

Phase Equilibria in the Systems Methyl 1,1-Dimethylethyl Ether + Benzene and + Toluene

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Pure-component vapor pressures and vapor–liquid equilibrium data at 94 kPa have been determined for the binary systems methyl 1,1-dimethylethyl ether + benzene and methyl 1,1-dimethylethyl ether + toluene. The systems exhibit regular behavior and a slight positive deviation from ideality, and no azeotrope is present. The data were correlated by the Wisniak–Tamir equation, and the appropriate parameters are reported.

The Reformulated Gasoline Program of the United States requires that gasoline must fulfill strict requirements on ozone-forming and air toxic emissions. These goals are achieved today by addition of oxygenates such as methyl 1,1-dimethylethyl ether (MTBE), ethyl 1,1-dimethylethyl ether (ETBE), methanol, and ethanol. MTBE is the primary oxygenated compound used around the world. Although aromatics such as benzene and toluene may be present in small concentrations in a typical gasoline, they represent fundamental examples of mixtures of MTBE with an aromatic compound. Vapor–liquid equilibrium data for the system MTBE + benzene have been reported at (323.17, 343.15, and 363.05) K by Jin et al. (1985) and at 313.15 K by Lozano et. (1997). For the system MTBE + toluene, vapor–liquid equilibrium data have been reported at 363.15 K by Plura et al. (1979). The isothermal data published in the literature suggest that both systems present small positive deviations from ideality, behave essentially as regular solutions, and present no azeotrope. The present work was undertaken to measure vapor–liquid equilibria (VLE) data for the title systems for which isobaric data are not available. It is also part of our experimental program to determine vapor–liquid equilibrium data for binary and ternary systems composed of an oxygenate and one or more gasoline components.

Experimental Section

Purity of Materials. Methyl 1,1-dimethylethyl ether (99.95 mass %), benzene (99.9+ mass %), and toluene (99.80 mass %) were purchased from Aldrich. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1. Appropriate precautions were taken when handling MTBE, in order to avoid peroxide formation, and benzene, a human carcinogen.

Apparatus and Procedure. An all-glass vapor–liquid equilibrium apparatus model 601, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the

Table 1. Mole Percent GLC Purities (mass %), Refractive Index n_D at the Na D Line, and Normal Boiling Points T of Pure Components

component (purity/mass %)	$n_D(293.15\text{ K})$	T/K
methyl 1,1-dimethylethyl ether (99.95)	1.369 22 ^a	327.85 ^a
	1.369 0 ^b	328.35 ^b
benzene (99.96)	1.500 72 ^a	353.18 ^a
	1.501 11 ^c	353.21 ^c
toluene (99.80)	1.496 88 ^a	383.65 ^a
	1.496 94 ^c	383.76 ^c

^a Measured. ^b TRC Tables, a-6040. ^c TRC Tables, a-3200.

equilibrium determinations. In this circulation-method apparatus, the solution is heated to its boiling point by a 250-W immersion heater (Cottrell pump). The vapor–liquid mixture flows through an extended contact line that guarantees an intense phase exchange and then enters a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The temperature in the VLE still has been determined with a Systemtechnik S1224 digital temperature meter and a Pt100 Ω probe calibrated at the Swedish Statens Provningsanstalt with the IPTS-68 temperature scale. The accuracy is estimated as ± 0.02 K. The total pressure of the system is controlled by a vacuum pump capable to work under vacuum up to 0.25 kPa. The pressure has been measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22-mm diameter precision tubing with catheterometer reading); the overall accuracy is estimated as ± 0.02 kPa. On the average the system reaches equilibrium conditions after 1–2 h of operation. Samples, taken by syringing 1.0 μL after the system had achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a Tsp model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector, and detector temperatures were (343.15, 413.15, 493.15) K for the system MTBE + benzene and

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Table 2. Experimental Vapor–Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + Benzene (2) at 94 kPa

<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	γ_1	γ_2	$-B_{11}/\text{cm}^3\text{mol}^{-1}$	$-B_{22}/\text{cm}^3\text{mol}^{-1}$	$-B_{12}/\text{cm}^3\text{mol}^{-1}$
350.77	0.000	0.000		1.000			
350.07	0.015	0.037	1.199	0.999	1005	988	985
349.24	0.034	0.079	1.174	0.998	1011	994	991
348.56	0.051	0.115	1.149	0.997	1016	999	995
347.98	0.064	0.142	1.148	0.998	1021	1003	1000
347.15	0.085	0.181	1.122	1.001	1027	1010	1006
346.80	0.093	0.197	1.123	1.001	1029	1012	1008
345.76	0.121	0.246	1.112	1.002	1037	1020	1016
344.96	0.146	0.285	1.098	1.001	1043	1026	1022
343.82	0.177	0.332	1.085	1.007	1052	1035	1031
342.64	0.210	0.387	1.103	1.001	1062	1044	1040
340.91	0.267	0.462	1.088	1.000	1076	1058	1053
339.35	0.323	0.529	1.074	0.999	1088	1070	1066
337.15	0.412	0.614	1.043	1.014	1107	1089	1084
335.43	0.480	0.670	1.029	1.037	1122	1103	1098
333.40	0.574	0.744	1.014	1.057	1139	1121	1116
332.07	0.632	0.786	1.014	1.067	1151	1133	1127
330.54	0.714	0.847	1.015	1.035	1165	1147	1141
328.98	0.802	0.900	1.008	1.029	1180	1162	1155
327.67	0.885	0.943	0.997	1.060	1192	1174	1168
326.80	0.944	0.973	0.992	1.058	1201	1183	1176
326.25	0.978	0.989	0.991	1.084	1206	1188	1181
326.06	0.992	0.996	0.988	1.251	1208	1190	1183
325.60	1.000	1.000	1.000				

(373.15, 423.15, 543.15) K for the system MTBE + toluene. Very good separation was achieved under these conditions, and calibration analyses were carried out with synthetic mixtures to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fits had a correlation coefficient R^2 better than 0.99 and a mole fraction standard deviation of 4×10^{-4} for the system MTBE + benzene and of 6×10^{-4} for the system MTBE + toluene. At least three analyses were made of each composition. Concentration measurements were accurate to better than ± 0.001 mole fraction.

Results

The temperature T and liquid-phase x_i and vapor-phase y_i mole fraction measurements at $P = 94$ kPa are reported in Tables 2 and 3 and Figures 1–4, together with the activity coefficients γ_i , which were calculated from the following equation (Van Ness and Abbott, 1982)

$$\ln \gamma_i = \ln \left(\frac{P y_i}{P_i^0 x_i} \right) + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + \frac{P}{2RT} \sum_k \sum_j y_j V_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

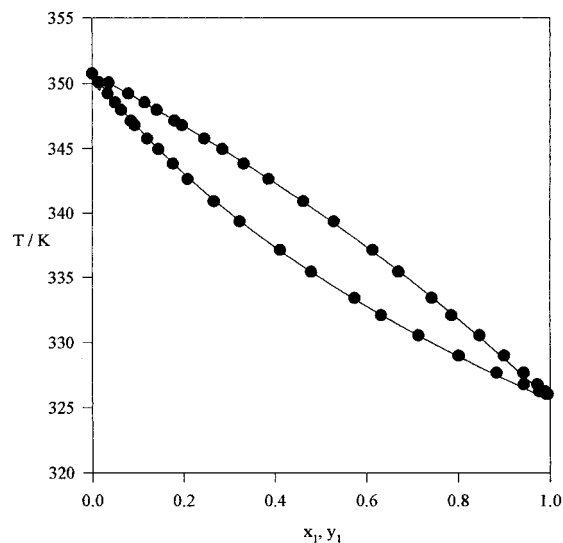
where T and P are the boiling point and the total pressure, V_i^L is the molar liquid volume of component i , P_i^0 is the pure-component vapor pressure, B_{ii} and B_{ij} are the second virial coefficients of the pure gases, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \quad (2)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure-component vapor pressures P_i^0 were determined experimentally as a function of the temperature, using the same equipment as that for obtaining the VLE data; the pertinent results appear in Table 4.

Table 3. Experimental Vapor–Liquid Equilibrium Data for Methyl 1,1-Dimethylethyl Ether (1) + Toluene (3) at 94 kPa

<i>T</i> /K	<i>x</i> ₁	<i>y</i> ₁	γ_1	γ_3	$-B_{11}/\text{cm}^3\text{mol}^{-1}$	$-B_{33}/\text{cm}^3\text{mol}^{-1}$	$-B_{13}/\text{cm}^3\text{mol}^{-1}$
381.04	0.000	0.000		1.000			
380.47	0.004	0.021	1.214	0.999	816	1221	998
378.74	0.017	0.083	1.165	0.996	826	1236	1010
377.24	0.029	0.132	1.137	0.996	834	1249	1020
375.24	0.046	0.193	1.117	0.998	845	1267	1034
373.00	0.064	0.260	1.128	0.996	857	1287	1050
370.62	0.085	0.328	1.125	0.994	871	1310	1068
369.13	0.098	0.366	1.133	0.994	880	1324	1079
367.07	0.118	0.420	1.130	0.990	892	1344	1095
364.86	0.141	0.474	1.127	0.988	906	1366	1112
362.89	0.163	0.516	1.113	0.992	918	1387	1128
360.71	0.187	0.557	1.107	1.000	932	1410	1146
358.93	0.209	0.595	1.102	0.996	944	1429	1161
357.55	0.225	0.621	1.108	0.994	953	1444	1173
355.77	0.252	0.653	1.090	0.999	965	1465	1189
353.12	0.291	0.696	1.077	1.009	983	1496	1213
350.83	0.326	0.731	1.072	1.016	1000	1523	1234
348.83	0.363	0.767	1.063	0.998	1014	1548	1253
345.66	0.428	0.809	1.037	1.020	1038	1589	1284
342.41	0.489	0.849	1.044	1.012	1063	1632	1317
340.53	0.530	0.873	1.046	0.988	1079	1658	1337
337.28	0.611	0.906	1.034	0.997	1106	1705	1373
335.18	0.670	0.928	1.028	0.980	1124	1737	1397
332.81	0.749	0.949	1.011	0.986	1145	1774	1425
330.53	0.811	0.967	1.020	0.938	1165	1810	1452
329.21	0.866	0.976	1.005	0.999	1178	1832	1469
327.79	0.919	0.985	0.999	1.099	1191	1856	1486
327.06	0.954	0.990	0.990	1.369	1198	1869	1496
326.37	0.979	0.993	0.990	1.974	1205	1881	1505
326.05	0.990	0.995	0.991	2.951	1208	1886	1509
325.60	1.000	1.000	1.000				

**Figure 1.** Boiling-point diagram for the system methyl 1,1-dimethylethyl ether (1) + benzene (2) at 94 kPa: experimental data (●); smoothed curve obtained from the regular model (—).

The measured vapor pressures were correlated using the Antoine equation

$$\log(P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \quad (3)$$

where the Antoine constants A_i , B_i , and C_i are reported in Table 5. The vapor pressures were correlated with an average percentual deviation in pressure (APDP) of 0.07% for methyl 1,1-dimethylethyl ether and 0.03% for toluene and benzene. The parameters presented in Table 5 predict

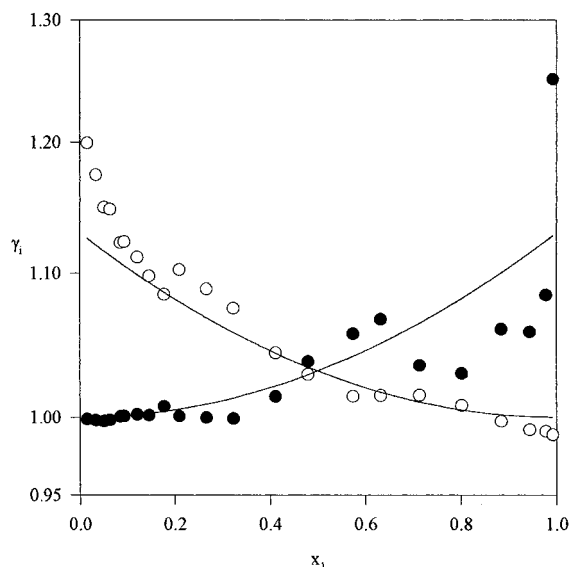


Figure 2. Activity-coefficient plot for the system methyl 1,1-dimethylethyl ether (1) + benzene (2) at 94 kPa: γ_1 calculated from experimental data (○); γ_2 calculated from experimental data (●); smoothed curve obtained from the regular model, eq 4 (—).

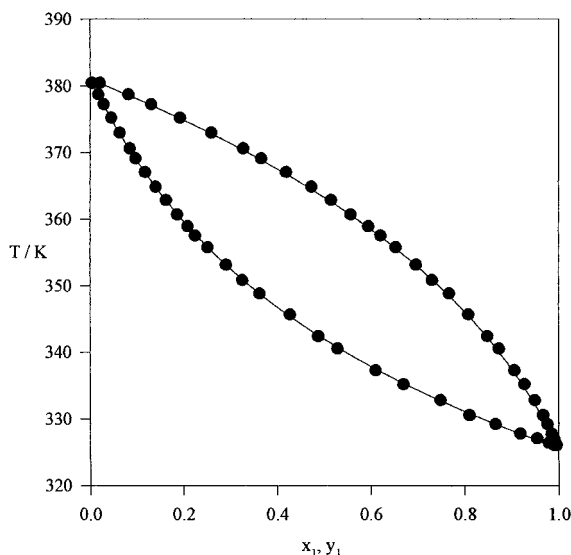


Figure 3. Boiling-point diagram for the system methyl 1,1-dimethylethyl ether (1) + toluene (3) at 94 kPa: experimental data (●); smoothed curve obtained from the regular model (—).

very well the experimental vapor pressures measured by Ambrose (1981) for benzene [APDP = 0.27%] and by Myers et al. (1979) for toluene [APDP = 0.49%], and by Wu et al. (1991) for MTBE [APDP = 0.53%]; however, larger differences were found with the data of Ambrose et al. (1976) for MTBE [APDP = 1.03%]. A graphical comparison of the vapor pressure data measured in this work and other references is presented in Figure 5. The molar virial coefficients B_{ij} and B_{jj} were estimated by the method of Hayden and O'Connell (1975), using the molecular parameters suggested by Prausnitz et al. (1980) and assuming the association and solvation parameters to be negligible. Critical properties of both components were taken from DIPPR (Daubert and Danner, 1989), and liquid volumes were estimated from the Rackett relation (Smith and Van Ness, 1987), which uses only critical properties of the compound. The last two terms in eq 1 contributed less than 6% to the activity coefficients in both binaries, and their influence was important only at very dilute concentrations.

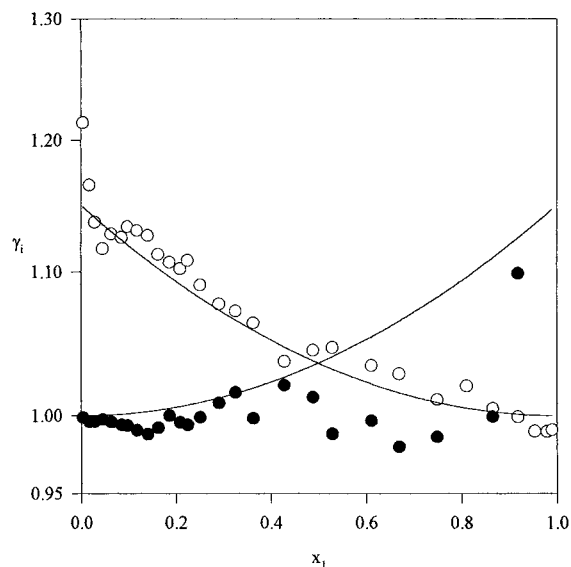


Figure 4. Activity-coefficient plot for the system methyl 1,1-dimethylethyl ether (1) + toluene (3) at 94 kPa: γ_1 calculated from experimental data (○); γ_2 calculated from experimental data (●); smoothed curve obtained from the regular model (—).

Table 4. Experimental Vapor Pressures Determined for the Pure Species

MTBE		benzene		toluene	
<i>T</i> /K	<i>P</i> /kPa	<i>T</i> /K	<i>P</i> /kPa	<i>T</i> /K	<i>P</i> /kPa
299.11	35.01	295.78	11.42	320.32	10.94
301.17	38.02	305.91	18.03	330.37	16.63
302.47	40.06	311.70	23.04	336.36	21.08
305.42	45.04	316.69	28.16	341.04	25.16
307.16	48.19	320.44	32.65	346.38	30.63
308.68	51.07	323.21	36.31	351.49	36.71
311.10	56.04	325.82	40.04	354.05	40.12
312.99	60.16	329.32	45.56	356.47	43.56
314.33	63.27	332.49	51.07	359.18	47.69
315.98	67.21	335.41	56.62	361.93	52.21
317.20	70.22	337.18	60.16	365.41	58.42
319.07	75.08	339.37	64.85	367.98	63.35
320.95	80.19	341.72	70.18	370.20	67.89
323.13	86.54	343.83	75.28	372.05	71.88
324.37	90.22	345.77	80.15	373.97	76.20
325.75	94.49	348.34	87.06	376.49	82.21
327.85	101.33	350.93	94.49	379.09	88.82
		353.18	101.33	380.92	93.71
				383.65	101.33

Table 5. Antoine Coefficients, Eq 3^a

compound	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether	5.860 78	1032.988	59.880
benzene	6.088 17	1243.256	48.640
toluene	6.223 72	1432.925	43.929

^a Obtained from the correlation of experimental vapor-pressure data.

The calculated activity coefficients are reported in Tables 2 and 3 and are estimated to be accurate to within 3%.

As seen from Tables 2 and 3 and Figures 2 and 4, the binary systems formed by methyl 1,1-dimethylethyl ether (1) + benzene (2), and + toluene (3) behave as essentially ideal, with activity coefficients slightly greater than unity. The thermodynamic consistency of the systems was checked using the point-to-point test proposed by Van Ness et al. (1973), as modified by Fredenslund et al. (1977); for both systems the consistency criteria is met with a one-parameter Legendre polynomial, or regular model, which reduces the functionality of the excess Gibbs energy G^E to

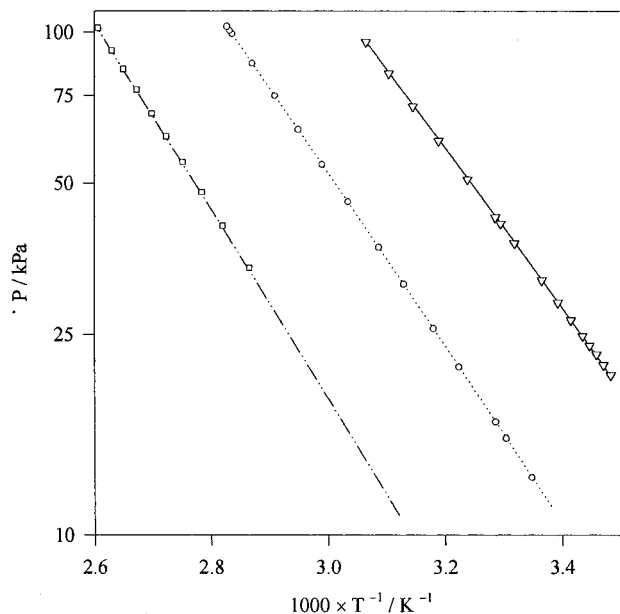


Figure 5. Comparison of correlated vapor pressures with other references: experimental data of Ambrose et al. (1976) for 1,1-dimethylethyl ether (∇); experimental data of Ambrose (1981) for benzene (\circ); experimental data of Myers et al. (1979) for toluene (\square). Predicted by eq 3 and parameters in Table 5 for methyl 1,1-dimethylethyl ether (—), for benzene (\cdots), and for toluene ($-\cdots-$).

Table 6. Consistency Results

binary system	100 MAD(y) ^a	MAD(P)/ kPa ^b	A ^c
methyl 1,1-dimethylethyl ether (1) + benzene (2)	0.31	0.33	0.122
methyl 1,1-dimethylethyl ether (1) + toluene (3)	0.36	0.37	0.139

^a MAD(y): mean average deviation in vapor-phase composition residuals, $y = y_{\text{calcd}} - y_{\text{exptl}}$. ^b MAD(P): mean average deviation in pressure, $P = P_{\text{calcd}} - P_{\text{exptl}}$. ^c A : parameter in eq 4.

the following symmetric relation

$$\frac{G^E}{RT} = Ax_1x_2 \quad (4)$$

for which consistency statistics, and the A parameter, are given in Table 6. In addition, consistency residuals are reasonably distributed, as can be seen in Figures 6 and 7.

Following the model of consistency (eq 4), it can be established that the systems measured in this work behave like regular solutions, in excellent agreement with the results of Plura et al. (1979) for the system methyl 1,1-dimethylethyl ether (1) + toluene (2) at 333.15 K, for which a value of $A = 0.137$ was found in eq 4. Although eq 4 provides satisfactory thermodynamic consistency according to the test criteria, as shown by Figures 6 and 7, the correlation does not fit the data of experimental activity coefficients too well, as depicted by Figures 2 and 4. Higher-order terms in the Legendre polynomial were rejected because although the consistency criteria was satisfied, the polynomial wriggle yielded an absurd dependence of activity coefficients in composition. The scattering of the experimental activity coefficients in Figures 2 and 4 may be explained in terms of the order of magnitude of the limiting activity coefficients (γ_i^∞) that, being close to the unity, are largely affected by experimental errors, which, in turn, are magnified by the narrow scale of the figures. It should be noted that in common nonideal

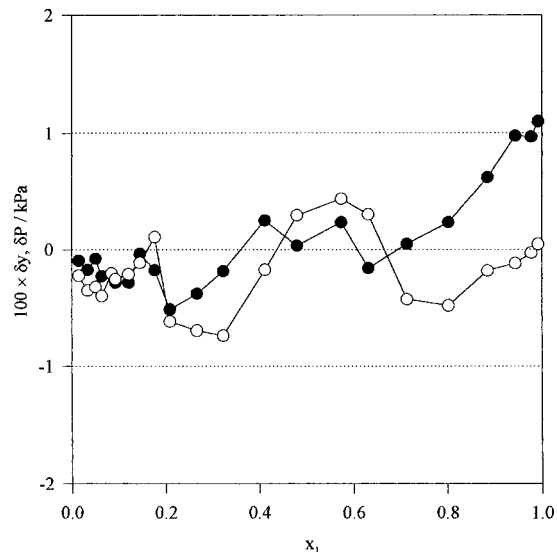


Figure 6. Consistency residuals for the system methyl 1,1-dimethylethyl ether (1) + benzene (2) at 94 kPa: pressure residuals, $P/\text{kPa} = P_{\text{calcd}} - P_{\text{exptl}}$ (\bullet); vapor-phase composition residuals, $y = y_{\text{calcd}} - y_{\text{exptl}}$ (\circ).

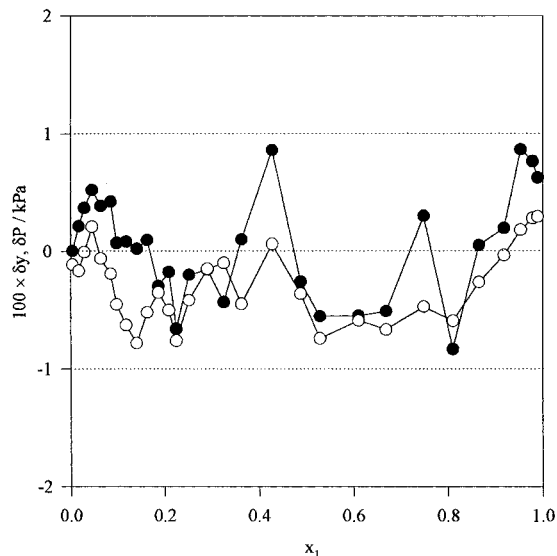


Figure 7. Consistency residuals for the system methyl 1,1-dimethylethyl ether (1) + toluene (3) at 94 kPa: pressure residuals, $P/\text{kPa} = P_{\text{calcd}} - P_{\text{exptl}}$ (\bullet). Vapor-phase composition residuals, $y = y_{\text{calcd}} - y_{\text{exptl}}$ (\circ).

Table 7. Coefficients in Correlation of Boiling Points, Eq 6, for the Systems Methyl 1,1-Dimethylethyl Ether (1) + Benzene (2) and Methyl 1,1-Dimethylethyl Ether (1) + Toluene (3) at 94 kPa, Average Deviation, and Root-Mean-Square Deviations in Temperature, rmsd

system	C_0	C_1	C_2	max dev/K ^a	avg dev/K ^b	rmsd/K ^c
1 + 2	-13.45	9.14	2.98	0.51	0.16	0.05
1 + 3	-46.53	28.68	-3.85	0.92	0.24	0.06

^a Maximum deviation ^b Average deviation. ^c Root-mean-square deviation.

systems (where $\gamma_i^\infty > 2$) the activity coefficient plot shows a wider scale, where absolute errors similar to those obtained in this work are masked by the order of magnitude of i .

The boiling-point temperatures of the solution at 94 kPa were correlated with its composition by the equation

proposed by Wisniak and Tamir (1976)

$$TK = x_1 T_1^0 + x_2 T_2^0 + x_1 x_2 \sum_{k=1}^m C_k (x_1 - x_2)^k \quad (5)$$

In this equation T_i^0/K is the boiling point of the pure component i at the operating pressure and m is the number of terms in the series expansion of $(x_1 - x_2)$. The various constants of eq 5 are reported in Table 7, which also contains information indicating the degree of goodness of the correlation.

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