882 *J. Chem. Eng. Data* **2000,** *45,* 882−886

Isobaric Vapor−Liquid Equilibria for the Binary System 3-Methylpentane + Ethanol and for the Ternary System 2-Methyl-2-propanol + Ethanol + 3-Methylpentane at 101.3 kPa

Carmen Gabaldón, Vicente Martínez-Soria, Paula Marzal, and Juan B. Montón*

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

Isobaric vapor−liquid equilibria data were measured for the 3-methylpentane + ethanol binary system and 2-methyl-2-propanol + ethanol + 3-methylpentane ternary system at 101.3 kPa in a temperature range from 329 to 356 K. The data were found to be thermodynamically consistent according to the Van Ness−Byer−Gibbs method for the binary system and according to the McDermott−Ellis method for the ternary one. The binary system shows a minimum boiling azeotrope that boils at 327.9 K and contains 71.4 mol % 3-methylpentane. The binary interaction parameters obtained from this work and literature data are used to predict the vapor−liquid equilibrium for the ternary system using the UNIQUAC, NRTL, and Wilson models. The ternary system is well predicted from binary data.

Introduction

Environmental legislation around the world has forced the reformulation of gasolines to phase out the lead additives and to reduce the reactive evaporative and exhaust emissions. Alkanols and ethers have been shown to be substances with excellent antiknock and pollution-reducing capabilities. The commonly used oxygenated additives are methyl 1,1-dimethylethyl ether (MTBE) and light alkanols such as methanol and ethanol. 2-Methyl-2-propanol (TBA) is added in the oxygenated gasolines with ethanol to avoid the formation of two liquid phases in the presence of small quantities of water. Phase equilibrium data of oxygenated and hydrocarbon mixtures are important to predict the vapor-phase composition that would be in equilibrium with gasoline mixtures, for which isoparaffins may constitute up to 30 wt %. The systems reported here constitute a particular case of such mixtures.

In this work, isobaric vapor−liquid data at 101.3 kPa for the binary system 3-methylpentane (1) + ethanol (2) and the ternary system TBA (1) + ethanol (2) + 3-methylpentane (3) have been obtained, tested for thermodynamic consistency and vapor−liquid equilibrium (VLE) modeled. For these systems no VLE data have been previously reported, as far as we know.

Experimental Section

Chemicals. High-purity 2-methyl-2-propanol (TBA) and 3-methylpentane from Aldrich Chemical Co. and ethanol from Prolabo were used without further purification. The purities of all chemicals, checked by gas chromatography (GC), were 3-methylpentane, 100.0 mass %; TBA, 99.9 mass %; and ethanol, 100.0 mass %. TBA and ethanol were dehydrated by using zeolite A (4 Å). Experimental densities of the pure liquids at 298.15 K were measured in a digital precision densimeter, Anton Paar DMA55. The refractive indexes at 298.15 K were measured using an Abbe refractometer (ATAGO 3T). Temperature was controlled to ±0.01 K with a thermostated bath. The accuracies in density and refractive index measurements were ±0.01 kg·m^{-3} and ±0.0002, respectively. The boiling points were determined using the apparatus described below. The experimental values of these properties are listed in Table 1 together with the literature values.

Table 1. Density, *d*, Refractive Index, n_D, and Normal Boiling Point, T_b, of the 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.
TBA	775.40[a]	775.43[a,b]	1.3851	1.3859[c]	355.6	355.52[d]
ethanol	785.04	785.07[g]	1.3592	1.3594[c]	351.6	351.45[d]
3-methylpentane	659.51	660.04[e]	1.3738	1.3739[c]	336.3	336.43[f]

[a] Measured at 303.15 K. [b] Hales et al.[1] [c] Daubert and Danner.[2] [d] Ambrose and Sprake.[3] [e] Awwad and Pethrick.[4] [f] Willingham et al.[5] [g] Papanastasiou and Ziogas.[6]

Apparatus and Procedures. The equilibrium vessel used in this work (Labodest model, Fischer Labor und Verfahrenstechnik) is an all-glass, dynamic recirculating still described by Walas,[7] equipped with a Cottrell circulation pump. Apparatus and procedures details have been described in another work.[8] The uncertainty in equilibrium temperature and pressure was ±0.1 K and ±0.01 kPa, respectively.

Analysis. All the samples of liquid and condensed vapor were analyzed by using a Hewlett-Packard 5890 S-II gas chromatograph (GC) with a flame ionization detector as described in previous work.[8] The GC was calibrated with gravimetrically prepared standard solutions. Twenty binary and 60 ternary samples covering the entire composition range were prepared to calibrate the GC. The standard deviation in the mole fraction was usually less than 0.001.

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* Corresponding author. E-mail: juan.b.monton@uv.es.

10.1021/je000005b CCC: $19.00

Table 2. Antoine Coefficients, Eq 1

compound	A_i	B_i	C_i
TBA[a]	14.8533	2649.89	−96.69
ethanol[a]	16.4298	3545.95	−51.36
3-methylpentane[b]	14.3708	2999.76	−28.69

[a] Aucejo et al.[8] [b] Loras et al.[9]

Table 3. Experimental Vapor−Liquid Equilibrium Data for 3-Methylpentane (1) + Ethanol (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}
351.6	0.000	0.000					
350.4	0.005	0.044	6.730	1.006	1146	961	585
349.5	0.009	0.091	7.144	0.995	1154	972	588
347.6	0.018	0.167	6.778	0.991	1170	997	595
346.0	0.025	0.236	7.157	0.977	1184	1018	602
341.0	0.043	0.375	7.632	0.998	1231	1089	622
337.9	0.067	0.469	6.771	0.991	1261	1136	636
334.9	0.100	0.552	5.809	0.989	1291	1186	649
332.9	0.135	0.588	4.869	1.034	1312	1221	658
331.4	0.181	0.625	4.047	1.064	1328	1248	665
330.2	0.237	0.656	3.361	1.107	1341	1270	670
329.5	0.281	0.671	2.958	1.162	1348	1284	674
328.8	0.336	0.680	2.564	1.261	1356	1297	677
328.5	0.395	0.687	2.224	1.375	1359	1303	679
328.1	0.478	0.701	1.901	1.548	1364	1311	680
328.0	0.545	0.709	1.691	1.740	1365	1313	681
328.0	0.596	0.710	1.548	1.953	1365	1313	681
328.0	0.698	0.715	1.330	2.573	1365	1313	681
328.0	0.723	0.712	1.280	2.825	1365	1313	681
328.0	0.770	0.718	1.212	3.335	1365	1313	681
328.1	0.820	0.710	1.121	4.370	1364	1311	680
328.2	0.865	0.732	1.092	5.365	1363	1309	680
328.6	0.919	0.751	1.040	8.156	1358	1301	678
330.4	0.969	0.812	1.007	14.800	1338	1267	670
336.3	1.000	1.000					

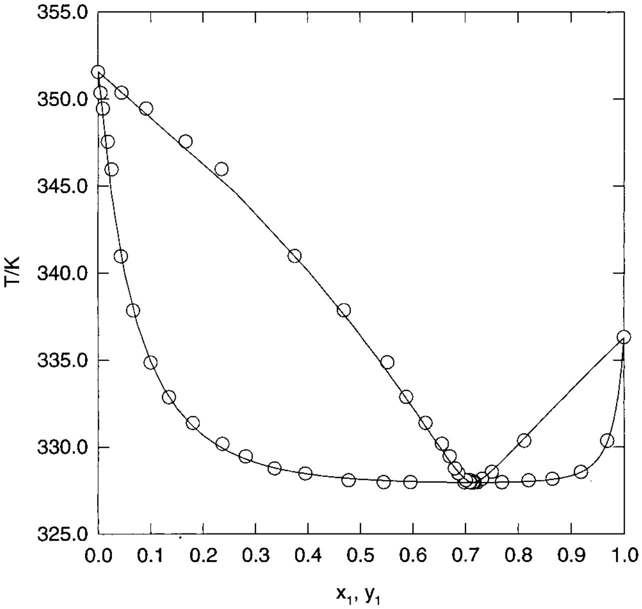

Figure 1. Temperature versus composition (x_1, y_1) for the system 3-methylpentane (1) + ethanol (2) at 101.3 kPa: ○, experimental; —, Wilson model.

Results and Discussion

Vapor pressures $P_i°$ were calculated with the Antoine equation

$$\ln(P_i°/\mathrm{kPa}) = A - \frac{B}{(C + T/\mathrm{K})} \qquad (1)$$

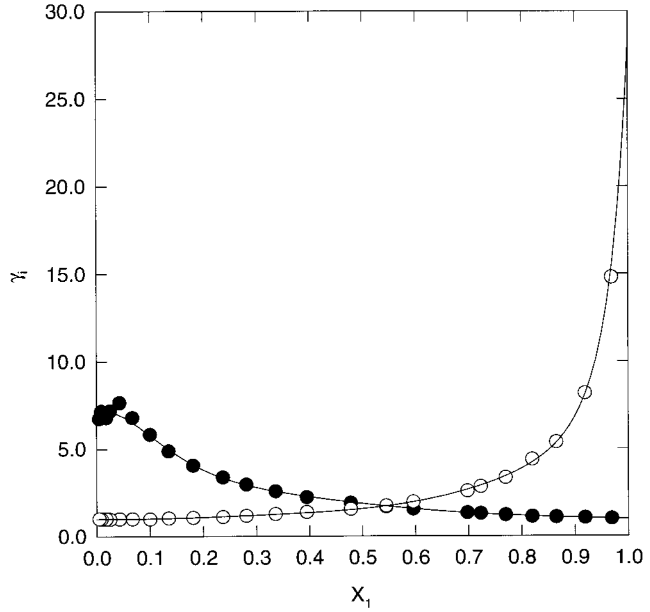

Figure 2. Activity coefficient plot for the system 3-methylpentane (1) +ethanol (2) at 101.3 kPa: ●, γ_1; ○, γ_2; —, smoothed with the Legendre polynomial used in consistency test.

Table 4. Correlation Parameters for Activity Coefficients, Activity Coefficients at Infinite Dilution γ_i^∞, and Mean Absolute Deviations MAD(y) and MAD(T) for the Binary System 3-Methylpentane(1) + Ethanol (2) at 101.3 KPa

model	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	α_{ij}	γ_1^∞	γ_2^∞	MAD-(y)	MAD-(T)/K
Wilson	1537.29	9412.87		9.61	23.52	0.0083	0.23
NRTL	5903.23	3481.14	0.42	7.81	16.95	0.0099	0.32
UNIQUAC	4313.99	−488.64		8.06	12.11	0.0172	0.55

The Antoine constants for TBA, ethanol, and 3-methylpentane were taken from Aucejo et al.[9] and Loras et al.[10] and are summarized in Table 2.

Binary System. The experimental VLE data for the binary system are given in Table 3 and Figure 1. The system presents a minimum boiling azeotrope. Figure 2 shows the experimental liquid-phase activity coefficients, γ_i, that were calculated from

$$\ln \gamma_i = \ln\left(\frac{P y_i}{x_i P_i°}\right) + (B_{ii} - v_i^{\mathrm{L}})(P - P_i°)/RT + (P/2RT)\sum_1^n \sum_1^n y_j y_k (2\delta_{ji} - \delta_{jk}) \qquad (2)$$

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \qquad (3)$$

where 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, and B_{ij} is the cross second virial coefficient. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell[11] using the molecular parameters suggested by Prausnitz et al.[12] Critical properties of all components were taken from Daubert and Danner.[2] The last two terms in eq 2 contributed less than 5.5% to the activity coefficient. As can be observed from the activity coefficients (Figure 2), the system shows positive deviations from ideality.

The thermodynamic consistency of the VLE experimental data was checked by the point-to-point test of Van Ness−Byer−Gibbs[13] using a five-order Legendre polynomial for

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

								$\mathrm{cm^3 \cdot mol^{-1}}$					
T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3	$-B_{11}$	$-B_{22}$	$-B_{33}$	$-B_{12}$	$-B_{13}$	$-B_{23}$
329.5	0.042	0.107	0.033	0.215	2.371	5.132	1.094	1475	1284	1348	1717	1006	674
328.8	0.050	0.264	0.021	0.256	1.325	2.552	1.334	1485	1297	1356	1737	1012	677
328.8	0.050	0.467	0.014	0.285	0.920	1.600	1.836	1485	1297	1356	1737	1012	677
330.2	0.051	0.670	0.013	0.317	0.744	1.163	2.909	1464	1270	1341	1698	1001	670
343.4	0.050	0.913	0.025	0.685	0.816	1.038	6.576	1287	1054	1208	1386	908	612
338.7	0.099	0.823	0.043	0.530	0.865	1.083	5.170	1346	1124	1253	1486	940	632
332.6	0.102	0.721	0.029	0.351	0.743	1.073	3.946	1429	1226	1315	1634	983	659
330.7	0.101	0.614	0.028	0.302	0.786	1.183	2.807	1457	1261	1335	1684	997	668
329.8	0.102	0.509	0.030	0.278	0.881	1.367	2.183	1470	1278	1345	1709	1004	672
329.4	0.102	0.401	0.034	0.257	1.027	1.637	1.771	1476	1286	1349	1720	1007	674
329.5	0.104	0.299	0.040	0.235	1.169	2.006	1.502	1475	1284	1348	1717	1006	674
329.9	0.104	0.192	0.051	0.235	1.462	3.045	1.242	1469	1276	1344	1706	1003	672
331.0	0.100	0.089	0.076	0.155	2.167	4.150	1.120	1452	1255	1332	1676	995	667
331.8	0.217	0.094	0.130	0.112	1.652	2.750	1.265	1441	1241	1323	1655	989	663
331.2	0.211	0.199	0.098	0.175	1.305	2.073	1.447	1450	1252	1330	1671	993	666
331.0	0.208	0.302	0.080	0.209	1.087	1.646	1.717	1452	1255	1332	1676	995	667
331.2	0.203	0.413	0.067	0.241	0.933	1.374	2.115	1450	1252	1330	1671	993	666
332.2	0.211	0.509	0.065	0.276	0.831	1.218	2.681	1435	1233	1319	1644	986	661
337.1	0.216	0.658	0.084	0.381	0.834	1.047	4.184	1367	1149	1269	1523	951	639
344.6	0.201	0.754	0.114	0.582	0.874	1.017	5.415	1272	1037	1197	1362	900	607
341.6	0.311	0.605	0.156	0.410	0.878	1.010	4.512	1309	1080	1225	1423	920	620
335.7	0.308	0.501	0.122	0.284	0.904	1.090	3.197	1386	1172	1283	1556	960	645
333.6	0.314	0.391	0.122	0.229	0.979	1.236	2.405	1415	1208	1304	1608	976	655
332.6	0.309	0.278	0.126	0.184	1.081	1.467	1.875	1429	1226	1315	1634	983	659
332.6	0.320	0.175	0.148	0.137	1.228	1.725	1.592	1429	1226	1315	1634	983	659
334.0	0.410	0.070	0.216	0.060	1.311	1.795	1.498	1409	1201	1300	1598	973	653
333.9	0.407	0.205	0.176	0.138	1.078	1.405	1.909	1411	1203	1301	1600	973	653
335.1	0.404	0.326	0.171	0.197	0.995	1.194	2.444	1394	1183	1289	1570	965	648
338.7	0.419	0.431	0.195	0.275	0.929	1.077	3.309	1346	1124	1253	1486	940	632
348.7	0.404	0.566	0.284	0.493	0.917	0.975	5.282	1225	982	1161	1285	875	591
346.2	0.533	0.404	0.355	0.327	0.965	0.998	3.840	1254	1015	1183	1331	890	601
339.7	0.533	0.299	0.270	0.200	0.969	1.080	2.881	1333	1108	1243	1464	933	628
336.5	0.521	0.189	0.246	0.126	1.044	1.234	2.169	1375	1159	1275	1537	955	642
335.6	0.531	0.034	0.276	0.027	1.203	1.533	1.643	1387	1174	1284	1558	961	646
337.7	0.608	0.104	0.305	0.073	1.055	1.238	2.079	1359	1140	1263	1509	946	636
339.8	0.597	0.218	0.293	0.145	0.937	1.071	2.768	1332	1107	1242	1461	932	627
350.5	0.601	0.371	0.476	0.345	0.964	0.966	4.422	1205	960	1145	1253	864	584
346.9	0.714	0.211	0.487	0.171	0.963	0.972	3.384	1246	1006	1176	1318	886	598
340.2	0.719	0.050	0.393	0.036	1.029	1.142	2.213	1327	1101	1238	1453	929	626
346.6	0.802	0.111	0.564	0.090	1.006	0.976	3.009	1249	1010	1179	1323	888	599
350.5	0.890	0.061	0.722	0.059	0.991	1.006	3.011	1205	960	1145	1253	864	584

the excess Gibbs free energy. The objective function selected to minimize was the sum of the squared relative deviations in the total pressure. The consistency criteria in this test is that the mean absolute deviation (MAD) between calculated and measured mole fractions of component 1 in the vapor phase, MAD(y), is less than 0.01, and that deviations scatter randomly about zero. To check the absence of bias in the data, a graphical inspection of the error in y_1 is performed; y_1 residuals are plotted versus x_1 in Figure 3. Experimental VLE data were found to be thermodynamically consistent according to this test, with a value of MAD(y) of 0.0060, and a sum of y_1 residuals (BIAS) of 0.004.

The activity coefficients were correlated with the Wilson, NRTL, and UNIQUAC equations.[14] The binary parameters were obtained by minimizing the objective function

$$\mathrm{OF} = \sum_{i=1}^{N} \left(\left| \frac{T_i^{\mathrm{expt}} - T_i^{\mathrm{calc}}}{T_i^{\mathrm{expt}}} \right| + \left| y_i^{\mathrm{expt}} - y_i^{\mathrm{calc}} \right| \right) \qquad (4)$$

where N is the number of data points. The parameters A_{12}, A_{21}, and α_{12} for the correlation equations, mean absolute deviations, and activity coefficients at infinite dilution γ_i^∞ are given in Table 4. The best fit was obtained with the Wilson equation. An azeotropic composition and temperature were calculated with the Wilson equation at the conditions $x_1 = 0.714$ and $T = 327.95$ K.

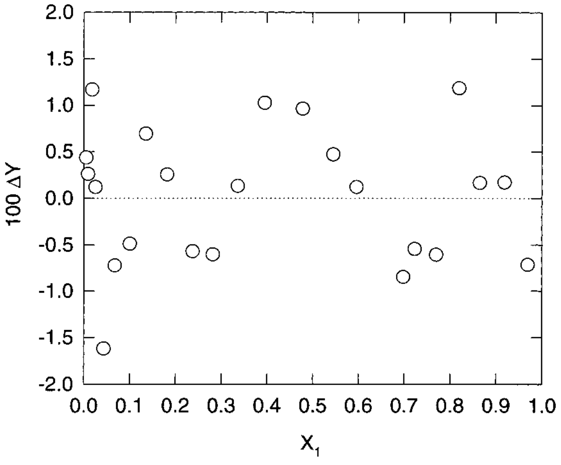

Figure 3. Deviation between calculated and measured vapor-phase mole fraction y_1 versus liquid-phase mole fraction x_1 for the system 3-methylpentane (1) + ethanol (2) at 101.3 kPa.

Ternary System. The VLE data for the ternary system are shown in Table 5 and Figure 4. The activity coefficients γ_i were calculated from eq 2. The last two terms in eq 2 contributed less than 4.5% to the activity coefficient. The ternary data were found to be thermodynamically consistent as tested by the McDermott−Ellis method[15] modified by Wisniak and Tamir.[16] The test requires that $D_i < D_{\max}$ for every experimental point. Values calculated of $D_{\max}$ −

Table 6. Correlation of Experimental Ternary Data with Wilson, NRTL, and UNIQUAC Equations Using Binary Interaction Parameters for TBA (1) + Ethanol (2) + 3-Methylpentane (3) at 101.3 kPa

model	ij	A_{ij}/J·mol^{-1}	A_{ji}/J·mol^{-1}	α_{ij}	system	MAD(y_1)	MAD(y_2)	MAD(y_3)	max dev in y	MAD(T)/K
Wilson	1−2[a]	784.630	−343.430		1 + 2 + 3	0.0033	0.0059	0.0083	0.034	0.16
	1−3[b]	5634.38	146.56							
	2−3	9412.87	1537.29							
NRTL	1−2[a]	−989.00	714.30	0.30	1 + 2 + 3	0.0036	0.0040	0.0068	0.029	0.15
	1−3[b]	1968.56	4530.95	0.674						
	2−3	3481.14	5903.23	0.42						
UNIQUAC	1−2[a]	194.90	−195.04		1 + 2 + 3	0.0058	0.0057	0.0108	0.026	0.34
	1−3[b]	−1015.96	2933.79							
	2−3	−488.64	4313.99							

[a] Aucejo et al.[8] [b] Gabaldón et al.[16]

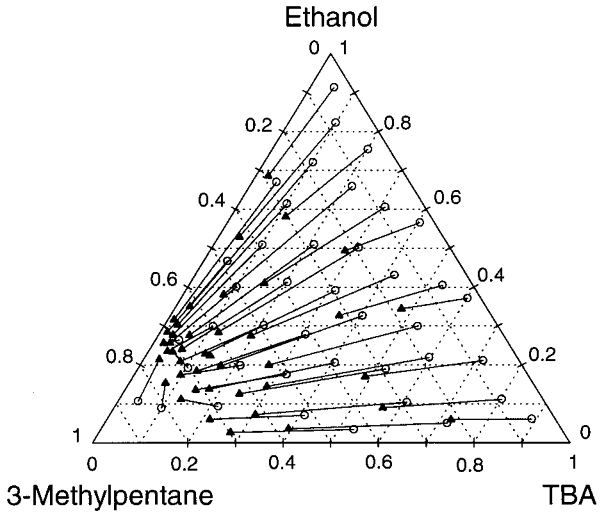

Figure 4. Vapor−liquid equilibrium tie lines for the TBA (1) + ethanol (2) + 3-methylpentane (3) system at 101.3 kPa: ○, liquid-phase mole fraction; ▲, vapor phase mole fraction.

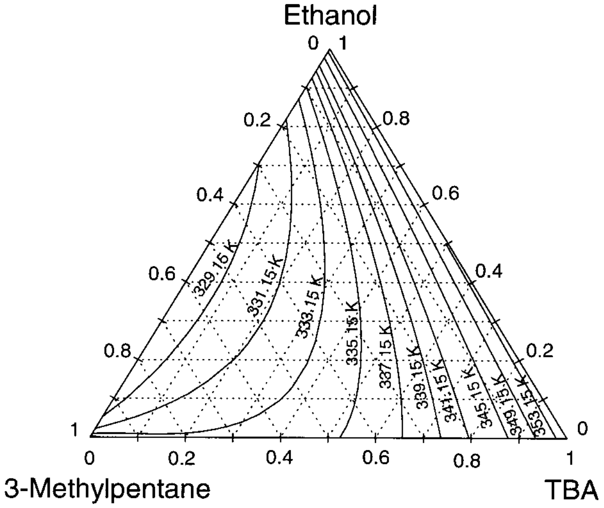

Figure 5. Boiling isotherms for the TBA (1) + ethanol (2) + 3-methylpentane (3) system at 101.3 kPa calculated with the Wilson model as a function of the liquid mole fraction.

D_i were >0 for every experimental point with a mean value of 0.055.

Vapor−liquid equilibrium for the ternary system has been predicted by using the Wilson, NRTL, and UNIQUAC models for the activity coefficients of the components with the binary interaction parameters obtained from the regression of binary data. The values of the binary interaction parameters have been taken from this study and from the literature[8,9] and are summarized in Table 6 for the readers' convenience. Table 6 also lists the mean absolute deviations between experimental and calculated temperatures and vapor-phase mole fractions of the components, and the maximum deviations in vapor-phase mole fractions. The three models yield similar deviations, with each representing the data successfully. Thus, the models can be used to predict the vapor-phase compositions and boiling points from liquid-phase compositions at the system pressure. As an example, boiling isotherms calculated with the Wilson model are presented in Figure 5.

Acknowledgment

Sonia Lora's help is gratefully acknowledged.

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Received for review January 14, 2000. Accepted June 2, 2000. Financial support by MEC, Spain, (Project No. PB96-0788) is acknowledged.

JE000005B