

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

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,

$$V^E = V - x_1V_1 - x_2V_2. \quad (1)$$

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 + butane⁵ 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 insensi-

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	H	-	-	-
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	N	-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	H	-	-	-
04886	298.150	0.1013	DE	H	-	-	-
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	-	-	-

tivity of such data to pressure. A pressure of 0.1013 MPa was assumed for those data sets.

Previous papers¹ 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 K¹—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

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

(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 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-

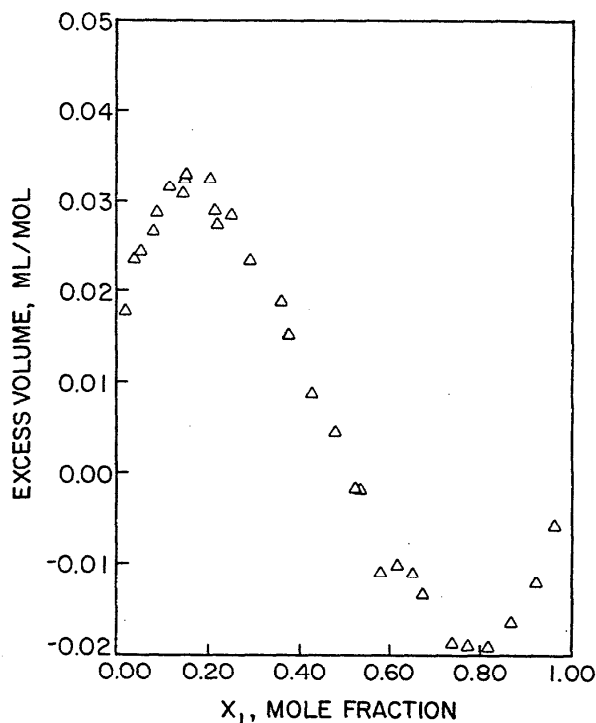


FIG. 1. Typical shape of the V^E vs x_1 curve for the methanol(1) + benzene(2) system at 298.15 K, MRL 41405.

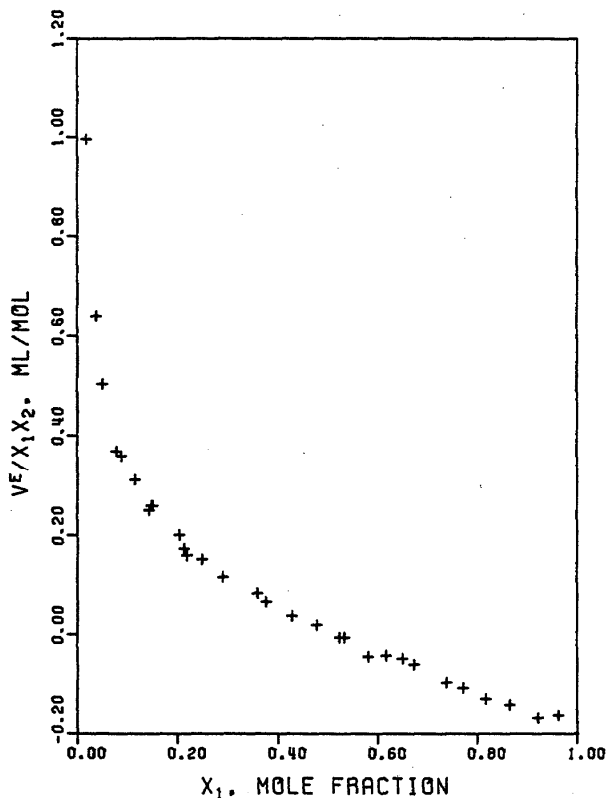


FIG. 2. Typical shape of the V^E/x_1x_2 vs x_1 curve for the methanol(1) + benzene(2) system at 298.15 K, MRL 41405.

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., <i>Anales de Quimica</i> , 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, K., <i>Journal of Chemical Physics</i> , 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		

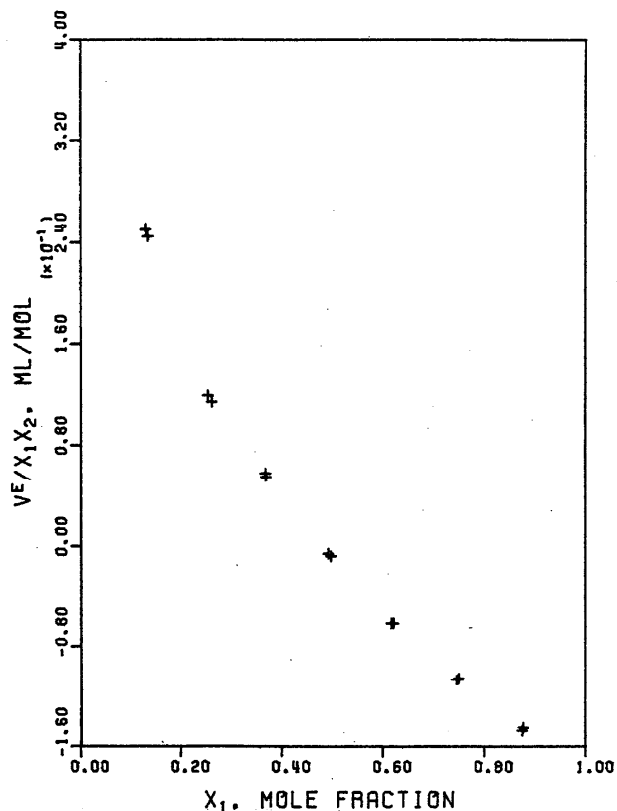
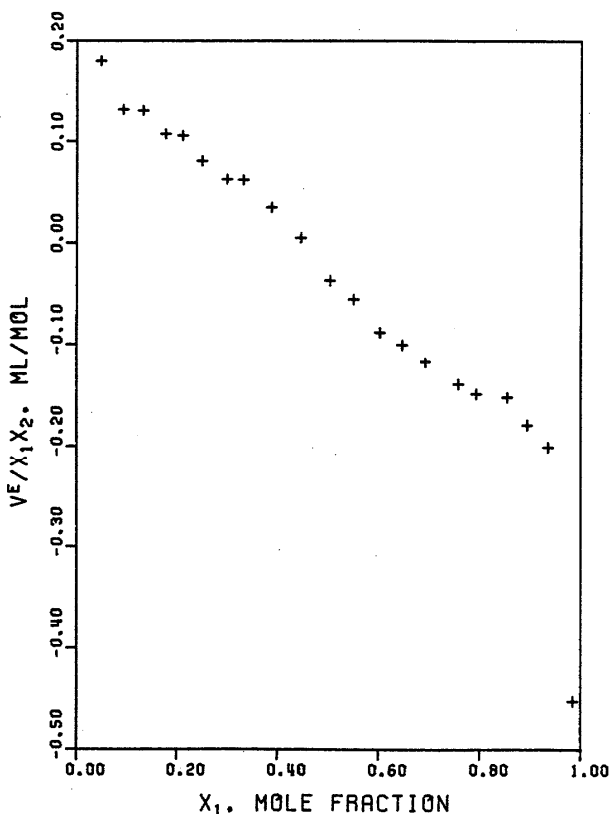
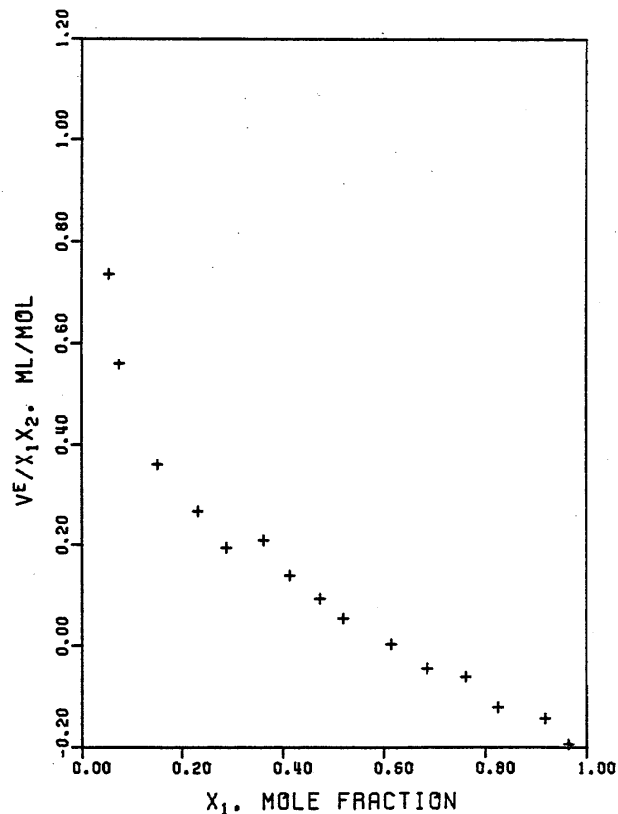

 FIG. 4. Best data set at 298.15 K for methanol(1) + benzene(2). Data of Wood *et al.*, MRL 18139.

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

 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

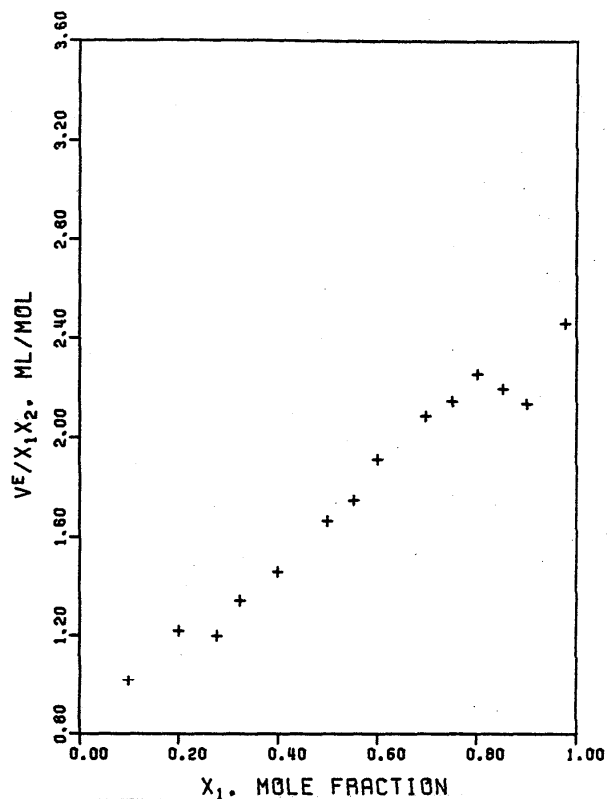


FIG. 6. Data of Campbell and Anand for the methanol(1) + cyclohexane(2) system at 319.15 K, MRL 4886.

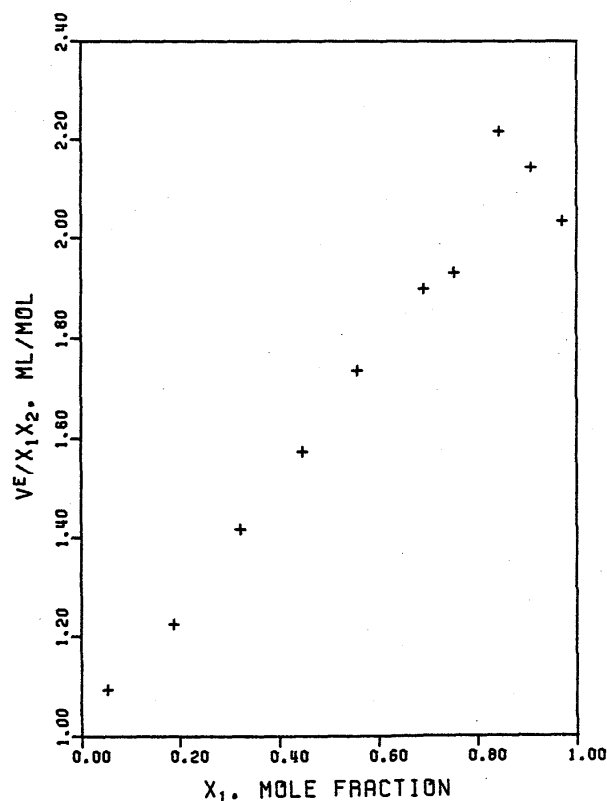


FIG. 7. Data of Campbell and Anand for the methanol(1) + cyclohexane(2) system at 323.15 K, MRL 4886.

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

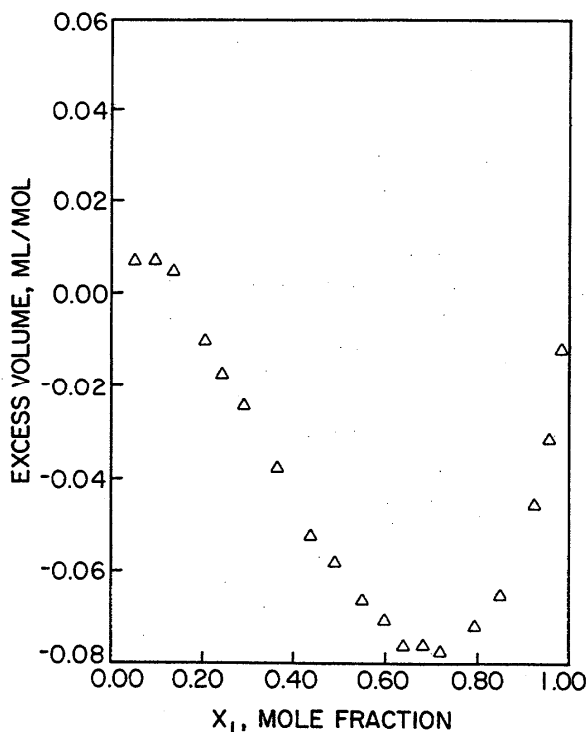
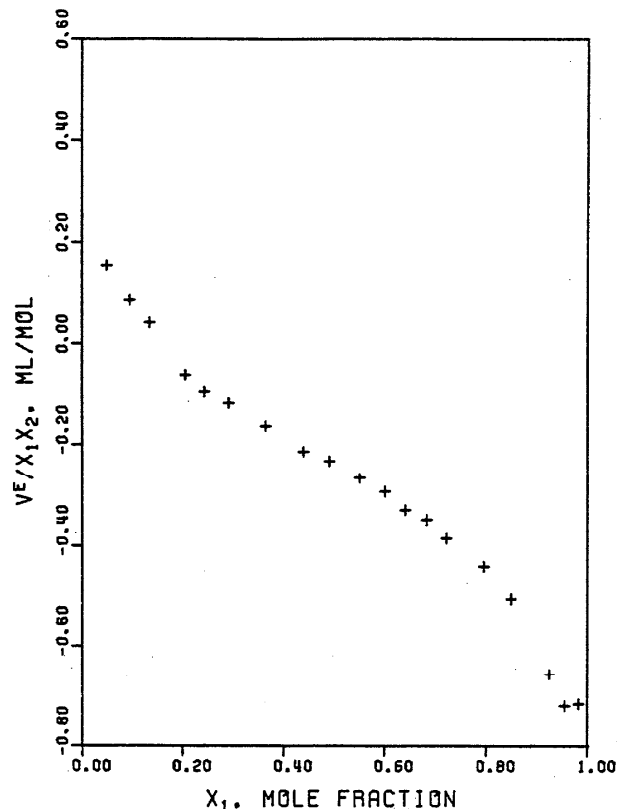

 FIG. 8. V^E values from Ocon *et al.* for the methanol(1) + toluene(2) system at 293.15 K, MRL 1398.

 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		

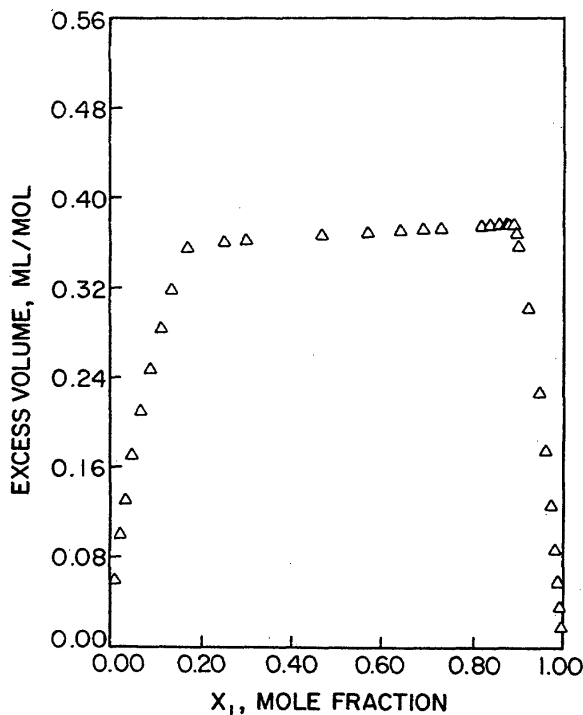


FIG. 10. V^E values from Treszczanowicz and Benson for methanol (1) + heptane(2) at 298.15 K, MRL 40893.

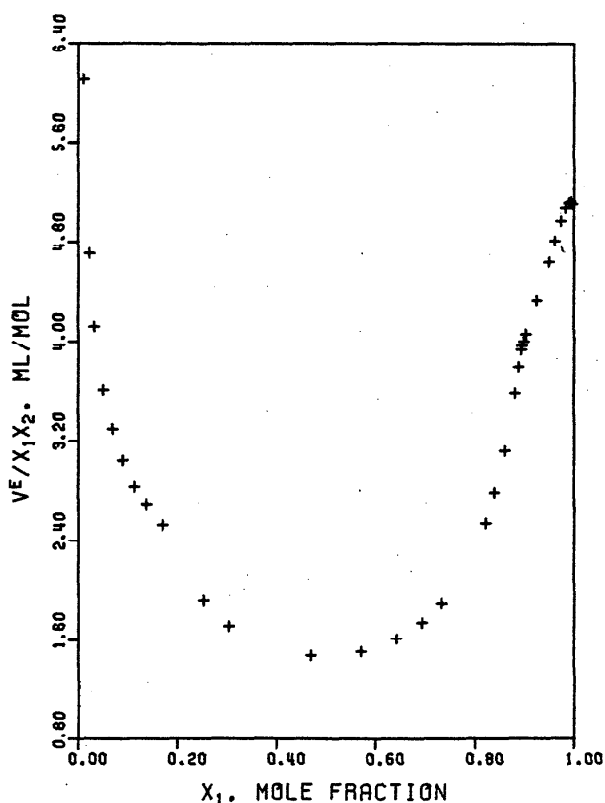


FIG. 11. V^E/x_1x_2 plot of the data in Fig. 10.

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

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

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,

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

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 + acetylene,³ methanol + ethane,⁴ and the methanol + butane⁵ 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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 18543. N. Perrakis, *J. Chim. Phys. Phys. Chim. Biol.* **22**, 280 (1925).
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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 .

11. Acknowledgments

This work was supported by the Office of Standard Reference Data of the National Bureau of Standards with funds supplied by the National Science Foundation (under Agreement No. PRM-8005187-AO1) and by the Industrial Participants in the Thermodynamics Research Laboratory.

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²B. D. Smith, O. Muthu, and A. Dewan, *J. Phys. Chem. Ref. Data* **12**, 381 (1983); **12**, 389 (1983); **12**, 395 (1983).

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⁵L. B. Petty and J. M. Smith, *Ind. Eng. Chem.* **47**, 1258 (1955).

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⁷A. N. Campbell and S.C. Anand, *Can. J. Chem.* **50**, 479 (1972).

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

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The heat 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 enthalpy; heat of mixing; hydrocarbons; methanol.

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1. Introduction

Previous papers^{1,2} have evaluated the vapor-liquid equilibrium (VLE), heat of mixing (H^E) and volume change of mixing data for selected 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 new correlations; and designers who need the best available data to design process equipment.

This report extends that work to include the excess enthalpy data for the important alcohol + hydrocarbon systems. As in the preceding evaluation papers, an attempt is

made to establish selected values of H^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 enthalpy is related to the mixture and pure component molar enthalpies by

$$H^E = H - x_1H_1 - x_2H_2.$$

The procedures used to evaluate the accuracy of H^E data have been described and illustrated in detail in the first and third articles 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 search. Useable data were found for hydrocarbons in the C₂ to C₈ carbon number range.

3. Summary of Evaluation Results

The evaluation results for all the methanol + hydrocarbon excess enthalpy data sets 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 sets to the literature citations in the Bibliography at the end of this paper. The data sets listed for each system are ordered with respect to temperature. In many cases, the data

Table 1. Summary list for excess enthalpy data

LITERATURE REFERENCE	T, K	P, MPA	QUALITY RATING	SCATTER RATING	% DEVIATION FROM HE VS. X(1)=0.25	X(1)=0.50	1/T CURVE X(1)=0.75
METHANOL(1) + ETHANE(2)							
41770	298.150	6.9000	ABC	E	-	-	-
METHANOL(1) + PROPANE(2)							
41669	298.150	2.9850	ABC	E	-	-	-
METHANOL(1) + BUTANE(2)							
41665	298.150	2.9850	ABC	E	-	-	-
METHANOL(1) + PENTANE(2)							
41444	298.150	0.1700	ABC	E	-	-	-
METHANOL(1) + BENZENE(2)							
01325	293.150	0.1013	DE	H	-	-	-
18302	297.400	0.1013	B	G	1.1	-1.1	-3.6
00050	298.150	0.1013	DE	M	-	-	-
00682	298.150	0.1013	C	G	2.1	5.1	-4.7
00686	298.150	0.2100	A	E	0.0	0.0	0.0
01028	298.150	0.1013	B	G	2.5	1.6	5.0
01052	298.150	0.1013	B	S	-3.0	-0.3	-4.7
01115	298.150	0.1013	C	F	2.5	4.2	5.3
01213	298.150	0.1013	D	F	8.1	3.3	-3.3
01953	298.150	0.1013	C	F	3.2	2.3	-0.5
03633	298.150	0.1013	C	F	1.1	0.2	-1.0
03647	298.150	0.1013	DE	M	-	-	-
04761	298.150	0.1013	E	S	5.3	14.4	17.5
04857	298.150	0.1013	C	F	-2.2	-0.3	-4.9
04882	298.150	0.1013	C	F	-0.4	0.0	-2.5
05123	298.150	0.1013	D	M	2.0	2.1	0.7
23943	298.150	0.1013	B	G	-0.4	-1.0	-3.4
00686	308.150	0.2100	A	E	0.0	0.0	0.0
01052	308.150	0.1013	B	S	-0.8	-1.7	-2.7
05307	308.150	0.1013	E	F	-10.1	-12.5	-13.8
00686	318.150	0.2100	A	E	0.0	0.0	0.0
01052	318.150	0.1013	B	S	-2.4	-1.2	-2.7
03633	318.150	0.1013	B	G	1.6	2.1	-1.5
04857	318.150	0.1013	C	F	-2.3	-1.1	-1.7
METHANOL(1) + CYCLOHEXANE(2)							
02762	298.150	0.1013	E	U	-	-	-
10643	298.150	0.1013	ABC	E	-	-	-
02762	308.150	0.1013	E	U	-	-	-
02762	320.150	0.1013	E	U	-	-	-
05768	323.650	0.1013	CDE	F	-	-	-
METHANOL(1) + HEXANE(2)							
01080	298.150	0.2100	ABC	E	-	-	-
01080	303.150	0.2100	ABC	E	-	-	-
01080	306.850	0.2100	A	E	0.0	0.0	0.0
01080	313.150	0.2100	B	G	0.0	0.4	0.3
01080	318.150	0.2100	B	G	0.7	0.0	0.1
04846	318.150	0.1013	D	M	-0.3	-1.4	-2.0
01080	323.150	0.2100	B	G	0.0	0.0	0.0
METHANOL(1) + TOLUENE(2)							
00686	298.150	0.2100	A	E	0.0	0.0	0.0
01953	298.150	0.1013	C	F	3.7	1.9	1.8
08717	298.150	0.1013	E	M	7.4	13.0	8.7
00686	308.130	0.2100	A	E	0.0	0.0	0.0
08717	308.150	0.1013	D	H	-6.0	-2.4	-3.7
00686	318.150	0.2100	A	E	0.0	0.0	0.0
METHANOL(1) + HEPTANE(2)							
05308	298.150	0.1013	DE	M	-	-	-
01080	303.150	0.2100	ABC	E	-	-	-
05307	308.150	0.1013	DE	M	-	-	-
01080	318.150	0.2100	ABC	E	-	-	-
05307	318.150	0.1013	CDE	F	-	-	-
01080	333.150	0.2100	ABC	E	-	-	-
METHANOL(1) + ETHYLBENZENE(2)							
00686	298.150	0.2100	ABC	E	-	-	-
00686	308.150	0.2100	ABC	E	-	-	-
00686	318.150	0.2100	ABC	E	-	-	-
METHANOL(1) + P-XYLENE(2)							
41007	298.150	0.1700	ABC	E	-	-	-

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 in Table 1.

Previous papers¹ 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 case, 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 H^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" H^E vs $1/T$ curves at three mole fractions: $x_1 = 0.25, 0.50,$ and 0.75 . 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 of the best curve value. The test compares data sets at the same temperature and also at different temperatures.

The use of an H^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 H^E data sets for correlation or design purposes 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 H^E vs $1/T$ plots can be made for the comparison test, it is necessary to select the best point values at each temperature where multiple data sets appear. Tables 2-4 and Figs. 1-3 for the methanol + benzene system at 298.15 K illustrate the tabulations and plots which can be produced to support those choices.

The S code letter in the tables is the scatter rating. That scatter rating letter also appears above the point symbol in the corresponding figures.

The ET (equipment type) code in the three tables denotes the type of calorimeter used to measure the set of data. In the three figures, the equipment type is denoted by the symbol. A description of each equipment type, and the assignments for the numerical codes in Tables 2-4, and the symbols in the corresponding figures, are given in the benzene + cyclohexane H^E report.¹ A brief description of the

numerical codes appearing in Tables 2-4 follows:

- 01 McGlashan batch vessel;
- 02 Scatchard batch vessel;
- 04 miscellaneous batch vessels;
- 05 Van Ness semi-batch vessel;
- 06 miscellaneous semi-batch vessels.

In a batch vessel, both pure components are initially present in the vessel and then mixed by some technique such as rocking the vessel, breaking a glass ampoule, etc. A semi-batch vessel is one where only one component is initially present in the vessel and the second component is titrated into the vessel in increments, but no material is withdrawn from the vessel during the run.

The Tschner and Strazielle (MRL 4761) points in Tables 2-4 and Figs. 1-3 were obtained from light scattering data rather than calorimetrically.

Table 2. Magnitude listings for the methanol(1) + benzene(2) system at 298.15 K and $x_1 = 0.25$

MRL number	Codes S ET	Authors	Year	Excess enthalpy J/mol
1052	S 04	Brown, Fock, Smith	1969	690.5
4857	F 01	Williamson, Scott	1960	696.0
4882	F 02	Vesely, Pick	1969	709.0
23943	G 05	Coca Prados	1969	709.0
686	E 05	Mrazek, Van Ness	1961	712.0
3633	F 04	Vesely, Hynek, Svoboda, Holub	1974	720.0
5123	M 06	Hanson, VanWinkle	1960	726.0
682	G 04	Goates, Snow, James	1961	727.0
1028	G 06	Schnaible	1955	730.0
1115	F 06	Murti, Van Winkle	1958	730.0
1953	F 06	Tsao, Smith	1953	734.8
4761	S	Fechner, Strazielle	1972	750.0
1213	F 06	Deshpande, Pandya	1965	770.0

Table 3. Magnitude listings for the methanol(1) + benzene(2) system at 298.15 K and $x_1 = 0.50$

MRL number	Codes S ET	Authors	Year	Excess enthalpy J/mol
23943	G 05	Coca Prados	1969	615.8
1052	S 04	Brown, Fock, Smith	1969	620.0
4857	F 01	Williamson, Scott	1960	620.0
686	E 05	Mrazek, Van Ness	1961	621.7
4882	F 02	Vesely, Pick	1969	622.0
3633	F 04	Vesely, Hynek, Svoboda, Holub	1974	623.2
1028	G 06	Schnaible	1955	631.4
5123	M 06	Hanson, VanWinkle	1960	634.8
1953	F 06	Tsao, Smith	1953	635.8
1213	F 06	Deshpande, Pandya	1965	642.0
1115	F 06	Murti, Van Winkle	1958	648.0
682	G 04	Goates, Snow, James	1961	653.3
4761	S	Fechner, Strazielle	1972	711.0

Table 4. Magnitude listings for the methanol(1) + benzene(2) system at 298.15 K and $x_1 = 0.75$

MRL number	Codes S ET	Authors	Year	Excess enthalpy J/mol
4857	F 01	Williamson, Scott	1960	344.0
1052	S 04	Brown, Fock, Smith	1969	345.0
682	G 04	Goates, Snow, James	1961	345.0
23943	G 05	Coca Prados	1969	349.4
1213	F 06	Deshpande, Pandya	1965	350.0
4882	F 02	Vesely, Pick	1969	352.8
3633	F 04	Vesely, Hynek, Svoboda, Holub	1974	358.2
1953	F 06	Tsao, Smith	1953	360.0
686	E 05	Mrazek, Van Ness	1961	361.8
5123	M 06	Hanson, VanWinkle	1960	364.5
1028	G 06	Schnaible	1955	380.0
1115	F 06	Murti, Van Winkle	1958	381.0
4761	S	Fechner, Strazielle	1972	425.0

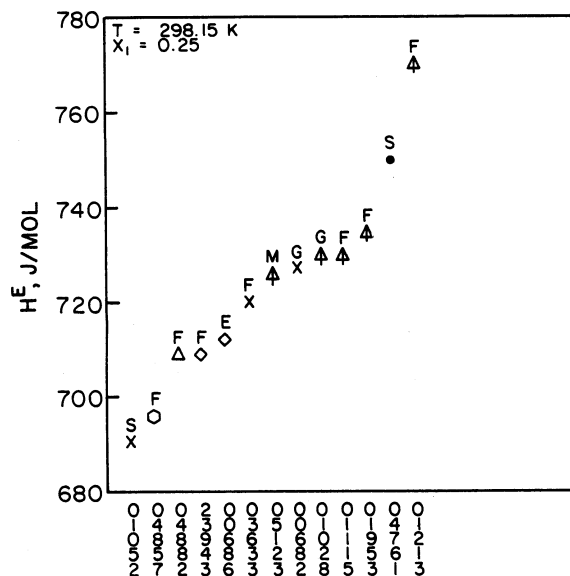


Fig. 1. Magnitude comparison plot for the methanol(1) + benzene(2) system at 298.15 K and $x_1 = 0.25$.

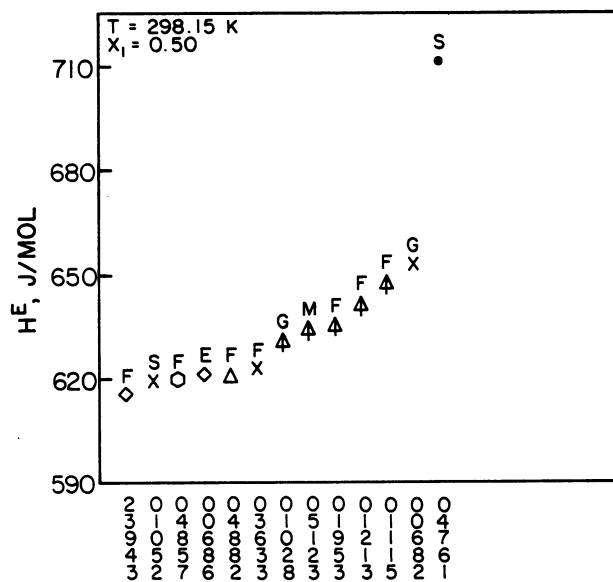


Fig. 2. Magnitude comparison plot for the methanol(1) + benzene(2) system at 298.15 K and $x_1 = 0.50$.

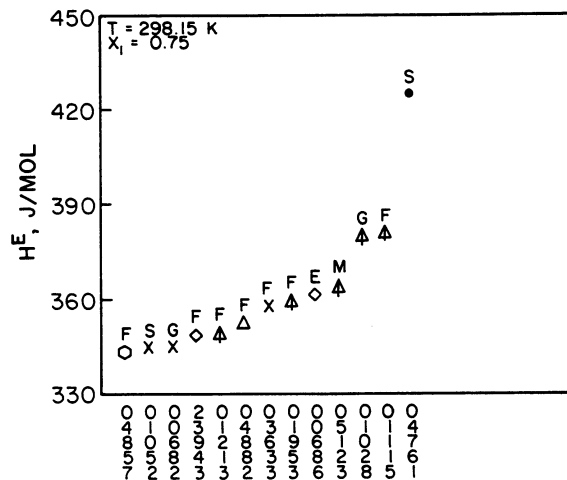


Fig. 3. Magnitude comparison plot for the methanol(1) + benzene(2) system at 298.15 K and $x_1 = 0.75$.

Table 5. Best curve H^E values for the methanol(1) + benzene(2) system

T, K	$1/T \times 10^2$	Values from best curves		
		$x_1=0.25$	$x_1=0.50$	$x_1=0.75$
297.40	0.3362	703.0	614.0	358.0
298.15	0.3354	712.0	621.7	361.8
308.15	0.3245	832.0	732.6	422.5
318.15	0.3143	953.0	850.0	505.6

Only one methanol + benzene data set at 298.15 K was given an E rating (Mrazek and Van Ness, MRL 686). The Van Ness semi-batch vessel used for that data set has been proven in extensive use by many investigators. As can be seen in Figs. 1–3, that data set avoids the extremes among the rather widely scattered points. Hence, it is reasonable to select that data set as being most representative for the methanol + benzene system at 298.15 K.

Even though the number of data sets at other temperatures are insufficient to require tables and plots such as Tables 2–4 and Figs. 1–3, the reasons for selecting the Mrazek and Van Ness set at 298.15 also lead to the selection of their data sets at 308.15 and 318.15 K.

The best H^E vs $1/T$ curves at $x_1 = 0.25, 0.50,$ and 0.75 drawn through the three Mrazek and Van Ness data sets at 298.15, 308.15, and 318.15 K have a negative slope and are slightly concave upward. The values read from those curves are tabulated in Table 5. Note that the curves were extrapolated slightly to the point for the MRL 18302 set at 297.4 K.

As can be seen from Table 1, H^E vs $1/T$ curves could be established for only two other systems besides methanol + benzene: the methanol + hexane and the methanol + toluene binaries. The upper critical solution temperature for the methanol + cyclohexane system is 45.87 °C (319.02 K) (Campbell and Kartzmark, MRL 5768), and only one useable set of data above that temperature is available; the partial miscibility gap in the Touhara *et al.* (MRL 10643) data set at 298.15 K includes the $x_1 = 0.25, 0.50,$ and 0.75 points. A similar situation exists for the methanol + heptane system where five of the six available data sets fall below the upper critical solution temperature of about 51.2 °C (324.35 K)³.

The methanol + hexane data are dominated by the data sets of Savini, Winterhalter, and Van Ness (MRL 1080). They provide two sets (at 298.15 and 303.15 K) below and four sets above the critical solution temperature, which they found to be just above 33.7 °C (306.85 K). As in the case of

Table 6. Best curve H^E values for the methanol(1) + hexane(2) system

T, K	$1/T \times 10^2$	Values from best curves		
		$x_1=0.25$	$x_1=0.50$	$x_1=0.75$
306.85	0.3259	602.0	635.0	551.1
313.15	0.3193	673.0	705.5	592.0
318.15	0.3143	742.0	767.1	627.0
323.15	0.3095	816.0	830.0	664.0

Table 7. Best curve H^E values for the methanol(1) + toluene(2) system

T, K	$1/T \times 10^2$	Values from best curves		
		$x_1=0.25$	$x_1=0.50$	$x_1=0.75$
298.15	0.3354	704.0	622.5	376.2
308.15	0.3245	846.0	758.0	459.0
318.15	0.3143	981.7	891.0	549.0

the methanol + benzene system, the H^E vs $1/T$ curves fit the four miscible data set points better if they are slightly curved and concave upwards. The values read from those curves are tabulated in Table 6.

The three Mrazek and Van Ness (MRL 686) data sets were used to establish the best curves for the methanol + toluene system. Points from those curves appear in Table 7. The Tsao and Smith (MRL 1953) data set has H^E and H^E/x_1x_2 vs x_1 curves worthy of an E scatter rating except for a large gap in the data above $x_1 = 0.81$; that data set lies close to the curve through the Mrazek *et al.* points. The two Mason and Washburn sets (MRL 8717) present no points below $x_1 = 0.20$, and they differ considerably from the Mrazek *et al.* data sets.

It is not necessary to tabulate best curve values for the methanol + ethylbenzene system; the best values available are those provided by the only three available data sets from Mrazek and Van Ness (MRL 686).

5. Best Data Sets

Two excellent calorimeters have been applied extensively to the measurement of H^E data for methanol + hydrocarbon binaries. The flow calorimeter developed by Christensen and co-workers has been used at 298.15 for the binaries containing methanol with ethane, propane, butane, pentane, and para-xylene. Those single data sets are not confirmed by data from other sources but, based on the very accurate performance of the Christensen vessel on the well-established benzene + cyclohexane system,¹ it is highly probable that those data sets are accurate.

A similar situation exists for the methanol + ethylbenzene system. The only data for that system are the three sets at 298.15, 308.15, and 318.15 K obtained with the Van Ness semi-batch vessel. Based on the proven performance of that vessel on other systems, it is reasonable to assume those data sets are accurate.

The Van Ness vessel has also applied to the methanol + benzene, hexane, toluene and heptane binaries; as discussed in the previous section, the resulting data have been selected as the superior data sets in each instance. The methanol + cyclohexane binary is the only methanol + hydrocarbon system with H^E data which does not have data sets from the Christensen or the Van Ness vessels.

Tables 8–33 and Figs. 4–29 present the best available methanol + hydrocarbon data sets in the order in which they appear in Table 1. All of the sets obtained with the Christensen and the Van Ness apparatuses are shown. For the methanol + cyclohexane system, the Touhara *et al.*

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

SYSTEM. Methanol(1) + Ethane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 6.9000 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. McFall, T. A., Post, M. E., Christensen, J. J., Izatt, R. M., Journal of Chemical Thermodynamics, 13(5), 441 (1981). (MRL 41770)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0202	131.9	0.4541	14.2
0.0399	136.2	0.4894	4.9
0.0592	134.4	0.5230	-1.8
0.0782	127.4	0.5552	-5.2
0.0968	117.6	0.5859	-7.0
0.1150	111.3	0.6154	-4.6
0.1504	94.0	0.6707	1.0
0.1676	88.7	0.7216	7.0
0.2011	80.2	0.7687	16.1
0.2333	71.2	0.8123	19.9
0.2490	67.3	0.8529	23.4
0.2943	56.1	0.8907	22.1
0.3374	43.4	0.9260	18.8
0.3782	35.9	0.9590	12.3
0.4171	25.4	0.9901	4.2

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

SYSTEM. Methanol(1) + Propane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 2.9850 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. Post, M. E., McFall, T. A., Christensen, J. J., Izatt, R. M., Journal of Chemical Thermodynamics, 13(1), 77 (1981). (MRL 41669)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0429	228.7	0.5737	356.0
0.1036	289.9	0.6041	350.0
0.1603	326.1	0.6330	341.8
0.2134	346.3	0.6607	332.4
0.2633	359.6	0.6870	322.1
0.3102	367.0	0.7364	297.8
0.3544	374.9	0.7818	269.6
0.3960	374.5	0.8235	235.2
0.4094	374.1	0.8620	202.3
0.4355	374.9	0.8978	163.2
0.4481	372.6	0.9310	117.0
0.4728	372.2	0.9619	69.2
0.5081	370.7	0.9908	18.5
0.5417	363.3		

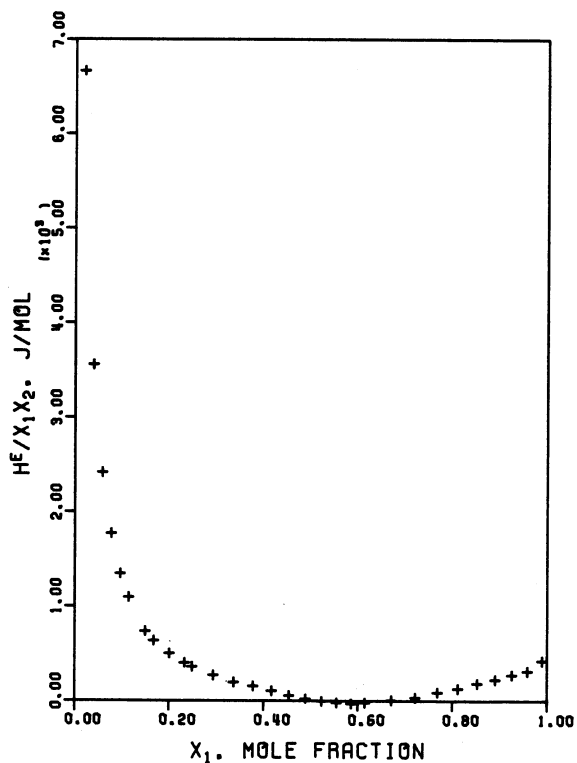
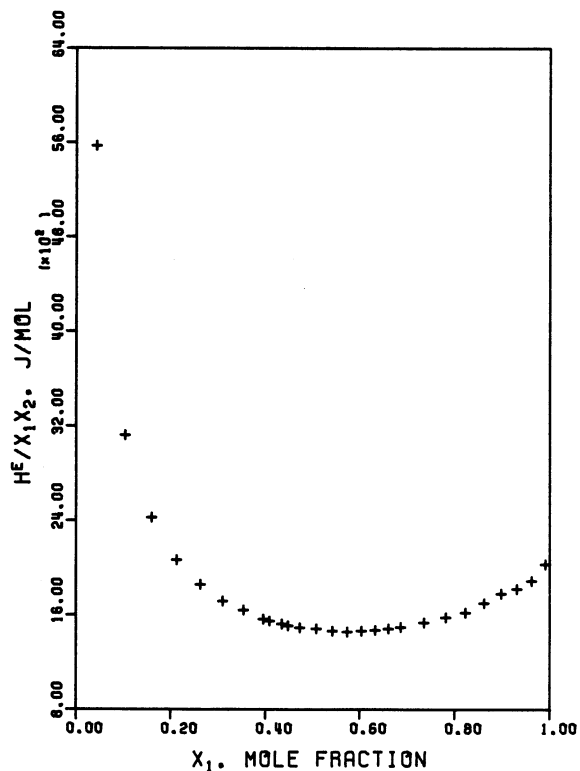
FIG. 4. Data of McFall *et al.* for the methanol(1) + ethane(2) system at 298.15 K, MRL 41770.FIG. 5. Data of Post *et al.* for the methanol(1) + propane(2) system at 298.15 K, MRL 41669.

Table 10. Only data set for the methanol(1) + butane(2) system

SYSTEM. Methanol(1) + Butane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 2.9850 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. McFall, T. A., Post, M. E., Collins, S. G., Christensen, J. J., Izatt, R. M., Journal of Chemical Thermodynamics, 13(1), 41 (1981). (MRL 41665)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0485	269.9	0.5403	487.6
0.0717	296.3	0.5947	480.1
0.1162	349.3	0.6440	466.0
0.1375	368.4	0.6890	446.3
0.1583	387.0	0.7302	424.2
0.1981	417.5	0.7680	392.7
0.2541	451.3	0.8290	333.3
0.3059	465.4	0.8653	285.9
0.3541	474.6	0.8985	234.2
0.3990	488.0	0.9291	177.0
0.4410	488.7	0.9574	118.5
0.4802	494.5		

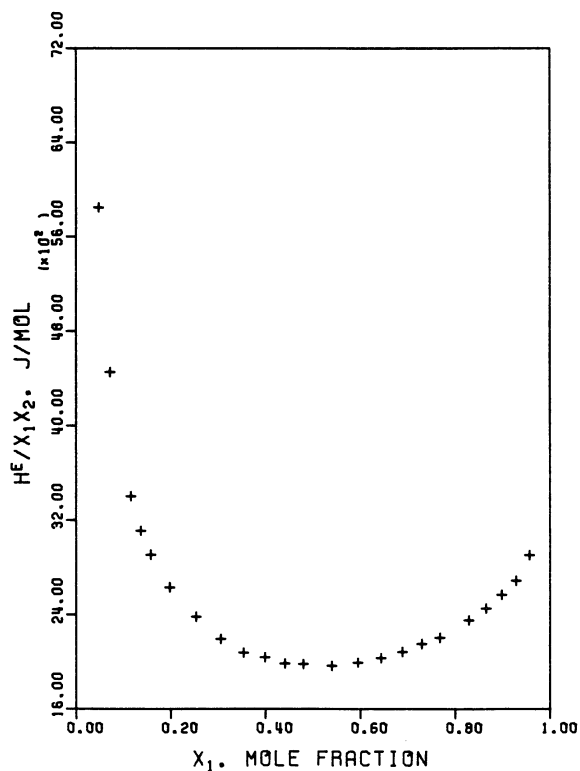

 FIG. 6. Data of McFall *et al.* for the methanol(1) + butane(2) system at 298.15 K, MRL 41665.

Table 11. Only data set for the methanol(1) + pentane(2) system

SYSTEM. Methanol(1) + Pentane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.1700 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. Collins, S. G., Christensen, J. J., Izatt, R. M., Hanks, R. W., Journal of Chemical Thermodynamics, 12(7), 609 (1980). (MRL 41444)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0238	160.4	0.6820	509.0
0.0772	302.6	0.6994	499.1
0.1270	366.6	0.7399	479.4
0.1956	435.3	0.7767	444.0
0.2374	454.4	0.8151	418.4
0.3325	500.7	0.8411	374.8
0.4141	517.0	0.8693	338.8
0.4723	528.6	0.8904	296.5
0.5119	538.5	0.9196	239.8
0.5486	528.3	0.9419	176.3
0.5718	533.8	0.9587	139.0
0.6150	532.1	0.9627	126.3
0.6545	514.1	0.9822	65.9

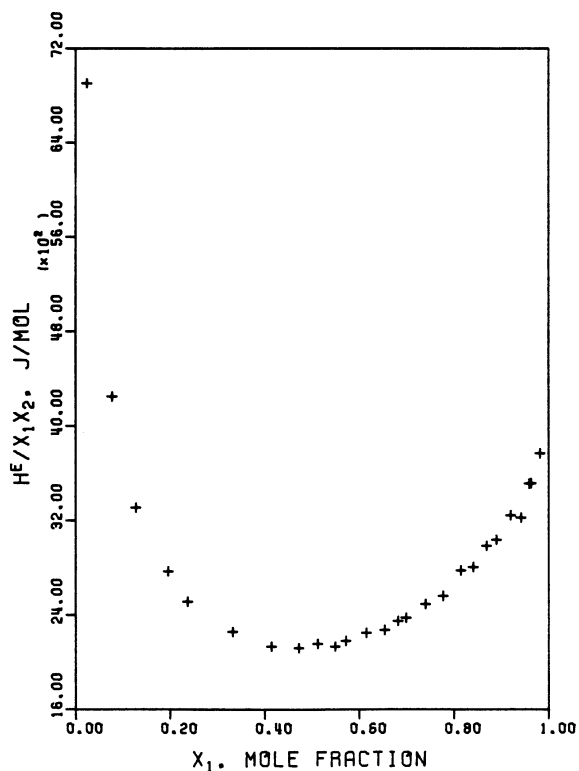

 FIG. 7. Data of Collins *et al.* for the methanol(1) + pentane(2) system at 298.15 K, MRL 41444.

Table 12. Selected data set for the methanol(1) + benzene(2) system at 298.15 K

SYSTEM. Methanol(1) + Benzene(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0210	244.2	0.5760	555.9
0.0370	360.5	0.6250	507.1
0.0690	502.4	0.6870	441.9
0.1030	586.2	0.7230	397.7
0.1460	651.3	0.7710	332.6
0.2110	700.1	0.8250	258.2
0.2820	716.4	0.8710	193.1
0.3740	695.5	0.9230	116.3
0.4500	655.9	0.9480	76.8
0.5120	614.1		

Table 13. Selected data set for the methanol(1) + benzene(2) system at 308.15 K

SYSTEM. Methanol(1) + Benzene(2)			
TEMPERATURE. 308.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0330	374.5	0.4490	774.6
0.0500	479.2	0.5060	725.7
0.0740	583.8	0.5510	681.5
0.1070	679.2	0.5900	639.6
0.1480	753.6	0.6500	567.5
0.2010	807.1	0.6970	500.1
0.2420	828.1	0.7680	395.4
0.2750	835.0	0.8230	304.7
0.3130	835.0	0.8800	209.3
0.3640	821.1	0.9380	109.3
0.4120	797.8	0.9760	41.9

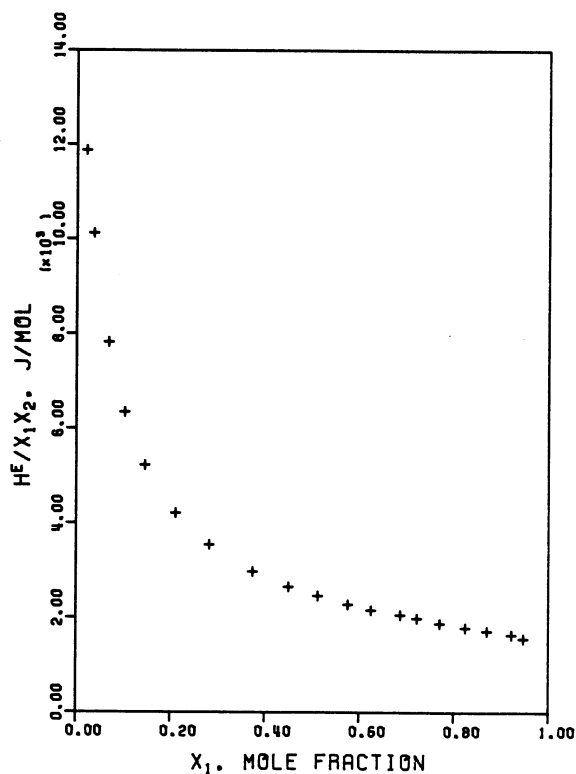
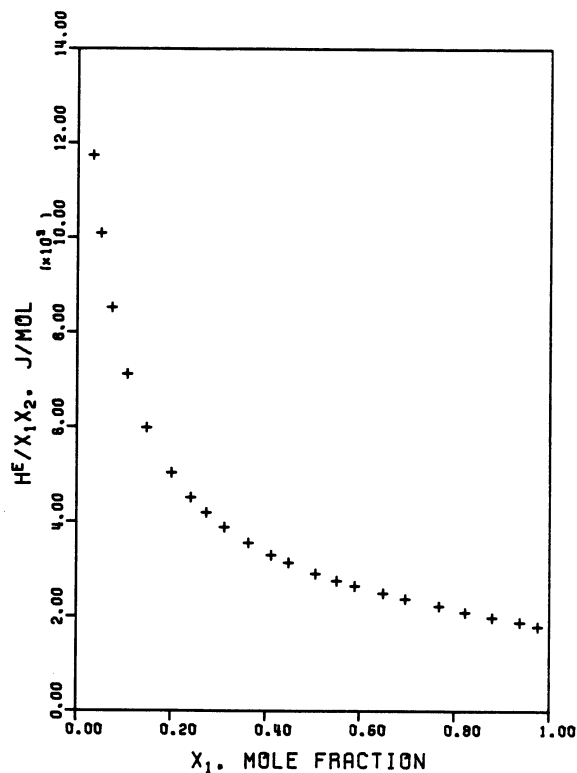
FIG. 8. Data of Mrazek *et al.* for the methanol(1) + benzene(2) system at 298.15 K, MRL 686.FIG. 9. Data of Mrazek *et al.* for the methanol(1) + benzene(2) system at 308.15 K, MRL 686.

Table 14. Selected data set for the methanol(1) + benzene(2) system at 318.15 K

SYSTEM. Methanol(1) + Benzene(2)			
TEMPERATURE. 318.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0540	537.3	0.5120	839.7
0.0690	621.0	0.5610	783.9
0.0940	725.7	0.5990	735.0
0.1280	814.1	0.6580	651.3
0.1670	883.9	0.7020	590.8
0.2200	935.1	0.7440	516.4
0.2610	956.0	0.8080	395.4
0.2930	963.0	0.8560	302.4
0.3240	960.6	0.9030	207.0
0.3520	953.7	0.9480	111.6
0.4080	928.1	0.9800	41.9
0.4600	888.5		

Table 15. Data set for the partially miscible methanol(1) + cyclohexane(2) system at 298.15

SYSTEM. Methanol(1) + Cyclohexane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.1013 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Touhara, H., Ikeda, M., Nakanishi, K., Watanabe, N., Journal of Chemical Thermodynamics, 7, 887 (1975). (MRL 10643)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0060	91.3	0.4988	467.6
0.0081	92.9	0.5289	471.5
0.0120	109.4	0.5560	474.7
0.0169	130.6	0.8246	459.0
0.0298	175.9	0.8562	445.0
0.0476	249.2	0.8806	400.9
0.0913	332.9	0.8970	364.6
0.1118	363.9	0.9117	328.9
0.2160	409.4	0.9276	284.7
0.2900	424.3	0.9477	219.4
0.3561	440.2	0.9645	151.7
0.4086	449.7	0.9856	67.0
0.4643	463.9		

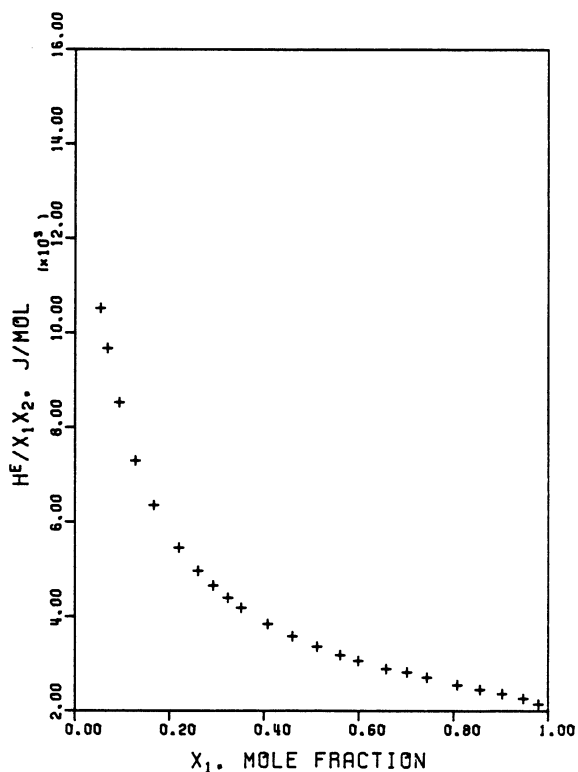
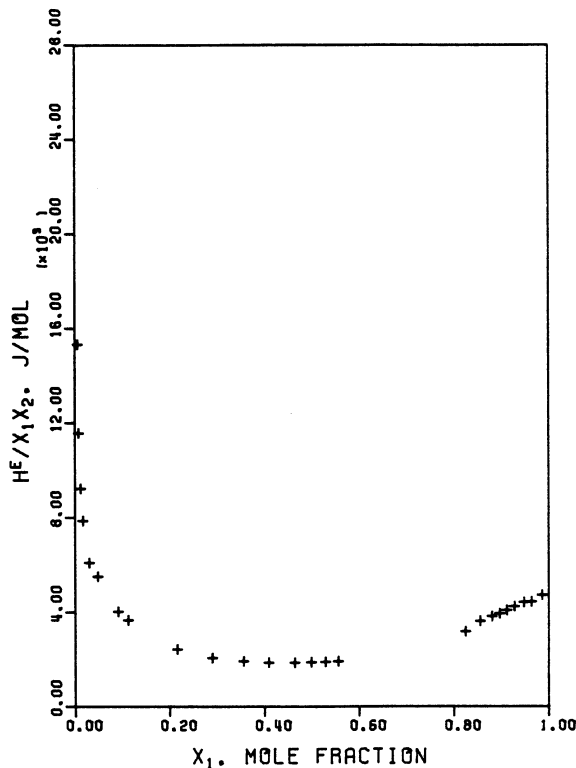

 FIG. 10. Data of Mrazek *et al.* for the methanol(1) + benzene(2) system at 318.15 K, MRL 686.

 FIG. 11. Data of Touhara *et al.* for the methanol(1) + cyclohexane(2) system at 298.15 K, MRL 10643.

Table 16. Only useable data set above the critical solution temperature for the methanol(1) + cyclohexane(2) system

SYSTEM. Methanol(1) + Cyclohexane(2)			
TEMPERATURE. 323.65 K		PRESSURE. 0.1013 MPa	
QUALITY RATING. CDE		SCATTER. Fair	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Campbell, A. N., Kartzmark, E. M., Canadian Journal of Chemistry, 47, 619 (1969). (MRL 5768)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0699	857.7	0.6314	1129.7
0.1301	1005.4	0.7233	1033.9
0.2426	1188.3	0.8052	828.9
0.3126	1240.1	0.8680	650.6
0.4190	1228.0	0.9080	558.1
0.5205	1241.4	0.9583	291.2

Table 17. Data set for the partially miscible methanol(1) + hexane(2) system at 298.15 K

SYSTEM. Methanol(1) + Hexane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0360	273.3	0.6276	491.8
0.0516	309.1	0.6839	487.2
0.0715	345.8	0.7383	482.6
0.1048	394.6	0.7750	479.2
0.1254	420.1	0.8190	452.2
0.1658	461.3	0.8462	419.3
0.1992	487.2	0.8700	383.2
0.2207	501.9	0.9004	325.8
0.2518	516.0	0.9296	225.4
0.3570	512.7	0.9593	164.6
0.4835	503.8	0.9847	67.9
0.5477	498.4		

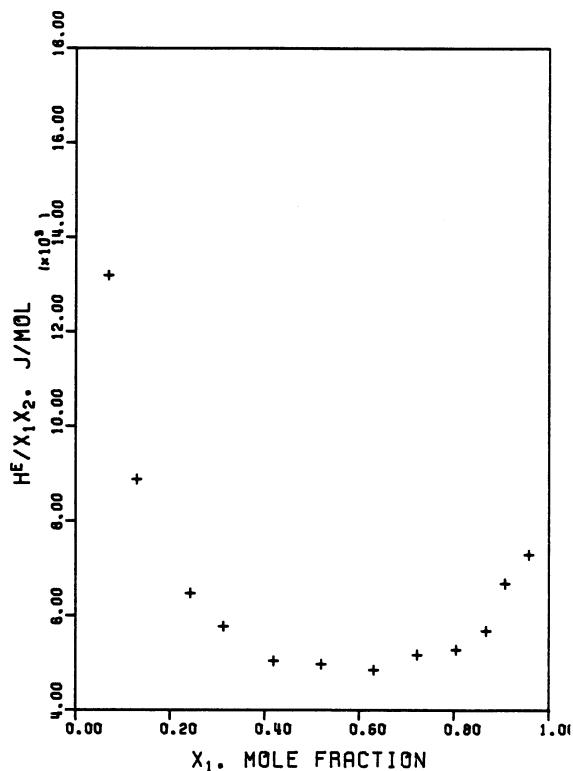
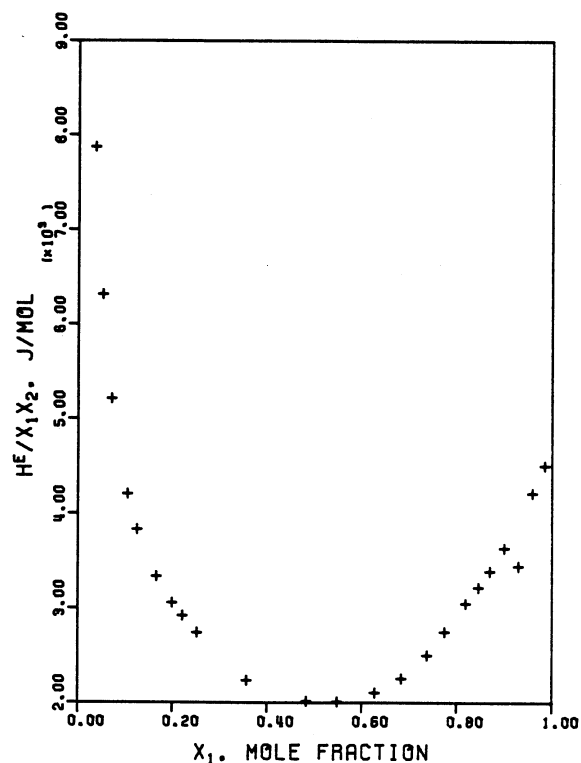
FIG. 12. Data of Campbell *et al.* for the methanol(1) + cyclohexane(2) system at 323.65 K, MRL 5768.FIG. 13. Data of Savini *et al.* for the methanol(1) + hexane(2) system at 298.15 K, MRL 1080.

Table 18. Data set for the partially miscible methanol(1) + hexane(2) system at 303.15 K

SYSTEM. Methanol(1) + Hexane(2)			
TEMPERATURE. 303.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0104	176.0	0.6092	555.0
0.0141	206.6	0.6586	548.3
0.0187	234.5	0.6964	543.2
0.0249	263.3	0.7282	538.7
0.0318	288.7	0.7492	533.0
0.0388	310.3	0.7602	525.7
0.0460	329.8	0.7701	518.2
0.0562	351.9	0.7872	503.7
0.1010	430.1	0.8112	479.5
0.1503	488.4	0.8352	449.9
0.1968	529.2	0.8584	415.2
0.2892	579.6	0.8888	359.9
0.3004	583.1	0.9101	312.7
0.3143	587.7	0.9317	256.0
0.3187	588.0	0.9474	208.3
0.3365	590.1	0.9637	152.5
0.4592	575.6	0.9792	92.5
0.5484	563.2		

Table 19. Data set for the miscible methanol(1) + hexane(2) system at 306.85 K

SYSTEM. Methanol(1) + Hexane(2)			
TEMPERATURE. 306.85 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			

x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0154	230.3	0.5191	632.2
0.0239	278.9	0.5504	626.7
0.0377	333.7	0.5782	621.3
0.0573	387.2	0.6030	615.3
0.0810	434.5	0.6450	602.8
0.1115	482.3	0.6940	584.2
0.1437	521.2	0.7565	549.5
0.1734	549.7	0.7871	522.0
0.2144	580.7	0.8282	473.5
0.2530	603.0	0.8503	440.8
0.2981	621.7	0.8737	399.6
0.3364	632.1	0.9002	343.9
0.3821	639.2	0.9308	264.3
0.4186	640.8	0.9580	176.6
0.4519	640.0	0.9790	95.4
0.4882	636.6		

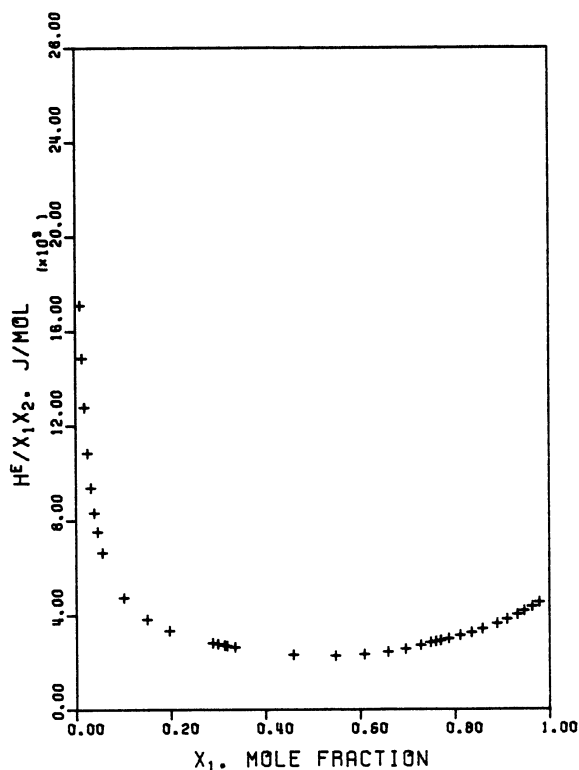
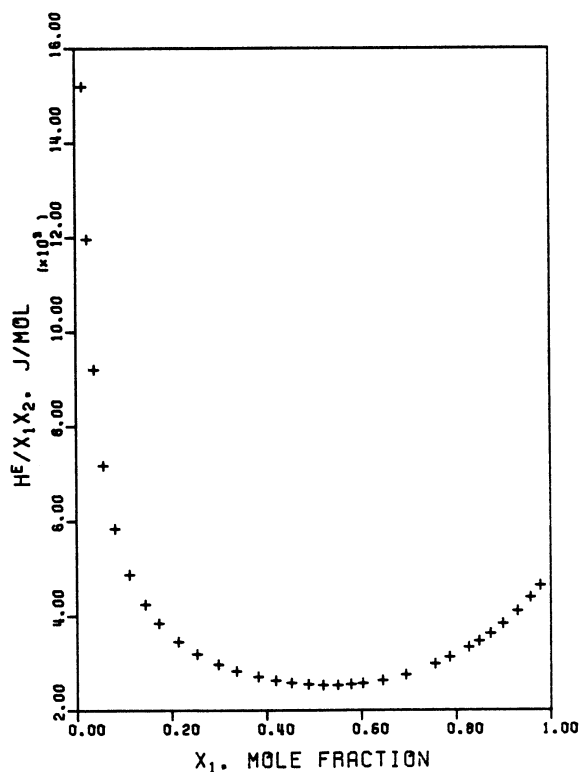

 FIG. 14. Data of Savini *et al.* for the methanol(1) + hexane(2) system at 303.15 K, MRL 1080.

 FIG. 15. Data of Savini *et al.* for the methanol(1) + hexane(2) system at 306.85 K, MRL 1080.

Table 20. Data set for the miscible methanol(1) + hexane(2) system at 313.15 K

SYSTEM. Methanol(1) + Hexane(2)			
TEMPERATURE. 313.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. B		SCATTER. Good	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.4 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.3 %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0294	384.2	0.7945	547.4
0.0985	531.0	0.8140	521.9
0.2127	656.8	0.8339	492.3
0.3515	712.2	0.8568	452.9
0.4581	714.9	0.8775	411.4
0.5510	697.8	0.9023	354.2
0.6163	676.3	0.9252	291.8
0.6629	654.7	0.9442	231.6
0.6957	635.4	0.9636	161.5
0.7280	612.3	0.9762	110.0
0.7511	592.7		

Table 21. Data set for the miscible methanol(1) + hexane(2) system at 318.15 K

SYSTEM. Methanol(1) + Hexane(2)			
TEMPERATURE. 318.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. B		SCATTER. Good	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.7 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.1 %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0152	264.1	0.7208	655.1
0.0249	345.4	0.7465	630.6
0.0322	388.2	0.7873	583.9
0.0390	421.2	0.8040	561.0
0.1438	657.2	0.8223	533.0
0.2797	758.8	0.8395	504.0
0.3850	780.5	0.8656	453.4
0.4822	772.3	0.8876	404.0
0.5603	749.9	0.9108	343.3
0.6180	724.8	0.9337	274.5
0.6576	702.4	0.9535	204.7
0.6906	679.1	0.9700	139.2

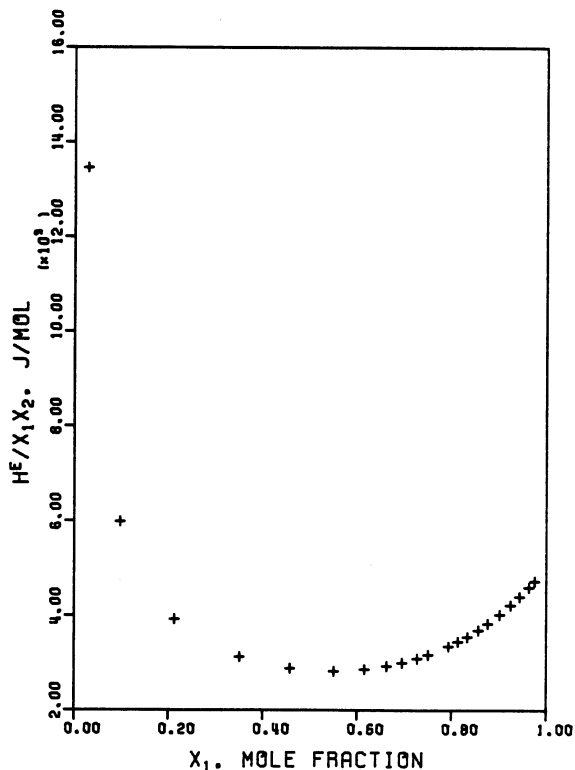
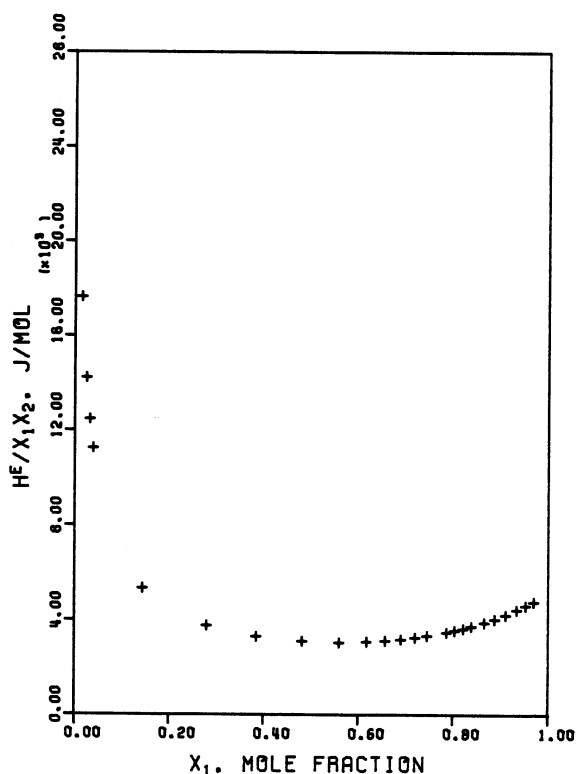
FIG. 16. Data of Savini *et al.* for the methanol(1) + hexane(2) system at 313.15 K, MRL 1080.FIG. 17. Data of Savini *et al.* for the methanol(1) + hexane(2) system at 318.15 K, MRL 1080.

Table 22. Data set for the miscible methanol(1) + hexane(2) system at 323.15 K

SYSTEM. Methanol(1) + Hexane(2)			
TEMPERATURE. 323.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. B		SCATTER. Good	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0284	410.6	0.7438	669.7
0.1044	663.7	0.7848	619.3
0.2272	804.1	0.8016	594.2
0.3714	848.7	0.8225	559.9
0.4759	837.3	0.8418	523.9
0.5622	806.6	0.8664	472.0
0.6206	775.1	0.8891	417.1
0.6634	745.1	0.9137	348.8
0.6959	718.3	0.9408	259.8
0.7240	691.1	0.9622	177.3

Table 23. Selected data set for the methanol(1) + toluene(2) system at 298.15 K

SYSTEM. Methanol(1) + Toluene(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0220	267.5	0.5410	590.8
0.0430	404.7	0.5800	558.2
0.0790	535.0	0.6190	521.0
0.1340	635.0	0.6570	483.8
0.1970	693.1	0.7150	418.7
0.2580	704.8	0.7740	346.6
0.3220	704.8	0.8210	281.4
0.3810	688.5	0.8750	204.7
0.4280	667.6	0.9290	121.0
0.4860	632.7	0.9760	41.9
0.5020	621.0		

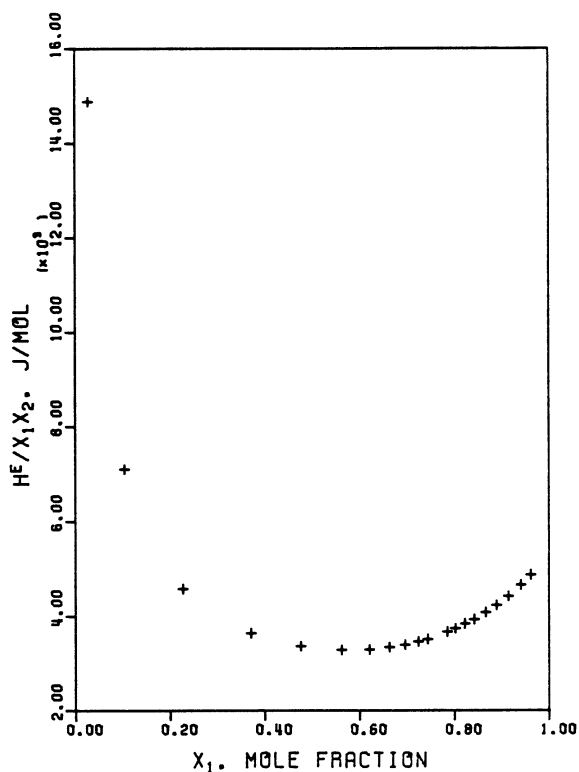
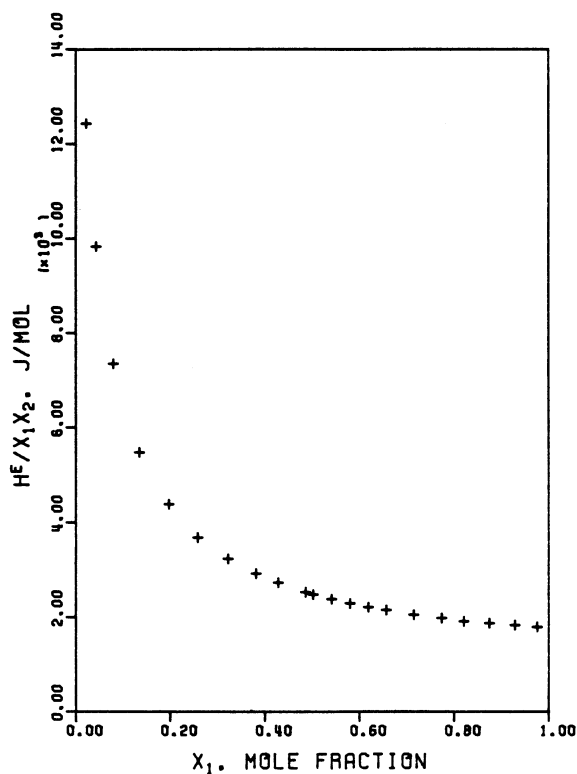

 FIG. 18. Data of Savini *et al.* for the methanol(1) + hexane(2) system at 323.15 K, MRL 1080.

 FIG. 19. Data of Mrazek *et al.* for the methanol(1) + toluene(2) system at 298.15 K, MRL 686.

Table 24. Selected data set for the methanol(1) + toluene(2) system at 308.13 K

SYSTEM. Methanol(1) + Toluene(2)			
TEMPERATURE. 308.13 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0400	428.0	0.5000	758.3
0.0710	583.8	0.5540	709.4
0.1040	686.2	0.6010	660.6
0.1540	774.6	0.6390	616.4
0.2230	835.0	0.6710	576.8
0.2710	849.0	0.7200	504.7
0.3060	853.6	0.7700	428.0
0.3400	849.0	0.8180	348.9
0.3790	835.0	0.8700	260.5
0.4140	816.4	0.9230	160.5
0.4610	788.5	0.9730	58.1

Table 25. Selected data set for the methanol(1) + toluene(2) system at 318.15 K

SYSTEM. Methanol(1) + Toluene(2)			
TEMPERATURE. 318.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. A		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		0.0 %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		0.0 %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0430	490.8	0.5000	890.9
0.0580	583.8	0.5500	839.7
0.0870	718.7	0.5960	783.9
0.1190	818.8	0.6340	732.7
0.1630	907.1	0.6660	688.5
0.2200	965.3	0.7140	611.7
0.2720	988.6	0.7750	502.4
0.3070	993.2	0.8480	355.9
0.3410	988.6	0.9120	216.3
0.3720	979.2	0.9710	74.4
0.4420	939.7		

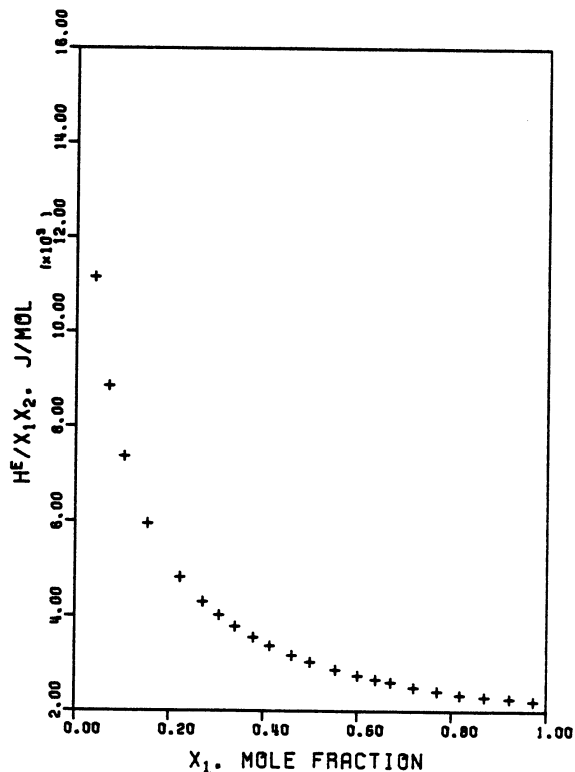
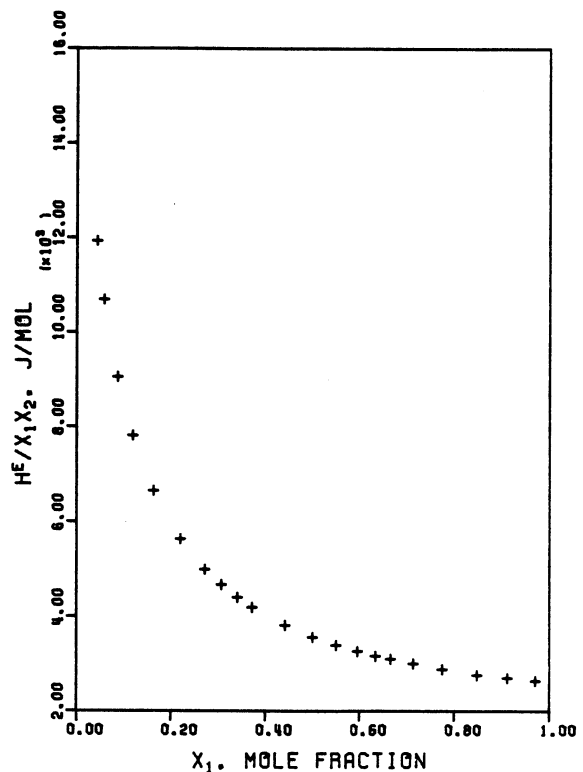
FIG. 20. Data of Mrazek *et al.* for the methanol(1) + toluene(2) system at 308.13 K, MRL 686.FIG. 21. Data of Mrazek *et al.* for the methanol(1) + toluene(2) system at 318.15 K, MRL 686.

Table 26. Partial data set for the partially miscible methanol(1) + heptane(2) system at 298.15 K

SYSTEM. Methanol(1) + Heptane(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.1013 MPa	
QUALITY RATING. DE		SCATTER. Marginal	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Savini, C. G., Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, New York, 1963. (MRL 5308)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0004	8.3	0.0979	405.6
0.0008	17.9	0.1091	420.2
0.0011	26.1	0.1219	433.0
0.0015	33.6	0.1332	447.7
0.0019	43.4	0.1453	456.9
0.0023	52.0	0.1548	460.0
0.0028	61.5	0.1659	463.0
0.0033	70.9	0.1765	467.9
0.0038	80.1	0.1850	470.4
0.0045	91.5	0.1955	471.6
0.0050	100.4	0.2058	471.0
0.0056	109.1	0.2107	474.4
0.0080	141.9	0.2276	469.9
0.0270	256.7	0.2381	469.5
0.0416	301.4	0.2619	466.3
0.0524	328.3	0.2838	463.4
0.0637	351.7	0.3047	460.9
0.0750	371.5	0.4276	443.3
0.0870	390.8	0.5129	431.0

Table 27. Selected data set for the partially miscible methanol(1) + heptane(2) system at 303.15 K

SYSTEM. Methanol(1) + Heptane(2)			
TEMPERATURE. 303.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0107	181.8	0.6103	468.1
0.0153	221.1	0.6536	459.0
0.0209	255.1	0.6950	450.2
0.0285	289.4	0.7243	444.2
0.0327	304.8	0.7600	436.5
0.0371	324.0	0.8759	409.3
0.0771	414.6	0.8986	373.4
0.1246	485.1	0.9196	322.1
0.1973	544.8	0.9407	259.6
0.3356	525.6	0.9638	174.9
0.4566	500.1	0.9819	94.2
0.5473	481.3	0.9939	33.3

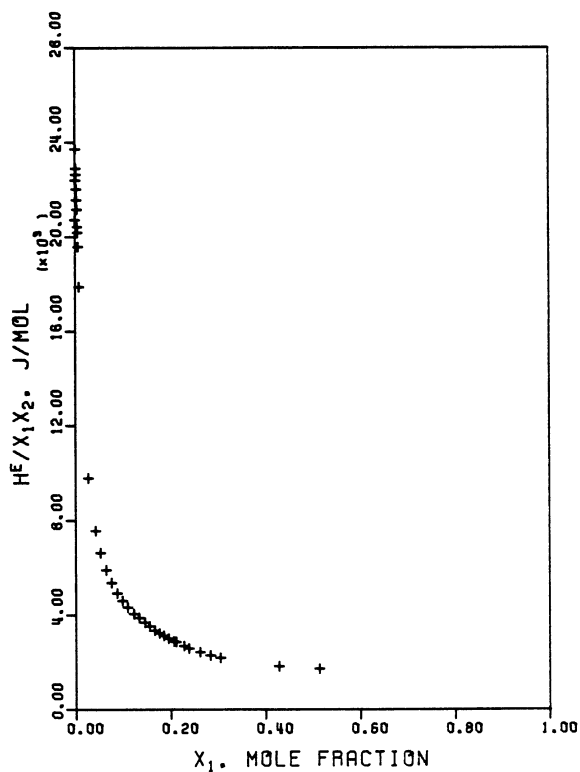


FIG. 22. Data of Savini for the methanol(1) + heptane(2) system at 298.15 K, MRL 5308.

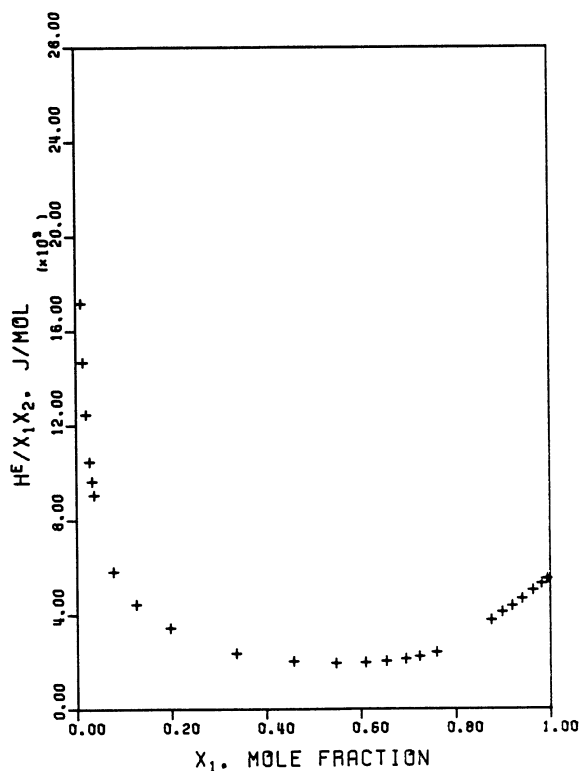

 FIG. 23. Data of Savini *et al.* for the methanol(1) + heptane(2) system at 303.15 K, MRL 1080.

Table 28. Selected data set for the partially miscible methanol(1) + heptane(2) system at 318.15 K

SYSTEM. Methanol(1) + Heptane(2)			
TEMPERATURE. 318.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0204	324.3	0.7724	594.6
0.0249	360.8	0.8309	558.4
0.0288	387.6	0.8469	531.1
0.0383	442.9	0.8674	490.5
0.0734	560.0	0.8843	452.7
0.1185	653.9	0.9040	400.8
0.1934	741.8	0.9173	360.9
0.2820	792.6	0.9307	317.1
0.3979	764.7	0.9430	272.6
0.4694	733.2	0.9537	229.7
0.5580	693.4	0.9645	183.9
0.6233	663.2	0.9711	153.0
0.6852	634.9	0.9784	117.4
0.7255	616.6	0.9841	87.3

Table 29. Selected data set for the partially miscible methanol(1) + heptane(2) system at 333.15 K

SYSTEM. Methanol(1) + Heptane(2)			
TEMPERATURE. 333.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. Savini, C. G., Winterhalter, D. R., Van Ness, H. C., Journal of Chemical and Engineering Data, 10(2), 171 (1965). (MRL 1080)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0266	461.7	0.6533	904.5
0.0298	495.3	0.6990	855.7
0.0326	520.5	0.7342	812.2
0.0348	538.8	0.8187	676.5
0.0429	601.6	0.8376	637.2
0.0505	644.9	0.8527	601.9
0.0668	723.6	0.8686	561.9
0.0915	809.4	0.8854	514.9
0.1495	933.2	0.9040	456.4
0.2352	1026.0	0.9225	390.8
0.3271	1061.0	0.9426	309.2
0.4135	1055.0	0.9594	231.7
0.4794	1031.0	0.9756	147.4
0.5457	993.3	0.9897	65.4
0.6103	944.6		

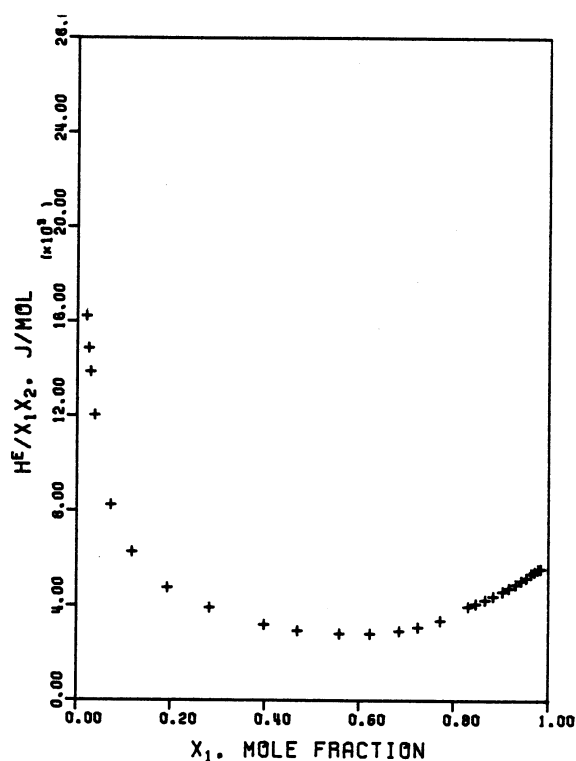
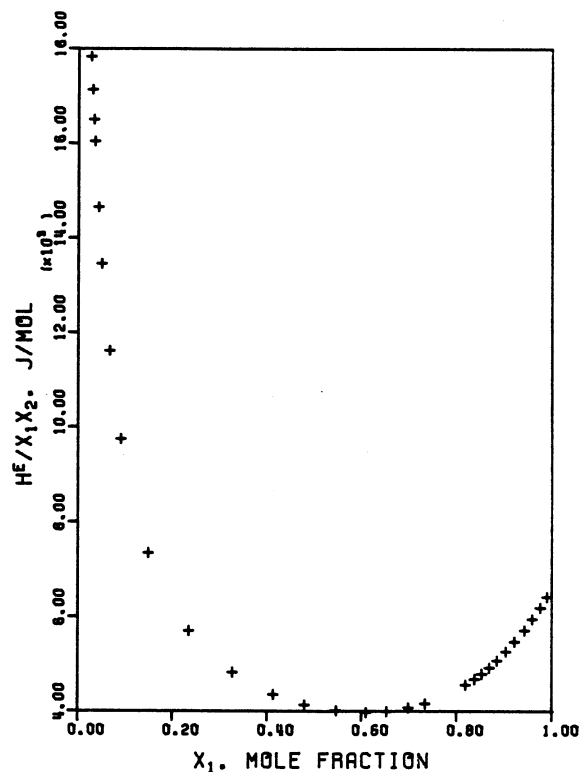
FIG. 24. Data of Savini *et al.* for the methanol(1) + heptane(2) system at 318.15 K, MRL 1080.FIG. 25. Data of Savini *et al.* for the methanol(1) + heptane(2) system at 333.15 K, MRL 1080.

Table 30. Only data set for the methanol(1) + ethylbenzene(2) system at 298.15 K

SYSTEM. Methanol(1) + Ethylbenzene(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0280	316.3	0.4750	693.1
0.0390	388.4	0.5160	667.6
0.0520	453.6	0.5520	642.0
0.0710	523.3	0.6020	600.1
0.0980	590.8	0.6450	562.9
0.1270	642.0	0.7090	493.1
0.1670	688.5	0.7530	437.3
0.2140	721.1	0.8110	353.6
0.2670	739.7	0.8580	281.4
0.3260	742.0	0.9210	169.8
0.3760	732.7	0.9610	88.4
0.4260	716.4		

Table 31. Only data set for the methanol(1) + ethylbenzene(2) system at 308.15 K

SYSTEM. Methanol(1) + Ethylbenzene(2)			
TEMPERATURE. 308.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$. -- %			
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$. -- %			
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0380	435.0	0.5040	814.1
0.0520	521.0	0.5440	781.5
0.0700	609.4	0.5980	728.0
0.0950	693.1	0.6410	679.2
0.1270	765.3	0.7050	597.8
0.1660	825.7	0.7730	486.1
0.2130	865.3	0.8140	416.4
0.2660	888.5	0.8600	328.0
0.3260	893.2	0.9220	195.4
0.3880	879.2	0.9650	90.7
0.4500	851.3		

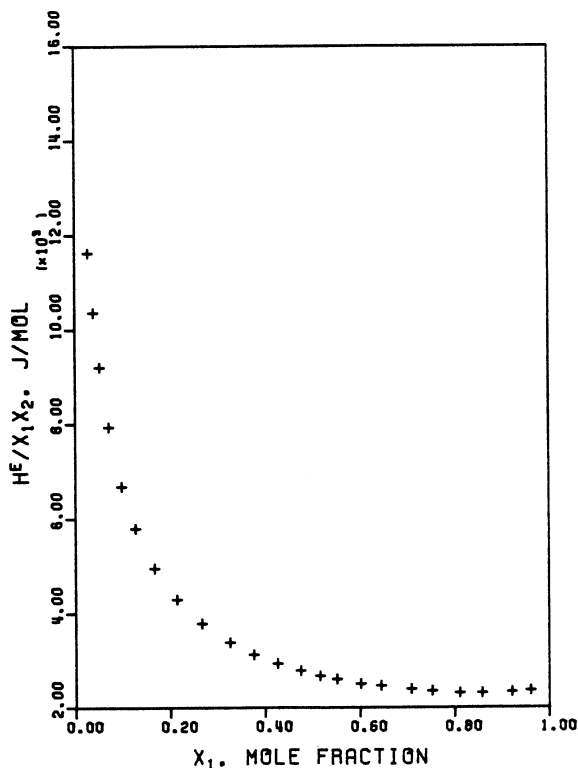
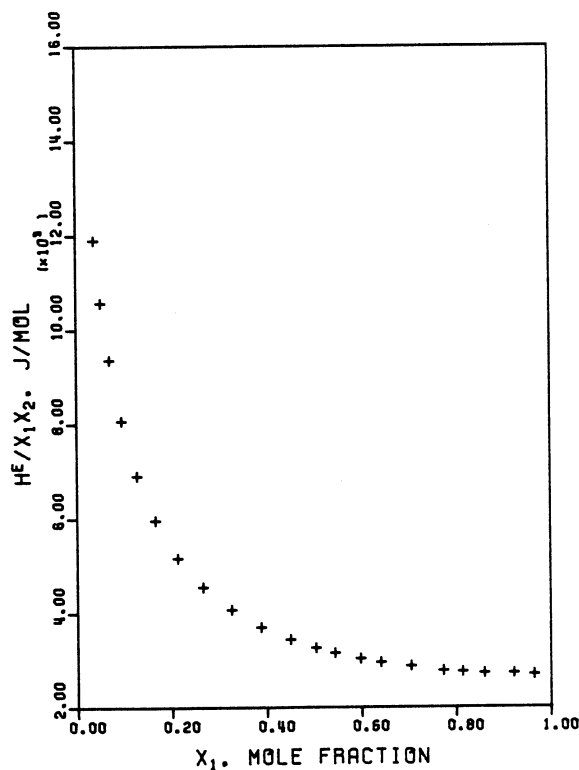
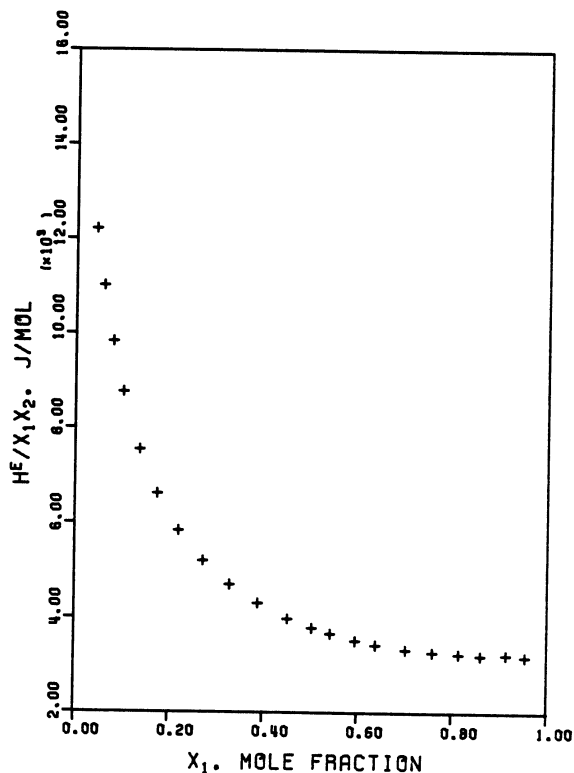
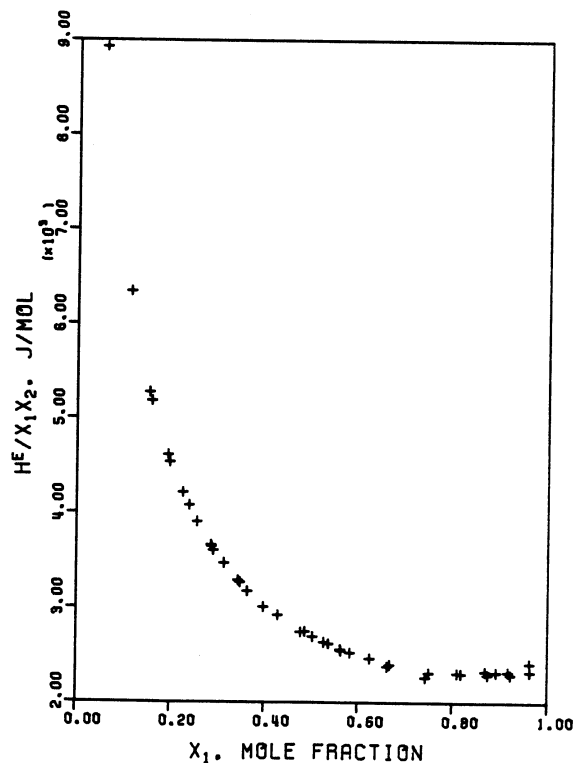

 FIG. 26. Data of Mrazek *et al.* for the methanol(1) + ethylbenzene(2) system at 298.15 K, MRL 686.

 FIG. 27. Data of Mrazek *et al.* for the methanol(1) + ethylbenzene(2) system at 308.15 K, MRL 686.

Table 32. Only data set for the methanol(1) + ethylbenzene(2) system at 318.15 K

SYSTEM. Methanol(1) + Ethylbenzene(2)			
TEMPERATURE. 318.15 K		PRESSURE. 0.2100 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Mrazek, R. V., Van Ness, H. C., AIChE Journal, 7, 190 (1961). (MRL 686)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0430	502.4	0.5040	946.7
0.0600	621.0	0.5430	909.5
0.0800	723.4	0.5960	846.7
0.1020	802.5	0.6390	790.8
0.1370	890.9	0.7030	695.5
0.1750	956.0	0.7600	597.8
0.2200	1002.5	0.8150	488.5
0.2720	1030.4	0.8610	383.8
0.3290	1037.4	0.9150	251.2
0.3890	1023.4	0.9550	137.2
0.4520	986.2		

Table 33. Only data set for the methanol(1) + para-xylene (2) system at 298.15 K

SYSTEM. Methanol(1) + p-Xylene(2)			
TEMPERATURE. 298.15 K		PRESSURE. 0.1700 MPa	
QUALITY RATING. ABC		SCATTER. Excellent	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.25$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.50$.		-- %	
DEVIATION FROM HE VS. 1/T CURVE AT $x(1) = 0.75$.		-- %	
REFERENCE. Christensen, J. J., Rossiter, B. E., O'Neill, T. K., Hanks, R. W., Journal of Chemical Thermodynamics, 10(9), 829 (1978). (MRL 41007)			
x(1) mole fraction	EXCESS ENTHALPY J/mol	x(1) mole fraction	EXCESS ENTHALPY J/mol
0.0574	482.9	0.5282	656.9
0.1135	637.7	0.5381	650.6
0.1530	682.9	0.5631	628.4
0.1581	689.4	0.5632	629.4
0.1926	717.1	0.5636	626.5
0.1970	717.7	0.5845	613.1
0.2253	736.0	0.6265	576.7
0.2394	743.3	0.6633	531.7
0.2564	744.4	0.6677	532.5
0.2860	747.9	0.7437	431.4
0.2867	745.8	0.7508	433.1
0.2914	744.4	0.8110	354.2
0.3142	747.5	0.8188	342.2
0.3437	742.3	0.8698	263.6
0.3481	742.3	0.8755	250.3
0.3645	735.9	0.8931	221.4
0.3981	721.6	0.9182	174.8
0.4291	716.0	0.9234	162.4
0.4785	684.4	0.9628	86.5
0.4866	686.5	0.9644	79.8
0.5037	674.2		

FIG. 28. Data of Mrazek *et al.* for the methanol(1) + ethylbenzene(2) system at 318.15 K, MRL 686.FIG. 29. Data of Christensen *et al.* for the methanol(1) + para-xylene(2) system at 298.15 K, MRL 41007.

(MRL 10643) data set below the critical solution temperature, and the Campbell *et al.* (MRL 5768) data set above the critical solution temperature, are shown. The Campbell *et al.* set is the only one above the critical solution temperature of 319.02 K. (Note: $A \times 10^3$ notation by the figure ordinate scale means the decimal must be shifted three places to the right.)

TABLE 34. Bibliography for excess enthalpy data

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6. Experimental Measurements Needed

With the benzene + cyclohexane system¹ and the cyclohexane + hexane system² both well established as test systems for new calorimeters, there is little incentive to acquire enough data to establish a methanol + hydrocarbon binary (such as methanol + benzene) as another test system.

The work by Van Ness and co-workers at the Rensselaer Polytechnic Institute, and by Christensen and co-workers at Brigham Young University, has produced more good data for the methanol + hydrocarbon binaries than is usually available for such a group of systems. However, both the correlator and the designer need H^E data over as wide a temperature range as possible, and that is the area where further experimental work is justified for those binaries for which one or more good data sets already exist.

To complete the data base for the correlator, additional data are needed for the methanol + cyclohexane system, both above and below the critical solution temperature. That is the only binary listed in Table 1 for which no reliable data set exists in the miscible region.

7. Other Data Set Tabulations

Only the best data sets 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.

8. Bibliography

Table 34 is the bibliography for the excess enthalpy data for the methanol + hydrocarbon system. The identifying numbers in Table 34 are the Laboratory's Master Reference List (MRL) numbers. The MRL numbers relate the literature documents listed in Table 34 to the individual data sets listed in Table 1.

Sometimes documents report data in graphical form only. Even though such data sets cannot be transcribed and processed, their citations usually are included in Table 34 in order to provide comprehensive coverage of the literature data.

9. Acknowledgments

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10. References

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