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Phase Equilibria in the Systems 2-Methyl-2-propanol + Methyl 1,1-Dimethylpropyl Ether and 2-Methylpentane + 2-Methyl-2-propanol + Methyl 1,1-Dimethylpropyl Ether

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Consistent vapor−liquid equilibrium data for the binary and ternary systems 2-methyl-2-propanol (TBA) + methyl 1,1-dimethylpropyl ether (TAME) at temperatures from 353 to 359 K and 2-methylpentane + 2-methyl-2-propanol (TBA) + methyl 1,1-dimethylpropyl ether (TAME) from 332 to 353 K are reported at 101.3 kPa. The results indicate that the systems deviate positively from ideality and that only the binary system presents an azeotrope. The ternary system is well predicted from binary data. The activity coefficients and boiling points of the solutions were correlated with composition by Wilson, UNIQUAC, NRTL, and Wisniak−Tamir equations.

Introduction

Ethers and alkanols are used as gasoline additives to provide antiknock quality and help to reduce harmful emissions from combustion. They may be used individually or in combination. Light alkanols such as methanol and ethanol are commonly used in combination with 2-methyl-2-propanol (TBA) to avoid the formation of two liquid phases in the presence of small quantities of water. Methyl 1,1-dimethylethyl ether (MTBE) is currently the primary oxygenated compound being used in reformulated gasolines. However, potential and documented contamination of water resources by MTBE has become a major public issue over the past few years. Restrictions on the use of MTBE have been proposed and alternative oxygenates sought, particularly of higher carbon number to reduce the affinity for water. Methyl 1,1-dimethylpropyl ether (TAME) is effective at reducing automotive CO emissions and has been considered a good alternative to MTBE as a gasoline additive.

Phase equilibrium data on 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 ternary system 2-methylpentane (1) + TBA (2) + TAME (3) and the constituent binary system TBA (2) + TAME (3) at 101.3 kPa. For these systems no VLE data have been previously published. For the other binary constituent systems 2-methylpentane (1) + TAME (3) and 2-methylpentane (1) + TBA (2), VLE data at 101.3 kPa have already been reported by Aucejo et al. (1998) and Aucejo et al. (1999), respectively. Both systems present positive deviations from ideality; the first one presents a minimum boiling point azeotrope, and the second one can be described as a symmetric solution and presents no azeotrope.

Experimental Section

Chemicals. 2-Methylpentane (99+ mass %, GC grade), TBA (99.5 mass %, HPLC grade), and TAME (97 mass %) were purchased from Aldrich Chemie Co. 2-Methylpentane and TBA were used without further purification after chromatography failed to show any significant impurities. TAME was purified to 99.9+ mass % by batch distillation in a Fischer SPALTROHR-column HMS-500, controlled by a Fischer System D301-C. The densities of the pure liquids were measured at 298.15 K using 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. The temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements are $\pm 0.01\ \mathrm{kg \cdot m^{-3}}$ 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, up to 120 kPa, 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

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

component	d(298.15 K) /kg·m^{-3}		n_D(298.15 K)		T_b(101.3 kPa)/K	
	exptl	lit.	exptl	lit.	exptl	lit.
2-methylpentane	648.39	648.86[a]	1.3689	1.3687[b]	333.4	333.41[b]
2-methyl-2-propanol	775.40[c]	775.43[c,d]	1.3851	1.3859[b]	355.6	355.52[e]
methyl 1,1-dimethylpropyl ether	765.94	765.77[f]	1.3858	1.3859[b]	359.3	359.33[g]

[a] Awwad and Pethrick (1983). [b] DIPPR (Daubert and Danner, 1989). [c] Measured to 303.15 K. [d] Hales et al. (1983). [e] Ambrose and Sprake (1970). [f] Linek (1987). [g] Martínez-Ageitos (1996).

Table 2. Antoine Coefficients, Eq 1

compound	A_i	B_i	C_i
2-methylpentane[a]	14.0614	2791.52	37.75
2-methyl-2-propanol[b]	14.8533	2649.89	96.69
methyl 1,1-dimethylpropyl ether[a]	14.3501	3111.28	39.52

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

Table 3. Experimental Vapor−Liquid Equilibrium Data for TBA (2) + TAME (3) at 101.3 kPa

T/K	x_2	y_3	γ_2	γ_3	B_{22}/ cm^3·mol^{-1}	B_{33}/ cm^3·mol^{-1}	B_{23}/ cm^3·mol^{-1}
359.30	0.000	0.000		1.000			
358.25	0.021	0.043	1.821	1.006	−1125	−1366	−1229
357.15	0.052	0.098	1.794	1.010	−1136	−1377	−1238
356.15	0.099	0.172	1.700	1.005	−1146	−1387	−1247
355.15	0.149	0.234	1.602	1.014	−1156	−1397	−1255
354.55	0.198	0.282	1.483	1.027	−1162	−1403	−1261
353.95	0.248	0.328	1.410	1.043	−1168	−1410	−1266
353.55	0.297	0.367	1.336	1.065	−1172	−1414	−1269
353.25	0.347	0.406	1.282	1.084	−1175	−1417	−1272
353.05	0.395	0.444	1.237	1.104	−1177	−1419	−1274
352.95	0.440	0.475	1.195	1.128	−1179	−1420	−1274
352.85	0.491	0.507	1.147	1.169	−1180	−1421	−1275
352.85	0.541	0.549	1.127	1.187	−1180	−1421	−1275
352.85	0.581	0.576	1.102	1.221	−1180	−1421	−1275
352.95	0.645	0.627	1.076	1.265	−1179	−1420	−1274
353.15	0.696	0.665	1.050	1.316	−1176	−1418	−1273
353.35	0.745	0.710	1.037	1.357	−1174	−1416	−1271
353.65	0.793	0.755	1.026	1.394	−1171	−1413	−1268
353.95	0.842	0.805	1.018	1.440	−1168	−1410	−1266
354.35	0.892	0.859	1.010	1.505	−1164	−1406	−1262
354.85	0.943	0.924	1.007	1.522	−1159	−1400	−1258
355.25	0.974	0.964	1.002	1.566	−1155	−1396	−1254
355.60	1.000	1.000	1.000				

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 that allowed one to withdraw small-volume samples (1.0 μL) in a system under partial vacuum or under overpressure conditions.

Analysis. The compositions 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. The column, injector, and detector temperatures were 343, 423, and 473 K 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 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.

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

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

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 and Figure 1. Figure 2 shows the activity coefficients γ_i that were calculated from the following equation (Van Ness and Abbott, 1982):

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i°} + \frac{(B_{ii} - V_i^{\text{L}})(P - P_i°)}{RT} + \frac{P}{2RT}\sum\sum y_i y_k (2\delta_{ji} - \delta_{jk}) \tag{2}$$

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

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{3}$$

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 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) and are shown in Table 3. 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 less than 2.5% for the system TBA + TAME. The calculated activity coefficients reported in Table 3 are estimated to be accurate to within ± 3%. The results reported in that table indicate that the measured system exhibits positive deviation from ideal behavior and an azeotrope is present at $x_1 \approx 0.54$ and $T = 352.85$ K.

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). The pertinent statistics required by the Fredenslund test together with the number of parameters of the Legendre polynomial used for consistency are shown in Table 4.

The parameters of the Wilson, NRTL, and UNIQUAC equations were obtained by minimizing the following

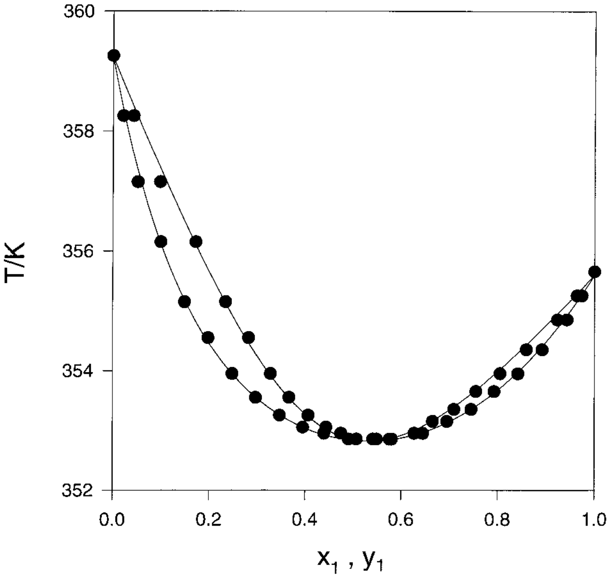

Figure 1. Boiling temperature diagram for the system TBA (1) + TAME (2) at 101.3 kPa: experimental data (●); smoothed with the Legendre polynomial used in the consistency test (—).

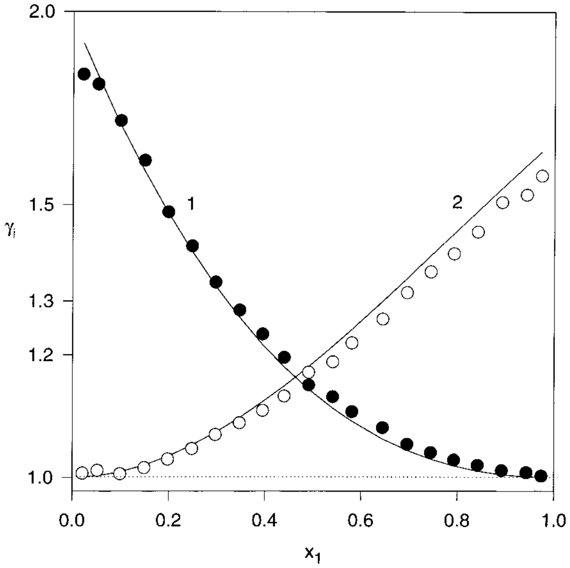

Figure 2. Activity coefficient plot for the system TBA (1) + TAME (2) at 101.3 kPa: γ_1 (●); γ_2 (○); smoothed with the Legendre polynomial used in the consistency test (—).

Table 4. Consistency Test for the Binary Mixture TBA (2) + TAME (3)

n	100 × MAD(y_2)[a]	MAD(P)[b]/kPa
2	0.44	0.19

[a] Mean absolute deviation in vapor-phase composition. [b] Mean absolute deviation in pressure.

objective function (OF):

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

and are reported in Table 5, together with the pertinent statistics of VLE interpolation, for the data of the system 2-methylpentane (1) + TAME (3) reported in Aucejo et al. (1998) and for the data of the system TBA (2) + TAME (3) reported in this work. Inspection of the results given in Table 5 shows that all models are adequate to predict the binary data.

Table 5. Parameters and Deviations between Experimental and Calculated Values for Different G^E Models for the Binary Systems 2-Methylpentane (1) + TAME (3) and TBA (2) + TAME (3)

				bubble-point pressures		dew-point pressures	
model	A_{ij}/ J·mol^{-1}	A_{ji}/ J·mol^{-1}	α_{ij}	ΔP[a]/ %	100 × Δy[b]	ΔP[a]/ %	100 × Δx[b]
		2-Methylpentane (1) + TAME (3)[e]					
Wilson[c]	−575.18	1112.85		0.24	0.81	0.90	0.90
NRTL	−504.22	953.38	0.2	0.21	0.88	0.88	1.00
UNIQUAC[d]	−377.67	509.97		0.21	0.87	0.87	0.99
		TBA (2) + TAME (3)					
Wilson[c]	2634.43	−646.82		0.23	0.40	0.20	0.44
NRTL	−163.00	2120.81	0.3	0.24	0.39	0.21	0.43
UNIQUAC[d]	−937.11	1774.84		0.20	0.42	0.20	0.47

[a] Average percent deviation in pressure $\Delta P = 100/N \sum_i^N |P_i^{\mathrm{expt}} - P_i^{\mathrm{calc}}|/P_i^{\mathrm{expt}}$ (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 the data of Aucejo et al. (1998).

Ternary System. The VLE data for the ternary system are shown in Table 6 and Figure 3. The activity coefficients γ_i were calculated from eq 2, and the molar virial coefficients were estimated as well as 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

$$D = \sum_{i=1}^{N} (x_{ia} + x_{ib})(\ln \gamma_{ia} - \ln \gamma_{ib}) \quad (5)$$

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

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

The errors in the measurements Δx, ΔP, and ΔT were as previously indicated.

The 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 (1) + TBA (2) were used from the data of Aucejo et al. (1999), and corresponding parameters of the systems 2-methylpentane (1) + TAME (2) and TBA (2) + TAME (3) were calculated in this work. Table 7 shows the pertinent statistics of VLE interpolation. The three models yield similar deviations, representing the data successfully.

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

Table 6. Experimental Vapor−Liquid Equilibrium Data for 2-Methylpentane (1) + TBA (2) + TAME (3) at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	B_{11}/ $\text{cm}^3\cdot\text{mol}^{-1}$	B_{22}/ $\text{cm}^3\cdot\text{mol}^{-1}$	B_{33}/ $\text{cm}^3\cdot\text{mol}^{-1}$	B_{12}/ $\text{cm}^3\cdot\text{mol}^{-1}$	B_{13}/ $\text{cm}^3\cdot\text{mol}^{-1}$	B_{23}/ $\text{cm}^3\cdot\text{mol}^{-1}$
331.95	0.928	0.048	0.901	0.090	1.013	5.182	0.966	−1318	−1438	−1672	−986	−1463	−1483
335.85	0.726	0.048	0.816	0.081	1.044	3.876	0.949	−1277	−1383	−1620	−958	−1418	−1440
340.45	0.522	0.046	0.698	0.074	1.086	3.022	0.942	−1232	−1323	−1562	−926	−1368	−1392
345.85	0.319	0.045	0.521	0.074	1.139	2.428	0.955	−1182	−1257	−1498	−891	−1312	−1339
353.35	0.108	0.030	0.234	0.058	1.239	2.100	0.976	−1118	−1174	−1416	−845	−1241	−1271
350.05	0.151	0.090	0.308	0.142	1.269	1.977	0.952	−1145	−1210	−1451	−865	−1271	−1300
349.85	0.145	0.109	0.295	0.164	1.272	1.887	0.960	−1147	−1212	−1453	−866	−1273	−1302
344.95	0.292	0.106	0.487	0.144	1.192	2.096	0.946	−1190	−1268	−1508	−897	−1321	−1348
342.15	0.386	0.103	0.584	0.136	1.171	2.289	0.927	−1216	−1302	−1541	−915	−1350	−1375
339.35	0.497	0.101	0.669	0.130	1.128	2.528	0.927	−1243	−1337	−1575	−934	−1379	−1404
336.85	0.602	0.105	0.735	0.130	1.101	2.726	0.926	−1267	−1370	−1607	−951	−1407	−1430
334.55	0.710	0.101	0.792	0.127	1.077	3.059	0.938	−1291	−1401	−1637	−967	−1433	−1454
332.85	0.801	0.099	0.835	0.125	1.059	3.332	0.934	−1308	−1425	−1659	−980	−1452	−1473
332.95	0.710	0.189	0.799	0.162	1.140	2.244	0.909	−1307	−1423	−1658	−979	−1451	−1472
335.05	0.608	0.191	0.743	0.170	1.163	2.121	0.925	−1286	−1394	−1630	−964	−1427	−1449
337.35	0.501	0.194	0.675	0.180	1.198	1.991	0.940	−1262	−1363	−1600	−948	−1401	−1424
339.95	0.399	0.200	0.600	0.194	1.241	1.845	0.934	−1237	−1329	−1568	−930	−1373	−1397
342.85	0.297	0.198	0.506	0.207	1.294	1.752	0.939	−1209	−1293	−1533	−910	−1342	−1368
347.65	0.157	0.200	0.322	0.239	1.362	1.642	0.968	−1166	−1236	−1477	−880	−1294	−1322
351.45	0.048	0.271	0.125	0.328	1.581	1.426	1.010	−1133	−1194	−1436	−857	−1258	−1288
348.85	0.099	0.293	0.238	0.316	1.544	1.408	1.001	−1156	−1223	−1464	−872	−1283	−1311
344.95	0.194	0.302	0.395	0.281	1.459	1.428	0.992	−1190	−1268	−1508	−897	−1321	−1348
341.55	0.294	0.304	0.520	0.252	1.396	1.471	0.977	−1222	−1309	−1548	−919	−1356	−1381
338.55	0.391	0.311	0.615	0.233	1.350	1.519	0.972	−1251	−1347	−1585	−939	−1388	−1412
335.85	0.490	0.315	0.690	0.218	1.309	1.585	0.983	−1277	−1383	−1620	−958	−1418	−1440
332.55	0.635	0.316	0.781	0.198	1.263	1.676	0.976	−1312	−1429	−1663	−982	−1456	−1476
334.55	0.495	0.405	0.722	0.232	1.408	1.394	1.007	−1291	−1401	−1637	−967	−1433	−1454
337.15	0.390	0.424	0.651	0.255	1.493	1.299	1.006	−1264	−1366	−1603	−949	−1403	−1427
340.25	0.294	0.418	0.555	0.282	1.544	1.269	1.013	−1234	−1325	−1564	−928	−1370	−1394
343.45	0.210	0.394	0.438	0.310	1.559	1.288	1.027	−1204	−1286	−1526	−906	−1336	−1362
350.05	0.059	0.386	0.162	0.391	1.713	1.259	1.059	−1145	−1210	−1451	−865	−1271	−1300
347.75	0.094	0.494	0.260	0.415	1.848	1.147	1.111	−1165	−1235	−1476	−879	−1293	−1321
343.25	0.191	0.496	0.440	0.351	1.734	1.166	1.089	−1206	−1288	−1528	−908	−1338	−1364
339.45	0.290	0.501	0.575	0.304	1.658	1.182	1.070	−1242	−1336	−1574	−933	−1378	−1403
334.65	0.442	0.508	0.720	0.256	1.568	1.221	1.050	−1290	−1400	−1635	−967	−1432	−1453
337.85	0.299	0.600	0.620	0.320	1.821	1.115	1.147	−1257	−1356	−1594	−944	−1396	−1419
342.35	0.194	0.601	0.487	0.373	1.938	1.063	1.147	−1214	−1299	−1539	−914	−1348	−1373
349.05	0.061	0.600	0.201	0.497	2.122	1.071	1.207	−1154	−1221	−1462	−871	−1281	−1309
346.45	0.101	0.701	0.331	0.497	2.263	1.020	1.279	−1177	−1250	−1491	−887	−1306	−1334
339.05	0.248	0.705	0.606	0.363	2.070	1.021	1.213	−1246	−1341	−1579	−936	−1383	−1407
345.85	0.106	0.797	0.386	0.526	2.566	0.973	1.366	−1182	−1257	−1498	−891	−1312	−1339
349.25	0.057	0.894	0.266	0.679	2.973	0.974	1.526	−1152	−1218	−1460	−870	−1279	−1308

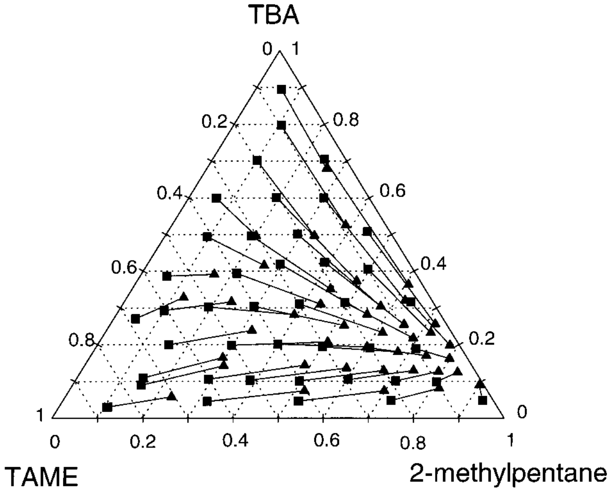

Figure 3. Diagram of VLE for the ternary system 2-methylpentane (1) + TBA (2) + TAME (3) at 101.3 kPa: (■) liquid-phase mole fractions; (▲) vapor-phase mole fractions.

Wisniak and Tamir (1976)

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

where 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, and A, B, C, and D are ternary constants. Tamir (1981) has suggested the following equation, of the same structure, for the direct correlation of ternary data, without the use of binary data:

$$T/\text{K} = \sum_{i=1}^{3} x_i T_i^\circ + x_1 x_2 [A_{12} + B_{12}(x_1 - x_2) + C_{12}(x_1 - x_2)^2 + \ldots] + x_1 x_3 [A_{13} + B_{13}(x_1 - x_3) + C_{13}(x_1 - x_3)^2 + \ldots] + x_2 x_3 [A_{23} + B_{23}(x_2 - x_3) + C_{23}(x_2 - x_3)^2 + \ldots] \quad (8)$$

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 8, which also contains information indicating the degree of goodness of the correlation. The values of the binary constants for the two binaries 2-methylpentane (1) + TAME (3) and 2-methylpen-

Table 7. 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]	−14.98	5658.90		1 + 2 + 3	0.60	1.46	0.80	1.18	1.40	0.96
	1 + 3[d]	−575.18	1112.85								
	2 + 3[d]	2634.43	−646.82								
NRTL	1 + 2[c]	4362.09	983.72	0.47	1 + 2 + 3	0.48	1.56	0.74	1.39	1.62	0.91
	1 + 3[d]	−504.22	953.38	0.20							
	2 + 3[d]	−163.00	2120.81	0.30							
UNIQUAC[b]	1 + 2[c]	2844.32	−1030.28		1 + 2 + 3	1.18	1.60	0.86	1.02	1.50	1.00
	1 + 3[d]	−377.67	509.97								
	2 + 3[d]	−937.11	1774.84								

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

Table 8. Coefficients in Correlation of Boiling Points in Eqs 7 and 8 and 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
−43.42	0.00	0.00	0.00	0.42	0.20	0.034

Binary Constants

system	C_0	C_1	C_2	max. dev/K	avg dev/K	rmsd[a]/K
2-methylpentane (1) + TBA (2)[b]	−42.25	18.00	−43.88	0.90	0.38	0.102
2-methylpentane (1) + TAME (3)[c]	−13.42	5.13	−1.22	0.11	0.04	0.012
TBA (2) + TAME (3)	−17.36	10.51	−13.78	0.55	0.23	0.061

B. Equation 8 (Direct Fit)

ij	A_{ij}	B_{ij}	C_{ij}	max. dev/K	avg dev/K	rmsd[a]/K
1−2	−45.75	18.65	−31.98	0.40	0.13	0.025
1−3	−18.30	4.43	−0.50			
2−3	−19.96	7.44	−6.92			

[a] rmsd (*T*/K): root mean square deviation, $\{\sum(T_{\text{exp}} - T_{\text{cal}})^2\}^{0.5}/N$. [b] Recalculated constants from data of Aucejo et al. (1999). [c] Recalculated constants from data of Aucejo et al. (1998).

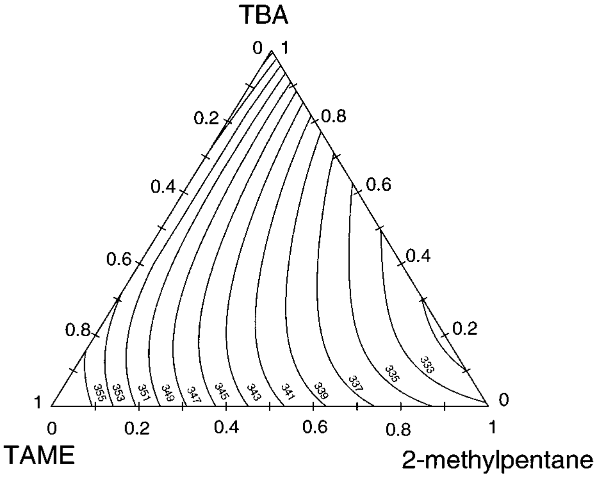

Figure 4. Isotherms (K) for the ternary system 2-methylpentane (1) + TBA (2) + TAME (3) at 101.3 kPa, calculated with direct fit, eq 8.

tane (1) +TBA (2) were recalculated in this work from the data of Aucejo et al. (1998) and Aucejo et al. (1999), respectively. Corresponding parameters of the system TBA (2) + TAME (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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