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

Sonia Loras, Antonio Aucejo,* and Rosa Muñoz

Departamento de Ingeniería Química, Falcultad de Química, Universitat de València,
Burjassot, 46100 Valencia, Spain

Consistent vapor−liquid equilibrium data for the binary and ternary systems methyl 1,1-dimethylethyl ether (MTBE) + 2-methyl-2-propanol (TBA) and methyl 1,1-dimethylethyl ether (MTBE) + 2-methylpentane + 2-methyl-2-propanol (TBA) are reported at 101.3 kPa at temperatures in the range 328 to 356 K. The results indicate that the systems deviate positively from ideality and that no azeotrope is present. The activity coefficients of the solutions were correlated with composition by Wilson, NRTL, and UNIQUAC models. It is shown that the models allow a very good prediction of the phase equilibrium of the ternary system using the pertinent parameters of the binary system. In addition, the Wisniak−Tamir relations were used for correlating bubble-point temperatures.

Introduction

Alcohol + ether + alkane systems are of interest as model mixtures for gasoline where the alcohol and the ether components act as antiknocking agents substituting the formerly used lead compounds to reduce pollution. Gasoline including about 7 to 15% methyl 1,1-dimethylethyl ether (MTBE) has been used for a high-performance premium gasoline. However, it has been recommended that gasoline additives be not only pure MTBE but also mixtures with alcohols for high-octane gasoline.

In this research, for the knowledge of the phase behavior of alkanes with MTBE and alcohol mixtures, isobaric vapor−liquid equilibrium (VLE) data of the ternary system MTBE (1) + 2-methylpentane (2) + 2-methyl-2-propanol (TBA) (3) and the constituent binary system MTBE (1) + TBA (3) at 101.3 kPa have been measured. Isobaric VLE data at 101.3 kPa for the binary system have been reported previously by Churkin et al. (1979) and by Zong et al. (1987). Both references present contradictory information about the system MTBE + TBA; in the first one nonazeotropic behavior is observed, while the results of Zong et al. indicate the presence of a minimum boiling point. For this reason, it has been considered of interest to measure the VLE data of this binary system at the same conditions. For the ternary system no VLE data have been previously published. VLE data at 101.3 kPa of the other binary constituent systems MTBE (1) + 2-methylpentane (2) and 2-methylpentane (2) + TBA (3) have already been reported by Aucejo et al. (1998) and Aucejo et al. (1999a), respectively. Both systems present positive deviations from ideality, and also each one presents a minimum-boiling azeotrope; the first one behaves essentially as a symmetric solution, and the second deviates remarkably from ideal behavior.

Experimental Section

Chemicals. MTBE (99.8 mass %, HPLC grade), 2-methylpentane (99+ mass %, GC grade), and TBA (99.5 mass %, HPLC grade) were purchased from Aldrich Chemical Co. The chemicals were used without further purification after chromatography failed to show any significant impurities. The densities of the pure liquids were measured at 298.15 K with an Anton Paar DMA 55 densimeter. The refractive indexes of the pure liquids were measured at 298.15 K in an Abbe refractometer, Atago 3T. Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are ±0.01 $kg·m^{-3}$ and ±0.0002, respectively. The experimental values of these properties and the boiling points are given in Table 1, together with those given in the literature.

Apparatus and Procedures. An all-glass Fischer LABODEST vapor−liquid equilibrium apparatus model 602/D, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. The equilibrium vessel was a dynamic-recirculating still described by Walas (1985), equipped with a Cottrell circulation pump. The still 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 sample extractions were carried out with special syringes, which withdrew small-volume samples (1.0 μL) from a system either under partial vacuum or under overpressure conditions.

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* Corresponding author. Fax: +34 96 386 48 98. E-mail: Antonio Aucejo@uv.es.

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Table 1. Density *d*, Refractive Index n_D, and Normal Boiling Point T_b of the Chemicals

	d(298.15 K)/kg·m^{-3}		n_D(298.15 K)		T_b(101.3 kPa)/K	
	exptl	lit.	exptl	lit.	exptl	lit.
methyl 1,1-dimethylethyl ether	735.20	735.28[a]	1.3664	1.3663[a]	328.2	328.11[b]
2-methylpentane	648.39	648.86[c]	1.3689	1.3687[a]	333.4	333.41[a]
2-methyl-2-propanol	775.40[d]	775.43[d,e]	1.3851	1.3859[a]	355.6	355.52[f]

[a] DIPPR (Daubert and Danner, 1989). [b] Martínez-Ageitos (1996). [c] Awwad and Pethrick (1983). [d] Measured at 303.15 K. [e] Hales et al. (1983). [f] Ambrose and Sprake (1970).

Table 2. Antoine Coefficients, Eq 1

compound	A_i	B_i	C_i
methyl 1,1-dimethylethyl ether[a]	14.6212	3022.19	26.03
2-methylpentane[a]	14.0614	2791.52	37.75
2-methyl-2-propanol[b]	14.8533	2649.89	96.69

[a] Aucejo et al. (1998). [b] Aucejo et al. (1999a).

Table 3. Experimental Vapor−Liquid Equilibrium Data for MTBE (1) + TBA (3) at 101.3 kPa

T/K	x_1	y_1	γ_1	γ_3	$-B_{11}$/ cm^3·mol^{-1}	$-B_{33}$/ cm^3·mol^{-1}	$-B_{13}$/ cm^3·mol^{-1}
328.20	1.000	1.000	1.000				
328.45	0.980	0.989	1.000	1.713	1138	1490	1295
328.75	0.949	0.973	1.006	1.656	1136	1485	1292
329.55	0.898	0.949	1.012	1.514	1129	1473	1284
330.25	0.846	0.926	1.025	1.399	1123	1463	1278
331.15	0.793	0.902	1.036	1.322	1115	1450	1269
331.95	0.743	0.880	1.053	1.257	1109	1438	1262
332.75	0.688	0.856	1.079	1.203	1102	1426	1254
333.85	0.637	0.832	1.096	1.141	1093	1411	1244
334.75	0.587	0.809	1.125	1.095	1086	1398	1236
335.85	0.538	0.783	1.150	1.058	1077	1383	1226
336.95	0.488	0.754	1.182	1.031	1068	1368	1216
338.15	0.439	0.719	1.208	1.021	1059	1352	1206
339.15	0.405	0.692	1.224	1.009	1051	1339	1197
340.45	0.359	0.654	1.257	0.995	1041	1323	1186
341.95	0.311	0.606	1.288	0.988	1030	1304	1174
343.75	0.260	0.539	1.304	0.997	1017	1282	1159
345.85	0.206	0.476	1.371	0.969	1002	1257	1142
347.85	0.156	0.390	1.406	0.977	988	1234	1127
350.05	0.107	0.290	1.424	0.986	973	1210	1110
352.45	0.059	0.170	1.430	0.994	957	1184	1092
354.05	0.028	0.086	1.444	0.998	947	1167	1080
355.60	0.000	0.000		1.000			

Analysis. The compositions of the liquid- and condensed-vapor-phase samples were determined using a CE Instruments GC 8000 Top gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 30 m, 0.454 mm i.d., capillary column, DB-MTBE (J&W Scientific). The GC response peaks were processed with Chrom-Card for Windows, Version 1.20. The column, injector, and detector temperatures were 323, 498, and 523 K, respectively, for the two 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 liquid and vapor composition; the standard deviation in the mole fraction was usually <0.001.

Results and Discussion

Vapor pressures $P_i°$ were calculated with the Antoine equation, whose parameters A_i, B_i, and C_i are reported in Table 2.

$$\ln(P_i°/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \qquad (1)$$

The Antoine constants for MTBE and 2-methylpentane were taken from Aucejo et al. (1998). For TBA, the values given in Aucejo et al. (1999a) were used.

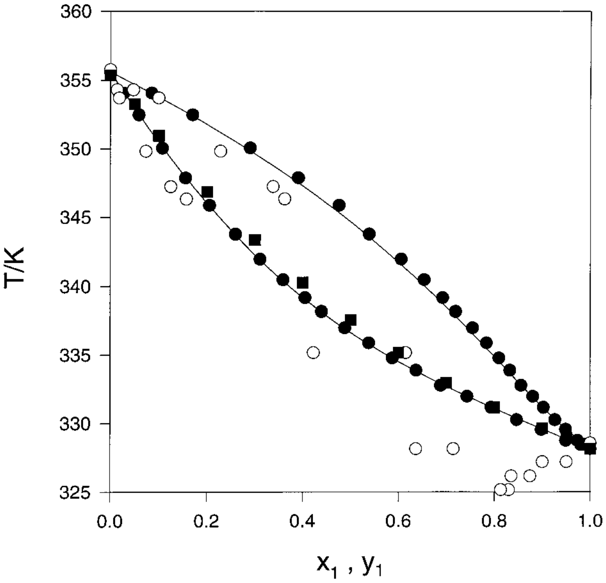

Figure 1. Boiling temperature diagram for the system MTBE (1) + TBA (3) at 101.3 kPa. Experimental data: this work (●); Churkin et al. (1979) (■); Zong et al. (1987) (○). Smoothed with the Legendre polynomial used in the consistency test (—).

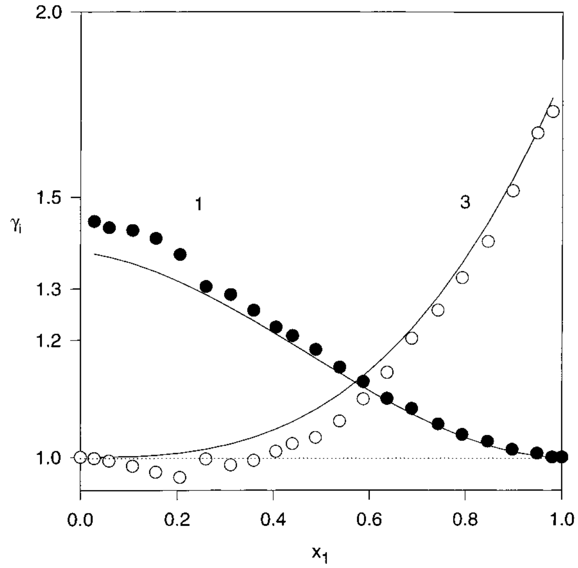

Figure 2. Activity coefficient plot for the system MTBE (1) + TBA (3) at 101.3 kPa: γ_1 (●); γ_3 (○); smoothed with the Legendre polynomial used in the consistency test (—).

Binary System. The temperature T and the liquid-phase x_i and vapor-phase y_i mole fractions at 101.3 kPa are reported in Table 3. Figure 1 shows a graphical comparison between the boiling-point temperatures measured for the system MTBE (1) + TBA (3) in this work and those

Table 4. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models for the Binary Systems MTBE (1) + 2-Methylpentane (2) and MTBE (1) + TBA (3)

				bubble-point pressures		dew-point pressures	
model	A_{ij}/ J·mol^{-1}	A_{ji}/ J·mol^{-1}	α_{ij}	ΔP^a/%	$100\Delta y^b$	ΔP^a/%	$100\Delta x^b$
		MTBE (1) + 2-Methylpentane (2)[e]					
Wilson[c]	523.28	22.45		0.11	0.05	0.11	0.05
NRTL	272.05	265.27	0.2	0.11	0.05	0.11	0.05
UNIQUAC[d]	−119.81	261.33		0.10	0.05	0.11	0.06
		MTBE (1) + TBA (3)					
Wilson[c]	−687.80	2263.48		0.56	0.84	1.34	1.17
NRTL	3080.07	−1211.97	0.3	0.13	0.76	0.96	0.91
UNIQUAC[d]	2267.27	−1295.30		0.32	0.61	0.95	0.64

[a] Average percentage deviation in pressure $\Delta P = 100/N\sum_i^N |P_i^{\exp} - P_i^{\text{calc}}|/P_i^{\exp}$ (N = number of data points). [b] Average absolute deviation in vapor- and liquid-phase composition. [c] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [d] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990). [e] Parameters calculated from data of Aucejo et al. (1998).

determined by Churkin et al. (1979) and by Zong et al. (1987). It is seen that there is good agreement between the data of Churkin et al. and the data of this work, although it should be pointed out that the data of Churkin et al. do not include experimental determination of vapor-phase compositions. Nevertheless, the data of Zong et al. present an azeotropic behavior of the system, which cannot be observed in our data.

Figure 2 shows the activity coefficients γ_i that were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^\circ} + \frac{(B_{ii} - V_i^{\mathrm{L}})(P - P_i^\circ)}{RT} + \frac{P}{2RT}\sum_j \sum_k y_i y_k (2\delta_{ji} - \delta_{jk}) \quad (2)$$

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° is the vapor pressure, B_{ij} is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \quad (3)$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation 2 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 the

Table 5. Experimental Vapor−Liquid Equilibrium Data for MTBE (1) + 2-Methylpentane (2) + TBA (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{11}$/ cm^3·mol^{-1}	$-B_{22}$/ cm^2·mol^{-1}	$-B_{33}$/ cm^3·mol^{-1}	$-B_{12}$/ cm^3·mol^{-1}	$-B_{13}$/ cm^3·mol^{-1}	$-B_{23}$/ cm^3·mol^{-1}
328.65	0.719	0.233	0.735	0.234	1.006	1.164	2.067	1137	1354	1487	1217	1293	1011
328.95	0.890	0.047	0.915	0.052	1.003	1.276	1.616	1134	1351	1482	1215	1290	1009
329.15	0.500	0.432	0.524	0.424	1.016	1.119	2.379	1132	1348	1479	1213	1288	1008
329.35	0.598	0.292	0.622	0.310	1.002	1.204	1.889	1131	1346	1476	1211	1286	1006
329.65	0.397	0.493	0.420	0.499	1.008	1.136	2.252	1128	1343	1472	1208	1283	1004
329.75	0.310	0.643	0.340	0.607	1.044	1.056	3.376	1127	1342	1470	1207	1282	1003
329.85	0.780	0.091	0.827	0.107	1.005	1.321	1.520	1126	1341	1469	1206	1281	1002
330.15	0.197	0.708	0.215	0.689	1.025	1.076	2.998	1124	1337	1464	1203	1279	1000
330.25	0.301	0.514	0.323	0.557	1.002	1.195	1.925	1123	1336	1463	1202	1278	999
330.25	0.502	0.299	0.540	0.352	1.007	1.297	1.606	1123	1336	1463	1202	1278	999
330.55	0.096	0.809	0.107	0.784	1.038	1.057	3.357	1120	1333	1458	1199	1275	997
330.65	0.096	0.713	0.105	0.749	1.014	1.142	2.231	1120	1332	1457	1199	1274	996
330.65	0.195	0.593	0.211	0.648	1.001	1.188	1.936	1120	1332	1457	1199	1274	996
330.65	0.389	0.381	0.421	0.450	1.002	1.288	1.614	1120	1332	1457	1199	1274	996
330.75	0.589	0.190	0.648	0.242	1.014	1.385	1.431	1119	1331	1455	1198	1273	995
330.75	0.692	0.099	0.769	0.130	1.024	1.426	1.389	1119	1331	1455	1198	1273	995
331.15	0.047	0.904	0.056	0.859	1.091	1.017	4.967	1115	1327	1450	1194	1269	992
331.15	0.047	0.685	0.053	0.771	1.008	1.206	1.877	1115	1327	1450	1194	1269	992
331.15	0.302	0.397	0.341	0.507	1.027	1.368	1.435	1115	1327	1450	1194	1269	992
331.25	0.096	0.601	0.107	0.716	1.009	1.272	1.661	1114	1326	1448	1193	1268	992
331.25	0.195	0.498	0.218	0.612	1.014	1.313	1.567	1114	1326	1448	1193	1268	992
331.65	0.500	0.200	0.578	0.279	1.036	1.476	1.314	1111	1321	1442	1189	1264	989
331.95	0.394	0.286	0.454	0.393	1.023	1.437	1.304	1109	1318	1438	1186	1262	986
332.15	0.095	0.497	0.112	0.679	1.036	1.420	1.392	1107	1316	1435	1185	1260	985
332.35	0.195	0.392	0.234	0.567	1.047	1.497	1.297	1105	1314	1432	1183	1258	983
332.95	0.048	0.477	0.058	0.708	1.041	1.505	1.290	1100	1307	1423	1177	1252	979
333.05	0.304	0.288	0.371	0.438	1.047	1.544	1.207	1100	1306	1422	1176	1251	978
333.05	0.391	0.200	0.492	0.324	1.079	1.644	1.163	1100	1306	1422	1176	1251	978
333.45	0.095	0.397	0.120	0.639	1.065	1.608	1.213	1096	1302	1416	1173	1248	975
333.65	0.497	0.101	0.645	0.173	1.093	1.714	1.134	1095	1300	1414	1171	1246	974
333.65	0.576	0.051	0.745	0.087	1.091	1.694	1.128	1095	1300	1414	1171	1246	974
334.35	0.192	0.284	0.255	0.506	1.097	1.731	1.114	1089	1293	1404	1165	1240	969
334.75	0.301	0.189	0.414	0.355	1.120	1.808	1.083	1086	1289	1398	1161	1236	966
335.55	0.095	0.293	0.134	0.580	1.125	1.859	1.081	1079	1281	1387	1154	1229	960
336.85	0.047	0.273	0.071	0.609	1.139	2.011	1.031	1069	1267	1370	1143	1217	951
336.85	0.389	0.061	0.605	0.138	1.191	2.052	1.013	1069	1267	1370	1143	1217	951
337.85	0.297	0.092	0.480	0.224	1.204	2.139	1.003	1061	1257	1356	1134	1209	944
338.05	0.193	0.147	0.316	0.368	1.210	2.180	0.988	1060	1255	1354	1132	1207	943
339.05	0.092	0.179	0.157	0.473	1.220	2.248	1.000	1052	1246	1341	1124	1198	936
342.25	0.193	0.057	0.393	0.190	1.330	2.582	0.952	1028	1215	1300	1097	1171	914
343.25	0.092	0.093	0.192	0.326	1.326	2.645	0.971	1021	1206	1288	1089	1163	908
348.15	0.046	0.048	0.120	0.226	1.454	3.106	0.966	986	1162	1231	1051	1124	877

Table 6. Correlation of Experimental Ternary Data with Wilson, NRTL, and UNIQUAC Equations Using Binary Interaction Parameters

						bubble-point pressures			dew-point pressures		
model	ij	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	α_{ij}	system	ΔP[e]/%	$100 \times \Delta y_1$[f]	$100 \times \Delta y_2$[f]	ΔP[e]/%	$100 \times \Delta x_1$[f]	$100 \times \Delta x_2$[f]
Wilson[a]	1−2[c]	523.28	22.45								
	1−3[c]	−687.80	2263.48		1+2+3	0.59	0.24	0.77	1.35	0.57	0.73
	2−3[d]	−14.98	5658.90								
NRTL	1−2[c]	272.05	265.27	0.20							
	1−3[c]	3080.07	−1211.97	0.30	1+2+3	0.47	0.27	0.67	1.15	0.51	0.97
	2−3[d]	4362.09	983.72	0.47							
UNIQUAC[b]	1−2[c]	−119.81	261.33								
	1−3[c]	2267.27	−1295.30		1+2+3	0.72	0.32	0.77	1.08	0.41	0.87
	2−3[d]	2844.32	−1030.28								

[a] Liquid volumes have been estimated from the Rackett equation (Rackett, 1970). [b] Volume and surface parameters from DECHEMA (Gmehling and Onken, 1990). [c] Calculated in this work. [d] Aucejo et al. (1999a). [e] Average percentage deviation in bubble and dew pressures $\Delta P = 100/N\sum_i^N |P_i^{\text{exp}} - P_i^{\text{calc}}|/P_i^{\text{exp}}$ (N = number of data points). [f] Average absolute deviation in composition $\Delta y = 1/N\sum_i^N |y_i^{\text{exp}} - y_i^{\text{calc}}|$; $\Delta x = 1/N\sum_i^N |x_i^{\text{exp}} - x_i^{\text{calc}}|$.

liquid volumes of the pure components are incompressible over the pressure range under consideration. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell (1975) using the molecular parameters suggested by Prausnitz et al. (1980). The critical properties of all components were taken from DIPPR (Daubert and Danner, 1989). The last two terms in eq 2, particularly the second one that expresses the correction due to the nonideal behavior of the vapor phase, contributed <4.5% for the system MTBE + TBA; their influence was important only at very dilute concentrations. The calculated activity coefficients reported in Table 3 are estimated to be accurate to within ±3%. The results reported in Table 3 indicate that the measured system exhibits positive deviations from ideal behavior and no azeotrope is present.

The VLE data reported in Table 3 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 Legendre polynomial with two parameters. The average deviations of pressure and vapor composition obtained with the Fredenslund et al. test were MADy_1 = 0.0069 and MADP = 0.23 kPa.

The parameters of the Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following objective function (OF)

$$\mathrm{OF} = \sum_{i=1}^{N} 100\left(\left|\frac{P_i^{\text{exptl}} - P_i^{\text{calc}}}{P_i^{\text{exptl}}}\right| + \left|y_i^{\text{exptl}} - y_i^{\text{calc}}\right|\right) \tag{4}$$

and are reported in Table 4, together with the pertinent statistics of VLE interpolation, for the data of the system MTBE (1) + 2-methylpentane (2) reported in Aucejo et al. (1998) and for the data of the system MTBE (1) + TBA (3) reported in this work. Inspection of the results given in Table 4 shows that all models are adequate to predict the binary data.

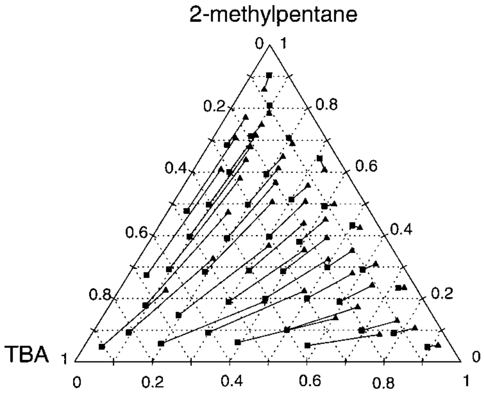

Figure 3. Diagram of VLE for the ternary system MTBE (1) + 2-methylpentane (2) + TBA (3) at 101.3 kPa: (■) liquid phase mole fractions; (▲) vapor phase mole fractions.

Ternary System. The VLE data for the ternary system are shown in Table 5 and Figure 3. The activity coefficients γ_i were calculated from eq 2, and the molar virial coefficients were estimated in the same way as that for the binary system. The ternary data were found to be thermodynamically consistent, as tested by the L−W method of Wisniak (1993) and the McDermott−Ellis method (1965) modified by Wisniak and Tamir (1977). The test requires that $D < D_{\max}$ for every experimental point, where the local deviation D is given by

$$D_i = \sum_{i=1}^{n}(x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \tag{5}$$

where n is the number of components. The maximum deviation $D_{\max}$ is given by

$$\begin{aligned} D_{\max} = {} & \sum_{i=1}^{n}(x_{ia} + x_{ib})\left(\frac{1}{x_{ia}} + \frac{1}{y_{ia}} + \frac{1}{x_{ib}} + \frac{1}{y_{ib}}\right)\Delta x + \\ & \sum_{i=1}^{n}(x_{ia} + x_{ib})\frac{\Delta P}{P} + 2\sum_{i=1}^{n}|\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \\ & \sum_{i=1}^{n}(x_{ia} + x_{ib})B_j\{(T_a + C_j)^{-2} + (T_b + C_j)^{-2}\}\Delta T \end{aligned} \tag{6}$$

The accuracies of the measurements of Δx, ΔP, and ΔT were as indicated previously.

Vapor−liquid equilibrium was correlated by using Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters. The values of the binary interaction parameters for the binary 2-methylpentane (2) + TBA (3) were used from Aucejo et al. (1999a), and the corresponding parameters of the systems MTBE (1) + 2-methylpentane (2) and MTBE (1) + TBA (3) were calculated in this work and appear in Table 4. Table 6 shows the pertinent statistics of VLE correlation. The three models yield similar deviations, with each model representing the data successfully.

Boiling Isotherms Correlation. The boiling points of the systems were correlated by the equation proposed

Table 7. Coefficients in Correlation of Boiling Points, Eqs 7 and 8, Maximum, Average and Root Mean Square Deviations in Temperature (rmsd)

A. Equation 7 (Fit from Binary Constants)

A	*B*	*C*	*D*	max. dev/K	avg dev/K	rmsd[a]/K
12.85	2.74	4.06	0.00	0.57	0.15	0.032

Binary Constants

system	C_0	C_1	C_2	max. dev/K	avg dev/K	rmsd[a]/K
MTBE (1) + 2-methylpentane (2)[b]	−6.69	1.90	−0.75	0.08	0.02	0.007
MTBE (1) + TBA (3)	−20.80	6.92	−1.55	0.12	0.04	0.012
2-methylpentane (2) + TBA (3)[c]	−42.25	18.00	−43.88	0.90	0.38	0.102

B. Equation 8 (Direct Fit)

ij	A_{ij}	B_{ij}	C_{ij}	max. dev/K	avg dev/K	rmsd[a]/K
1−2	−5.59	1.89	−7.63	0.44	0.13	0.026
1−3	−18.49	8.89	−4.55			
2−3	−42.88	19.77	−32.61			

[a] Root mean square deviation, $\{\sum(T_{\mathrm{exp}} - T_{\mathrm{cal}})^2\}^{0.5}/N$. [b] Recalculated constants from data for Aucejo et al. (1998). [c] Constants from Aucejo et al. (1999b).

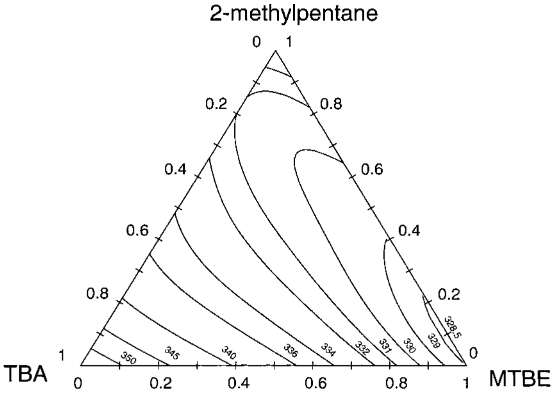

Figure 4. Isotherms for the ternary system MTBE (1) + 2-methylpentane (2) + TBA (3) at 101.3 kPa, calculated with direct fit of eq 8.

by Wisniak and Tamir (1976)

$$T = \sum_{i=1}^{n} x_i T_i^\circ + \sum_{i,j=1}^{n} [x_i x_j \sum_{k=0}^{m} C_k (x_i - x_j)^k] + x_1 x_2 x_3 [A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + ...] \quad (7)$$

In this equation n is the number of components ($n = 2$ or 3), T_i° is the boiling point of the pure component i, and m is the number of terms considered in the series expansion of $(x_i - x_j)$. C_k are the binary constants, whereas A, B, C, and D are ternary constants. The following equation, of the same structure, has been suggested by Tamir (1981) for the direct correlation of ternary data, without the use of binary data:

$$T = \sum_{i=1}^{n} x_i T_i^\circ + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (8)$$

In eq 8 the coefficients A_{ij}, B_{ij}, and C_{ij} are not binary constants; instead, they are multicomponent parameters determined directly from the data. Direct correlation of $T(x)$ for ternary mixtures can be very efficient, as reflected by a lower percent average deviation and root mean square deviation (rmsd) and a smaller number of parameters than those for eq 7. The various constants of eqs 7 and 8 are reported in Table 7, which also contains information indicating the quality of the correlation. The values of the binary constants for MTBE (1) + 2-methylpentane (2) were recalculated from the data of Aucejo et al. (1998). For the binary system 2-methylpentane (2) + TBA (3), the binary constants were taken from Aucejo et al. (1999b). The corresponding parameters of the system MTBE (1) + TBA (3) were calculated from the data of this work. Figure 4 shows the boiling isotherms for the ternary system calculated by direct fit, which gives a better fit.

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