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Isobaric Vapor−Liquid Equilibrium in the Systems 2-Methylpentane + Methyl 1,1-Dimethylethyl Ether, + Ethyl 1,1-Dimethylethyl Ether, and + Methyl 1,1-Dimethylpropyl Ether

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Vapor−liquid equilibrium data for the binary systems 2-methylpentane + methyl 1,1-dimethylethyl ether (MTBE), + ethyl 1,1-dimethylethyl ether (ETBE), and + methyl 1,1-dimethylpropyl ether (TAME) are reported at 101.3 kPa, including pure component vapor pressures. The measured systems, which deviate slightly from ideal behavior, can be described as symmetric regular solutions, and only the system 2-methylpentane + MTBE presents an azeotrope. Boiling points are correlated with the Wisniak−Tamir equation.

Introduction

Amendments of the U.S. Clean Air Act in 1990 have mandated that new gasoline formulations be sold in highly polluted areas of the country, with oxygenated gasolines being supplied particularly during the winter. Methyl 1,1-dimethylethyl ether (MTBE) is the primary oxygenated compound being used to reformulate gasolines to improve their octane rating and pollution-reducing capability. However, potential and documented contamination of water resources by MTBE has become a major public issue over the past few years, and restrictions in its use as additive are expected. MTBE readily dissolves in water, can move rapidly through soils and aquifers, is resistant to microbial decomposition, and is difficult to remove in water treatment. The U.S. Environmental Protection Agency has classified it as a possible human carcinogen. Finally, it is reported to have an unpleasant taste and odor in water. These factors have caused widespread concern that drinking water supplies and human health may be at risk, a situation that promotes further research with other ethers as potential additives. Methyl 1,1-dimethylpropyl ether (TAME) is an additive that is effective at reducing automotive CO emissions. In addition, ethanol-based ethers provide refiners with greater flexibility and economic advantages in making reformulated gasoline. Ethyl 1,1-dimethylethyl ether (ETBE) shows good characteristics as a gasoline additive, including low volatility, low water solubility, high octane value, excellent distillation curve response, large reductions in carbon monoxide (CO) and hydrocarbon (HC) emissions, and superior drive-ability.

Phase equilibrium data of oxygenated mixtures are important for predicting the vapor-phase composition that would be in equilibrium with hydrocarbon mixtures, and the systems reported here constitute examples of such mixtures. The present work was undertaken to measure vapor−liquid equilibrium (VLE) data of the entitled systems at 101.3 kPa, for which no data have been previously published.

Experimental Section

Chemicals. 2-Methylpentane (99+ mass %), MTBE (99.8 mass %, HPLC grade), and TAME (97 mass %) were purchased from Aldrich Ltd., and ETBE (96+ mass %) was purchased from Tokyo Chemical Industry Co. Ltd. (Japan). 2-Methylpentane and MTBE were used without further purification after chromatography failed to show any significant impurities. ETBE and TAME were purified to 99.9+ mass %, in a 1 m height × 30 mm diameter Normschliffgerätebau adiabatic column (packed with 3 × 3 mm SS spirals) working at a 1:100 reflux ratio. The properties and purity (as determined by GLC) of the pure components, as used for VLE measurements, appear in Table 1. Appropriate precautions were taken when handling ethers in order to avoid peroxide formation.

Apparatus and Procedure. The equilibrium vessel was an all-glass, dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Germany), is capable of handling pressures from 0.25 to 400 kPa and temperatures up to 523 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact during boiling and also in contact with the temperature sensing element. The equilibrium temperature was measured with a digital Fischer thermometer with an accuracy of ±0.1 K. The apparatus is equipped with two digital sensors of pressure: one for the low-pressure zone with an accuracy of ±0.01 kPa and another one for the high pressures with an accuracy of ±0.1 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. The manometers were calibrated using the vapor pressure of ultrapure water. The still was operated under constant pressure until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 60 min or longer. Then, samples of liquid and condensate were taken for analysis. The

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Table 1. Purities (mass %), Refractive Index n_D, and Normal Boiling Points T_b of Pure Components

component (purity/mass %)	n_D (298.15 K)		T_b (101.3 kPa)/K	
	exptl	lit.	exptl	lit.
2-methylpentane (99+)	1.3689	1.3687[a]	333.4	333.37[b]
methyl 1,1-dimethylethyl ether (99.80)	1.3664	1.3663[b]	328.2	328.11[c]
ethyl 1,1-dimethylethyl ether (99.95)	1.3730	1.3729[a]	345.8	345.86[d]
methyl 1,1-dimethylpropyl ether (99.97)	1.3858	1.3859[a]	359.3	359.33[c]

[a] DIPPR (Daubert and Danner, 1989). [b] TRC Tables, a-6040. [c] Martínez-Ageitos (1996). [d] Krähenbühl and Gmehling (1994).

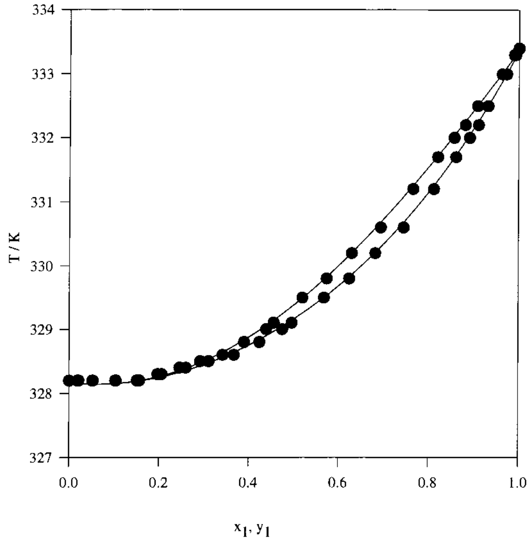

Figure 1. Experimental data for the system 2-methylpentane (1) + MTBE (2) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 (—).

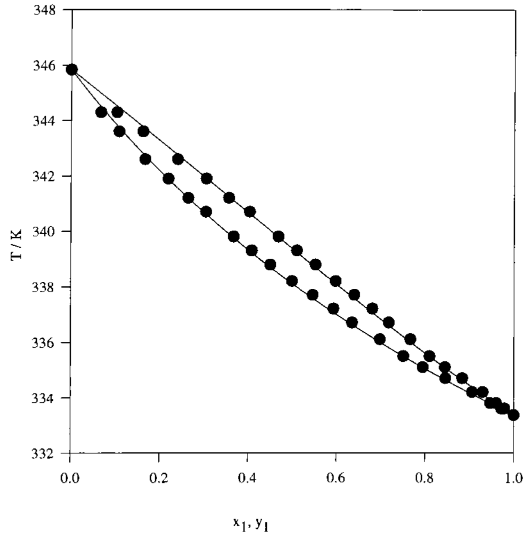

Figure 2. Experimental data for the system 2-methylpentane (1) + ETBE (3) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 (—).

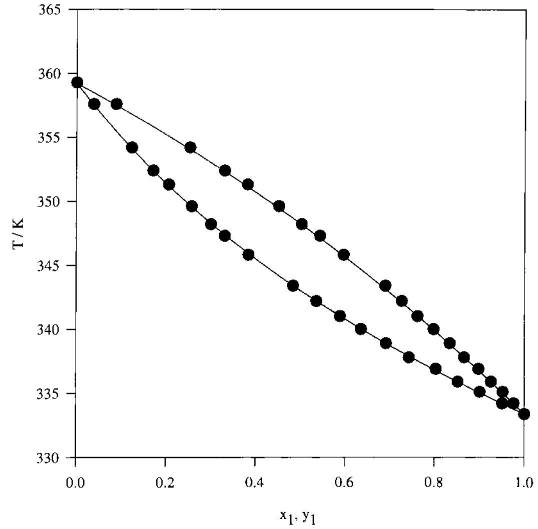

Figure 3. Experimental data for the system 2-methylpentane (1) + TAME (4) at 101.3 kPa. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 (—).

Table 2. Experimental Vapor–Liquid Equilibrium Data for 2-Methylpentane (1) + MTBE (2) at 101.3 KPa

T/K	x_1	y_1	γ_1	γ_2	$-B_{11}$/cm^3 mol^{-1}	$-B_{22}$/cm^3 mol^{-1}	$-B_{12}$/cm^3 mol^{-1}
328.2	0.000	0.000		1.000	1359	1187	1252
328.2	0.019	0.020	1.237	0.998	1359	1187	1252
328.2	0.020	0.021	1.234	0.998	1359	1187	1252
328.2	0.052	0.053	1.198	0.998	1359	1187	1252
328.2	0.104	0.103	1.164	1.000	1359	1187	1252
328.2	0.156	0.151	1.137	1.005	1359	1187	1252
328.3	0.206	0.197	1.120	1.007	1358	1186	1251
328.4	0.260	0.246	1.105	1.012	1356	1185	1250
328.5	0.311	0.292	1.092	1.017	1355	1184	1249
328.6	0.367	0.342	1.081	1.026	1354	1183	1248
328.8	0.424	0.390	1.060	1.038	1352	1182	1246
329.0	0.475	0.439	1.055	1.038	1349	1179	1243
329.1	0.496	0.456	1.049	1.048	1349	1179	1243
329.5	0.568	0.520	1.032	1.066	1344	1175	1239
329.8	0.624	0.574	1.027	1.077	1341	1172	1236
330.2	0.682	0.630	1.019	1.092	1337	1168	1232
330.6	0.745	0.694	1.014	1.113	1332	1165	1228
331.2	0.812	0.766	1.008	1.133	1326	1159	1222
331.7	0.861	0.821	1.003	1.154	1320	1155	1218
332.0	0.891	0.857	1.000	1.162	1316	1151	1214
332.2	0.911	0.882	1.003	1.170	1315	1150	1213
332.5	0.932	0.909	1.001	1.170	1312	1147	1210
333.0	0.973	0.963	1.001	1.181	1307	1143	1205
333.3	0.993	0.990	0.999	1.220	1303	1140	1202
333.4	1.000	1.000	1.000		1302	1139	1202

sample extractions were carried out with special syringes that allowed one to withdraw small volume samples (1.0 μL) in a system under partial vacuum or under overpressure conditions.

Analysis. Mole fractions of the liquid- and condensed vapor-phase samples were determined using a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60 m, 0.2 mm i.d., fused silica capillary column, SUPELCOWAX 10. The GC response peaks were integrated with a Hewlett-Packard 3396 integrator. Column, injector, and detector temperatures were 333, 373, and 413 K for all the systems. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. At least three analyses were made of each vapor composition; the standard deviation in the mole fraction was usually less than 0.001.

Results and Discussion

The temperature T, the liquid-phase x_i, and vapor-phase y_i mole fractions at 101.3 kPa are reported in Figures 1, 2, and 3 and in Tables 2, 3, and 4. Figures 4, 5, and 6 show the activity coefficients γ_i that, for the system 2-methyl-

Table 3. Experimental Vapor−Liquid Equilibrium Data for 2-Methylpentane (1) + ETBE (3) at 101.3 KPa (Vapor Phase Considered Ideal)

T/K	x_1	y_1	γ_1	γ_3
345.8	0.000	0.000		1.000
344.3	0.067	0.103	1.098	1.009
343.6	0.108	0.162	1.094	1.009
342.6	0.167	0.240	1.080	1.011
341.9	0.219	0.305	1.069	1.009
341.2	0.264	0.356	1.057	1.015
340.7	0.304	0.403	1.055	1.011
339.8	0.367	0.468	1.043	1.020
339.3	0.408	0.510	1.038	1.021
338.8	0.450	0.552	1.034	1.022
338.2	0.499	0.598	1.029	1.026
337.7	0.546	0.640	1.023	1.031
337.2	0.593	0.681	1.018	1.036
336.7	0.635	0.718	1.018	1.039
336.1	0.698	0.767	1.008	1.059
335.5	0.751	0.810	1.008	1.068
335.1	0.795	0.845	1.006	1.073
334.7	0.846	0.884	1.002	1.083
334.2	0.906	0.930	1.000	1.089
333.8	0.947	0.960	1.000	1.119
333.6	0.972	0.979	1.000	1.120
333.4	1.000	1.000	1.000	

Table 4. Experimental Vapor−Liquid Equilibrium Data for 2-Methylpentane (1) + TAME (4) at 101.3 kPa (Vapor Phase Considered Ideal)

T/K	x_1	y_1	γ_1	γ_4
359.3	0.000	0.000		1.000
357.6	0.038	0.088	1.132	0.996
354.2	0.123	0.253	1.105	0.995
352.4	0.171	0.331	1.093	0.998
351.3	0.206	0.382	1.081	0.997
349.6	0.257	0.452	1.076	0.998
348.2	0.300	0.503	1.068	1.005
347.3	0.331	0.544	1.074	0.994
345.8	0.384	0.597	1.062	1.002
343.4	0.484	0.690	1.046	0.997
342.2	0.536	0.727	1.031	1.017
341.0	0.589	0.762	1.020	1.043
340.0	0.636	0.798	1.020	1.034
338.9	0.692	0.834	1.013	1.044
337.8	0.743	0.866	1.014	1.049
336.9	0.803	0.898	1.000	1.075
335.9	0.852	0.926	1.003	1.076
335.1	0.901	0.952	1.000	1.073
334.2	0.951	0.976	0.999	1.119
333.4	1.000	1.000	1.000	

pentane (1) + MTBE (2), were calculated from the following equation (Van Ness and Abbott, 1982)

$$\ln \gamma_i = \ln\frac{y_iP}{x_iP_i^0} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^0)}{RT} + y_j^2\frac{\delta_{ij}P}{RT} \qquad (1)$$

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

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

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 1 is valid at low and moderate pressures when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration.

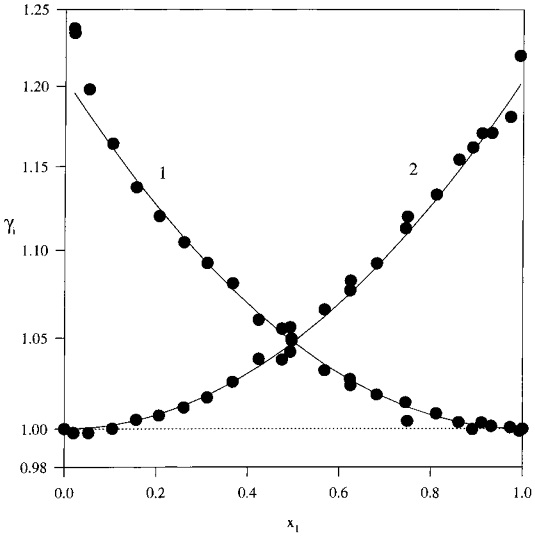

Figure 4. Activity coefficient plot of the system 2-methylpentane (1) + MTBE (2) at 101.3 kPa, calculated from experimental data. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 (—).

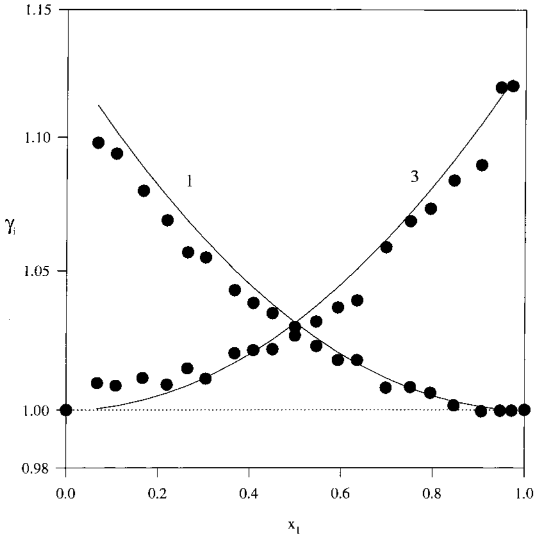

Figure 5. Activity coefficient plot of the system 2-methylpentane (1) + ETBE (3) at 101.3 kPa, calculated from experimental data. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 (—).

For the systems 2-methylpentane (1) + ETBE (3) and 2-methylpentane (1) + TAME (4), activity coefficients were calculated according to the ideal relation (Van Ness and Abbott, 1982)

$$\gamma_i = \frac{y_iP}{x_iP_i^0} \qquad (3)$$

because, on one hand, the low pressure makes this assumption reasonable and, on the other hand, as discussed by Reich et al. (1998a), the scarce physical information available for mixtures of ETBE and TAME with alkanes does not allow a reliable estimation of the second virial coefficient.

The pure component vapor pressure P_i^0 for ETBE was taken from Reich et al. (1998a). For 2-methylpentane,

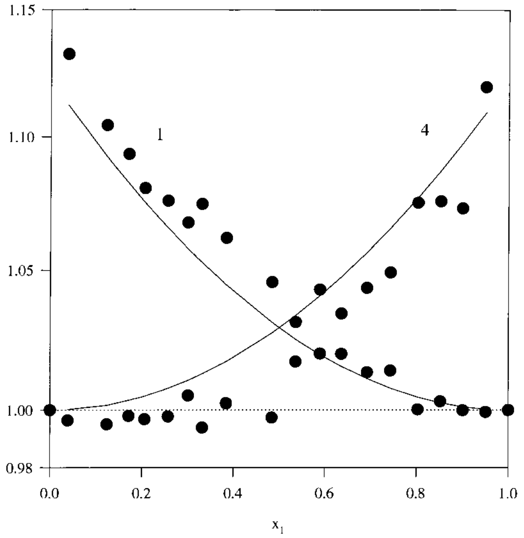

Figure 6. Activity coefficient plot of the system 2-methylpentane (1) + TAME (4) at 101.3 kPa, calculated from experimental data. Experimental data (●). Smoothed data using the regular model with the parameters given in Table 7, eq 5 (—).

Table 5. Experimental Vapor Pressures Determined for Pure Species

2-methylpentane		MTBE		TAME	
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
310.0	45.10	315.4	65.04	313.8	20.16
312.9	50.23	317.3	69.55	319.2	25.11
315.4	55.05	319.4	74.96	323.8	30.08
317.9	60.14	321.3	80.06	327.9	35.14
320.1	65.07	322.9	84.71	331.5	40.13
322.2	70.02	324.7	90.01	334.7	45.11
324.3	75.21	326.3	95.07	337.7	50.14
326.2	80.08	328.0	100.61	340.5	55.17
328.0	85.05	328.2	101.33	343.0	60.15
329.7	89.99	329.3	105.10	345.4	65.10
331.4	95.03	330.7	110.01	347.6	70.12
333.0	100.23	332.1	115.15	349.7	74.96
333.4	101.33	333.4	120.03	351.7	80.02
333.7	102.30	335.9	129.90	353.6	85.02
334.5	104.85	338.3	140.00	355.4	89.93
336.0	110.00	340.5	149.70	357.2	95.07
337.4	115.02	342.6	159.70	359.3	101.33
338.7	119.83	344.7	169.80	360.4	104.88
340.0	124.73	346.6	179.90	362.0	110.04
342.6	134.90	348.5	189.80		
343.8	139.90	350.2	199.70		
346.1	149.80	351.9	209.70		
347.2	154.70	353.5	219.70		
348.3	159.70	355.1	229.30		
349.3	164.40	356.7	239.70		
350.4	169.60	358.2	249.90		
353.4	184.80	359.6	260.00		
355.2	194.40	361.0	269.60		
356.2	199.80	362.4	279.80		
358.0	210.10	363.6	289.50		
358.9	215.20	365.0	300.00		
359.7	220.10				

MTBE, and TAME, pure component vapor pressures 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 5. The measured vapor pressures were correlated using the Antoine equation

$$\log(P_i^0/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \qquad (4)$$

whose parameters A_i, B_i, and C_i are reported in Table 6.

Table 6. Antoine Coefficients, Eq 4

compound	A_i	B_i	C_i
2-methylpentane[a]	6.106 78	1212.34	37.75
methyl 1,1-dimethylethyl ether[a]	6.349 91	1312.52	26.03
ethyl 1,1-dimethylethyl ether[b]	5.966 51	1151.73	55.06
methyl 1,1-dimethylpropyl ether[a]	6.232 18	1351.21	39.52

[a] Antoine's parameters were calculated from the experimental data in Table 5. [b] Reich et al. (1998a).

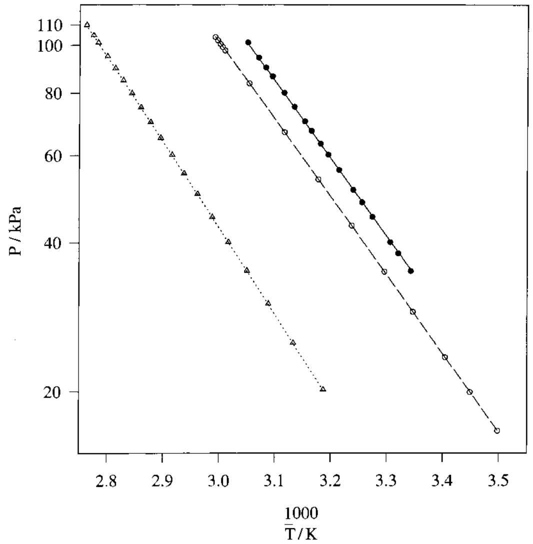

Figure 7. Comparison of correlated vapor pressures with other references. Experimental data reported by Boublík et al. (1984) for 2-methylpentane (○). Experimental data of Reich et al. (1998b) for MTBE (●). Experimental data of Krähenbuhl and Gmehling (1994) for TAME (△). Predicted by eq 4 and parameters in Table 6 for MTBE (—), for 2-methylpentane (---) and for TAME (···).

The vapor pressures were correlated with an mean absolute deviation [MADP] of 0.13% for 2-methylpentane, 0.07% for MTBE, and 0.05% for TAME. In addition, the parameters presented in Table 6 give a fair prediction of the experimental vapor pressures reported by Boublík et al. (1984) for 2-methylpentane (MADP = 0.12%), by Reich et al. (1998b) for MTBE (MADP = 0.37%), and by Krähenbühl and Gmehling (1994) for TAME (MADP = 0.30%), as shown in Figure 7. When required, the molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) assuming the association parameter η to be zero. Critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 1, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed less than 2% for the system 2-methylpentane (1) + MTBE (2) at 101.3 kPa; in general, their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Tables 2, 3, and 4 are estimated to be accurate to within ±2%. The results reported in these tables indicate that the measured systems exhibit moderate positive deviations from ideal behavior. An azeotrope composition is present in the system 2-methylpentane (1) + MTBE (2) at $x_1 \approx 0.08$ and $T = 328.2$ K.

The vapor–liquid equilibria data reported in Tables 2, 3, and 4 were found to be thermodynamically consistent by the point-to-point method of Van Ness et al. (1973), as modified by Fredenslund et al. (1977). Consistency was achieved using a one-parameter (zeroth-order) Legendre polynomial, the regular model, which reduces the func-

Table 7. Consistency Test for the Various Experimental Systems Considered in VLE Measurements

system	A^a	$100 \times \text{MADy}_1{}^b$	MADP^c/kPa
1 + 2	0.186	0.1	0.13
1 + 3	0.122	0.1	0.25
1 + 4	0.115	0.3	0.16

[a] Zeroth order Legendre polynomial (or Porter model) parameter in eq 5. [b] Average absolute deviation in vapor-phase composition. [c] Average absolute deviation in pressure.

Table 8. Coefficients in Correlation of Boiling Points, Eq 6. Average Deviation, Standard Deviation, and Maximum Deviation in Temperature

system	C_0	C_1	C_2	avg dev./K^a	σ/K^b	max dev./K^c
1 + 2	−6.611	−1.411	−0.724	0.03	0.03	0.11
1 + 3	−5.517	2.080	−2.065	0.03	0.03	0.11
1 + 4	−13.500	5.080	−0.823	0.04	0.04	0.11

[a] Average deviation. [b] Standard deviation. [c] Maximum deviation.

tionality of the excess Gibbs energy G^E to the following symmetric relation

$$G^E = Ax_1x_2 \qquad (5)$$

The parameter A in eq 5, together with the pertinent statistics required by the Fredenslund et al. test, are shown in Table 7 for the different systems considered in this work. From Table 7 it is concluded that eq 5 gives an excellent fit to the data.

The variation of activity coefficients with composition appears in Figures 4, 5, and 6. Inspection of these figures shows a symmetric trend of experimental activity coefficients that, in high dilution ranges, are approximately equivalent for both components in each binary system. In addition, from the figures, it is clear that activity coefficients exhibit intersection about the composition $x_1 = 0.5$ and are reasonably represented by eq 5. Thus, according to the present experimental data and the pertinent consistency test, it is concluded that the systems can be satisfactorily explained by regular solution behavior.

The boiling point temperatures of each system at 101.3 kPa were well-correlated with mole fractions by the equation proposed by Wisniak and Tamir (1976):

$$T/\text{K} = x_1T_1^0/\text{K} + x_2T_2^0/\text{K} + x_1x_2\sum_{k=0}^{m} C_k(x_1 - x_2)^k \qquad (6)$$

In this equation T_i^0/K is the boiling point of the pure component i and m is the number of terms used in the series expansion of $(x_1 - x_2)$, usually two. The various constants of eq 6 are reported in Table 8, with information indicating the goodness of fit of the correlation.

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