IUPAC-NIST Solubility Data Series 69. Ternary Alcohol–Hydrocarbon–Water Systems

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The mutual solubilities of ternary systems containing alcohols, hydrocarbons and water are reviewed. An exhaustive search of the literature was attempted for numerical data on all alcohols and hydrocarbons which are liquid at STP. Data were found for alcohols with up to nine carbon atoms, but mostly with fewer than four carbons. Data for a variety of hydrocarbon structural types were found including alkane, alkene, and arene. A total of 205 original studies treating 116 ternary systems which have been published through 1992 are compiled. For 47 systems sufficient data were available to allow critical evaluation. All solubility data are expressed as mass and mole fractions as well as the originally reported units. Similar reviews of the related binary systems have previously been prepared for the Solubility Data Series. © *1999 American Institute of Physics and American Chemical Society.* [S0047-2689(99)00304-9]

Key words: aqueous solutions; hydrocarbons; solubility alcohols.

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*Note: an asterisk (*) indicates presence of a Critical Evaluation

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1. Preface to the Volume

This volume of IUPAC Solubility Data Series on ternary alcohol–hydrocarbon–water systems is the continuation of previous works on binary systems. Alcohol–water systems were presented as Vol. 15 of the Series, Ref. 1; hydrocarbon–water systems were presented as Vols. 37 and 38 of the Series, Refs. 2 and 3 and alcohol–hydrocarbon systems were presented as Vol. 56 of the Series, Ref. 4.

This volume surveys solubility data (along saturation curve and phases in equilibrium) which have been published in the open literature up to the end of 1992. The alcohols are those to nine carbon atoms, the most common are methanol, ethanol, propanols, and butanols. The hydrocarbons include those with three or more carbon atoms and of all structural types (aliphatic, aromatic, unsaturated, etc.) which are liquids at room temperature and pressure.

A total of 205 original studies of 116 ternary systems are compiled. Components of these systems were always well-defined substances. From these, it has been possible to make critical evaluations for 47 systems. Only numerical data are given because data published originally in graphical form are inherently imprecise, especially given the high precision of the tabulated data for many systems. The literature contains a large amount of imprecise and conflicting data. Where possible, recommended or tentative values of composition along saturation curves and for phases in equilibrium are given, but and in many cases this cannot be done because of insufficient information. This volume is the result of a careful search of the chemical literature. The goal of that search was to include all published data for the systems indicated in the title. Each Critical Evaluation includes a closing date for the literature for that system, generally December, 1992. In spite of these efforts, some published measurements may have been missed. The editors will appreciate having their attention brought to any omitted source of solubility data for inclusion in future volumes.

For purposes of comparison, all original results are expressed in mass and mole fraction as well as in the units given by the original investigators. Conversions, where they have been made, are clearly attributed to the compiler and the sources of any data not provided by the original investigators are specified. Definitions of mass and mole fraction as well as their relation to other common measures of solubility are given in the Introduction to the Solubility Data Series: Solubility of Liquids in Liquids in this volume. A table of conversion formulas is included at the end of the Introduction.

The reported ternary data often form miscibility gaps with one pair of partially miscible components (type 1) e.g., ethanol–hydrocarbon–water or propanol–hydrocarbon–water systems or miscibility gap with two pairs of partially miscible components (type 2) e.g., methanol–hydrocarbon–water or 1-butanol–hydrocarbon–water systems. In this volume the alcohol is reported always as the first component, the hydrocarbon as the second, and water as the third. For each group (alcohols, hydrocarbons), substances are ordered by increasing number of carbon atoms. In brackets, after each compound name synonyms are given. Each system begins on a separate page; first, the critical evaluation is presented together with a graphical representation of the system at one selected temperature. This is followed by compilation of original papers. Critical evaluations are presented only for systems where two or more independent determinations of solubility allow comparison of experimental data. The concentration along the saturation curve as well as the concentration of phases in equilibrium are always expressed in mole and mass fractions of alcohol and hydrocarbon. Concentration of water may be calculated from the mass balance (sum of concentration is always equal 1.0). The indexes $'$ and $''$ express the phase number; $'$ describes organic-rich or hydrocarbon-rich phase, while $''$ describes water-rich or hydrocarbon-poor phase. Among the references in several evaluations occurs the Russian compilation of Kafarov (ed.), "Spravochnik po Rastvorimosti,"[5] which contains only numerical data without any explanatory text; the English translation of this compilation was published as a handbook on solubility.[6]

The editors would like to thank Andrzej Bok (Thermodynamics Data Center, Warsaw, Poland) for preparing computer programs for presentation of the tables; Professor John W. Lorimer (Ontario, Canada) for valuable discussions and for preparing the addresses of translated Russian papers and all members of IUPAC Commission on Solubility Data (Vol. 8) for discussions.

1.1. References to the Preface

[1] A. F. M. Barton, ed., *Solubility Data Series*, Vol. 15, Alcohols with Water (Pergamon, New York, 1984).

[2] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

[3] D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).

[4] D. G. Shaw, A. Skrzecz, J. W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol. 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

[5] V. V. Kafarov, ed., *Spravochnik po Rastvorimosti*, Vol. 2, Troinye, Mnogokomponentnye Sistemy, Kniga II (Izd. Akademii Nauk SSSR, Moskva, 1963).

[6] H. Stephen and T. Stephen, eds., *Solubilities of Inorganic and Organic Compounds* (Pergamon, New York, 1963).

2. Introduction to the Solubility Data Series. Solubility of Liquids in Liquids

2.1. The Nature of the Project

The Solubility Data project (SDP) has as its aim a comprehensive review of published data for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled for each publication on data sheets in a uniform format. The data for each system are evaluated and, where data from independent sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

This series is concerned primarily with liquid–liquid systems, but a limited number or related solid–liquid, fluid–fluid, and multicomponent (organic-water-salt) systems are included where it is considered logical and appropriate. Solubilities at elevated and low temperatures and at elevated pressures have also been included, as it is considered inappropriate to establish artificial limits on the data presented if they are considered relevant or useful.

For some systems, the two components may be miscible in all proportions at certain temperatures and pressures. Data on reported miscibility gaps and upper and lower critical solution temperatures are included where appropriate and when available.

2.2. Compilations and Evaluations

The formats for the compilations and critical evaluations have been standardized for all volumes. A description of these formats follows.

2.2.1. Compilations

The format used for the compilations is, for the most part, self-explanatory. A compilation sheet is divided into boxes, with detailed contents described below.

Components

Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The Chemical Abstracts name is also included if this differs from the IUPAC name, as are trivial names if appropriate. IUPAC and common names are cross-referenced to Chemical Abstracts names in the System Index.

The formula is given either in terms of the IUPAC or Hill[1] system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered on a given compilation sheet according to:

(a) saturating components;
(b) nonsaturating components in alphanumerical order;
(c) solvents in alphanumerical order.

The saturating components are arranged in order according to the IUPAC 18-column periodic table with two additional rows:

Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements
Columns 3 to 12: transition elements
Columns 13 to 17: boron, carbon, nitrogen groups; chalcogenides, halogens
Column 18: noble gases
Row 1: Ce to Lu
Row 2: Th to the end of the known elements, in order of atomic number.

Organic compounds within each Hill formula are ordered in the following succession:

(a) by degree of unsaturation
(b) by order of increasing chain length in the parent hydrocarbon
(c) by order of increasing chain length of hydrocarbon branches
(d) numerically by position of unsaturation
(e) numerically by position by substitution
(f) alphabetically by IUPAC name.

Example:

C_5H_8	cyclopentane
	2-methyl-1,3-butadiene
	1,4-pentadiene
	1-pentyne
C_5H_{10}	cyclopentane
	3-methyl-1-butene
	2-methyl-2-butene

	1-pentene
	2-pentene
C_5H_{12}	2,2-dimethylpropane
	2-methylbutane
	pentane
$C_5H_{12}O$	2,2-dimethyl-1-propanol
	2-methyl-1-butanol
	2-methyl-2-butanol
	3-methyl-1-butanol
	3-methyl-2-butanol
	1-pentanol
	2-pentanol
	3-pentanol
$C_6H_{12}O$	cyclohexanol
	4-methyl-1-penten-3-ol
	1-hexen-3-ol
	4-hexen-3-ol

Deuterated (^2H) compounds follow immediately the corresponding H compounds.

Original Measurements

References are abbreviated in the forms given by Chemical Abstracts Service Source Index (CASSI). Names originally in other than Roman alphabets are given as transliterated by Chemical Abstracts. In the case of multiple entries (for example, translations) an asterisk indicated the publication used for compilation of the data.

Variables

Ranges of temperature, pressure, etc., are indicated here.

Prepared by

The names of all compilers are given here.

Experimental Data

Components are described as (1), (2), etc., as defined in the ''Components'' box. Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass percent for weight percent; mol dm^{-3} for molar; etc. In most cases, both mass and molar values are given. Usually, only one type of value (e.g., mass percent) is found in the original paper, and the compiler has added the other type of value (e.g., mole percent) from computer calculations based on 1989 atomic weights.[2] Temperatures are expressed as t/°C, t/°F, or T/K as in the original; if necessary, conversions to T/K are made, sometimes in the compilations, and always in the critical evaluation. However, the author's units are expressed according to IUPAC recommendations[3] as far as possible.

Errors in calculations, fitting equations, etc., are noted, and where possible corrected. Material inserted by the compiler is identified by the word ''compiler'' or by the compiler's name in parentheses or in a footnote. In addition, compiler-calculated values of mole or mass fractions are included if the original data do not use these units. If densities are reported in the original paper, conversions from concentrations to mole fractions are included, but otherwise this is done in the evaluation, with the values and sources of the densities being quoted and referenced.

Details of smoothing equations (with limits) are included if they are present in the original publication and if the temperature or pressure ranges are wide enough to justify this procedure and if the compiler finds that the equations are consistent with the data.

The precision of the original data is preserved when derived quantities are calculated, if necessary by the inclusion of one additional significant figure. In some cases graphs have been included, either to illustrate presented data more clearly, or if this is the only information in the original. Full grids are not usually inserted as it is not intended that users should read data from the graphs.

Method

The apparatus and procedure are mentioned briefly. Abbreviations used in Chemical Abstracts are often used here to save space, reference being made to sources of further detail if these are cited in the original paper.

Source and Purity of Materials

For each component, referred to as (1), (2), etc., the following information (in this order and in abbreviated form) is provided if available in the original paper: source and specified method of preparation; properties; degree of purity.

Estimated Error

If estimated errors were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors (identified by ''compiler'' or the compiler's name in parentheses or in a footnote) from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on Ku and Eisenhart.[4]

Comments and/or Additional Data

Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References

The format for these follows the format for the Original Measurements box, except that final page numbers are omitted. References (usually cited in the original paper) are given where relevant to interpretation of the compiled data, or where cross-reference can be made to other compilations.

2.2.2. Evaluations

The evaluator's task is to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend ''best'' values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. There are only three boxes on a typical evaluation sheet, and these are described below.

Components

The format is the same as on the Compilation sheets.

Evaluator

The name and affiliation of the evaluator(s) and date up to which the literature was checked.

Critical Evaluation

(a) Critical text. The evaluator checks that the compiled data are correct, assesses their reliability and quality, estimates errors where necessary, and recommends numerical values based on all the published data (including theses, reports, and patents) for each given system. Thus, the evaluator reviews the merits or shortcomings of the various data. Only published data are considered. Documented rejection of some published data may occur at this stage, and the corresponding compilations may be removed.

The solubility of comparatively few systems is known with sufficient accuracy to enable a set of recommended values to be presented. Although many systems have been studied by at least two workers, the range of temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different but internally consistent sets of results at the same temperature, although both sets of results were obtained by reliable methods. In such cases, a definitive assessment may not be possible. In some cases, two or more sets of data have been classified as tentative even though the sets are mutually inconsistent.

(b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets, stating the limits within which it should be used.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are reported as tentative if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However, references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here, including all those publications appearing in the accompanying compilation sheets and those which, by virtue of their poor precision, have been rejected and not compiled.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in SI units[3] when the data can be converted accurately.

2.3. Quantities and Units Used in Compilation and Evaluation of Solubility Data

2.3.1. Mixtures, Solutions and Solubilities

A *mixture*[5,6] describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way.

A *solution*[5,6] describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent*, and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fraction of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a solute 1 (solid, liquid or gas) is the analytical composition of a saturated solution, expressed in terms of the proportion of the designated solute in a designated solvent.[7]

''Saturated'' implies equilibrium with respect to the processes of dissolution and demixing; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the same substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the reference states used for definition of activities, activity coefficients and osmotic coefficients. Note that the composition of a saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components.

2.3.2. Physicochemical Quantities and Units

Solubilities of solids have been the subject of research for a long time, and have been expressed in a great many ways, as described below. In each case, specification of the temperature and either partial or total pressure of the saturating gaseous component is necessary. The nomenclature and units

TABLE 1. Interconversions between quantities used as measures of solubilities c-component systems containing c-1 solutes i and single solvent c (ρ—density of solution; M_i—molar masses of i. For relations for two-component systems, set summations to 0.)

	x_i	w_i	m_i	c_i
$x_i=$	x_i	$\dfrac{1}{1+\dfrac{M_i}{M_c}\left\{\dfrac{1}{w_i}-1+\sum\limits_{j\neq 1}^{c-1}\left(\dfrac{M_c}{M_j}-1\right)\dfrac{w_j}{w_i}\right\}}$	$\dfrac{1}{1+\dfrac{1}{m_iM_c}+\sum\limits_{j\neq i}^{c-1}\dfrac{m_j}{m_i}}$	$\dfrac{1}{1+\dfrac{1}{M_c}\left(\dfrac{\rho}{c_i}-M_i\right)+\sum\limits_{j\neq i}^{c-1}\dfrac{c_j}{c_i}\left(1-\dfrac{M_j}{M_c}\right)}$
$w_i=$	$\dfrac{1}{1+\dfrac{M_c}{M_i}\left\{\dfrac{1}{x_i}-1+\sum\limits_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right\}}$	w_i	$\dfrac{1}{1+\dfrac{1}{m_iM_i}\left(1+\sum\limits_{j\neq i}^{c-1}m_jM_j\right)}$	$\dfrac{c_iM_i}{\rho}$
$m_i=$	$\dfrac{1}{M_c\left(\dfrac{1}{x_i}-1-\sum\limits_{j\neq i}^{c-1}\dfrac{x_j}{x_i}\right)}$	$\dfrac{1}{M_i\left(\dfrac{1}{w_i}-1-\sum\limits_{j\neq i}^{c-1}\dfrac{w_j}{w_i}\right)}$	m_i	$\dfrac{1}{\dfrac{1}{c_i}\left(\rho-\sum\limits_{j\neq i}^{c-1}c_jM_j\right)-M_i}$
$c_i=$	$\dfrac{\rho}{M_i+M_c\left\{\dfrac{1}{x_i}-1+\sum\limits_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right\}}$	$\dfrac{\rho w_i}{M_i}$	$\dfrac{\rho}{\dfrac{1}{m_i}\left(1+\sum\limits_{j\neq i}^{c-1}m_jM_j\right)+M_j}$	c_i

follow, where possible, IUPAC *Green Book*.[3] A few quantities follow the ISO standards[8] or the German standard;[9] see a review by Cvitas[10] for details.

A note on nomenclature

The nomenclature of the IUPAC *Green Book*[3] calls the solute component B and the solvent component A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing equations given here with those in the *Green Book.*

1. *Mole fraction* of substance 1, x_1 or x (1) (condensed phases), y_1 (gases):

$$x_1=n_1\bigg/\sum_{s=1}^{c}n_s \qquad (1)$$

where n_s is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole percent* of substance 1 is 100 x_1.

2. *Ionic mole fractions* of salt i, x_{i+}, x_{i-}:
For a mixture of s binary salts i, each of which ionizes completely into υ_{s+} cations and υ_{s-} anions, with $\upsilon_s=\upsilon_{s+}+\upsilon_{s-}$ and a mixture of p nonelectrolytes j, of which some may be solvent components, a generalization of the definition in Ref. 11 gives

$$x_{i+}=\frac{\upsilon_i+x_i}{1+\sum\limits_{i=1}^{s}(\upsilon_i-1)x_s}, \quad x_{i-}=\frac{\upsilon_i-x_{i+}}{\upsilon_{i+}} \quad i=1\ldots s \qquad (2)$$

$$x_j'=\frac{x_j}{1+\sum\limits_{i=1}^{s}(\upsilon_i-1)x_i}, \quad j=(s+1),\ldots,p. \qquad (3)$$

The sum of these mole fractions is unity, so that, with $c=s+p$,

$$\sum_{i=1}^{s}(x_{i+}+x_{i-})+\sum_{i=s+1}^{c}x_i'=1. \qquad (4)$$

General conversions to other units in multicomponent systems are complicated. For a three-component system containing nonelectrolyte 1, electrolyte 2, and solvent 3,

$$x_1=\frac{\upsilon_{2+}x_1'}{\upsilon_{2+}-(\upsilon_2-1)x_{2+}}, \quad x_2=\frac{x_{2+}}{\upsilon_{2+}-(\upsilon_2-1)x_{2+}}. \qquad (5)$$

These relations are used in solubility equations for salts, and for tabulation of salt effects on solubilities of gases (see below).

3. *Mass fraction* of substance 1, w_1 or $w(1)$:

$$w_1=g_1\bigg/\sum_{s=1}^{c}g_s \qquad (6)$$

where g_s is the mass of substance s. *Mass percent* of substance 1 is 100 w_1. The equivalent terms *weight fraction, weight percent*, and *g(1)/100 g solution* are no longer used.

4. *Molality* of solute 1 in a solvent 2, m_1:

$$m_1=n_1/n_2M_2 \qquad (7)$$

SI base units: mol kg^{-1}. Here, M_2 is the molar mass of the solvent.

5. *Aquamolality, Solvomolality* of substance 1 in a mixed solvent with components, 2, 3,[12] $m_1^{(3)}$:

$$m_1^{(3)}=m_1\bar{M}/M_3 \qquad (8)$$

SI base units: mol kg^{-1}. Here, the average molar mass of the solvent is

$$\bar{M}=x_2'M_2+(1-x_2')M_3 \tag{9}$$

and x_2' is the solvent mole fraction of component 2. This term is used most frequently in discussing comparative solubilities in water (component 2) and heavy water (component 3) and in their mixtures.

6. *Amount concentration* if solute 1 in a solution of volume V, c_1:

$$c_1=[\text{formula of solute}]=n_1/V \tag{10}$$

SI base units: mol m^{-3}. The symbol c_1 is preferred to [formula of solute], but both are used. The old terms *molarity, molar*, and *moles per unit volume* are no longer used.

7. *Mass concentration* of solute 1 in a solution of volume V, r_1: SI base units: kg m^{-3}.

$$\rho_1=g_1/V. \tag{11}$$

8. *Mole ratio*, $r_{\mathrm{A,B}}$ (dimensionless)[10]

$$r_{\mathrm{A,B}}=n_1/n_2. \tag{12}$$

Mass ratio, symbol $\zeta_{\mathrm{A,B}}$, may be defined analogously.[10]

Mole and mass fractions are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions between pairs of these quantities can be carried out using the equations given in Table 1 at the end of this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

9. *Density*, ρ:

$$\rho=g/V \tag{13}$$

SI base units: kg m^{-3}. Here g is the total mass of the system.

10. *Relative density*, $d=\rho/\rho°$: the ratio of the density of a mixture at temperature t, pressure p to the density of a reference substance at temperature t', pressure p'. For liquid solutions, the reference substance is often water at 4 °C, 1 bar. (In some cases 1 atm is used instead of 1 bar.) The term *specific gravity* is no longer used.

Thermodynamics of Solubility

Thermodynamic analysis of solubility phenomena provides a rational basis for the construction of functions to represent solubility data, and thus aids in evaluation, and sometimes enables thermodynamic quantities to be extracted. Both these aims are often difficult to achieve because of a lack of experimental or theoretical activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve examination of a large body of data that is not directly relevant to solubility. Where possible, procedures for evaluation are based on established thermodynamic methods. Specific procedures used in a particular volume will be described in the Preface to this volume.

2.4. References for the Introduction

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[8] ISO Standards Handbook, *Quantities and Units* (International Standards Organization, Geneva, 1993).

[9] German Standard, DIN 1310, *Zusammungsetzung von Mischphasen* (Beuth Verlag, Berlin, 1984).

[10] T. Cvitaŝ, Chem. Int. **17**, 123 (1995).

[11] R. A. Robinson and R. H. Stokes, *Electroyte Solutions* (Butterworths, London, 1959), 2nd ed.

[12] J. W. Lorimer, in R. Cohen-Adad and J. W. Lorimer, *Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)*, IUPAC Solubility Data Series, Vol. 47 (Pergamon, Oxford, UK, 1991), p. 495.

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3. Methanol + Water

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Propane (*n*-propane); C_3H_8; [74-98-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

K. Noda, K. Sato, K. Nagatsuka, and K. Ishida, J. Chem. Eng. Jpn. **8**, 492–3 (1975).

Variables:

T/K=273–293

Compiled by:

A. Skrzecz

3.1. Methanol + Water + Propane

Experimental Data

Compositions of coexisting phases

		x'_1	x'_3	x''_1	x''_2	w'_1	w'_2	w'_3	w''_1	w''_2
t/°C	T/K (compiler)	organic-rich phase (compiler)		water-rich phase (compiler)		organic-rich phase			water-rich phase	
0.0	273.2	0.004	0.995	0.397	0.005	0.003	0.997	0.0002	0.537	0.009
		0.007	0.992	0.510	0.010	0.005	0.995	0.0003	0.643	0.017
		0.019	0.979	0.677	0.023	0.014	0.985	0.0008	0.772	0.036
		0.038	0.960	0.754	0.036	0.028	0.971	0.001	0.818	0.054
		0.147	0.848	0.851	0.099	0.112	0.886	0.002	0.838	0.134
20.0	293.2	0.007	0.992	0.276	0.003	0.005	0.994	0.0006	0.402	0.007
		0.015	0.983	0.458	0.010	0.011	0.988	0.0008	0.594	0.018
		0.019	0.978	0.493	0.014	0.014	0.985	0.001	0.624	0.025
		0.035	0.961	0.639	0.041	0.026	0.972	0.0015	0.730	0.064
		0.066	0.929	0.718	0.115	0.049	0.949	0.002	0.740	0.163

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used, similar to that reported in Ref. 1. Samples of each phase were analyzed by glc on a 3 mm diameter by 3 m long column packed with Poropak R and using H_2 as a carrier gas. Each sample was injected several times and the composition was determined from chromatogram areas. Care was taken to avoid contamination by the surroundings, especially water vapor.

Source and Purity of Materials:

(1) source not specified, commercially available; guaranteed reagent; used as received.
(2) Takachiho Chemical Industry Co., Ltd; standard reagent; used as received.
(3) distilled.

Estimated Error:

Not reported.

References:

[1] K. Ishida, Bull. Chem. Soc. Jpn. **29**, 956 (1956).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Butane (*n*-butane); C_4H_{10}; [106-97-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

K. Noda, K. Sato, K. Nagatsuka, and K. Ishida, J. Chem. Eng. Jpn. **8**, 492–3 (1975).

Variables:

T/K=273–293

Compiled by:

A. Skrzecz

3.2. Methanol + Water + Butane

Experimental Data

Compositions of coexisting phases

		x'_1	x'_3	x''_1	x''_2	w'_1	w'_2	w'_3	w''_1	w''_2
t/°C	T/K (compiler)	organic-rich phase (compiler)		water-rich phase (compiler)		organic-rich phase			water-rich phase	
0.0	273.2	0.011	0.988	0.584	0.007	0.006	0.994	0.0003	0.707	0.015
		0.020	0.979	0.729	0.019	0.011	0.989	0.0004	0.805	0.039
		0.037	0.961	0.811	0.044	0.021	0.978	0.0006	0.834	0.082
		0.063	0.934	0.843	0.073	0.036	0.963	0.0007	0.824	0.130
		0.100	0.897	0.835	0.123	0.058	0.941	0.0008	0.772	0.206
		0.105	0.892	0.834	0.131	0.061	0.938	0.0008	0.764	0.218
20.0	293.2	0.007	0.991	0.270	0.001	0.004	0.996	0.0004	0.396	0.003
		0.014	0.984	0.510	0.005	0.008	0.991	0.0006	0.644	0.011
		0.020	0.978	0.626	0.010	0.011	0.988	0.0007	0.737	0.022
		0.023	0.974	0.650	0.013	0.013	0.986	0.0008	0.753	0.027
		0.041	0.956	0.723	0.023	0.023	0.976	0.001	0.797	0.046
		0.060	0.937	0.759	0.056	0.034	0.965	0.001	0.787	0.105
		0.082	0.914	0.783	0.092	0.047	0.951	0.0015	0.768	0.163
		0.121	0.873	0.751	0.177	0.071	0.927	0.002	0.675	0.289

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used, similar to that reported in Ref. 1. Samples of each phase were analyzed by glc on a 3 mm diam by 3 m long column packed with Poropak R and using H_2 as a carrier gas. Each sample was injected several times and the composition was determined from chromatogram areas. Care was taken to avoid contamination by the surroundings, especially water vapor.

Source and Purity of Materials:

(1) source not specified, commercially available; guaranteed reagent; used as received.
(2) Takachiho Chemical Industry Co., Ltd; standard reagent; used as received.
(3) distilled.

Estimated Error:

Not reported.

References:

[1] K. Ishida, Bull. Chem. Soc. Jpn. **29**, 956 (1956).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Isoprene (2-methyl-1,3-butadiene, isopentadiene); C_5H_8; [78-79-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
T. M. Lesteva, S. K. Ogorodnikov and V. I. Morozova, Zh. Prikl. Khim. (Leningrad) 39, 2134–6 (1966). [Eng. transl. Russ. J. Phys. Appl. Chem. (Leningrad) 39, 2002–5 (1966)].

Variables:
T/K=288

Compiled by:
A. Skrzecz

3.3. Methanol + Water + 2-Methyl-1, 3-butadiene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
15.0	288.2	0.0000	0.0002	0.0000	0.0008
		0.0595	0.0006	0.101	0.002
		0.1241	0.0006	0.201	0.002
		0.1652	0.0006	0.260	0.002
		0.2809	0.0010	0.409	0.003
		0.2709	0.0010	0.397	0.003
		0.3490	0.0010	0.487	0.003
		0.0646	0.0011	0.109	0.004
		0.1824	0.0015	0.283	0.005
		0.2768	0.0023	0.403	0.007
		0.3443	0.0037	0.479	0.011
		0.3690	0.0045	0.505	0.013
		0.4245	0.0090	0.557	0.025
		0.5098	0.0152	0.630	0.040
		0.5679	0.0227	0.671	0.057
		0.5197	0.0225	0.630	0.058
		0.5560	0.0318	0.650	0.079
		0.6050	0.0384	0.682	0.092
		0.6077	0.0393	0.683	0.094
		0.6351	0.0530	0.688	0.122
		0.6575	0.0720	0.683	0.159
		0.6653	0.0930	0.666	0.198
		0.6647	0.0936	0.665	0.199
		0.6780	0.1026	0.665	0.214
		0.6685	0.1090	0.652	0.226
		0.6694	0.1251	0.637	0.253
		0.6825	0.1346	0.637	0.267
		0.6675	0.1443	0.618	0.284
		0.6602	0.1724	0.589	0.327
		0.6434	0.1772	0.574	0.336
		0.6473	0.2106	0.551	0.381
		0.6263	0.2383	0.518	0.419
		0.5841	0.3033	0.452	0.499
		0.5807	0.3105	0.446	0.507
		0.5204	0.3991	0.368	0.600
		0.5060	0.4103	0.355	0.612
		0.4833	0.4388	0.331	0.639
		0.4546	0.4758	0.302	0.672
		0.3983	0.5478	0.250	0.731
		0.3991	0.5579	0.248	0.737
		0.3464	0.6294	0.204	0.788
		0.2448	0.7232	0.136	0.854
		0.1909	0.7957	0.101	0.895
		0.0000	0.9989	0.0000	0.9997

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
15.0	288.2	0.0000	0.9962	0.0406	0.0003	0.000	0.999	0.070	0.001
		0.0000	0.9925	0.0917	0.0006	0.000	0.998	0.152	0.002
		0.0000	0.9888	0.1551	0.0003	0.000	0.997	0.246	0.001
		0.0063	0.9899	0.1796	0.0003	0.003	0.996	0.280	0.001
		0.0063	0.9862	0.2203	0.0006	0.003	0.995	0.334	0.002
		0.0147	0.9779	0.4678	0.0081	0.007	0.991	0.600	0.022
		0.0412	0.9478	0.5592	0.0169	0.020	0.977	0.671	0.043
		0.0614	0.9314	0.5904	0.0264	0.030	0.968	0.685	0.065
		0.2587	0.7252	0.2587	0.7252	0.143	0.852	0.143	0.852[a]

[a] Critical point of solution estimated by the authors.

Auxiliary Information

Method/Apparatus/Procedure:

The standard titration method was used to construct the binodal curve. Refractive indexes and densities of points on the binodal curve were measured. Ternary mixtures of known composition were shaken in the thermostat for 1 h. After separation, refractive indexes and densities of both phases were measured and concentrations were calculated from calibration curves prepared during solubility measurements. The results of the analysis of the water-rich phase were checked for a few points by redistillation and further analysis of distillate by glc and the Karl Fischer methods.

Source and Purity of Materials:

(1) source not specified; distilled several times on laboratory columns; purity 99.85%–99.90%.
(2) source not specified; distilled several times on laboratory columns; purity 99.85%–99.90%.
(3) not specified.

Estimated Error:

temp. ±0.1 °C.

Components:	Evaluated by:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1] (2) Benzene: C_6H_6; [71-43-2] (3) Water; H_2O; [7732-18-5]	A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.05)

3.4. Methanol + Water + Benzene

Critical Evaluation:

A survey of reported compositions along the saturation curves (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system methanol–benzene–water is given in Table 2.

TABLE 2. Summary of experimental data for the system methanol–benzene–water

Author(s), year	T/K	Type of data[a]	Ref.
Bancroft, 1895	293	sat. (3)	1
Holmes, 1918	288	sat. (1)	2
Perrakis, 1925	293	sat. (11)	3
Barbaudy, 1926	298	Eq. (3)	4
Ormandy *et al.*, 1934	288	sat. (5)	5
Sata and Niwase, 1937	292–304	sat. (15)	6
Leikola, 1940	299	sat. (3)	7
Staveley *et al.*, 1951	288–341	sat. (49)	8
Francis, 1954	295	sat. (16)	9
Udovenko and Mazanko, 1963	289–341	sat. (32), Eq. (44)	10
Bundantseva *et al.*, 1976	293	sat. (5), Eq. (10)	11
Triday, 1984	293	sat. (27), Eq. (10)	12
Letcher *et al.*, 1990	298	sat. (13), Eq. (5)	13

[a] Number of experimental points in parentheses.

Saturation curves

The ternary system methanol–benzene–water forms a miscibility gap of type 1. The system was the object of 13 studies over the temperature range 288–341 K. This critical evaluation is based on the original papers with the exception of data of Bancroft,[1] Ormandy, *et al.*,[5] and Leikola,[7] which were taken from the handbook of Kafarov;[14] these data sets were also taken into account during evaluation but are not reported as compilation sheets because they do not contribute further to knowledge of the system. Data of Perrakis[3] at 293 K show a larger miscibility gap than other studies; maximum mole fraction of methanol is larger by about 0.1 than any other data at this temperature. Data of Bancroft[1] were reported in volume % and were not recalculated. Therefore these data are rejected and are not reported as a compilation table. All experimental data of Letcher *et al.*[13] were presented only in graphical form and therefore were not reported as a separate compilation sheet. Data of Francis[9] at 295 K show a slightly smaller miscibility gap than data at 293 K (in agreement with general expectations), while data published during the period 1918–40 are all very close to the binodal curve describing saturation at 293 K, even though they were measured over the range 288–299 K. Of the three related binary systems, only benzene–water shows partially miscibility. The data for this system were reported, compiled, and critically evaluated in a previously published SDS volume.[15] The recommended values of mutual solubility at 293.2 K, from Ref. 15, are: $x_2'=0.9975$ and $x_2''=0.000\,406$. Only the papers of Budantseva *et al.*[11] and Triday[12] reported mutual solubility of the binary system. These values at 293.2 K[11] and at 293.0 K[12] are the same in both references: $x_2'=0.9974$, $x_2''=0.0004$ and are in excellent agreement with recommended data, Ref. 15. Characteristic points on the binodal curve of the system methanol–benzene–water at selected temperatures, reported in literature, are presented in Table 3. At the point of maximum methanol concentration the errors estimated by the evaluator are 0.005 and 0.015 mole fraction of methanol and benzene, respectively. The composition of plait points at 293 K reported in Refs. 11 and 12, differed by 0.04 mole fraction of methanol and benzene (the plait point reported by Triday[12] was calculated by Hand's method).[16]

TABLE 3. Characteristic points on the binodal curve of the system methanol–benzene–water

	Max. CH_3OH concentration			Plait points		
T/K	x_1	x_2	Ref.	x_1	x_2	Ref.
293.0	0.6181	0.1371	12	0.406	0.523	12
293.2	0.6320	0.1462	11	0.441	0.482	11
298.2	—	—		0.4743	0.4106	4
298.2	0.62	0.14	13	0.47	0.44	13
303.2	0.5949	0.1499	10	0.470	0.420	10
318.2	0.5662	0.1542	10	0.467	0.389	10
333.2	0.5345	0.1082	10	0.465	0.357	10

The temperature 293 K was selected for presentation of the behavior of the system. (The temperature difference between 293.2 and 293.0 K was neglected in binodal curve parameters calculations.) All together 72 experimental points on the saturation curve[11,12] (the water-rich and benzene-rich branches were treated together) were used to construct the fitting equation:

$$x_1=0.96828+0.11825\ln(x_2)-0.852\,77x_2-0.122\,05x_2^2.$$

The standard error of estimate was 0.0421. The compositions on the saturation curve calculated by the fitting equation are presented in the Table 4 for selected concentrations of benzene. The results of calculations (solid line) are presented graphically in Fig. 1 together with all experimental data reported at 293.2 K.

TABLE 4. Calculated compositions along the saturation curve at 293.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 406 Ref. 15	0.4294	0.5000
0.1506	0.0010	0.4145	0.5200
0.4152	0.0100	0.3993	0.5400
0.4886	0.0200	0.3839	0.5600
0.5533	0.0400	0.3682	0.5800
0.5840	0.0600	0.3523	0.6000
0.6006	0.0800	0.3361	0.6200
0.6095	0.1000	0.3197	0.6400
0.6135	0.1200	0.3031	0.6600
0.6140	0.1400	0.2864	0.6800
0.6120	0.1600	0.2694	0.7000
0.6080	0.1800	0.2522	0.7200
0.6025	0.2000	0.2348	0.7400
0.5957	0.2200	0.2172	0.7600
0.5878	0.2400	0.1995	0.7800
0.5790	0.2600	0.1816	0.8000
0.5694	0.2800	0.1635	0.8200
0.5591	0.3000	0.1452	0.8400
0.5482	0.3200	0.1268	0.8600
0.5367	0.3400	0.1082	0.8800
0.5247	0.3600	0.0895	0.9000
0.5122	0.3800	0.0706	0.9200
0.4993	0.4000	0.0515	0.9400
0.4860	0.4200	0.0323	0.9600
0.4723	0.4400	0.0130	0.9800
0.4584	0.4600	0.0032	0.9900
0.4440	0.4800	0.0000	0.9975 Ref. 15

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–benzene–water were reported in five references as 6 isotherms, Refs. 4, 10, 11, 12, 13, over the temperature range 293–333 K. The tie lines cover the full area of the miscibility gap. There is a large difference of mole fraction of methanol between the benzene-rich and water-rich phases. The reported data are consistent within each data set. Changes of tie line direction were observed with temperature. With decreasing temperature the water concentration in the benzene-poor phase also decreased for a similar composition of benzene-rich phase. This may be observed in data reported in Refs. 10, 11, 12. At 293 K equilibrium data of Budantseva *et al.*[11] and Triday[12] differ one from the other. For similar composition of benzene-rich phase the measured composition of water-rich phase reported by Triday[12] contains much more methanol than the equivalent mixture reported by Budantseva *et al.*[11] All equilibrium data are considered tentative. The experimental plait points reported in literature are presented above in Table 2. The experimental points at 293.2 K, both saturation and equilibrium data, Refs. 11 and 12, are presented in Fig. 1.

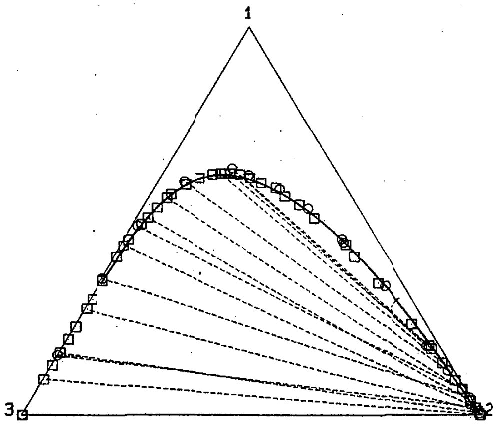

FIG. 1. Phase diagram of the system methanol (1)—benzene (2)—water (3) at 293.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 11, □—experimental data, Ref. 12, dashed lines—experimental tie lines, Refs. 11 and 12.

References:

[1]W. D. Bancroft, Phys. Rev. 3, 205 (1895).

[2]J. Holmes, J. Chem. Soc. 113, 263 (1918).

[3]N. Perrakis, J. Chim. Phys. Phys. Chim. Biol. 22, 280 (1925).

[4]J. Barbaudy, C. R. Hebd, Seances Acad. Sci. 182, 1279 (1926).

[5]W. R. Ormandy, T. W. M. Pond, and W. R. Davies, J. Inst. Petrol. Technol. 20, 308 (1934).

[6]N. Sata and Y. Niwase, Bull. Chem. Soc. Jpn. 12, 86 (1937).

[7]E. Leikola, Suomen Kemistil B. 13, 13 (1940).

[8]L. A. K. Staveley, R. G. S. Johns, and B. C. Moore, J. Chem. Soc. 2516 (1951).

[9]A. W. Francis, Ind. Eng. Chem. 46, 205 (1954).

[10]V. V. Udovenko and T. E. Mazanko, Zh. Fiz. Khim. 37, 2324 (1963).

[11]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI 438-76, 1 (1976).

[12]J. O. Triday, J. Chem. Eng. Data 29, 321 (1984).

[13]T. M. Letcher, J. Sewry, and S. Radloff, S. Afr. J. Chem 43, 56 (1990).

[14]V. V. Kafarov, ed., *Spravochnik po Rastvorimosti* Vol. 2. Troinye, Mnogokomponentnye Sistemy, Kniga II (Izd. Akademii Nauk SSSR, Moskva, 1963).

[15]D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

[16]D. B. Hand, J. Phys Chem. 34, 1961 (1930).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Benzene; C_6H_6 [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
J. Barbaudy, C. R. Hebd. Seances Acad. Sci. 182, 1279–81 (1926).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hyrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.0925	0.8961	0.5192	0.0343	0.0405	0.9567	0.6080	0.0980
		0.0961	0.8918	0.5377	0.0409	0.0422	0.9548	0.6150	0.1140
		0.0933	0.8953	0.5240	0.0359	0.0409	0.9563	0.6100	0.1020[a]
		0.4743	0.4106	0.4743	0.4106	0.3080	0.6500	0.3080	0.6500[b]

[a]Equal density of both phases (interpolated by the author).
[b]Plait point.

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. After separation, density and refractive index of each phase were measured. Compositions of coexisting phases were determined as intersections of constant density and constant refractive index lines. Nine tie lines are presented graphically. Only two of them and critical point are reported as numerical values and presented above. The procedure was described for ethanol–benzene–water system in Ref. 1.

Source and Purity of Materials:
(1) source not specified.
(2) source not specified.
(3) source not specified.

Estimated Error:
Not reported.

References:
[1]J. Barbaudy, Bull. Soc. Chim. Fr. 49, 371 (1926).

Components:

(1) Methanol (methyl alcohol); Ch_4O; [67-56-1]
(2) Benzene; C_6H_6 [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. Sata and Y. Niwase, Bull. Chem. Soc. Jpn. **12**, 86–95 (1937).

Variables:

T/K=292–304

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)			
23.0	296.2	0.4282	0.5026	0.2530	0.7240
26.0	299.2	0.4249	0.5001	0.2520	0.7230
30.0	303.2	0.4198	0.4939	0.2510	0.7200
19.0	292.2	0.4996	0.4095	0.3225	0.6445
23.5	296.7	0.4986	0.4092	0.3221	0.6444
24.0	297.2	0.4969	0.4078	0.3217	0.6436
28.0	301.2	0.4952	0.4064	0.3213	0.6428
31.0	304.2	0.4934	0.4049	0.3209	0.6419
30.0	303.2	0.4906	0.4031	0.3200	0.6410
25.5	298.7	0.5491	0.3384	0.3820	0.5740
22.0	295.2	0.5460	0.3368	0.3810	0.5730
30.0	303.2	0.5449	0.3356	0.3810	0.5720
25.0	298.2	0.6089	0.2503	0.4690	0.4700
29.0	302.2	0.6059	0.2491	0.4680	0.4690
30.0	303.2	0.6029	0.2478	0.4670	0.4680

Auxiliary Information

Method/Apparatus/Procedure:

Alcohol was added to a known amount of water–benzene mixture until one layer was obtained.

Source and Purity of Materials:

(1) Merck, "very pure," without acetone; used as received.
(2) source not specified; used as received.
(3) not specified.

Estimated Error:

Not reported.

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. A. K. Staveley, R. G. S. Johns, and B. C. Moore, J. Chem. Soc. 2516–23 (1951).

Variables:

T/K=288–341

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (complier)	x_1	x_2	w_1	w_2
				(compiler)	
26.0	299.15	0.0113	0.985 63	0.004 68	0.994 61
33.5	306.65	0.0113	0.984 74	0.004 68	0.994 40
37.7	310.85	0.0113	0.984 08	0.004 68	0.994 24
46.1	319.25	0.0113	0.982 52	0.004 69	0.993 87
60.1	333.25	0.0113	0.979 245	0.004 70	0.993 09
20.0	293.15	0.0226	0.974 52	0.009 42	0.989 91
32.4	305.55	0.0226	0.972 89	0.009 43	0.989 51
42.0	315.15	0.0226	0.971 19	0.009 44	0.989 10
49.8	322.95	0.0226	0.968 53	0.009 46	0.988 45
56.4	329.55	0.0226	0.967 60	0.009 47	0.988 22
28.7	301.85	0.0332	0.962 65	0.013 94	0.985 08
34.5	307.65	0.0332	0.961 72	0.013 95	0.984 85
40.1	313.25	0.0332	0.960 72	0.013 96	0.984 61
47.9	321.05	0.0332	0.959 03	0.013 98	0.984 19
56.5	329.65	0.0332	0.956 62	0.014 00	0.983 58
28.4	301.55	0.0412	0.954 49	0.017 40	0.981 59
32.2	305.35	0.0412	0.954 075	0.017 41	0.981 48
44.6	317.75	0.0412	0.951 375	0.017 44	0.980 80
52.0	325.15	0.0412	0.949 68	0.017 47	0.980 37
62.8	335.95	0.0412	0.946 52	0.017 51	0.979 57
22.5	295.65	0.0458	0.950 13	0.019 37	0.979 66
41.1	314.25	0.0458	0.946 76	0.019 42	0.978 80
47.4	320.55	0.0458	0.945 03	0.019 45	0.978 36
64.1	337.25	0.0458	0.940 09	0.019 53	0.977 09
67.6	340.75	0.0458	0.939 11	0.019 54	0.976 84
23.7	296.85	0.0568	0.936 79	0.024 23	0.974 23
31.6	304.75	0.0568	0.935 31	0.024 26	0.973 85
37.9	311.05	0.0568	0.933 89	0.024 29	0.973 47
47.8	320.95	0.0568	0.931 49	0.024 33	0.972 85
50.7	323.85	0.0568	0.930 69	0.024 35	0.972 64
22.2	295.35	0.0781	0.913 62	0.033 81	0.964 18
32.7	305.85	0.0781	0.911 27	0.033 87	0.963 53
46.2	319.35	0.0781	0.908 42	0.033 95	0.962 75
53.1	326.25	0.0781	0.906 59	0.034 00	0.962 25
61.6	334.75	0.0781	0.903 74	0.034 08	0.961 46
15.0	288.15	0.1047	0.885 86	0.046 13	0.951 53
22.2	295.35	0.1047	0.884 48	0.046 18	0.951 13
35.6	308.75	0.1047	0.880 67	0.046 33	0.950 03
43.7	316.85	0.1047	0.878 85	0.046 40	0.949 50

Auxiliary Information

Method/Apparatus/Procedure:

The synthetic method was used. Mixtures were prepared in sealed tubes; water was added from a weighed pipette to a known mass of alcohol–benzene mixture.

Source and Purity of Materials:

(1) source not specified; dried by refluxing over freshly ignited lime, and then with magnesium, distilled.
(2) source not specified; chemically purified, crystallized, distilled, dried over phosphoric anhydride.
(3) not specified.

Estimated Error:

composition <0.2%; temp. <0.2 °C.

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. W. Francis, Ind. Eng. Chem. **46**, 205–7 (1954).

Variables:

T/K=295

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
22	295	0.120	0.001	0.195	0.005
		0.244	0.004	0.360	0.015
		0.407	0.011	0.535	0.035
		0.524	0.036	0.610	0.102
		0.561	0.052	0.620	0.140
		0.585	0.072	0.613	0.185
		0.599	0.077	0.618	0.194
		0.603	0.144	0.550	0.320
		0.589	0.205	0.489	0.415
		0.574	0.254	0.445	0.480
		0.474	0.411	0.308	0.650
		0.356	0.565	0.200	0.775
		0.253	0.678	0.130	0.850
		0.161	0.794	0.076	0.912
		0.112	0.868	0.050	0.945
		0.094	0.894	0.041	0.956

Auxiliary Information

Method/Apparatus/Procedure:

The experimental procedure was not reported. Temperature was reported to be in the range 21–23 °C. Data were presented as a part of quaternary data of methanol–benzene–aniline–water system.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified.
(3) source not specified.

Estimated Error:

temp. ±1 °C.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
V. V. Udovenko and T. F. Mazanko, Zh. Fiz. Khim. **37**, 2324–7 (1963).

Variables:
T/K=289–341

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
25.79	298.94	0.2862	0.6652	0.1479	0.8380
30.42	303.57	0.2849	0.6622	0.1477	0.8369
40.55	313.70	0.2831	0.6582	0.1474	0.8354
46.52	319.67	0.2816	0.6544	0.1472	0.8340
56.60	329.75	0.2791	0.6486	0.1468	0.8318
63.20	336.35	0.2773	0.6446	0.1465	0.8303
25.00	298.15	0.4065	0.5001	0.2422	0.7265
29.89	303.04	0.4036	0.4966	0.2416	0.7248
38.63	311.78	0.3973	0.4889	0.2403	0.7210
49.00	322.15	0.3886	0.4783	0.2385	0.7156
60.78	333.93	0.3806	0.4684	0.2368	0.7104
21.27	294.42	0.5579	0.2973	0.4090	0.5313
26.42	299.57	0.5532	0.2947	0.4076	0.5294
36.80	309.95	0.5419	0.2887	0.4041	0.5249
46.25	319.40	0.5323	0.2836	0.4011	0.5209
52.52	325.67	0.5199	0.2770	0.3971	0.5157
61.09	334.24	0.5065	0.2698	0.3926	0.5099
23.20	296.35	0.5844	0.2304	0.4675	0.4492
31.20	304.35	0.5734	0.2260	0.4635	0.4453
40.24	313.39	0.5597	0.2206	0.4584	0.4404
46.28	319.43	0.5495	0.2166	0.4545	0.4367
54.41	327.56	0.5341	0.2105	0.4485	0.4309
63.81	336.96	0.5168	0.2037	0.4415	0.4242
24.18	297.33	0.6028	0.1828	0.5157	0.3812
31.22	304.37	0.5918	0.1794	0.5111	0.3778
40.45	313.60	0.5756	0.1745	0.5042	0.3727
50.23	323.38	0.5579	0.1691	0.4965	0.3669
56.07	329.22	0.5453	0.1654	0.4908	0.3628
60.00	333.15	0.5366	0.1627	0.4868	0.3598
22.80	295.95	0.6103	0.1125	0.5866	0.2636
26.28	299.43	0.6034	0.1112	0.5830	0.2620
31.00	304.15	0.5862	0.1080	0.5739	0.2578
42.40	315.55	0.5622	0.1036	0.5607	0.2519
54.65	327.80	0.5339	0.0984	0.5445	0.2446
67.40	340.55	0.5027	0.0926	0.5258	0.2362
24.85	298.00	0.5735	0.0607	0.6186	0.1595
28.20	301.35	0.5596	0.0592	0.6094	0.1572
35.15	308.30	0.5427	0.0574	0.5980	0.1542
47.83	320.98	0.5113	0.0541	0.5761	0.1486
59.22	332.37	0.4820	0.0510	0.5548	0.1430
21.40	294.55	0.0588	0.0006	0.0998	0.0024
31.51	304.66	0.0587	0.0006	0.0997	0.0026
38.69	311.84	0.0587	0.0007	0.0997	0.0029
46.03	319.18	0.0588	0.0008	0.0997	0.0032
54.00	327.15	0.0587	0.0009	0.0996	0.0037
61.40	334.55	0.0588	0.0011	0.0996	0.0044
23.00	296.15	0.1032	0.0007	0.1695	0.0030
30.64	303.79	0.1032	0.0008	0.1694	0.0034
41.51	314.66	0.1032	0.0011	0.1693	0.0043
47.38	320.53	0.1031	0.0012	0.1692	0.0046
54.80	327.95	0.1031	0.0014	0.1691	0.0055
62.05	335.20	0.1031	0.0015	0.1690	0.0062
20.85	294.00	0.1792	0.0013	0.2786	0.0050
32.40	305.55	0.1791	0.0016	0.2783	0.0061
39.54	312.69	0.1791	0.0019	0.2780	0.0070
45.00	318.15	0.1791	0.0021	0.2778	0.0079
53.23	326.38	0.1790	0.0024	0.2775	0.0090
58.40	331.55	0.1790	0.0027	0.2772	0.0101
19.20	292.35	0.2437	0.0020	0.3623	0.0073
33.98	307.13	0.2435	0.0028	0.3613	0.0100
39.80	312.95	0.2434	0.0036	0.3603	0.0128
45.83	318.98	0.2432	0.0042	0.3595	0.0150
52.45	325.60	0.2430	0.0050	0.3584	0.0180
65.40	338.55	0.2427	0.0065	0.3565	0.0234
16.26	289.41	0.3407	0.0052	0.4725	0.0175
30.19	303.34	0.3398	0.0079	0.4682	0.0265
45.82	318.97	0.3389	0.0103	0.4643	0.0345
57.20	330.35	0.3379	0.0134	0.4595	0.0446
65.85	339.00	0.3372	0.0156	0.4562	0.0514
22.60	295.75	0.4511	0.0138	0.5742	0.0429
30.82	303.97	0.4500	0.0163	0.5697	0.0504
38.00	311.15	0.4489	0.0188	0.5653	0.0578
45.15	318.30	0.4477	0.0216	0.5605	0.0659
50.63	323.78	0.4467	0.0238	0.5567	0.0722
55.10	328.25	0.4445	0.0284	0.5487	0.0854
60.62	333.77	0.4430	0.0316	0.5433	0.0945
20.27	293.42	0.5396	0.0395	0.6184	0.1104
25.24	298.39	0.5372	0.0439	0.6106	0.1217
36.51	309.66	0.5331	0.0512	0.5979	0.1400
44.55	317.70	0.5277	0.0607	0.5817	0.1632
56.85	330.00	0.5190	0.0763	0.5565	0.1995
63.33	336.48	0.5120	0.0889	0.5372	0.2273

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
30	303.2	0.0133	0.9846	0.0303	0.0006	0.0055	0.9940	0.0525	0.0025
		0.0228	0.9730	0.0589	0.0007	0.0095	0.9895	0.1000	0.0030
		0.0345	0.9592	0.1088	0.0008	0.0145	0.9840	0.1780	0.0030
		0.0459	0.9457	0.1738	0.0016	0.0195	0.9785	0.2710	0.0060
		0.0595	0.9301	0.2712	0.0040	0.0255	0.9720	0.3940	0.0140
		0.0739	0.9138	0.3631	0.0082	0.0320	0.9650	0.4930	0.0270
		0.0913	0.8965	0.4460	0.0170	0.0400	0.9570	0.5650	0.0525
		0.1104	0.8756	0.5049	0.0311	0.0490	0.9475	0.6000	0.0900
		0.1186	0.8655	0.5432	0.0482	0.0530	0.9430	0.6100	0.1320
		0.1328	0.8495	0.5734	0.0742	0.0600	0.9355	0.6020	0.1900
		0.2167	0.7502	0.5938	0.1123	0.1050	0.8860	0.5750	0.2650
		0.2297	0.7305	0.5949	0.1499	0.1130	0.8760	0.5390	0.3310
		0.3671	0.5692	0.5599	0.2622	0.2050	0.7750	0.4310	0.4920
		0.4696	0.4197	0.4696	0.4197	0.3020	0.6580	0.3020	0.6580[a]
45	318.2	0.0145	0.9813	0.0273	0.0006	0.0060	0.9930	0.0475	0.0025
		0.0227	0.9709	0.0589	0.0007	0.0095	0.9890	0.1000	0.0030
		0.0356	0.9560	0.1103	0.0013	0.0150	0.9830	0.1800	0.0050
		0.0491	0.9363	0.1684	0.0024	0.0210	0.9755	0.2630	0.0090
		0.0646	0.9149	0.2611	0.0056	0.0280	0.9670	0.3800	0.0200
		0.0862	0.8896	0.3130	0.0082	0.0380	0.9560	0.4380	0.0280
		0.1110	0.8575	0.4030	0.0154	0.0500	0.9420	0.5250	0.0490
		0.1290	0.8360	0.4317	0.0187	0.0590	0.9320	0.5490	0.0580
		0.1326	0.8287	0.4856	0.0341	0.0610	0.9290	0.5790	0.0990
		0.1559	0.8023	0.5133	0.0466	0.0730	0.9160	0.5870	0.1300
		0.2059	0.7501	0.5518	0.0921	0.1000	0.8880	0.5650	0.2300
		0.2727	0.6753	0.5662	0.1542	0.1400	0.8450	0.5150	0.3420
		0.3607	0.5634	0.5507	0.2467	0.2030	0.7730	0.4350	0.4750
		0.4670	0.3893	0.4670	0.3893	0.3120	0.6340	0.3120	0.6340[a]
60	333.2	0.0144	0.9729	0.0212	0.0007	0.0060	0.9910	0.0370	0.0030
		0.0238	0.9635	0.0560	0.0012	0.0100	0.9870	0.0950	0.0050
		0.0491	0.9343	0.1038	0.0015	0.0210	0.9750	0.1700	0.0060
		0.0534	0.9259	0.1614	0.0026	0.0230	0.9720	0.2530	0.0100
		0.0751	0.8965	0.2187	0.0046	0.0330	0.9600	0.3280	0.0170
		0.0899	0.8781	0.2978	0.0087	0.0400	0.9520	0.4200	0.0300
		0.1065	0.8580	0.3344	0.0123	0.0480	0.9430	0.4570	0.0410
		0.1082	0.8525	0.3764	0.0178	0.0490	0.9410	0.4950	0.0570
		0.1303	0.8273	0.4250	0.0262	0.0600	0.9290	0.5330	0.0800
		0.1866	0.7618	0.4706	0.0417	0.0900	0.8960	0.5560	0.1200
		0.2220	0.7242	0.4900	0.0540	0.1100	0.8750	0.5580	0.1500
		0.2380	0.7021	0.5186	0.0747	0.1200	0.8630	0.5580	0.1960
		0.2668	0.6615	0.5346	0.1082	0.1390	0.8400	0.5350	0.2640
		0.3610	0.5239	0.5271	0.1948	0.2120	0.7500	0.4550	0.4100
		0.4099	0.4615	0.5020	0.2607	0.2550	0.7000	0.3950	0.5000
		0.4648	0.3566	0.4648	0.3566	0.3240	0.6060	0.3240	0.6060[a]

[a] Critical point of solubility.

Auxiliary Information

Method/Apparatus/Procedure:

Solubility was measured by Alekseev's method.[1] Seven solubility temperature curves of constant alcohol–benzene ratio and another seven curves of constant alcohol–water ratio were constructed. Phase equilibrium was determined by comparison of density with calibration curves obtained for saturation solutions. Critical points of solubility were obtained by Alekseev's method.[1]

Source and Purity of Materials:

(1) source not specified; b.p = 63.85 °C at 750 Torr, d(30 °C,4 °C) = 0.7832, n(25 °C,D) = 1.3267.

(2) source not spcified; b.p. = 79.00 °C at 752 Torr, d(30 °C,4 °C) = 0.8680, n(25 °C,D) = 1.4980.

(3) not specified.

Estimated Error:

Not reported.

References:

[1] V. F. Alekseev, Gornyi Zh. **2**, 385 (1885).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **438-76**, 1–12 (1976).

Variables:
T/K=293

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)
20	293.2	0.331	0.626	0.176	0.811
		0.450	0.474	0.273	0.701
		0.528	0.362	0.359	0.599
		0.578	0.276	0.434	0.505
		0.614	0.191	0.516	0.392

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1 hydrocarbon-rich phase	x'_2 hydrocarbon-rich phase	x''_1 water-rich phase	x''_2 water-rich phase	w'_1 hydrocarbon-rich phase (compiler)	w'_2 hydrocarbon-rich phase (compiler)	w''_1 water-rich phase (compiler)	w''_2 water-rich phase (compiler)
20	293.2	0.0000	0.9974	0.0000	0.0004	0.0000	0.9994	0.0000	0.0017
		0.0192	0.9782	0.1538	0.0003	0.0080	0.9914	0.2441	0.0012
		0.0450	0.9508	0.3498	0.0015	0.0190	0.9800	0.4871	0.0051
		0.0674	0.9243	0.4814	0.0128	0.0290	0.9690	0.6040	0.0392
		0.1145	0.8711	0.5972	0.0560	0.0510	0.9454	0.6430	0.1470
		0.1775	0.7941	0.6320	0.1462	0.0834	0.9091	0.5678	0.3202
		0.4410	0.4820	0.4410	0.4820	0.2658	0.7081	0.2658	0.7081[a]

[a] Critical point of solubility.

Auxiliary Information

Method/Apparatus/Procedure:
The titration method was used to determine binodal curve. The synthetic method was used to determine phase equilibria. The mole fraction of hydrocarbon in the charge before separation was about 0.30. After separation phases were analyzed by glc to determine methanol and hydrocarbon; concentration of water was determined by the Karl Fischer method.

Source and Purity of Materials:
(1) source not specified.
(2) source not specified; distilled; purity>99.9%.
(3) not specified.

Estimated Error:
Not reported.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Benzene; C_6H_6 ; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
J. O. Triday, J. Chem. Eng. Data **29**, 321–4 (1984).

Variables:
T/K=293

Compiled By:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
24.8	293.0	0.0000	0.0004	0.0000	0.0017
		0.1277	0.0025	0.2050	0.0098
		0.1956	0.0028	0.2995	0.0105
		0.2271	0.0029	0.3404	0.0106
		0.2973	0.0042	0.4246	0.0146
		0.3445	0.0047	0.4772	0.0159
		0.4055	0.0055	0.5406	0.0179
		0.4473	0.0105	0.5751	0.0329
		0.4867	0.0187	0.6006	0.0563
		0.5284	0.0316	0.6196	0.0903
		0.5644	0.0443	0.6325	0.1210
		0.5896	0.0632	0.6280	0.1641
		0.6063	0.0862	0.6128	0.2124
		0.6151	0.1117	0.5909	0.2616
		0.6181	0.1371	0.5671	0.3066
		0.6060	0.1977	0.5057	0.4022
		0.5940	0.2282	0.4751	0.4450
		0.5816	0.2665	0.4417	0.4934
		0.5595	0.2965	0.4104	0.5302
		0.5378	0.3386	0.3754	0.5761
		0.5025	0.3880	0.3328	0.6264
		0.4357	0.4897	0.2607	0.7142
		0.3392	0.6072	0.1834	0.8003
		0.2884	0.6698	0.1483	0.8396
		0.2337	0.7341	0.1145	0.8767
		0.0895	0.8992	0.0391	0.9581
		0.0000	0.9974	0.0000	0.9994

Compositions of coexisting phases

t/°C (compiler)	T/K	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
24.8	293.0	0.0007	0.9967	0.0914	0.0020	0.0003	0.9991	0.1508	0.0080
		0.0055	0.9915	0.1603	0.0026	0.0023	0.9970	0.2515	0.0099
		0.0114	0.9852	0.2734	0.0036	0.0047	0.9945	0.3970	0.0127
		0.0199	0.9760	0.4322	0.0073	0.0083	0.9908	0.5649	0.0233
		0.0371	0.9574	0.5033	0.0245	0.0156	0.9831	0.6075	0.0721
		0.0667	0.9249	0.5547	0.0400	0.0287	0.9693	0.6303	0.1108
		0.1339	0.8500	0.6182	0.1279	0.0604	0.9355	0.5763	0.2907
		0.1708	0.8080	0.6187	0.1496	0.0793	0.9151	0.5556	0.3275
		0.1789	0.7986	0.6161	0.1698	0.0837	0.9104	0.5355	0.3598
		0.406	0.523	0.406	0.523	0.2359	0.7409	0.2359	0.7409[a]

[a] Author's plait point.

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine the binodal curve. Binary homogeneous samples of known composition were titrated in a thermostated glass-stoppered bottle with the small portions of the third component from Kimax microburette (with an accuracy of 0.01 cm^3). The mass of the titrant was calculated from its volume and density. Liquid–liquid equilibrium was measured in the thermostated cell of 250 cm^3 capacity with magnetic stirrer for the mixtures resulting equal volumes of both phases. After separation, both phases were analyzed by measuring the refractive indexes and comparing results with a calibration curve obtained earlier for saturated mixtures. Plait point was calculated by the author by the Hand's method.[1]

Source and Purity of Materials:

(1) AnalaR; distilled in a high-efficiency packed column; ρ(293 K)/(g cm^{-3})=0.7911, n(293 K)=1.3290.

(2) Merck, analytical-grade; certificated purity > 99.5%; used as received; ρ(293 K)/(g cm^{-3})=0.8790, n(293 K)=1.5011.

(3) de-ionized and distilled.

Estimated Error:

temp. ±0.1 K; composition ±0.0005 mole fraction.

References:

[1] D. B. Hand, J. Phys. Chem. **34**, 1961 (1930).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]

(2) Cyclohexene; C_6H_{10}; [110-83-8]

(3) Water; H_2O; [7732-18-5]

Evaluated by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.04)

3.5. Methanol + Water + Cyclohexene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system methanol–cyclohexene–water is given in Table 5.

TABLE 5. Summary of experimental data for the system methanol–cyclohexene–water

Author(s)	T/K	Type of data[a]	Ref.
Washburn *et al.*, 1940	298	sat. (16), eq. (7)	1
Budantseva *et al.*, 1976	293	sat. (6), eq. (9)	2

[a] Number of experimental points in parentheses.

Saturation curve

The system methanol–cyclohexene–water forms a large miscibility gap of type 1 covering the majority of the concentration triangle. Compositions along the saturation curves reported in both references were obtained by the titration method. Experimental data within each data set, measured at various temperatures, as well as between data sets, are consistent. Only one binary system, cyclohexene–water, forms miscibility gap. Binary data of this system were compiled and critically evaluated in a previously published SDS volume.[3] The recommended, Ref. 3, values of mutual solubility at 298 K are $x_2'=0.9983$ and $x_2''=0.000\ 035$. Budantseva *et al.*[2] report data of mutual solubility at 293.2 K which are almost equal $x_2'=0.9981$, $x_2''=0.000\ 05$. The saturation curves for both temperatures are located very closely to one to another, a temperature difference 5 K is not significant. Maximum methanol concentration on saturation curve is observed at the region close to $x_1=0.78$, $x_2=0.14$. All experimental data, reported at 293 and 298 K in the two references are treated as tentative.

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–cyclohexene–water were reported in both references. After separation, phases in equilibrium were analyzed. Washburn *et al.*[1] reported that the hydrocarbon-rich phase did not contain water, which presumably was the result of analytical limitations (self constructed refractive index–composition curve). Budantseva *et al.*[2] used more precise analytical methods (glc—for methanol and cyclohexene and the Karl Fischer—for water). Their results seem more reliable. The plait point of the system reported at 293.2 K,[1] was $x_1=0.504$, $x_2=0.477$. The miscibility gap of the binary cyclohexene–methanol system may exist at temperatures below 270 K, but this region was not studied in Ref. 4. The equilibrium data are treated as tentative. Experimental data of Budantseva *et al.*[2] at 293.2 K are presented in Fig. 2.

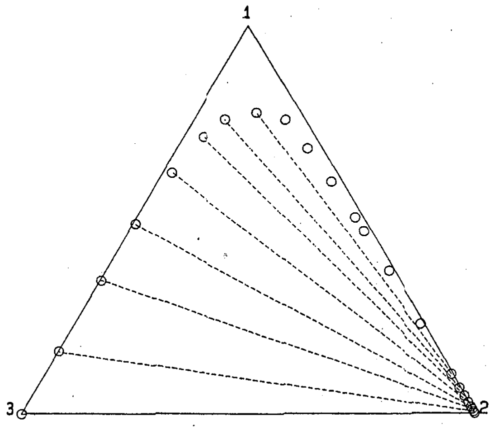

FIG. 2. Phase diagram of the system methanol (1)—cyclohexene (2)—water (3) at 293.2 K. ○—experimental data, Ref. 2, dashed lines—experimental tie lines, Ref. 2.

References:

[1]E. R. Washburn, C. L. Graham, G. B. Arnold, and L. F. Transue, J. Am. Chem. Soc. **62**, 1454 (1940).

[2]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **438-76**, 1 (1976).

[3]D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

[4]D. G. Shaw, A. Skrzecz, J. W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol. 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

Components:

(1) Methanol (mel alcohol); CH_4O; [67-56-1]
(2) Cyclohexene; C_6H_{10}; [110-83-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

E. R. Washburn, C. L. Graham, G. B. Arnold, and L. F. Transue, J. Am. Chem. Soc. **62**, 1454–7 (1940)

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.15	0.2372	0.7585	0.1086	0.8903
		0.3974	0.5937	0.2065	0.7909
		0.5341	0.4514	0.3143	0.6809
		0.6426	0.3366	0.4235	0.5688
		0.7308	0.2317	0.5430	0.4413
		0.7866	0.1397	0.6631	0.3020
		0.7761	0.0731	0.7404	0.1787
		0.7333	0.0401	0.7611	0.1067
		0.6709	0.0231	0.7436	0.0657
		0.6007	0.0117	0.7079	0.0352
		0.5175	0.0064	0.6456	0.0205
		0.4196	0.0025	0.5587	0.0087
		0.3429	0.0013	0.4796	0.0048
		0.2497	0.0005	0.3712	0.0020
		0.1574	0.0002	0.2492	0.0010
		0.0923	0.0001	0.1531	0.0005

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.15	0.0026	0.9974	0.0563	0.0000	0.001	0.999	0.096	0.000
		0.0051	0.9949	0.1086	0.0002	0.002	0.998	0.178	0.001
		0.0051	0.9949	0.1723	0.0002	0.002	0.998	0.270	0.001
		0.0077	0.9923	0.2018	0.0003	0.003	0.997	0.310	0.001
		0.0102	0.9898	0.2734	0.0008	0.004	0.996	0.400	0.003
		0.0302	0.9698	0.6373	0.0171	0.012	0.988	0.728	0.050
		0.0521	0.9479	0.7252	0.0372	0.021	0.979	0.760	0.100

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, as described in Ref. 1, was used. The titrant, from a weighed pipette, was added to the weighed binary mixture of known composition and the mixture was kept in a thermostated bath. To confirm that the end-point was reached the mixture was shaken automatically for at least 15 min and then reexamined. The plot of refractive index against composition was then used to find compositions of equilibrium phases. The refractive indexes were determined at the temperature of 30.0 °C to eliminate an opalescence.

Source and Purity of Materials:

(1) Eastman Kodak Company, commercial grade; dried by refluxing over active lime, twice distilled; d(25 °C,4 °C) =0.7866, n(25 °C,D)=1.326 59.

(2) Eastman Kodak Company, commercial grade; distilled in an atmosphere of purified N_2, collected in dried nitrogen-filled bottles; d(25 °C,4 °C)=0.8056, n(25 °C,D)=1.4434.

(3) not specified.

Estimated Error:

temp. ±0.05 °C.

References:

[1]E. R. Washburn and A. E. Beguin, J. Am. Chem. Soc. **62**, 579 (1940).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Cyclohexene; C_6H_{10}; [110-83-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **438–76**, 1–12 (1976).

Variables:
$T/\mathrm{K}=293$

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

$t/°\mathrm{C}$	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
20	293.2	0.230	0.761	0.105	0.892
		0.368	0.618	0.188	0.808
		0.469	0.513	0.261	0.733
		0.595	0.380	0.376	0.615
		0.680	0.287	0.474	0.513
		0.754	0.202	0.582	0.399

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
$t/°\mathrm{C}$	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
20	293.2	0.0000	0.9981	0.0000	0.00005	0.0000	0.9996	0.0000	0.00023
		0.0045	0.9937	0.1603	0.0005	0.0018	0.9978	0.2531	0.0020
		0.0103	0.9877	0.3437	0.0019	0.0040	0.9955	0.4797	0.0068
		0.0165	0.9813	0.4885	0.0058	0.0065	0.9930	0.6202	0.0189
		0.0284	0.9690	0.6185	0.0190	0.0113	0.9881	0.7101	0.0559
		0.0447	0.9522	0.7107	0.0435	0.0180	0.9813	0.7400	0.1161
		0.0655	0.9306	0.7561	0.0700	0.0267	0.9724	0.7317	0.1737
		0.1004	0.8945	0.7736	0.1295	0.0419	0.9569	0.6669	0.2862
		0.5040	0.4770	0.5040	0.4770	0.2901	0.7038	0.2901	0.7038[a]

[a] Critical point of solubility.

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine binodal curve. The synthetic method was used to determine phase equilibria. The mole fraction of hydrocarbon in the charge before separation was about 030. After separation phases were analyzed by glc to determine methanol and hydrocarbon; concentration of water was determined by the Karl Fischer method.

Source and Purity of Materials:
(1) source not specified.
(2) source not specified; distilled; purity > 99.9%.
(3) not specified.

Estimated Error:
Not reported.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.04)

3.6. Methanol + Water + Cyclohexane

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of methanol between phases (dist.) for the system methanol–cyclohexane–water is given in Table 5.

TABLE 6. Summary of experimental data for the system methanol–cyclohexane–water

Author(s)	T/K	Type of data[a]	Ref.
Washburn and Spencer, 1934	298	sat. (16), dist. (6)	1
Budantseva *et al.*, 1976	293	eq. (10)	2
Letcher *et al.*, 1991	298	sat. (12), eq. (3)	3
Plackov and Stern, 1992	298	sat. (14), eq. (7)	4

[a] Number of experimental points in parentheses.

Saturation curves

The system methanol–cyclohexane–water forms a large miscibility gap of type 2 covering the majority of the concentration triangle. Two binary systems, cyclohexane–water and cyclohexane–methanol, form miscibility gaps. The data of these binary systems were compiled and critically evaluated in previously published SDS volumes, Refs. 5 and 6, respectively. The recommended values[5] of mutual solubility of the cyclohexane–water system at 298.2 K are: $x''_2=1.2\cdot 10^{-5}$ and $x'_3=3.7\cdot 10^{-4}$. The mutual solubility at 298.2 K and upper critical solubility temperature of the methanol–cyclohexane system calculated on the basis of Ref. 6 are: $x'_1=0.128$ and $x''_1=0.822$ and 318.7 K. Reported data on the saturation curves describe mainly the cyclohexane-poor phase; there are few experimental points in the cyclohexane-rich region. Data for both temperatures are in agreement with one another with the exception of the Washburn and Spencer data[1] in the cyclohexane-rich phase, which presents too high concentration of water. All experimental solubility and equilibrium data at 298 K in cyclohexane-poor phase[1,3,4] were described by the equation:

$$x_1=1.07468+0.05543\ \ln(x_3)-1.07833x_3\,.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0030. The equation is valid in the region of $0.02<x_3<0.50$. The points on the saturation curve calculated by the above equation for the selected concentrations of water in the mixture together with the recommended data of binary systems are presented in Table 7 and in Fig. 3 as solid line.

TABLE 7. Calculated compositions along the saturation curve at 298.2 K

x_1	x_3	x_1	x_3
0.822	0.178 Ref. 6	0.6844	0.3000
0.8363	0.0200	0.6665	0.3200
0.8531	0.0400	0.6483	0.3400
0.8540	0.0600	0.6299	0.3600
0.8484	0.0800	0.6113	0.3800
0.8392	0.1000	0.5926	0.4000
0.8278	0.1200	0.5737	0.4200
0.8147	0.1400	0.5547	0.4400
0.8006	0.1600	0.5356	0.4600
0.7855	0.1800	0.5164	0.4800
0.7698	0.2000	0.4971	0.5000
0.7535	0.2200	0.0000	0.999988 Ref. 5
0.7368	0.2400	0.0000	0.00037 Ref. 5
0.7197	0.2600	0.128	0.0000 Ref. 6
0.7022	0.2800		

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–cyclohexane–water were reported in Refs 2, 3, and 4. In Ref. 1 the distribution of methanol between two phases (hydrocarbon-rich and hydrocarbon-poor) was reported. The lines reported by Letcher *et al.*[3] were measured at the pressure of 94.7 kPa, but the influence of such pressure difference (6.6 kPa) on liquid–liquid equilibria may be neglected. The experimental tie lines of Budantseva *et al.*, Ref. 2, even they were measured at 293.2 K, are in agreement with tie lines of Plackov and Stern,[4] measured at a little higher temperature of 298.2 K. The three tie lines presented by Letcher *et al*[3] were measured with the accuracy 0.01 mole fraction, as was reported in the paper and are not consistent with data of Ref. 4. Therefore data of Plackov and Stern,[4] in the opinion of evaluator, appear reliable and are considered as tentative. They are presented in Fig. 3.

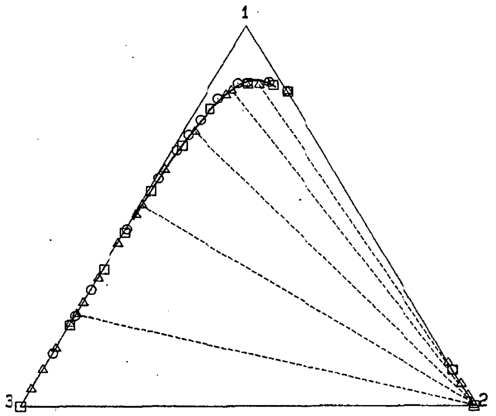

FIG. 3. Phase diagram of the system methanol (1)—cyclohexane (2)—water (3) at 298.2 K. ○—experimental data, Ref. 1, □—experimental data, Ref. 3, △—experimental data, Ref. 4, dashed lines—tie lines, Ref. 4.

References:

[1]E. R. Washburn and H. C. Spencer, J. Am. Chem. Soc. **56**, 361 (1934).

[2]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **433–76**, 1 (1976).

[3]T. M. Letcher, P. Siswana, and S. E. Radloff, S. Afr. J. Chem. **44**, 118 (1991).

[4]D. Plackov and I. Stern, Fluid. Phase Equilib. **71**, 189 (1992).

[5]D. G. Shaw, ed., *Solubility Data Series*, Vol 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon New York, 1989).

[6]D. G. Shaw, A. Skrzecz, J. W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3)Water; H_2O; [7732-18-5]

Original Measurements:

E. R. Washburn and H. C. Spencer, J. Am. Chem. Soc. 56, 361–4 (1934).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
25.0	298.2	0.1398	0.0002	0.2241	0.0010
		0.2372	0.0005	0.3556	0.0019
		0.3058	0.0008	0.4383	0.0031
		0.4663	0.0025	0.6043	0.0086
		0.5979	0.0056	0.7156	0.0176
		0.6699	0.0100	0.7645	0.0301
		0.7106	0.0151	0.7857	0.0437
		0.7504	0.0219	0.8018	0.0614
		0.8072	0.0340	0.8188	0.0906
		0.8464	0.0580	0.8041	0.1448
25.0	298.2	0.8491	0.0780	0.7754	0.1872
		0.8501	0.1237	0.7145	0.2731
		0.8264	0.1736	0.6445	0.3555
		0.0935	0.9065	0.0378	0.9622
		0.0395	0.9406	0.0157	0.9799
		0.0233	0.9683	0.0091	0.9891

Distribution of methanol in methanol–cyclohexane–water system

t/°C	T/K (compiler)	w_1' hydrocarbon-rich phase	w_1'' water-rich phase
25.0	298.2	0.0005	0.032
		0.0025	0.151
		0.0040	0.268
		0.0050	0.349
		0.0065	0.388
		0.0070	0.418

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to obtain points on the saturation curve. A flask containing weighted amounts of two liquids was suspended in a temperature controlled water bath and the third liquid added by means of a glass dropper which was thrust through a cork stopper. The flask was shaken after each addition of the third liquid and sufficient time allowed for equilibrium to be reached. In order to ensure complete saturation near the end-point, the bath was warmed a few tenths of a degree so that complete solution occurred and then cooled to 24.8 °C. The refractive index of each saturated mixture was measured. The tie lines were determined as recorded in Refs. 1 and 2. Refractive indexes and concentrations of methanol in phases in equilibrium were reported in the paper.

Source and Purity of Materials:

(1) synthetic from Merck Co.; refluxed over freshly ignited lime, distilled, $d(25\ °C,4\ °C)=0.786\ 73$, $n(25\ °C,D)=1.326\ 60$.
(2) Eastman Kodak Co., "best grade;" crystallized, distilled, dried over Na, distilled; $d(25\ °C,4\ °C)=0.773\ 54$, $n(25\ °C,D)=1.423\ 70$, f.p.$=6.10$ °C.
(3) distilled.

Estimated Error:

temp. ±0.1 °C (estimated by the compiler).

References:

[1]E. R. Washburn, V. Hnizda, and R. D. Vold, J. Am. Chem. Soc. **53**, 3237 (1931).
[2]R. D. Vold and E. R. Washburn, J. Am. Chem. Soc. **54**, 4217 (1932).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **438–76**, 1-12 (1976).

Variables:

T/K=293

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K(compiler)	x'_1 hydrocarbon-rich phase	x'_2 hydrocarbon-rich phase	x''_1 hydrocarbon-poor phase	x''_2 hydrocarbon-poor phase	w'_1 hydrocarbon-rich phase (compiler)	w'_2 hydrocarbon-rich phase (compiler)	w''_1 hydrocarbon-poor phase (compiler)	w''_2 hydrocarbon-poor phase (compiler)
20	293.2	0.0000	0.999 53	0.0000	0.000 015	0.0000	0.999 90	0.0000	0.000 070
		0.0030	0.9965	0.1935	0.0000	0.0011	0.9987	0.2991	0.0002
		0.0058	0.9937	0.3605	0.0005	0.0022	0.9977	0.4999	0.0018
		0.0086	0.9909	0.4990	0.0020	0.0033	0.9966	0.6358	0.0067
		0.0130	0.9861	0.6310	0.0062	0.0050	0.9948	0.7413	0.0191
		0.0181	0.9810	0.7284	0.0130	0.0070	0.9928	0.8023	0.0376
		0.0268	0.9723	0.8000	0.0253	0.0104	0.9894	0.8293	0.0689
		0.0394	0.9597	0.8409	0.0461	0.0154	0.9844	0.8200	0.1181
		0.0798	0.9193	0.8717	0.0808	0.0320	0.9678	0.7849	0.1911
		0.1390	0.8610	0.8570	0.1430	0.0579	0.9421	0.6953	0.3047

Auxiliary Information

Method/Apparatus/Procedure:

The synthetic method was used. The mole fraction of hydrocarbon in the charge before separation was about 0.30. After separation phases were analyzed by glc to determine methanol and hydrocarbon; concentration of water was determined by the Karl Fischer method.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified; distilled; purity >99.9%.
(3) not specified.

Estimated Error:

Not reported.

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. M. Letcher, P. Sisvana, and S. E. Radloff, S. Afr. J. Chem. **44**, 118–21 (1991).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C (compiler)	T/K	x_1	x_2	w_1	w_2
				(compiler)	
25.0	298.2	0.000	0.000	0.000	0.000
		0.212	0.001	0.323	0.004
		0.360	0.002	0.497	0.007
		0.457	0.003	0.595	0.010
		0.565	0.006	0.687	0.019
		0.682	0.016	0.763	0.047
		0.780	0.029	0.809	0.079
		0.845	0.080	0.770	0.191
		0.842	0.136	0.695	0.295
		0.825	0.175	0.642	0.358
		0.093	0.907	0.038	0.962
		0.000	0.999	0.0000	0.9998

Compositions of coexisting phases

t/°C (compiler)	T/K	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
25.0	298.2	0.025	0.974	0.323	0.001	0.010	0.990	0.458	0.004
		0.051	0.949	0.533	0.005	0.020	0.980	0.661	0.016
		0.074	0.926	0.737	0.023	0.030	0.970	0.790	0.065

Auxiliary Information

Method/Apparatus/Procedure:

The points on the binodal curve were determined by the titration method, as described in Ref. 1. The formation of a cloudy mixture was observed visually on shaking after addition of a known mass of the third component; syringes were precisely weighed. Tie line compositions were determined by the refractive index method,[2] and a complementary method using the Karl Fischer titration.[3] Measurements were made at pressure of 94.7 kPa.

Source and Purity of Materials:

(1) Merck; AR grade; refluxed with Mg and I_2, distilled; purity >99.9 mole % by glc.
(2) BDH; Gold label grade; used as received; purity >99.9 mole % by glc.
(3) not specified.

Estimated Error:

composition ± 0.005 mole fraction (birodal curve), ± 0.01 mole fraction (tie lines).

References:

[1] T. M. Letcher, S. Wootten, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037 (1986).
[2] S. W. Briggs and F. W. Comings, Ind. Eng. Chem. **35**, 411 (1993).
[3] T. M. Letcher, P. Siswana, P. van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053 (1989).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

D. Plackov and I. Stern, Fluid Phase Equilib. **71**, 189–209 (1992).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
				(compiler)	
25	298.2	0.1114	0.8886	0.0456	0.9544
		0.8250	0.1750	0.6422	0.3578
		0.8495	0.1195	0.7194	0.2658
		0.8462	0.0760	0.7766	0.1832
		0.8158	0.0472	0.8023	0.1219
		0.6196	0.0091	0.7270	0.0280
		0.5050	0.0033	0.6391	0.0110
		0.4289	0.0019	0.5689	0.0066
		0.3365	0.0010	0.4729	0.0037
		0.2713	0.0005	0.3978	0.0019
		0.2149	0.0004	0.3270	0.0016
		0.1524	0.0003	0.2421	0.0013
		0.0961	0.0003	0.1589	0.0013
		0.0454	0.0002	0.0779	0.0009

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
25	298.2	0.0006	0.9988	0.100	0.000	0.0002	0.9996	0.165	0.000
		0.0019	0.9975	0.242	0.001	0.0007	0.9991	0.361	0.004
		0.0047	0.9948	0.369	0.001	0.0018	0.9981	0.508	0.004
		0.0064	0.9931	0.529	0.005	0.0024	0.9974	0.658	0.016
		0.0097	0.9898	0.719	0.025	0.0037	0.9962	0.774	0.071
		0.0276	0.9720	0.828	0.053	0.0107	0.9892	0.801	0.135
		0.0567	0.9430	0.843	0.106	0.0224	0.9776	0.733	0.242

Auxiliary Information

Method/Apparatus/Procedure:

Binodal compositions were determined by titration with the corresponding, less-soluble component until the appearance of turbidity.[1] The analytical method was used for determination of tie-lines. This was based on refractive indexes and densities of the samples, Ref. 1, combined with the oxidation of the alcohol with an excess of potassium dichromate and determination of unreduced dichromate with $Na_2S_2O_3$. Alcohol in the organic layer was determined after extraction with water.

Source and Purity of Materials:

(1) Kemika (Zagreb); analytical grade; presumably used as received; $n=1.3624$, $\rho(25\ °C)=787.7$ kg/m^3, b.p.=64.6 °C.
(2) Kemika (Zagreb); purity not specified; presumably used as received; $n=1.4232$, $\rho(25\ °C)=773.9$ kg/m^3, b.p.=80.0 °C.
(3) twice distilled in the presence of $KMnO_4$.

Estimated Error:

composition < 0.0005 mass fraction, binodal, (relative); composition ± 2%, tie line.

References:

[1] D. Plackov and I. Stern, Fluid Phase Equilib. **57**, 327 (1990).

Components:
(1) Methanol (methyl alcohol);CH_4O; [67-56-1]
(2) 1-Hexene; C_6H_{12}; [592-41-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **438-76**, 1-12 (1976).

Variables:
T/K=293

Compiled by:
A. Skrzecz

3.7. Methanol + Water + 1-Hexene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
20	293.2	0.229	0.762	0.102	0.895
		0.392	0.593	0.200	0.795
		0.513	0.465	0.294	0.699
		0.614	0.357	0.392	0.598
		0.690	0.275	0.482	0.504
		0.746	0.203	0.570	0.408

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1 hydrocarbon-rich phase	x'_2 hydrocarbon-rich phase	x''_1 water-rich phase	x''_2 water-rich phase	w'_1 hydrocarbon-rich phase (compiler)	w'_2 hydrocarbon-rich phase (compiler)	w''_1 water-rich phase (compiler)	w''_2 water-rich phase (compiler)
20	293.2	0.0000	0.9984	0.0000	0.000 01	0.0000	0.999 66	0.0000	0.000 05
		0.0049	0.9937	0.1564	0.0000	0.0019	0.9978	0.2479	0.0002
		0.0120	0.9866	0.3359	0.0004	0.0046	0.9951	0.4730	0.0015
		0.0194	0.9792	0.4973	0.0021	0.0075	0.9922	0.6341	0.0070
		0.0359	0.9623	0.6227	0.0088	0.0140	0.9856	0.7300	0.0271
		0.0566	0.9407	0.7250	0.0218	0.0224	0.9770	0.7841	0.0619
		0.0830	0.9134	0.7703	0.0421	0.0334	0.9658	0.7810	0.1121
		0.1469	0.8468	0.7885	0.1038	0.0619	0.9366	0.7030	0.2431
		0.1988	0.7931	0.7736	0.1529	0.0869	0.9111	0.6359	0.3301
		0.5200	0.4580	0.5200	0.4580	0.2997	0.6932	0.2997	0.6932[a]

[a]Critical point of solubility.

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine binodal curve. The synthetic method was used to determine phase equilibria. The mole fraction of hydrocarbon in the charge before separation was about 0.30. After separation phases were analyzed by glc to determine methanol and hydrocarbon; concentration of water was determined by the Karl Fischer method.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified; distilled; purity >99.9%.
(3) not specified.

Estimated Error:

Not reported.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Hexane (n-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.04)

3.8. Methanol + Water + Hexane

Critical Evaluation

A survey of reported in the literature compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system methanol–hexane–water is given in Table 8.

TABLE 8. Summary of experimental data for the system methanol–hexane–water

Author(s)	T/K	Type of data[a]	Ref.
Bonner, 1909	273	sat. (11)	1
Suhrmann and Walter, 1951	311–323	sat. (7)	2
Kogan *et al.*, 1956	283,293	Eq. (9)	3
Budantseva *et al.*, 1976	293	Eq. (10)	4

[a]Number of experimental points in parentheses.

Saturation curve

The system methanol–hexane–water forms a large miscibility gap of type 2 covering the majority of the concentration triangle. Two binary systems, hexane–water and hexane–methanol, are partially miscible at the reported temperatures. The data for these binary systems were compiled and critically evaluated in previously published SDS volumes, Refs. 5 and 6, respectively. The recommended, values[5] of mutual solubility for the hexane water system at 293.2 K are: $x'_2=0.999\ 47$ and $x''_2=2.5\cdot 10^{-6}$. The binary data reported in Ref. 4, $x'_2=0.999\ 63$ and $x''_2=3\cdot 10^{-6}$, are in very close agreement. The recommended upper critical solution temperature and mutual solubilities at 293.2 K of the methanol–hexane system calculated on the basis of Ref. 6 are: 306.8 K and $x'_1=0.210$, $x''_1=0.822$. These recommended solubilities are exactly the mean value of experimental data reported in Refs. 3 and 4 which were also used in evaluation of the binary system. Concentration differences, in mole fraction, in hexane-rich phase are about 0.03 and in hexane-poor phase—0.006 and 0.02. Measurements along the saturation curve only were reported by Bonner[1] at 273 K and Suhrmann and Walter[2] in the range 311–323 K. This last paper shows the influence of water on the upper critical solution temperature of the system methanol–hexane. In the other studies phases in equilibrium were presented which may also be treated as points on saturation curve. The data for the hydrocarbon-poor phase on the saturation curve[3,4] in the region $x_3<0.33$ were described by the equation:

$$x=1.08162+0.04830\ \ln(x_3)-1.09286x_3\,.$$

The least-squares method was used and the standard error of estimate was 0.0026. For the selected concentrations of water in the mixture this part of saturation curve was calculated and the results are presented in Table 9 and in Fig. 4 as solid line. The part of the saturation curve (hydrocarbon-poor branch) in the region of $x_1<0.65$ presents very low concentration of hydrocarbon and on the basis of reported papers the relationship between concentrations of methanol and hexane may be treated as linear. The maximum concentration of methanol in hexane-poor phase of saturation curve, estimated on the basis of Ref. 4, is $x_1=0.88$ and $x_2=0.08$ within an accuracy 0.01 mole fraction. The experimental points of hexane-rich branch of saturation curve contain a very small amount of water and therefore were not described (concentration of water was smaller than 0.0001 mass fraction, Ref. 3).

TABLE 9. Calculated compositions along the saturation curve at 293.2 K (hexane-poor phase)

x_1	x_3	x_1	x_3
0.210	0.0000 Ref. 6	0.8021	0.1800
0.822	0.0000 Ref. 6	0.7853	0.2000
0.8483	0.0100	0.7681	0.2200
0.8708	0.0200	0.7504	0.2400
0.8824	0.0400	0.7324	0.2600
0.8802	0.0600	0.7141	0.2800
0.8722	0.0800	0.6956	0.3000
0.8611	0.1000	0.6769	0.3200
0.8481	0.1200	0.0000	0.999 997 5 Ref. 5
0.8337	0.1400	0.0000	0.000 53 Ref. 5
0.8183	0.1600		

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–hexane–water were reported in Refs. 3 and 4 at 283.2 and 293.2 K, respectively. The phases, when equilibrium was reached, were separated and then analyzed in various ways: methanol was determined by reaction with phthalic anhydride, Ref. 3, or by glc, Ref. 4; water was determined by the Karl Fischer reaction.[3,4] The compositions of phases in equilibrium reported in both Refs. 3 and 4 are consistent with one another. They are presented in Fig. 4.

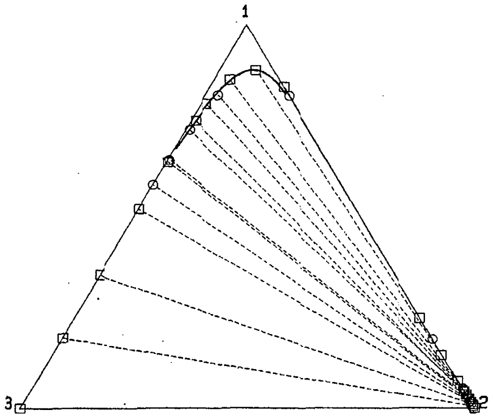

FIG. 4. Phase diagram of the system methanol (1)—hexane (2)—water (3) at 293.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 3, □—experimental data, Ref. 4, dashed lines—experimental tie lines, Refs. 3 and 4.

References:

[1] W. D. Bonner, J. Phys. Chem. 14, 738 (1909–1910).
[2] R. Suhrmann and R. Walter, Abh. Braunschw. Wiss. Ges. 3, 135 (1951).
[3] V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim (Leningrad) 29, 1387 (1956).
[4] L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI 433–76, 1 (1976).
[5] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).
[6] D. G. Shaw, A. Skrzecz, J. W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol. 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910).

Variables:

T/K=273

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)
0.0	273.2	0.9018	0.0731	0.8106	0.1767
		0.8950	0.0549	0.8358	0.1379
		0.8762	0.0394	0.8510	0.1030
		0.8674	0.0303	0.8619	0.0809
		0.8540	0.0245	0.8642	0.0667
		0.8288	0.0172	0.8619	0.0481
		0.8256	0.0163	0.8615	0.0457
		0.7857	0.0106	0.8459	0.0308
		0.7650	0.0096	0.8337	0.0283
		0.7040	0.0064	0.7964	0.0193
		0.5004	0.0017	0.6375	0.0058

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogenous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled; n(14 °C) =1.330 70.
(2) Kahlbaum; presumably dried and distilled; n(14 °C) =1.383 82.
(3) not specified.

Estimated Error:

accuracy of weighing 0.0001 g.

Components:

(1) Methanol (methyl alcohol);CH_4O; [67-56-1]
(2) Hexane (n-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

R. Sahrmann and R. Walter, Abh. Braunschw. Wiss. Ges. **3**, 135–52 (1951).

Variables:

$T/K=311-323$

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

$t/°C$	T/K (compiler)	vol% of H_2O	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)
38.1	311.25	0.173	0.5299	0.4680	0.2961	0.7033
40.0	313.15	0.276	0.5293	0.4675	0.2960	0.7030
42.0	315.15	0.378	0.5286	0.4669	0.2958	0.7028
44.1	317.25	0.476	0.5280	0.4664	0.2957	0.7025
48.0	321.15	0.667	0.5268	0.4653	0.2955	0.7020
48.1	321.25	0.680	0.5267	0.4652	0.2955	0.7019
50.1	323.25	0.778	0.5261	0.4647	0.2954	0.7017

Auxiliary Information

Method/Apparatus/Procedure:

To the binary methanol–hexane mixture of constant composition (74.1 vol. % of hexane) known amounts of water were added and the turbidity temperature was measured. A linear relationship was obtained for change of turbidity temperature with number of moles of water in 1000 moles of methanol.

Source and Purity of Materials:

(1) Riedel de Haen and Merck, pure for analysis grade; dried over CaO for 2 weeks, distilled over $Mg(ClO_4)_2$; b.p. =64.78 °C, n(18 °C,D)=1.3292, d(16.3 °C,4 °C) =0.7950–0.7955.
(2) Ruhrchemie Holten; distilled three times; b.p.=68.8 °C, d(20 °C,4 °C)=0.6608.
(3) not specified.

Estimated Error:

temp. ±0.1 °C.

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim. (Leningrad) **29**, 1387–92 (1956).

Variables:

$T/K=283-293$

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

$t/ °C$	T/K (compiler)	x'_1 hydrocarbon-rich phase (compiler)	x'_2 hydrocarbon-rich phase (compiler)	x''_1 hydrocarbon-poor phase (compiler)	x''_2 hydrocarbon-poor phase (compiler)	w'_1 hydrocarbon-rich phase	w'_2 hydrocarbon-rich phase	w''_1 hydrocarbon-poor phase	w''_2 hydrocarbon-poor phase
10.0	283.15	0.1217	0.8783	0.8748	0.1252	0.049	0.951	0.722	0.278
		0.0342	0.9658	0.8236	0.0201	0.013	0.987	0.853	0.056
		0.0251	0.9749	0.7303	0.0067	0.0095	0.9905	0.815	0.020
		0.0064	0.9936	0.5840	0.0000	0.0024	0.9976	0.714	0.000
20.0	293.15	0.1811	0.8189	0.8157	0.1843	0.076	0.924	0.622	0.378
		0.0520	0.9480	0.8177	0.0278	0.020	0.980	0.835	0.0763
		0.0470	0.9530	0.7270	0.0080	0.018	0.982	0.810	0.024
		0.0316	0.9684	0.6480	0.0032	0.012	0.988	0.760	0.010
		0.0186	0.9814	0.5829	0.0006	0.007	0.993	0.712	0.002

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. The two phase mixture was periodically shaken in a thermostated burette with water jacket for several hours. The phases were removed for analysis after separation. Methanol was determined by reaction with phthalic anhydride; water was determined by the Karl Fischer method. Water concentration in hydrocarbon-rich phase was smaller than 0.01–0.02%.

Source and Purity of Materials:

(1) source not specified, pure grade; distilled; contained <0.01% of water; n(20 °C)=1.3391.
(2) source not specified; used as received; b.p.=68.7 °C, n(20 °C)=1.3753.
(3) not specified.

Estimated Error:

temp. ±0.05 °C; soly.<±1% (relative error of methanol concentration).

Components:
(1) Methanol (methyl alcohol); CH^{4}O; [67-56-1]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **438-76**, 1–12 (1976).

Variables:
T/K=293

Compiled by:
A. Skrzecz

Experimental Data

Compositions of coexisting phases

		x_1'	x_2'	x'	x_2''	w_1'	w_2'	w_1''	w_2''
t/ °C	T/K (compiler)	hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
20	293.2	0.0000	0.99963	0.0000	0.000003	0.0000	0.99992	0.0000	0.000014
		0.0051	0.9944	0.1847	0.0000	0.0019	0.9980	0.2872	0.0001
		0.0099	0.9896	0.3497	0.0001	0.0037	0.9962	0.4887	0.0004
		0.0160	0.9835	0.5206	0.0008	0.0060	0.9939	0.6575	0.0027
		0.0246	0.9749	0.6428	0.0025	0.0093	0.9906	0.7572	0.0079
		0.0362	0.9629	0.7513	0.0091	0.0138	0.9860	0.8252	0.0269
		0.0444	0.9547	0.7958	0.0126	0.0170	0.9828	0.8489	0.0362
		0.0718	0.9268	0.8576	0.0336	0.0280	0.9717	0.8498	0.0895
		0.1394	0.8590	0.8822	0.0785	0.0569	0.9427	0.7909	0.1893
		0.2360	0.7640	0.8390	0.1610	0.1030	0.8970	0.6596	0.3404

Auxiliary Information

Method/Apparatus/Procedure:

The synthetic method was used. The mole fraction of hydrocarbon in the charge before separation was about 0.30. After separation phases were analyzed by glc to determine methanol and hydrocarbon; concentration of water was determined by the Karl Fischer method.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified; distilled; purity >99.9%.
(3) not specified.

Estimated Error:

Not reported.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Toluene (methylbenzene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.03)

3.9. Methanol + Water + Toluene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of methanol between phases (distr.) for the system methanol–toluene–water is given in Table 10.

TABLE 10. Summary of experimental data for the system methanol–toluene–water

Author(s)	T/K	Type of data[a]	Ref.
Mason and Washburn, 1937	298	sol. (13), distr. (7)	1
Leikola, 1940	293	sol. (8)	2
Letcher and Siswana, 1992	298	sol. (14), Eq. (6)	3

[a] Number of experimental points in parentheses.

Saturation curve

The system methanol–toluene–water forms a miscibility gap of type 1. Only one binary system, toluene–water, is partially miscible. Data for this system were compiled and critically evaluated in a previously published SDS volume.[4] The recommended values of mutual solubility of toluene–water system at 298.2 K are: $x_2'=0.9972$ and $x_2''=0.000104$, by Ref. 4. This critical evaluation is based on the original papers with the exception of data of Leikola,[2] which were taken from the handbook of Kafarov;[5] this data set was also taken into account during evaluation but is not reported as a compilation sheet because it does not contribute further to knowledge of the system. The end points of saturation curve[3] were reported to be $x_2=0.999$ and pure water which is inconsistent with recommended values but within the accuracy of experimental measurements (0.001 mole fraction) stated by the authors. The experimental saturation data reported in Refs. 1 and 3 at 298.2 K show similar behavior of the system with differences in the most difficult to measure region, close to the plait point. In this region, $0.15<x_2<0.6$, Mason and Washburn[1] reported a slightly larger miscibility gap (about 0.04 mole fraction of water) than did Letcher and Siswana.[3] Leikola[2] at 293.2 K presents a smaller solubility gap than Ref. 1, but a little larger than Ref. 3. It seems, that results of Letcher and Siswana[3] at 298 K are the most reasonable. Therefore only data of Ref. 3 presenting saturation and equilibrium data were used to derive the equation:

$$x_1=1.0652+0.1260\ \ln(x_2)-1.1183x_2+0.0591x_2^2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0070. The equation is valid in the region of $0.02<x_2<0.94$. Selected points on the saturation curve, calculated by this equation together with the "best" values of Ref. 4 are presented in Table 11 and as solid line in Fig. 5. The water-rich branch of saturation curve contains only a small amount of toluene ($x_2<0.0001$) and toluene was not detected in either study. These experimental points are not described by any model. The maximum methanol concentration observed on the saturation curve at 298 K was $x_1=0.68\pm0.01$.

TABLE 11. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x	x_2
0.0000	0.000 104 Ref. 4	0.4335	0.500
0.5499	0.020	0.4173	0.520
0.6150	0.040	0.4009	0.540
0.6438	0.060	0.3844	0.560
0.6579	0.080	0.3678	0.580
0.6638	0.100	0.3511	0.600
0.6647	0.120	0.3343	0.620
0.6621	0.140	0.3175	0.640
0.6569	0.160	0.3005	0.660
0.6498	0.180	0.2835	0.680
0.6411	0.200	0.2664	0.700
0.6313	0.220	0.2493	0.720
0.6204	0.240	0.2321	0.740
0.6087	0.260	0.2148	0.760
0.5963	0.280	0.1976	0.780
0.5833	0.300	0.1803	0.800
0.5698	0.320	0.1629	0.820
0.5559	0.340	0.1456	0.840
0.5415	0.360	0.1282	0.860
0.5269	0.380	0.1108	0.880
0.5119	0.400	0.0933	0.900
0.4966	0.420	0.0759	0.920
0.4811	0.440	0.0584	0.940
0.4654	0.460	0.0000	0.9972 Ref. 4
0.4496	0.480		

Phases in equilibrium

Compositions of coexisting phases in equilibrium of the ternary system methanol–toluene–water were reported only in Ref. 3. The tie lines are consistent with one another. They are considered tentative. Experimental tie lines together with all experimental saturation points at 298.2 K are presented in Fig. 5. The calculated plait point of the system at 293.2 K, Ref. 3, was $x_1=0.43$, $x_2=0.50$.

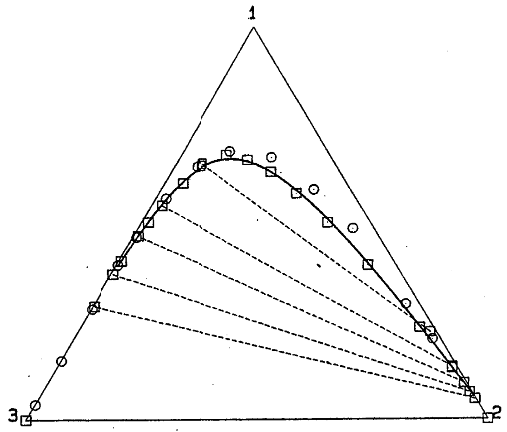

FIG. 5. Phase diagram of the system methanol (1)—toluene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 1, □—experimental data, Ref. 3, dashed lines—experimental tie lines, Ref. 3.

References:

[1] L. S. Mason and E. R. Washburn, J. Am. Chem. Soc. **59**, 2076 (1937).

[2] E. Leikola, Suomen Kemistil. B **13**, 13 (1940).

[3] T. M. Letcher and P. M. Siswana, Fluid Phase Equilib. **74**, 203 (1992).

[4] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon New York, 1989).

[5] V. V. Kafarov, ed., *Spravochnik po Rastvorimosti*, Vol. 2, Troinye, Mnogokomponentnye Sistemy, Kniga II (Izd. Akademii Nauk SSSR, Moskva, 1963).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Toluene (methylbenzene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. S. Mason and E. R. Washburn, J. Am. Chem. Soc. 59, 2076–7 (1937).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25	298.2	0.2040	0.7785	0.0832	0.9128
		0.2937	0.6766	0.1302	0.8624
		0.4869	0.4675	0.2622	0.7240
		0.5867	0.3343	0.3684	0.6037
		0.6686	0.2021	0.5056	0.4394
		0.6841	0.1033	0.6215	0.2699
		0.6454	0.0491	0.6735	0.1472
		0.5648	0.0215	0.6573	0.0720
		0.4657	0.0077	0.5940	0.0283
		0.3948	0.0035	0.5312	0.0137
		0.2828	0.0012	0.4106	0.0050
		0.1510	0.0003	0.2400	0.0014
		0.0389	0.0001	0.0672	0.0006

Distribution of methanol in methanol–toluene–water system

t/°C	T/K (compiler)	w_1' hydrocarbon-rich phase	w_1'' water-rich phase
25	298.2	0.000	0.025
		0.001	0.101
		0.002	0.154
		0.002	0.220
		0.004	0.322
		0.008	0.406
		0.022	0.428

Auxiliary Information

Method/Apparatus/Procedure:
The titration method was used. Water was added to binary alcohol–toluene mixtures of known composition until the saturation point was reached. The refractive indexes of these mixtures were determined with an immersion refractometer and then were used to construct the refractive index/composition curve, which was used further to find compositions of equilibrium phases.

Source and Purity of Materials:
(1) synthetically prepared; dried over lime, distilled; $d(25\ ^\circ C, 4\ ^\circ C)=0.78672$, $n(25\ ^\circ C, D)=1.326\ 60$.
(2) Mallinckrodt, reagent grade; dried over Na, distilled; $d(25\ ^\circ C, 4\ ^\circ C)=0.862\ 16$, $n(25\ ^\circ C, D)=1.493\ 75$.
(3) distilled from $KMnO_4$.

Estimated Error:
Not reported.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Toluene (methylbenzene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
T. M. Letcher and P. M. Siswana, Fluid Phase Equilib. 74, 203–17 (1992).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25.0	298.2	0.000	0.000	0.000	0.000
		0.405	0.006	0.538	0.023
		0.504	0.014	0.618	0.049
		0.604	0.038	0.660	0.119
		0.648	0.057	0.663	0.168
		0.675	0.100	0.620	0.264
		0.662	0.153	0.549	0.365
		0.632	0.219	0.470	0.468
		0.577	0.301	0.382	0.573
		0.502	0.406	0.292	0.678
		0.393	0.546	0.197	0.786
		0.234	0.736	0.099	0.894
		0.130	0.857	0.050	0.947
		0.000	0.999	0.000	0.9998

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.000	0.999	0.000	0.000	0.000	0.9998	0.000	0.000
		0.051	0.946	0.290	0.002	0.018	0.981	0.418	0.008
		0.068	0.926	0.372	0.004	0.025	0.974	0.507	0.016
		0.092	0.902	0.469	0.010	0.034	0.965	0.593	0.036
		0.133	0.856	0.547	0.022	0.051	0.946	0.642	0.074
		0.222	0.765	0.653	0.057	0.091	0.906	0.666	0.167

Auxiliary Information

Method/Apparatus/Procedure:

The points on the binodal curve were determined by the formation of a cloudy mixture on shaking after the addition of a known mass of one component to a mixture of known masses of the other two components. Precision weighing syringes were used as described in Ref. 1. Tie line compositions were determined by the refractive index method reported in Ref. 2 and a complementary method using the Karl Fischer titrations as reported in Ref. 3.

Source and Purity of Materials:

(1) Merck, AR grade; distilled, dried by refluxing with Mg and I_2; purity better than 99.6 mole % by glc; $d=0.786\ 88$, $n=1.3265$.
(2) BDH; used as received; purity better than 99.6 mole % by glc.
(3) not specified.

Estimated Error:

estimated comp. 0.005 mole fraction on the binodal curve and 0.01 mole fraction for tie lines (estimated by the authors).

References:

[1] T. M. Letcher, S. Wootten, B. Shuttleworth, and C. Heward, J. Chem. Thermodyn. 18, 1037 (1986).
[2] S. W. Briggs and E. W. Comings, Ind. Eng. Chem. 35, 411 (1943).
[3] T. M. Letcher, P. M Siswana, P. Van der Watt, and S. Radloff, J. Chem. Thermodyn. 21, 1053 (1989).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) 1-Heptene; C_7H_{14}; [592-76-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. M. Letcher, B. C. Bricknell, J. D. Sewry, and S. E. Radloff, J. Chem. Eng. Data 39, 320–3 (1994).

Variables:

$T/K=298$

Compiled by:

A. Skrzecz

3.10. Methanol + Water + 1-Heptene

Experimental Data

Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25.0	298.2	0.000	1.000	0.000	1.000
		0.264	0.731	0.105	0.894
		0.454	0.539	0.215	0.783
		0.601	0.390	0.334	0.664
		0.707	0.283	0.448	0.549
		0.772	0.210	0.542	0.451
		0.805	0.165	0.606	0.381
		0.834	0.102	0.705	0.264
		0.827	0.053	0.782	0.154
		0.750	0.020	0.797	0.065
		0.554	0.012	0.664	0.044
		0.396	0.010	0.521	0.040
		0.239	0.006	0.351	0.027
		0.049	0.001	0.084	0.005
		0.000	0.000	0.000	0.000

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
$t/°C$	T/K (compiler)	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.375	0.618	0.690	0.301	0.165	0.833	0.427	0.570
		0.240	0.754	0.805	0.165	0.094	0.905	0.606	0.381
		0.184	0.811	0.757	0.020	0.069	0.930	0.802	0.065
		0.116	0.881	0.571	0.017	0.041	0.958	0.668	0.061

Auxiliary Information

Method/Apparatus/Procedure:

The experimental methods have been described in Ref. 1. No more details were reported in the paper.

Source and Purity of Materials:

(1) source not specified.
(2) Aldrich; distilled; purity >99.8 mole % by glc., $\rho=0.692\ 65\ g\ cm^{-3}$.
(3) not specified.

Estimated Error:

Not reported.

[1] T. M. Letcher and P. M. Siswana, Fluid Phase Equilib. 74, 203 (1992).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Evaluated by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.03)

3.11. Methanol + Water + Heptane

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system methanol–heptane-water is given in Table 12.

TABLE 12. Summary of experimental data for the system methanol–heptane–water

Author(s)	T/K	Type of data[a]	Ref.
Bonner, 1909	273	sat. (7)	1
Kogan *et al.*, 1956	283, 293	Eq. (8)	2
Budantseva *et al.*, 1976	293, 313	Eq. (19)	3
Letcher *et al.*, 1986	298	sat. (8), Eq. (3)	4

[a]Number of experimental points in parentheses.

Saturation curve

The ternary system methanol–heptane–water forms a very large miscibility gap of type 2 covering the majority of the concentration triangle. The system was studied at five temperatures in the range 273.2–298.2 K. Two binary systems, heptane–water and methanol–heptane form miscibility gap at the reported temperatures. Data for these binaries were compiled and critically evaluated in previously published SDS volumes, Refs. 5 and 6, respectively. In the binary methanol–heptane system the upper critical solution temperature is 324.3±0.2 K.[6] This may be a reason for the large dispersion of solubility reported in the ternary system at temperatures over 300 K. Kogan *et al.*,[2] Budantseva *et al.*,[3] and Letcher *et al.*,[4] also report mutual solubility data for the binary methanol–heptane system; Refs. 3 and 4 report the same methanol concentration (0.176 mole fraction) at 293 and 298 K, respectively. Recommended solubilities of the binaries differ from those reported for the ternary system. The ternary data lack of one component in the phase. This is the result of very low concentrations (<0.001 mole fraction). The ternary solubilities reported in all data sets are consistent with one another. The data are considered tentative. The temperature 293.2 K was selected for presentation of the system behavior. The experimental saturation curve at 293.2 K is presented in Fig. 6. At this temperature the recommended values of mutual solubility are $x_2''=4.3\cdot 10^{-7}$, $x_3'=5.0\cdot 10^{-4}$, Ref. 5, for heptane–water system and $x_1''=0.1364$, $x_1'=0.9037$, Ref. 6, for methanol–heptane system. A fitting equation for the saturation curve was not derived because of the law quality of the experimental data. In a few studies the ternary compositions were reported as the binaries, the concentration of the third component was not detectable by the analytical method used. This situation was observed in hydrocarbon-rich phase as well as in hydrocarbon-poor phase.

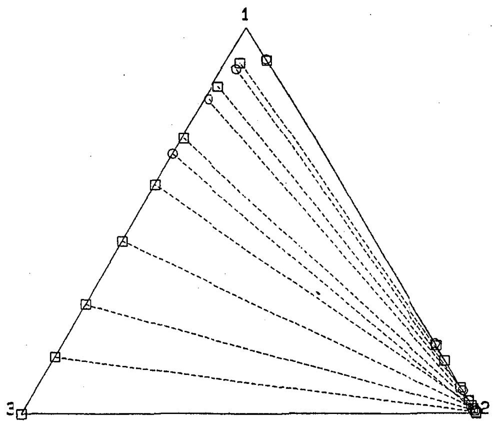

FIG. 6. Phase diagram of the system methanol (1)—heptane (2)—water (3) at 293.2 K. ○—experimental data, Ref. 2, □—experimental data, Ref. 3, dashed lines—experimental tie lines, Refs. 2 and 3.

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–heptane–water were reported in the temperature range 283–313 K. The tie lines cover the whole area of miscibility gap. The reported equilibrium data sets are consistent with one another. All experimental points at 293.2 K, Refs. 2 and 3, are reported in Fig. 6.

References:

[1]W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).
[2]V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim. (Leningrad) **29**, 1387 (1956).
[3]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **437-76**, 1 (1976).
[4]T. M. Letcher, S. Wootton, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn **18**, 1037 (1986).
[5]D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).
[6]D. G. Shaw, A. Skrzecz, I. W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol. 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910).

Variables:
T/K=273

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
0.0	273.2	0.9283	0.0600	0.8270	0.1671
		0.9217	0.0434	0.8557	0.1261
		0.9109	0.0363	0.8641	0.1077
		0.9045	0.0263	0.8818	0.0803
		0.9010	0.0210	0.8915	0.0651
		0.8908	0.0155	0.8980	0.0490
		0.8610	0.0112	0.8895	0.0362
		0.8183	0.0077	0.8703	0.0257
		0.6321	0.0026	0.7475	0.0096

Auxiliary Information

Method/Apparatus/Procedure:
In a tube 1 cm diam and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water-hydrocarbon mixture and the weight of alcohol necessary to make a homogeneous solution. The mass of binary water-hydrocarbon mixture was about 1 g; the mass of alcohol–up to 5 g.

Source and Purity of Materials:
(1) Kahlbaum; presumably dried and distilled; n(14 °C) =1.330 70.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:
accuracy of weighing 0.0001 g.

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim. (Leningrad) **29**, 1387–92 (1956).

Variables:
T/K=283–293

Compiled by:
A. Skrzecz

Experimental Data
Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)		hydrocarbon-rich phase		hydrocarbon-poor phase	
10.0	283.15	0.1099	0.8901	0.9217	0.0783	0.038	0.962	0.790	0.210
		0.0246	0.9754	0.8491	0.0177	0.008	0.992	0.867	0.0565
		0.0124	0.9876	0.7706	0.0053	0.004	0.996	0.844	0.018
		0.0093	0.9907	0.6988	0.0025	0.003	0.997	0.799	0.009
20.0	293.15	0.1810	0.8190	0.9159	0.0841	0.066	0.934	0.777	0.223
		0.0600	0.9400	0.8893	0.0322	0.020	0.980	0.860	0.0973
		0.0336	0.9664	0.8095	0.0096	0.011	0.989	0.860	0.032
		0.0065	0.9935	0.6672	0.0000	0.0021	0.9979	0.781	0.000

Auxiliary Information

Method/Apparatus/Procedure:
The analytical method was used. The two phase mixture was periodically shaken in a thermostated burette with water jacket for several hours. The phases were removed for analysis after separation. Methanol was determined by reaction with phthalic anhydride; water was determined by the Karl Fischer method. Water concentration in hydrocarbon-rich phase was smaller than 0.01–0.02%.

Source and Purity of Materials:
(1) source not specified, pure grade; distilled; contained <0.01% of water; n(20 °C)=1.3391.
(2) source not specified; used as received; b.p.=98.4 °C, n(20 °C)=1.3877.
(3) not specified.

Estimated Error:
temp. ±0.05 °C; soly. <±1% (relative error of methanol concentration).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **437–76**, 1-13 (1976).

Variables:

T/K=293–313

Compiled By:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
20	293.2	0.0000	0.9995	0.0000	0.000 003	0.0000	0.999 91	0.0000	0.000 02
		0.0031	0.9964	0.1473	0.000 02	0.0010	0.9989	0.2350	0.000 10
		0.0072	0.9922	0.2841	0.0001	0.0023	0.9976	0.4136	0.0005
		0.0133	0.9861	0.4468	0.0002	0.0043	0.9956	0.5892	0.0008
		0.0215	0.9779	0.5895	0.0009	0.0070	0.9929	0.7166	0.0034
		0.0336	0.9658	0.7075	0.0040	0.0110	0.9889	0.8020	0.0142
		0.0676	0.9314	0.8431	0.0154	0.0227	0.9771	0.8684	0.0496
		0.1373	0.8612	0.9053	0.0334	0.0485	0.9512	0.8670	0.1000
		0.1760	0.8240	0.9120	0.0880	0.0639	0.9361	0.7682	0.2318
40	313.2	0.0000	0.9993	0.0000	0.000 01	0.0000	0.999 87	0.0000	0.000 06
		0.0041	0.9950	0.1508	0.000 02	0.0013	0.9985	0.2400	0.000 10
		0.0100	0.9889	0.3119	0.0001	0.0032	0.9966	0.4462	0.0004
		0.0168	0.9819	0.4608	0.0004	0.0054	0.9943	0.6024	0.0016
		0.0281	0.9704	0.5902	0.0017	0.0092	0.9906	0.7154	0.0064
		0.0467	0.9516	0.7382	0.0078	0.0154	0.9842	0.8153	0.0269
		0.0945	0.9036	0.8502	0.0214	0.0323	0.9673	0.8594	0.0676
		0.1400	0.8578	0.8971	0.0416	0.0496	0.9500	0.8450	0.1225
		0.2250	0.7725	0.8845	0.1005	0.0852	0.9143	0.7327	0.2603
		0.2950	0.7050	0.8350	0.1650	0.1180	0.8820	0.6181	0.3819

Auxiliary Information

Method/Apparatus/Procedure:

The method was described in Ref. 1. No more details were reported in the paper.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified.
(3) not specified.

Estimated Error:

Not reported.

References:

[1]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Zh. Fiz. Khim. **49**, 1849 (1975).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. M. Letcher, S. Wootton, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037–42 (1986).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions of the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
				(compiler)	
25	298.2	0.040	0.000	0.069	0.000
		0.144	0.000	0.230	0.000
		0.339	0.001	0.475	0.004
		0.580	0.002	0.706	0.008
		0.848	0.026	0.848	0.081
		0.880	0.038	0.842	0.114
		0.893	0.099	0.740	0.256
		0.176	0.824	0.064	0.936

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
25	298.2	0.115	0.885	0.886	0.042	0.040	0.960	0.838	0.124
		0.060	0.940	0.695	0.005	0.020	0.980	0.790	0.018
		0.003	0.997	0.400	0.000	0.001	0.999	0.542	0.000

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, adapted from Ref. 1, was used to determine the coexistence curve. The third component was added from a weighed gas-tight syringe to a weighed mixture of the other two components in 100 mL long-neck flask until one drop (weighing less than 0.01 g) resulted in cloudiness. The flask was immersed in a well controlled water bath and shaken continuously. Refractive indexes of these mixtures were measured at 298.3 K to ensure that separation did not take place. Tie lines were determined from mixtures of known composition in the immiscible region. The flasks were shaken well and the phases allowed to separate. Refractive indexes of samples of both phases were measured and related to compositions on the coexistence curve. Each tie line was checked to ensure that it passed through the composition of the overall mixture.

Source and Purity of Materials:

(1) Merck, Uvasol grade; dried with magnesium metal activated with iodine, distilled.
(2) Analytical Carbo Erba, purity 99.5 mole %; purified by passing through columns containing silica gel and basic alumina.
(3) de-ionized.

Estimated Error:

composition ±0.005 mole fraction for measured points, ±0.01 mole fraction for tie-lines extremities in the worst case (authors).

References:

[1]S. W. Briggs and E. W. Commings, Ind. Eng. Chem. **35**, 411 (1943).

Components:	Evaluated by:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1] (2) *p*-Xylene (1,4-dimethylbenzene, 1,4-xylene); C_8H_{10}; [106-42-3] (3) Water; H_2O; [7732-18-5]	A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.03)

3.12. Methanol + Water + *p*-Xylene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) for the system methanol–*p*-xylene–water is given in Table 13.

TABLE 13. Summary of experimental data for the system methanol–*p*-xylene–water

Author(s)	*T*/K	Type of data[a]	Ref.
Leikola, 1940	294	sat. (4)	1
Letcher, *et al.*, 1989	298	sat. (17), Eq. (5)	2

[a] Number of experimental points in parentheses.

Saturation curve

The system methanol–*p*-xylene–water forms a miscibility gap of type 1. Only one binary system, *p*-xylene–water, is partially miscible. The data for this system were compiled and critically evaluated in a previously published SDS volumes, Ref. 3. The recommended values of mutual solubility of *p*-xylene–water system at 298.2 K are: $x_2'=0.9974$ and $x_2''=0.000\ 031$. The data of Leikola[1] taken from the handbook of Kafarov,[4] were also taken into account during evaluation but are not reported as compilation sheet because they do not contribute further to knowledge of the system. All experimental saturation data are consistent. The data of Letcher *et al.*[2] describe the whole binodal curve. The end points of saturation curve, Ref. 2, were reported to be $x_2=0.998$ and pure water which is inconsistent with recommended values. Data for the water-rich phase in the range of low methanol concentrations, Ref. 2, were reported to be *p*-xylene free. All these results are within the accuracy of experimental measurements which were stated by the authors to be 0.005 mole fraction. Phase equilibrium data, Ref. 2, were also used to construct the saturation curve with the exception of one point ($x_1=0.058$ $x_2=0.916$) which appears to contain experimental error. Data at 298.2 K, Ref. 2, presenting both phases (organic-rich and water-rich) were fitted by the equation:

$$x_1=1.1424+0.1264\ \ln(x_2)-1.2561x_2+0.1108x_2^2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0194. The points on the saturation curve calculated by this equation for the selected concentrations of *p*-xylene together with the "best" values of Ref. 3 are presented in Table 14.

TABLE 14. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 031 Ref. 3	0.4365	0.5200
0.6228	0.0200	0.4185	0.5400
0.6855	0.0400	0.4004	0.5600
0.7118	0.0600	0.3823	0.5800
0.7234	0.0800	0.3641	0.6000
0.7269	0.1000	0.3458	0.6200
0.7253	0.1200	0.3275	0.6400
0.7202	0.1400	0.3091	0.6600
0.7126	0.1600	0.2907	0.6800
0.7031	0.1800	0.2723	0.7000
0.6922	0.2000	0.2539	0.7200
0.6800	0.2200	0.2355	0.7400
0.6669	0.2400	0.2171	0.7600
0.6530	0.2600	0.1986	0.7800
0.6385	0.2800	0.1802	0.8000
0.6234	0.3000	0.1618	0.8200
0.6078	0.3200	0.1434	0.8400
0.5918	0.3400	0.1250	0.8600
0.5754	0.3600	0.1067	0.8800
0.5588	0.3800	0.0883	0.9000
0.5419	0.4000	0.0700	0.9200
0.5247	0.4200	0.0517	0.9400
0.5074	0.4400	0.0335	0.9600
0.4899	0.4600	0.0153	0.9800
0.4722	0.4800	0.0000	0.9974 Ref. 3
0.4544	0.5000		

Phases in equilibrium

Compositions of coexisting phases in equilibrium of the ternary system methanol–*p*-xylene–water were reported only by Letcher *et al.*[2] The tie lines are consistent with one another and cover the whole area of the miscibility gap. One point for organic-rich phase ($x_1=0.058$, $x_2=0.916$) appears to contain any experimental error. The phase equilibrium data are considered tentative. All experimental saturation points together with experimental tie lines at 298.2 K are presented in Fig. 7. The plait point of the system at 298.2 K, calculated by Letcher and Siswana[5] was reported to be $x_1=0.46$, $x_2=0.49$.

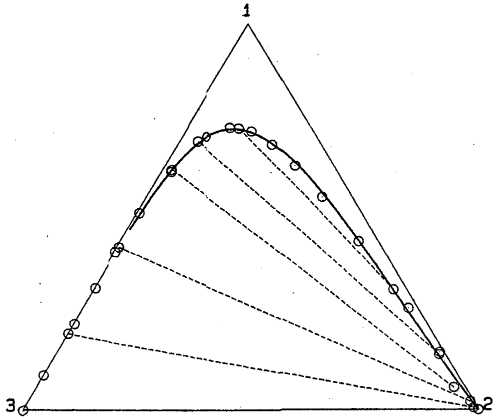

FIG. 7. Phase diagram of the system methanol (1)—*p*-xylene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, O—experimental data, Ref. 2, dashed lines—experimental tie lines, Ref. 2.

References:

[1] E. Leikola, Suomen. Kemistil. B **13**, 13 (1940).

[2] T. M. Letcher, P. M. Siswana, P. van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053 (1989).

[3] D. G. Shaw ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons, C_8 to C_{36} (Pergamon, New York, 1989).

[4] V. V. Kafarov, ed., *Spravochnik po Rastvormosti*, Vol. 2, Troinye, Mnogokomponentny e Sistemy, Kniga II (Izd. Akademii Nauk SSSR, Moskva, 1963).

[5] T. M. Letcher, and P. M. Siswana, Fluid Phase Equilib. **74**, 203 (1992).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) *p*-Xylene (1,4-dimethylbenzene, 1,4-xylene); C_8H_{10}; [106-42-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. M. Letcher, P. M. Siswana, P. van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053–60 (1989).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions of the saturation curve

t/°C	T/K	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25.0	298.2	0.000	0.998	0.000	0.9997
		0.150	0.840	0.051	0.947
		0.263	0.716	0.099	0.896
		0.433	0.523	0.198	0.791
		0.548	0.385	0.294	0.685
		0.629	0.285	0.388	0.582
		0.686	0.207	0.479	0.479
		0.721	0.145	0.565	0.376
		0.730	0.095	0.639	0.275
		0.707	0.053	0.695	0.173
		0.615	0.021	0.692	0.078
		0.508	0.005	0.636	0.021
		0.407	0.003	0.544	0.013
		0.315	0.001	0.448	0.005
		0.224	0.001	0.338	0.005
		0.090	0.000	0.150	0.000
		0.000	0.000	0.000	0.000

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C (compiler)	T/K	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.310	0.660	0.728	0.115	0.123	0.870	0.608	0.318
		0.144	0.842	0.695	0.039	0.049	0.948	0.714	0.133
		0.058	0.916	0.620	0.019	0.019	0.977	0.700	0.071
		0.021	0.970	0.419	0.005	0.006	0.992	0.552	0.022
		0.005	0.985	0.199	0.000	0.002	0.997	0.306	0.000

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine binodal curve. A binary mixture of known composition was titrated with the third component until cloudiness was observed. Tie line compositions were related to the coexistence curve; water was determined by the Karl Fischer titration. The methods were described in Ref. 1.

Source and Purity of Materials:

(1) source not specified; used as received.
(2) source not specified; recrystallized three times.
(3) not specified.

Estimated Error:

comp. <0.005 mole fraction (estimated authors' precision on binodal curve), <0.01 mole fraction (estimated authors' precision of tie lines).

References:

[1] T. M. Letcher, S. Wootten, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037 (1986).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Xylene (mixture of isomers); C_8H_{10}; [1330-20-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
J. Hartley, J. Soc. Chem. Ind. (London) **69**, 60–1 (1950).

Variables:
T/K=293–323

Compiled by:
A. Skrzecz

3.13. Methanol + Water + Xylene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
20	293.2	0.419	0.553	0.185	0.808
		0.696	0.229	0.465	0.507
		0.765	0.092	0.666	0.264
		0.758	0.062	0.711	0.194
		0.725	0.039	0.735	0.130
		0.696	0.029	0.736	0.100
		0.611	0.013	0.706	0.050
		0.356	0.002	0.492	0.010
30	303.2	0.416	0.548	0.185	0.806
		0.686	0.226	0.462	0.505
		0.749	0.089	0.660	0.260
		0.742	0.061	0.703	0.192
		0.701	0.038	0.721	0.128
		0.680	0.028	0.726	0.099
		0.611	0.014	0.703	0.054
		0.356	0.003	0.491	0.012
50	323.2	0.243	0.719	0.092	0.900
		0.412	0.544	0.184	0.805
		0.708	0.155	0.545	0.396
		0.721	0.102	0.622	0.292
		0.710	0.065	0.675	0.205
		0.671	0.035	0.705	0.121
		0.545	0.009	0.660	0.036
		0.417	0.002	0.556	0.009

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2'	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
20	293.2	0.101	0.888	0.636	0.015	0.033	0.965	0.721	0.057
30	303.2	0.106	0.883	0.638	0.018	0.035	0.963	0.715	0.068
50	323.2	0.146	0.833	0.637	0.024	0.050	0.946	0.702	0.088

Concentration of xylene and water in coexisting phases

t/°C	T/K (compiler)	w_2' hydrocarbon-rich phase	w_2'' water-rich phase
20	293.2	0.983	0.517
		0.982	0.353
		0.977	0.254
		0.965	0.222
30	303.2	0.985	0.525
		0.977	0.351
		0.970	0.256
		0.963	0.217

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used. Binary mixtures of known volumes were titrated with the third component in glass-stoppered bottles until after vigorously shaking, the mixture became turbid. The equilibrium phases were determined by titrating with water binary methanol–xylene mixtures. The xylene-rich phase was at the beginning the lower layer, but addition of water caused this phase to separate as the upper layer. To determine tie lines, mixtures of known composition were immersed in a thermostat bath, shaken, and after separation one component of each phase was analyzed. Water, in the alcohol-rich phase, was analyzed by the Karl Fischer reagent and xylene, in the hydrocarbon-rich phase, was determined by extraction with water. The results were presented on a Gibbs triangle together with binodal curve.

Source and Purity of Materials:

(1) BDH, sulphur free; distilled; fraction boiling at the range 140–2 °C was used.
(2) source not specified; absolute alcohol; used as received.
(3) distilled.

Estimated Error:

temp. ±0.5 °C (temperature of the bath).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) 2,2,4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.05)

3.14. Methanol + Water +2,2,4-Trimethylpentane

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system methanol–2,2,4-trimethylpentane–water is given in Table 15.

TABLE 15. Summary of experimental data for the system methanol–2,2,4-trimethylpentane–water

Author(s)	T/K	Type of data[a]	Ref.
Buchowski and Teperek, 1959	291, 293	sat. (21), eq. (18)	1
Budantseva *et al.*, 1976	293	eq. (6)	2

[a] Number of experimental points in parentheses.

Saturation curve

The system methanol–2,2,4-trimethylpentane–water forms a large miscibility gap of type 2 covering the majority of the concentration triangle. Two binary systems 2,2,4-trimethylpentane–water and 2,2,4-trimethylpentane–methanol are partially miscible. The data for these systems were compiled and critically evaluated in previously, published SDS volumes, Refs. 3 and 4. The recommended values of mutual solubility of 2,2,4-trimethylpentane–water system, Ref. 3, and methanol–2,2,4-trimethylpentane system, Ref. 4, at 293 K are: $x_2'=0.9995$, $x_2''=3\cdot10^{-7}$ and $x_2'=0.890$, $x_2''=0.224$, respectively. (The mutual solubilities of methanol–2,2,4-trimethylpentane system, reported in both papers[1,2] were also considered during evaluation of this binary system in Ref. 4.) Compositions along the saturation curve at 291.2 and 293.2 K by Buchowski and Teperek[1] were obtained by the titration method. They are consistent within each data set, as well as with one another. The paper of Budantseva *et al.*[2] contains information about phases in equilibrium at 293.2 K only. The hydrocarbon-poor phase shows smaller miscibility while the hydrocarbon-rich phase shows larger solubility[2] than data of Ref. 1 at the same temperature and than the "best" binary solubilities by Ref. 4. The data of Buchowski and Teperek[1] were well documented (description of the method, description of pure substances properties and purity) while data of Ref. 2 were reported without any auxiliary information. Therefore data of Ref. 1 appear reliable, but all are considered as tentative.

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–2,2,4-trimethylpentane–water were reported in both references. Tie lines cover nearly the whole range of miscibility gap. In the paper of Buchowski and Teperek[1] the reported hydrocarbon-rich phase did not contain detectable water (water concentration in the hydrocarbon-rich phase was neglected because solubility of water in 2,2,4-trimethylpentane is lower than 0.000 5 mass fraction, Ref. 1). The data from Refs. 1 and 2 show slightly different directions of the tie lines. All of them are considered as tentative. To present system behavior, experimental data along the saturation curve and experimental compositions of coexisting phases in equilibrium at 293.2 K, are presented in Fig. 8.

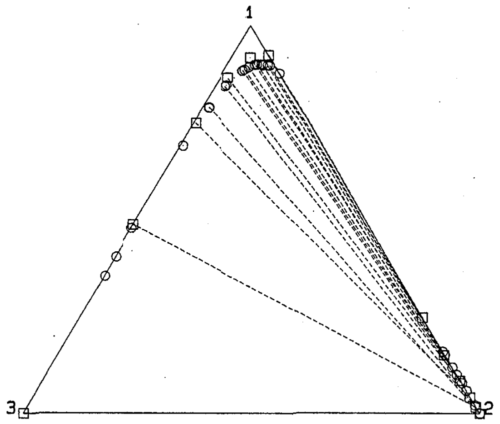

FIG. 8. Phase diagram of the system methanol (1)—2,2,4-trimethylpentane (2)—water (3) at 293.2 K. ○—experimental data, Ref. 1, □—experimental data, Ref. 2, dashed lines—experimental tie lines, Refs. 1 and 2.

References:

[1] H. Buchowski and J. Teperek, Rocz. Chem. **33**, 1093 (1959).
[2] L. S. Budantseva, T.M. Lesteva, and M.S. Nemtsov, Dep. Doc. VINITI **437–76**, 1 (1976).
[3] D.G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).
[4] D. G. Shaw, A. Skrzecz, J. W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol. 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

Components:	**Original Measurements:**
(1) Methanol (methyl alcohol); CH_4O; [67-56-1] (2) 2,2,4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1] (3) Water; H_2O; [7732-18-5]	H. Buchowski and J. Teperek, Rocz. Chem. **33**, 1093–8 (1959).
Variables: T/K=291–293	**Compiled by:** A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
18	291.2	0.8786	0.1214	0.670	0.330
		0.9071	0.0780	0.760	0.233
		0.9054	0.0639	0.787	0.198
		0.9002	0.0558	0.801	0.177
		0.8940	0.0442	0.823	0.145
		0.8880	0.0350	0.841	0.118
		0.8359	0.0200	0.846	0.072
		0.7192	0.0073	0.800	0.029
		0.6227	0.0007	0.744	0.003
		0.3985	0.0004	0.540	0.002
		0.3076	0.0002	0.441	0.001
20	293.2	0.8747	0.1253	0.662	0.338
		0.8988	0.0740	0.763	0.224
		0.8970	0.0606	0.789	0.190
		0.8811	0.0408	0.823	0.136
		0.8441	0.0251	0.838	0.089
		0.7845	0.0135	0.829	0.051
		0.6875	0.0057	0.781	0.023
		0.4769	0.0007	0.617	0.003
		0.4033	0.0004	0.545	0.002
		0.3538	0.0002	0.493	0.001

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)		hydrocarbon-rich phase		hydrocarbon-poor phase	
18	291.2	0.1773	0.8227	0.8736	0.1214	0.057	0.943	0.670	0.330
		0.1054	0.8946	0.9025	0.0705	0.032	0.968	0.772	0.215
		0.1524	0.8476	0.9055	0.0775	0.048	0.952	0.760	0.232
		0.0869	0.9131	0.9045	0.0519	0.026	0.974	0.812	0.166
		0.0806	0.9194	0.8971	0.0415	0.024	0.976	0.831	0.137
		0.0678	0.9322	0.8856	0.0346	0.020	0.980	0.841	0.117
		0.0448	0.9552	0.8535	0.0231	0.013	0.987	0.849	0.082
		0.0415	0.9585	0.8353	0.0197	0.012	0.988	0.847	0.071
		0.0000	1.0000	0.7200	0.0060	0.000	1.000	0.804	0.024
20	293.2	0.1580	0.8420	0.8950	0.0940	0.050	0.950	0.724	0.271
		0.1495	0.8505	0.8957	0.0891	0.047	0.953	0.733	0.260
		0.1175	0.8825	0.8961	0.0784	0.036	0.964	0.753	0.235
		0.0993	0.9007	0.8933	0.0649	0.030	0.970	0.781	0.201
		0.0838	0.9162	0.8910	0.0501	0.025	0.975	0.808	0.162
		0.0774	0.9226	0.8848	0.0440	0.023	0.977	0.818	0.145
		0.0581	0.9419	0.8821	0.0415	0.017	0.983	0.822	0.138
		0.0211	0.9789	0.8411	0.0236	0.006	0.994	0.840	0.084
		0.0000	1.0000	0.7860	0.0135	0.000	1.000	0.830	0.051

Auxiliary Information

Method/Apparatus/Procedure:

Solubility was measured by the titration method. Known masses of methanol and water were titrated with 2,2,4-trimethylpentane until turbidity was observed. The mass of hydrocarbon was determinated from mass balance of the mixture. To obtain equilibrium data, known masses of components were shaken and allowed to stand for over 2 h. Refractive indexes of the hydrocarbon-rich phase were measured and phase composition was read from the calibration curve of the binary methanol–2,2,4-trimethylpentane mixture. Water concentration in the hydrocarbon-rich phase was neglected because the solubility of water in 2,2,4-trimethylpentane is lower than 0.000 05 mass fraction.[1] Concentration of the water-rich phase was determined graphically from a large scale ternary diagram from the binodal curve, composition of hydrocarbon-rich phase and total composition of starting mixture.

Source and Purity of Materials:

(1) F. O. Ch. Gliwice, pure grade; boiled with I_2 and Mg to remove water, distilled; middle fraction was used; $n(20\ °C)=1.3288$, $\rho(20\ °C)=0.7915$ g/c^3.

(2) obtained from the Physical Chemistry Department of Warsaw University, high purity grade; distilled only to remove water; $n(20\ °C)=1.3914$, $\rho(20\ °C)=0.6920$ g/cm^3.

(3) doubly distilled.

Estimated Error:

temp. ±0.5 °C.

References:

[1] A. Weissberger, E. S. Proskauer, I. A. Riddick, and E. E. Toops, *Organic Solvents*, 2nd ed. (New York, 1995).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) 2,2,4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep. Doc. VINITI **437–76**, 1–13 (1976).

Variables:

T/K=293

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
20	293.2	0.0000	0.999 56	0.0000	0.000 0003	0.0000	0.999 931	0.0000	0.000 002
		0.0162	0.9831	0.4855	0.0002	0.0046	0.9953	0.6262	0.0009
		0.0414	0.9579	0.7456	0.0043	0.0120	0.9879	0.8270	0.0170
		0.0836	0.9152	0.8636	0.0180	0.0250	0.9748	0.8685	0.0645
		0.1493	0.8490	0.9158	0.0411	0.0470	0.9527	0.8428	0.1349
		0.2460	0.7540	0.9220	0.0780	0.0838	0.9162	0.7683	0.2317

Auxiliary Information

Method/Apparatus/Procedure:

The method was described in Ref. 1. No more details were reported in the paper.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified.
(3) not specified.

Estimated Error:

Not reported.

References:

[1]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Zh. Fiz. Khim. **49**, 1849 (1975).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Octane (n-octane); C_8H_{18}; [111-65-9]
(3) Water; H_2O; [7732-18-5]

Evaluated by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.04)

3.15. Methanol + Water + Octane

Critical Evaluation:

A survey of reported compositions along the saturation curve and compositions of coexisting phases in equilibrium (eq.) for the system methanol–octane–water is given in Table 16.

TABLE 16. Summary of experimental data for the system methanol–octane–water

Author(s)	T/K	Type of data[a]	Ref.
Kogan *et al.*, 1956	283, 293	eq. (12)	1
Budantseva *et al.*, 1976	293	eq. (10)	2

[a]Number of experimental points in parentheses.

Saturation curve

The ternary system methanol–octane–water forms a large miscibility gap of type 2 covering the majority of the concentration triangle. Compositions along the saturation curves were not reported independently in the references; the saturation curves can be constructed on the bases of equilibrium compositions. Two binary systems, octane–water and octane–methanol, form miscibility gaps. The data for these systems were compiled and critically evaluated in previously published SDS volumes, Refs. 3 and 4, respectively. The recommended, Ref. 3, values of mutual solubility of octane–water system at 293 K[4] are: $x_2''=9.9\cdot 10^{-8}$ and $x_2'=0.9995$. The mutual solubility of methanol–octane system at 293 K,[4] are: $x_1''=0.944$ and $x_1'=0.105$. The binary data reported by Budantseva *et al.*[2] are: $x_2''=2.0\cdot 10^{-7}$, $x_2'=0.999\ 57$ and $x_1''=0.960$, $x_1'=0.155$, respectively.

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system methanol–octane–water were reported in both references. The experimental procedure was reported only in Ref. 1. After separation, methanol was determined by reaction with phthalic anhydride; water—with the Karl Fischer reagent. The compositions of phases in equilibrium reported in Refs. 1 and 2 are consistent with one another, they are treated as tentative and those at 293.2 K are presented in Fig. 9.

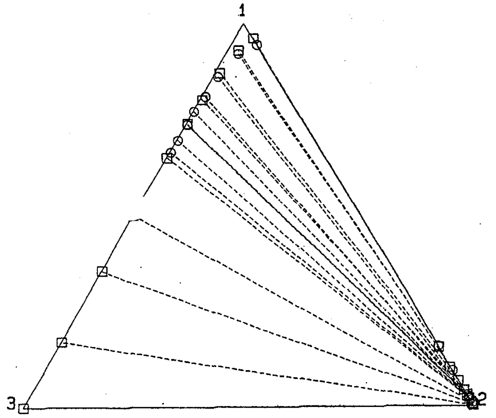

FIG. 9. Phase diagram of the system methanol (1)—octane (2)—water (3) at 293.2 K. ○—experimental data, Ref. 1, □—experimental data, Ref. 2, dashed lines—experimental tie lines, Ref. 2.

References:

[1] V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim. (Leningrad) **29**, 1387 (1956).

[2] L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Dep Doc. VINITI **437–76**, 1 (1976).

[3] D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).

[4] D. G. Shaw, A. Skrzecz, W. Lorimer, and A. Maczynski, eds., *Solubility Data Series*, Vol. 56, Alcohols with Hydrocarbons (Pergamon, New York, 1994).

Components:

(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) Octane (*n*-octane); C_8H_{18}; [111-65-9]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim. (Leningrad) **29**, 1387–92 (1956).

Variables:

T/K=283–293

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)		hydrocarbon-rich phase		hydrocarbon-poor phase	
10.0	283.15	0.0742	0.9258	0.9507	0.0493	0.022	0.978	0.844	0.156
		0.0482	0.9518	0.9107	0.0211	0.014	0.986	0.889	0.0736
		0.0245	0.9755	0.8106	0.0063	0.007	0.993	0.866	0.024
		0.0245	0.9755	0.6856	0.0000	0.007	0.993	0.795	0.000
20.0	293.15	0.1580	0.8420	0.9431	0.0569	0.050	0.950	0.823	0.177
		0.0931	0.9069	0.9197	0.0275	0.028	0.972	0.878	0.0937
		0.0242	0.9758	0.8602	0.0114	0.0069	0.9931	0.8840	0.0418
		0.0141	0.9859	0.8098	0.0079	0.004	0.996	0.861	0.030
		0.0141	0.9859	0.7708	0.0020	0.004	0.996	0.851	0.008
		0.0211	0.9789	0.7368	0.0028	0.006	0.994	0.825	0.011
		0.0176	0.9824	0.6955	0.0027	0.005	0.995	0.795	0.011
		0.0176	0.9824	0.6645	0.0022	0.005	0.995	0.773	0.009

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. The two phase mixture was periodically shaken in a thermostated burette with water jacket for several hours. The phases were removed for analysis after separation. Methanol was determined by reaction with phthalic anhydride; water was determined by the Karl Fischer method. Water concentration in the hydrocarbon-rich phase was smaller than 0.01–0.02%.

Source and Purity of Materials:

(1) source not specified, pure grade; distilled; contained <0.01% of water; $n(20\ ^\circ C) = 1.3391$.
(2) source not specified; used as received; b.p. = 125.4°C, $n(20\ ^\circ C) = 1.3976$.
(3) not specified.

Estimated Error:

temp. ±0.05 °C; soly. <±1% (relative error of methanol concentration).

Components:	Original Measurements:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1] (2) Octane (*n*-octane); C_8H_{18}; [111-65-9] (3) Water; H_2O; [7732-18-5]	L. S. Budantseva, T. M. Lesteva and M. S. Nemtsov, Dep. Doc. VINITI **437–76**, 1–13 (1976).
Variables: T/K=293	**Compiled by:** A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
20	293.2	0.0000	0.99957	0.0000	0.000 000 2	0.0000	0.999 932	0.0000	0.000 001
		0.0018	0.9975	0.1722	0.000 02	0.0005	0.9994	0.2700	0.000 11
		0.0050	0.9943	0.3554	0.0001	0.0014	0.9985	0.4949	0.0005
		0.0092	0.9901	0.4995	0.0002	0.0026	0.9973	0.6392	0.0009
		0.0182	0.9811	0.6501	0.0009	0.0052	0.9947	0.7652	0.0038
		0.0279	0.9714	0.7390	0.0027	0.0080	0.9919	0.8268	0.0108
		0.0414	0.9579	0.8016	0.0052	0.0120	0.9879	0.8631	0.0200
		0.0671	0.9322	0.8694	0.0109	0.0198	0.9801	0.8912	0.0398
		0.1022	0.8966	0.9283	0.0233	0.0310	0.9688	0.8938	0.0800
		0.1550	0.8450	0.9600	0.0400	0.0489	0.9511	0.8707	0.1293

Auxiliary Information

Method/Apparatus/Procedure:

The method was described in Ref. 1. No more details were reported in the paper.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified.
(3) not specified.

Estimated Error:

Not reported.

References:

[1]L. S. Budantseva, T. M. Lesteva, and M. S. Nemtsov, Zh. Fiz. Khim. **49**, 1849 (1975).

Components:	Original Measurements:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1] (2) Mesitylene (1,3,5-trimethylbenzene); C_9H_{12}; [108-67-8] (3) Water; H_2O; [7732-18-5]	T.M. Letcher and P.M. Siswana, Fluid Phase Equilib. **74**, 203–17 (1992).
Variables: T/K=298	**Compiled By:** A. Skrzecz

3.16. Methanol + Water + Mesitylene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
				(compiler)	
25.0	298.2	0.000	0.000	0.000	0.000
		0.360	0.001	0.498	0.005
		0.457	0.002	0.595	0.010
		0.565	0.005	0.684	0.023
		0.734	0.022	0.770	0.087
		0.788	0.043	0.755	0.154
		0.796	0.053	0.737	0.184
		0.807	0.092	0.668	0.285
		0.792	0.141	0.583	0.389
		0.747	0.202	0.487	0.494
		0.682	0.273	0.394	0.591
		0.595	0.370	0.297	0.693
		0.471	0.503	0.199	0.795
		0.292	0.690	0.101	0.895
		0.163	0.826	0.050	0.948
		0.000	0.999	0.000	0.9998

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		hydrocarbon-poor phase		hydrocarbon-rich phase (compiler)		hydrocarbon-poor phase (compiler)	
25.0	298.2	0.000	0.999	0.000	0.000	0.000	0.9998	0.000	0.000
		0.090	0.905	0.533	0.001	0.026	0.973	0.667	0.005
		0.140	0.852	0.663	0.010	0.042	0.957	0.750	0.042
		0.200	0.790	0.755	0.023	0.063	0.935	0.781	0.089
		0.208	0.717	0.800	0.056	0.071	0.915	0.733	0.193
		0.408	0.573	0.795	0.135	0.159	0.837	0.593	0.378

Auxiliary Information

Method/Apparatus/Procedure:

The points on the binodal curve were determined by the formation of a cloudy mixture on shaking after the addition of a known mass of one component to a mixture of known masses of the other two components. Precision weighing syringes were used as described in Ref. 1. Tie line compositions were determined by the refractive index method reported in Ref. 2 and a complementary method using the Karl Fischer titrations as reported in Ref. 3.

Source and Purity of Materials:

(1) Merck, AR grade; distilled, dried by refluxing with Mg and I_2; purity better than 99.6 mole % by glc; $d=0.786\,88$, $n=1.3265$.

(2) BDH; used as received; purity better than 99.6 mole % by glc.

(3) not specified.

Estimated Error:

estimated comp. 0.005 mole fraction on the binodal curve and 0.01 mole fraction for tie lines (estimated by the authors).

References:

[1] T. M. Letcher, S. Wooten, B. Shuttleworth, and C. Heward, J. Chem. Thermodyn. **18**, 1037 (1986).

[2] S. W. Briggs and E. W. Comings, Ind. Eng. Chem. **35**, 411 (1943).

[3] T. M. Letcher, P. M. Siswana, P. Van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053 (1989).

Components:	**Original Measurements:**
(1) Methanol (methyl alcohol); CH_4O; [67-56-1] (2) Nonane (*n*-nonane); C_9H_{20}; [111-84-2] (3) Water; H_2O; [7732-18-5]	V. B. Kogan, I. V. Deizenrot, T. A. Kulbyaeva, and V. M. Fridman, Zh. Prikl. Khim. (Leningrad) **29**, 1387–92 (1956).
Variables: T/K=283–293	**Compiled by:** A. Skrzecz

3.17. Methanol + Water + Nonane

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-lean phase (compiler)		hydrocarbon-rich phase (compiler)		hydrocarbon-lean phase		hydrocarbon-rich phase	
10.0	283.15	0.9615	0.0385	0.0965	0.9035	0.862	0.138	0.026	0.974
		0.9458	0.0183	0.0501	0.9499	0.910	0.0706	0.013	0.987
		0.8957	0.0081	0.0464	0.9536	0.912	0.0329	0.012	0.988
		0.7512	0.0000	0.0236	0.9764	0.843	0.000	0.006	0.994
20.0	293.15	0.9562	0.0438	0.1034	0.8966	0.845	0.155	0.028	0.972
		0.9370	0.0220	0.0861	0.9139	0.894	0.0840	0.023	0.977
		0.9238	0.0138	0.0381	0.9619	0.911	0.0544	0.0098	0.9902
		0.7725	0.0009	0.0158	0.9842	0.855	0.004	0.0040	0.9960

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. The two phase mixture was periodically shaken in a thermostated burette with water jacket for several hours. The phases were removed for analysis after separation. Methanol was determined by reaction with phthalic anhydride; water was determined by the Karl Fischer method. Water concentration in the hydrocarbon-rich phase was smaller than 0.01–0.02%.

Source and Purity of Materials:

(1) source not specified, pure grade; distilled; contained <0.01% of water; $n(20\ ^\circ C)=1.3391$.

(2) source not specified; used as received; b.p.$=150.5\ ^\circ C$, $n(25\ ^\circ C)=1.4035$.

(3) not specified.

Estimated Error:

temp. ±0.05 °C; soly. <±1% (relative error of methanol concentration).

Components:
(1) Methanol (methyl alcohol); CH_4O; [67-56-1]
(2) 1-Methylnaphthalene; $C_{11}H_{10}$; [90-12-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements
C. F. Prutton, T. J. Walsh, and A. M. Desai, Ind. Eng. Chem. **42**, 1210–7 (1950).

Variables:
T/K=298 and 308

Compiled by:
A. Skrzecz

3.18. Methanol + Water + 1-Methylnaphthalene

Experimental Data

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon -rich phase		water -rich phase	
25.0	298.15	0.0000	1.0000	0.0000	0.0000	0.000	1.000	0.000	0.000
		0.0429	0.9571	0.2726	0.0000	0.010	0.990	0.400	0.000
		0.0511	0.9489	0.3957	0.0000	0.012	0.988	0.538	0.000
		0.0752	0.9248	0.6273	0.0058	0.018	0.982	0.730	0.030
		0.1022	0.8978	0.6928	0.0134	0.025	0.975	0.755	0.065
		0.1207	0.8793	0.7356	0.0242	0.030	0.970	0.752	0.110
		—	—	0.8023	0.0487	—	—	0.728	0.196
		—	—	0.8173	0.0555	—	—	0.720	0.217
		—	—	0.7973	0.1196	—	—	0.580	0.386
		—	—	0.7910	0.1507	—	—	0.530	0.448
35.0	308.15	0.0000	1.0000	0.0000	0.0000	0.000	1.000	0.000	0.000
		0.0511	0.9489	0.3957	0.0000	0.012	0.988	0.538	0.000
		0.0752	0.9248	0.6229	0.0078	0.018	0.982	0.720	0.040
		0.1022	0.8978	0.6885	0.0156	0.025	0.975	0.745	0.075
		—	—	0.7118	0.0188	—	—	0.752	0.088
		—	—	0.7741	0.0389	—	—	0.736	0.164
		—	—	0.7948	0.0552	—	—	0.707	0.218
		—	—	0.7993	0.0824	—	—	0.649	0.297
		—	—	0.7934	0.1189	—	—	0.579	0.385
		—	—	0.7390	0.1915	—	—	0.454	0.522
		—	—	0.6184	0.3223	—	—	0.297	0.687
		—	—	0.5184	0.4457	—	—	0.206	0.786
		—	—	0.4506	0.5494	—	—	0.156	0.844
		0.2021	0.7979	—	—	0.054	0.946	—	—
		0.3376	0.6624	—	—	0.103	0.897	—	—

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. Samples in 4 oz. oil sample bottles were agitated in a constant temperature bath for at least 12 h before phase separation. Samples of each phase were taken for analysis by a rubber bulb pipette. Water was determined by the Karl Fischer reagent, hydrocarbons as the caustic-insoluble fraction, methanol–by the difference.

Source and Purity of Materials:

(1) Barker C.P. analyzed absolute; purity 99.5%; water-free by the Karl Fischer.
(2) (a) Eastman Kodak Co.; distillation range 238–240 °C, contained about 5% of 2-methylnaphthalene isomer. (b) prepared in the laboratory from the crude material; extracted with NaOH aq., refluxed with Na distilled; fraction boiling at 240 °C was collected; contained about 10% of 2-methylnaphtalene isomer.
(3) not specified.

Estimated Error:

temp. ± 0.01 °C.

4. Ethanol+Water

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.05)

4.1. Ethanol + Water + Benzene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of ethanol between phases (distr.) for the system ethanol–benzene–water is given in Table 17.

TABLE 17. Summary of experimental data for the system ethanol–benzene–water

Author(s)	T/K	Type of data[a]	Ref.
Taylor, 1896	298	sat. (14), eq. (6)	1
Lincoln, 1899	298	sat. (13)	2
Bonner, 1909	288	sat. (12)	3
Holmes, 1918	288	sat. (1)	4
Sidgwick and Spurrell, 1920	273–298	sat. (32)	5
Wehrmann, 1921	263–303	sat. (33)	6
Perrakis, 1925	294	sat. (11)	7
Barbaudy, 1926	298	sat. (9)	8
Barbaudy, 1926	298–338	sat. (26), eq. (13)	9
Wright, 1926	284–296	sat. (7)	10
Barbaudy, 1927	338–342	eq. (6)	11
Washburn *et al.*, 1931	298	sat. (16), distr. (9)	12
Tarasenkov and Polozhentseva, 1932	293	eq. (6)	13
Sata and Kimura, 1935	303	sat. (7)	14
Varteressian and Fenske, 1936	298	sat. (10), eq. (14)	15
Bancroft and Hubard, 1942	298	sat. (4), eq. (12)	16
Staveley *et al.*, 1951	274–342	sat. (45)	17
Chang and Moulton, 1953	298	sat. (12), eq. (11)	18
Morachevskii and Belousov, 1958	293–337	eq. (35)	19
Mertslin *et al.*, 1961	299	sat. (20), distr. (12)	20
Ross and Patterson, 1979	293	eq. (9)	21
Brandani *et al.*, 1985	303–328	eq. (34)	22
Letcher *et al.*, 1990	298	sat. (13), eq. (5)	23

[a]Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–benzene–water forms a miscibility gap of type 1. Data for the system were reported in 23 references over the temperature range 263–342 K. The system is evaluated on the basis of the original papers. Only one binary system, benzene–water, is partially miscible. The data for this system were compiled and critically evaluated in a previously published SDS volume, Ref. 24. These recommended values of mutual solubility at 293 K are $x_2'=0.9975$, $x_2''=0.000\ 406$; at 298 K–$x_2'=0.9970$, $x_2''=0.000\ 409$ and at 333 K–$x_2'=0.991\ 04$, $x_2''=0.000\ 534$. Only the paper of Barbaudy, Ref. 9 at 333.2 K reported mutual solubility of the binary system: $x_2'=0.9893$ and $x_2''=0.0005$. This is in agreement with the recommended values, Ref. 24. The results of Taylor,[1] Lincon,[2] Perrakis,[7] Tarasenkov and Polozhentseva,[13] and Letcher *et al.*[23] are not reported as compilation tables. The data of Taylor[1] and Lincon[2] at 298.2 K published at 1896 and 1899, were reported as volume ratios. These data were recalculated to mole fractions, and they were taken into account for this evaluation; they are in agreement with other data sets at the same temperature. Data of Perrakis[7] at 294 K present a significantly larger miscibility gap than any other data at 293 K and therefore these data are rejected as are other alcohol–benzene–water systems presented in Ref. 7. Data of Tarasenkov and Polozhentseva[13] were obtained for this evaluation from Tarasenkov and Paulsen.[25] These data present a much smaller miscibility gap (at maximum ethanol concentration of about 0.03 mole fraction of C_2H_5OH) which is inconsistent with all other experimental data and an unreasonable large solubility of water in benzene (solubility of benzene in water estimated on the basis of these data seems to rech value $x_2''=0.94$). Therefore, this data set is rejected. All experimental data of Letcher *et al.*[23] were presented in the paper in graphical form only and therefore were not compiled. The miscibility gap decreased with the increasing temperature. This behavior is observed in all studies at more than one temperature.[5,6,9,17,19,22] Data reported by Brandani *et al.*[22] show a slightly smaller miscibility gap than other data at 303.2 K (Wehrmann, Ref. 6, and Sata and Kimura, Ref. 14) and at 313.2 K (Morachevskii and Belousov, Ref. 19). The reported data are consistent within each data set and for each study. All data on the saturation curve are treated as tentative. Characteristic points on the binodal curve at selected temperatures, reported or estimated for plait points and for maximum ethanol concentration, are presented in Table 18. At the point of maximum ethanol concentration the errors estimated by the evaluator are 0.005 and 0.015 mole fraction for ethanol and benzene, respectively.

TABLE 18. Characteristic points on the binodal curve of the system ethanol–benzene–water

	Max. C_2H_5OH concentration			Plait points		
T/K	x_1	x_2	Ref.	x_1	x_2	Ref.
288.2	0.438	0.198	3	0.389	0.413	3
293.2	0.435	0.195	6	-	-	
298.2	0.418	0.211	16	0.391	0.318	9
298.2	0.416	0.181	15	0.393	0.322	15
298.2	0.419	0.244	18	0.398	0.325	18
298.2	0.40	0.20	23	0.38	0.37	23
299.2	0.425	0.262	20	0.395	0.343	20
303.2	0.385	0.154	22	0.365	0.353	22
303.2	0.412	0.226	6	-	-	
313.2	0.384	0.198	19	0.344	0.330	22
328.2	0.354	0.271	22	0.354	0.271	22
338.2	0.344	0.212	9	0.344	0.212	9

The temperature of 298.2 K, a standard temperature in which various alcohol–hydrocarbon–water systems are presented, was chosen to present the behavior of the system. Saturation and equilibrium data of Refs. 1, 2, 5, 8, 9, 15, 16, and 18, water-rich and hydrocarbon-rich branches were described together by the equation:

$$x_1=0.541\,21+0.062\,76\ln(x_2)-0.083\,61x_2-0.468\,57x_2^2.$$

The least-squares method was used and the standard error of estimate was 0.0106. The proposed equation is not appropriate for the binodal curve at >0.98 mole fraction of benzene. The compositions on the saturation curve calculated by the proposed equation are presented in Table 19 for selected concentrations of benzene in the mixture. The results of the calculations (solid line) are also presented graphically in Fig. 10 together with selected experimental data, Refs. 5, 8, 9, 15, 16, 18, reported at 298.2 K

TABLE 19. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 409 Ref. 24	0.3388	0.5000
0.1076	0.0010	0.3300	0.5200
0.2513	0.0100	0.3208	0.5400
0.2938	0.0200	0.3111	0.5600
0.3351	0.0400	0.3009	0.5800
0.3579	0.0600	0.2903	0.6000
0.3730	0.0800	0.2793	0.6200
0.3837	0.1000	0.2678	0.6400
0.3914	0.1200	0.2558	0.6600
0.3969	0.1400	0.2435	0.6800
0.4008	0.1600	0.2307	0.7000
0.4034	0.1800	0.2175	0.7200
0.4047	0.2000	0.2039	0.7400
0.4051	0.2200	0.1898	0.7600
0.4046	0.2400	0.1753	0.7800
0.4033	0.2600	0.1604	0.8000
0.4012	0.2800	0.1451	0.8200
0.3984	0.3000	0.1294	0.8400
0.3950	0.3200	0.1133	0.8600
0.3909	0.3400	0.0967	0.8800
0.3863	0.3600	0.0798	0.9000
0.3811	0.3800	0.0625	0.9200
0.3753	0.4000	0.0447	0.9400
0.3690	0.4200	0.0265	0.9600
0.3622	0.4400	0.0080	0.9800
0.3549	0.4600	0.0000	0.9970 Ref. 24
0.3471	0.4800		

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system ethanol–benzene–water were reported in 11 references over the temperature range 293–342 K as 20 data sets (mainly isotherms). The tie lines cover the full area of miscibility gap. Reported data are consistent within each data set. Only data of Tarasenkov and Polozhentseva[13] were rejected; these tie lines were inconsistent with all others. Vapor–liquid–liquid equilibria or boiling points of two-phase mixtures are reported in the papers of Barbaudy[11] at 101 kPa and of Morachevskii and Belousov[19] at temperatures 308.2, 318.2, 328.2, and 337.2 K. These data sets are consistent with other equilibrium data at lower temperatures. Changes of tie line direction are observed with temperature. With increasing temperature the water concentration in benzene-poor phase decreases for similar composition of benzene-rich phase; at temperatures over 333 K the concentration (in mole fraction) of ethanol in both phases in equilibrium reaches nearly the same values. This may be observed in data sets reported in Refs. 9, 11, 19, and 22. The equilibrium compositions of both phases of Ross and Patterson at 293.2 K[21] (referring also to density and surface tension of phases in equilibrium), are identical with those of Morachevskii and Belousov.[19] The reported experimental plait points are presented in Table 17. All equilibrium data are treated as tentative. Selected experimental points at 298.2 K, both saturation and equilibrium data, are presented in Fig. 10.

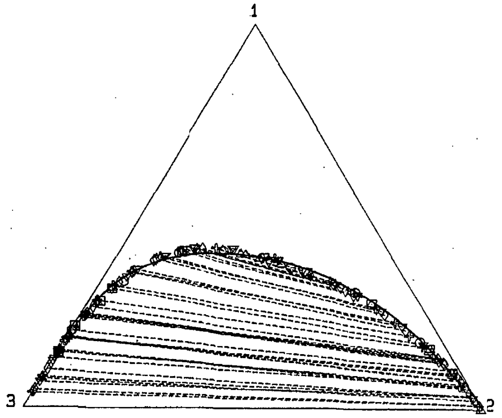

FIG. 10. Phase diagram of the system ethanol (1)—benzene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 5, □—experimental data, Ref. 8, △—experimental data, Ref. 9, ◇—experimental data, Ref. 15, ✣—experimental data, Ref. 16, ▽—experimental data, Ref. 18, dashed lines—experimental tie lines. Refs. 9, 15, 16, and 18.

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[23] T. M. Letcher, J. Sewry, and S. Radloff, S. Afr. J. Chem. **43**, 56 (1990).
[24] D. G. Shaw, ed., *Solubility Data Series* Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).
[25] D. N. Tarasenkov and I. A. Paulsen, Acta Physicochim. URSS **11**, 75 (1939).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

W. D. Bonner, J. Phys. Chem. **14**, 738-89 (1909-1910)

Variables:

T/K=273

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2	
		(compiler)		(compiler)		
15.0	288.2	0.2165	0.7412	0.1453	0.8436	
		0.3328	0.5166	0.2625	0.6910	
		0.3886	0.4126	0.3333	0.6000	plait point
		0.4271	0.2906	0.4145	0.4783	
		0.4381	0.1978	0.4784	0.3662	
		0.4365	0.1409	0.5192	0.2841	
		0.4251	0.1019	0.5430	0.2207	
		0.4003	0.0759	0.5455	0.1755	
		0.3854	0.0599	0.5475	0.1443	
		0.3433	0.0360	0.5305	0.0944	
		0.2920	0.0181	0.4929	0.0517	
		0.1898	0.0038	0.3711	0.0126	

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogenous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:

accuracy of weighing 0.0001 g.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. V. Sidgwick and W. J. Spurrell, J. Chem. Soc. **117**, 1397–404 (1920).

Variables:

T/K=272–312

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
30.7	303.85	0.1496	0.8080	0.0974	0.8918
26.1	299.25	0.1698	0.7822	0.1121	0.8755
23.9	297.05	0.1781	0.7719	0.1182	0.8688
16.1	289.25	0.1974	0.7467	0.1329	0.8524
11.0	284.15	0.2084	0.7328	0.1414	0.8430
5.2	278.35	0.2212	0.7164	0.1515	0.8318
2.0	275.15	0.2283	0.7070	0.1572	0.8254
28.3	301.45	0.2978	0.5781	0.2245	0.7389
22.7	295.85	0.3074	0.5645	0.2338	0.7281
17.6	290.75	0.3177	0.5501	0.2440	0.7163
12.9	286.05	0.3286	0.5346	0.2550	0.7035
8.5	281.65	0.3404	0.5179	0.2672	0.6893
4.5	277.65	0.3529	0.5000	0.2805	0.6738
39.2	312.35	0.3428	0.4395	0.2922	0.6352
32.1	305.25	0.3547	0.4200	0.3071	0.6166
19.6	292.75	0.3805	0.3777	0.3411	0.5741
9.2	282.35	0.4188	0.3152	0.3961	0.5055
5.2	278.35	0.4363	0.2865	0.4234	0.4714
1.6	274.75	0.4507	0.2628	0.4470	0.4419
29.5	302.65	0.3985	0.2523	0.4139	0.4443
20.3	293.45	0.4227	0.2071	0.4601	0.3823
15.2	288.35	0.4338	0.1860	0.4832	0.3512
7.75	280.90	0.4480	0.1595	0.5138	0.3102
3.00	276.15	0.4550	0.1464	0.5296	0.2890
−1.25	271.90	0.4609	0.1353	0.5434	0.2704
25.3	298.45	0.4047	0.1322	0.4997	0.2767
21.2	294.35	0.4094	0.1220	0.5120	0.2588
17.3	290.45	0.4135	0.1134	0.5229	0.2431
13.5	286.65	0.4169	0.1058	0.5325	0.2291
9.9	283.05	0.4200	0.0992	0.5411	0.2167
6.5	279.65	0.4227	0.0934	0.5488	0.2055
1.95	275.10	0.4263	0.0857	0.5591	0.1906
15.4	288.55	0.3336	0.0402	0.5159	0.1053
12.15	285.30	0.3343	0.0382	0.5187	0.1005
7.1	280.25	0.3354	0.0350	0.5233	0.0925
2.3	275.45	0.3363	0.0322	0.5272	0.0856
−0.40	272.75	0.3367	0.0310	0.5289	0.0827
25.0	298.15	0.1994	0.0030	0.3861	0.0100

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
0.0	273.2	0.2333	0.7008	0.1612	0.8210
		0.4561	0.2542	0.4559	0.4308
		0.4592	0.1385	0.5393	0.2759
		0.4277	0.0828	0.5631	0.1848
		0.3366	0.0312	0.5286	0.0832
1.0	274.2	0.2305	0.7044	0.1590	0.8235
		0.4531	0.2590	0.4510	0.4370
		0.4580	0.1407	0.5366	0.2795
		0.4270	0.0843	0.5611	0.1878
		0.3365	0.0317	0.5279	0.0844
2.0	275.2	0.2283	0.7073	0.1572	0.8255
		0.4493	0.2652	0.4446	0.4450
		0.4564	0.1438	0.5328	0.2846
		0.4262	0.0859	0.5589	0.1910
		0.3363	0.0322	0.5273	0.0855
3.0	276.2	0.2259	0.7103	0.1553	0.8276
		0.4448	0.2726	0.4372	0.4542
		0.4551	0.1461	0.5299	0.2885
		0.4254	0.0877	0.5564	0.1945
		0.3361	0.0327	0.5266	0.0868
4.0	277.2	0.2238	0.7130	0.1536	0.8295
		0.4411	0.2787	0.4311	0.4618
		0.4536	0.1490	0.5264	0.2932
		0.4247	0.0892	0.5544	0.1975
		0.3360	0.0332	0.5258	0.0881
5.0	278.2	0.2227	0.7145	0.1527	0.8305
		0.3508	0.5031	0.2782	0.6765
		0.4374	0.2847	0.4252	0.4692
		0.4520	0.1520	0.5228	0.2981
		0.4239	0.0909	0.5521	0.2008
		0.3358	0.0338	0.5250	0.0895
15.0	288.2	0.1997	0.7439	0.1346	0.8505
		0.3235	0.5418	0.2498	0.7095
		0.3944	0.3550	0.3604	0.5500
		0.4339	0.1858	0.4834	0.3510
		0.4158	0.1083	0.5293	0.2338
		0.3336	0.0399	0.5162	0.1047
25.0	298.2	0.1739	0.7771	0.1151	0.8722
		0.3036	0.5701	0.2300	0.7325
		0.3686	0.3972	0.3251	0.5941
		0.4109	0.2291	0.4370	0.4132
		0.4052	0.1310	0.5011	0.2746
		0.3305	0.0488	0.5039	0.1261
		0.1994	0.0030	0.3861	0.0100

Auxiliary Information

Method/Apparents/Procedur:

The apparatus consisted of Beckmann tube with air-jacket, thermometer and stirrer. Known amounts of aqueous alcohol mixture of known composition and benzene were placed in a tube. Aqueous alcohol mixtures were prepared gravimetrically. Components were added from an accurate pipette, which had been carefully graduated by weight. The reported temperatures (the mean of two or three observations) were those at which the liquid separated into two layers. The results, for the round temperatures, were interpolated by the authors from the curves. Concentrations were reported as alcohol mass concentration in alcohol–water mixture used in the experiment and benzene mass concentration in the solution which became turbid. The temperatures at which benzene crystallized from the investigated mixtures of know composition were reported also in the paper.

Source and Purity of Materials:

(1) source not specified, ordinary ''absolute'' alcohol; distilled from lime, water concentration was determined from the density using ''last edition of Beilstein's Handbuch der Organische Chemie,'' 99.5% alcohol was obtained by treatment with anhydrous copper sulphate and redistillation.
(2) source not specified; freed of thiophene by sulphuric acid, frozen out seven times, distilled over sodium.
(3) not specified.

Estimated Error:

Not reported.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Meassurement:

F. Wehrmann, Z. Elektrochem. **27**, 379–93 (1921).

Variables:

$T/K = 263-303$

Complied by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
−10	263.2	0.1846	0.0014	0.3653	0.0048
	263.2	0.3298	0.0142	0.5403	0.0394
	263.2	0.4115	0.0433	0.5895	0.1051
	263.2	0.4885	0.1010	0.5955	0.2088
	263.2	0.4579	0.3745	0.3953	0.5481
0	273.2	0.0347	0.0007	0.0839	0.0029
	273.2	0.1022	0.0009	0.2249	0.0035
	273.2	0.1781	0.0026	0.3541	0.0087
	273.2	0.2528	0.0081	0.4550	0.0247
	273.2	0.3176	0.0164	0.5242	0.0459
	273.2	0.3994	0.0538	0.5669	0.1295
	273.2	0.4702	0.1287	0.5562	0.2582
	273.2	0.3772	0.4810	0.3022	0.6534
	273.2	0.1035	0.8871	0.0642	0.9335
10	283.2	0.1785	0.0040	0.3534	0.0135
	283.2	0.3116	0.0191	0.5145	0.0534
	283.2	0.3948	0.0627	0.5536	0.1490
	283.2	0.4554	0.1573	0.5213	0.3053
	283.2	0.3416	0.5314	0.2643	0.6973
20	293.2	0.0346	0.0008	0.0837	0.0032
	293.2	0.1020	0.0024	0.2235	0.0089
	293.2	0.2501	0.0117	0.4477	0.0356
	293.2	0.3088	0.0262	0.5035	0.0725
	293.2	0.3890	0.0803	0.5310	0.1858
	293.2	0.4353	0.1845	0.4853	0.3489
	293.2	0.3150	0.5567	0.2406	0.7210
	293.2	0.0220	0.9760	0.0131	0.9864
30	303.2	0.0703	0.0021	0.1609	0.0083
	303.2	0.1772	0.0075	0.3483	0.0251
	303.2	0.3074	0.0316	0.4962	0.0866
	303.2	0.3869	0.0842	0.5252	0.1939
	303.2	0.4123	0.2257	0.4402	0.4086
	303.2	0.2890	0.6027	0.2135	0.7552

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used Binary alcohol–water mixtures of known concentration and volume were put into Erlenmayer flasks, immersed in a constant temperature bath and then titrated with benzene until constant cloudiness was observed. Concentrations of alcohol–water mixtures were determined by density measurements. Results were reported in volume percentage.

Source and Purity of Materials:

(1) source not specified; chemically pure grade; used as received; $d(15\ °C) = 0.8835$.
(2) source not specified.
(3) not specified.

Estimated Error:

concentration ±0.3% relative error.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2)Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
J. Barbaudy, Bull. Soc. Chim. Fr. 39, 371–82 (1926).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
25.00	298.15	0.4080	0.1360	0.4994	0.2823
		0.3112	0.0332	0.4988	0.0903
		0.2774	0.0241	0.4690	0.0691
		0.2100	0.0046	0.4000	0.0150
		0.3543	0.4403	0.3000	0.6320
		0.1442	0.0014	0.3000	0.0050
		0.2734	0.6206	0.2000	0.7697
		0.1551	0.8063	0.1009	0.8893
		0.0938	0.8861	0.0585	0.9366

Auxiliary Information

Method/Apparatus/Procedure:
The mixtures were prepared by weight (corrections on weighing in air were taken into account). Densities and refractive indexes of ternary liquid mixtures were measured. No further details were reported in the paper.

Source and Purity of Materials:
(1) source not specified; distilled over Na; d(25 °C,4 °C) = 0.785 06, n(25 °C,D) = 1.3592.
(2) Toluene, without thiophene; b.p. = 80.3 °C, d(25 °C,4 °C) = 0.873 63, n(25 °C,D) = 1.497 95.
(3) not specified.

Estimated Error:
Not reported.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
J. Barbaudy, Recl. Trav. Chim. Pays-Bas Belg. 45, 207–13 (1926).

Variables:
T/K=298–338

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)			
25.00	298.15	0.0000	0.9957	0.0000	0.9990
		0.0938	0.8857	0.0585	0.9365
		0.1553	0.8074	0.1009	0.8896
		0.2734	0.6206	0.2000	0.7697
		0.3543	0.4403	0.3000	0.6320
		0.4017	0.2825	0.4000	0.4770
		0.4080	0.1360	0.4994	0.2823
		0.3112	0.0332	0.4988	0.0903
		0.2742	0.0204	0.4690	0.0591
		0.2100	0.0046	0.4000	0.0150
		0.1442	0.0014	0.3000	0.0050
60.0	333.15	0.0000	0.0500	0.0000	0.1858
		0.1919	0.0126	0.3660	0.0407
		0.2287	0.0228	0.4083	0.0690
		0.2638	0.0381	0.4386	0.1074
		0.2977	0.0658	0.4523	0.1695
		0.3227	0.0856	0.4615	0.2076
		0.3413	0.1376	0.4385	0.2997
		0.3576	0.2187	0.4000	0.4147
		0.3566	0.2226	0.3968	0.4200
		0.3559	0.2254	0.3946	0.4238
		0.3531	0.3138	0.3477	0.5240
		0.3340	0.3944	0.3012	0.6030
		0.3180	0.4562	0.2695	0.6556
		0.2439	0.6329	0.1787	0.7861
		0.0000	0.9893	0.0000	0.9975

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K(compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.0226	0.9727	0.0766	0.0000	0.0135	0.9854	0.1750	0.0000
		0.0523	0.9376	0.1484	0.0016	0.0318	0.9658	0.3070	0.0055
		0.0856	0.9004	0.1819	0.0027	0.0529	0.9437	0.3600	0.0090
		0.3337	0.2946	0.4040	0.2698	0.3410	0.5105	0.4085	0.4625
		0.3914	0.3176	0.3914	0.3176	0.3750	0.5160	0.3750	0.5160[a]
65.0	338.15	0.2300	0.6727	0.2171	0.0190	0.1633	0.8097	0.3962	0.0587
		0.2314	0.6507	0.2224	0.0201	0.1676	0.7990	0.4023	0.0618
		0.3082	0.4864	0.2977	0.0667	0.2540	0.6798	0.4515	0.1715
		0.3437	0.3007	0.3384	0.1434	0.3463	0.5136	0.4315	0.3101
		0.3430	0.2970	0.3376	0.1488	0.3474	0.5100	0.4269	0.3191
		0.3490	0.2592	0.3397	0.1718	0.3706	0.4667	0.4132	0.3544
		0.3437	0.2547	0.3424	0.1735	0.3686	0.4630	0.4146	0.3562
		0.3438	0.2121	0.3438	0.2121	0.3920	0.4100	0.3920	0.4100[a]

[a] Plait point.

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to find points on saturation curve. Samples of the binary benzene–ethanol mixture (30 mL at 25 °C and 10 mL in tubes with double walls and air jacket to eliminate heat transfer) were immersed in a thermostat, titrated with aqueous ethanol and refractive indexes were measured until the second phase appeared. The analytical method was used to determine coexisting phases. About 100–150 mL of mixture was placed in a 200 mL flask in a thermostat, agitated for more than 1 h, left for 8–48 h for separation and then density and refractive index of each phase were measured.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified.
(3) source not specified.

Estimated Error:

Not reported.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

R. Wright, J. Chem. Soc. **129**, 1203–6 (1926).

Variables:

T/K=284–296

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
11.2	284.35	0.2767	0.0156	0.477 15	0.0457
13.2	286.35	0.2765	0.0164	0.4761	0.0478
15.5	288.65	0.2762	0.0173	0.474 75	0.0505
18.0	291.15	0.2760	0.0182	0.4735	0.0530
20.0	293.15	0.2758	0.0189	0.4726	0.0548
20.2	293.35	0.2757	0.0193	0.471 95	0.0561
22.6	295.75	0.2753	0.0206	0.470 15	0.0597

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used. Solubility was determined by adding a weighed quantity of benzene from a burette to a definite weight of alcohol–water mixture (about 12 g of 50% by weight of the aqueous alcohol) in a stoppered tube and raising the temperature until turbidity disappeared.

Source and Purity of Materials:

(1) not specified.
(2) not specified.
(3) not specified.

Estimated Error:

temp. ±0.1 °C.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6 [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Meassurement:

J. Barbaudy, J. Chim. Phys. **24**, 1–23 (1927).

Variables:

T/K=338–342

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
69.0	342.15	0.0007	0.9865	0.0108	0.0007	0.0004	0.9966	0.027	0.003
68.0	341.15	0.0067	0.9805	0.0278	0.0010	0.0040	0.9930	0.068	0.004
67.0	340.15	0.0199	0.9631	0.0481	0.0012	0.0120	0.9840	0.114	0.005
66.0	339.15	0.0458	0.9333	0.0775	0.0016	0.0280	0.9670	0.176	0.006
65.5	338.65	0.0832	0.8881	0.1000	0.0019	0.0520	0.9410	0.220	0.007
65.0	338.15	0.1407	0.8198	0.1609	0.0059	0.0910	0.8990	0.324	0.020

Auxiliary Information

Method/Apparatus/Procedure:

Compositions of coexisting phases at boiling temperatures were determined as intersections of boiling isotherms in homogeneous and heterogeneous regions. Boiling temperatures were measured for over 100 ternary mixtures.

Source and Purity of Materials:

(1) source not specified.
(2) source not specified.
(3) not specified.

Estimated Error:

Not reported.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

E. R. Washburn, V. Hnizda, and R. Vold, J. Am. Chem. Soc. **53**, 3237–44 (1931).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
24.5	297.7	0.1287	0.8432	0.082	0.911
		0.1537	0.8070	0.100	0.890
		0.1925	0.7541	0.129	0.857
		0.2506	0.6564	0.179	0.795
		0.3235	0.5294	0.253	0.702
		0.3493	0.4571	0.291	0.646
		0.3804	0.3728	0.343	0.570
		0.4158	0.2723	0.416	0.462
		0.4161	0.2180	0.448	0.398
		0.4119	0.1345	0.504	0.279
		0.3991	0.1045	0.518	0.230
		0.3334	0.0438	0.512	0.114
		0.2692	0.0174	0.466	0.051
		0.1934	0.0064	0.374	0.021
		0.1441	0.0024	0.299	0.0083
		0.1203	0.0016	0.258	0.0057

Distribution of ethanol in ethanol–benzene–water system

t/°C	T/K (compiler)	w'_1 hydrocarbon-rich phase	w''_1 water-rich phase
25.0	298.2	0.007	0.025
		0.012	0.106
		0.016	0.164
		0.024	0.243
		0.039	0.318
		0.054	0.370
		0.070	0.405
		0.084	0.443
		0.098	0.573

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used. Binary alcohol–benzene mixtures of known composition, prepared from calibrated pipettes in 125 mL glass-stoppered bottles, were mixed, and titrated with water to a permanent cloudiness at room temperature (24.5 °C). The amount of water was 0.66–5.77 mL (added from a 10 mL burette graduated to 0.01 mL) and 17.1–112.7 mL (added from a calibrated 50 mL burette). The refractive indexes of mixtures were measured at 25.0 °C by Abbe refractometer and used to construct the plot of refractive index against composition which was further used to find compositions of equilibrium phases. Phase equilibrium data were reported in incomplete form. The mixtures of 25.0 mL of benzene and 25.0 mL of water were shaken and then suspended in the constant temperature bath to reach equilibrium. When the phases were transparent, refractive indexes of each layer were measured and compositions of the phases were calculated.

Source and Purity of Materials:

(1) standard commercial grade of absolute alcohol; dried with CaO and Ca until density measurements showed it to be better than 99.3%.
(2) Mallinckrodt, reagent quality; dried with Na, distilled.
(3) redistilled from $KMnO_4$.

Estimated Error:

temp. ±0.1 °C.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

N. Sata and O. Kimura, Bull. Chem. Soc. Jpn. **10**, 409–20 (1935).

Variables:

T/K = 303

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
30	303.2	0.219	0.718	0.150	0.833
		0.350	0.459	0.291	0.647
		0.409	0.269	0.413	0.460
		0.403	0.132	0.498	0.277
		0.333	0.044	0.511	0.114
		0.232	0.010	0.426	0.031
		0.133	0.002	0.280	0.006

Auxiliary Information

Method/Apparatus/Procedure:

Samples of known composition (by volume) were prepared in glass tubes (diameter—15 mm, length—200 mm) and sealed. These were placed in a thermostat and turbidity was observed after some (not reported) time. Eight series of measurements were made. The volume of alcohol was 2.00, 5.00, or 10.00 cm^3. The volume of second component was constant in the series, while the volume of the third component differed 0.05–0.02 cm^3 from point to point. The results were reported in the paper as the volumes of each component added into the tube.

Source and Purity of Materials:

(1) source not specified, 95% commercial reagent; purified with $KMnO_4$, refluxed 1 day with CaO, distilled; purity 99.53%, d(25 °C) = 0.7865.
(2) Merck, pure crystallized; distilled over Na.
(3) doubly distilled.

Estimated Error:

sol. ±0.01 cm^3 (authors), ±(0.0001–0.005) mass fraction (compiler).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

K. A. Varteressian and M. R. Fenske, Ind. Eng. Chem. **28**, 928–33 (1936).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.15	0.0416	0.0002	0.0998	0.0010
		0.1150	0.0010	0.2488	0.0036
		0.1873	0.0033	0.3677	0.0111
		0.2761	0.0193	0.4724	0.0561
		0.3280	0.0399	0.5103	0.1052
		0.3572	0.0571	0.5230	0.1417
		0.3855	0.0860	0.5224	0.1976
		0.3930	0.3222	0.3740	0.5200
		0.3852	0.3418	0.3595	0.5409
		0.3086	0.5461	0.2390	0.7170

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.15	0.0101	0.9877	0.0471	0.0003	0.0060	0.9935	0.1120	0.0013
		0.0308	0.9628	0.0996	0.0007	0.0185	0.9800	0.2200	0.0028
		0.0576	0.9340	0.1495	0.0015	0.0350	0.9630	0.3090	0.0053
		0.0725	0.9150	0.1821	0.0030	0.0445	0.9525	0.3600	0.0102
		0.0733	0.9142	0.1849	0.0033	0.0450	0.9520	0.3640	0.0110
		0.1171	0.8586	0.2398	0.0109	0.0740	0.9200	0.4350	0.0335
		0.1192	0.8546	0.2453	0.0121	0.0755	0.9180	0.4410	0.0370
		0.1320	0.8360	0.2625	0.0162	0.0845	0.9075	0.4590	0.0480
		0.2034	0.7309	0.3539	0.0548	0.1385	0.8440	0.5220	0.1370
		0.2452	0.6631	0.3884	0.0898	0.1745	0.8000	0.5215	0.2045
		0.3162	0.5319	0.4150	0.1693	0.2475	0.7060	0.4800	0.3320
		0.3247	0.5115	0.4155	0.1813	0.2585	0.6905	0.4720	0.3490
		0.3489	0.4501	0.4125	0.2265	0.2930	0.6410	0.4400	0.4095
		0.393	0.322	0.393	0.322	0.374	0.520	0.374	0.520[a]

[a] Critical composition.

Auxiliary Information

Method/Apparatus/Procedure:

The synthetic method was used. Refractive indexes were measured in saturation as well as equilibrium experiments.

Source and Purity of Materials:

(1) Barrett Co., thiophene-free, boiling range 1 °C: distilled, the middle portion was taken for the next distillation; b.p. =80.15 °C, d(25 °C,4 °C)=0.8727, n(25 °C,D)=1.4976.
(2) U.S. Ind. Alcohol Co.; used as received; purity 99.8–99.9% by density measurements; b.p.=78.28 °C, d(25 °C,4 °C) =0.7852, n(25 °C,D)=1.3598.
(3) doubly distilled; n(25 °C,D)=1.3326.

Estimated Error:

temp. ±0.05 °C.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
W. D. Bancroft and S. S. Hubard, J. Am. Chem. Soc. **64**, 347–53 (1942).

Variables:
$T/K=298$

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.2	0.1702	0.0032	0.3411	00109
		0.4105	0.1349	0.5025	02799
		0.3919	0.3509	0.3604	05471
		0.3246	0.5168	0.2570	06939

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
$t/°C$	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.2	0.0101	0.9856	0.0382	0.0005	0.006	0.993	0.092	0.002
		0.0332	0.9583	0.0797	0.0005	0.020	0.978	0.181	0.002
		0.0586	0.9206	0.1298	0.0014	0.036	0.959	0.275	0.005
		0.0912	0.8842	0.1813	0.0039	0.057	0.937	0.358	0.013
		0.1294	0.8347	0.2354	0.0100	0.083	0.908	0.430	0.031
		0.1334	0.8269	0.2407	0.0111	0.086	0.904	0.436	0.034
		0.1609	0.7887	0.2789	0.0183	0.106	0.881	0.477	0.053
		0.1894	0.7462	0.3173	0.0337	0.128	0.855	0.505	0.091
		0.2244	0.6983	0.3551	0.0540	0.156	0.823	0.524	0.135
		0.2622	0.6355	0.3938	0.0958	0.190	0.781	0.521	0.215
		0.2934	0.5810	0.4106	0.1331	0.221	0.742	0.504	0.277
		0.3309	0.5030	0.4177	0.2105	0.265	0.683	0.454	0.388

Auxiliary Information

Method/Apparatus/Procedure:

The binodal curve was prepared by the titration method in glass-stoppered thermostated flasks. The end-point was taken as the first appearance of cloudiness (when water was the saturating liquid) and the first appearance of tiny drops (when benzene was the saturating liquid). The phase equilibrium data were obtained by the authors' new procedure described in the paper. A binary homogenous mixture of known composition was added to a known amount of the phase until homogenization was observed. Then the phase composition was calculated, by trial-and-error method, using the authors knowledge about binodal curve. Data reported in Refs. 1 and 2 were included in the description of the saturation curve.

Source and Purity of Materials:

(1) source not specified; absolute alcohol; dried with CaO, distilled.
(2) source not specified; thiophene-free grade; dried with CaO, distilled.
(3) distilled.

Estimated Error:

temp. ±0.1 °C.

References:

[1] A. T. Lincoln, J. Phys. Chem. **4**, 161 (1990)
[2] K. A. Varteressian and M. R. Fenske, Ind. Eng. Chem **28**, 928 (1936).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
L. A. K. Staveley, R. G. S. Johns, and B C. Moore, J. Chem. Soc. 2516–23 (1951).

Variables:
$T/K=274–342$

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
27.2	300.35	0.006 44	0.990 44	0.003 82	0.995 46
34.4	307.55	0.006 44	0.989 60	0.003 82	0.995 26
42.2	315.35	0.006 44	0.988 27	0.003 82	0.994 95
53.7	326.35	0.006 44	0.985 54	0.003 83	0.994 30
55.2	328.35	0.006 44	0.985 05	0.003 83	0.994 19
66.5	339.65	0.006 44	0.981 37	0.003 84	0.993 31
14.7	287.35	0.0143	0.983 69	0.008 50	0.991 04
32.6	305.75	0.0143	0.981 60	0.008 51	0.990 54
37.4	310.55	0.0143	0.980 68	0.008 52	0.990 31
46.4	319.55	0.0143	0.978 73	0.008 53	0.989 84
51.6	324.75	0.0143	0.977 38	0.008 54	0.989 52
68.7	341.35	0.0143	0.971 42	0.008 58	0.988 07
26.1	299.25	0.0183	0.978 28	0.010 90	0.988 30
39.1	312.25	0.0183	0.976 145	0.010 92	0.987 78
45.4	318.55	0.0183	0.974 79	0.010 93	0.987 45
51.6	324.75	0.0183	0.973 43	0.010 94	0.987 12
60.6	333.75	0.0183	0.970 83	0.010 97	0.986 49
67.7	340.85	0.0183	0.968 64	0.010 99	0.985 95
18.7	291.85	0.024 65	0.971 77	0.014 73	0.984 44
23.1	296.25	0.024 65	0.971 16	0.014 73	0.984 29
26.6	299.75	0.024 65	0.970 67	0.014 74	0.984 17
32.1	305.25	0.024 65	0.969 78	0.014 75	0.983 95
41.6	314.75	0.024 65	0.968 25	0.014 77	0.983 57
57.3	330.45	0.024 65	0.965 76	0.014 80	0.982 95
61.7	334.85	0.024 65	0.964 09	0.014 82	0.982 54
68.4	341.55	0.024 65	0.962 60	0.014 83	0.982 17
16.7	289.35	0.029 86	0.965 43	0.017 89	0.981 00
32.3	305.45	0.029 86	0.963 13	0.017 93	0.980 43
43.4	316.55	0.029 86	0.961 76	0.017 95	0.980 08
55.6	328.75	0.029 86	0.959 61	0.017 98	0.979 54
11.5	284.65	0.042 13	0.951 91	0.025 40	0.973 19
27.9	301.05	0.042 13	0.949 60	0.025 45	0.972 60
38.6	311.75	0.042 13	0.948 25	0.025 48	0.972 25
38.8	311.95	0.042 13	0.948 17	0.025 48	0.972 23
39.0	312.15	0.042 13	0.947 83	0.025 48	0.972 14
62.1	335.25	0.042 13	0.943 25	0.025 58	0.970 95
1.3	274.45	0.0563	0.937 81	0.034 15	0.964 46
12.2	285.35	0.0563	0.935 95	0.034 20	0.963 96
27.5	300.65	0.0563	0.933 57	0.034 26	0.963 33
48.6	321.75	0.0563	0.928 93	0.034 39	0.962 08
13.0	286.15	0.0691	0.921 60	0.042 25	0.955 52
21.4	294.55	0.0691	0.919 78	0.042 31	0.955 02
32.6	305.75	0.0691	0.917 33	0.042 40	0.954 35
41.6	314.75	0.0691	0.914 30	0.042 50	0.953 51
56.5	329.65	0.0691	0.911 47	0.042 60	0.952 72

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

Y. C. Chang and R. W. Moulton, Ind Eng. Chem. **45**, 2350–61 (1953).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.2	0.1213	0.0012	0.2600	0.0043
		0.1496	0.0027	0.3080	0.0095
		0.1735	0.0038	0.3458	0.0129
		0.2737	0.0179	0.4711	0.0521
		0.3430	0.0486	0.5171	0.1242
		0.3978	0.1055	0.5160	0.2320
		0.4175	0.1639	0.4860	0.3235
		0.4177	0.2482	0.4310	0.4342
		0.3879	0.3617	0.3529	0.5580
		0.2947	0.5708	0.2241	0.7359
		0.2597	0.6379	0.1880	0.7830
		0.1508	0.8094	0.0980	0.8919

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.2	0.0310	0.9630	0.0676	0.0005	0.0186	0.9800	0.1561	0.0019
		0.0629	0.9233	0.1445	0.0018	0.0385	0.9582	0.3001	0.0065
		0.0994	0.8813	0.2001	0.0052	0.0621	0.9332	0.3850	0.0171
		0.1238	0.8425	0.2424	0.0094	0.0791	0.9125	0.4400	0.0288
		0.1671	0.7867	0.3097	0.0329	0.1100	0.8781	0.4975	0.0895
		0.2141	0.7181	0.3621	0.0621	0.1468	0.8350	0.5228	0.1521
		0.2542	0.6516	0.3964	0.1028	0.1821	0.7915	0.5172	0.2273
		0.2957	0.5788	0.4140	0.1423	0.2230	0.7400	0.4995	0.2911
		0.3081	0.5579	0.4176	0.1606	0.2358	0.7241	0.4885	0.3185
		0.3601	0.4268	0.4186	0.2439	0.3085	0.6201	0.4342	0.4289
		0.3980	0.3248	0.3980	0.3248	0.3765	0.5210	0.3765	0.5210[a]

[a] Plait point.

Auxiliary Information

Method/Apparatus/Procedure:

The synthetic method was used. Mixtures were prepared in sealed tubes; water was added from a weighted pipette to a known mass of alcohol–benzene mixture.

Source and Purity of Materials:

(1) source not specified; dried by refluxing over freshly ignited lime, and then with magnesium, distilled.
(2) source not specified; chemically purified, crystallized, distilled, dried over phosphoric anhydride.
(3) not specified.

Estimated Error:

composition <0.2%; temp. <0.2 °C.

Auxiliary Information

Method/Apparatus/Procedure:

The cloud point method, as described in Ref. 1, was used. Binary alcohol–benzene mixtures were titrated with water to a sudden appearance of cloudiness. The end point was observed against a bright light as a background. Refractive indexes were measured at 25.5 °C with an Abbe refractometer. To obtain equilibrium, mixtures of known composition were overheated to about 35 °C and placed into a thermostat. When equilibrium was reached and the layers were clear in a bright light, phases were sampled, refractive indexes at 25.5 °C were measured and compositions were determined on the basis of charts obtained in saturation studies.

Source and Pority of Materials:

(1) source not specified, absolute alcohol; dehydrated by magnesium ethoxide method; b.p.=78.3 °C; n(25 °C,D) =1.3596; d(25 °C,4 °C)=0.7851.

(2) source not specified, reagent grade; dehydrated with Na wire, distilled; b.p.=80.1 °C; n(25 °C,D)=1.4978; d(25 °C,4 °C) =0.8725.

(3) distilled.

Estimated Error:

temp. ±0.1 °C (temperature of the bath), composition accuracy 0.5% in the center part of the binodal curve.

References:

[1]S. F. Taylor, J. Phys. Chem. 1, 461 (1897).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Benzene; C_6H_6; [71-43-2] (3) Water; H_2O; [7732-18-5]	A. G. Morachevskii and V. P. Belousov, Vestn. Leningr. Univ., Ser. 4: Fiz. Khim. 4, 117–25 (1958).
Variables: T/K=293–337	**Compiled by:** A. Skrzecz

Experimental Data

Compositions of coexisting phases

		x_2'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
20	293.2	0.3376	0.4941	0.4268	0.1971	0.272	0.675	0.470	0.368
		0.2809	0.6145	0.4180	0.1334	0.206	0.764	0.510	0.276
		0.2484	0.6785	0.3976	0.0941	0.174	0.806	0.526	0.211
		0.1633	0.7938	0.3179	0.0353	0.107	0.882	0.504	0.095
		0.1152	0.8565	0.2489	0.0118	0.073	0.920	0.446	0.036
		0.0762	0.9072	0.1881	0.0042	0.047	0.949	0.368	0.014
		0.0414	0.9501	0.1327	0.0017	0.025	0.973	0.280	0.006
		0.0118	0.9839	0.0637	0.0005	0.007	0.992	0.148	0.002
40	313.2	0.0201	0.9756	0.0642	0.0008	0.012	0.987	0.149	0.003
		0.0572	0.9261	0.1176	0.0016	0.035	0.961	0.253	0.006
		0.1062	0.8655	0.1792	0.0057	0.067	0.926	0.353	0.019
		0.1680	0.7929	0.2495	0.0184	0.110	0.880	0.440	0.055
		0.2550	0.6554	0.3273	0.0533	0.182	0.793	0.496	0.137
		0.3621	0.3801	0.3842	0.1979	0.327	0.582	0.435	0.380
60	333.2	0.0848	0.8866	0.1107	0.0022	0.053	0.940	0.240	0.008
		0.2118	0.7210	0.2300	0.0187	0.145	0.837	0.414	0.057
		0.2973	0.5312	0.3010	0.0527	0.235	0.712	0.468	0.139
		0.3393	0.3808	0.3424	0.0988	0.310	0.590	0.470	0.230

Compositions of coexisting phases (liquid–liquid–vapor-equilibria)

			x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
P/kPa	t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.6	35	308.2	0.014	0.982	0.056	0.001	0.0083	0.9907	0.1313	0.0040
28.3			0.080	0.899	0.154	0.003	0.0496	0.9453	0.3151	0.0104
28.8			0.145	0.816	0.241	0.015	0.0939	0.8962	0.4324	0.0456
29.2			0.197	0.746	0.298	0.033	0.1327	0.8522	0.4841	0.0909
28.9			0.255	0.649	0.348	0.064	0.1831	0.7900	0.5070	0.1581
28.5			0.320	0.508	0.386	0.124	0.2563	0.6898	0.4899	0.2669
39.7	45	318.2	0.017	0.979	0.051	0.001	0.0101	0.9889	0.1205	0.0040
44.8			0.086	0.889	0.140	0.003	0.0536	0.9403	0.2915	0.0106
45.9			0.156	0.801	0.217	0.012	0.1019	0.8871	0.4027	0.0378
46.1			0.213	0.727	0.270	0.027	0.1450	0.8390	0.4571	0.0775
45.9			0.270	0.619	0.320	0.053	0.1981	0.7701	0.4885	0.1372
60.3	55	328.2	0.023	0.972	0.044	0.001	0.0137	0.9851	0.1050	0.0040
67.3			0.092	0.879	0.124	0.003	0.0577	0.9352	0.2636	0.0108
68.8			0.164	0.789	0.195	0.010	0.1079	0.8800	0.3730	0.0324
69.7			0.222	0.704	0.250	0.022	0.1537	0.8263	0.4371	0.0652
69.4			0.278	0.586	0.300	0.047	0.2098	0.7500	0.4724	0.1255
84.5	64	337.2	0.020	0.971	0.037	0.001	0.0120	0.9859	0.0892	0.0041
95.7			0.099	0.873	0.108	0.002	0.0623	0.9309	0.2351	0.0074
97.6			0.174	0.776	0.172	0.008	0.1153	0.8718	0.3398	0.0268
98.5			0.228	0.685	0.235	0.020	0.1602	0.8159	0.4195	0.0605
98.4			0.284	0.563	0.280	0.042	0.2187	0.7352	0.4543	0.1155

Auxiliary Information

Method/Apparatus/Procedure:

Mixtures of known total composition were placed in a thermostat for about 2 h. After phase separation, samples of each phase were taken for analysis using heat-jacketed pipettes. Composition of each phase at different temperatures was found by determinations of the total amount of benzene in a sample combined with tie line data at 20 °C for the mixture investigated. Total amount of benzene was determined by adding a known amount of cyclohexane and 80% H_2SO_4. This caused separation to an acid–water–alcohol phase and a benzene–cyclohexane phase, the refractive index of which was measured. Benzene concentrations were calculated from the benzene–cyclohexane refractive index calibration curve. Tie lines at 20 °C were found by the method described above combined with the binodal curve data at 20 °C determined by isothermal titration method. Liquid–liquid equilibrium data were presented together with vapor pressure and vapor composition over two-liquid mixtures.

Source and Purity of Materials:

(1) source not specified; absolute alcohol was obtained by azeotropic dehydration with C_6H_6; $d(20\ °C,4\ °C)=0.7895$, $n(20\ °C,D)=1.3614$; in most of experiments distillate (containing water) was used; water concentration was determined densimetrically and taken into account in composition determinations.

(2) source not specified; pure for analysis grade, without thiophene; washed with H_2SO_4, H_2O, dried over $CaCl_2$, distilled; b.p.=80.10 °C, $d(20\ °C,4\ °C)=0.8791$, $n(20\ °C,D)=1.5010$.

(3) not specified.

Estimated Error:

temp. <±0.1 °C, error of analytical method <0.5%.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

R. V. Mertslin, N. I. Nikurashina, and L. A. Kamaevskaya, Zh. Fiz. Khim. **35**, 2628–32 (1961).

Variables:

T/K=299

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
26	299.2	0.1169	0.0014	0.2520	0.0050
		0.1873	0.0033	0.3677	0.0111
		0.2155	0.0066	0.4060	0.0210
		0.2738	0.0180	0.4710	0.0525
		0.3280	0.0399	0.5103	0.1052
		0.3569	0.0570	0.5228	0.1415
		0.3854	0.0857	0.5226	0.1970
		0.4052	0.1107	0.5180	0.2400
		0.4076	0.1167	0.5150	0.2500
		0.4107	0.1350	0.5026	0.2800
		0.4116	0.2140	0.4470	0.3940
		0.4247	0.2621	0.4283	0.4482
		0.3930	0.3222	0.3740	0.5200
		0.3950	0.3427	0.3662	0.5387[a]
		0.3706	0.4246	0.3166	0.6150
		0.3559	0.4590	0.2950	0.6450
		0.3086	0.5461	0.2390	0.7170
		0.3098	0.5619	0.2360	0.7258
		0.2629	0.6611	0.1860	0.7930
		0.1283	0.8397	0.0820	0.9100

[a] Critical solubility point.

Distribution of ethanol in ethanol–benzene–water system

t/°C	T/K (compiler)	w_1' hydrocarbon-rich phase	w_2'' water-rich phase
26	299.2	0.0660	0.0050
		0.1380	0.0100
		0.2150	0.0200
		0.2960	0.0300
		0.3780	0.0560
		0.4530	0.0800
		0.4930	0.1060
		0.5130	0.1380
		0.5230	0.1810
		0.5230	0.1810
		0.5200	0.2060
		0.5160	0.2180

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine the binodal curve. The refractive indexes of mixtures were measured at 26 °C using an IRF-22 refractometer to construct the calibration curve, *which was then used to find the concentration of* ethanol in both phases at equilibrium.

Source and Purity of Materials:

(1) source not specified, "absolute;" distilled; b.p = 78.1 °C; $n(26\ °C,D) = 1.3596$.
(2) source not specified; doubly distilled; b.p = 80.0 °C, $n(26\ °C,D) = 1.4975$.
(3) doubly distilled.

Estimated Error:

Not reported.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

S. Ross and R. E. Patterson J. Chem. Eng. Data **24**, 111-5 (1979).

Variables:

T/K = 298

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

		x	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
20.0	293.15	0.0000	1.0000	0.0000	0.0000	0.000	1.000	0.000	0.000
		0.0118	0.9839	0.0637	0.0005	0.007	0.992	0.148	0.002
		0.0414	0.9501	0.1327	0.0017	0.025	0.973	0.280	0.006
		0.0762	0.9072	0.1881	0.0042	0.047	0.949	0.368	0.014
		0.1152	0.8565	0.2489	0.0118	0.073	0.920	0.446	0.036
		0.1633	0.7938	0.3179	0.0353	0.107	0.882	0.504	0.095
		0.2484	0.6786	0.3976	0.0941	0.174	0.806	0.526	0.211
		0.2809	0.6145	0.4180	0.1334	0.206	0.764	0.510	0.276
		0.3376	0.4941	0.4268	0.1971	0.272	0.675	0.470	0.368

Auxiliary Information

Method/Apparatus/Procedure:

Mixtures of known composition (close to the midpoint) and mass of about 90 g were prepared by weighing into flasks with tightly fitting ground-glass stoppers. The solutions were shaken several times and placed in a thermostat for at least 24 h. Then density and surface tension of both phases as well as interfacial tension were measured.

Source and Purity of Materials:

(1) source not specified, absolute alcohol; dried with Mg, distilled; $\rho(20\ °C) = 0.7895\ g\ cm^{-3}$, b.p. = 77.9–78.1 °C, $n(20\ °C,D) = 1.3612$.
(2) source not specified, reagent grade; passed through a column of activated alumina into a bottle containing Na, distilled, (first and last portions of distillate were discarded); $\rho(20\ °C) = 0.8792\ g\ cm^{-3}$, b.p. = 79.5–79.8 °C, $n(20\ °C,D) = 1.5011$.
(3) distilled, redistilled from $KMnO_4$, acidified with phosphoric acid, redistilled, (all distillations under N_2 atmosphere).

Estimated Error:

temp. ±0.05 °C.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Benzene; C_6H_6; [71-43-2]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
V. Brandani, A. Chianese, and M. Rossi, J. Chem. Eng. Data **30**, 27–9 (1985).

Variables:
T/K=303–328

Complied by:
A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
30.00	303.15	0.015	0.971	0.055	0.001	0.009	0.988	0.129	0.004
		0.053	0.935	0.133	0.003	0.032	0.965	0.279	0.011
		0.123	0.846	0.233	0.015	0.078	0.914	0.422	0.046
		0.138	0.816	0.243	0.015	0.090	0.899	0.435	0.046
		0.166	0.781	0.273	0.025	0.110	0.876	0.463	0.072
		0.194	0.725	0.315	0.039	0.133	0.845	0.497	0.104
		0.203	0.712	0.314	0.051	0.141	0.836	0.484	0.133
		0.242	0.662	0.343	0.082	0.173	0.801	0.485	0.197
		0.274	0.595	0.370	0.127	0.205	0.756	0.473	0.275
		0.288	0.555	0.376	0.162	0.223	0.729	0.452	0.330
		0.302	0.545	0.385	0.154	0.235	0.719	0.466	0.316
		0.302	0.526	0.377	0.179	0.239	0.707	0.441	0.355
		0.349	0.415	0.378	0.256	0.305	0.615	0.396	0.454
		0.365	0.353	0.365	0.353	0.340	0.557	0.340	0.557[a]
40.00	313.15	0.019	0.971	0.052	0.001	0.011	0.986	0.123	0.004
		0.065	0.918	0.129	0.004	0.040	0.956	0.272	0.014
		0.149	0.806	0.210	0.014	0.097	0.891	0.391	0.044
		0.163	0.776	0.233	0.016	0.108	0.876	0.421	0.049
		0.200	0.709	0.270	0.025	0.139	0.836	0.459	0.072
		0.228	0.674	0.305	0.039	0.162	0.811	0.486	0.105
		0.230	0.670	0.306	0.054	0.164	0.808	0.472	0.141
		0.265	0.592	0.324	0.094	0.200	0.758	0.456	0.224
		0.316	0.472	0.357	0.197	0.264	0.667	0.413	0.386
		0.324	0.436	0.356	0.237	0.280	0.639	0.388	0.438
		0.344	0.330	0.344	0.330	0.334	0.543	0.334	0.543[a]
55.00	328.15	0.026	0.960	0.046	0.002	0.016	0.981	0.109	0.008
		0.029	0.957	0.049	0.002	0.017	0.979	0.116	0.008
		0.094	0.875	0.125	0.005	0.059	0.933	0.264	0.018
		0.181	0.755	0.197	0.014	0.122	0.861	0.372	0.045
		0.183	0.747	0.209	0.017	0.124	0.858	0.387	0.053
		0.203	0.711	0.223	0.015	0.141	0.836	0.407	0.050
		0.241	0.643	0.256	0.024	0.175	0.792	0.443	0.070
		0.267	0.596	0.293	0.034	0.201	0.759	0.477	0.094
		0.268	0.581	0.287	0.060	0.204	0.751	0.446	0.158
		0.302	0.476	0.316	0.127	0.253	0.675	0.422	0.287
		0.344	0.351	0.343	0.151	0.325	0.562	0.430	0.321
		0.354	0.271	0.354	0.271	0.369	0.479	0.369	0.479[a]

[a] Plait point estimated by the authors.

Auxiliary Information

Method/Apparatus/Procedure:
The analytical method was used. Mixtures were stirred in an equilibrium cell fitted with a jacket for the circulating fluid and equipped with a mechanical stirrer. After equilibrium was reached each layer was withdrawn with a syringe and the composition was determined by glc (Carlo Erba Fractovap 2400 T, 2 m Poropak column, thermal conductivity detector; peak areas were measured with S-3380 Hewlett–Packard integrator). Calibration curves were prepared for the compositions closed to solubility curve at 20 °C. Each reported result is a mean of four analysis.

Source and Purity of Materials:
(1) source not specified, reagent grade; used as received.
(2) source not specified, reagent grade; used as received.
(3) doubly distilled.

Estimated Error:
temp. ±0.05 °C; composition accuracy ±1%.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexene; C_6H_{10}; [110-83-8]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.05)

4.2. Ethanol + Water +Cyclohexene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system ethanol–cyclohexene–water is given in Table 20.

TABLE 20. Summary of experimental data for the system ethanol–cyclohexene–water

Author(s)	T/K	Type of data[a]	Ref.
Washburn *et al.*, 1940	298	sat. (12), eq. (6)	1
Kretschmer and Wiebe, 1945	228–298	sat. (9)	2

[a] Number of experimental points in parentheses.

Saturation curve

The system ethanol–cyclohexene–water forms a miscibility gap of type 1. Compositions along the saturation curves reported in both references were obtained by the titration method. Experimental data within each data set, measured at various temperatures, as well as both data sets, are consistent. The experimental results at 228, 273, and 298 K in the paper of Washburn *et al.*,[1] were expressed as the water tolerance of the alcohol–hydrocarbon mixture. Only one binary system, cyclohexene–water, forms a miscibility gap. Binary data of this system were compiled and critically evaluated in a previously published SDS volume.[3] The recommended, Ref. 3, values of mutual solubility at 298 K are: $x_2'=0.9983$ and $x_2''=0.000\,035$. Binary solubility data were not reported together with ternary data in any of the references discussed. Compositions of coexisting phases in equilibrium at 298.2 K, Ref. 1, are consistent with those measured along the saturation curve. Experimental results reported at lower temperatures by Kretschmer and Wiebe[2] are in agreement with the general expectation, at lower temperature the solubility gap increases. The maximum ethanol concentration is observed on the saturation curve at 298.2 K. It was reported to be $x_1=0.559$ and $x_2=0.157$.

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system ethanol–cyclohexene–water were presented only in Ref. 1. The reported tie lines cover the whole range of miscibility gap. In the paper of Washburn *et al.*[1] two points reported for the hydrocarbon-rich phase did not contain water ($x_2=0.9947$ and $x_2=0.9460$). This presumably was the result of analytical limitations (self constructed refractive index–composition curve). Experimental compositions along the saturation curve and experimental compositions of coexisting phases in equilibrium at 298.2 K are treated as tentative and are presented in Fig. 11.

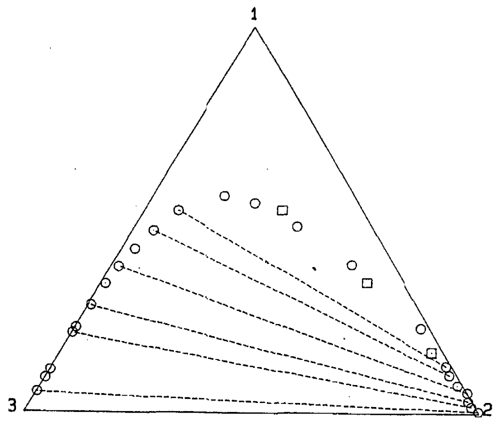

FIG. 11. Phase diagram of the system ethanol (1)—cyclohexene (2)—water (3) at 298.2 K. ○—experimental data, Ref. 1, □—experimental data, Ref. 2, dashed lines—experimental tie lines, Ref. 1.

References:

[1] E. R. Washburn, C. L. Graham, G. B. Arnold, and L. F. Transue, J. Am. Chem. Soc. **62**, 1454 (1940).
[2] C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. **37**, 1130 (1945).
[3] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexene; C_6H_{10}; [110-83-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

E. R. Washburn, C. L. Graham, G. B. Arnold, and L. F. Transue, J. Am. Chem. Soc. **62**, 1454–7 (1940).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.15	0.0727	0.9155	0.0425	0.9548
		0.2195	0.7607	0.1386	0.8565
		0.3827	0.5229	0.2831	0.6896
		0.4811	0.3537	0.4090	0.5361
		0.5415	0.2315	0.5192	0.3957
		0.5592	0.1570	0.5886	0.2946
		0.5213	0.0733	0.6431	0.1613
		0.4215	0.0285	0.6132	0.0739
		0.3313	0.0105	0.5454	0.0308
		0.2189	0.0017	0.4156	0.0059
		0.1098	0.0004	0.2394	0.0017
		0.0884	0.0003	0.1985	0.0012

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.15	0.0053	0.9947	0.0521	0.0007	0.003	0.997	0.123	0.003
		0.0176	0.9734	0.2054	0.0009	0.010	0.988	0.397	0.003
		0.0314	0.9596	0.2762	0.0057	0.018	0.980	0.487	0.018
		0.0540	0.9460	0.3753	0.0166	0.031	0.969	0.584	0.046
		0.0992	0.8836	0.4689	0.0461	0.059	0.937	0.633	0.111
		0.1219	0.8653	0.5209	0.0731	0.073	0.924	0.643	0.161

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, as described in Ref. 1, was used. The titrant, from a weighed pipette, was added to the weighed binary mixture of known composition and the mixture was kept in a thermostated bath. To confirm that the end-point was reached the mixture was shaken automatically for at least 15 min and then reexamined. The plot of refractive index against composition was then used to find compositions of equilibrium phases. The refractive indexes were determinated at the temperature of 30.0 °C to eliminate an opalescence.

Source and Purity of Materials:

(1) Eastman Kodak Company, commercial grade; dried by refluxing over active lime, twice distilled; $d(25\ °C, 4\ °C) = 0.7851$, $n(25\ °C, D) = 1.359\,42$.
(2) Eastman Kodak Company, commercial grade; distilled in an atmosphere of purified N_2, collected in dried nitrogen-filled bottles; $d(25\ °C, 4\ °C) = 0.8056$, $n(25\ °C, D) = 1.4434$.
(3) not specified.

Estimated Error:

temp. ±0.05 °C.

References:

[1] E. R. Washburn and A. E. Beguin, J. Am. Chem. Soc. **62**, 579 (1940).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexene; C_6H_{10}; [110-83-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. **37**, 1130–2 (1945).

Variables:

T/K=228–298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)
−45.0	228.2	0.5967	0.3420	0.4849	0.4956
		0.3586	0.6166	0.2443	0.7491
		0.1610	0.8304	0.0979	0.9001
0.0	273.2	0.5531	0.3170	0.4731	0.4835
		0.3463	0.5954	0.2420	0.7420
		0.1593	0.8218	0.0976	0.8979
25.0	298.2	0.5234	0.3000	0.4643	0.4745
		0.3371	0.5797	0.2403	0.7366
		0.1581	0.8156	0.0974	0.8962

Comments and Additional Data

Water tolerance (S) was described with probable error <0.5% at the range −45–25 °C by the equation: $\log(S) = a - b/(T/\mathrm{K})$. The parameters (a,b) were determined from plots. Water tolerance was defined as: $S = H_2O\%$ by volume·(100 - Hydrocarbon % by volume in the blend)/100

vol % hydrocarbon	a	b
90	1.312	477.5
75	2.051	530.4
50	2.332	487.6

Auxiliary Information

Method/Apparatus/Procedure:

A glass tube with stirrer containing the ternary mixture was immersed in a bath, the temperature of which could be varied. Mixtures were prepared directly in the tube, by special pipettes at 15.5 °C. Precautions to exclude moisture and to prevent evaporation were observed. No correction was made for the slight expansion in volume when alcohol was mixed with hydrocarbon. In the paper the experimental results were expressed as the water tolerance of the alcohol–hydrocarbon blend. For practical purposes water tolerance was defined as the volume per cent of water which can be added before separation occurs.

Source and Purity of Materials:

(1) source not specified; anhydrous ethanol.
(2) source not specified; b.p.=82.55–82.65 °C.
(3) not specified.

Estimated Error:

temp. within about 0.3 °C (duplicate determinations); composition <0.2% relative of volume fraction.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Evaluated by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.04)

4.3. Ethanol + Water + Cyclohexane

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of ethanol between phases (distr.) for the system ethanol–cyclohexane–water is given in Table 21.

TABLE 21. Summary of experimental data for the system ethanol–cyclohexane–water

Author(s)	T/K	Type of data[a]	Ref.
Vold and Washburn, 1932	298	sat. (16), distr. (8)	1
Tarasenkov and Paulsen, 1937	273, 298	sat. (19)	2
Tarasenkov and Paulsen, 1939	298	eq. (3)	3
Kretschmer and Wiebe, 1945	228–298	sat. (5)	4
Connemann *et al.*, 1990	303–335	eq. (6)	5
Moriyoshi *et al.*, 1991	298, 323	eq. (36)	6
Letcher *et al.*, 1991	298	sat. (17), eq. (6)	7
Plackov and Stern, 1992	298	sat. (21), eq. (6)	8

[a]Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–cyclohexane–water forms a miscibility gap of type 1. Eight studies of the system in the temperature range 228–335 K were reported; seven studies included measurements at 298 K. A growing saturation gap with the decreasing temperature is well observed from 298 to 335 K. The maximum ethanol concentration changes from 0.628 (298 K), through 0.598 (323 K) to 0.547 (335 K). The temperature 298.2 K was selected to present the behavior of the system. Only one binary system, cyclohexane–water, forms a miscibility gap. The data for this binary system were compiled and critically evaluated in a previously published SDS volume, Ref. 9; the recommended values of mutual solubility at 298.2 K are: $x_2''=1.2\cdot10^{-5}$ and $x_3'=3.7\cdot10^{-4}$.

The end points of saturation curve were reported to be pure cyclohexane and water.[6,7] For the water-rich phase and ethanol concentrations up to about 0.16 mole fraction the system was reported to be cyclohexane free.[6,7] All these results are within the accuracy of experimental measurements which were stated by the authors to be 0.001 mole fraction. The experimental point on saturation curve $x_2=0.0002$ by Vold and Washburn,[1] appears to contain experimental error and was rejected. All saturation data sets are consistent within each reference as well as with one another. Experimental solubility and equilibrium data reported at 298.2 K ($0.001<x_2<0.98$), for both water-rich and hydrocarbon-rich branches, were described by the equation:

$$x_1=1.021\,89+0.131\,29\,\ln(x_2)-1.019\,99x_2\,.$$

The least-squares method was used and the standard error of estimate was 0.0198. Compositions on the saturation curve calculated by this equation for selected concentrations of cyclohexane in the mixture are presented in Table 22 and in Fig. 12.

TABLE 22. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 012 Ref. 9	0.4209	0.5000
0.1140	0.0010	0.4056	0.5200
0.4071	0.0100	0.3902	0.5400
0.4879	0.0200	0.3746	0.5600
0.5585	0.0400	0.3588	0.5800
0.5913	0.0600	0.3428	0.6000
0.6087	0.0800	0.3267	0.6200
0.6176	0.1000	0.3105	0.6400
0.6211	0.1200	0.2941	0.6600
0.6210	0.1400	0.2777	0.6800
0.6181	0.1600	0.2611	0.7000
0.6132	0.1800	0.2444	0.7200
0.6066	0.2000	0.2276	0.7400
0.5987	0.2200	0.2107	0.7600
0.5897	0.2400	0.1937	0.7800
0.5798	0.2600	0.1766	0.8000
0.5692	0.2800	0.1594	0.8200
0.5578	0.3000	0.1422	0.8400
0.5459	0.3200	0.1249	0.8600
0.5335	0.3400	0.1075	0.8800
0.5206	0.3600	0.0901	0.9000
0.5073	0.3800	0.0725	0.9200
0.4936	0.4000	0.0550	0.9400
0.4796	0.4200	0.0373	0.9600
0.4653	0.4400	0.0196	0.9800
0.4507	0.4600	0.0000	0.999 63 Ref. 9
0.4359	0.4800		

Phases in equilibrium

Compositions of coexisting phases in equilibrium of the ternary system ethanol–cyclohexane–water were reported for the temperature range 298–335 K. The tie lines cover the full area of miscibility gap. The reported plait point calculated in Ref. 5 at 334.1 K was $x_1=0.437$ and $x_2=0.416$. Phase equilibrium data of Tarasenkov and Paulsen,[3] are inconsistent with saturation curve and are rejected. The other reported equilibrium data sets are consistent with one another, and within each data set. The small differences in tie lines are the result of experimental errors of phase analysis. The data for phases in equilibrium are considered tentative. The experimental tie lines at 298.2 K as well as all experimental points on saturation curve, Refs. 4, 6, 7 and 8, at 298.2 K, are reported in Fig. 12.

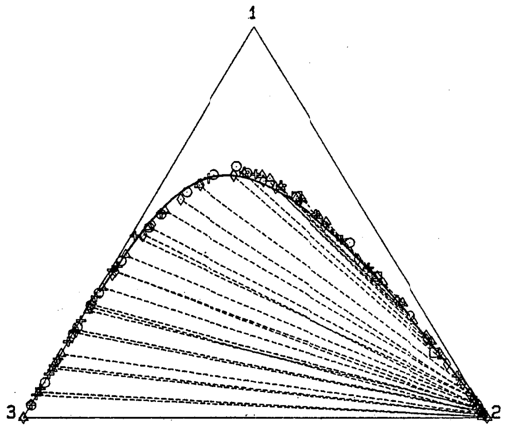

FIG. 12. Phase diagram of the system ethanol (1)—cyclohexane (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 1, □—experimental data, Ref. 4, △—experimental data, Ref. 6, ◇—experimental data, Ref. 7, ✣—experimental data, Ref. 8, dashed lines—experimental tie lines, Refs. 4, 6, 7, and 8.

References:

[1] R. D. Vold and E. R. Washburn, J. Am. Chem. Soc. **54**, 4217 (1932).

[2] D. N. Tarasenkov and I. A. Paulsen, Zh. Obshch. Khim. **7**, 2143 (1937).

[3] D. N. Tarasenkov and I. A. Paulsen, Acta Physicochim. URSS **9**, 75 (1939).

[4] C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. **37**, 1130 (1945).

[5] M. Connemann, J. Gaube, L. Karrer, A. Pfennig, and U. Reuter, Fluid Phase Equilib. **60**, 99 (1990).

[6] T. Moriyoshi, Y. Uosaki, K. Takahashi, and T. Yamakawa, J. Chem. Thermodyn. **23**, 37 (1991).

[7] T. M. Letcher, P. Siswana, and S. E. Radloff, S. Afr. J. Chem. **44**, 118 (1991).

[8] D. Plackov and I. Stern, Fluid Phase Equilib. **71**, 189 (1992).

[9] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Cyclohexane; C_6H_{12}; [110-82-7] (3) Water; H_2O; [7732-18-5]	R. D. Vold and E. R. Washburn, J. Am. Chem. Soc. **54**, 4217–25 (1932).
Variables:	**Compiled by:**
T/K=298	A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25	298.2	0.0314	0.0007	0.0763	0.0032
		0.0898	0.0014	0.2005	0.0059
		0.2143	0.0002	0.4106	0.0008
		0.2309	0.0016	0.4324	0.0054
		0.2868	0.0025	0.5038	0.0081
		0.3184	0.0044	0.5385	0.0136
		0.4014	0.0110	0.6163	0.0309
		0.4876	0.0278	0.6699	0.0698
		0.5213	0.0368	0.6847	0.0884
		0.5781	0.0634	0.6931	0.1388
		0.6226	0.1023	0.6789	0.2038
		0.6435	0.1399	0.6541	0.2598
		0.6269	0.1706	0.6159	0.3063
		0.5656	0.3056	0.4817	0.4754
		0.4485	0.4799	0.3314	0.6479
		0.2606	0.7039	0.1670	0.8241

Distribution of ethanol in ethanol–cyclohexane–water system

t/°C	T/K (compiler)	w'_1 hydrocarbon-rich phase	w''_1 water-rich phase
25.00	298.15	0.000	0.0072
		0.000	0.0330
		0.000	0.0368
		—	0.0665
		0.0020	0.1274
		0.0037	0.1880
		0.0064	0.2810
		0.0120	0.4360

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to obtain points on the saturation curve. A 100 mL flask containing weighed amounts of ethanol and cyclohexane was suspended in a temperature controlled water bath at 24.8 °C and water was added from a weighed pipette until phase separation occurred. The appearance of a second phase was taken as the end-point. After each addition of water the flask was shaken for 30 s and then allowed to stand for at least 5 min. The flask was open only during addition of water from the pipette. The change of weight due to evaporation was no larger than 0.3%. Refractive index of each saturated mixture was measured at 25.0 °C, 0.2 °C above the titration temperature in order to assure homogeneous solutions. To determine the distribution of ethanol between water and organic phases, mixtures of 10 mL of water and different amounts of ethanol were prepared in glass-stoppered bottles, suspended in a thermostat 25.00 °C for 12 h and then the refractive indexes of both phases were measured and compared with those obtained for saturation mixtures.

Source and Purity of Materials:

(1) source not specified; absolute-standard commercial grade; refluxed over freshly ignited lime, distilled from an all-glass apparatus until density showed it to be 99.91% alcohol by Ref. 1.
(2) Eastman Kodak Co.; the best grade; fractionally crystallized, distilled, dried over Na, distilled; $\rho=0.773\ 79\ \mathrm{g/cm^3}$, f.p. $=6.20$ °C.
(3) double distilled over $KMnO_4$.

Estimated Error:

temp. ±0.2 K (estimated by the compiler).

References:

[1] *International Critical Tables*, Vol. 3 (McGraw Hill, New York, 1929).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexene; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

D. N. Tarasenkov and I. A. Paulsen, Zh. Obshch. Khim. 7, 2143–8 (1937).

Variables:

T/K=273–298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
0.0	273.15	0.2316	0.7426	0.1449	0.8488
		0.3521	0.5680	0.2478	0.7302
		0.4245	0.5131	0.3062	0.6762
		0.6001	0.3085	0.5003	0.4699
		0.6636	0.1900	0.6214	0.3250
		0.6298	0.0699	0.7198	0.1460
		0.5971	0.0533	0.7184	0.1171
		0.4920	0.0182	0.6863	0.0465
		0.4288	0.0090	0.6447	0.0247
		0.3228	0.0040	0.5441	0.0122
		0.1682	0.0006	0.3402	0.0023
20.0	298.15	0.4477	0.4797	0.3310	0.6480
		0.5658	0.3056	0.4818	0.4754
		0.6110	0.2388	0.5524	0.3945
		0.6329	0.2050	0.5911	0.3497
		0.6357	0.1401	0.6491	0.2614
		0.6004	0.0773	0.6920	0.1627
		0.5212	0.0369	0.6845	0.0885
		0.3806	0.0075	0.6007	0.0217

Auxiliary Information

Method/Apparatus/Procedure:

A titration method similar to that in Ref. 1 was used. A flask of 100 mL capacity containing a binary cyclohexane–alcohol mixture of known composition, by weight, was placed in a thermostat. The mixture was titrated with water from a microburette with a scale of 0.01 mL, until opalescence, emulsion or turbidity was observed. Samples of the same binary composition were titrated several times.

Source and Purity of Materials:

(1) source not specified; purity of 99.97% for 3 points of the lower alcohol concentration at each temperature and purity of 92.64% for all other points.
(2) source not specified; distilled; b.p. $=80.9$ °C, $d(20\ °\mathrm{C},4\ °\mathrm{C})=0.7744$.
(3) source not specified.

Estimated Error:

temp. ±0.05 °C.

References:

[1] R. E. Washburn, J. Am. Soc. **53**, 3237 (1931).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
D. N. Tarasenkov and I. A. Paulsen, Acta Physicochim. URSS 9, 75–86 (1939).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.2	0.0110	0.9743	0.2530	0.0036	0.0061	0.9907	0.4598	0.0119
		0.0278	0.9563	0.3284	0.0044	0.0156	0.9809	0.5498	0.0135
		0.1607	0.7915	0.6135	0.1125	0.0989	0.8896	0.6624	0.2219

Auxiliary Information

Method/Apparatus/Procedure:
Not described. The data were also reported in Refs. 1 and 2.

Source and Purity of Materials:
(1) source not specified.
(2) source not specified.
(3) source not specified.

Estimated Error:
Not reported.

References:
[1]D. N. Tarasenkov and I. A. Paulsen, Zh. Obshch. Khim. 7, 2143 (1937).
[2]D. N. Tarasenkov and I. A. Paulsen, Zh. Obshch. Khim. 8, 76 (1938).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. 37, 1130–2 (1945).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)
−45.0	228.2	0.8347	0.1495	0.7493	0.2452[a]
0.0	273.2	0.6991	0.1252	0.7015	0.2295[a]
25.0	298.2	0.5680	0.3052	0.4834	0.4745
		0.3604	0.5809	0.2495	0.7346
		0.1662	0.8037	0.1010	0.8919

[a]Solution in equilibrium with solid cyclohexane.

Comments and Additional Data

Water tolerance (S) was described with probable error < 0.5% at the range −45–25 °C by the equation: $\log(S)=a-b/(T/\mathrm{K})$. The parameters ($a$,$b$) were determined from plots. Water tolerance was defined as: $S=H_2O$ % by volume·(100-Hydrocarbon % by volume in the blend)/100

vol % hydrocarbon	a	b
90	1.856	628.7
75	2.421	693.4
50	2.850	693.4
25	6.328	1526.0

at the range −45–0 °C; solution in equilibrium with solid cyclohexane.

Auxiliary Information

Method/Apparatus/Procedure:
A glass tube with stirrer containing the ternary mixture was immersed in a bath, the temperature of which could be varied. Mixtures were prepared directly in the tube, by special pipettes at 15.5 °C. Precautions to exclude moisture and to prevent evaporation were observed. No correction was made for the slight expansion in volume when alcohol was mixed with hydrocarbon. In the paper the experimental results were expressed as the water tolerance of the alcohol–hydrocarbon blend. For practical purposes water tolerance was defined as the volume per cent of water which can be added before separation occurs.

Source and Purity of Materials:
(1) source not specified; anhydrous ethanol.
(2) source not specified; b.p.=78–81 °C.
(3) not specified.

Estimated Error:
temp. within about 0.3 °C (duplicate determinations); composition <0.2% relative of volume fraction.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

M. Connemann, J. Gaube, L. Karrer, A. Pfennig, and U. Reuter, Fluid Phase Equilib. **60**, 99–118 (1990).

Variables:

T/K=303–335

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C (compiler)	T/K	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		organic-rich phase		water-rich phase		organic-rich phase (compiler)		water-rich phase (compiler)	
30.0	303.2	0.027	0.969	0.337	0.004	0.015	0.984	0.560	0.012
61.4	334.6	0.074	0.910	0.424	0.019	0.042	0.954	0.627	0.051
60.5	333.7	0.146	0.826	0.521	0.080	0.083	0.906	0.633	0.178
61.6	334.8	0.200	0.757	0.547	0.140	0.125	0.864	0.591	0.276
61.5	334.7	0.316	0.601	0.515	0.262	0.213	0.759	0.476	0.443
60.9	334.1	0.437	0.416	0.437	0.416	0.348	0.606	0.348	0.606[a]

[a] Plait point evaluated by the authors.

Auxiliary Information

Method/Apparatus/Procedure:

An equilibration cell with magnetic stirrer and a jacket for circulating thermostated fluid was used. Temperature was measured with a PT-100 resistance thermometer. After phase separation, samples of each phase were withdrawn with a syringe, dissolved in a known amount of 2-propanol and analyzed. Walter was determined by the Karl Fischer titration; the mass ratio of ethanol to cyclohexane was determined by glc using a peak-area calibration curve prepared earlier.

Source and Purity of Materials:

(1) Merck, Chromato-quality; dried over molecular sieves 3A; purity >99.8 mole %, impurities: organic <0.001 mass fraction, water <0.000 45 mass fraction by the Karl Fischer titration.
(2) Merck, Chromato-quality; dried over molecular sieves 3A; purity >99.8 mole %, impurities: organic <0.002 mass fraction, water <0.000 001 mass fraction by the Karl Fischer titration.
(3) distilled three times.

Estimated Error:

temp. ±0.1 K.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Cyclohexane; C_6H_{12}; [110-82-7]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. Moriyoshi, Y. Uosaki, K. Takahashi, and T. Yamakawa, J. Chem. Thermodyn. **23**, 37–42 (1991).

Variables:

T/K=298 and 323

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C (compiler)	T/K	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000
		0.0020	0.9870	0.0640	0.0000	0.0011	0.9965	0.1488	0.0000
		0.0070	0.9840	0.1250	0.0000	0.0039	0.9942	0.2676	0.0000
		0.0110	0.9750	0.1640	0.0000	0.0061	0.9908	0.3341	0.0000
		0.0170	0.9750	0.2250	0.0010	0.0094	0.9888	0.4249	0.0035
		0.0260	0.9640	0.2740	0.0030	0.0145	0.9833	0.4874	0.0097
		0.0270	0.9630	0.3320	0.0050	0.0151	0.9827	0.5530	0.0152
		0.0380	0.9530	0.4180	0.0120	0.0213	0.9767	0.6306	0.0331
		0.0510	0.9440	0.4890	0.0260	0.0287	0.9702	0.6734	0.0654
		0.0630	0.9320	0.5310	0.0400	0.0356	0.9633	0.6880	0.0947
		0.0910	0.8980	0.5980	0.0790	0.0524	0.9451	0.6884	0.1661
		0.1570	0.8240	0.6250	0.1650	0.0940	0.9015	0.6197	0.2989
		0.1950	0.7830	0.6220	0.2050	0.1193	0.8754	0.5845	0.3519
		0.2210	0.7640	0.6130	0.2260	0.1305	0.8634	0.5630	0.3792
		0.2470	0.7180	0.5910	0.2590	0.1571	0.8342	0.5264	0.4214
		0.2930	0.6690	0.5600	0.3200	0.1915	0.7988	0.4700	0.4906
		0.3460	0.6010	0.5180	0.3790	0.2362	0.7496	0.4142	0.5536
		0.3620	0.5810	0.5030	0.4030	0.2504	0.7342	0.3942	0.5770
50.00	323.15	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000
		0.0180	0.9820	0.1300	0.0000	0.0099	0.9901	0.2765	0.0000
		0.0260	0.9700	0.1820	0.0010	0.0144	0.9847	0.3616	0.0036
		0.0380	0.9600	0.2670	0.0030	0.0212	0.9784	0.4785	0.0098
		0.0480	0.9500	0.3210	0.0060	0.0269	0.9727	0.5394	0.0184
		0.0570	0.9400	0.3650	0.0080	0.0321	0.9672	0.5842	0.0234
		0.0620	0.9350	0.3920	0.0120	0.0350	0.9643	0.6059	0.0339
		0.0730	0.9230	0.4280	0.0210	0.0415	0.9577	0.6277	0.0563
		0.0760	0.9190	0.4480	0.0220	0.0433	0.9556	0.6442	0.0578
		0.0890	0.8990	0.4780	0.0370	0.0513	0.9460	0.6501	0.0919
		0.1250	0.8610	0.5470	0.0800	0.0734	0.9234	0.6520	0.1742
		0.1300	0.8540	0.5520	0.0850	0.0766	0.9197	0.6500	0.1829
		0.1580	0.8210	0.5780	0.1150	0.0948	0.9002	0.6365	0.2313
		0.1870	0.7820	0.5890	0.1230	0.1149	0.8777	0.6358	0.2426
		0.2300	0.7300	0.5980	0.1290	0.1456	0.8445	0.6359	0.2506
		0.2810	0.6620	0.5870	0.1740	0.1858	0.7995	0.5880	0.3184
		0.3800	0.5380	0.5530	0.2750	0.2724	0.7046	0.4926	0.4475
		0.4230	0.4830	0.5290	0.3230	0.3152	0.6574	0.4495	0.5014

Components:	Original Measurements:
(1) *Ethanol (ethyl alcohol)*; C_2H_6O; [64-17-5] (2) Cyclohexane; C_6H_{12}; [110-82-7] (3) Water; H_2O; [7732-18-5]	T. M. Letcher, P. Siswana, and S. E. Radloff, Afr. J. Chem **44**, 118–21 (1991).
Variables: T/k=298	**Compiled by:** A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C (compiler)	T/K	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25.0	298.2	0.000	0.000	0.000	0.000
		0.144	0.001	0.300	0.004
		0.207	0.001	0.399	0.004
		0.280	0.004	0.494	0.013
		0.366	0.010	0.583	0.029
		0.466	0.024	0.657	0.062
		0.495	0.030	0.673	0.075
		0.597	0.083	0.683	0.174
		0.621	0.146	0.634	0.272
		0.607	0.215	0.568	0.367
		0.560	0.307	0.477	0.478
		0.492	0.404	0.387	0.581
		0.406	0.518	0.294	0.685
		0.298	0.655	0.197	0.791
		0.165	0.815	0.099	0.896
		0.088	0.903	0.051	0.947
		0.000	0.999	0.0000	0.9998

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C (compiler)	T/K	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.008	0.990	0.282	0.004	0.004	0.995	0.496	0.013
		0.015	0.982	0.374	0.012	0.008	0.991	0.588	0.034
		0.028	0.970	0.469	0.025	0.016	0.984	0.658	0.064
		0.061	0.930	0.560	0.059	0.035	0.963	0.686	0.132
		0.137	0.845	0.621	0.145	0.081	0.915	0.635	0271
		0.200	0.770	0.590	0.249	0.124	0.869	0.533	0.411

Auxiliary Information

Method/Apparatus/Procedure:

The method was similar to that described in Ref. 1. After equilibrium was reached, both phases were analyzed by glc using acetone as an internal standard (a glass column (diameter 3.2 mm, 2 m long) packed with PEG-6000 Shimalite TPA; 353 K, He flow rate 0.33 mL/s). Compositions were determined from the peak-area diagram.

Source and Purity of Materials:

(1) source and purification procedure was described in Ref. 2.
(2) Dojin Chemical. Co.; spectrograde, used as received; refractive index agreed to within 0.005 with literature values.
(3) de-ionized, distilled over KMnO4, redistilled, by Ref. 1.

Estimated Error:

composition <±0.001 mass fraction.

References:

[1] T. Moriyoshi, Y. Uosaki, H. Matsuura, and W. Nishimoto, J. Chem Thermodyn. **20**, 551 (1988).

[2] T. Moriyoshi, T. Sakamoto, and Y. Uosaki, J. Chem. Thermodyn. **27**, 947 (1989).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Cyclohexane; C_6H_{12}; [110-82-7] (3) Water; H_2O; [7732-18-5]	D. Plackov and I. Stern, Fluid. Phase. Equilib. **71**, 189–209 (1992).
Variables:	**Compiled by:**
T/K=298	A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25	298.2	0.0433	0.9506	0.0243	0.9744
		0.1058	0.8826	0.0614	0.9360
		0.1890	0.7851	0.1157	0.8781
		0.2915	0.6653	0.1913	0.7976
		0.3824	0.5531	0.2697	0.7125
		0.4553	0.4600	0.3426	0.6324
		0.5204	0.3726	0.4187	0.5476
		0.5588	0.3181	0.4703	0.4891
		0.5945	0.2590	0.5285	0.4206
		0.6230	0.1915	0.5960	0.3347
		0.6284	0.1653	0.6215	0.2987
		0.6125	0.0939	0.6814	0.1908
		0.5235	0.0366	0.6867	0.0877
		0.3864	0.0105	0.6024	0.0299
		0.3073	0.0044	0.5258	0.0138
		0.2471	0.0021	0.4538	0.0070
		0.1931	0.0008	0.3788	0.0029
		0.1491	0.0005	0.3090	0.0019
		0.1111	0.0004	0.2419	0.0016
		0.0735	0.0002	0.1685	0.0008
		0.0334	0.0002	0.0811	0.0009

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C	T/K (compiler)	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25	298.2	0.003	0.994	0.057	0.000	0.002	0.998	0.134	0.000
		0.007	0.990	0.132	0.000	0.004	0.996	0.280	0.000
		0.015	0.982	0.218	0.003	0.008	0.991	0.413	0.010
		0.021	0.976	0.290	0.004	0.012	0.988	0.506	0.013
		0.032	0.964	0.377	0.005	0.018	0.981	0.601	0.015
		0.051	0.943	0.465	0.009	0.029	0.970	0.677	0.024

Auxiliary Information

Method/Apparatus/Procedure:

The points on the binodal curve were determined by the titration method, as described in Ref. 1. The formation of a cloudy mixture was observed visually on shaking after addition of a known mass of the third component; syringes were precisely weighed. Tie line compositions were determined by the refractive index method,[2] and a complementary method using the Karl Fischer titration.[3] Measurements were made at pressure of 94.7 kPa.

Source and Purity of Materials:

(1) Merck: AR grade; refluxed with Mg and I_2, distilled; purity >99.9 mole % by glc.
(2) BDH; Gold label grade; used as received; purity >99.9 mole % by glc.
(3) not specified.

Estimated Error:

composition ±0.005 mole fraction (binodal curve), ±0.01 mole fraction (tie lines).

References:

[1] T. M. Letcher, S. Wooten, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037 (1986).
[2] S. W. Briggs and E. W. Comings, Ind. Eng. Chem. **35**, 411 (1943).
[3] T. M. Letcher, P. Siswana, P. van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053 (1989).

Auxiliary Information

Method/Apparatus/Procedure

Binodal compositions were determined by titration with the corresponding, less-soluble component until the appearance of turbidity, Ref. 1. The analytical method was used for determination of tie-lines. This was based on refractive indexes and densities of the samples, Ref. 1, combined with the oxidation of the alcohol with an excess of potassium dichromate and determination of unreduced dichromate with $Na_2S_2O_3$. Alcohol in the organic layer was determined after extraction with water.

Source and Purity of Materials:

(1) Kemika (Zagreb); analytical grade; presumably used as received; $n=1.3593$, $\rho(25\ °C)=787.0\ kg/m^3$, b.p.=79.1 °C.
(2) Kemika (Zagreb); purity not specified; presumably used as received; $n=1.4232$, $\rho(25\ °C)=773.9\ kg/m^3$, b.p.=80.0 °C.
(3) twice distilled in the presence of $KMnO_4$.

Estimated Error:

composition <0.0005 mass fraction, binodal, (relative); composition ±2%, tie line.

References:

[1] D. Plackov and I. Stern, Fluid Phase Equilib. **57**, 327 (1990).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) 2,2-Dimethylbutane (neohexane); C_6H_{14}; [75-83-2] (3) Water; H_2O; [7732-18-5]	C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. **37**, 1130–2 (1945).
Variables: $T/K=228-298$	**Compiled by:** A. Skrzecz

4.4. Ethanol + Water + 2,2-Dimethylbutane

Experimental Data

Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
−45.0	228.2	0.6168	0.3178	0.4987	0.4806
		0.3824	0.5911	0.2552	0.7379
		0.1759	0.8158	0.1032	0.8949
0.0	273.2	0.5814	0.2996	0.4893	0.4716
		0.3713	0.5740	0.2532	0.7322
		0.1742	0.8078	0.1029	0.8929
25.0	298.2	0.5596	0.2883	0.4831	0.4656
		0.3640	0.5627	0.2519	0.7283
		0.1730	0.8021	0.1028	0.8914

Comments and Additional Data

Water tolerance (S) was described with probable error <0.5% at the range −45–25 °C by the equation: $\log(S)=a-b/(T/K)$. The parameters (a, b) were determined from plots. Water tolerance was defined as: $S=H_2O$ by volume·(100−Hydrocarbon % by volume in the blend)/100

vol % hydrocarbon	a	b
90	1.235	473.1
75	1.679	444.9
50	1.911	388.5

Auxiliary Information

Method/Apparatus/Procedure:

A glass tube with stirrer containing the ternary mixture was immersed in a bath, the temperature of which could be varied. Mixtures were prepared directly in the tube by special pipettes at 15.5 °C. Precautions to exclude moisture and to prevent evaporation were observed. No correction was made for the slight expansion in volume when alcohol was mixed with hydrocarbon. In the paper the experimental results were expressed as the water tolerance of the alcohol–hydrocarbon blend. For practical purposes water tolerance was defined as the volume percent of water which can be added before separation occurs.

Source and Purity of Materials:

(1) source not specified; anhydrous ethanol.
(2) source not specified; b.p.=49.7 °C.
(3) not specified.

Estimated Error:

temp. within about 0.3 °C (duplicate determinations), composition <0.2% relative of volume fraction.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water (hydrogen oxide); H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.04)

4.5. Ethanol + Water + Hexane

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of ethanol between phases (distr.) for the system ethanol–hexane–water is given in Table 23.

TABLE 23. Summary of experimental data for the system ethanol–hexane–water

Author(s)	T/K	p/MPa	Type of data[a]	Ref.
Bonner, 1909	273		sat. (12)	1
Ormandy and Craven, 1922	242–304		sat. (25)	2
Tarasenkov and Paulsen, 1937	273, 298		sat. (25), eq. (2)	3
Mertslin *et al.*, 1961	293		sat. (8), distr. (18)	4
Vorobeva and Karapetyants, 1966	298		sat. (16), eq. (9)	5
Ross and Patterson, 1979	293		eq. (9)	6
Moriyoshi *et al.*, 1988	298	0.1–200	eq. (53)	7

[a] Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–hexane–water forms a miscibility gap of type 1. The data are discussed on the basis of original papers with the exception of data of Ormandy and Craven,[2] which were taken from the handbook of Kafarov,[8] these data were also taken into account during evaluation but are not reported as compilation sheet because they do not contribute further to knowledge of the system. The influence of pressure over the range 0.1–200 MPa at 298 K was also studied;[7] the maximum concentration of ethanol on the saturation curve varies from $x_1=0.660$ at $p=0.1$ MPa to $x_1=0.711$ at $p=200$ MPa. Only the binary system hexane–water forms a miscibility gap. Data for this binary system were compiled and critically evaluated in a previously published SDS volume.[9] The values of mutual solubility of hexane–water system recommended at 298.2 K are: $x_2'=2.3\cdot 10^{-6}$ and $x_2''=0.999\,53$. The data of Tarasenkov and Paulsen at 273 and 298 K,[3] show larger miscibility gaps than any other data set; they are inconsistent and therefore rejected. The measurements of Vorobeva and Karapetyants,[5] and Ross and Patterson,[6] were made with the accuracy of 0.001 mass fraction, and therefore the reported solubilities of binary system hexane–water in these references are outlayers. One of experimental points measured by Mertslin *et al.*,[4] ($x_1=0.5582$, $x_2=0.3033$) is inconsistent and therefore is also rejected. Data of Bonner[1] measured at 273 K show a slightly larger immiscibility region which is in agreement with general expectation. A maximum value of ethanol concentration on the saturation curve of $x_1=0.66$ is observed at 298.2 K (Refs. 5 and 7). The temperature 298.2 K was selected to present the phase behavior; the data sets of Vorobeva and Karapetyants,[5] and Moriyoshi *et al.*[7] are consistent. These data were described by the equation:

$$x_1=1.04385+0.126\,03\ \ln(x_2)-1.046\,56\,x_2\,.$$

The least-squares method was used and the standard error of estimate was 0.0165. Compositions on the saturation curve calculated by the proposed equation are presented in Table 24 for selected concentrations of hexane in the mixture. The results of calculations (solid line) are presented graphically in Fig. 13 together with experimental data reported at 298.2 K.

TABLE 24. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	$2.3\cdot 10^{-6}$ Ref. 9	0.4172	0.5200
0.3709	0.0050	0.4010	0.5400
0.4530	0.0100	0.3847	0.5600
0.5299	0.0200	0.3682	0.5800
0.5963	0.0400	0.3515	0.6000
0.6265	0.0600	0.3347	0.6200
0.6418	0.0800	0.3178	0.6400
0.6490	0.1000	0.3008	0.6600
0.6510	0.1200	0.2836	0.6800
0.6495	0.1400	0.2663	0.7000
0.6454	0.1600	0.2489	0.7200
0.6393	0.1800	0.2314	0.7400
0.6317	0.2000	0.2139	0.7600
0.6228	0.2200	0.1962	0.7800
0.6128	0.2400	0.1785	0.8000
0.6020	0.2600	0.1607	0.8200
0.5904	0.2800	0.1428	0.8400
0.5781	0.3000	0.1248	0.8600
0.5653	0.3200	0.1068	0.8800
0.5521	0.3400	0.0887	0.9000
0.5383	0.3600	0.0705	0.9200
0.5242	0.3800	0.0523	0.9400
0.5097	0.4000	0.0340	0.9600
0.4950	0.4200	0.0157	0.9800
0.4799	0.4400	0.0065	0.9900
0.4646	0.4600	0.0019	0.9950
0.4490	0.4800	0.0000	0.99953 Ref. 9
0.4332	0.5000		

Phases in equilibrium

The phases in equilibrium were measured at 293 and 298 K over the pressure range 0.1–200 MPa. The tie lines of Ref. 3 are inconsistent and are rejected. The other tie lines cover the whole miscibility gap and are consistent within each data set, within each region and between the regions. The differences between compositions of the phases in equilibrium reported in Refs. 5 and 7 do not exceed 0.01 mole fraction. The solubility plait point of the system was reported only by Vorobeva and Karapetyants[5] at 298.2 K (($x_1=0.478$, $x_2=0.437$) and by Bonner[1] at 273.2 K ($x_1=0.498$, $x_2=0.414$). The experimental tie lines at 298.2 K are presented in Fig. 13 together with the saturation curve.

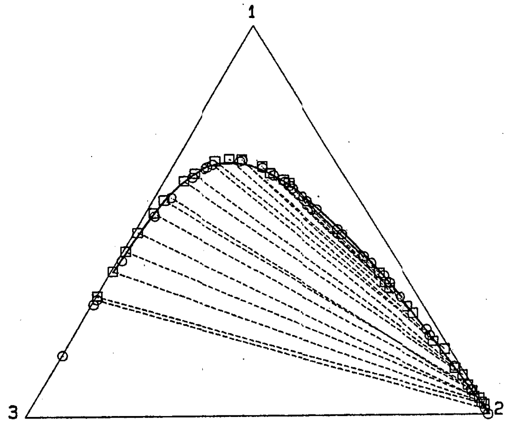

FIG. 13. Phase diagram of the system ethanol (1)—hexane (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental results of Ref. 5, □—experimental results of Ref. 7, dashed lines—experimental tie lines, Refs. 5 and 7.

References:

[1] W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).
[2] W. R. Ormandy and E. C. Craven, J. Inst. Petrol. Technol **8**, 181, 213 (1922).
[3] D. N. Tarasenkov and I. A. Paulsen, Zh. Obshch. Khim. **7**, 2143 (1937).
[4] R. V. Mertslin, N. I. Nikurashina, and V. A. Petrov, Zh. Fiz. Khim. **35**, 2770 (1961).
[5] A. I. Vorobeva and M. Kh. Karapetyants, Zh. Fiz. Khim. **40**, 3018 (1966).
[6] S. Ross and R. E. Patterson, J. Chem. Eng. Data **24**, 111 (1979).
[7] T. Moriyoshi, Y. Uosaki, H. Matsuura, and W. Nishimoto, J. Chem. Thermodyn, **20**, 551 (1988).
[8] V. V. Kafarov, ed., *Spravochnik po Rastvorimosti*, Vol. 2, Troinye, Mnogokomponentnye Sistemy, Part II (Izd. Akademii Nauk SSSR, Moskva, 1963).
[9] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements;

W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910).

Variables:

T/K=273

Complied by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)	
0.0	273.2	0.4978	0.4375	0.3711	0.6101	plait point
		0.5139	0.4142	0.3902	0.5884	
		0.6706	0.1893	0.6212	0.3280	
		0.6822	0.1588	0.6551	0.2853	
		0.6901	0.1112	0.7072	0.2132	
		0.6724	0.0810	0.7306	0.1646	
		0.6496	0.0557	0.7475	0.1199	
		0.6386	0.0484	0.7500	0.1062	
		0.5989	0.0327	0.7448	0.0761	
		0.5548	0.0202	0.7312	0.0497	
		0.4928	0.0121	0.6949	0.0320	
		0.2946	0.0021	0.5136	0.0068	

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogeneous solution. The mass of binary water–hydrocarbon mixture, was about 1 g the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled; n(14 °C) = 1.383 82.
(3) not specified.

Estimated Error:

accuracy of weighting 0.0001 g.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
D. N. Tarasenkov and I. A. Paulsen, Zh. Obshch. Khim. **7**, 2143–8 (1937).

Variables:
T/K=273–298

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
0.0	273.15	0.1125	0.8536	0.0653	0.9270
		0.5730	0.3741	0.4430	0.5410
		0.6592	0.3000	0.5332	0.4539
		0.7371	0.2189	0.6334	0.3518
		0.7658	0.1199	0.7401	0.2167
		0.7310	0.0585	0.7922	0.1186
		0.6730	0.0364	0.7874	0.0796
		0.6715	0.0332	0.7908	0.0732
		0.6001	0.0167	0.7682	0.0400
		0.4897	0.0080	0.6985	0.0213
		0.4807	0.0058	0.6943	0.0157
		0.3745	0.0031	0.6004	0.0094
		0.2297	0.0012	0.4312	0.0042
25.0	298.15	0.0545	0.9014	0.0310	0.9592
		0.2843	0.6564	0.1852	0.7997
		0.4866	0.4420	0.3628	0.6164
		0.4971	0.4195	0.3782	0.5970
		0.6336	0.2994	0.5194	0.4591
		0.7321	0.1617	0.6803	0.2811
		0.7024	0.0896	0.7384	0.1761
		0.6602	0.0611	0.7473	0.1293
		0.5879	0.0342	0.7352	0.0800
		0.4709	0.0135	0.6749	0.0361
		0.3200	0.0059	0.5381	0.0186
		0.1870	0.0033	0.3668	0.0121

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.0	298.15	0.0015	0.9700	0.1916	0.0006	0.0008	0.9931	0.3767	0.0023
		0.0316	0.9434	0.3531	0.0097	0.0175	0.9771	0.5692	0.0291

Auxiliary Information

Method/Apparatus/Procedure:

A titration method similar to that in Ref. 1 was used. A flask of 100 mL capacity containing a binary hexane–alcohol mixture of known composition, by weight, was placed in a thermostat. The mixture was titrated with water from a microburette with a scale of 0.01 mL, until opalescence, emulsion or turbidity was observed. Samples of the same binary composition were titrated several times. Compositions of coexisting phases were obtained by an analytical method similar to that in Ref. 2. Experimental points were located on the binodal curve obtained by the authors. The ternary mixture became homogenous when the hexane concentration reached 79.4 mass % at 0 °C and 74.73 mass % at 25 °C.

Source and Purity of Materials:

(1) source not specified; purity of 99.97% for 3 points of the lower alcohol concentration at each temperature and purity of 92.64% for all other points.
(2) source not specified; distilled; b.p.=68.85 °C, $d(20\ °C,4\ °C)=0.6898$.
(3) source not specified.

Estimated Error:

temp. ±0.05 °C.

References:

[1] R. E. Washburn. J. Am. Soc. **53**, 3237 (1931).
[2] D. N. Tarasenkov and E. N. Polozhentseva, Zh. Obshch. Khim. **2**, 84 (1932)

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
R. V. Mertslin, N. I. Nikurashina, and V. A. Petrov, Zh. Fiz. Khim. **35**, 2770-4 (1961). [Eng. transl. Russ. J. Phys. Chem. **35**, 1359–72 (1961)].

Variables:
T/K=293

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
20	293.2	0.3683	0.0048	0.5918	0.0143
		0.6543	0.0873	0.7122	0.1778
		0.6892	0.1224	0.6949	0.2308
		0.6327	0.2259	0.5697	0.3805
		0.5582	0.3033	0.4732	0.4809
		0.5054	0.4056	0.3891	0.5841
		0.4907	0.4234	0.3728	0.6017
		0.4824	0.4391	0.3615	0.6155

Distribution of ethanol in ethanol-hexane–water system

t/°C	T/K (compiler)	w_1' hydrocarbon-rich phase	w_1'' water-rich phase
20	293.2	0.2125	0.5675
		0.1325	0.6400
		0.0600	0.7300
		0.0200	0.6125
		0.0150	0.5650
		0.0125	0.5175
		0.0100	0.4775
		0.0075	0.4400
		0.0075	0.4125
		0.0060	0.3830
		0.0055	0.3625
		0.0055	0.3450
		0.0050	0.3250
		0.0050	0.3100
		0.0040	0.2925
		0.0040	0.2700
		0.0030	0.2550
		0.0030	0.2325

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine the binodal curve. The refractive indexes of mixtures were measured to construct the calibration curve, which was then used to find the concentration of ethanol in both phases at equilibrium.

Source and Purity of Materials:

(1) source not specified, dehydrated; distilled; b.p.=78.0 °C, n(20 °C,D)=1.3596.
(2) source not specified; doubly distilled; b.p.=68.5 °C, n(26 °C,D)=1.3751.
(3) doubly distilled.

Estimated Error:

Not reported.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
A. I. Vorobeva and M. Kh. Karapetyants, Zh. Fiz. Khim. **40**, 3018-23 (1966).
[Eng. transl. Russ. J. Phys. Chem. **40**, 1619–22 (1966)].

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Values

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25	298.2	0.0000	0.9952	0.000	0.999
		0.2200	0.7548	0.134	0.860
		0.3391	0.6147	0.225	0.763
		0.465	0.4526	0.346	0.630
		0.5294	0.3677	0.421	0.547
		0.5915	0.2777	0.509	0.447
		0.6021	0.2630	0.525	0.429
		0.6378	0.1977	0.595	0.345
		0.6542	0.1415	0.655	0.265
		0.6393	0.0786	0.713	0.164
		0.6361	0.0735	0.717	0.155
		0.6141	0.0562	0.724	0.124
		0.5153	0.0233	0.697	0.059
		0.4007	0.0090	0.618	0.026
		0.2886	0.0040	0.504	0.013
		0.1588	0.0005	0.325	0.002

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25	298.2	0.013	0.982	0.301	0.005	0.007	0.992	0.518	0.015
		0.065	0.926	0.562	0.036	0.036	0.962	0.714	0.086
		0.125	0.861	0.646	0.087	0.072	0.925	0.707	0.179
		0.205	0.769	0.657	0.145	0.124	0.870	0.653	0.270
		0.303	0.657	0.618	0.230	0.196	0.794	0.558	0.388
		0.358	0.593	0.584	0.287	0.241	0.746	0.499	0.458
		0.390	0.551	0.563	0.320	0.270	0.714	0.466	0.496
		0.408	0.526	0.551	0.336	0.288	0.694	0.450	0.514
		0.478	0.437	0.478	0.437	0.360	0.615	0.360	0.615

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, Ref. 1, was used to determine solubility of the mixtures. The third component was added to the binary homogenous mixture until cloudiness was first observed. Density of the saturated mixtures was measured; these results were graphed. To obtain equilibrium, ternary mixtures were stirred in a thermostated vessel for several hours. After phase separation, the density of each phase was measured and composition was determined from the graphs prepared earlier. Concentration at the critical point was found by method described in Ref. 2. Water included in ethanol was taken into account in all measurements.

Source and Purity of Materials:

(1) source not specified, "rectificate grade;" distilled; water concentration was determined by the Karl Fischer method.
(2) source not specified; b.p.=68.7 °C, $n(20\ ^\circ\mathrm{C,D})=1.3753$.
(3) not specified.

Estimated Error:

solubility ±0.001 mass fraction.

References:

[1] W. D. Bancroft, Phys. Rev. **3**, 21 (1896).
[2] E. N. Zilberman, Zh. Fiz. Khim. **26**, 1458 (1952).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

S. Ross and R. E. Patterson, J. Chem. Eng. Data **24**, 111–5 (1979).

Variables:

$T/\mathrm{K}=298$

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

$t/^\circ\mathrm{C}$	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
20.0	293.15	0.0000	1.0000	0.0000	0.0000	0.000	1.000	0.000	0.000
		0.0056	0.9944	0.1056	0.0000	0.003	0.997	0.232	0.000
		0.0093	0.9907	0.1586	0.0003	0.005	0.995	0.325	0.001
		0.0112	0.9888	0.1957	0.0005	0.006	0.994	0.383	0.002
		0.0149	0.9851	0.2358	0.0009	0.008	0.992	0.440	0.003
		0.0222	0.9778	0.2980	0.0018	0.012	0.988	0.518	0.006
		0.0368	0.9632	0.3914	0.0068	0.020	0.980	0.612	0.020
		0.1063	0.8892	0.5819	0.0349	0.060	0.939	0.730	0.082
		0.2170	0.7577	0.6710	0.1681	0.132	0.862	0.640	0.300

Auxiliary Information

Method/Apparatus/Procedure:

Mixtures of known composition (close to the midpoint) and mass of about 90 g were prepared by weighing into flasks with tightly fitting ground-glass stoppers. The solutions were shaken several times and placed in a thermostat for at least 24 h. Then density and surface tension of both phases as well as interfacial tension were measured.

Source and Purity of Materials:

(1) source not specified, absolute alcohol; dried with Mg, distilled; $\rho(20\ ^\circ\mathrm{C})=0.7895\ \mathrm{g\ cm^{-3}}$, b.p.=77.9–78.1 °C, $n(20\ ^\circ\mathrm{C,D})=1.3612$.
(2) source not specified, reagent grade; passed through a column of activated alumina distilled, (first and last portions of distillate were discarded; $\rho(20\ ^\circ\mathrm{C})=0.6595\ \mathrm{g\ cm^{-3}}$, b.p. =68.4–68.5 °C, $n(20\ ^\circ\mathrm{C,D})=1.3749$.
(3) distilled, redistilled from $KMnO_4$, acidified with phosphoric acid, redistilled, (all distillations under N_2 atmosphere).

Estimated Error:

temp. ±0.05 °C.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Hexane (*n*-hexane); C_6H_{14}; [110-54-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. Moriyoshi, Y. Uosaki, H. Matsuura, and W. Nishimoto, J. Chem. Thermodyn. **20**, 551–7 (1988).

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C (compiler)	T/K	p/MPa	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
			hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.00	298.15	0.1	0.026	0.974	0.310	0.001	0.014	0.986	0.533	0.003
			0.031	0.966	0.373	0.003	0.017	0.983	0.599	0.009
			0.042	0.956	0.425	0.005	0.023	0.977	0.647	0.014
			0.046	0.943	0.473	0.007	0.025	0.972	0.686	0.019
			0.062	0.930	0.523	0.017	0.034	0.964	0.712	0.043
			0.076	0.914	0.556	0.023	0.042	0.955	0.728	0.056
			0.102	0.890	0.605	0.042	0.058	0.941	0.736	0.096
			0.120	0.865	0.624	0.056	0.069	0.928	0.731	0.123
			0.170	0.818	0.655	0.088	0.100	0.898	0.712	0.179
			0.190	0.784	0.660	0.116	0.114	0.880	0.684	0.225
			0.262	0.705	0.659	0.143	0.164	0.828	0.656	0.266
			0.279	0.683	0.641	0.195	0.178	0.813	0.599	0.341
			0.326	0.621	0.624	0.220	0.216	0.770	0.569	0.375
			0.341	0.605	0.607	0.257	0.228	0.758	0.532	0.421
			0.364	0.581	0.599	0.272	0.247	0.738	0.517	0.439
		50	0.022	0.978	0.329	0.001	0.012	0.988	0.555	0.003
			0.038	0.959	0.450	0.006	0.021	0.979	0.668	0.017
			0.049	0.950	0.513	0.012	0.027	0.973	0.711	0.031
			0.064	0.930	0.558	0.019	0.035	0.963	0.735	0.047
			0.065	0.935	0.569	0.024	0.036	0.964	0.736	0.058
			0.074	0.916	0.603	0.034	0.041	0.957	0.746	0.079
			0.105	0.892	0.644	0.057	0.059	0.940	0.742	0.123
			0.208	0.775	0.674	0.131	0.125	0.871	0.677	0.246
			0.254	0.718	0.653	0.194	0.158	0.835	0.607	0.337
		100	0.019	0.978	0.346	0.001	0.010	0.989	0.574	0.003
			0.034	0.965	0.457	0.006	0.018	0.981	0.674	0.017
			0.036	0.964	0.515	0.011	0.020	0.980	0.714	0.029
			0.046	0.953	0.559	0.018	0.025	0.975	0.737	0.044
			0.057	0.943	0.589	0.025	0.031	0.969	0.749	0.059
			0.063	0.934	0.603	0.028	0.035	0.965	0.754	0.065
			0.076	0.912	0.643	0.043	0.043	0.955	0.760	0.095
			0.173	0.814	0.688	0.118	0.102	0.895	0.699	0.224
			0.203	0.779	0.677	0.160	0.122	0.874	0.651	0.288
			0.249	0.725	0.658	0.204	0.154	0.840	0.602	0.349
		150	0.024	0.974	0.456	0.004	0.013	0.987	0.676	0.011
			0.029	0.971	0.516	0.011	0.016	0.984	0.715	0.029
			0.039	0.961	0.559	0.016	0.021	0.979	0.740	0.040
			0.041	0.959	0.576	0.019	0.022	0.978	0.748	0.046
			0.046	0.954	0.605	0.026	0.025	0.975	0.758	0.061
			0.064	0.936	0.646	0.041	0.035	0.965	0.764	0.091
			0.176	0.813	0.692	0.145	0.103	0.894	0.674	0.264
			0.204	0.779	0.688	0.168	0.122	0.874	0.650	0.297
		200	0.015	0.975	0.411	0.002	0.008	0.990	0.638	0.006
			0.020	0.975	0.475	0.006	0.011	0.988	0.689	0.016
			0.023	0.975	0.512	0.010	0.012	0.987	0.713	0.026
			0.031	0.969	0.561	0.015	0.017	0.983	0.743	0.037
			0.056	0.932	0.649	0.036	0.031	0.966	0.773	0.080
			0.091	0.904	0.695	0.071	0.051	0.948	0.756	0.144
			0.151	0.839	0.711	0.126	0.088	0.910	0.704	0.233
			0.200	0.790	0.695	0.174	0.119	0.879	0.648	0.304

Auxiliary Information

Method/Apparatus/Procedure:

The experimental apparatus consisted of a high-pressure equilibrium cell, two hand operated pumps, a pressure exchanger, and two pressure gauges. The equilibrium cell, a stainless-steel cylinder of 50 cm^3 capacity, with mechanical stirrer was immersed in a thermostat. The mixtures, prepared by mass, were stirred under the desired conditions for at least 8 h and then allowed to settle for 2 h. Samples of each layer were withdrawn for glc analysis (glass column, 3.2 mm i.d., 150 cm long, packed with PEG-6000 Shimalite F; T/K=343; thermal-conductivity detector equipped with electronic integrator). Acetone was used as an inert standard. Compositions were determined from the peak-area ratio and the calibration curve. Analysis of each phase were done at least twice.

Source and Purity of Materials:

(1) source not specified; dried by refluxing with CaO, followed by the Lund–Bjerrum magnesium method, distilled.
(2) source not specified; shaken with conc. H_2SO_4, neutralized with aq. NaOH, dried over $CaCl_2$, distilled.
(3) de-ionized, distilled over $KMnO_4$, redistilled.

Estimated Error:

temp. ±0.002 K (control of the thermostat); press. ±0.1 MPa; composition ±0.003 mass fraction.

Components:	Evaluated by
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Toluene (methylbenzene); C_7H_8; [108-88-3] (3) Water; H_2O; [7732-18-5]	A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.05)

4.6. Ethanol + Water + Toluene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of ethanol between phases (distr.) for the system ethanol–toluene–water is given in Table 25.

TABLE 25. Summary of experimental data for the system ethanol–toluene–water

Author(s)	T/K	Type of data[a]	Ref.
Curtis, 1897	273	sat. (7)	1
Bonner, 1909	273	sat. (8)	2
Ormandy and Craven, 1921	243–303	sat. (48)	3
Tarasenkov and Polozhentseva, 1932	273–313	eq. (14)	4
Washburn *et al.*, 1939	298	sat. (17), distr. (9)	5
Leikola, 1940	293	sat. (8)	6
Mondain-Monval and Quiquerez, 1940	298	eq. (8)	7
Arzhanov *et al.*, 1975	348–357	eq. (6)	8
Borisova *et al.*, 1978	293–353	eq. (17)	9
Bevia *et al.* 1985	298	sat. (10)	10
Ricna *et al.* 1989	278–323	sat. (7), eq. (37)	11
Letcher and Siswana, 1992	298	sat. (15), eq. (6)	12

[a]Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–toluene–water forms a miscibility gap of type 1. There are 12 references for this system over the temperature range 243–353 K. This evaluation was made on the basis of original papers with the exception of data of Ormandy and Craven,[3] Tarasenkov and Polozhentseva,[4] and Leikola,[6] which were taken from the handbook of Kafarov;[13] these data were also taken into account during evaluation but are not reported as compilation sheet because they do not contribute further to knowledge of the system. Only the binary system toluene–water is partially miscible. The data for this system were compiled and critically evaluated in a previously published SDS volume.[14] The recommended values of mutual solubility at 298 K are: $x_2'=0.9972$ and $x_2''=0.000\,0104$. The papers of Borisova *et al.*,[9] ($x_2'=0.9976$ and $x_2''=0.0001$ at 293.2 K) and Letcher and Siswana,[12] ($x_2'=0.999$ and $x_2''=0.000$ at 298.2 K) report mutual solubility of the binary system. Accuracy of experimental data reported in Ref. 12 was stated by the authors to be 0.005 mole fraction, so these data are consistent. The water-rich phase, Ricna *et al.*[11] is reported to be toluene free over a wide range of temperatures and water concentrations. This indicates that their experimental accuracy was in the range of 0.001–0.005 mole fraction; lower than reported (0.0001 mole fraction). Data of Arzhanov *et al.*[8] and Borisova *et al.*[9] reported for the temperature range 348–357 K describe the vapor–liquid–liquid equilibrium. (The boiling temperatures of two-phase mixture of Ref. 8 were estimated from authors graph.) The point ($x_1=0.5536$ and $x_2=0213$) on saturation curve at 278.2 K, Rican *et al.*[1] appears to contain a typing error and is rejected. Data reported for 273.2, 293.2, 313.2 K by Tarasenkov and Polozhentseva[4] contain errors for the toluene-rich phase; the experimental points are inconsistent with saturation curve in the region of low concentration of ethanol. These data are also rejected. Data of Borisova *et al.*,[9] at 293.2 K, close to the plait point, show a miscibility gap similar to the data at 273 K and larger than data of Leikola.[6] All other data for the saturation curve are consistent with one another. Ormandy and Craven[3] reported seven isotherms which clearly show the temperature dependence of the saturation data in the range 243–303 K. Characteristic points on the binodal curve of the system ethanol–toluene–water at selected temperatures, reported in literature, are presented in Table 26. At the maximum ethanol concentration point, the errors estimated by the evaluator are to be 0.005 and 0.015 mole fraction of ethanol and benzene, respectively.

TABLE 26. Characteristic points on the binodal curve of the system ethanol–toluene–water

	Max. C_2H_5OH concentration			Plait points		
T/K	x_1	x_2	Ref.	x_1	x_2	Ref.
243.2	0.573	0.168	3	—	—	
258.2	0.541	0.113	3	—	—	
273.2	0.523	0.143	3	—	—	
273.2	0.520	0.128	2	—	—	
278.2	0.512	0.161	3	—	—	
278.2	0.505	0.100	11	—	—	
288.2	0.493	0.193	3	—	—	
293.2	0.475	0.166	6	—	—	
293.2	0.503	0.197	9	0.464	0.357	9
298.2	0.474	0.123	3	0.423	0.341	7
298.2	0.473	0.127	11	—	—	
298.2	0.472	0.159	12	0.41	0.36	12
303.2	0.465	0.139	3	—	—	
323.2	0.425	0.160	11	—	—	
347.6	0.415	0.166	9	0.403	0.228	9
347.7	—	—		0.342	0.219	8

The temperature of 298.2 K was selected to present the behavior of the system. All experimental saturation and equilibrium points at 298.2 K water-rich and benzene-rich branches together, were described by the equation:

$$x_1=0.718\,83+0.092\,81\ln(x_2)-0.488\,76x_2-0.230\,41x_2^2.$$

The least-squares method was used and the standard error of estimate was 0.0125. The compositions on the saturation curve calculated by the proposed equation are presented in Table 27 for selected concentrations to toluene in the mixture. The results of calculations (solid line) are also presented graphically in Fig. 14 together with all experimental data reported at 298.2 K.

TABLE 27. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 0104 Ref. 14	0.3525	0.5000
0.0773	0.0010	0.3417	0.5200
0.2865	0.0100	0.3305	0.5400
0.3459	0.0200	0.3191	0.5600
0.4002	0.0400	0.3073	0.5800
0.4276	0.0600	0.2952	0.6000
0.4438	0.0800	0.2829	0.6200
0.4540	0.1000	0.2702	0.6400
0.4601	0.1200	0.2573	0.6600
0.4634	0.1400	0.2441	0.6800
0.4647	0.1600	0.2307	0.7000
0.4642	0.1800	0.2170	0.7200
0.4625	0.2000	0.2030	0.7400
0.4596	0.2200	0.1888	0.7600
0.4558	0.2400	0.1743	0.7800
0.4512	0.2600	0.1596	0.8000
0.4458	0.2800	0.1447	0.8200
0.4397	0.3000	0.1295	0.8400
0.4331	0.3200	0.1141	0.8600
0.4259	0.3400	0.0984	0.8800
0.4182	0.3600	0.0825	0.9000
0.4100	0.3800	0.0664	0.9200
0.4014	0.4000	0.0501	0.9400
0.3924	0.4200	0.0335	0.9600
0.3830	0.4400	0.0167	0.9800
0.3732	0.4600	0.0082	0.9900
0.3630	0.4800	0.0000	0.9972 Ref. 14

Phases in equilibrium

Compositions of the coexisting phases in equilibrium for the ternary system ethanol–toluene–water were reported in six references over the temperature range 273–357 K as 11 data sets. Two of these data sets, of Arzhanov *et al.*,[8] and Borisova *et al.*,[9] were measured at the boiling temperatures of two-phase mixtures at atmospheric pressure. Data reported by Tarasenkov and Polozhentseva[4] contain errors in the toluene-rich phase, as discussed above, and are rejected. Equilibrium phases for a boiling point of 248.2 K, Borisova *et al.*[9] contain presumably an analytical error. This tie line is inconsistent within the data set; other tie lines at boiling temperatures, Refs. 8 and 9, are consistent and cover the full miscibility gap. Other reported data are consistent within each data set. The distribution of ethanol (direction of tie lines) between the phases changes with temperature and at the boiling point (348–357 K) the concentration of ethanol in both phases becomes nearly the same. The reported plait points are presented above in Table 2. All equilibrium data are treated as tentative. All experimental points at 298.2 K, both saturation and equilibrium data,[3,5,7,10,11,12] are presented in Fig. 14.

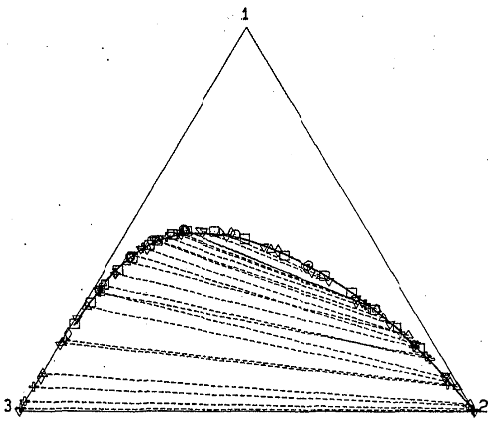

FIG. 14. Phase diagram of the system ethanol (1)—toluene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ◇—experimental data, Ref. 10, ○—experimental data, Ref. 3, ♧—experimental data, Ref. 11, □—experimental data, Ref. 5, ▽—experimental data, Ref. 12, △—experimental data, Ref. 7, dashed lines—experimental tie lines, Refs. 7, 11, and 12.

References:

[1] C. B. Curtis, J. Phys. Chem. **2**, 371 (1897-1898).
[2] W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).
[3] W. R. Ormandy and E. C. Craven, J. Inst. Pet. Technol. **7**, 325, 422 (1921).
[4] D. N. Tarasenkov and E. N. Polozhentseva, Zh. Obshch. Khim. **2**, 84 (1932).
[5] R. E. Washburn, A. E. Beguin, and O. C. Beckord, J. Am. Chem. Soc. **61**, 1694 (1939).
[6] E. Leikola, Suom. Kemistil. B **13**, 13 (1940).
[7] P. Mondain-Monval and J. Quiquerez, Bull. Soc. Chim. Fr., Mem. **7**, 240 (1940).
[8] P. G. Arzhanov, L. F. Komarova, and Yu. N. Garber, Zh. Prikl. Khim. (Leningrad) **48**, 2089 (1975).
[9] I. A. Borisova, V. G. Vatskova, A. I. Gorbunov, and N. M Sokolov, Khim. Prom-st (Moscow) 347 (1978)
[10] F. R. Beva, D. P. Rico, and V. G. Yagues, Fluid Phase Equilibria **23**, 269 (1985).
[11] K. Ricna, J. Matous, J. P. Novak, and V. Kubicek, Collect. Czech. Chem. Commun. **54**, 581 (1989).
[12] T. M. Letcher and P. M. Siswana, Fluid Phase Equilib. **74**, 203 (1992).
[13] V. V. Kafarov, ed., *Spravochnik po Rastvorimosti*, Vol. 2, Troinye, Mnogokomponentnye Sistemy, Part II (Izd. Akademii Nauk SSSR, Moskva, 1963).
[14] D. G. Shaw, ed., *Solubility Data Series*, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 Pergamon, New York, 1989).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Toluene (methylbenzene); C_7H_8; [108-88-3] (3) Water; H_2O; [7732-18-5]	W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910).

Variables:	**Compiled by:**
T/K=273	A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (compiler)	w_2 (compiler)
0.0	273.2	0.3900	0.4764	0.2795	0.6830
		0.4451	0.3793	0.3498	0.5962
		0.4849	0.3023	0.4135	0.5155
		0.5198	0.1275	0.5695	0.2794
		0.4937	0.0748	0.6080	0.1842
		0.4202	0.0339	0.5990	0.0966
		0.3831	0.0226	0.5798	0.0685
		0.3224	0.0098	0.5345	0.0326
		0.2463	0.0042	0.4496	0.0154

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogenous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:

accuracy of weighing 0.0001 g.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Toluene (methylbenzene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

R.E. Washburn, A. E. Beguin, and O. C. Beckord, J Am. Chem. Soc. **61**, 1694–5 (1939).

Variables:

T/K = 298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.2	0.1662	0.7975	0.0936	0.8984
		0.2194	0.7195	0.1304	0.8554
		0.2668	0.6464	0.1674	0.8113
		0.3106	0.5737	0.2066	0.7633
		0.3543	0.4935	0.2529	0.7046
		0.4074	0.3780	0.3266	0.6061
		0.4497	0.2712	0.4083	0.4926
		0.4695	0.1952	0.4737	0.3940
		0.4695	0.1310	0.5289	0.2952
		0.4604	0.1033	0.5496	0.2467
		0.4449	0.0787	0.5642	0.1996
		0.4333	0.0674	0.5676	0.1766
		0.4022	0.0459	0.5665	0.1294
		0.3697	0.0314	0.5546	0.0941
		0.3315	0.0199	0.5304	0.0637
		0.3155	0.0162	0.5173	0.0533
		0.2843	0.0108	0.4889	0.0372
		0.2284	0.0047	0.4243	0.0175

Distribution of ethanol in ethanol–toluene–water system

t/°C	T/K (compiler)	w_1' hydrocarbon-rich phase	w_1'' water-rich phase
25.0	298.2	0.002	0.110
		0.007	0.192
		0.013	0.257
		0.027	0.352
		0.047	0.417
		0.053	0.469
		0.065	0.500
		0.082	0.533
		0.094	0.556

Auxiliary Information

Method/Apparatus/Procedure:

The solubility curve was determined in a constant temperature bath by a titration method similar to that reported in Refs. 1–3. Refractive indexes were measured with an Abbe refractometer at the same temperature and presented as a concentration function in a graph. This graph was used to determine the concentration of alcohol in the samples of each phase when equilibrium had been reached. Phase equilibrium data were reported only as distribution of ethanol.

Source and Purity of Materials:

(1) source not specified; commercial grade absolute ethanol; refluxed over lime, distilled; d(25 °C,4 °C) = 0.7851, n(25 °C,D) = 1.359 40.
(2) source not specified; analytical reagent grade; dried over Na, distilled; d(25 °C,4 °C) = 0.8608, n(25 °C,D) = 1.493 71.
(3) distilled over $KMnO_4$.

Estimated Error:

temp. ±0.1 °C.

References:

[1] E. R. Washburn, V. Hnizda, and R. Vold, J. Am Chem. Soc. **53**, 3237 (1931).
[2] R. Vold and E. R. Washburn, J. Am. Chem. Soc. **54**, 4217 (1932).
[3] E. R. Washburn and H. C. Spencer, J. Am. Chem. Soc. **56**, 361 (1934).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Toluene (methylbenzene); C_7H_8 ; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
P. Mondain-Monaval, and J. Quicuerez, Bull. Soc. Chim. Fr., Mem. 7, 240–53 (1940).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data
Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1 hydrocarbon-rich phase (complier)	x'_2	x''_1 water-rich phase (complier)	x''_2	w'_1 hydrocarbon-rich phase	w'_2	w''_1 water-rich phase	w''_2
25.00	298.15	0.020	0.980	0.0994	0.0002	0.010	0.990	0.220	0.001
	298.15	0.066	0.930	0.179	0.002	0.034	0.965	0.355	0.009
	298.15	0.078	0.908	0.274	0.008	0.041	0.956	0.480	0.029
	298.15	0.199	0.757	0.391	0.038	0.115	0.875	0.566	0.111
	298.15	0.246	0.675	0.445	0.079	0.151	0.830	0.564	0.200
	298.15	0.269	0.649	0.472	0.127	0.168	0.812	0.535	0.287
	298.15	0.354	0.486	0.466	0.210	0.255	0.700	0.460	0.415
	298.15	0.423	0.341	0.423	0.341	0.353	0.570	0.353	0.570[a]

[a] Plait point.

Auxiliary Information

Method/Apparatus/Procedure:
The analytical method was used. A sample of 100 mL of a ternary mixture, prepared by weight, was placed in a thermostat, agitated many times and then left for several hours to separate. The density and refractive index of each phase was measured. Inversion of density was observed.

Source and Purity of Materials:
(1) source not specified; $d(25\ °C,4\ °C)=0.7853$.
(2) obtained in the laboratory; $d(24\ °C,4\ °C)=0.8622$.
(3) not specified.

Estimated Error:
temp. ±0.02 °C.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Toluene (methylbenzene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
P. G. Arzhanov, L. F. Komarova, and Yu. N. Garber, Zh. Prikl. Khim. (Leningrad) **48**, 2089–91 (1975). [Eng. transl. Russ. J. Appl. Chem. (Leningrad) **48**, 2160–2 (1975)].

Variables:
T/K=348–353

Compiled by:
A. Skrzecz

Experimental Data
Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1 hydrocarbon-rich phase	x'_2	x''_1 water-rich phase	x''_2	w'_1 hydrocarbon-rich phase (compiler)	w'_2	w''_1 water-rich phase (compiler)	w''_2
80.0	353.2	0.075	0.925	0.085	0.000	0.039	0.961	0.192	0.000
76.5	349.7	0.139	0.815	0.144	0.003	0.078	0.912	0.298	0.012
75.5	348.7	0.205	0.705	0.220	0.006	0.124	0.854	0.412	0.022
75.1	348.3	0.261	0.603	0.263	0.015	0.172	0.793	0.457	0.052
74.7	347.9	0.290	0.530	0.283	0.030	0.204	0.746	0.463	0.098
74.5	347.7	0.342	0.219	0.342	0.219	0.359	0.460	0.359	0.460

Auxiliary Information

Method/Apparatus/Procedure:
The analytical method was used. The equilibrium was investigated at the boiling temperature at 760 Torr. The samples were taken for glc analysis through heated capillaries. Analysis: column 2 m long and 4 mm diameter filled with polichrom with 15% polyethyleneglycoladipinate; 100 °C; H_2 100 mL/min; internal standard and homogenizer–acetone. Boiling temperatures of the two-phase mixture at 760 Torr were estimated from the authors' graph.

Source and Purity of Materials:
(1) Source not specified; purified in the laboratory; b.p.=78.3 ±0.1 °C, $n(20\ °C,D)=1.3614$; the properties were in agreement with literature data, purity was checked by glc analysis.
(2) source not specified; purified in the laboratory; b.p.=110.7 ±0.1 °C, $n(20\ °C,D)=1.4969$; the properties were in agreement with literature data, purity was checked by glc analysis.
(3) double distilled.

Estimated Error:
pressure ±0.1 Torr.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Toluene (methylbenzene); C_7H_8 ; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
I. A. Borisova, V. G. Vatskova, A. I. Gorbunov, and N. M. Sokolov, Khim. Prom-st (Moscow) 347 (1978).

Variables:
T/K=293–253

Compiled by:
A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase (complier)		water-rich phase (complier)		hydrocarbon-rich phase		water-rich phase	
20	293.2	0.0000	0.9976	0.0000	0.0001	0.0000	0.9995	0.0000	0.0005
		0.0209	0.9751	0.0767	0.0005	0.0106	0.9886	0.1750	0.0022
		0.0485	0.9441	0.2067	0.0011	0.0250	0.9735	0.3986	0.0041
		0.0797	0.9058	0.2253	0.0047	0.0420	0.9550	0.4205	0.0175
		0.1066	0.8790	0.2546	0.0084	0.0570	0.9400	0.4550	0.0300
		0.1866	0.7907	0.3533	0.0225	0.1050	0.8900	0.5500	0.0700
		0.2548	0.6822	0.4629	0.0778	0.1550	0.8300	0.5800	0.1950
		0.3769	0.5097	0.5027	0.1966	0.2616	0.7076	0.4960	0.3880
		0.4643	0.3570	0.4643	0.3570	0.3720	0.5720	0.3720	0.5720[a]
80.0	353.2	0.0600	0.9152	0.0442	0.0007	0.0316	0.9633	0.1055	0.0034[b]
79.0	352.2	0.0650	0.9098	0.0510	0.0008	0.0343	0.9605	0.1205	0.0037[b]
78.0	351.2	0.0700	0.9001	0.0634	0.0009	0.0372	0.9566	0.1471	0.0042[b]
77.0	350.2	0.0869	0.8780	0.0858	0.0012	0.0468	0.9458	0.1927	0.0054[b]
76.0	349.2	0.1101	0.8480	0.1201	0.0030	0.0604	0.9306	0.2560	0.0128[b]
75.0	348.2	0.1366	0.8020	0.2122	0.0158	0.0774	0.9090	0.3888	0.0580[b]
74.5	347.7	0.2801	0.6000	0.3302	0.0660	0.1834	0.7859	0.4728	0.1891[b]
74.4	347.6	0.3910	0.3401	0.4146	0.1659	0.3324	0.5782	0.4554	0.3644[b]
74.3	347.5	0.4031	0.2276	0.4031	0.2276	0.4020	0.4540	0.4020	0.4540[a,b,c]

[a] Critical solubility point.
[b] Temperatures are the boiling temperatures of the two-phase mixtures.
[c] Boiling temperature estimated by the compiler.

Auxiliary Information

Method/Apparatus/Procedure:

The method of description of concentration of phases in equilibrium was the same as reported in Ref. 1. No more details were reported in the paper.

Source and Purity of Materials:

(1) source not specified; properties were in agreement with literature data.
(2) source not specified; properties were in agreement with literature data.
(3) Not specified.

Estimated Error:

Not reported.

References:

[1] A S. Mozzhukhin, L. A. Serafimov, and V. A. Mitropolskaya, Zh. Fiz. Khim. **41**, 1687 (1967).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Toluene (methylbenzene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
F. R. Bevia, D. P. Rico, and V. G. Yagues, Fluid Phase Equilib. **23**, 269–92 (1985).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.0	298.2	0.0878	0.0022	0.196	0.010
		0.2028	0.0034	0.390	0.013
		0.3608	0.0296	0.548	0.090
		0.4245	0.0666	0.561	0.176
		0.4623	0.1221	0.532	0.281
		0.4646	0.2344	0.442	0.446
		0.4195	0.3584	0.343	0.586
		0.3659	0.4608	0.270	0.680
		0.2867	0.5963	0.188	0.782
		0.1721	0.7830	0.098	0.892

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. The quaternary system ethanol–toluene–water–chloroform was investigated. Mixtures of known composition representing the chosen ratios of components were vigorously stirred for at least 2 h and then allowed to separate. The refractive indexes of both phases were measured in a thermostated ERMA Abbe refractometer and the results were plotted as function of ethanol concentration. Solubility in the ternary system was calculated from these plots.

Source and Purity of Materials:

(1) Merck, analytical reagent grade; volatile impurities <0.1 mass % by glc.
(2) Merck, analytical reagent grade; volatile impurities <0.1 mass % by glc.
(3) not specified.

Estimated Error:

temp. ±0.1 °C.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Methylbenzene (toluene); C_7H_8; [108-88-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

K. Ricna, J. Matous, J. P. Novac, and V. Kubicek, Collect. Czech. Chem. Commun. 54, 581–5 (1989).

Variables:

T/K=278

Compiled By:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
5.0	278.15	0.8620	0.0356	0.8857	0.0732
		0.7072	0.0587	0.7719	0.1281
		0.5725	0.1045	0.6306	0.2302
		0.3597	0.1978	0.3875	0.4261
		0.2220	0.2780	0.2280	0.5711
		0.0923	0.4151	0.0832	0.7443
		0.0213	0.4251	0.0196	0.7814

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
5.0	278.15	0.0000	0.9938	0.9980	0.0013	0.0000	0.9988	0.9971	0.0026
		0.0000	0.9783	0.9921	0.0052	0.0000	0.9957	0.9886	0.0104
		0.0000	0.9763	0.9919	0.0051	0.0000	0.9953	0.9887	0.0102
		0.0000	0.9447	0.9888	0.0036	0.0000	0.9887	0.9898	0.0072
		0.0000	0.8855	0.9744	0.0050	0.0000	0.9753	0.9818	0.0101
		0.0000	0.8197	0.9546	0.0053	0.0000	0.9588	0.9732	0.0108
		0.0061	0.7283	0.9080	0.0168	0.0039	0.9298	0.9351	0.0346
		0.0255	0.6037	0.8516	0.0235	0.0185	0.8763	0.8988	0.0496
		0.0361	0.5554	0.8331	0.0310	0.0276	0.8501	0.8786	0.0654
		0.0442	0.5171	0.8091	0.0418	0.0354	0.8274	0.8508	0.0879
		0.0655	0.4727	0.7895	0.0369	0.0550	0.7935	0.8478	0.0793
		0.0996	0.3951	0.7435	0.0512	0.0916	0.7267	0.8028	0.1106
25.0	298.15	0.0000	0.9930	0.9973	0.0014	0.0000	0.9986	0.9967	0.0028
		0.0000	0.9745	0.9932	0.0020	0.0000	0.9949	0.9941	0.0040
		0.0000	0.9364	0.9770	0.0072	0.0000	0.9869	0.9794	0.0144
		0.0072	0.8082	0.9062	0.0232	0.0042	0.9532	0.9245	0.0473
		0.0176	0.6710	0.8236	0.0332	0.0119	0.9059	0.8706	0.0702
		0.0170	0.6530	0.8349	0.0295	0.0117	0.8994	0.8817	0.0623
		0.0305	0.6093	0.7857	0.0460	0.0219	0.8767	0.8327	0.0975
		0.0571	0.5171	0.7374	0.0586	0.0454	0.8222	0.7892	0.1254
		0.0947	0.4518	0.6349	0.0963	0.0806	0.7686	0.6808	0.2065
		0.1172	0.4227	0.6200	0.1000	0.1026	0.7399	0.6670	0.2152
		0.1265	0.4009	0.6194	0.0998	0.1136	0.7203	0.6669	0.2149
50.0	323.15	0.0000	0.9928	0.9960	0.0013	0.0000	0.9986	0.9963	0.0026
		0.0000	0.9908	0.9927	0.0038	0.0000	0.9982	0.9910	0.0076
		0.0000	0.9674	0.9803	0.0058	0.0000	0.9935	0.9829	0.0116
		0.0000	0.9534	0.9757	0.0027	0.0000	0.9905	0.9860	0.0055
		0.0030	0.9447	0.9672	0.0073	0.0016	0.9877	0.9752	0.0147
		0.0047	0.8252	0.8669	0.0275	0.0027	0.9586	0.9000	0.0571
		0.0068	0.7929	0.8333	0.0439	0.0041	0.9491	0.8598	0.0906
		0.0081	0.7481	0.7961	0.0488	0.0051	0.9353	0.8342	0.1023
		0.0331	0.6856	0.7719	0.0552	0.0219	0.9055	0.8126	0.1162
		0.0306	0.6403	0.7294	0.0655	0.0213	0.8894	0.7755	0.1393
		0.0428	0.6082	0.6888	0.0764	0.0307	0.8716	0.7379	0.1637
		0.1021	0.5045	0.5390	0.1570	0.0807	0.7977	0.5546	0.3231
		0.1256	0.4592	0.4553	0.2033	0.1041	0.7613	0.4574	0.4085
		0.1603	0.4146	0.3320	0.2726	0.1387	0.7175	0.3218	0.5284

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used for solubility measurements. Water was added from a calibrated hypodermic syringe (controlled by a micrometer screw) to a binary ethanol–toluene mixture of known mass and composition until persistent turbidity was observed. The direct analytical method was used for liquid–liquid equilibrium measurements. A mixture was stirred vigorously for 2–3 h in a thermostated cell,[1] and after phase separation samples were taken for analysis. A small amount of tetrahydrofuran was added as an internal standard and homogenization agent in glc analysis. Calibration standards were analyzed separately for each phase prior to each sample analysis by glc. Conditions of the glc analysis were: glass column (2.5 mm i.d., 1.5 m), Poropak Q, 200 °C, carrier gas H_2, thermal conductivity detector.

Source and Purity of Materials:

(1) source not specified "extra fine;" distilled with benzene; 0.1% H_2O by the Karl Fischer method; $\rho(25\ °C) = 0.784\ 98\ g\ cm^{-3}$, $n(25\ °C,D) = 1.3605$.
(2) Lachema Neratovice, A. R. grade; shaken five times with H_2SO_4 conc., three times with H_2O, then with NaOH, dried with Na, distilled; $\rho(25\ °C) = 0.861\ 24\ g/cm^3$, $n(25\ °C,D) = 1.4939$.
(3) doubly distilled.

Estimated Error:

temp. ±0.05 K.

Components: (1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Toluene (methylbenzene); C_7H_8; [108-88-3] (3) Water; H_2O; [7732-18-5]	**Original Measurements:** T. M. Letcher and P. M. Siswana, Fluid Phase Equilib. **74**, 203–17 (1992).
Variables: T/K=298	**Compiled by:** A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25.0	298.2	0.000	0.000	0.000	0.000
		0.174	0.001	0.349	0.004
		0.242	0.003	0.445	0.011
		0.319	0.014	0.525	0.046
		0.404	0.041	0.575	0.117
		0.424	0.053	0.577	0.144
		0.460	0.099	0.554	0.238
		0.472	0.159	0.505	0.340
		0.456	0.228	0.440	0.440
		0.430	0.323	0.367	0.551
		0.378	0.441	0.284	0.663
		0.296	0.591	0.194	0.777
		0.174	0.785	0.099	0.892
		0.094	0.889	0.050	0.946
		0.000	0.999	0.000	0.9998

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K(compiler)	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.000	0.999	0.000	0.000	0.000	0.9998	0.000	0.000
		0.341	0.510	0.470	0.170	0.240	0.719	0.494	0.358
		0.285	0.610	0.466	0.112	0.184	0.789	0.545	0.262
		0.230	0.697	0.445	0.070	0.139	0.844	0.572	0.185
		0.178	0.778	0.410	0.042	0.102	0.889	0.579	0.119
		0.090	0.890	0.315	0.012	0.048	0.940	0.523	0.040

Auxiliary Information

Method/Apparatus/Procedure:

The points on the binodal curve were determined by the formation of a cloudy mixture on shaking after the addition of a known mass of one component to a mixture of known masses of the other two components. Precision weighing syringes were used as described in Ref. 1. Tie line compositions were determined by the refractive index method reported in Ref. 2 and a complementary method using the Karl Fischer titrations as reported in Ref. 3.

Source and Purity of Materials:

(1) Merck, AR grade; AR grade; distilled, dried by refluxing with Mg and I_2; purity better than 99.6 mole % by glc; d =0.78524, n=1.3594.

(2) BDH; used as received; purity better than 99.6 mole % by glc.

(3) not specified.

Estimated Error:

estimated comp. 0.005 mole fraction on the binodal curve and 0.01 mole fraction for tie lines (estimated by the authors).

References:

[1] T. M. Letcher, S. Wooten, B. Shuttleworth, and C. Heward, J. Chem. Thermodyn. **18**, 1037 (1986).

[2] S. W. Briggs and E. W. Comings, Ind. Eng. Chem. **35**, 411 (1943).

[3] T. M. Letcher, P. M. Siswana, P. Van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053 (1989).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Methylcyclohexane (hexahydrotoluene); C_7H_{14}; [108-87-2] (3) Water; H_2O; [7732-18-5]	C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. 37, 1130–2 (1945).
Variables: T/K=228–298	**Compiled by:** A. Skrzecz

4.7. Ethanol + Water + Methylcyclohexane

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	x_2
		(complier)		(complier)	
−45.0	228.2	0.8952	0.0527	0.7251	0.2327
		0.8320	0.1470	0.5030	0.4843
		0.6471	0.3429	0.2562	0.7399
0.0	273.2	0.8580	0.0505	0.7005	0.2248
		0.8091	0.1429	0.4946	0.4761
		0.6366	0.3373	0.2545	0.7351
25.0	298.2	0.8349	0.0492	0.6850	0.2198
		0.7922	0.1399	0.4882	0.4700
		0.6275	0.3325	0.2530	0.7308

Comments and Additional Data

Water tolerance (S) was described with probable error < 0.5% at the range −45–25 °C by the equation: $\log(S)=a-b/(T/\mathrm{K})$. The parameters ($a,b$) were determined from plots. Water tolerance was defined as: $S=\mathrm{H_2O}$ % by volume·(100-Hydrocarbon % by volume in the blend)/100.

vol % hydrocarbon	a	b
75	2.058	587.6
50	2.210	504.9
25	2.047	347.3

Auxiliary Information

Method/Apparatus/Procedure:

A glass tube with stirrer containing the ternary mixture was immersed in a bath, the temperature of which could be varied. Mixtures were prepared directly in the tube, by special pipettes at 15.5 °C. Precautions to exclude moisture and to prevent evaporation were observed. No correction was made for the slight expansion in volume when alcohol was mixed with hydrocarbon. In the paper the experimental results were expressed as the water tolerance of the alcohol–hydrocarbon blend. For practical purposes water tolerance was defined as the volume percent of water which can be added before separation occurs.

Source and Purity of Materials:

(1) source not specified; anhydrous ethanol.
(2) source not specified; b.p.=99.85–100 °C.
(3) not specified.

Estimated Error:

temp. within about 0.3 °C (duplicate determinations), composition <0.2% relative of volume fraction.

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) 1-Heptene; C_7H_{14}; [592-76-7] (3) Water; H_2O; [7732-18-5]	T. M. Letcher, B. C. Bricknell, I. D. Sewry, and S. E. Radloff, J. Chem. Eng. Data 39, 320–3 (1994).
Variables: T/K=298	**Compiled by:** A. Skrzecz

4.8. Ethanol + Water + 1-Heptene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
				(compiler)	
25.0	298.2	0.000	1.000	0.000	1.000
		0.202	0.770	0.109	0.885
		0.361	0.579	0.223	0.762
		0.455	0.457	0.311	0.666
		0.538	0.342	0.409	0.555
		0.596	0.248	0.503	0.446
		0.628	0.171	0.586	0.340
		0.637	0.113	0.653	0.247
		0.611	0.063	0.700	0.154
		0.513	0.022	0.692	0.063
		0.412	0.013	0.620	0.042
		0.300	0.010	0.507	0.036
		0.239	0.005	0.438	0.020
		0.047	0.001	0.112	0.005
		0.000	0.000	0.000	0.000

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1	x_2	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.365	0.578	0.595	0.246	0.225	0.761	0.504	0.444
		0.330	0.620	0.627	0.175	0.197	0.791	0.582	0.346
		0.262	0.700	0.639	0.121	0.148	0.843	0.645	0.260
		0.228	0.743	0.555	0.033	0.125	0.869	0.706	0.089
		0.193	0.783	0.442	0.017	0.103	0.892	0.641	0.053
		0.099	0.890	0.239	0.005	0.049	0.948	0.438	0.020

Auxiliary Information

Method/Apparatus/Procedure:

The experimental methods have been described in Ref. 1. No more details were reported in the paper.

Source and Purity of Materials:

(1) source not specifed.
(2) Aldrich; distilled; purity >99.8 mole % by glc, $\rho = 0.692\ 65$ g cm^{-3}.
(3) not specified.

Estimated Error:

Not reported.

References:

[1] T. M. Letcher and F. M. Siswana, Fluid Phase Equilib. **74**, 203 (1992).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water (hydrogen oxide); H_2O; [7732-18-5]

Evaluted by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.03)

4.9. Ethanol + Water + Heptane

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.), compositions of coexisting phases in equilibrium (eq.) and distribution of ethanol between phases (distr.) for the system ethanol–heptane–water is given in Table 28.

TABLE 28. Summary of experimental data for the system ethanol–heptane–water

Author(s)	T/K	Type of data[a]	Ref.
Bonner, 1909	273	sat. (9)	1
Schweppe and Lorah, 1954	303	sat. (24), distr. (7)	2
Vorobeva and Karapetyants, 1966	298	sat. (15), eq.(9)	3
Letcher *et al.*, 1986	298	sat. (8), eq.(3)	4

[a] Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–heptane–water forms a large miscibility gap of type 1 covering the majority of the concentration triangle. The system was investigated by four groups over the temperature range 273–303 K; the saturation data are consistent with one another. Only the heptane–water binary system forms a miscibility gap. The data of this system were compiled and critically evaluated in a previously published SDS volume,[5] the recommended values at 298 K are: $x_2''=4.3\cdot 10^{-7}$ and $x_3'=5.6\cdot 10^{-4}$. The data reported by Schweppe and Lorah,[2] at 303 K, and Vorobeva and Karapetyants,[3] at 298 K, include solubility of the binary system heptane–water; $x_2''=0.0003$ and $x_3'<0.005$, respectively. These values are less precise and do not agree with the recommended data reported in Ref. 5. All experimental solubility and equilibrium data reported at 298 K in Refs. 3 and 4, were described by the equation:

$$x_1=1.1136+0.1319\ \ln(x_2)-1.2083x_2+0.0932x_2^2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0087. The selected points on the saturation curve, calculated by the above equation together with the "best" values of Ref. 5 are presented in Table 29 as in Fig. 1 as solid line.

TABLE 29. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 000 43 Ref. 5	0.4242	0.5200
0.5735	0.0200	0.4070	0.5400
0.6408	0.0400	0.3897	0.5600
0.6703	0.0600	0.3723	0.5800
0.6844	0.0800	0.3548	0.6000
0.6900	0.1000	0.3372	0.6200
0.6903	0.1200	0.3196	0.6400
0.6869	0.1400	0.3019	0.6600
0.6809	0.1600	0.2842	0.6800
0.6729	0.1800	0.2664	0.7000
0.6634	0.2000	0.2486	0.7200
0.6526	0.2200	0.2308	0.7400
0.6407	0.2400	0.2129	0.7600
0.6281	0.2600	0.1951	0.7800
0.6147	0.2800	0.1772	0.8000
0.6007	0.3000	0.1593	0.8200
0.5862	0.3200	0.1414	0.8400
0.5713	0.3400	0.1235	0.8600
0.5559	0.3600	0.1056	0.8800
0.5403	0.3800	0.0877	0.9000
0.5243	0.4000	0.0699	0.9200
0.5081	0.4200	0.0520	0.9400
0.4917	0.4400	0.0341	0.9600
0.4751	0.4600	0.0163	0.9800
0.4583	0.4800	0.0000	0.999 44 Ref. 5
0.4413	0.5000		

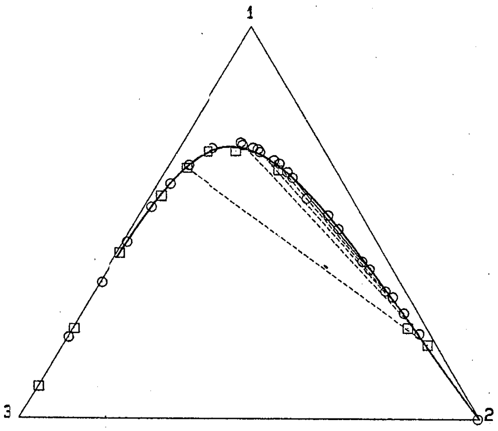

FIG. 15. Phase diagram of the system ethanol (1)—heptane (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 3 □—experimental data, Ref. 4, dashed lines—experimental tie lines, Refs. 3 and 4.

References:

[1]W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).

[2]J. L. Schweppe and J. R. Lorah, Ind. Eng. Chem. **46**, 2391 (1954).

[3]A. I. Vorobeva and M. Kh. Karapetyants, Zh. Fiz. Khim. **40**, 3018 (1966).

[4]T. M. Letcher, S. Wootton, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037 (1986).

[5]D. G. Shaw, ed., *Solubility Data Series,* Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C_5 to C_7 (Pergamon, New York, 1989).

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system ethanol–heptane–water were reported in Refs. 3 and 4 at 298.2 K. The reported equilibrium data sets are not consistent with one another, although they are consistent within each data set. The data for phases in equilibrium differ very much from one another; they are treated as doubtful. Part of experimental tie lines from both discussed references are crossing one another and therefore they are rejected and not reported in Fig. 15. These tie lines cover the region of high heptane concentration (>0.79 mole fraction) in the heptane-rich phase.

The plait point at 298.2 K reported in Ref. 3 is $x_1=0.517$ and $x_2=0.409$.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910).

Variables:

T/K=273

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K(compiler)	x_1 (compiler)	x_2 (compiler)	w_1 (complier)	w_2 (complier)
0.0	273.2	0.5662	0.3557	0.4131	0.5646
		0.7044	0.1695	0.6276	0.3285
		0.7289	0.1126	0.7037	0.2364
		0.7145	0.0736	0.7462	0.1673
		0.7030	0.0656	0.7509	0.1524
		0.6640	0.0438	0.7601	0.1092
		0.6086	0.0250	0.7549	0.0674
		0.5797	0.0176	0.7475	0.0495
		0.4939	0.0092	0.6974	0.0281

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogenous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated error:

accuracy of weighing 0.0001 g.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2)Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

J. L. Schweppe and J.R. Lorah, Ind. Eng. Chem. **46**, 2391–2 (1954).

Variables:

T/K=303

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
30.00	303.15	0.2061	0.7890	0.1071	0.8919
		0.3650	0.6296	0.2102	0.7886
		0.4437	0.5078	0.2831	0.7048
		0.5318	0.4133	0.3662	0.6190
		0.5996	0.3124	0.4565	0.5173
		0.6226	0.2892	0.4841	0.4891
		0.6865	0.1889	0.5990	0.3585
		0.6687	0.2222	0.5597	0.4046
		0.6298	0.2674	0.5032	0.4647
		0.6997	0.1458	0.6495	0.2944
		0.7090	0.1137	0.6913	0.2411
		0.6963	0.0784	0.7292	0.1785
		0.6912	0.0636	0.7469	0.1495
		0.6477	0.0398	0.7563	0.1010
		0.4764	0.0073	0.6862	0.0230
		0.4957	0.0073	0.7021	0.0226
		0.5784	0.0135	0.7537	0.0384
		0.6367	0.0253	0.7727	0.0669
		0.6587	0.0394	0.7638	0.0993
		0.2808	0.0005	0.4988	0.0021
		0.1155	0.0002	0.2502	0.0009
		0.3727	0.0026	0.5986	0.0090
		0.0000	0.0003	0.0000	0.0016
		0.2738	0.0005	0.4901	0.0019

Distribution of ethanol in ethanol–heptane–water system

t/°C	T/K (compiler)	w_1' hydrocarbon-rich phase	w_1'' water-rich phase
30.00	303.15	0.029	0.106
		0.032	0.290
		0.050	0.392
		0.050	0.460
		—	0.624
		0.055	0.752
		0.145	0.663

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Heptane (*n*-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

A. I. Vorobeva and M. Kh. Karapetyants, Zh. Fiz. Khim. **40**, 3018–23 (1966). [Eng. transl. Russ. J. Phys. Chem. **40**, 1619–22 (1966)].

Variables:

T/K=298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25	298.2	0.0000	0.9945	0.000	0.999
		0.3108	0.6535	0.178	0.814
		0.4828	0.4488	0.325	0.657
		0.5591	0.3415	0.417	0.554
		0.6474	0.2381	0.535	0.428
		0.6843	0.1730	0.613	0.337
		0.6877	0.1609	0.627	0.319
		0.7009	0.1279	0.670	0.266
		0.6868	0.0730	0.731	0.169
		0.6432	0.0413	0.751	0.105
		0.5959	0.0257	0.745	0.070
		0.5372	0.0151	0.721	0.044
		0.4486	0.0081	0.661	0.026
		0.3467	0.0022	0.572	0.008
		0.2070	0.0010	0.399	0.004

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hyrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25	298.2	0.000	1.000	0.365	0.003	<0.001	1.000	0.591	0.009
		0.030	0.970	0.492	0.008	0.014	0.986	0.697	0.026
		0.128	0.857	0.692	0.086	0.064	0.933	0.716	0.194
		0.218	0.758	0.695	0.135	0.116	0.879	0.659	0.278
		0.270	0.698	0.677	0.181	0.150	0.843	0.601	0.350
		0.326	0.630	0.656	0.222	0.190	0.800	0.553	0.407
		0.381	0.568	0.626	0.266	0.233	0.755	0.502	0.464
		0.401	0.542	0.612	0.284	0.250	0.736	0.482	0.486
		0.517	0.409	0.517	0.409	0.360	0.620	0.360	0.620

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used. Third component (hexane or water) was added to the binary alcohol solutions, respectively, held in a temperature controlled bath until a cloud point was observed. The solutions were prepared by weight, using an analytical balance. Density and refractive index measurements were made for the mixture and then plotted separately for each component. Then tie lines were determined by analytical method. The two-phase mixtures were placed in a thermostated bath and agitated periodically. After phase separation, densities of both phases were measured and concentrations were read from the plots. Phase equilibrium data were reported in incomplete form; only distribution of ethanol between water and heptane was reported.

Source and Purity of Materials:

(1) U.S. Industrial Chemicals, Inc., U.S.P., 200-proof; n(20 °C)=1.3579; used as received.
(2) Philips Petroleum Co., pure grade; purity>99 mole %, n(20 °C)=1.3835.
(3) distilled.

Estimated Error:

temp. ±0.03 °C.

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, Ref. 1, was used to determine solubility of the mixtures. The third component was added to the binary homogenous mixture until cloudiness was first observed. Density of the saturated mixtures was measured; these results were graphed. To obtain equilibrium, ternary mixtures were stirred in a thermostated vessel for several hours. After phase separation, the density of each phase was measured and composition was determined from the graphs prepared earlier. Concentration at the critical point was found by method described in Ref. 2. Water included in ethanol was taken into account in all measurements.

Source and Purity of Materials:

(1) source not specified, "rectificate grade:" distilled; water concentration was determined by the Karl Fischer method.
(2) source not specified; b.p. = 98.4 °C, $n(20\ °C,D) = 1.3877$.
(3) not specified.

Estimated Error:

solubility ±0.001 mass fraction.

References:

[1] W. D. Bancroft, Phys. Rev. **3**, 21 (1896).
[2] E. N. Zilberman, Zh. Fiz. Khim. **26**, 1458 (1952).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Heptane (n-heptane); C_7H_{16}; [142-82-5]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. M. Letcher, S. Wootton, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037–42 (1986).

Variables:

T/K = 298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C (compiler)	T/K	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25	298.2	0.082	0.000	0.186	0.000
		0.229	0.002	0.429	0.008
		0.421	0.006	0.640	0.020
		0.565	0.022	0.730	0.062
		0.678	0.067	0.734	0.158
		0.680	0.128	0.658	0.269
		0.631	0.244	0.521	0.438
		0.232	0.726	0.127	0.864

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w''_1	w'_2	w''_1	w''_2
t/°C (compiler)	T/K	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25	298.2	0.190	0.790	0.636	0.041	0.099	0.897	0.747	0.105
		0.110	0.875	0.418	0.006	0.054	0.943	0.637	0.020
		0.078	0.912	0.138	0.002	0.038	0.960	0.288	0.009

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, adapted from Ref. 1, was used to determine the coexistence curve. The third component was added from a weighed gas-tight syringe to a weighed mixture of the other two components in 100 mL long-neck flask until one drop (weighing less than 0.01 g) resulted in cloudiness. The flask was immersed in a well controlled water bath and shaken continuously. Refractive indexes of these mixtures were measured at 298.3 K to ensure that separation did not take place. Tie lines were determined from mixtures of known composition in the immiscible region. The flasks were shaken well and the phases allowed to separate. Refractive indexes of samples of both phases were measured and related to compositions on the coexistence curve. Each tie line was checked to ensure that it passed through the composition of the overall mixture.

Source and Purity of Materials:

(1) NCP, South Africa, absolute grade; dried with magnesium metal activated with iodine, distilled.
(2) Analytical Carbo Erba, purity 99.5 mole %; purified by passing through columns containing silica gel and basic alumina.
(3) de-ionized.

Estimated Error:

composition ±0.005 mole fraction for measured points, ±0.01 mole fraction for tie-lines extremities in the worst case (authors).

References:

[1] S. W. Briggs and E. W. Commings, Ind. Eng. Chem. **35**, 411 (1943).

Components:	**Evaluated by:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) *m*-Xylene (1,3-dimethylbenzene, 1,3-xylene); C_8H_{10}; [108-38-3] (3) Water; H_2O; [7732-18-5]	A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.04)

4.10. Ethanol + Water + *m*-Xylene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system ethanol–*m*-xylene–water is given in Table 30.

TABLE 30. Summary of experimental data for the system ethanol–*m*-xylene–water

Author(s)	*T*/K	Type of data[a]	Ref.
Bonner, 1909	273	sat. (10)	1
Holt and Bell, 1914	273–373	sat.(43)	2
Mochalov, 1937	273, 323	eq.(12)	3
Leikola, 1940	293	sat. (6)	4
Mondain-Monval and Quiquerez, 1940	298	sat. (22), eq. (8)	5
Nam *et al.*, 1972	298	sat. (16), eq. (10)	6

[a] Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–*m*-xylene–water forms a miscibility gap of type 1. This critical evaluation is based on the original papers with the exception of data of Mochalov[3] and Leikola[4] which were taken from the handbooks of Seidel and Linke[7] and Kafarov,[8] respectively; these data sets were also taken into account during evaluation but are not reported as compilation sheets because they do not contribute further to knowledge of the system. Data of Holt and Bell[2] measured over a wide temperature range, show a decreasing miscibility gap with increasing temperature which is in agreement with the general expectation. The points $x_1=0.4706$ at 336.2 K and $x_1=0.3956$ at 373.2 K are incompatible with other data and presumably contain experimental errors. Data of Leikola[4] for 293 K are close to the data for 298.2 K, with the exception of one experimental point $x_1=0.561$, $x_2=0.243$, which presumably contains an experimental error. Other solubility data are consistent within each data set, at the same temperature as well as with one another. Nam *et al.*,[6] checked their experiments in two ways: repetition of experiment with another mixture and by reappearance of turbidity by lowering the temperature; so these data are considered more reliable. Equilibrium compositions of both phases, reported in Ref. 6, are consistent with saturation measurements. Only one binary system, *m*-xylene–water, forms a miscibility gap. This system was compiled and critically evaluated in a previously published SDS vol. 38, Ref. 9. These recommended values are: $x_2'=0.000\,0344$ and $x_2''=0.9989$ at 273 K; $x_2'=0.000\,029$ and $x_2''=0.9978$ at 293 K and $x_2'=0.000\,027$ and $x_2''=0.9974$ at 298 K. All experimental data are treated as tentative. Data reported at 298.2 K by Mondain-Monval and Quiquerez[5] and Nam *et al.*,[6] $x_2<0.96$ (water-rich and hydrocarbon-rich branches were treated together), were used to construct the fitting equation:

$$x_1=0.765\,79+0.087\,29\ln(x_2)-0.495\,55x_2-0.284\,48x_2^2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0164. Selected points on the saturation curve, calculated by this equation together with the recommended values of Ref. 9 are presented in Table 31 and in Fig. 16 as the solid line. Experimental points at 298.2 K are also shown.

TABLE 31. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 027 Ref. 9	0.3983	0.4800
0.1623	0.0010	0.3864	0.5000
0.3588	0.0100	0.3741	0.5200
0.4143	0.0200	0.3615	0.5400
0.4645	0.0400	0.3485	0.5600
0.4894	0.0600	0.3351	0.5800
0.5038	0.0800	0.3215	0.6000
0.5124	0.1000	0.3075	0.6200
0.5171	0.1200	0.2932	0.6400
0.5192	0.1400	0.2785	0.6600
0.5192	0.1600	0.2636	0.6800
0.5177	0.1800	0.2484	0.7000
0.5148	0.2000	0.2328	0.7200
0.5108	0.2200	0.2170	0.7400
0.5059	0.2400	0.2009	0.7600
0.5001	0.2600	0.1845	0.7800
0.4936	0.2800	0.1678	0.8000
0.4864	0.3000	0.1508	0.8200
0.4789	0.3200	0.1336	0.8400
0.4702	0.3400	0.1160	0.8600
0.4613	0.3600	0.0982	0.8800
0.4519	0.3800	0.0802	0.9000
0.4421	0.4000	0.0618	0.9200
0.4318	0.4200	0.0432	0.9400
0.4210	0.4400	0.0243	0.9600
0.4099	0.4600	0.0000	0.9974 Ref. 9

Phases in equilibrium

The equilibrium data for the ternary system ethanol–*m*-xylene–water were reported in the papers of Mochalov,[3] Mondain-Monval and Quiquerez,[5] and Nam *et al.*[6] At 298.2 K data of Mondain-Monval and Quiquerez[5] covered the region closer to the plait point, while data of Nam *et al.*[6] covered the region from low methanol concentrations to the equilibrium point ($x_1=0.412$, $x_2=0.024$ in water-rich phase). The results are consistent within each data set but there is significant disagreement between the first tie line of Ref. 5 ($x_1''=0.261$ and $x=0.002$) and the tie lines reported by Nam *et al.*[6] Other reported tie lines are consistent. Systematic changes in the partition coefficient of ethanol are observed with temperature. Characteristic points on the binodal curve, plait point and maximum ethanol concentration, reported or estimated, are presented at selected temperatures in Table 32. The errors of maximum ethanol concentration point estimated by the evaluator are 0.01 and 0.02 mole fraction of ethanol and *m*-xylene, respectively.

TABLE 32. Characteristic points on binodal curve of the system ethanol–*m*-xylene–water

	Max. C_2H_5OH concentration			Plait points		
T/K	x_1	x_2	Ref.	x_1	x_2	Ref.
273.2	0.59	0.19	1	0.549	0.329	3
298.2	0.53	0.15	5	0.470	0.324	5
298.2	0.53	0.13	6	—	—	
314.2	0.51	0.15	2	—	—	
323.2	—	—		0.492	0.274	3
336.2	0.46	0.16	2	—	—	

The experimental data for phase equilibria at 298.2 K are considered tentative and are presented in the Fig. 16.

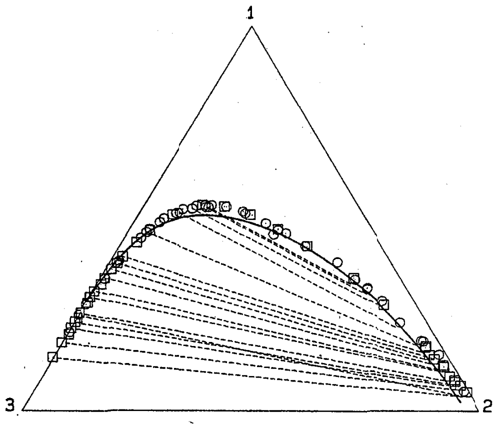

FIG. 16. Phase diagram of the system ethanol (1)—*m*-xylene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 5, □—experimental data, Ref. 6, dashed lines—experimental tie lines, Refs. 5 and 6.

References:

[1]W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).

[2]A. Holt and N. M. Bell, J. Chem. Soc. **105**, 633 (1914).

[3]K. I. Mochalov, Izv. Biol. Nauchno-Issled. Inst. Molotov. Gos. Univ. **11**, 25 (1937).

[4]E. Leikola, Suomen Kemistil. B **13**, 13 (1940).

[5]P. I. Mondain-Monval and J. Quiquerez, Bull. Soc. Chim. Fr. Mem. **7**, 240 (1940).

[6]S. Nam, T. Hayakawa, and S. Fujita, J. Chem. Eng. Jpn. 5, 327 (1972).

[7]A. Seidel and W. F. Linke, *Solubilities of Inorganic and Organic Compounds*, Supplement to the Third Edition, Am. Chem. Soc., D (Ban Nostrand Co., New York, 1952).

[8]V. V. Kafarov, ed., *Spravochnik po Rastvorimosti*, Vol. 2. Troinye, Mnogokomponentnye Sistemy, Kniga II (Izd. Akademii Nauk SSSR, Moskva, 1963).

[9]D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) *m*-Xylene (1,3-dimethylbenzene, 1,3-xylene); C_8H_{10}; [108-38-3] (3) Water; H_2O; [7732-18-5]	W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910)
Variables: T/K=273	**Compiled by:** A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
0.0	273.2	0.4350	0.4704	0.2795	0.6967
		0.5548	0.2714	0.4444	0.5011
		0.5912	0.1911	0.5294	0.3944
		0.6028	0.1170	0.6139	0.2745
		0.5772	0.0835	0.6396	0.2133
		0.5387	0.0490	0.6627	0.1390
		0.5036	0.0302	0.6667	0.0920
		0.4684	0.0223	0.6516	0.0714
		0.3953	0.0114	0.6047	0.0403
		0.3177	0.0027	0.5387	0.0106

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water-hydrocarbon mixture and the weight of alcohol necessary to make a homogeneous solution. The mass of binary water-hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:

accuracy of weighing 0.0001 g.

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) *m*-Xylene (1,3-dimethylbenzene, 1,3-xylene); C_8H_{10}; [108-38-3] (3) Water; H_2O; [7732-18-5]	A. Holt and N. M Bell, J. Chem. Soc. **105**, 633–9 (1914).
Variables: T/K=273–373	**Compiled by:** A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1 (compiler)	w_2 (compiler)
0	273.2	0.4112	0.4918	0.2598	0.7162
		0.5335	0.3189	0.4023	0.5542
		0.5827	0.2323	0.4895	0.4497
		0.5961	0.1783	0.5443	0.3752
		0.5907	0.1446	0.5749	0.3243
		0.6002	0.1196	0.6091	0.2797
		0.5843	0.0873	0.6393	0.2201
		0.5522	0.0600	0.6557	0.1642
		0.5271	0.0450	0.6604	0.1299
		0.5143	0.0362	0.6649	0.1079
19	292.2	0.4043	0.4836	0.2587	0.7132
		0.5069	0.3031	0.3961	0.5458
		0.5344	0.2131	0.4753	0.4368
		0.5471	0.1636	0.5275	0.3635
		0.5637	0.1318	0.5714	0.3079
		0.5452	0.1087	0.5856	0.2691
		0.5398	0.0922	0.6023	0.2371
		0.5200	0.0691	0.6191	0.1896
		0.4731	0.0404	0.6254	0.1231
		0.4289	0.0223	0.6172	0.0740
41	314.2	0.3853	0.4608	0.2556	0.7045
		0.4719	0.2822	0.3873	0.5338
		0.4963	0.1979	0.4630	0.4255
		0.5075	0.1517	0.5124	0.3530
		0.5075	0.1214	0.5443	0.3001
		0.5007	0.0998	0.5645	0.2593
		0.4661	0.0557	0.5964	0.1643
		0.4437	0.0442	0.5949	0.1366
		0.4122	0.0336	0.5836	0.1096
		0.4035	0.0268	0.5864	0.0898
63	336.2	0.3708	0.4435	0.2530	0.6974
		0.4167	0.3322	0.3254	0.5979
		0.4706	0.2814	0.3870	0.5333
		0.4522	0.2163	0.4186	0.4614
		0.4606	0.1836	0.4503	0.4137
		0.4644	0.1587	0.4751	0.3741
		0.4564	0.1248	0.5028	0.3168
		0.4566	0.0993	0.5315	0.2664
		0.4495	0.0766	0.5540	0.2176
		0.4035	0.0419	0.5628	0.1347
100	373.2	0.3956	0.1881	0.3988	0.4370
		0.3824	0.0759	0.4972	0.2274
		0.4097	0.0375	0.5752	0.1213

Distribution of *m*-xylene in ethanol—*m*-xylene—water system

t/°C	T/K (compiler)	x_2' hydrocarbon-rich phase (compiler)	x_2'' water-rich phase (compiler)
0	273.2	0.8018	0.0093
0	273.2	0.6995	0.0229
19	292.2	0.8212	0.0105
19	292.2	0.5840	0.0527

Auxiliary Information

Method/Apparatus/Procedure:

To a known volume of *m*-xylene small portions of alcohol were added. After each addition of alcohol, water was added until a distinct milkiness was observed. The mixture was kept at constant temperature and was shaken repeatedly.

Source and Purity of Materials:

(1) source not specified; ''absolute'' ethyl alcohol; used as received.
(2) source not specified; ''nearly pure'' *m*-xylene; used as received.
(3) distilled.

Estimated Error:

Not reported.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *m*-Xylene (1,3-dimethylbenzene, 1,3-xylene); C_8H_{10}; [108-38-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
P. Mondain-Monval and J. Quiquerez, Bull. Soc. Chim. Fr. Mem. 7, 240–53 (1940).

Variables:
T/K=298

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.00	298.15	0.2039	0.0006	0.3948	0.0029
	298.15	0.2763	0.0036	0.4880	0.0145
	298.15	0.3433	0.0105	0.5536	0.0389
	298.15	0.3887	0.0176	0.5876	0.0614
	298.15	0.4485	0.0344	0.6144	0.1086
	298.15	0.4717	0.0421	0.6216	0.1279
	298.15	0.4992	0.0592	0.6175	0.1689
	298.15	0.4895	0.0553	0.6158	0.1602
	298.15	0.5132	0.0783	0.6014	0.2114
	298.15	0.5238	0.0917	0.5915	0.2387
	298.15	0.5323	0.1163	0.5680	0.2857
	298.15	0.5345	0.1343	0.5490	0.3180
	298.15	0.5344	0.1479	0.5347	0.3410
	298.15	0.5304	0.1818	0.4995	0.3945
	298.15	0.5185	0.2237	0.4569	0.4543
	298.15	0.5133	0.2312	0.4479	0.4649
	298.15	0.4877	0.2887	0.3932	0.5363
	298.15	0.4613	0.3456	0.3463	0.5972
	298.15	0.4287	0.4037	0.3009	0.6531
	298.15	0.3870	0.4940	0.2462	0.7242
	298.15	0.3163	0.5931	0.1843	0.7952
	298.15	0.1803	0.7874	0.0898	0.9039

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.051	0.938	0.261	0.002	0.023	0.975	0.470	0.010
	298.15	0.146	0.838	0.395	0.019	0.070	0.927	0.591	0.066
	298.15	0.182	0.782	0.475	0.044	0.091	0.902	0.621	0.133
	298.15	0.229	0.713	0.526	0.090	0.121	0.867	0.595	0.235
	298.15	0.285	0.646	0.537	0.115	0.158	0.827	0.573	0.282
	298.15	0.320	0.592	0.541	0.142	0.186	0.794	0.545	0.330
	298.15	0.342	0.555	0.541	0.148	0.206	0.770	0.539	0.340
	298.15	0.470	0.324	0.470	0.324	0.362	0.576	0.362	0.576[a]

[a] Plait point.

Auxiliary Information

Method/Apparatus/Procedure:

The analytical method was used. 100 mL of ternary mixture, prepared by weight, was placed in thermostat, agitated many times and then leave for several hours to separate. The density and refractive index of each phase was measured. Inversion of density was observed.

Source and Purity of Materials:

(1) source not specified; d(25 °C,4 °C)=0.7853.
(2) source not specified; d(25 °C, 4 °C)=0.8593, b.p. =138.1 °C at 739 Torr.
(3) not specified.

Estimated Error:

temp. ±0.02 °C.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *m*-Xylene (1,3-dimethylebenzene, 1,3-xylene); C_8H_{10}; [108-38-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
S Nam, T. Hayakawa, and S. Fujita, J. Chem. Eng. Jpn. 5, 327–34 (1972).

Variables:
T/K = 298

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.00	298.15	0.1678	0.8001	0.0829	0.9109
		0.2748	0.6548	0.1517	0.8331
		0.3464	0.5499	0.2094	0.7661
		0.4281	0.4081	0.2988	0.6565
		0.4730	0.3222	0.3651	0.5731
		0.5102	0.2433	0.4371	0.4803
		0.5310	0.1772	0.5040	0.3877
		0.5349	0.1275	0.5567	0.3059
		0.5097	0.0729	0.6061	0.1998
		0.4685	0.0447	0.6150	0.1351
		0.4368	0.0309	0.6100	0.0993
		0.3816	0.0175	0.5809	0.0613
		0.3284	0.0096	0.5388	0.0364
		0.2806	0.0052	0.4907	0.0210
		0.2410	0.0028	0.4437	0.0117
		0.1988	0.0015	0.3861	0.0065

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.049	0.945	0.1506	0.0008	0.022	0.977	0.311	0.004
		0.066	0.923	0.1888	0.0015	0.030	0.968	0.371	0.007
		0.076	0.907	0.2272	0.0021	0.035	0.962	0.426	0.009
		0.080	0.903	0.2430	0.0031	0.037	0.960	0.446	0.013
		0.090	0.888	0.2662	0.0044	0.042	0.954	0.474	0.018
		0.114	0.864	0.3068	0.0069	0.054	0.942	0.519	0.027
		0.118	0.860	0.3221	0.0084	0.056	0.940	0.534	0.032
		0.134	0.834	0.3562	0.0129	0.065	0.929	0.563	0.047
		0.145	0.818	0.3789	0.0164	0.071	0.922	0.580	0.058
		0.164	0.800	0.4118	0.0239	0.081	0.912	0.599	0.080

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine solubility curve. A binary ethanol–xylene mixture of known composition was prepared in a conical flask with silicone stopper to prevent evaporation. The mixture was placed in a thermostated vessel, agitated by a magnetic stirrer and titrated through a needle of the syringe with water until two phases were observed. The result was checked by another ternary mixture, of the same composition as above: (a) titrated with one of the pure components until the turbidity disappeared, (b) by reappearance of turbidity by lowering the temperature about 0.5 °C. The two-phase mixture was placed in a 50 mL glass-stoppered test tube at temperature of 25 °C, shaken vigorously, kept for nearly 2 h in a constant temperature water bath, and after separation each layer was pipetted for sampling. Refractive index and density of each phase were measured and composition was found from the calibration curves constructed during solubility measurements. When mixtures were not separated clearly after several hours, a centrifuge was used to obtain separation.

Source and Purity of Materials:

(1) Wako Pure Chemical Inst. Ltd., guaranteed reagent; $\rho(25\ °C) = 785.32\ kg\ m^{-3}$, $n(25\ °C,D) = 1.3600$; used as received.
(2) Kishida Chem. Ltd., guaranteed reagent; $\rho(25\ °C) = 859.88\ kg\ m^{-3}$, $n(25\ °C,D) = 1.4940$; used as received.
(3) ion exchanged, distilled.

Estimated Error:

temp. ±0.02 °C and ±0.1 °C (near plait point).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *o*-Xylene (1,2-dimethylbenzene, 1,2-xylene); C_8H_{10}; [95-47-6]
(3) Water; H_2O; [7732-18-5]

Evaluated by:
A. Skrzecz (1995.04)

4.11. Ethanol + Water + *o*-Xylene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system ethanol–*o*-xylene–water is given in Table 33.

TABLE 33. Summary of experimental data for the system ethanol-*o*-xylene–water

Author(s)	T/K	Type of data[a]	Ref.
Bonner, 1909	273	sat. (10)	1
Nam *et al.*, 1972	298	sat. (16), eq. (10)	2

[a]Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–*o*-xylene–water forms a miscibility gap of type 1. The system was measured at temperatures 273 and 298 K in two references. Only one binary system, *o*-xylene–water forms a miscibility gap. Binary data were compiled and critically evaluated in a previously published SDS volume.[3] The recommended values of mutual solubility of the *o*-xylene–water system at 298 K are: $x_2'=0.9974$ and $x_2''=0.000\,029\,3$.[3] Binary data were not reported together with the ternary system and data reported in the both references are far from the binary systems. Experimental errors were ±0.05 mass % (estimated by the evaluator) for data reported in Ref. 1 and ±0.1 mass % (estimated by the authors) for data reported in Ref. 2. Experimental data for phases in equilibrium, reported in Ref. 2, were also used to construct the binodal curve. Although the composition of the *o*-xylene-rich phase is outside the saturation measurements and is scattered, the data appear to be consistent within one another. The data reported from both references appear consistent although they were measured at different temperatures. The system shows increasing solubility with temperature. Data at both temperatures are treated as tentative. The data at 298.2 K (Ref. 2) were described by the equation:

$$x_1=0.746\,15+0.086\,71\ln(x_2)-0.437\,11x_2-0.325\,75x_2^2.$$

The least-squares method was used. The standard error of estimate was 0.0127. The model is not valid in the region of high concentration of *o*-xylene ($x_2>0.98$). Compositions on the saturation curve calculated by the equation are presented in Table 34 for selected concentrations of *o*-xylene in the mixture. The results of calculations (solid line) are presented also graphically (Fig. 17) together with all experimental data reported at 298.2 K.

TABLE 34. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 0293 Ref. 3	0.3861	0.5000
0.1468	0.0010	0.3741	0.5200
0.3424	0.0100	0.3617	0.5400
0.3981	0.0200	0.3489	0.5600
0.4490	0.0400	0.3358	0.5800
0.4748	0.0600	0.3223	0.6000
0.4901	0.0800	0.3085	0.6200
0.4995	0.1000	0.2943	0.6400
0.5052	0.1200	0.2797	0.6600
0.5081	0.1400	0.2648	0.6800
0.5090	0.1600	0.2496	0.7000
0.5082	0.1800	0.2341	0.7200
0.5061	0.2000	0.2182	0.7400
0.5029	0.2200	0.2020	0.7600
0.4987	0.2400	0.1855	0.7800
0.4937	0.2600	0.1686	0.8000
0.4878	0.2800	0.1515	0.8200
0.4813	0.3000	0.1340	0.8400
0.4741	0.3200	0.1162	0.8600
0.4663	0.3400	0.0981	0.8800
0.4580	0.3600	0.0797	0.9000
0.4491	0.3800	0.0611	0.9200
0.4397	0.4000	0.0421	0.9400
0.4299	0.4200	0.0228	0.9600
0.4196	0.4400	0.0032	0.9800
0.4088	0.4600	0.0000	0.9974 Ref. 3
0.3976	0.4800		

Phases in equilibrium

For the ternary system ethanol–*o*-xylene–water, phases, in equilibrium were measured only in Ref. 2 at temperature 298.2 K. The tie lines cover the middle area of miscibility gap and are consistent with one another. They are considered tentative. The plait point was not reported. All experimental data reported at 298.2 K, Ref. 2, are presented in Fig. 17.

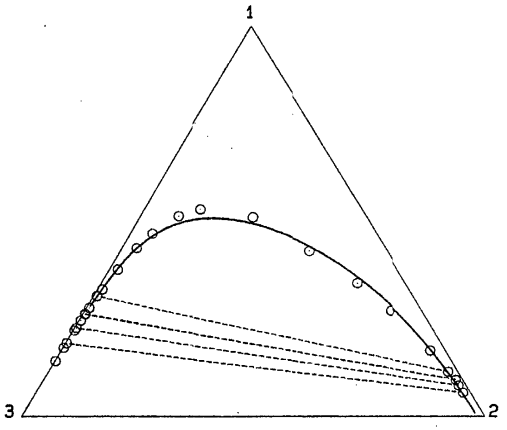

FIG. 17. Phase diagram of the system ethanol (1)—*o*-xylene (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, O—experimental results of Ref. 2, dashed lines—experimental tie lines, Ref. 2.

References:

[1] W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).

[2] S. Nam, T. Hayakawa, and S. Fujita, J. Chem. Eng. Jpn. **5**, 327 (1972).

[3] D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *o*-Xylene (1,2-dimethylbenzene, 1,2-xylene); C_8H_{10}; [95-47-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910)

Variables:

T/K=273

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K	x_1	x_2	w_1	w_2
0.0	273.2	0.4153	0.4972	0.2604	0.7182
		0.5053	0.3972	0.3464	0.6275
		0.6030	0.2120	0.5181	0.4198
		0.5977	0.1544	0.5690	0.3388
		0.5873	0.1124	0.6094	0.2687
		0.5580	0.0677	0.6485	0.1814
		0.5252	0.0434	0.6616	0.1259
		0.4615	0.0230	0.6445	0.0739
		0.4116	0.0109	0.6212	0.0379
		0.3232	0.0037	0.5434	0.0142

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogenous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:

accuracy of weighting 0.001 g.

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *o*-Xylene (1,2-dimethylbenzene, 1,2-xylene); C_8H_{10}; [95-47-6]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

S. Nam, T. Hayakawa, and S. Fujita, J. Chem. Eng. Jpn. **5**, 327–34 (1972).

Variables:

$T/K = 298$

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.00	298.15	0.1710	0.7960	0.0847	0.9089
		0.2727	0.6577	0.1502	0.8348
		0.3432	0.5521	0.2072	0.7681
		0.4255	0.4106	0.2964	0.6590
		0.5110	0.2465	0.4353	0.4839
		0.5312	0.1251	0.5568	0.3023
		0.5143	0.0827	0.5963	0.2210
		0.4700	0.0472	0.6124	0.1416
		0.4333	0.0314	0.6060	0.1013
		0.3785	0.0177	0.5774	0.0624
		0.3275	0.0098	0.5377	0.0369
		0.2801	0.0053	0.4900	0.0212
		0.2479	0.0033	0.4521	0.0140
		0.2225	0.0023	0.4192	0.0099
		0.1777	0.0012	0.3543	0.0056
		0.1439	0.0006	0.2999	0.0030

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
$t/°C$	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.061	0.922	0.190	0.002	0.028	0.969	0.372	0.008
		0.080	0.903	0.229	0.003	0.037	0.960	0.428	0.012
		0.095	0.889	0.265	0.004	0.044	0.953	0.472	0.018
		0.095	0.889	0.264	0.005	0.044	0.953	0.471	0.019
		0.116	0.862	0.310	0.007	0.055	0.941	0.522	0.029
		0.102	0.876	0.306	0.008	0.048	0.948	0.517	0.030
		0.130	0.849	0.362	0.014	0.062	0.934	0.566	0.052
		0.147	0.816	0.403	0.023	0.072	0.921	0.592	0.079
		0.167	0.796	0.448	0.036	0.083	0.910	0.611	0.114

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine solubility curve. A binary ethanol–xylene mixture of known composition was prepared in a conical flask with silicone stopper to prevent evaporation. The mixture was placed in a thermostated vessel, agitated by a magnetic stirrer and titrated through a needle of the syringe with water until two phases were observed. The result was checked by another ternary mixture, of the same composition as above: (a) titrated with one of the pure components until the turbidity disappeared, (b) by reappearance of turbidity by lowering the temperature about 0.5 °C. The two-phase mixture was placed in a 50 mL glass-stoppered test tube at temperature of 25 °C, shaken vigorously, kept for nearly 2 h in a constant temperature water bath, and after separation each layer was pipetted for sampling. Refractive index and density of each phase were measured and composition was found from the calibration curves constructed during solubility measurements. When mixtures were not separated clearly after several hours, a centrifuge was used to obtain separation.

Source and Purity of Materials:

(1) Wako Pure Chemical Inst. Ltd., guaranteed reagent; $\rho(25\ °C) = 785.32\ kg\ m^{-3}$, $n(25\ °C,D) = 1.3600$; used as received.
(2) Kishida Chem. Ltd., guaranteed reagent; $\rho(25\ °C) = 870.29\ kg\ m^{-3}$, $n(25\ °C,D) = 1.50175$; used as received.
(3) ion exchanged, distilled.

Estimated Error:

temp. ±0.02 °C and ±0.1 °C (near plait point).

Components:	Evaluated by:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) *p*-Xylene (1,4-dimethylbenzene, 1,4-xylene); C_8H_{10}; [106-42-3] (3) Water; H_2O; [7732-18-5]	A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw Poland (1997.04)

4.12. Ethanol + Water + *p*-Xylene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system the system ethanol–*p*-xylene–water is given in Table 35.

TABLE 35. Summary of experimental data for the system ethanol–*p*-xylene–water

Author(s)	*T*/K	Type of data[a]	Ref.
Bonner, 1909	288	sat. (12)	1
Nam *et al.*, 1972	298	sat. (16), eq. (9)	2
Letcher *et al.*, 1989	298	sat.(15), eq. (6)	3

[a] Number of experimental points in parentheses.

Saturation curve

The system ethanol–*p*-xylene–water forms a miscibility gap of type 1. Solubility data for the saturation curve obtained by the titration method were reported in all three references. Data for phases in equilibrium, reported in Refs. 2 and 3, were also used for construction of the binodal curve. Only one binary pair of components, *p*-xylene–water, is partially miscible. Data of this system were compiled and critically evaluated in a previously published SDS volume.[4] The recommended, values of mutual solubility of *p*-xylene–water system at 298.2 K are: $x_2''=3.1\cdot 10^{-5}$ and $x_2'=0.9974$. The end points of the saturation curve, Ref. 3, were reported to be $x_1=0.000$, $x_2=0.998$ and $x_1=0.065$, $x_2=0.000$, which suggests that ethanol is only partially soluble in water. These numerical results are within the accuracy of experimental measurements which was stated by the authors to be 0.005 mole fraction, however, they are not adequate to describe the region of low ethanol concentration. Data of Bonner, Ref. 1, reported at 288.2 K, are consistent with the results of Refs. 2 and 3. All experimental saturation data reported at 298.2 K[2,3] are in agreement. For $x_2>0.003$, the results were fitted to the equation:

$$x_1=0.845\,30+0.111\,30\,\ln(x_2)-0.704\,79x_2-0.144\,88x_2^2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0246. Selected points on the saturation curve, calculated by this equation together with the "best" values of Ref. 4 are presented in Table 36. Experimental points at 298.2 K are also presented in Fig. 18.

TABLE 36. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	0.000 031 Ref. 4	0.3795	0.5000
0.0758	0.0010	0.3668	0.5200
0.3257	0.0100	0.3539	0.5400
0.3957	0.0200	0.3406	0.5600
0.4586	0.0400	0.3272	0.5800
0.4894	0.0600	0.3134	0.6000
0.5069	0.0800	0.2994	0.6200
0.5171	0.1000	0.2852	0.6400
0.5226	0.1200	0.2708	0.6600
0.5250	0.1400	0.2561	0.6800
0.5249	0.1600	0.2413	0.7000
0.5229	0.1800	0.2262	0.7200
0.5194	0.2000	0.2109	0.7400
0.5147	0.2200	0.1954	0.7600
0.5090	0.2400	0.1798	0.7800
0.5023	0.2600	0.1639	0.8000
0.4949	0.2800	0.1479	0.8200
0.4868	0.3000	0.1316	0.8400
0.4781	0.3200	0.1152	0.8600
0.4688	0.3400	0.0987	0.8800
0.4591	0.3600	0.0819	0.9000
0.4489	0.3800	0.0650	0.9200
0.4382	0.4000	0.0479	0.9400
0.4272	0.4200	0.0306	0.9600
0.4158	0.4400	0.0132	0.9800
0.4040	0.4600	0.0044	0.9900
0.3919	0.4800	0.0000	0.9974 Ref. 4

Phases in equilibrium

Compositions of equilibrium phases of the ternary system ethanol–*p*-xylene–water at 298.2 K were reported in Refs. 2 and 3. These data are presented in Fig. 18. The reported tie lines cross one another. For similar compositions of the hydrocarbon-rich phase, the concentration of ethanol at equilibrium in the water-rich phase is always reported to be lower by Nam *et al.*,[2] than by Letcher *et al.*,[3] e.g.: $x_1'=0.044$ $x_2'=0.939$, $x_1''=0.0728$ $x_2''=0.0004$ (Ref. 2) and $x_1'=0.031$ $x_2'=0.960$, $x_1''=0.0292$ $x_2''=0.0007$ (Ref. 3) or $x_1'=0.163$ $x_2'=0.806$, $x_1''=0.4457$ $x_2''=0.0369$ (Ref. 2) and $x_1'=0.168$ $x_2'=0.795$, $x_1''=0.514$ $x_2''=0.074$ (Ref. 3). These equilibrium data sets are not consistent with one another, although each is internally consistent. The plait point of the system at 298.2 K, calculated by Letcher and Siswana[5] was reported to be $x_1=0.48$ $x_2=0.35$. The plait point reported by Bonner at 288.2 K[1] was $x_1=0.486$, $x_2=0.340$. The equilibrium and saturation data are presented together with calculated binodal curve in Fig. 18.

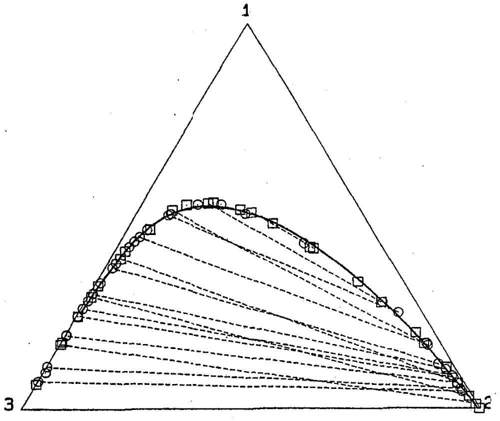

FIG. 18. Phase diagram of the system ethanol (1)—*p*-xylene (2)—water (3) at 298.2 K. Solid line—calculated binodal curve, ○—experimental results of Ref. 2, □—experimental results of Ref. 3, dashed lines—experimental tie lines, Refs. 2 and 3.

References:

[1] W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).
[2] S. Nam, T. Hayakawa, and S. Fujita, J. Chem. Eng. Jpn. **5**, 327 (1972).
[3] T. M. Letcher, P. M. Siswana, P. van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053 (1989).
[4] D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).
[5] T. M. Letcher and P. M. Siswana, Fluid Phase Equilib. **74**, 203 (1992).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *p*-Xylene (1,4-dimethylbenzene, 1,4-xylene); C_8H_{10}; [106-42-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910).

Variables:

T/K=273

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2	w_1 (compiler)	w_2	
15.0	288.2	0.3768	0.5161	0.2343	0.7397	
		0.4732	0.3581	0.3468	0.6048	
		0.4856	0.3401	0.3631	0.5860	plait point
		0.5238	0.2629	0.4318	0.4994	
		0.5532	0.1734	0.5220	0.3772	
		0.5572	0.1318	0.5671	0.3091	
		0.5280	0.0630	0.6337	0.1744	
		0.5040	0.0464	0.6407	0.1358	
		0.4753	0.0353	0.6354	0.1086	
		0.4308	0.0222	0.6190	0.0735	
		0.3625	0.0103	0.5741	0.0375	

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment. Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogenous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:

accuracy of weighing 0.0001 g.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *p*-Xylene (1,4-dimethylbenzene, 1,4-xylene); C_8H_{10}; [106-42-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
S. Nam, T. Hayakawa, and S. Fujita, J. Chem. Eng. Jpn. 5, 327–34 (1972).

Variables:
$T/K=298$

Compiled by:
A. Skrzecz

Experimental Data

Compositions along the saturation curve

$t/°C$	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
25.00	298.15	0.1685	0.8004	0.0832	0.9108
		0.2750	0.6529	0.1521	0.8323
		0.0963	0.0050	0.2097	0.0250
		0.4276	0.4062	0.2993	0.6552
		0.5057	0.2401	0.4365	0.4777
		0.5297	0.1761	0.5042	0.3863
		0.5292	0.1257	0.5548	0.3037
		0.5049	0.0755	0.5990	0.2063
		0.4636	0.0441	0.6119	0.1340
		0.4206	0.0266	0.6025	0.0879
		0.4339	0.0309	0.6073	0.0998
		0.3789	0.0175	0.5783	0.0615
		0.3277	0.0096	0.5381	0.0364
		0.2815	0.0052	0.4918	0.0208
		0.2399	0.0028	0.4423	0.0117
		0.1930	0.0015	0.3774	0.0066

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
$t/°C$	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25.00	298.15	0.044	0.939	0.3728	0.0004	0.020	0.977	0.167	0.002
		0.051	0.932	0.1113	0.0006	0.023	0.974	0.242	0.003
		0.066	0.918	0.1917	0.0011	0.030	0.967	0.376	0.005
		0.080	0.903	0.2413	0.0028	0.037	0.960	0.444	0.012
		0.086	0.897	0.2613	0.0036	0.040	0.957	0.469	0.015
		0.102	0.876	0.3000	0.0064	0.048	0.948	0.512	0.025
		0.115	0.853	0.3671	0.0154	0.055	0.939	0.570	0.055
		0.163	0.806	0.4457	0.0369	0.080	0.914	0.608	0.116
		0.247	0.701	0.5013	0.0720	0.131	0.858	0.601	0.199

Auxiliary Information

Method/Apparatus/Procedure:
The titration method was used to determine solubility curve. A binary ethanol–xylene mixture of known composition was prepared in a conical flask with silicone stopper to prevent evaporation. The mixture was placed in a thermostated vessel, agitated by a magnetic stirrer and titrated through a needle of the syringe with water until two phases were observed. The result was checked by another ternary mixture, of the same composition as above: (a) titrated with one of the pure components until the turbidity disappeared, (b) by reappearance of turbidity by lowering the temperature about 0.5 °C. The two-phase mixture was placed in a 50 mL glass-stoppered test tube at temperature of 25 °C, shaken vigorously, kept for nearly 2 h in a constant temperature water bath, and after separation each layer was pipetted for sampling. Refractive index and density of each phase were measured and composition was found from the calibration curves constructed during solubility measurements. When mixtures were not separated clearly after several hours, a centrifuge was used to obtain separation.

Source and Purity of Materials:
(1) Wako Pure Chemical Inst. Ltd., guaranteed reagent; $\rho(25\ °C)=785.32\ kg\ m^{-3}$, $n(25\ °C,D)=1.3600$; used as received.
(2) Kishida Chem. Ltd., guaranteed reagent; $\rho(25\ °C)=856.65\ kg\ m^{-3}$, $n(25\ °C,D)=1.4916$; used as received.
(3) ion exchanged, distilled.

Estimated Error:
temp. ±0.02 °C and ±0.1 °C (near plait point).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) *p*-Xylene (1,4-dimethylbenzene, 1,4-xylene); C_8H_{10}; [106-42-3]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

T. M. Letcher, P. M. Siswana, P. van der Watt, and S. Radloff, J. Chem. Thermodyn. **21**, 1053–60 (1989).

Variables:

$T/K=298$

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

$t/°C$ (compiler)	T/K	x_1	x_2	w_1 (compiler)	w_2 (compiler)
25.0	298.2	0.000	0.998	0.000	0.9997
		0.107	0.875	0.050	0.946
		0.196	0.763	0.099	0.892
		0.328	0.572	0.195	0.782
		0.418	0.424	0.287	0.671
		0.479	0.312	0.374	0.562
		0.516	0.224	0.455	0.455
		0.534	0.157	0.525	0.356
		0.528	0.098	0.587	0.251
		0.465	0.050	0.604	0.150
		0.410	0.023	0.599	0.077
		0.320	0.008	0.532	0.031
		0.241	0.003	0.443	0.013
		0.174	0.001	0.349	0.005
		0.065	0.000	0.151	0.000

Compositions of coexisting phases

		x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
$t/°C$ (compiler)	T/K	hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.415	0.433	0.598	0.252	0.282	0.678	0.430	0.491
		0.275	0.650	0.532	0.147	0.153	0.831	0.534	0.340
		0.168	0.795	0.514	0.074	0.083	0.909	0.608	0.202
		0.066	0.919	0.391	0.022	0.030	0.967	0.582	0.076
		0.031	0.960	0.292	0.007	0.014	0.985	0.501	0.028
		0.011	0.985	0.168	0.001	0.005	0.994	0.339	0.005

Auxiliary Information

Method/Apparatus/Procedure:

The titration method was used to determine binodal curve. A binary mixture of known composition was titrated with the third component until cloudiness was observed. Tie line compositions were related to the coexistence curve; water was determined by the Karl Fischer titration. The methods were described in Ref. 1.

Source and Purity of Materials:

(1) source not specified; used as received.
(2) source not specified; recrystallized three times.
(3) not specified.

Estimated Error:

comp. <0.005 mole fraction (estimated authors' precision on binodal curve), <0.01 mole fraction (estimated authors' precision of tie lines).

References:

[1] T. M. Letcher, S. Wootten, B. Shuttleworth, and C. Heyward, J. Chem. Thermodyn. **18**, 1037 (1986).

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) 2,4,4-Trimethyl-1-pentene (alpha-diisobutylene); C_8H_{16}; [107-39-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. 37, 1130–2 (1945).

Variables:
T/K=228–298

Compiled by:
A. Skrzecz

4.13. Ethanol + Water + 2,4,4-Trimethyl-1-pentene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
−45.0	228.2	0.6682	0.2471	0.5127	0.4619
		0.4515	0.5010	0.2671	0.7219
0.0	273.2	0.6242	0.2309	0.5021	0.4523
		0.4355	0.4832	0.2648	0.7158
25.0	298.2	0.5984	0.2213	0.4954	0.4463
		0.4258	0.4725	0.2634	0.7120

Comments and Additional Data

Water tolerance (S) was described with probable error <0.5% at the range −45–25 °C by the equation: $\log(S)=a-b/(T/K)$. The parameters (a, b) were determined from plots. Water tolerance was defined as: $S=H_2O$ % by volume·(100−Hydrocarbon % by volume in the blend)/100.

vol % hydrocarbon	a	b
75	1.400	340.3
50	1.842	355.4

Auxiliary Information

Method/Apparatus/Procedure:

A glass tube with stirrer containing the ternary mixture was immersed in a bath, the temperature of which could be varied. Mixtures were prepared directly in the tube, by special pipettes at 15.5 °C. Precautions to exclude moisture and to prevent evaporation were observed. No correction was made for the slight expansion in volume when alcohol was mixed with hydrocarbon. In the paper the experimental results were expressed as the water tolerance of the alcohol–hydrocarbon blend. For practical purposes water tolerance was defined as the volume percent of water which can be added before separation occurs.

Source and Purity of Materials:

(1) source not specified; anhydrous ethanol.
(2) source not specified.
(3) not specified.

Estimated Error:

temp. within about 0.3 °C (duplicate determinations), composition <0.2% relative of volume fraction.

Components:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) 1-Octene; C_8H_{16}; [111-66-0]
(3) Water; H_2O; [7732-18-5]

Original Measurements:
J. Nowakowska, C. B. Kretschmer, and R. Wiebe, J. Chem. Eng. Data Ser. **1**, 42–5 (1956).

Variables:
T/K=273–298

Compiled by:
A. Skrzecz

4.14. Ethanol + Water + 1-Octene

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)			
0.0	273.2	0.0329	0.0000	0.080	0.000
		0.0515	0.0000	0.122	0.000
		0.0712	0.0000	0.164	0.000
		0.1164	0.0000	0.252	0.000
		0.1702	0.0000	0.344	0.000
		0.1967	0.0000	0.385	0.000
		0.2288	0.0002	0.431	0.001
		0.2472	0.0002	0.456	0.001
		0.2900	0.0005	0.510	0.002
		0.3610	0.0015	0.588	0.006
		0.4352	0.0041	0.655	0.015
		0.4720	0.0057	0.684	0.020
		0.6121	0.0230	0.755	0.069
		0.6821	0.0504	0.750	0.135
		0.6972	0.0650	0.735	0.167
		0.7073	0.1311	0.649	0.293
		0.6514	0.2406	0.509	0.458
		0.5339	0.3958	0.350	0.632
		0.3476	0.6144	0.187	0.805
20.0	298.2	0.0329	0.0000	0.080	0.000
		0.0515	0.0000	0.122	0.000
		0.0712	0.0000	0.164	0.000
		0.1164	0.0000	0.252	0.000
		0.1477	0.0000	0.307	0.000
		0.1508	0.0002	0.312	0.001
		0.1989	0.0002	0.388	0.001
		0.2240	0.0004	0.424	0.002
		0.2841	0.0009	0.502	0.004
		0.3837	0.0036	0.607	0.014
		0.4195	0.0054	0.638	0.020
		0.4701	0.0089	0.676	0.031
		0.5395	0.0161	0.717	0.052
		0.5606	0.0210	0.723	0.066
		0.6038	0.0340	0.729	0.100
		0.6560	0.0609	0.717	0.162
		0.6726	0.1248	0.637	0.288
		0.6202	0.2307	0.500	0.453
		0.5205	0.3874	0.347	0.629
		0.3332	0.6148	0.180	0.809

Compositions of coexisting phases

t/°C	T/K (compiler)	x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
0.0	273.2	0.005	0.995	0.1396	0.0002	0.002	0.998	0.293	0.001
		0.012	0.988	0.2334	0.0004	0.005	0.995	0.437	0.002
		0.019	0.981	0.3717	0.0015	0.008	0.992	0.599	0.006
		0.043	0.957	0.4807	0.0063	0.018	0.982	0.690	0.022
		0.068	0.927	0.5884	0.0188	0.029	0.970	0.747	0.058
		0.131	0.857	0.6996	0.0697	0.059	0.939	0.729	0.177
20.0	298.2	0.000	1.000	0.0566	0.0000	0.000	1.000	0.133	0.000
		0.010	0.984	0.1309	0.0000	0.004	0.995	0.278	0.000
		0.017	0.977	0.2358	0.0000	0.007	0.992	0.441	0.000
		0.033	0.955	0.3320	0.0012	0.014	0.984	0.523	0.005
		0.062	0.920	0.4587	0.0083	0.027	0.970	0.676	0.029
		0.105	0.872	0.5361	0.0263	0.047	0.949	0.731	0.080
		0.139	0.833	0.6303	0.0456	0.064	0.931	0.726	0.128
		0.222	0.731	0.6734	0.0932	0.110	0.881	0.679	0.229

Auxiliary Information

Method/Apparatus/Procedure:

Points on the binodal curve were obtained by titrating a known mixture of two components by the third component until turbidity appeared or disappeared. The mixtures were prepared by volume with calibrated pipettes and the results converted to weight percent. Over most of the composition range alcohol–hydrocarbon mixtures were titrated with water. For 25 °C, the end point was taken when the the mixture remained homogenous at 25.0 °C, but become turbid at 24.8 °C. The titrations at 0 °C were performed in small conical flasks with magnetic stirrers placed in Dewar vessel. Tie lines were determined through measurements of refractive index at 25 °C of both phases in equilibrium and comparison with the values obtained on binodal curve. For saturated solutions containing more than 40% ethanol the tie lines were obtained by measuring densities at 25 °C in a similar procedure. The experimental procedures were adapted mainly from Ref. 1.

Source and Purity of Materials:

(1) source not specified, commercial absolute grade; used as received; $\rho(25\ °\mathrm{C}) = 785.97\ \mathrm{kg\ m^{-3}}$, water concentration 0.30 mass % (water was taken into account in calculations of composition).
(2) Philips, pure grade purity >99 mole %; used as received; $\rho(25\ °\mathrm{C}) = 710.78\ \mathrm{kg\ m^{-3}}$.
(3) distilled.

Estimated Error:

conc. <0.1% (relative error) for ethanol in the region near 100% of hydrocarbon (tie lines).

References:

[1] E. R. Washburn, V. Hnizda, and R. Vold, J. Am. Chem. Soc. **53**, 3237 (1931)

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) 2,2,4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1]
(3) Water (hydrogen oxide); H_2O; [7732-18-5]

Evaluated by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1996.05)

4.15. Ethanol + Water + 2,2,4-Trimethylpentane

Critical Evaluation:

A survey of reported in the literature compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system ethanol–2,2,4-trimethylpentane–water is given in Table 37.

TABLE 37. Summary of experimental data for the system ethanol–2,2,4-trimethylpentane–water

Author(s)	T/K	Type of data[a]	Ref.
Kretschmer and Wiebe, 1945	228–298	sat. (12)	1
Nowakowska *et al.*, 1956	273–298	sat. (50), eq. (14)	2
Huber *et al.*, 1972	298	eq. (6)	3

[a] Number of experimental points in parentheses.

Saturation curve

The system ethanol–2,2,4-trimethylpentane–water forms a miscibility gap of type 1. Experimental points on the saturation curve were reported by Kretschmer and Wiebe[1] and Nowakowska *et al.*[2] In both references the saturation curves were obtained by the titration method. In Ref. 1 the experimental results at 228, 273, and 298 K were expressed as the water tolerance of the alcohol–hydrocarbon mixture. The binary 2,2,4-trimethylpentane–water system is only partially miscible. The data for this system were compiled and critically evaluated in a previously published SDS volume,[4] the binary solubility data were not reported together with ternary data in any of the references. The "best" (Ref. 4) values of mutual solubility at 293 and 298 K are: $x_2''=3\cdot10^{-7}$, $x_2'=0.9995$ and $x_2''=3.5\cdot10^{-7}$, $x_2'=0.9994$, respectively. Compositions of coexisting phases in equilibrium at 273 and 298 K (Refs. 2 and 3) were included and also used for data comparison on saturation curves. All data sets are consistent with one another. The temperature relationship of miscibility gap, (Refs. 1 and 2) is as expected one. At higher temperatures smaller miscibility gaps are found. The water-rich phase with low concentrations of ethanol ($x_1<0.20$), Ref. 2, was reported to be 2,2,4-trimethylpentane free, presumably due to the analytical methods used. The maximum ethanol concentration is observed on the saturation curve. At 298.2 K it reaches $x_1=0.71\pm0.01$ when $x_2=0.10\pm0.02$ mole fraction. All experimental solubility and equilibrium data reported at 298.2 K were used for calculation of the saturation curve. (Water-rich and hydrocarbon-rich branches were treated together.) These data were described by the equation:

$$x_1=1.021\,78+0.104\,50\ln(x_2)-1.018\,38x_2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0243. This equation describes the saturation curve for $x_2<0.95$ mole fraction. The points on the saturation curve, calculated by the above equation together with the "best" values from Ref. 4 are presented in Table 38 for selected concentration of 2,2,4-trimethylpentane in the mixture and in Fig. 19 as calculated binodal curve (solid line).

TABLE 38. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	$3.5\cdot10^{-7}$ Ref. 4	0.4563	0.4800
0.2989	0.0010	0.4402	0.5000
0.5303	0.0100	0.4239	0.5200
0.5926	0.0200	0.4075	0.5400
0.6447	0.0400	0.3909	0.5600
0.6667	0.0600	0.3742	0.5800
0.6764	0.0800	0.3574	0.6000
0.6793	0.1000	0.3404	0.6200
0.6780	0.1200	0.3234	0.6400
0.6737	0.1400	0.3062	0.6600
0.6673	0.1600	0.2890	0.6800
0.6593	0.1800	0.2716	0.7000
0.6499	0.2000	0.2542	0.7200

0.6395	0.2200	0.2367	0.7400
0.6282	0.2400	0.2191	0.7600
0.6162	0.2600	0.2015	0.7800
0.6036	0.2800	0.1838	0.8000
0.5904	0.3000	0.1660	0.8200
0.5768	0.3200	0.1481	0.8400
0.5628	0.3400	0.1302	0.8600
0.5484	0.3600	0.1122	0.8800
0.5337	0.3800	0.0942	0.9000
0.5187	0.4000	0.0762	0.9200
0.5034	0.4200	0.0580	0.9400
0.4879	0.4400	0.0535	0.9500
0.4722	0.4600	0.0000	0.9994 Ref. 4

Phases in equilibrium

Compositions of coexisting phases in equilibrium for the ternary system ethanol–2,2,4-trimethylpentane–water were presented in Refs. 2 and 3 and the reported tie lines cover the whole range of the miscibility gap. They were obtained by various analytical methods: refractive indexes, Ref. 2, or by glc, Ref. 3. The direction of tie lines differ slightly. They may be treated as tentative. Experimental tie lines together with all experimental saturation points at 298.2 K are presented in Fig. 19.

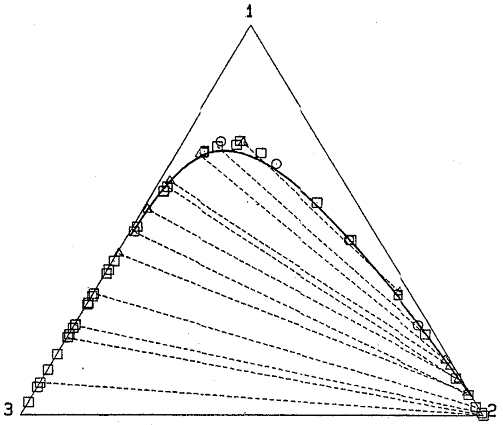

FIG. 19. Phase diagram of the system ethanol (1)—2,2,4-trimethylpentane (2)—water (3) at 298.2 K. Solid line—calculated saturation curve, ○—experimental data, Ref. 1, □—experimental data, Ref. 2, △—experimental data, Ref. 3, dashed lines—experimental tie lines, Refs. 2 and 3.

References:

[1] C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. **37**, 1130 (1945).

[2] J. Nowakowska, C. B. Kretschmer, and R. Wiebe, J. Chem. Eng. Data Ser. **1**, 42 (1956).

[3] J. F. K. Huber, C. A. M. Meijers, J. A. R. J. Hulsman, Anal. Chem. **44**, 111 (1972).

[4] D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) 2, 2, 4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

C. B. Kretschmer and R. Wiebe, Ind. Eng. Chem. **37**, 1130–2 (1945).

Variables:

T/K=228–298

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)		(compiler)	
−45.0	228.2	0.8028	0.0957	0.7434	0.2198
		0.7070	0.2529	0.5238	0.4646
		0.4737	0.5085	0.2720	0.7240
		0.2353	0.7578	0.1112	0.8876
0.0	273.2	0.7397	0.0882	0.7212	0.2132
		0.6709	0.2400	0.5157	0.4575
		0.4612	0.4950	0.2704	0.7196
		0.2329	0.7500	0.1110	0.8859
25.0	298.2	0.7032	0.0839	0.7072	0.2091
		0.6454	0.2309	0.5097	0.4521
		0.4517	0.4848	0.2691	0.7161
		0.2310	0.7438	0.1108	0.8845

Comments and Additional Data

Water tolerance (S) was described with probable error <0.5% at the range −45–25 °C by the equation: $\log(S)=a-b/(T/K)$. The parameters (a,b) were determined from plots. Water tolerance was defined as: $S=H_2O$ % by volume·(100-Hydrocarbon % by volume in the blend)/100

vol % hydrocarbon	a	b
90	1.383	553.5
75	1.894	554.5
50	2.151	504.4
25	2.001	352.5

Auxiliary Information

Method/Apparatus/Procedure:

A glass tube with stirrer containing the ternary mixture was immersed in a bath, the temperature of which could be varied. Mixtures were prepared directly in the tube, by special pipettes at 15.5 °C. Precautions to exclude moisture and to prevent evaporation were observed. No correction was made for the slight expansion in volume when alcohol was mixed with hydrocarbon. In the paper the experimental results were expressed as the water tolerance of the alcohol–hydrocarbon blend. For practical purposes water tolerance was defined as the volume per cent of water which can be added before separation occurs.

Source and Purity of Materials:

(1) source not specified; anhydrous ethanol.
(2) source not specified; b.p.=99.25 °C.
(3) not specified.

Estimated Error:

temp. within about 0.3 °C (duplicate determinations), composition <0.2% relative of volume fraction.

Components:	Original Measurements:
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) 2,2,4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1] (3) Water; H_2O; [7732-18-5]	J. Nowakowska, C. B. Kretschmer, and R. Wiebe, J. Chem. Eng. Data Ser. **1**, 42–5 (1956).
Variables: T/K=273–298	**Compiled by:** A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2 (compiler)	w_1	w_2
0.0	273.2	0.0515	0.0000	0.122	0.000
		0.1164	0.0000	0.252	0.000
		0.1733	0.0000	0.349	0.000
		0.1894	0.0000	0.374	0.000
		0.2216	0.0002	0.421	0.001
		0.2472	0.0002	0.456	0.001
		0.2746	0.0005	0.491	0.002
		0.2770	0.0005	0.494	0.002
		0.3539	0.0012	0.581	0.005
		0.3654	0.0012	0.593	0.005
		0.4196	0.0029	0.643	0.011
		0.4218	0.0029	0.645	0.011
		0.5320	0.0095	0.724	0.032
		0.5361	0.0095	0.727	0.032
		0.5697	0.0133	0.744	0.043
		0.5764	0.0137	0.748	0.044
		0.6289	0.0225	0.766	0.068
		0.6421	0.0227	0.774	0.068
		0.6587	0.0293	0.772	0.085
		0.7213	0.0642	0.748	0.165
		0.7335	0.1302	0.661	0.291
		0.7104	0.1871	0.585	0.382
		0.6727	0.2348	0.521	0.451
		0.6126	0.3147	0.431	0.549
		0.5030	0.4430	0.310	0.677
		0.3543	0.6166	0.187	0.807
20.0	298.2	0.0329	0.0000	0.080	0.000
		0.0712	0.0000	0.164	0.000
		0.1164	0.0000	0.252	0.000
		0.1556	0.0002	0.320	0.001
		0.2002	0.0002	0.390	0.001
		0.2066	0.0004	0.399	0.002
		0.2226	0.0004	0.422	0.002
		0.2833	0.0009	0.501	0.004
		0.2882	0.0009	0.507	0.004
		0.3045	0.0012	0.526	0.005
		0.3639	0.0025	0.589	0.010
		0.3742	0.0023	0.600	0.009
		0.3960	0.0036	0.619	0.014
		0.4848	0.0088	0.688	0.031
		0.5746	0.0205	0.733	0.065
		0.5760	0.0206	0.734	0.065
		0.6747	0.0598	0.728	0.160
		0.6780	0.0604	0.729	0.161
		0.7042	0.1246	0.652	0.286
		0.6942	0.1225	0.649	0.284
		0.6734	0.1841	0.568	0.385
		0.5460	0.3698	0.365	0.613
		0.4504	0.4892	0.267	0.719
		0.3095	0.6604	0.158	0.836

Compositions of coexisting phases

		x_1'	x_2'	x_1''	x_2''	w_1'	w_2'	w_1''	w_2''
t/°C	T/K (compiler)	hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
0.0	273.2	0.007	0.993	0.2331	0.0002	0.003	0.997	0.437	0.001
		0.022	0.978	0.3771	0.0018	0.009	0.991	0.604	0.007
		0.029	0.972	0.4737	0.0053	0.012	0.988	0.686	0.019
		0.057	0.937	0.5922	0.0152	0.024	0.975	0.756	0.048
		0.113	0.881	0.7044	0.0529	0.049	0.950	0.757	0.141
		0.150	0.839	0.7352	0.0760	0.067	0.931	0.737	0.189
		0.222	0.762	0.7274	0.1544	0.105	0.892	0.629	0.331
20.0	298.2	0.000	1.000	0.0825	0.0000	0.000	1.000	0.187	0.000
		0.000	1.000	0.1989	0.0002	0.000	1.000	0.388	0.001
		0.007	0.993	0.2310	0.0009	0.003	0.997	0.433	0.004
		0.022	0.972	0.3114	0.0012	0.009	0.990	0.534	0.005
		0.053	0.941	0.4729	0.0079	0.022	0.977	0.680	0.028
		0.095	0.893	0.5865	0.0228	0.041	0.957	0.737	0.071
		0.208	0.770	0.6903	0.0830	0.098	0.898	0.701	0.209

Auxiliary Information

Method/Apparatus/Procedure:

Points on the binodal curve were obtained by titrating a known mixture of two components by the third component until turbidity appeared or disappeared. The mixtures were prepared by volume with calibrated pipettes and the results converted to weight percent. Over most of the composition range alcohol–hydrocarbon mixtures were titrated with water. For 25 °C, the end point was taken when the the mixture remained homogenous at 25.0 °C, but become turbid at 24.8 °C. The titrations at 0 °C were performed in small conical flasks with magnetic stirrers placed in Dewar vessel. The lines were determined through measurements of refractive index at 25 °C of both phases in equilibrium and comparison with the values obtained on binodal curve. For saturated solutions containing more than 40% ethanol the tie lines were obtained by measuring densities at 25 °C in a similar procedure. The experimental procedures were adapted mainly from Ref. 1.

Source and Purity of Materials:

(1) source not specified, commercial absolute grade; used as received; $\rho(25\ °C)=785.97\ kgm^{-3}$, water concentration 0.30 mass % (water was taken into account in calculations of composition).

(2) source not specified, certified knock-rating grade; distilled to remove olefins, filtered by silica gel; $\rho(25\ °C)=687.74\ kg\ m^{-3}$.

(3) distilled.

Estimated Error:

conc.<0.1% (relative error) for ethanol in the region near 100% of hydrocarbon (tie lines).

References

[1]E. R. Washburn, V. Hnizda, and R. Vold, J. Am. Chem. Soc. **53**, 3237 (1931).

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) 2, 2, 4-Trimethylpentane (isooctane); C_8H_{18}; [540-84-1] (3) Water; H_2O; [7732-18-5]	J. F. K. Huber, C. A M. Meijers, and J. A. R. J. Hulsman, Anal. Chem. **44**, 111–6 (1972).
Variables: T/K=298	**Compiled by:** A. Skrzecz

Experimental Data

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x'	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase		water-rich phase		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)	
25.0	298.2	0.317	0.658	0.700	0.133	0.162	0.833	0.639	0.301
		0.142	0.847	0.671	0.051	0.063	0.935	0.740	0.140
		0.126	0.865	0.601	0.021	0.055	0.943	0.750	0.065
		0.093	0.900	0.529	0.009	0.040	0.959	0.723	0.030
		0.059	0.935	0.416	0.003	0.025	0.974	0.639	0.011
		0.037	0.961	0.296	0.002	0.015	0.984	0.514	0.009

Auxiliary Information

Method/Apparatus/Procedure:

Equilibrium was established in a thermostated vessel with a magnetic stirrer and the composition of each of the phases was determined analytically by glc. Data were obtained during measurements of partition coefficients for steroids in liquid-liquid systems.

Source and Purity of Materials:

(1) Merck Uvasole, spectroquality grade; used as received.
(2) Merck Uvasole, spectroquality grade; used as received.
(3) double distilled.

Estimated Error:

temp. ±0.1 °C.

Components:	**Original Measurements:**
(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5] (2) Octane (n-octane); C_8H_{18}; [111-65-9] (3) Water; H_2O; [7732-18-5]	A. I. Vorobeva and M. Kh. Karapetyants, Zh. Fiz. Khim. **40** 3018-23 (1966). [Eng. transl. Russ. J. Phys. Chem. **40**, 1619–22 (1966)].
Variables: T/K=298	**Compiled by:** A. Skrzecz

4.16. Ethanol + Water + Octane

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1	x_2	w_1	w_2
		(compiler)			
25	298.2	0.0000	0.9937	0.000	0.999
		0.3330	0.6374	0.173	0.821
		0.4845	0.4687	0.291	0.698
		0.6099	0.3172	0.428	0.552
		0.7023	0.2052	0.563	0.408
		0.7121	0.1830	0.590	0.376
		0.7449	0.1319	0.665	0.292
		0.7382	0.1196	0.677	0.272
		0.7339	0.0808	0.729	0.199
		0.7242	0.0670	0.745	0.171
		0.7240	0.0620	0.753	0.160
		0.6986	0.0452	0.767	0.123
		0.6756	0.0353	0.771	0.100
		0.5998	0.0173	0.757	0.054
		0.5169	0.0097	0.712	0.033
		0.4945	0.0068	0.700	0.024
		0.4521	0.0055	0.667	0.020
		0.2697	0.0009	0.484	0.004
		0.2191	0.0004	0.417	0.002
		0.1792	0.0002	0.358	0.001

Compositions of coexisting phases

t/°C	T/K (compiler)	x'_1	x'_2	x''_1	x''_2	w'_1	w'_2	w''_1	w''_2
		hydrocarbon-rich phase (compiler)		water-rich phase (compiler)		hydrocarbon-rich phase		water-rich phase	
25	298.2	0.000	1.000	0.472	0.006	0.000	1.000	0.684	0.020
		0.067	0.933	0.621	0.021	0.028	0.972	0.764	0.064
		0.106	0.888	0.680	0.037	0.046	0.953	0.770	0.105
		0.164	0.825	0.739	0.077	0.074	0.924	0.738	0.190
		0.351	0.624	0.714	0.186	0.184	0.811	0.588	0.380
		0.418	0.546	0.674	0.243	0.234	0.758	0.515	0.460
		0.493	0.461	0.622	0.306	0.298	0.691	0.442	0.538
		0.553	0.388	0.553	0.388	0.360	0.625	0.360	0.625

Auxiliary Information

Method/Apparatus/Procedure:

The titration method, Ref. 1, was used to determine solubility of the mixtures. The third component was added to the binary homogenous mixture until cloudiness was first observed. Density of the saturated mixtures was measured; these results were graphed. To obtain equilibrium, ternary mixtures were stirred in a thermostated vessel for several hours. After phase separation, the density of each phase was measured and composition was determined from the graphs prepared earlier. Concentration at the critical point was found by method described in Ref. 2. Water included in ethanol was taken into account in all measurements.

Source and Purity of Materials:

(1) source not specified, "rectificate grade;" distilled; water concentration was determined by the Karl Fischer method.
(2) source not specified; b.p. = 125.5 °C, $n(20\ °C, D) = 1.3976$.
(3) not specified.

Estimated Error:

solubility ±0.001 mass fraction.

References

[1] W. D. Bancroft, Phys. Rev. **3**, 21 (1896).
[2] E. N. Zilberman, Zh Fiz. Khim. **26**, 1458 (1952).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Mesitylene (1,3,5-trimethylbenzene); C_9H_{12}; [108-67-8]
(3) Water; H_2O; [7732-18-5]

Evaluated by:

A. Skrzecz, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland (1997.05)

4.17. Ethanol + Water + Mesitylene

Critical Evaluation:

A survey of reported compositions along the saturation curve (sat.) and compositions of coexisting phases in equilibrium (eq.) for the system ethanol–mesitylene–water is given in Table 39.

TABLE 39. Summary of experimental data for the system ethanol–mesitylene–water

Author(s)	T/K	Type of data[a]	Ref.
Bonner, 1909	273	sat. (10)	1
Letcher *et al.*, 1992	298	sat. (15), eq. (7)	2

[a] Number of experimental points in parentheses.

Saturation curve

The ternary system ethanol–mesitylene–water forms a miscibility gap of type 1. Data for the system were reported in two references and are evaluated on the basis of the original papers. Only one binary system mesitylene–water forms a miscibility gap. This system was compiled and critically evaluated in a previously published SDS volume.[3] The recommended value at 298 K is $x_2' = 7.4 \cdot 10^{-6}$; solubility of water in mesitylene was not reported. The miscibility gap reported by Bonner[1] at 273 K is larger than the one at 298 K, which is in agreement with general expectation. Experimental errors estimated by evaluator are ±0.0005 mole fraction for data reported in Ref. 1. The authors of Ref. 2 estimated their errors at 0.005 mole fraction for the binodal curve and 0.01 mole fraction for tie line compositions. Mutual solubility data for the misytylene–water system reported at 298.2 K together with the ternary data,[2] are $x_2' = 0.000$ and $x_2'' = 0.999$. They differ significantly from recommended values but are within the accuracy of experimental measurements. Data are consistent within each data set as well as between sets and are considered tentative. Data reported at 298.2 K by Letcher *et al.*[2] were described by the equation:

$$x_1 = 0.935\ 36 + 0.113\ 49\ \ln(x_2) - 0.889\ 03 x_2 - 0.049\ 05 x_2^2.$$

The parameters were calculated by the least-squares method and the standard error of estimate was 0.0082. Selected points on the saturation curve, calculated by the above equation together with the recommended value of Ref. 3 are presented in Table 40.

TABLE 40. Calculated compositions along the saturation curve at 298.2 K

x_1	x_2	x_1	x_2
0.0000	$7.4 \cdot 10^{-6}$ Ref. 3	0.3999	0.5000
0.1505	0.0010	0.3856	0.5200
0.4038	0.0100	0.3710	0.5400
0.4736	0.0200	0.3563	0.5600
0.5344	0.0400	0.3414	0.5800
0.5625	0.0600	0.3263	0.6000
0.5773	0.0800	0.3111	0.6200
0.5846	0.1000	0.2956	0.6400
0.5873	0.1200	0.2801	0.6600
0.5868	0.1400	0.2644	0.6800
0.5839	0.1600	0.2485	0.7000
0.5791	0.1800	0.2325	0.7200
0.5729	0.2000	0.2164	0.7400
0.5656	0.2200	0.2002	0.7600
0.5572	0.2400	0.1839	0.7800
0.5480	0.2600	0.1674	0.8000
0.5381	0.2800	0.1509	0.8200
0.5276	0.3000	0.1342	0.8400

0.5165	0.3200	0.1174	0.8600
0.5050	0.3400	0.1005	0.8800
0.4930	0.3600	0.0835	0.9000
0.4806	0.3800	0.0665	0.9200
0.4679	0.4000	0.0493	0.9400
0.4549	0.4200	0.0321	0.9600
0.4415	0.4400	0.0147	0.9800
0.4279	0.4600	0.0060	0.9900
0.4140	0.4800	0.0000	0.9990 Ref. 2

Phases in equilibrium

Equilibrium data for the ternary system ethanol–mesitylene–water were reported at 298.2 K only by Letcher *et al.*[2] They are consistent within the series. The plait point calculated by the authors (Ref. 2) was $x_1=0.50$, $x_2=0.35$, while the maximum concentration of ethanol on binodal curve was $x_1=0.60$. The plait point reported by Bonner at 273.2 K.[1] was $x_1=0.517$, $x_2=0.400$. The experimental data for phase equilibria are treated as tentative and are presented together with experimental points on saturation curve in Fig. 20.

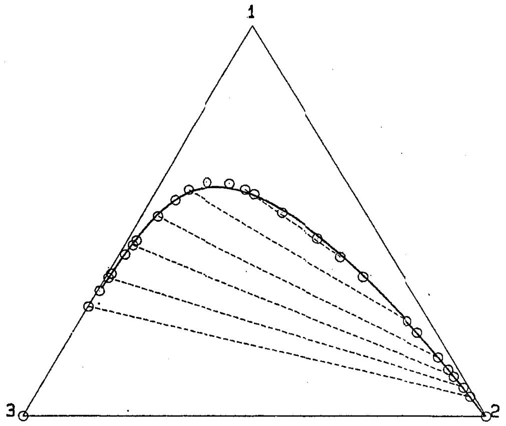

FIG. 20. Phase diagram of the system ethanol-mesitylene-water at 298.2 K Solid line—calculated saturation curve, ○—experimental data, Ref. 2.

References:

[1]W. D. Bonner, J. Phys. Chem. **14**, 738 (1909–1910).

[2]T. M. Letcher and P. M. Siswana, Fluid Phase Equilib, **74**, 203 (1992).

[3]D. G. Shaw, ed., *Solubility Data Series*, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C_8 to C_{36} (Pergamon, New York, 1989).

Components:

(1) Ethanol (ethyl alcohol); C_2H_6O; [64-17-5]
(2) Mesitylene (1,3,5-trimethylbenzene); C_9H_{12} ; [108-67-8]
(3) Water; H_2O; [7732-18-5]

Original Measurements:

W. D. Bonner, J. Phys. Chem. **14**, 738–89 (1909–1910)

Variables:

T/K=273

Compiled by:

A. Skrzecz

Experimental Data

Compositions along the saturation curve

t/°C	T/K (compiler)	x_1 (compiler)	x_2	w_1 (compiler)	w_2	
0.0	273.2	0.5170	0.4004	0.3243	0.6554	plait point
		0.5267	0.3767	0.3404	0.6352	
		0.6289	0.2236	0.4952	0.4594	
		0.6657	0.1448	0.5956	0.3381	
		0.6632	0.0879	0.6700	0.2317	
		0.6425	0.0595	0.7028	0.1697	
		0.5797	0.0238	0.7275	0.0779	
		0.5396	0.0165	0.7135	0.0570	
		0.5007	0.0091	0.6992	0.0331	
		0.3977	0.0048	0.6176	0.0195	

Auxiliary Information

Method/Apparatus/Procedure:

In a tube 1 cm diameter and 12 cm long known amount, by weight, of hydrocarbon and water were placed into a temperature controlled bath. The contents of the tube were stirred and alcohol was added gradually until a homogeneous solution was obtained. Observations were made visually through the telescope of a cathetometer. The samples were always weighed immediately before and after each experiment Concentrations were reported as weight of water in 1 g of binary water–hydrocarbon mixture and the weight of alcohol necessary to make a homogeneous solution. The mass of binary water–hydrocarbon mixture was about 1 g; the mass of alcohol—up to 5 g.

Source and Purity of Materials:

(1) Kahlbaum; presumably dried and distilled.
(2) Kahlbaum; presumably dried and distilled.
(3) not specified.

Estimated Error:

accuracy of weighing 0.0001 g.