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Liquid–Liquid Equilibria of the Ternary System Water + Propanoic Acid + Methyl Isobutyl Ketone at Various Temperatures

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Liquid–liquid equilibrium data are reported for the binary system water + methyl isobutyl ketone over the range 20–55 °C and for the ternary system water + propanoic acid + methyl isobutyl ketone at 25, 35, 45, and 55 °C. The NRTL and UNIQUAC equations have been fitted to the experimental data by optimizing their system-specific parameters; the goodness of fit is satisfactory in both cases.

Introduction

Because of the partial miscibility of methyl isobutyl ketone and water, this ketone is a possible extraction agent for the recovery of propanoic acid from aqueous solutions. To determine its efficiency in this role, we have measured the equilibrium compositions of the ternary mixture at 25, 35, 45, and 55 °C. No data on this ternary system have been found in the literature. The experimental data were correlated by fitting the NRTL and UNIQUAC models.

Experimental Section

Materials. Propanoic acid was obtained from Merck and methyl isobutyl ketone from Carlo Erba (purities >99.4% and >99.5%, respectively). Both were used without further purification. Water distilled three times was used in all the measurements.

Apparatus and Procedure. Solubility values for the construction of solubility curves were obtained by the cloud-point method in a thermostated cell equipped with a magnetic stirrer (*1*). The maximum deviation from the required temperature was ±0.05 K. At each temperature, tie lines covering the biphasic region of the composition diagram were determined. Equilibrium compositions were obtained in a jacketed cell, similar to that described above, with septum seals allowing samples to be withdrawn with hypodermic syringes. In each experiment, the components were mixed for 1 h and then left to reach equilibrium over the following 4 h.

The compositions of the conjugate phases were determined using a Perkin-Elmer Sigma 3 gas chromatograph with a thermal conductivity detector connected to a Perkin-Elmer Sigma 15 integration unit. Separation was performed in a stainless-steel 6 ft × 1/8 in. OD column packed with Chromosorb 102 80/100 through which helium of purity >99.998% was pumped at a flow rate of 35 cm^3/min. The oven and injector temperatures were 200 and 240 °C, respectively, and the detector current was 150 mA. Calibration was carried out using internal standards whose compositions lay close to the solubility curve. In all cases, the volume injected was 0.2 μL and the maximum error in the composition measurement mole fractions was verified as ±0.002.

Results

Figure 1 shows our mutual solubility results for water and methyl isobutyl ketone over the range 20–55 °C, alongside data due to Ginnings et al. (*2*), Gross et al. (*3*), Hlavaty and Linek (*4*), Iguchi and Fuse (*5*), Sherwood et al. (*6*), and Rajapakse et al. (*7*). The solubility of the ketone in the aqueous phase is practically temperature-independent, while the solubility of water in the organic phase increases with temperature.

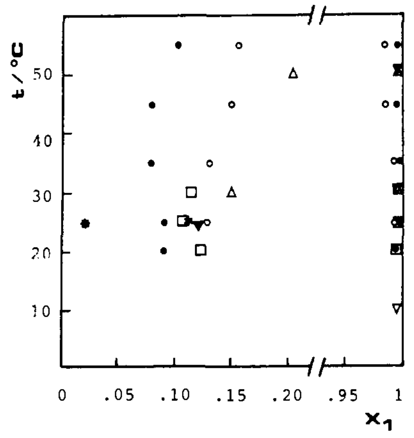

Figure 1. Solubility data for the mixture water + methyl isobutyl ketone: ○, this work; ▽, Gross et al. (*4*); □, Ginnings et al. (*3*); ▼, Hlavaty and Linek (*5*); *, Iguchi and Fuse (*6*); ●, Sherwood et al. (*7*); △, Rajapakse et al. (*8*).

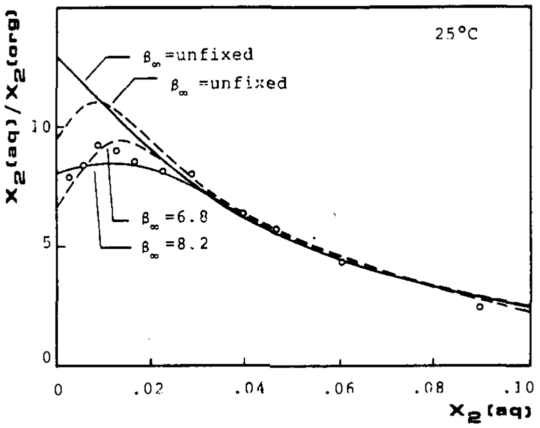

Figure 2. Influence of the value of β_∞ on the accuracy of NRTL and UNIQUAC curves in the low-concentration region, at 25 °C: ○, experimental; - - -, NRTL (α_{ij} = 0.1); —, UNIQUAC.

Table I shows the equilibrium compositions of the ternary mixture water + propanoic acid + methyl isobutyl ketone at 25, 35, 45, and 55 °C. The region of partial miscibility becomes smaller as temperature increases, this effect being more marked in the organic phase than in the aqueous phase.

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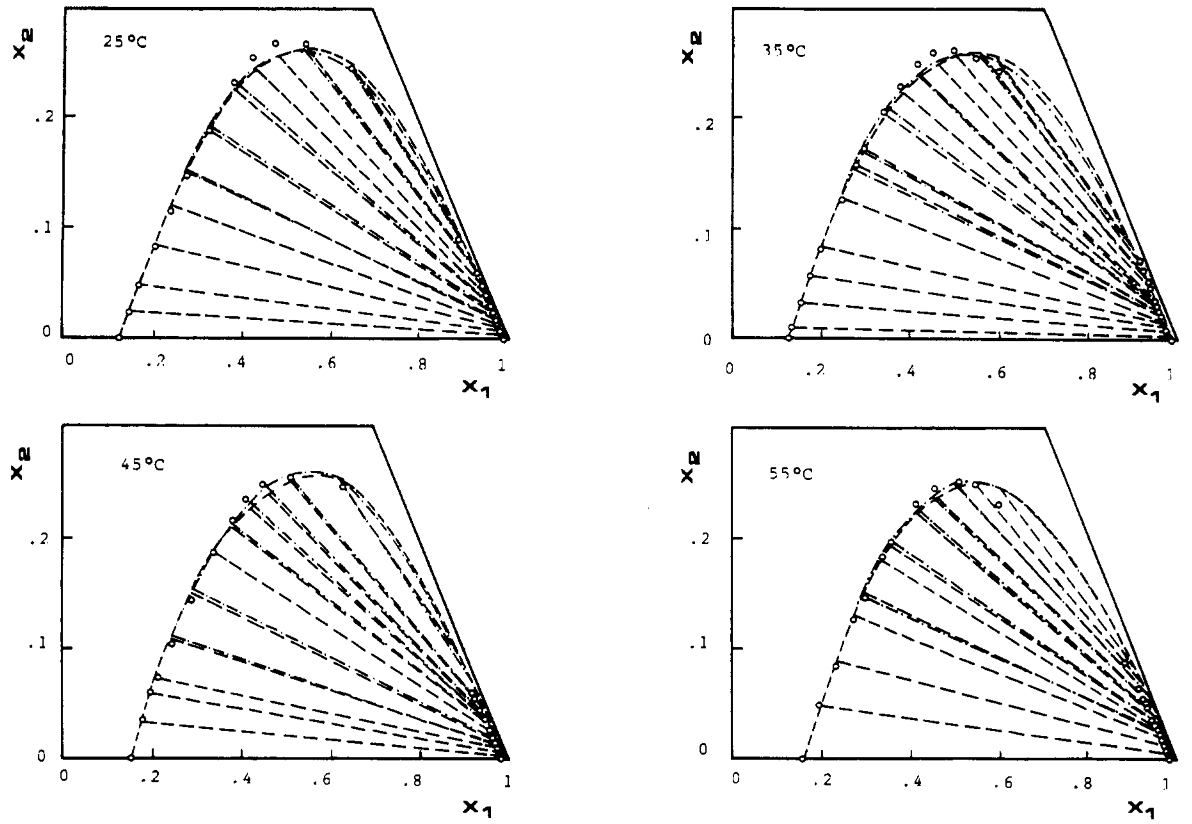

Figure 3. Binodal curves and tie lines calculated for the system water + propanoic acid + methyl isobutyl ketone at 25, 35, 45, and 55 °C using NRTL (α_{ij} = 0.1) (—) and UNIQUAC (- - -) equations, together with the corresponding experimental ends of the tie lines (○).

Table I. Experimental Liquid–Liquid Equilibrium Compositions for the Ternary System Water (1) + Propanoic Acid (2) + Methyl Isobutyl Ketone (3)

	organic phase		aqueous phase			organic phase		aqueous phase	
t/°C	x_1	x_2	x_1	x_2	t/°C	x_1	x_2	x_1	x_2
25.00	0.127	0.000	0.995	0.000	45.00	0.150	0.000	0.986	0.000
	0.150	0.024	0.992	0.003		0.180	0.036	0.983	0.003
	0.170	0.050	0.989	0.006		0.200	0.060	0.980	0.006
	0.203	0.083	0.986	0.009		0.215	0.074	0.976	0.010
	0.240	0.118	0.982	0.013		0.245	0.106	0.973	0.013
	0.275	0.148	0.976	0.017		0.290	0.146	0.968	0.017
	0.322	0.189	0.970	0.023		0.335	0.188	0.963	0.022
	0.380	0.233	0.964	0.029		0.375	0.218	0.955	0.028
	0.421	0.257	0.951	0.040		0.410	0.238	0.946	0.036
	0.470	0.268	0.944	0.047		0.448	0.250	0.935	0.043
	0.541	0.267	0.931	0.060		0.510	0.256	0.925	0.052
	0.645	0.226	0.889	0.090		0.625	0.247	0.915	0.058
35.00	0.130	0.000	0.993	0.000	55.00	0.156	0.000	0.985	0.000
	0.135	0.010	0.990	0.003		0.200	0.049	0.980	0.005
	0.154	0.034	0.987	0.006		0.235	0.084	0.974	0.011
	0.175	0.060	0.985	0.008		0.275	0.126	0.970	0.015
	0.200	0.082	0.981	0.012		0.300	0.146	0.968	0.017
	0.245	0.128	0.977	0.016		0.335	0.182	0.965	0.020
	0.278	0.158	0.974	0.019		0.357	0.198	0.960	0.024
	0.298	0.173	0.972	0.021		0.410	0.231	0.946	0.035
	0.340	0.206	0.966	0.026		0.455	0.244	0.935	0.046
	0.378	0.230	0.958	0.034		0.510	0.250	0.925	0.054
	0.415	0.250	0.954	0.038		0.550	0.247	0.914	0.064
	0.450	0.260	0.944	0.048		0.600	0.230	0.880	0.086
	0.500	0.262	0.939	0.052					
	0.550	0.256	0.925	0.064					
	0.600	0.244	0.915	0.073					

Correlation

The NRTL equation of Renon and Prausnitz (*8*) and the UNIQUAC equation of Abrams and Prausnitz (*9*) were both fitted to the experimental data using the computer program developed by Sørensen (*10*) to optimize the six system-specific parameters used by each of these models for ternary systems (two parameters per binary). The NRTL nonrandomness parameter α was successively assigned the fixed values 0.1, 0.2, and 0.3. The program optimizes the system-specific parameters of the equations by minimizing the objective function

$$F_x = \sum^{k} \min \sum^{i} \sum^{j} (x_{ijk} - \hat{x}_{ijk})^2 + Q \sum P_{\mathrm{n}}^{\,2} + |\ln ((\gamma_\infty^{\mathrm{I}}/\gamma_\infty^{\mathrm{II}})\beta_\infty)|^2 \quad (1)$$

in which the constant Q reduces the risk of multiple solutions

Table II. Correlation of Liquid–Liquid Equilibrium Data for the Ternary System Water + Propanoic Acid + Methyl Isobutyl Ketone: Numerical Values of the Goodness of Fit Functions *F* and $\Delta\beta$

model		25 °C		35 °C		45 °C		55 °C	
UNIQUAC	β_∞		8.2		4.3		9.7		10.5
	F	0.47	0.49	0.34	0.41	0.36	0.37	0.45	0.51
	$\Delta\beta$	21.4	5.5	65.1	16.6	10.8	9.5	20.4	8.2
NRTL	β_∞		6.8		4.1		9.5		8.1
($\alpha = 0.1$)	F	0.45	0.45	0.37	0.38	0.33	0.33	0.43	0.47
	$\Delta\beta$	16.7	4.9	78.6	13.3	9.6	9.5	25.8	7.8
NRTL	β_∞		7.5		4.1		9.5		8.4
($\alpha = 0.2$)	F	0.47	0.48	0.37	0.42	0.32	0.32	0.45	0.48
	$\Delta\beta$	22.4	4.5	73.3	14.2	9.8	9.6	29.0	7.8
NRTL	β_∞		8.7		4.7		10.3		9.5
($\alpha = 0.3$)	F	0.53	0.57	0.46	0.56	0.23	0.25	0.46	0.53
	$\Delta\beta$	12.9	7.0	92.9	18.9	12.3	9.5	35.4	7.9

Table III. NRTL Parameters ($\alpha = 0.1$) for the System Water (1) + Propanoic Acid (2) + Methyl Isobutyl Ketone (3) at 25, 35, 45, and 55 °C

t/°C	β_∞	i–j	a_{ij}	a_{ji}
25	6.8	1–2	2105.30	−1124.50
		1–3	1869.40	−321.51
		2–3	−1297.70	2043.30
35	4.1	1–2	2293.30	−1266.90
		1–3	2087.30	−360.52
		2–3	−1279.90	2143.50
45	9.5	1–2	2364.10	−1176.30
		1–3	1849.10	−357.80
		2–3	−33.71	64.14
55	8.1	1–2	2127.20	−1142.40
		1–3	1884.00	−358.42
		2–3	−1388.80	2075.40

Table IV. UNIQUAC Parameters for the System Water (1) + Propanoic Acid (2) + Methyl Isobutyl Ketone (3) at 25, 35, 45, and 55 °C

t/°C	β_∞	i–j	b_{ij}	b_{ji}
25	8.2	1–2	353.18	−171.90
		1–3	91.88	404.83
		2–3	−201.58	357.47
35	4.3	1–2	484.26	−230.52
		1–3	156.21	371.16
		2–3	−231.60	520.08
45	9.7	1–2	208.72	−21.14
		1–3	25.14	477.78
		2–3	167.94	−49.00
55	10.5	1–2	119.71	−27.97
		1–3	22.91	487.49
		2–3	145.59	−144.68

Table V. *r* and *q* Values for the UNIQUAC Equation

	r	q
methyl isobutyl ketone	4.596	3.952
propanoic acid	2.877	2.612
water	0.92	1.4

and β_∞ is the solute distribution ratio at infinite solution. The goodness of fit was measured by the residual function F and by $\Delta\beta$, the mean error of the solute distribution ratio:

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

$$\Delta\beta = 100\left(\sum^{k} |(\beta_k - \hat{\beta}_k)/\beta_k|^2 / M\right)^{1/2} \qquad (3)$$

In these equations M is the number of tie lines. For each temperature and model, numerous curves were fitted using different values of β_∞, and two were retained: the curve minimizing F and the curve minimizing $\Delta\beta$. Values of F and $\Delta\beta$ are listed for both these curves in Table II, which also shows the $\Delta\beta$ optimal values of β_∞. The $\Delta\beta$-optimal curves have poorer overall fit (F), but fit the data better in the region of low solute concentration. The NRTL equation fits best with $\alpha = 0.1$.

Tables III and IV list, for each temperature, the system-specific parameters of the NRTL and UNIQUAC equations obtained using the $\Delta\beta$-optimal value of β_∞. Figure 3 shows the experimental equilibrium data, those calculated using these equations, and the good fit obtained.

The values of r and q used for UNIQUAC calculations, which were derived from subgroup volumes and areas published by Magnussen et al. (*11*), are listed in Table V.

Conclusions

The solubility of methyl isobutyl ketone in water is practically temperature-independent and, over the range of temperatures considered here, is less than 2% by mole fraction. The solubility of water in the ketone increases slightly with temperature.

The data for the ternary system water + propanoic acid + methyl isobutyl ketone show that the ketone can be used as an extraction agent to recover propanoic acid from aqueous solutions. For this the best working temperature is 25 °C, at which the area of the biphasic region is greatest.

The NRTL and UNIQUAC equations have been fitted to the experimental data. The NRTL equation affords the better fit.

List of Symbols

a_{ij}	parameters for the NRTL correlation
b_{ij}	parameters for the UNIQUAC correlation
F	residual function for the NRTL and UNIQUAC correlations
F_z	objective function for the correlation
M	number of tie lines
P_n, Q	parameters (eq 1)
x_{ijk}	mole fraction of the ith component, jth phase, and kth tie line
$\hat{x}_{ijk}$	mole fraction of the ith component, jth phase, and kth tie line, calculated value
α	NRTL nonrandomness parameter
β_k	solute distribution ratio of the kth tie line
$\hat{\beta}_k$	solute distribution ratio of the kth tie line, calculated value
β_∞	solute distribution ratio of the kth tie line, at infinite dilution
$\Delta\beta$	mean error of the solute distribution ratio
γ	activity coefficient (phases I and II)

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