J. Chem. Eng. Data 1989, 34, 415–419

Liquid–Liquid Equilibria of the System Water + Acetic Acid + Methyl Isopropyl Ketone between 25 and 55 °C

José M. Correa, Antonio Blanco, and Alberto Arce*

Department of Chemical Engineering, University of Santiago de Compostela, Spain

This paper reports experimental data for the solubility of the binary mixture water + methyl isopropyl ketone at several temperatures in the range 20–55 °C, together with liquid–liquid equilibrium data for the ternary mixture water + acetic acid + methyl isopropyl ketone at 25, 35, 45 and 55 °C. NRTL and UNIQUAC equations were fitted satisfactorily to the experimental data for the ternary mixture, but UNIFAC predictions agreed only qualitatively with these data.

Introduction

To be able to evaluate methyl isopropyl ketone as an agent for the extraction of acetic acid from dilute aqueous solutions, we have obtained experimental liquid–liquid equilibrium data for the ternary mixture water + acetic acid + methyl isopropyl ketone (MIPK) at 25, 35, 45, and 55 °C (no such data have previously been published for this mixture). These data are also used to test NRTL (*1*) and UNIQUAC (*2*) (the most common semitheoretical equations) and the UNIFAC prediction method (*3*), the parameters obtained by Magnussen et al. (*4*) being used for the latter.

Experimental Section

Reagents. RPE grade acetic acid and methyl isopropyl ketone (from Carlo Erba) were used as supplied after being found chromatographically to be >99.8 and >99.0% pure, respectively. Water was triple-distilled.

Procedure. At each temperature, solubility curves were determined by the cloud-point method (*5*) in a magnetically stirred cell, Figure 1a, held constant to within ±0.05 °C of the desired temperature measured to ±0.01 °C by use of certified Siebert & Kühn thermometers (*6*). Tie-line data were obtained by use of a similar cell, shown in Figure 1b, with a lateral orifice closed by a septum: each mixture was stirred vigorously for 1 h and then left to attain equilibrium before samples of each phase were withdrawn through the septum by use of hypodermic needles. When necessary, samples were preheated to ensure miscibility before injection into the chromatograph. The compositions of the samples were determined in a Perkin-Elmer Sigma 3 gas chromatograph equipped with a thermal conductivity detector and a Perkin-Elmer Sigma 15 integrator. Stainless steel columns, 6 ft × 1/8 in. (outer diameter) packed with Chromosorb 102 80/100 were used with a high-purity (>99.998%) nitrogen carrier gas flow rate of 25 mL/min, an oven temperature of 180 °C, injector and detector temperatures of 240 °C, and a detector current of 65 mA. Calibration was carried out with ternary mixtures whose known compositions were close to the solubility curves. The maximum difference between measured and known composition of calibration samples was ±0.002 mole fraction.

Results

The solubilities determined for the binary mixture water + MIPK are shown in Figure 2 together with those reported by Gross et al. (*7*) and Ginnings et al. (*8*). The findings of all three studies agree well with regard the solubility of MIPK in water, which is practically independent of temperature. It is unknown why our results for the organic phase differ considerably from earlier data, though both sets show the solubility of water in MIPK to increase with temperature.

Table I. Binodal Compositions of the System Water + Acetic Acid + Methyl Isopropyl Ketone at 25 °C

mole fraction			mole fraction		
water	acetic acid	MIPK	water	acetic acid	MIPK
0.985	0.000	0.015	0.715	0.131	0.154
0.962	0.020	0.018	0.671	0.141	0.188
0.953	0.027	0.020	0.626	0.148	0.226
0.941	0.037	0.022	0.580	0.151	0.269
0.932	0.044	0.024	0.529	0.150	0.321
0.912	0.058	0.030	0.475	0.143	0.382
0.891	0.071	0.038	0.413	0.129	0.458
0.869	0.082	0.049	0.376	0.116	0.508
0.844	0.093	0.063	0.329	0.098	0.573
0.817	0.103	0.080	0.270	0.076	0.654
0.788	0.112	0.100	0.218	0.047	0.735
0.759	0.119	0.122	0.152	0.000	0.848
0.731	0.127	0.142			

Table II. Binodal Compositions of the System Water + Acetic Acid + Methyl Isopropyl Ketone at 35 °C

mole fraction			mole fraction		
water	acetic acid	MIPK	water	acetic acid	MIPK
0.987	0.000	0.013	0.716	0.131	0.153
0.976	0.009	0.015	0.674	0.140	0.186
0.965	0.019	0.016	0.631	0.146	0.223
0.953	0.028	0.019	0.584	0.149	0.267
0.943	0.036	0.021	0.533	0.149	0.318
0.932	0.044	0.024	0.472	0.144	0.384
0.913	0.058	0.029	0.426	0.133	0.441
0.891	0.071	0.038	0.367	0.116	0.517
0.870	0.082	0.048	0.319	0.098	0.583
0.845	0.093	0.062	0.264	0.074	0.662
0.817	0.103	0.080	0.202	0.043	0.755
0.788	0.112	0.100	0.162	0.000	0.838
0.744	0.124	0.132			

Table III. Binodal Compositions of the System Water + Acetic Acid + Methyl Isopropyl Ketone at 45 °C

mole fraction			mole fraction		
water	acetic acid	MIPK	water	acetic acid	MIPK
0.987	0.000	0.013	0.728	0.127	0.145
0.977	0.009	0.014	0.680	0.137	0.183
0.966	0.018	0.016	0.637	0.143	0.220
0.956	0.027	0.017	0.592	0.147	0.261
0.944	0.036	0.020	0.539	0.147	0.314
0.933	0.044	0.023	0.487	0.140	0.373
0.912	0.058	0.030	0.430	0.128	0.442
0.892	0.070	0.038	0.390	0.112	0.498
0.869	0.082	0.049	0.342	0.094	0.564
0.843	0.093	0.064	0.293	0.072	0.635
0.815	0.103	0.082	0.237	0.041	0.722
0.784	0.112	0.104	0.206	0.022	0.772
0.757	0.119	0.124	0.173	0.000	0.827

The compositions defining the binodal curves of the ternary mixture water + acetic acid + MIPK at the various tempera-

---

* Author to whom correspondence should be addressed.

0021-9568/89/1734-0415$01.50/0

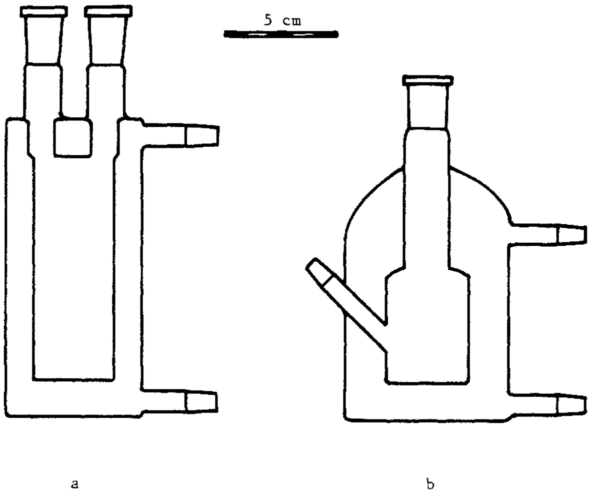

Figure 1. Sketch of the cells used. (a) Solubility cell. (b) Equilibrium cell.

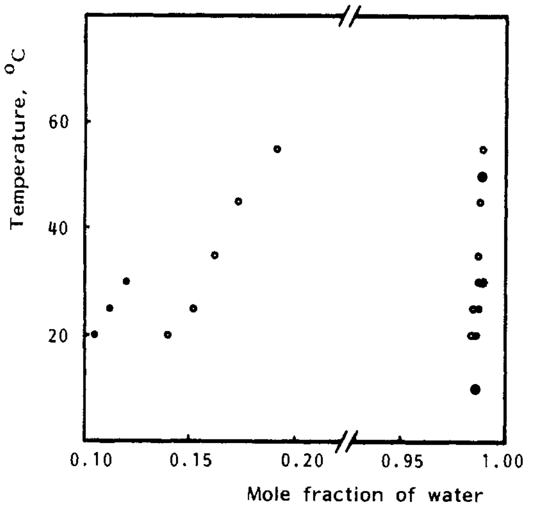

Figure 2. Solubility data for the mixture water + MIPK: O, this work; *, Gross et al. (*7*); ●, Ginnings et al. (*8*).

Table IV. Binodal Compositions of the System Water + Acetic Acid + Methyl Isopropyl Ketone at 55 °C

mole fraction			mole fraction		
water	acetic acid	MIPK	water	acetic acid	MIPK
0.989	0.000	0.011	0.725	0.126	0.149
0.979	0.009	0.012	0.687	0.134	0.179
0.967	0.018	0.015	0.648	0.139	0.213
0.955	0.027	0.018	0.603	0.143	0.254
0.943	0.036	0.021	0.554	0.142	0.304
0.932	0.044	0.024	0.497	0.137	0.366
0.913	0.058	0.029	0.441	0.122	0.437
0.892	0.070	0.038	0.399	0.110	0.491
0.868	0.082	0.050	0.359	0.093	0.548
0.842	0.093	0.065	0.317	0.070	0.613
0.813	0.102	0.085	0.267	0.043	0.690
0.783	0.111	0.106	0.191	0.000	0.809
0.753	0.119	0.128			

Table V. Liquid–Liquid Equilibria of the System Water + Acetic Acid + Methyl Isopropyl Ketone at 25, 35, 45, and 55 °C

	aqueous phase[a]			organic phase[a]		
temp, °C	water	acetic acid	MIPK	water	acetic acid	MIPK
25	0.974	0.009	0.017	0.186	0.031	0.783
	0.960	0.021	0.019	0.232	0.065	0.703
	0.947	0.031	0.022	0.301	0.094	0.605
	0.938	0.039	0.023	0.356	0.114	0.530
	0.918	0.054	0.028	0.431	0.134	0.435
	0.900	0.065	0.035	0.511	0.149	0.340
35	0.975	0.010	0.015	0.186	0.030	0.784
	0.961	0.021	0.018	0.245	0.062	0.693
	0.950	0.030	0.020	0.294	0.091	0.615
	0.939	0.039	0.022	0.349	0.115	0.536
	0.925	0.050	0.025	0.424	0.133	0.443
	0.911	0.059	0.030	0.499	0.149	0.352
45	0.976	0.010	0.014	0.222	0.030	0.748
	0.963	0.021	0.016	0.277	0.061	0.662
	0.950	0.031	0.019	0.320	0.088	0.592
	0.938	0.040	0.022	0.379	0.112	0.509
	0.925	0.049	0.026	0.437	0.132	0.431
	0.916	0.055	0.029	0.515	0.142	0.343
55	0.979	0.009	0.012	0.247	0.029	0.724
	0.968	0.018	0.014	0.305	0.058	0.637
	0.952	0.030	0.018	0.352	0.088	0.560
	0.935	0.042	0.023	0.407	0.109	0.484
	0.922	0.051	0.027	0.478	0.131	0.391
	0.909	0.060	0.031	0.552	0.143	0.305

[a] Mole fraction.

tures employed are listed in Tables I–IV, and Table V lists the compositions corresponding to the ends of tie lines. Figure 3, in which the experimental binodal curves and tie lines are drawn by using solid lines, shows that except for organic phases with very low concentrations of acetic acid, the solubilities are practically unaltered between 25 and 35 °C. On raising the temperature from 35 to 55 °C, the ketone-rich region of the binodal curve shifts slightly toward the vertex corresponding to water. At all temperatures, the ends of the experimental tie lines lie within mole fraction to the experimental binodal curves in spite of different methods having been used for their determination.

Correlation by the NRTL and UNIQUAC Equations

The NRTL (*1*) and UNIQUAC (*2*) equations were both fitted to the experimental data for the ternary mixture water + acetic acid + MIPK by using the computer program developed by Sørensen (*9*), the NRTL nonrandomness parameter α_{ij} being successively assigned the values 0.1, 0.2, and 0.3. For each given temperature, the system-specific parameters of the equation fitted are estimated by Sørensen's program by minimizing the objective function

$$F_x = \sum^{k} \min \sum^{i} \sum^{j} (x_{ijk} - \hat{x}_{ijk})^2 + Q\sum^{n} P_n{}^2 + \left[\ln\left(\frac{\hat{\gamma}^{\mathrm{I}}_{s\infty}}{\hat{\gamma}^{\mathrm{II}}_{s\infty}}\beta_\infty\right)\right]^2 \tag{1}$$

The overall procedure in which this program was used has been described elsewhere (*10*). Goodness of fit was measured by the residual function

$$F = 100[\sum^{k} \min \sum^{i} \sum^{j} (x_{ijk} - \hat{x}_{ijk})^2/6M]^{1/2} \tag{2}$$

and by the mean percentage error of the solute distribution ratio:

$$\Delta\beta = 100[\sum^{k}((\hat{\beta}_k - \beta_k)/\beta_k)^2/M]^{1/2} \tag{3}$$

Table VI lists the values of F and $\Delta\beta$ achieved at each temperature both without fixing β_∞, the solute distribution ratio at infinite dilution, and when β_∞ was fixed at the value minimizing $\Delta\beta$. In the latter case the overall goodness of fit as measured by F was in some cases slightly poorer, but the improvement in accuracy for low concentrations of acetic acid was considerable, as can be appreciated in Figure 4, which shows the experimental acetic acid distribution ratio at 35 °C together with those calculated by using the NRTL (α_{ij} = 0.3, which gave the best NRTL results) and UNIQUAC equations

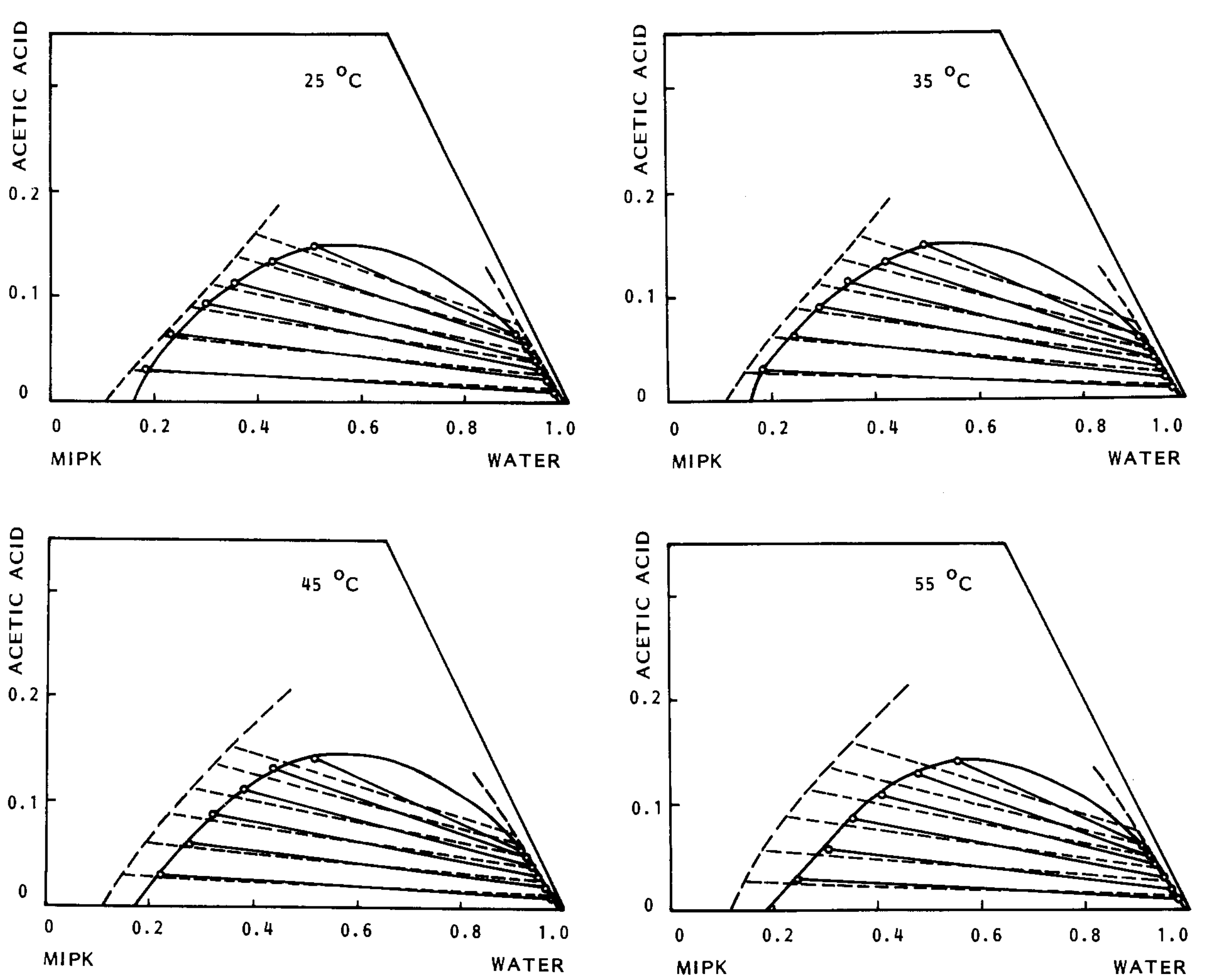

Figure 3. Binodal curves and tie lines for the system water + acetic acid + MIPK at 25, 35, 45, and 55 °C: —, experimental results; ---, UNIFAC predictions.

Table VI. Residuals F and $\Delta\beta$ of NRTL and UNIQUAC Equations Fitted to Liquid-Liquid Equilibrium Data for the System Water + Acetic Acid + Methyl Isopropyl Ketone at 25, 35, 45, and 55 °C

model		25 °C		35 °C		45 °C		55 °C	
NRTL (α_{ij} = 0.1)	β_∞		2.7		2.1		2.2		2.7
	F, %	0.31	0.32	0.35	0.35	0.41	0.41	0.40	0.40
	$\Delta\beta$, %	8.1	6.2	7.2	6.9	7.3	7.2	6.0	5.5
NRTL (α_{ij} = 0.2)	β_∞		2.7		2.2		3.6		2.8
	F, %	0.26	0.28	0.24	0.26	0.15	0.31	0.32	0.34
	$\Delta\beta$, %	9.0	5.8	9.0	6.4	8.8	6.3	7.1	5.2
NRTL (α_{ij} = 0.3)	β_∞		3.2		2.8		3.0		3.1
	F, %	0.14	0.14	0.13	0.13	0.19	0.17	0.21	0.23
	$\Delta\beta$, %	3.8	2.9	4.1	2.0	5.4	1.7	8.3	4.5
UNIQUAC	β_∞		2.9		2.6		2.5		2.8
	F, %	0.24	0.24	0.28	0.32	0.31	0.31	0.29	0.29
	$\Delta\beta$, %	3.6	3.7	8.6	2.6	7.0	4.0	4.8	4.8

with β_∞ unfixed and fixed at its optimal value. The NRTL results can be seen to be more accurate than the UNIQUAC equation.

Tables VII and VIII list the values of the system-specific parameters obtained for the NRTL and UNIQUAC equations at each temperature using the optimal value of β_∞. Figure 5 shows the experimental equilibrium data together with those calculated by the two equations (with α_{ij} = 0.3 for the NRTL equation).

Prediction of Equilibria by the UNIFAC Method

The equilibrium data of the ternary mixture were also predicted by the UNIFAC method (*3*) using the parameters obtained by Magnussen et al. (*4*). The overall procedure employed has been described elsewhere (*10*). The discrepancy between the experimental and predicted solubilities increases

Table VII. Optimized System-Specific Parameters of the NRTL Equation with α_{ij} = 0.3 for the System Water (1) + Acetic Acid (2) + Methyl Isopropyl Ketone (3) at 25, 35, 45, and 55 °C

temp, °C	β_∞	i–j	a_{ij}[a]	a_{ji}[a]
25	3.2	1–2	923.89	−450.61
		1–3	1093.10	401.57
		2–3	−104.38	269.57
35	2.8	1–2	983.54	−435.03
		1–3	1162.90	399.66
		2–3	−254.83	500.78
45	3.0	1–2	1293.40	−486.28
		1–3	1204.00	359.66
		2–3	−42.21	425.73
55	3.1	1–2	937.16	−446.47
		1–3	1298.50	319.65
		2–3	−309.91	520.97

[a] $a_{ij} = (g_{ij} - g_{jj})/R$, K.

with temperature because the predictions (dashed lines in Figure 3) are practically independent of temperature, whereas the observed concentration of ketone in the organic phase decreases as temperature rises.

Glossary

a_{ij}	NRTL binary interaction parameter, K
b_{ij}	UNIQUAC binary interaction parameter, K
F	residual defined by eq 2, mol %
F_x	objective function, eq 1
g_{ij}	energy of interaction between an i–j pair of molecules, J/mol
M	number of tie lines
P_n	parameter values (NRTL, UNIQUAC) in the penalty term of eq 1
q_i	component i UNIQUAC area parameter
Q	10^{-10}, constant in the penalty term of eq 1
r_i	component i UNIQUAC volume parameter
R	universal gas constant, J/(mol·K)
u_{ij}	UNIQUAC binary interaction parameter, J/mol
x	liquid-phase mole fraction

Greek Letters

α_{ij}	NRTL nonrandomness parameter
β	solute distribution ratio

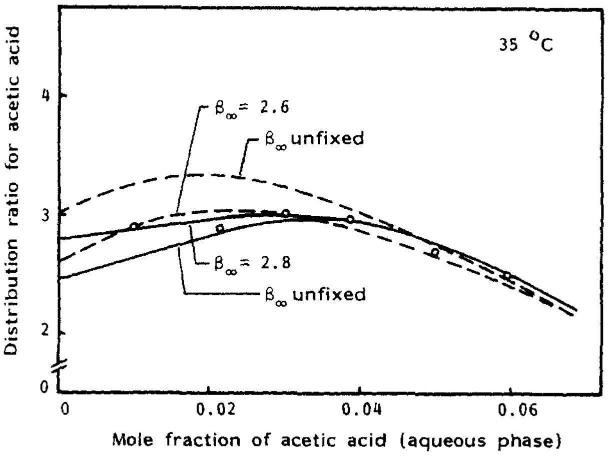

Figure 4. Influence of the value of β_∞ on the accuracy of NRTL and UNIQUAC curves in the low-concentration region at 35 °C: O, experimental; —, NRTL (α_{ij} = 0.3); ---, UNIQUAC.

Table VIII. Optimized System-Specific Parameters of the UNIQUAC Equation for the System Water (1) + Acetic Acid (2) + Methyl Isopropyl Ketone at 25, 35, 45, and 55 °C

temp, °C	β_∞	i–j	b_{ij}[a]	b_{ji}[a]
25	2.9	1–2	−83.75	−317.54
		1–3	72.71	404.41
		2–3	−50.35	−499.17
35	2.6	1–2	−117.73	−334.64
		1–3	93.19	386.97
		2–3	−25.14	−578.90
45	2.5	1–2	−183.85	−374.48
		1–3	135.96	322.05
		2–3	−44.73	−714.17
55	2.8	1–2	−93.80	−387.65
		1–3	147.96	287.53
		2–3	−79.40	−622.51

component	r_i	q_i
water	0.9200	1.4000
acetic acid	2.2024	2.0720
MIPK	3.9215	3.4120

[a] $b_{ij} = (u_{ij} - u_{jj})/R$, K.

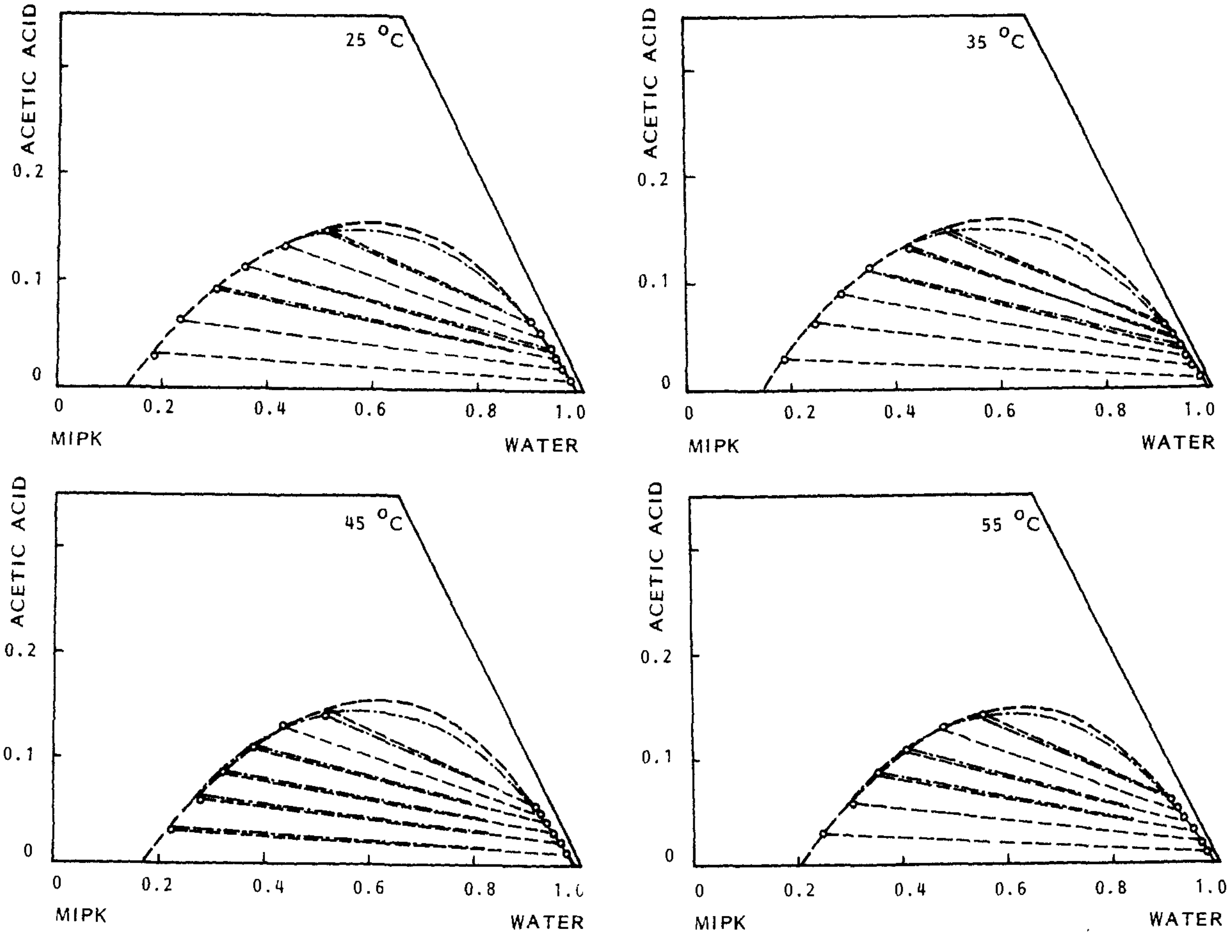

Figure 5. Binodal curves and tie lines calculated for the system water + acetic acid + methyl isopropyl ketone at 25, 35, 45, and 55 °C using the equations NRTL (α_{ij} = 0.3) (---) and UNIQUAC (–·–·), together with the corresponding experimental tie-line ends (O).

J. Chem. Eng. Data 1989, 34, 419-424

$\Delta\beta$	average error in solute distribution ratio
γ	activity coefficient

Subscripts

i, j	components i and j
j	phase j, eq 1 and 2
k	tie line k
n	1, 2, ..., NP (parameters, eq 1)
s	solute
∞	infinite dilution

Superscripts

$\hat{}$	calculated values
I, II	phases I and II, eq 1

Registry No. Acetic acid, 64-19-7; methyl isopropyl ketone, 563-80-4.

Literature Cited

(1) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135–144.
(2) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116–128.
(3) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086–1099.
(4) Magnussen, T.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20*, 331–339.
(5) Othmer, D. F.; White, R. E.; Trueger, E. *Ind. Eng. Chem.* **1941**, *33*, 1240–1248.
(6) Correa, J. M. Determinación, correlación y predicción del equilibrio líquido–líquido. Sistemas Agua + Acido acético + Cetonas. Doctoral Thesis, Universidad de Santiago de Compostela, Spain, 1985.
(7) Gross, P. M.; Rintelen, J. C.; Saylor, J. M. *J. Phys. Chem.* **1939**, *43*, 197–205.
(8) Ginnings, P. M.; Plonk, D.; Carter, E. *J. Am. Chem. Soc.* **1940**, *62*, 1923–1924.
(9) Sørensen, J. M. Correlation of liquid-liquid equilibrium data. Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark, 1980.
(10) Correa, J. M.; Arce, A.; Blanco, A.; Correa, A. *Fluid Phase Equilib.* **1987**, *32*, 151–162.

Received for review November 4, 1988. Accepted May 22, 1989.

High-Pressure Vapor–Liquid Equilibria of Mixtures of Nitrogen, Carbon Dioxide, and Cyclohexane

Steven K. Shibata[†] **and Stanley I. Sandler***

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Data are reported for the equilibrium phase compositions and densities of the carbon dioxide + cyclohexane and the nitrogen + cyclohexane systems at 366.5 and 410.9 K and for the nitrogen + carbon dioxide + cyclohexane system at the same temperatures at a variety of isobars. These data were modeled with the Peng–Robinson equation of state with generalized parameters. Good fits were obtained for the compositions in all three systems, but the predicted liquid-phase densities were in error by about 5%, as expected.

Introduction

The motivation for this research is to obtain experimental data on systems consisting of hydrocarbons and carbon dioxide, nitrogen, and other non-hydrocarbons, and to utilize these data in evaluating equations of state and their mixing rules. By determining both the compositions and the densities of the coexisting phases, equations of states and their mixing rules can be more stringently tested than with composition data alone.

The equipment used in these measurements is the double-recirculation cell with a maximum temperature of 300 °F and maximum pressure of 5000 psia described earlier (*1*). The key components of the apparatus are a 100-cm^3 through-windowed visual cell, recirculation pumps, and vibrating-tube density meters. The operating procedure for this equipment has also been described earlier (*1*) and will not be repeated here.

Experimental Results

Table I. Vapor–Liquid Equilibrium Data for the Carbon Dioxide + Cyclohexane Binary System

T, K	P, bar	x_{CO_2}	y_{CO_2}	ρ_L, g/cm^3	ρ_V, g/cm^3
366.5	1.71	0.0000	0.0000	0.7050	0.0077
366.4	17.52	0.0959	0.8984	0.7059	0.0288
366.4	34.69	0.1681	0.9374	0.7071	0.0593
366.5	51.91	0.2657	0.9495	0.7074	0.0940
366.5	68.86	0.3484	0.9515	0.7060	0.1349
366.6	86.37	0.4598	0.9500	0.7019	0.1831
366.5	103.60	0.5698	0.9402	0.6894	0.2476
366.5	125.11	0.7526	0.8977	0.6222	0.3986
366.4	128.00	0.7901	0.8732	0.5807	0.4515
410.8	4.43	0.0000	0.0000	0.6566	0.0114
410.8	17.18	0.0671	0.7166	0.6584	0.0294
410.9	34.44	0.1470	0.8295	0.6544	0.0570
410.9	51.51	0.2050	0.8593	0.6553	0.0866
410.8	69.28	0.2887	0.8850	0.6488	0.1198
410.9	86.51	0.3578	0.8861	0.6434	0.1614
410.9	104.02	0.4329	0.8777	0.6312	0.2046
410.9	120.56	0.5165	0.8636	0.6151	0.2579
410.9	138.14	0.6107	0.8320	0.5733	0.3434
410.8	144.41	0.6850	0.7846	0.5232	0.4115
410.9	145.10	0.7448	0.7671	0.4893	0.4321

Table I contains our unsmoothed, experimental data for the CO_2 + cyclohexane system at 366.5 and 410.9 K. Data for this system, at different temperatures, have been reported previously by Krichevskii and Sorina (*2*). Figures 1 and 2 are plots of composition and density for both data sets. Since the temperatures of the data sets are different, the data cannot be directly compared.

The data for the N_2 + cyclohexane system are tabulated in Table II. Two isotherms, 366.5 and 410.9 K, were measured for this system. The previously measured bubble-point data of Khodeeva (*3*) are plotted and compared with our experimental data in Figure 3, though the temperatures are not quite the same. Our density data are shown in Figure 4; there are no published density data for this system.

Tables III and IV contain our experimental, unsmoothed data for the N_2 + CO_2 + cyclohexane system at 366.5 and 410.9 K with data taken at four pressures, 68.9, 137.9, 206.8, and 275.7 bar, at both temperatures. No data for this system have been reported previously. Figures 5–8 are composition and density plots of these data sets.

[†] Present address: E. I. du Pont de Nemours & Company, Technical Group, Seaford, DE 19973.
* Author to whom correspondence should be addressed.

0021-9568/89/1734-0419$01.50/0