Evaluation of Binary Excess Volume Data for the Methanol + Hydrocarbon Systems

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The volume change of mixing data for the methanol + hydrocarbon binary mixtures have been compiled and the best sets of data identified. The needs for new experimental data have been defined.

Key words: excess volume; hydrocarbons; methanol; volume change of mixing.

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1. Introduction

Previous papers[1,2] have evaluated the vapor-liquid equilibrium (VLE), heat of mixing (H^E) and volume

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change of mixing (V^E) data for two C_6 hydrocarbon + C_6 hydrocarbon binary systems. The objective was to identify the best data sets and to define the most pressing needs for new experimental data. The reports were designed to meet the needs of three types of users: experimentalists who need well-established test systems to check new experimental apparatuses; correlators who need thermodynamically consistent sets of VLE, H^E, and V^E data to test and support new correlations; and designers who need the best available data to design process equipment.

This report extends that work to include the excess volume data for the important alcohol + hydrocarbon systems. As in the preceding evaluation papers, an attempt is made to establish selected values of V^E at mole fractions of 0.25, 0.50, and 0.75. Hopefully, the availability of selected values at three mole fractions will reduce the practice of comparing data sets at only the midpoint.

Whenever possible, recommended data sets are identified. If no data set can be recommended, the best data sets are identified. Needed new experimental measurements are defined when appropriate.

The excess volume is the difference between the mixture molar volume and the pure component volumes,

$$V^E = V - x_1 V_1 - x_2 V_2 . \tag{1}$$

The procedures used to evaluate the worthiness of V^E data have been described and illustrated in detail in the first and last articles of a series of four back-to-back articles published previously.[1]

2. Compounds Covered

Because of the large number of alcohol + hydrocarbon data sets in the literature, it was necessary to restrict the first part of the alcohol + hydrocarbon project to the methanol systems. Hydrocarbons of all carbon numbers were covered in a comprehensive literature research, but data of interest (V^E, mixture volume or mixture density) were found only for hydrocarbons in the C_5 to C_7 range. No data sets of any kind were found for hydrocarbons with more than seven carbon atoms. Volumetric data both below and above the critical temperature of the hydrocarbon components do exist in the literature for the methanol + acetylene,[3] methanol + ethane,[4] and the methanol + butane[5] systems. Those data are not given in a form which permitted conversion to V^E values and therefore had to be excluded from the project.

3. Summary of Evaluation Results

The evaluation results for all of the useful methanol + hydrocarbon excess volume data sets found are summarized in Table 1. Each set of data is represented by a single line in the table. The literature reference numbers are the Master Reference List (MRL) numbers which were assigned to the individual documents when they were retrieved. Those numbers key the data set to the literature citations in Table 11. The data sets listed for each system are ordered with respect to temperature. In most cases, the data were measured at atmospheric pressure and a specific experimental pressure was not reported because of the insensitivity of such data to pressure. A pressure of 0.1013 MPa was assumed for those data sets.

Table 1. Summary list for excess volume data

LITERATURE REFERENCE	T, K	P, MPA	QUALITY RATING	SCATTER RATING	100 (EXP. VALUE - CURVE VALUE)		
					X(1)=0.25	X(1)=0.50	X(1)=0.75
METHANOL(1) + PENTANE(2)							
00027	298.150	0.1013	CDE	F	-	-	-
METHANOL(1) + BENZENE(2)							
04487	279.150	0.1013	DE	M	-	-	-
23401	283.150	0.1013	DE	M	-	-	-
03227	293.150	0.1013	N	N	-	-	-
04998	293.150	0.1013	E	U	-	-	-
05250	293.150	0.1013	E	U	-	-	-
07610	293.150	0.1013	DE	M	-	-	-
18543	293.150	0.1013	DE	M	-	-	-
21323	293.150	0.1013	B	G	0.00	0.00	-0.14
23401	293.150	0.1013	D	M	-0.49	0.20	0.72
00687	296.150	0.1013	C	F	0.28	0.30	0.19
05014	298.150	0.1013	E	U	-	-	-
09589	298.150	0.1013	E	U	-	-	-
13489	298.150	0.1013	N	N	-	-	-
18139	298.150	0.1013	B	G	-0.06	0.00	0.00
41405	298.150	0.1013	B	E	0.21	0.39	0.14
04487	303.150	0.1013	DE	M	-	-	-
05250	303.150	0.1013	E	U	-	-	-
23401	303.150	0.1013	E	F	-1.13	-0.50	-0.40
05250	313.150	0.1013	E	U	-	-	-
23401	313.150	0.1013	DE	M	-	-	-
41405	313.150	0.1013	B	G	0.00	0.00	0.00
23401	323.150	0.1013	E	F	-1.22	-0.55	-0.53
METHANOL(1) + CYCLOHEXANE(2)							
04487	279.150	0.1013	BCD	G	-	-	-
03227	293.150	0.1013	N	N	-	-	-
04886	298.150	0.1013	DE	M	-	-	-
04886	298.150	0.1013	DE	M	-	-	-
04487	303.150	0.1013	ABC	E	-	-	-
04886	308.150	0.1013	CDE	F	-	-	-
04886	319.150	0.1013	CDE	F	-	-	-
04886	323.150	0.1013	CDE	F	-	-	-
METHANOL(1) + HEXANE(2)							
23528	293.150	0.1013	N	N	-	-	-
METHANOL(1) + TOLUENE(2)							
13016	252.050	0.1013	CDE	F	-	-	-
13016	273.150	0.1013	CDE	F	-	-	-
01398	293.150	0.1013	ABC	E	-	-	-
05250	293.150	0.1013	E	U	-	-	-
06408	293.150	0.1013	E	U	-	-	-
05077	298.150	0.1013	E	U	-	-	-
06408	298.150	0.1013	E	U	-	-	-
08717	298.150	0.1013	CDE	F	-	-	-
13016	298.150	0.1013	DE	M	-	-	-
05250	303.150	0.1013	DE	M	-	-	-
08717	308.150	0.1013	CDE	F	-	-	-
06408	310.950	0.1013	DE	M	-	-	-
05250	313.150	0.1013	DE	M	-	-	-
13016	322.850	0.1013	DE	M	-	-	-
06408	323.200	0.1013	E	U	-	-	-
06408	333.260	0.1013	E	U	-	-	-
METHANOL(1) + HEPTANE(2)							
20122	291.150	0.1013	E	U	-	-	-
03227	293.150	0.1013	N	N	-	-	-
13550	298.150	0.1013	N	N	-	-	-
40893	298.150	0.1013	ABC	E	-	-	-

Previous papers[1] have described the evaluation methods and the significance of the reported results. The five possible quality ratings range from A for excellent data to E for very bad data. An N means the data were not sufficient to support any evaluation test and therefore no quality rating could be assigned. A multiple-letter quality rating is assigned in those cases where the evaluation tests which could be performed eliminated some quality ratings but did not distinguish between the remaining ones. For example, a data set with an F (fair) scatter rating cannot have a quality rating of A or B. In the absence of the comparison test to further characterize the data set, a CDE quality rating is assigned. In any event, the quality rating assigned to a set of data represents a summary of the individual test results.

Only two kinds of tests are applied to V^E data. The first is a scatter rating which not only reflects scatter in the experimental data points but also reflects how well the shapes of the experimental data plots agree with the characteristic shape for the particular system. Seven scatter ratings are used: E = excellent, G = good, F = fair, M = marginal, U = unacceptable, S = smoothed, and N = none.

The second test is a comparison of the data set values to the "best" V^E vs T curves at three mole fractions: $x_1 = 0.25$, 0.50, and 0.75. Usually, the deviation of an experimental data set point from the best curve drawn by the evaluator through all the data sets' points is expressed as a percentage. (The procedure for locating the best curve has been described in the V^E paper in Ref. 1.) For the methanol + hydrocarbon systems, that approach was not feasible because some of the systems have S-shaped V^E curves and some of the V^E values involved in the calculation are close to zero. Hence, the deviation values in Table 1 are exposed as

$$100(\text{experimental value} - \text{best curve value}) .$$

Those deviation values show how far the individual data set points deviate from the best curves established by the evaluator. The test compares data sets at the same temperature and also at different temperatures.

The use of a V^E data set as a test system for a new experimental apparatus should be restricted to data sets with an A rating. A well-established test system requires multiple A-rated data sets at the given temperature.

The use of V^E data sets for correlation purposes usually should be restricted to those with a quality rating of A or B. In some cases one of the better C sets can be used when no A or B sets are available.

4. Selected Point Values

Before the three best V^E vs T curves can be drawn at mole fractions of 0.25, 0.50, and 0.75, it is necessary to select the best point values at each temperature where multiple data sets exist. Often there will be enough good data sets at a given temperature—e.g., 298.15 K[1]—to select a very firm value which positions the best curve accurately at that temperature. Unfortunately, that is not the case at any temperature for any of the methanol + hydrocarbon systems.

It was possible to establish V^E vs T curves only for the methanol + benzene system—but without any firmly established "anchor" points. The methanol + pentane and the methanol + hexane systems have only one set of data each. All of the data sets for the methanol + cyclohexane system except two are below the upper critical solution temperature of 45.87 °C (319.02 K),[6] and their regions of partial miscibility all include the $x_1 = 0.25$, 0.50, and 0.75 points. The methanol + toluene system is miscible over the 252.05–333.26 K range for which data are available, but the points obtained from the one set with an E scatter rating and the four sets with an F scatter rating were too scattered to permit the location of meaningful V^E vs T curves. As indicated by the reported V^E data, the methanol + heptane system is partially miscible over the 291.50–298.15 K range covered by the available four data sets, and three of those four data sets report data on only one side or the other of the region of partial miscibility, which includes the $x_1 = 0.25$, 0.50, and 0.75 points at all the data set temperatures.

There was no justification for anything but linear V^E vs T curves for the methanol + benzene system. As shown in Table 1, V^E values at 0.25, 0.50, and 0.75 mole fraction could be determined with some degree of certainty only for eight data sets. The three sets with G scatter ratings were used to locate the straight lines: the Ocon, Tojo, and Espada (MRL 21323) set at 293.15 K; the Wood, Langer, and Battino (MRL 18139) set at 298.15 K; and the Cibulka, Hynek, Holub, and Pick (MRL 41405) set at 313.50 K. At $x_1 = 0.25$, the Wood *et al.* set at 298.15 fell slightly below the straight line. At $x_1 = 0.75$, the Ocon *et al.* set at 293.15 K also fell below the line drawn.

Table 2. Best curve V^E values for the methanol(1) + benzene(2) system

t, °C	T, K	Values from best curves x_1=0.25	x_1=0.50	x_1=0.75
20	293.15	0.0171	−0.0095	−0.0242
23	296.15	0.0215	−0.0051	−0.0219
25	298.15	0.0244	−0.0022	−0.0204
30	303.15	0.0318	0.0050	−0.0166
40	313.15	0.0465	0.0195	−0.0089
50	323.15	0.0612	0.0340	−0.0012

Table 2 lists the V^E values read from the best curves at the three mole fractions. Because of the lack of multiple reliable data sets, at the various temperatures, those values are not firmly established as were the values for the benzene + cyclohexane system.[1] Nevertheless, the values indicate to the experimentalist what the V^E values appear to be at each temperature-mole fraction combination, based on the existing information in the literature. Those values will undoubtedly change to some degree as additional good data are reported.

5. Best Data Sets

Multiple data sets are available for only four methanol + hydrocarbon systems: methanol + benzene (22 sets), methanol + cyclohexane (eight sets), methanol + toluene (16 sets), and methanol + heptane (four sets).

Inspection of all the benzene + methanol data sets indicated that the V^E and V^E/x_1x_2 curves should have the shapes best illustrated by the Cibulka *et al.* data set (MRL 41405) at 298.15 K in Figs. 1 and 2. The three data sets used to establish the best V^E vs T curves are shown in Tables 3–5 and Figs. 3–5. The change in V^E with temperature was small and obscured by scatter in the data. However, it appears that the V^E curve is moving slowly toward positive deviation at all mole fractions. The maximum V^E value appears to increase, and the negative V^E value at the minimum appears to decrease slightly in absolute value, as the temperature increases from 293.15 to 313.15 K. The mole fractions at which the maximum and minimum V^E values occur appear to move slightly to the right (higher x_1 values) as temperature increases. Comparison of the V^E/x_1x_2 curves for the two Cibulka *et al.* data sets at 298.15 and 313.15 (MRL 41405) also indicates that V^E is moving toward larger positive values as temperature increases.

The methanol + cyclohexane system is partially misci-

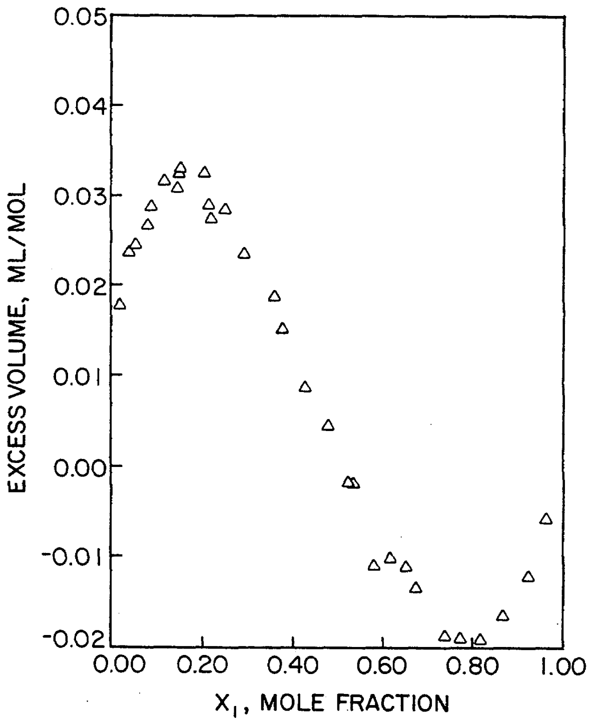

FIG. 1. Typical shape of the V^E vs x_1 curve for the methanol(1) + benzene(2) system at 298.15 K, MRL 41405.

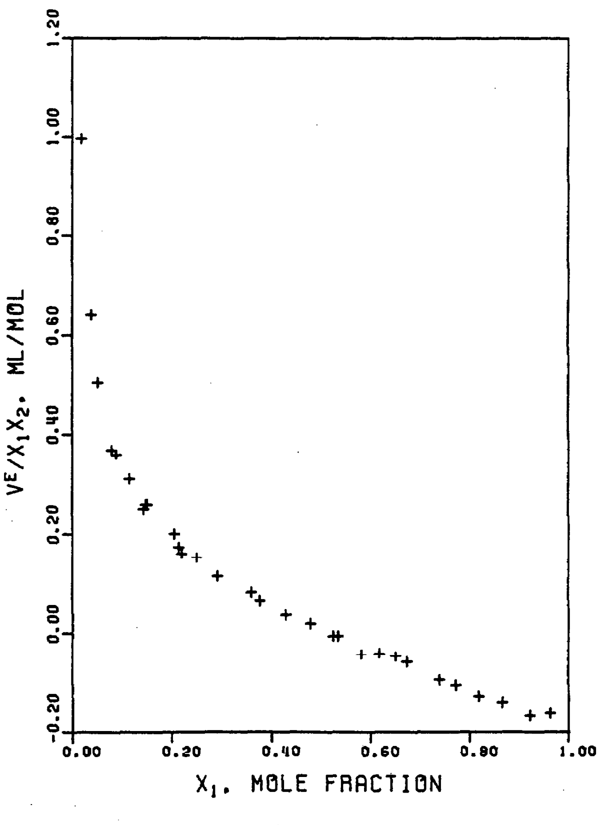

FIG. 2. Typical shape of the V^E/x_1x_2 vs x_1 curve for the methanol (1) + benzene(2) system at 298.15 K, MRL 41405.

Table 3. Best data set at 293.15 K for methanol(1) + benzene(2)

SYSTEM. Methanol(1) + Benzene(2)

TEMPERATURE. 293.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 40.468 2 = 88.878

QUALITY RATING. B SCATTER. Good

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. 0.00 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. 0.00 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -0.14 %

REFERENCE. Ocon, J., Tojo, G., Espada, L., Anales de Quimica, 65, 735 (1969). (MRL 21323)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0478	0.0082	0.5511	-0.0138
0.0921	0.0110	0.6030	-0.0211
0.1322	0.0150	0.6469	-0.0228
0.1770	0.0156	0.6934	-0.0251
0.2106	0.0175	0.7583	-0.0256
0.2498	0.0151	0.7928	-0.0245
0.2997	0.0131	0.8537	-0.0190
0.3325	0.0138	0.8944	-0.0169
0.3885	0.0084	0.9361	-0.0120
0.4462	0.0014	0.9852	-0.0066
0.5045	-0.0095		

ble below 319.02 K, based on the solubility data reported by Campbell and Kartzmark,[6] and Campbell and Anand.[7] Those and other papers by Campbell and co-workers, plus one listed in Table 11 by Campbell and Anand (MRL 4886), report extensive studies of the properties of the methanol + cyclohexane system. The latter paper reports five sets of V^E data (actually mixture density data), three below the critical solution temperature and two above. No other source reports data above the critical solution temperature. However, the four points reported by Stavely and Spice (MRL 3227) below 0.05 methanol mole fraction, and the

Table 4. Best data set at 298.15 K for methanol(1) + benzene(2)

SYSTEM. Methanol(1) + Benzene(2)

TEMPERATURE. 298.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 40.735 2 = 89.405

QUALITY RATING. B SCATTER. Good

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -0.06 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. 0.00 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. 0.00 %

REFERENCE. Wood, S. E., Langer, S., Battino, R., Journal of Chemical Physics, 32, 1389 (1960), (MRL 18139)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.1299	0.0283	0.6170	-0.0146
0.1346	0.0285	0.6214	-0.0145
0.2540	0.0227	0.7460	-0.0202
0.2623	0.0221	0.7489	-0.0200
0.3678	0.0134	0.7498	-0.0197
0.3689	0.0128	0.8746	-0.0162
0.4928	-0.0014	0.8775	-0.0156
0.4984	-0.0019		

Table 5. Best data set at 313.15 K for methanol(1) + benzene(2)

SYSTEM. Methanol(1) + Benzene(2)

TEMPERATURE. 313.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 41.489 2 = 91.083

QUALITY RATING. B SCATTER. Good

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. 0.00 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. 0.00 %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. 0.00 %

REFERENCE. Cibulka, I., Hynek, V., Holub, R., Pick, J., Collection of Czechoslovak Chemical Communications, 44(2), 295 (1979). (MRL 41405)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0555	0.0384	0.5205	0.0135
0.0762	0.0392	0.6150	0.0006
0.1522	0.0462	0.6863	-0.0097
0.2325	0.0475	0.7616	-0.0111
0.2876	0.0398	0.8255	-0.0174
0.3625	0.0482	0.9185	-0.0107
0.4142	0.0337	0.9641	-0.0067
0.4740	0.0232		

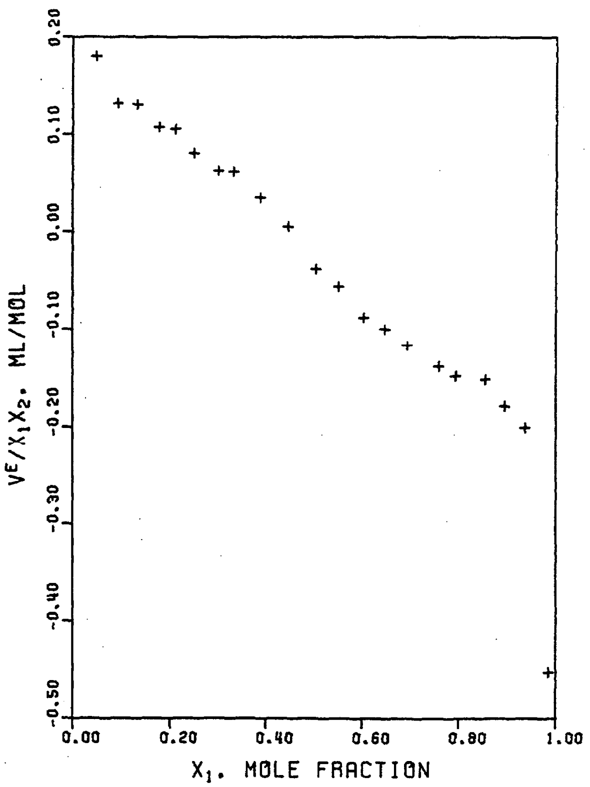

FIG. 3. Best data set at 293.15 K for methanol(1) + benzene(2). Data of Ocon *et al.*, MRL 21323.

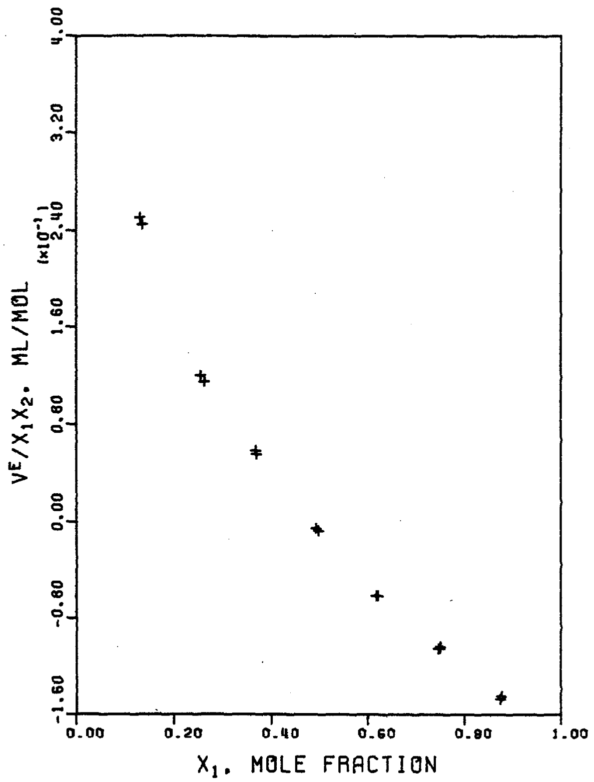

FIG. 4. Best data set at 298.15 K for methanol(1) + benzene(2). Data of Wood *et al.*, MRL 18139.

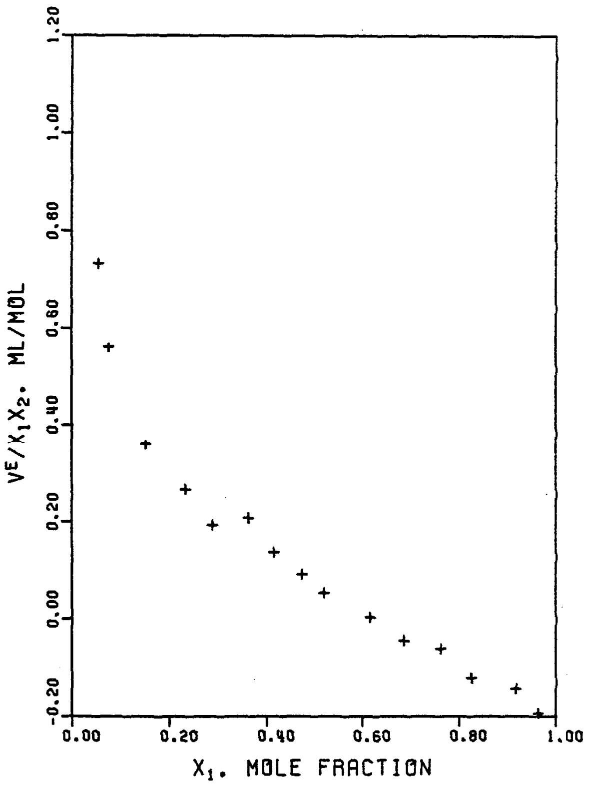

FIG. 5. Best data set at 313.15 K for methanol(1) + benzene(2). Data of Cibulka *et al.*, MRL 41405.

Table 6. Only data set at 319.15 K for methanol(1) + cyclohexane(2)

SYSTEM. Methanol(1) + Cyclohexane(2)

TEMPERATURE. 319.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 41.818 2 = 111.639

QUALITY RATING. CDE SCATTER. Fair

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -- %

REFERENCE. Campbell, A. N., Anand, S. C., Canadian Journal of Chemistry, 50, 1109 (1972). (MRL 4886)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0992	0.0910	0.6012	0.4580
0.2012	0.1960	0.6967	0.4410
0.2784	0.2410	0.7514	0.4010
0.3232	0.2930	0.8021	0.3580
0.4001	0.3510	0.8540	0.2740
0.4996	0.4160	0.9008	0.1910
0.5520	0.4320	0.9784	0.0520

two data sets reported by Harms (MRL 4487) at 279.15 and 303.15 K probably define the sides of the V^E curve better than do the Campbell and Anand sets below the critical solution temperature. Tables 6 and 7, and Figs. 6 and 7 show the two Campbell and Anand sets above the upper critical solution temperature.

The methanol + toluene system is miscible over the 252.05–333.26 K temperature range for which data are available. The Ocon *et al.* data set at 293.15 K (MRL 1398) shown in Table 8 and in Figs. 8 and 9 indicates that the V^E vs x_1 curve is S-shaped with a maximum at about 0.08 mole fraction methanol and a minimum at about 0.69. Unfortunately, none of the other data sets report V^E values below $x_1 = 0.10$ (only two of the other sets report values below

Table 7. Only data set at 323.15 K for methanol(1) + cyclohexane(2)

SYSTEM. Methanol(1) + Cyclohexane(2)

TEMPERATURE. 323.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 42.028 2 = 112.212

QUALITY RATING. CDE SCATTER. Fair

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -- %

REFERENCE. Campbell, A. N., Anand, S. C., Canadian Journal of Chemistry, 50, 1109 (1972). (MRL 4886)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0531	0.0550	0.6920	0.4050
0.1882	0.1870	0.7544	0.3580
0.3219	0.3090	0.8452	0.2900
0.4484	0.3890	0.9087	0.1780
0.5579	0.4280	0.9706	0.0580

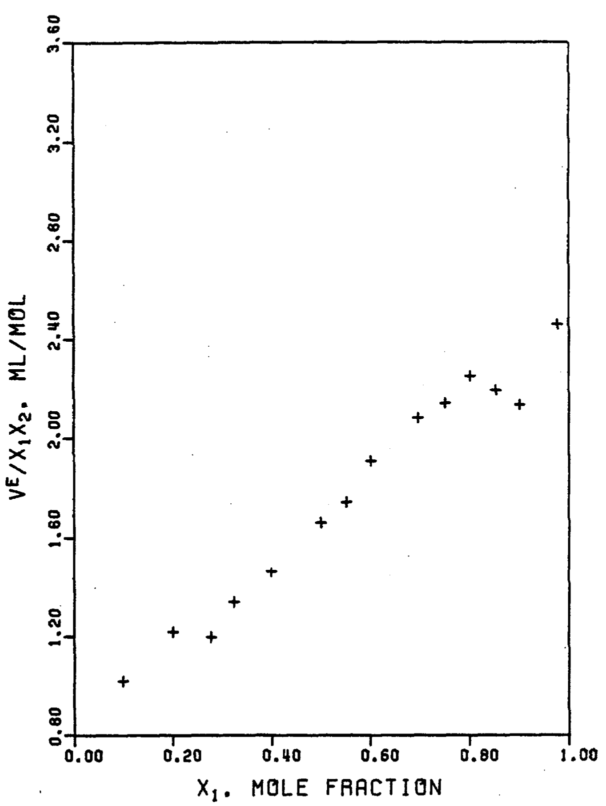

FIG. 6. Data of Campbell and Anand for the methanol(1) + cyclohexane(2) system at 319.15 K, MRL 4886.

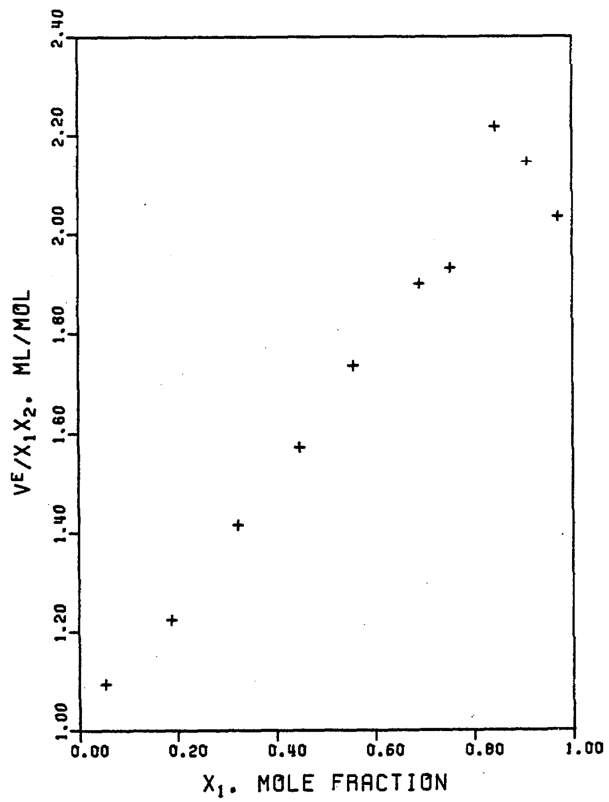

FIG. 7. Data of Campbell and Anand for the methanol(1) + cyclohexane(2) system at 323.15 K, MRL 4886.

Table 8. Only complete data set for the methanol(1) + toluene(2) system

SYSTEM. Methanol(1) + Toluene(2)

TEMPERATURE. 293.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 40.468 2 = 106.306

QUALITY RATING. ABC SCATTER. Excellent

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -- %

REFERENCE. Ocon, J., Tojo, G., Espada, L., Anales de Quimica, 65, 641 (1969). (MRL 1398)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0492	0.0072	0.6010	-0.0707
0.0945	0.0074	0.6415	-0.0763
0.1344	0.0049	0.6830	-0.0761
0.2052	-0.0101	0.7222	-0.0775
0.2429	-0.0174	0.7952	-0.0719
0.2910	-0.0242	0.8492	-0.0652
0.3640	-0.0377	0.9252	-0.0455
0.4388	-0.0526	0.9547	-0.0312
0.4913	-0.0582	0.9834	-0.0117
0.5512	-0.0664		

0.20) and hence the maximum indicated by the Ocon *et al.* data set (MRL 1398) is not confirmed by any other source. Those other data sets where the minimum point could be located with any certainty showed a minimum point in the $x_1 = 0.58–0.78$ range. The six data sets of a Mason and Washburn (MRL 8717) and Mason and Paxton (MRL 13016) indicate that the absolute value of the minimum V^E

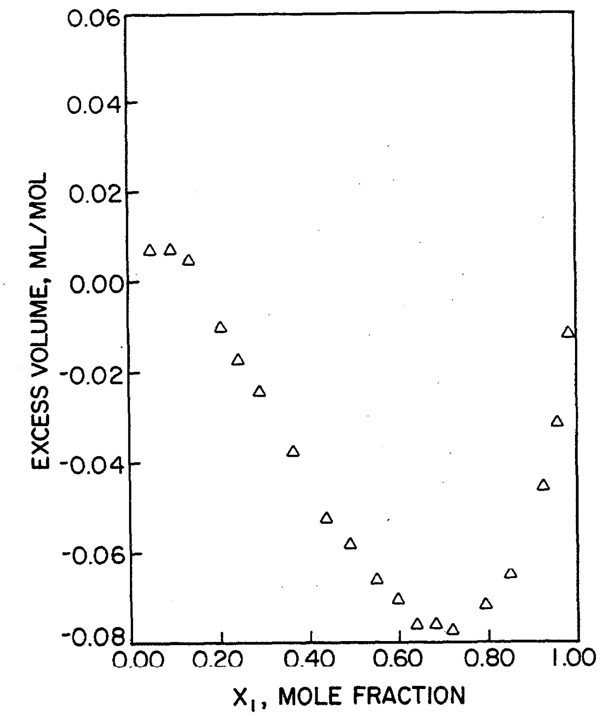

FIG. 8. V^E values from Ocon *et al.* for the methanol(1) + toluene(2) system at 293.15 K, MRL 1398.

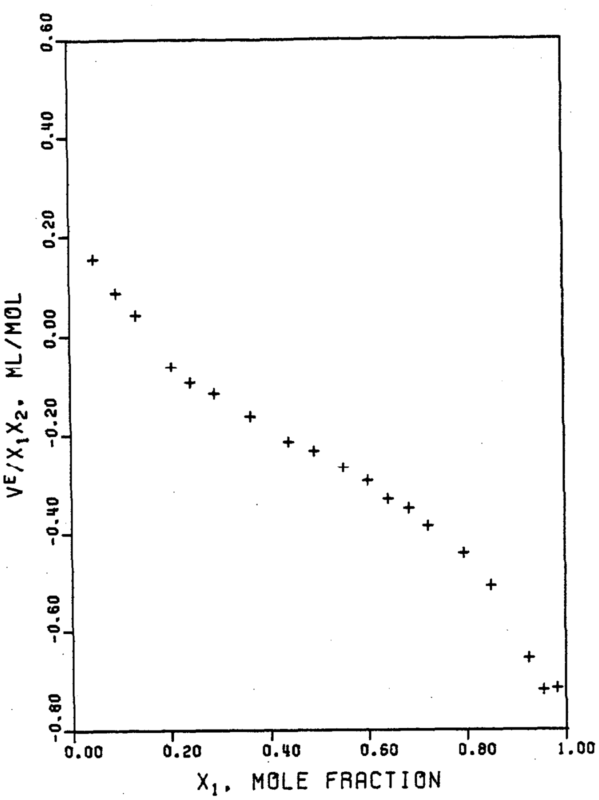

FIG. 9. V^E/x_1x_2 plot of the data in Fig. 8.

Table 9. Only complete data set for the methanol(1) + heptane(2) system

SYSTEM. Methanol(1) + Heptane(2)

TEMPERATURE. 298.15 K PRESSURE. 0.1013 MPa

MOLAR VOLUMES (ml/mol). 1 = 40.729 2 = 147.446

QUALITY RATING. ABC SCATTER. Excellent

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.25. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.50. -- %

DEVIATION FROM VE VS. T CURVE AT x(1) = 0.75. -- %

REFERENCE. Treszczanowicz, A. J., Benson, G. C., Journal of Chemical Thermodynamics, 9(12), 1189 (1977). (MRL 40893)

x(1) mole fraction	EXCESS VOLUME ml/mol	x(1) mole fraction	EXCESS VOLUME ml/mol
0.0098	0.0592	0.8396	0.3742
0.0216	0.0993	0.8600	0.3747
0.0324	0.1292	0.8810	0.3753
0.0498	0.1706	0.8884	0.3754
0.0682	0.2094	0.8930	0.3755
0.0890	0.2461	0.8942	0.3746
0.1133	0.2842	0.8977	0.3675
0.1371	0.3178	0.9029	0.3561
0.1687	0.3545	0.9248	0.3011
0.2506	0.3604	0.9487	0.2255
0.3021	0.3617	0.9625	0.1736
0.4691	0.3662	0.9742	0.1249
0.5713	0.3682	0.9827	0.0862
0.6417	0.3698	0.9886	0.0576
0.6934	0.3708	0.9931	0.0351
0.7325	0.3717	0.9966	0.0173
0.8207	0.3738		

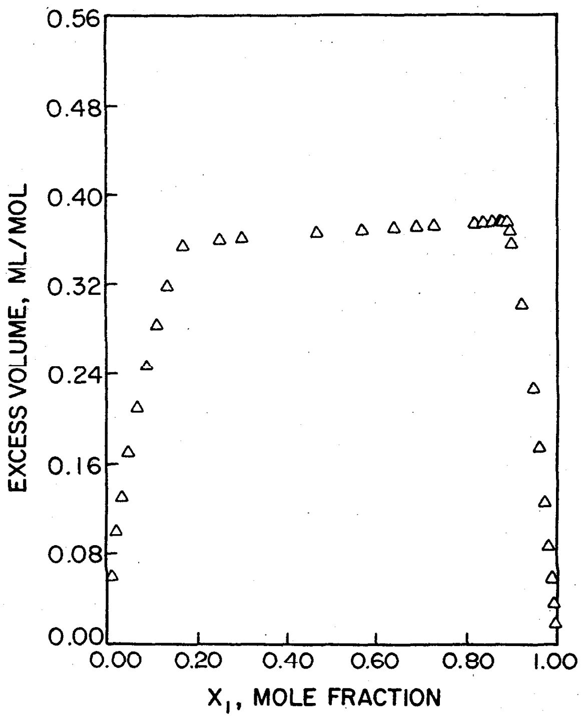

FIG. 10. V^E values from Treszczanowicz and Benson for methanol (1) + heptane(2) at 298.15 K, MRL 40893.

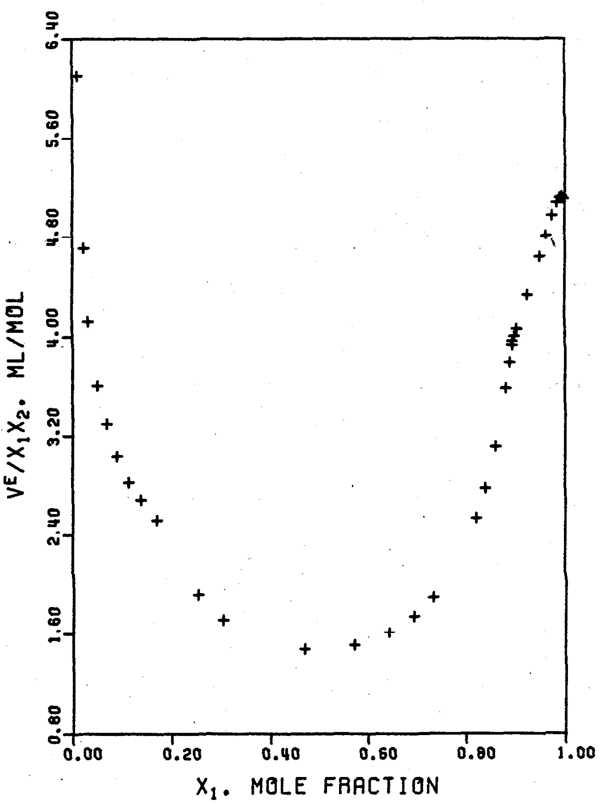

FIG. 11. V^E/x_1x_2 plot of the data in Fig. 10.

point decreases slowly as temperature increases, which implies that the system is moving toward positive deviation at all mole fractions. The data are too scattered to indicate which way the mole fraction of the minimum point changes with temperature.

The four sets of data listed in Table 1 for the methanol + heptane binary are all in the partially miscible temperature range. Only the set by Treszczanowicz and Benson (MRL 40893) is complete; the other three sources report only a few points on one side or the other of the two-phase region. Hence, the system is represented only by the Treszczanowicz and Benson data shown in Table 9 and Figs. 10 and 11.

6. Experimental Measurements Needed

Obviously, good experimental measurements are needed for any methanol + hydrocarbon binary system. However, insofar as experimentalists are concerned, new efforts should concentrate first on the methanol + benzene system. Dependable data are needed at 293.15, 298.15, and 313.15 K to firmly establish the best V^E vs T curve in that region but first, it would be wise to concentrate on 298.15 K until the behavior at that temperature is firmly established. That would provide a test system with an S-shaped V^E vs x_1 curve.

Correlators need firmly established V^E data for methanol plus each of at least three hydrocarbon types: aromatic, cycloalkane, and alkane. Also they need data for each system over as wide a temperature range as possible.

Miscibility gaps affect the choices of compounds and temperatures for the new cycloalkane and alkane data. The critical solution temperature is 45.87 °C (319.02 K)[6] for the methanol + cyclohexane system. The data of Campbell and Anand (MRL 4886) at 50 °C should be checked by duplicate measurements, and then new data should be accumulated at spaced temperatures up to the temperature limit of the apparatus being used.

The methanol + pentane system is miscible at 298.15 K (Tenn and Missen, MRL 27). Joerges *et al.* (MRL 23528) report a wide miscibility gap at 20 °C for the methanol + hexane system. Figure 10 shows the miscibility gap at 298.15 K for methanol + heptane. Systems with miscibility gaps must of course be handled by a general correlation of mixture properties but first a new correlation formalism should be tested on miscible systems. Hence, new experimental work should concentrate first on the methanol + pentane system, and then move to the partially miscible and miscible temperature ranges for methanol + hexane and heptane. Hexane complements benzene and cyclohexane better than does heptane for the initial tests of a new correlation formalism.

7. Pure Compound Densities

Pure Compound volume values are needed to calculate V^E values from

$$V^E = V - x_1V_1 - x_2V_2, \qquad (1)$$

when mixture density or volume values are reported. The author's pure compound values are always used if they are

Table 10. Pure compound density data

	Methanol	Heptane	Toluene
	183 to 341 K 52 points RMSD = 0.00036	183 to 384 K 123 points RMSD = 0.00023	179 to 400 K 253 points RMSD = 0.00033
A	0.10709171D+01	0.92942894D+00	0.11439199D+01
B	0.95429528D-03	0.75804070D-03	0.87978248D-03
C	0.49999952D-02	0.59999990D+01	0.60034208D+01
D	0.35699976D+03	0.54864941D+03	0.60689600D+03

given. If not, pure compound density values are obtained from an evaluated data file. The general procedures used to select and correlate the pure compound saturated liquid density data have been described in preceding papers.[1]

The pure compound volume values used for each set of data appear in the tabulation for the set (for examples, see Tables 3–9). When obtained from the evaluated data file, those values were calculated from a Francis equation,

$$\text{Density, g/ml} = A - BT - C/(E - T) \qquad (2)$$

correlation using constants such as those listed in Table 10. The Francis equation constants for benzene, cyclohexane, and hexane have been listed in previous papers.[1,2] The molar volume used for pentane for the single data set for methanol + pentane appears on the tabulation for that system. Table 10 presents the Francis equation constants for methanol, heptane, and toluene. The numbers of literature documents reporting liquid density or volume data for methanol, heptane, and toluene were 116, 50, and 111, respectively. The numbers of documents from which one or more data points were selected for fitting were 18, 46, and 78, respectively.

8. Data Set Tabulations

Only the best data for the various binary systems are tabulated in this paper. Copies of the tables and plots for the other data sets can be obtained from Professor Buford D. Smith, Box 1198, Washington University, St. Louis, Missouri 63130.

9. Bibliography

Table 11 is the bibliography for the excess volume data for the methanol + hydrocarbon systems covered by this evaluation project. As explained above, the literature data for the methanol + acetylane,[3] methanol + ethane,[4] and the methanol + butane[5] systems could not be evaluated as V^E data.

The identifying numbers in Table 11 are the Laboratory's Master Reference List (MRL) numbers. The MRL numbers relate the literature documents listed in Table 11 to the individual data sets listed in Table 1.

Sometimes documents report data in a form which does not permit transcription and evaluation. In most such cases, the data are presented only in graphical form. Even though their data sets do not appear in Table 1, such documents are listed in Table 11 to provide complete coverage of all the literature data.

TABLE 11. Bibliography for excess volume.

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10. Nomenclature

MRL	Acronym for Master Reference List.
RMSD	Acronym for root-mean-squared deviation.
V	Liquid molar volume of mixture.
V_i	Liquid molar volume of component i.
V^E	Excess volume. Defined by Eq. (1).
x_i	Liquid mole fraction of component i.

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