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Liquid−Liquid Equilibria of the Ternary Mixtures Water + Propanoic Acid + Methyl Ethyl Ketone and Water + Propanoic Acid + Methyl Propyl Ketone

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We report mutual solubilities of water + methyl ethyl ketone and water + methyl propyl ketone at temperatures between 25 and 55 °C, and binodal curves and liquid−liquid equilibria for water + propanoic acid + methyl ethyl ketone and water + propanoic acid + methyl propyl ketone in the same temperature range. UNIQUAC equations fitted the experimental data better than NRTL equations: the average rms phase composition error was 0.2% for UNIQUAC as compared to 0.3% for NRTL, and the rms relative error in the solute distribution ratio was 5% for UNIQUAC as compared to 7.5% for NRTL.

Introduction

With a view to evaluating the use of methyl ethyl ketone (MEK) and methyl propyl ketone (MPK) as agents for extraction of propanoic acid from aqueous solutions, we have measured solubilities and liquid−liquid equilibria of water + propanoic acid + methyl ethyl ketone at 25, 35, and 45 °C and water + propanoic acid + methyl propyl ketone at 25, 35, 45, and 55 °C. NRTL and UNIQUAC parameters were obtained from the results.

Experimental Section

Chemicals. MEK and MPK were purchased from Carlo Erba with purities better than 99.0% and 99.8%, respectively, and propanoic acid was from Merck with a purity better than 99.0%; these chemicals were used without further purification. Three times distilled, deionized water was obtained in our laboratory by the usual methods.

Procedure. Solubility curves were determined by the cloud-point method in a magnetically stirred cell whose temperature was both thermostated and measured with a precision of ±0.1 °C. Compositions defining the ends of tie lines were determined in a similar cell with a lateral orifice closed by a septum, through which samples of the separated phases in equilibrium were withdrawn using hypodermic syringes. In each experiment the ternary mixture to be separated was stirred vigorously for 1 h and left to settle for 4 h, which previous experiments had shown to be long enough for the phases to reach equilibrium. For diagrams of both cells, see Correa et al. (*1*).

Phase compositions were determined with a Perkin-Elmer Sigma 3 gas chromatograph with thermal conductivity detection and a Perkin-Elmer Sigma 15 integrator. Separation was performed in a 6 ft × 1/8 in. o.d. stainless steel column packed with Chromosorb 102 80/100, with a constant 35 cm^3/min flow of helium of purity >99.998%. The oven temperature was 190 °C for water + propanoic acid + MEK, and 200 °C for water + propanoic acid + MPK; for both mixtures the injection and detector temperatures were 240 °C and the detector current was 65 mA. The injection volume was always 0.2 μL. Calibration was carried out using ternary mixtures made up by mass to have compositions close to the solubility curve; the chromatographically measured mole fractions of the components in control mixtures differed by less than 0.002 from their known values. All analyses were performed in duplicate, and duplicates coincided to within 0.002 in mole fraction.

Table 1. Compositions on the Binodal Curve for the System Water (1) + Propanoic Acid (2) + Methyl Ethyl Ketone (3)

x_1	x_2	x_3	x_1	x_2	x_3
		t = 25 °C			
0.922	0.000	0.078	0.727	0.048	0.225
0.915	0.004	0.081	0.616	0.055	0.329
0.906	0.009	0.085	0.576	0.053	0.371
0.897	0.013	0.090	0.537	0.048	0.415
0.886	0.017	0.097	0.493	0.042	0.465
0.867	0.023	0.110	0.465	0.034	0.501
0.818	0.034	0.148	0.431	0.026	0.543
0.792	0.038	0.170	0.418	0.020	0.562
0.766	0.042	0.192	0.393	0.014	0.593
0.741	0.047	0.212	0.342	0.000	0.658
		t = 35 °C			
0.934	0.000	0.066	0.716	0.053	0.231
0.923	0.005	0.072	0.651	0.057	0.292
0.909	0.013	0.078	0.578	0.055	0.367
0.895	0.017	0.088	0.535	0.050	0.415
0.874	0.024	0.102	0.502	0.042	0.456
0.855	0.029	0.116	0.466	0.033	0.501
0.839	0.033	0.128	0.435	0.025	0.540
0.821	0.036	0.143	0.403	0.016	0.581
0.808	0.039	0.153	0.378	0.009	0.613
0.798	0.041	0.161	0.353	0.000	0.647
		t = 45 °C			
0.939	0.000	0.061	0.707	0.057	0.236
0.928	0.007	0.065	0.658	0.059	0.283
0.914	0.013	0.073	0.567	0.054	0.379
0.900	0.019	0.081	0.534	0.048	0.418
0.880	0.024	0.096	0.493	0.040	0.467
0.840	0.034	0.126	0.449	0.028	0.523
0.798	0.043	1.159	0.416	0.017	0.567
0.778	0.047	0.175	0.380	0.008	0.612
0.735	0.053	0.212	0.357	0.000	0.643

Results

Tables 1 and 2 list compositions corresponding to points on the binodal curves of the ternary mixtures studied at the working temperatures used. The points with zero propanoic acid concentration in these tables show that the solubility of the ketones in water was practically constant over the temperature range studied, while the solubility

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Table 2. Compositions on the Binodal Curve for the System Water (1) + Propanoic Acid (2) + Methyl Propyl Ketone (3)

x_1	x_2	x_3	x_1	x_2	x_3
		$t = 25$ °C			
0.987	0.000	0.013	0.698	0.170	0.132
0.977	0.010	0.013	0.652	0.185	0.163
0.968	0.018	0.014	0.589	0.198	0.213
0.959	0.027	0.014	0.542	0.201	0.257
0.946	0.038	0.016	0.493	0.198	0.309
0.937	0.045	0.018	0.467	0.192	0.341
0.928	0.052	0.020	0.442	0.186	0.372
0.919	0.058	0.023	0.392	0.166	0.442
0.904	0.068	0.028	0.361	0.149	0.490
0.889	0.077	0.034	0.313	0.128	0.559
0.872	0.087	0.041	0.275	0.106	0.619
0.844	0.102	0.054	0.240	0.086	0.674
0.815	0.117	0.068	0.182	0.054	0.764
0.770	0.139	0.091	0.154	0.032	0.814
0.727	0.158	0.155	0.140	0.000	0.860
		$t = 35$ °C			
0.989	0.000	0.011	0.718	0.158	0.124
0.982	0.006	0.012	0.632	0.186	0.182
0.977	0.011	0.012	0.575	0.194	0.231
0.971	0.016	0.013	0.528	0.193	0.279
0.963	0.024	0.013	0.448	0.175	0.377
0.956	0.030	0.014	0.427	0.166	0.407
0.948	0.037	0.015	0.401	0.154	0.445
0.936	0.047	0.017	0.367	0.137	0.496
0.916	0.063	0.021	0.303	0.110	0.587
0.883	0.079	0.038	0.273	0.091	0.636
0.853	0.095	0.052	0.241	0.075	0.684
0.822	0.111	0.067	0.213	0.058	0.729
0.803	0.121	0.076	0.166	0.023	0.849
0.758	0.142	0.100	0.151	0.000	0.842
		$t = 45$ °C			
0.990	0.000	0.010	0.721	0.154	0.125
0.982	0.007	0.011	0.760	0.172	0.168
0.978	0.011	0.011	0.624	0.180	0.196
0.972	0.017	0.011	0.561	0.184	0.255
0.961	0.026	0.013	0.532	0.182	0.286
0.953	0.032	0.015	0.499	0.176	0.325
0.945	0.039	0.016	0.471	0.164	0.363
0.932	0.048	0.020	0.440	0.153	0.407
0.911	0.062	0.027	0.378	0.127	0.495
0.876	0.082	0.042	0.344	0.113	0.543
0.858	0.091	0.051	0.314	0.097	0.589
0.822	0.110	0.068	0.282	0.080	0.638
0.785	0.127	0.088	0.213	0.028	0.759
0.749	0.143	0.108	0.180	0.000	0.820
		$t = 55$ °C			
0.990	0.000	0.010	0.775	0.127	0.098
0.980	0.009	0.011	0.729	0.146	0.125
0.974	0.014	0.012	0.641	0.173	0.186
0.965	0.021	0.014	0.569	0.179	0.252
0.959	0.027	0.014	0.525	0.178	0.297
0.950	0.033	0.017	0.483	0.167	0.350
0.940	0.041	0.019	0.438	0.156	0.406
0.929	0.048	0.023	0.395	0.144	0.461
0.916	0.056	0.028	0.360	0.130	0.510
0.900	0.066	0.034	0.324	0.112	0.564
0.884	0.075	0.041	0.279	0.090	0.631
0.866	0.084	0.050	0.253	0.061	0.686
0.849	0.093	0.058	0.220	0.031	0.749
0.812	0.111	0.077	0.211	0.000	0.789

of water in the ketones (MPK especially) increased with temperature. These solubility results are fairly close to previously published values (*2*–*10*) (within 0.7–10% for the temperatures used in our work) except for those reported by Siegelman and Sorum (*7*) for the organic phase of water + MEK mixtures, which differ by up to 21% from the corresponding findings of all other researchers. The compositions of the ends of tie lines are listed in Tables 3 and 4.

Table 3. Tie Lines for Liquid–Liquid Equilibria for Water (1) + Propanoic Acid (2) + Methyl Ethyl Ketone (3)

	organic phase		aqueous phase	
t/°C	x_1	x_2	x_1	x_2
25	0.416	0.017	0.915	0.004
	0.461	0.033	0.912	0.007
	0.524	0.047	0.903	0.010
	0.586	0.054	0.889	0.017
35	0.402	0.016	0.929	0.003
	0.436	0.028	0.928	0.005
	0.484	0.040	0.919	0.008
	0.517	0.051	0.912	0.011
	0.563	0.055	0.905	0.015
	0.618	0.057	0.894	0.019
45	0.418	0.019	0.933	0.004
	0.458	0.033	0.930	0.006
	0.505	0.047	0.923	0.010
	0.567	0.055	0.912	0.014
	0.618	0.059	0.902	0.018

Table 4. Tie Lines for Liquid–Liquid Equilibria for Water (1) + Propanoic Acid (2) + Methyl Propyl Ketone (3)

	organic phase		aqueous phase	
t/°C	x_1	x_2	x_1	x_2
25	0.238	0.061	0.980	0.006
	0.335	0.134	0.974	0.013
	0.420	0.182	0.964	0.023
	0.499	0.201	0.952	0.033
	0.583	0.202	0.938	0.046
	0.746	0.151	0.887	0.079
35	0.258	0.083	0.985	0.007
	0.359	0.139	0.976	0.014
	0.460	0.167	0.963	0.023
	0.519	0.187	0.953	0.031
	0.599	0.192	0.935	0.046
	0.715	0.161	0.906	0.067
45	0.262	0.065	0.982	0.006
	0.360	0.133	0.974	0.014
	0.495	0.165	0.963	0.024
	0.528	0.180	0.955	0.031
	0.627	0.182	0.933	0.048
	0.743	0.144	0.906	0.067
55	0.247	0.065	0.983	0.006
	0.306	0.108	0.981	0.010
	0.362	0.134	0.974	0.014
	0.408	0.146	0.970	0.017
	0.460	0.167	0.962	0.024
	0.540	0.178	0.954	0.032
	0.566	0.184	0.945	0.037
	0.641	0.174	0.933	0.047

Data Correlation

The NRTL (*11*) and UNIQUAC (*12*) models (see Appendix) were fitted to the experimental data for each system and temperature using Sørensen's (*13*–*15*) computer program. The NRTL equations were obtained for three prefixed values of the nonrandomness parameter α_{ij}: 0.1, 0.2, and 0.3. Optimizable parameters were found by minimizing the objective function

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

with or without the last term. In this equation, x_{ijk} and $\hat{x}_{ijk}$ are, respectively, the observed and calculated mole fractions of component i in phase j on tie line k, the second term on the right-hand side is a penalty term to reduce the risk of multiple solutions ($P_n = a_{ij}$ for the NRTL equation and b_{ij} for the UNIQUAC equation; Q is set to 10^{-10}), and the third term, in which β_∞ is the solute distribution ratio at infinite dilution and $\hat{\gamma}^{X}_{\mathrm{S}_\infty}$ is the calcu-

Table 5. Values of the Goodness-of-Fit Evaluators F and $\Delta\beta$ (Eqs 2 and 3) Achieved in Fitting UNIQUAC and NRTL Equations to the Experimental Data for Water + Propanoic Acid + Methyl Ethyl Ketone

model		$t = 25$ °C		$t = 35$ °C		$t = 45$ °C	
UNIQUAC	β_∞		5.9		6.3		6.7
	F (%)	0.10	0.11	0.12	0.12	0.10	0.10
	$\Delta\beta$ (%)	10.80	7.6	7.8	7.4	5.1	4.9
NRTL	β_∞		7.4		7.7		7.7
($\alpha_{ij} = 0.1$)	F (%)	0.17	0.22	0.23	0.25	0.21	0.24
	$\Delta\beta$ (%)	16.1	12.1	14.9	12.2	14.9	8.2
NRTL	β_∞		6.7		8.7		10.1
($\alpha_{ij} = 0.2$)	F (%)	0.11	0.20	0.19	0.30	0.15	0.31
	$\Delta\beta$ (%)	25.6	10.8	24.1	14.3	24.4	12.5
NRTL	β_∞		8.1		8.6		9.4
($\alpha_{ij} = 0.3$)	F (%)	0.08	0.03	0.16	0.28	0.12	0.28
	$\Delta\beta$ (%)	26.9	14.0	24.0	13.7	23.7	11.5

Table 6. Values of the Goodness-of-Fit Evaluators F and $\Delta\beta$ (Eqs 2 and 3) Achieved in Fitting UNIQUAC and NRTL Equations to the Experimental Data for Water + Propanoic Acid + Methyl Propyl Ketone

model		$t = 25$ °C		$t = 35$ °C		$t = 45$ °C		$t = 55$ °C	
UNIQUAC	β_∞		12.6		14.7		12.1		13.0
	F (%)	0.35	0.35	0.26	0.27	0.31	0.32	0.13	0.14
	$\Delta\beta$ (%)	6.5	6.4	5.7	3.4	4.9	4.6	1.6	1.3
NRTL	β_∞		9.7		11.5		9.7		2.2
($\alpha_{ij} = 0.1$)	F (%)	1.12	0.46	0.92	1.62	0.97	1.75	0.69	1.28
	$\Delta\beta$ (%)	16.1	6.8	40.3	12.1	60.7	18.6	48.8	7.6
NRTL	β_∞		13.3		16.5		12.8		12.8
($\alpha_{ij} = 0.2$)	F (%)	0.50	0.51	0.31	0.31	0.41	0.42	0.20	0.20
	$\Delta\beta$ (%)	18.6	8.6	5.1	4.0	10.4	6.4	3.3	1.8
NRTL	β_∞		12.3		16.0		11.7		13.1
($\alpha_{ij} = 0.3$)	F (%)	0.62	0.64	0.35	0.35	0.50	0.50	0.24	0.25
	$\Delta\beta$ (%)	49.5	9.6	9.1	4.8	15.0	7.2	11.3	2.5

lated activity coefficient of the solute at infinite dilution in phase X, accentuates deviation between the experimental and calculated results in the low solute concentration region.

Two *a posteriori* goodness-of-fit criteria were calculated: the rms error in mole fractions,

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

where M is the number of tie lines, and the rms relative error in the solute distribution ratio,

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

where β_k and $\hat{\beta}_k$ are, respectively, the experimental and calculated solute distribution ratios for tie line k.

When the β_∞ term was included in the objective function, the optimal value of β_∞ was identified by trial and error ("manually" optimized) as the value minimizing $\Delta\beta$.

Table 7. Values of the Parameters of the NRTL Equations Fitted to the Experimental Data for Water (1) + Propanoic Acid (2) + Methyl Ethyl Ketone (3)

t/°C	β_∞	α_{ij}	$i-j$	a_{ij}[a]/K	a_{ji}/K
25	7.4	0.1	1−2	−896.40	−114.30
			1−3	1330.60	−387.83
			2−3	−1332.80	768.35
35	7.7	0.1	1−2	−1028.10	−200.71
			1−3	1436.20	−421.33
			2−3	−1441.30	897.59
45	7.7	0.1	1−2	−1042.80	−5.61
			1−3	1537.60	−468.39
			2−3	−1400.60	1035.80

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

Table 8. Values of the Parameters of the NRTL Equations Fitted to the Experimental Data for Water (1) + Propanoic Acid (2) + Methyl Propyl Ketone (3)

t/°C	β_∞	α_{ij}	$i-j$	a_{ij}[a]/K	a_{ji}/K
25	13.3	0.2	1−2	1484.50	−657.54
			1−3	1204.10	117.57
			2−3	−524.73	535.34
35	16.5	0.2	1−2	1570.18	−757.18
			1−3	1269.80	138.60
			2−3	−374.70	72.29
45	12.8	0.2	1−2	1686.80	−790.66
			1−3	1329.70	111.06
			2−3	−355.17	137.27
55	12.8	0.2	1−2	1603.50	−800.63
			1−3	1382.30	132.14
			2−3	−64.25	−322.80

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

Table 9. Values of the Parameters of the UNIQUAC Equations Fitted to the Experimental Data for Water (1) + Propanoic Acid (2) + Methyl Ethyl Ketone (3)

t/°C	β_∞	$i-j$	b_{ij}[a]/K	b_{ji}/K
25	5.9	1−2	120.14	−142.34
		1−3	1.48	328.64
		2−3	91.94	−145.14
35	6.3	1−2	209.14	−155.44
		1−3	20.70	309.36
		2−3	192.44	−248.92
45	6.7	1−2	224.67	−207.78
		1−3	35.09	296.15
		2−3	87.45	−249.39

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

Table 10. Values of the Parameters of the UNIQUAC Equations Fitted to the Experimental Data for Water (1) + Propanoic Acid (2) + Methyl Propyl Ketone (3)

t/°C	β_∞	$i-j$	b_{ij}[a]/K	b_{ji}/K
25	12.6	1−2	14.32	−82.63
		1−3	114.63	301.47
		2−3	745.91	−488.84
35	14.7	1−2	348.32	−210.14
		1−3	93.12	381.32
		2−3	31.52	−110.86
45	12.1	1−2	201.50	−169.36
		1−3	132.16	309.51
		2−3	375.90	−110.86
55	13.0	1−2	242.72	−182.56
		1−3	101.85	377.04
		2−3	211.18	−289.25

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

Tables 5 and 6 list the values of F and $\Delta\beta$ of the curves fitted to the experimental data for each mixture and temperature. For curves optimized with the β_∞ term included in the objective function, the manually optimized value of β_∞ is also shown. Including the β_∞ term is generally preferable for these data, since the composition error F is increased only slightly overall, while the improvement in $\Delta\beta$ is considerable, especially for the NRTL model (and is moreover due largely to reduction of $|\hat{\beta}_k - \beta_k|$ in the low solute concentration region, which is of particular interest for separation operations). The UNIQUAC equation generally fitted better, especially in terms of $\Delta\beta$, than the NRTL equation (with which best results were achieved with $\alpha_{ij} = 0.1$ for the MEK mixture and $\alpha_{ij} = 0.2$ for the MPK mixture); Tables 7−10 list the optimized NRTL and UNIQUAC parameters, and Figures 1 and 2 show, for each ternary mixture and temperature, the experimental equilibrium data and the corresponding optimized UNIQUAC and NRTL curves.

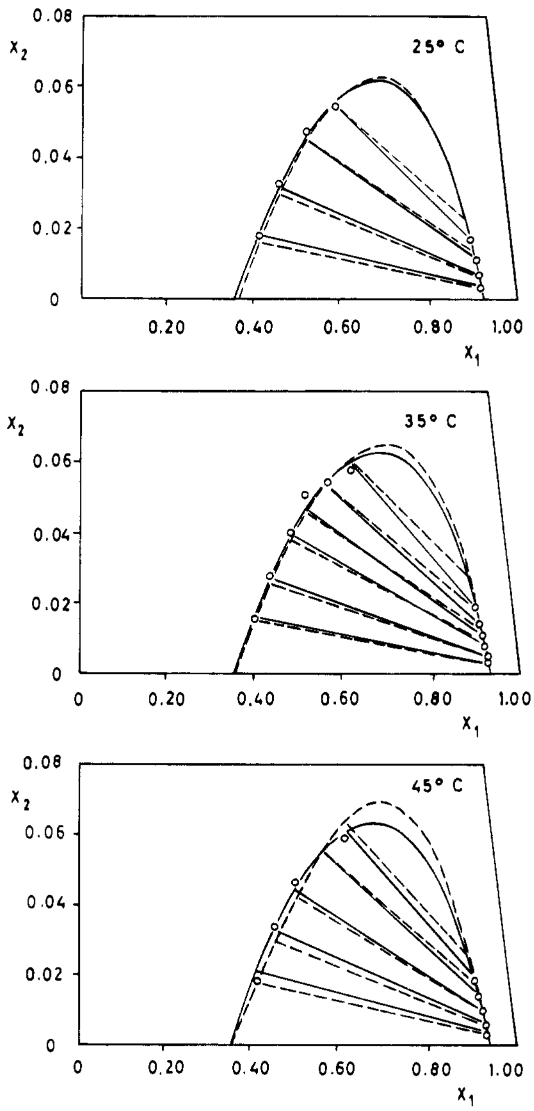

Figure 1. 1. Liquid–liquid equilibrium data for water (1) + propanoic acid (2) + methyl ethyl ketone (3) at 25, 35, and 45 °C: experimental equilibrium phase compositions (○) and calculated binodal curves and tie lines obtained by fitting UNIQUAC (—) and NRTL (- - -) equations (the latter with $\alpha_{ij} = 0.1$).

Conclusions

The experimentally determined liquid–liquid equilibria of the binary mixtures water + methyl ethyl ketone at temperatures of 25, 35, and 45 °C and water + methyl propyl ketone at temperatures of 25, 35, 45, and 55 °C show that in these temperature ranges the solubility of the ketone in water is practically independent of temperature, while the solubility of water in the ketones increases slightly with temperature.

Solubility and liquid–liquid equilibrium data were also determined experimentally for the ternary mixtures water + propanoic acid + methyl ethyl ketone at temperatures of 25, 35, and 45 °C and water + propanoic acid + methyl propyl ketone at temperatures of 25, 35, 45, and 55 °C. Fitting NRTL and UNIQUAC equations to the experimental liquid–liquid equilibrium data showed that, in general, the best fit was given by the UNIQUAC model.

In view of the high ratios between the concentrations of propanoic acid in the organic and the aqueous phases of these systems, both ketones are suitable for extraction of propanoic acid from aqueous solutions (though the use of MEK would be limited to very dilute solutions). The immiscible region is considerably greater with MPK than with MEK. In the range of temperature considered, this variable has practically no effect on either the size of the immiscible region or the slopes of tie lines.

Appendix: NRTL and UNIQUAC Equations

In both the following definitions, R is the universal gas constant (J/(mol·K)), T is temperature (K), G^E/RT is the dimensionless excess Gibbs energy of a mixture of n components indexed by subscripts i and j, and x_i is the mole fraction of component i.

NRTL Equation

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_j G_{ji} x_j}$$

$$i,j = 1, 2, ..., n \text{ (components)}$$

where τ_{ij} is given by

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}$$

(g_{ij} being a parameter characterizing the energy of interaction between components i and j; $g_{ji} = g_{ij}$) and G_{ji} is given by

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji})$$

(α_{ji} being related to the degree of nonrandomness of the mixture; $\alpha_{ji} = \alpha_{ij}$). The NRTL equation is fitted to composition data by optimizing the parameters $a_{ij} = T\tau_{ji}$.

UNIQUAC Equation

$$\frac{G^E}{RT} = \sum_i x_i \ln\frac{\phi_i}{X_i} + 5\sum_i Q_i x_i \ln\frac{\theta_i}{\phi_i} - \sum_i Q_i x_i \ln[\sum_j \theta_j \tau_{ji}]$$

$$i,j = 1, 2, ..., n \text{ (components)}$$

where τ_{ij} is given by

$$\tau_{ji} = \exp\left(-\frac{u_{ji} - u_{ii}}{RT}\right)$$

(u_{ij} being a parameter characterizing the energy of interaction between components i and j; $u_{ij} = u_{ji}$) and ϕ_i and θ_i are given by

$$\phi_i = \frac{x_i R_i}{\sum_j x_j R_j} \qquad \theta_i = \frac{x_i Q_i}{\sum_j x_j Q_j}$$

(the R_i and Q_i being parameters characterizing, respectively, the molecular volume and molecular surface area of pure component i). The UNIQUAC equation is fitted to composition data by optimizing the parameters $b_{ij} = (u_{ij} - u_{jj})/R$. For this work, the values of the structural parameters R_i and Q_i were taken from ref 16: $R_{H_2O} = 0.92$, $Q_{H_2O} = 1.40$; $R_{C_2H_5COOH} = 2.8768$, $Q_{C_2H_5COOH} = 2.612$; $R_{MEK} = 3.2479$, $Q_{MEK} = 2.876$; $R_{MPK} = 3.9223$, $Q_{MPK} = 3.416$.

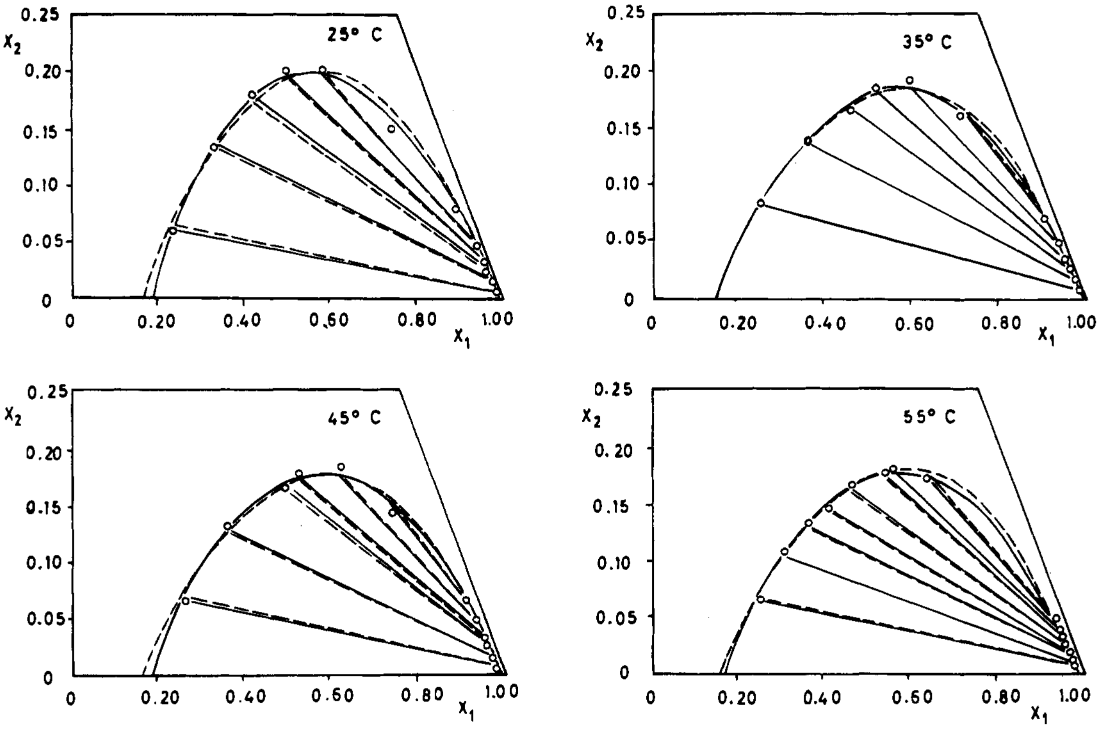

Figure 2. 2. Liquid–liquid equilibrium data for water (1) + propanoic acid (2) + methyl propyl ketone (3) at 25, 35, 45, and 55 °C: experimental equilibrium phase compositions (○) and calculated binodal curves and tielines obtained by fitting UNIQUAC (—) and NRTL (- - -) equations (the latter with $\alpha_{ij} = 0.2$).

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