J. Chem. Eng. Data **1999,** *44,* 35−39

Liquid−Liquid Equilibria of the Ternary Systems Water + Acetic Acid + Ethyl Acetate and Water + Acetic Acid + Isophorone (3,5,5-Trimethyl-2-cyclohexen-1-one)

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Liquid−liquid equilibria for the ternary systems water + acetic acid + ethyl acetate and water + acetic acid + isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) were measured over the temperature range (283 to 313) K. The results were used to estimate the interaction parameters between each of the three compounds of the systems studied for the NRTL and UNIQUAC models. The estimated interaction parameters were successfully used to predict the equilibrium compositions by the two models; experimental data were successfully reproduced. The UNIQUAC model was the most accurate in correlating the overall equilibrium composition of the studied systems. Also the NRTL model satisfactorily predicted the equilibrium composition. Isophorone experimentally resulted in a better extraction capacity for acetic acid and in a lower miscibility with water.

Introduction

The recovery of organic acids from dilute solutions resulting from fermentation processes and from spent or recycle solutions is industrially important, and many solvents have been tried to improve such recovery by means of liquid−liquid extraction (Arce et al.,1995; Briones et al., 1994; Dramur and Tatli, 1993). Several alcohols (Kirk and Othmer, 1992; Faihm et al., 1997), acetates, and ketones have been used as solvents for the recovery of acetic acid.

Precise liquid−liquid equilibrium data are required for extraction processes. Excess activity models, such as the nonrandom two-liquids model (NRTL) (Renon and Prausnitz, 1968) and the universal quasi-chemical theory (UNIQUAC) (Abrams and Prausnitz, 1975), have been successfully applied for the prediction of several liquid−liquid systems. In each case, the adjustable parameters were obtained by regressing the experimental data to the models and obtaining numerical values for the interaction parameters. The NRTL and UNIQUAC models depend on experimentally optimized interaction parameters between each two molecules in the system.

The objective of this work was to study the liquid−liquid phase equilibria of the ternary systems water + acetic acid + ethyl acetate and water + acetic acid + isophorone at several temperatures and to test the capability of the various equilibrium models to correlate these data. The compositions were measured at 283, 298, and 313 K and regressed by the NRTL and UNIQUAC models.

Previous works on these ternary systems are reported in the DECHEMA LLE data collection by Sørensen et al. (1984), based on old papers. These works are based on a lower number of data especially for the system water + acetic acid + isophorone.

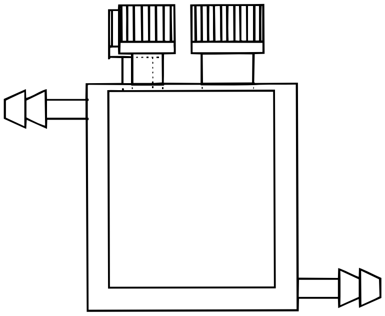

Figure 1. Apparatus.

Table 1. ***r* and *q* Values for the Used Compounds (Hansen et al., 1992)**

compound	r_i	q_i
water	0.9200	1.4000
acetic acid	0.9011	0.8480
ethyl acetate	3.4786	3.116
isophorone	5.9315	4.940

Experimental Section

***A. Chemicals*:** Acetic acid, >99.9%, supplied by Quantum Chemical Europe; water, bidistilled, supplied by Fluka Chemie; isophorone (3,5,5-trimethyl-2-cyclohexen-1-one), >97%, supplied by Sigma-Aldrich Co.; ethyl acetate, >99.5%, supplied by Fluka Chemie.

B. Apparatus and Procedure. The equilibrium runs were performed in a 200 mL extraction cell surrounded by a water jacket (see Figure 1). The water jacket was thermostatically controlled using an I. S. Co. crioterm 190 circulating thermostat. The temperature range for the

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10.1021/je9702910 CCC: $18.00

Table 2. Comparing Experimental and Predicted LLE Data for the Ternary System Water (1) + Acetic Acid (2) + Ethyl Acetate (3) (Where x = Molar Fraction)

aqueous phase						organic phase					
$100x_1$			$100x_2$			$100x_1$			$100x_2$		
exp	UNIQUAC	NRTL	exp	UNIQUAC	NRTL	exp	UNIQUAC	NRTL	exp	UNIQUAC	NRTL
$T = 283$ K											
88.299	87.859	87.698	7.592	7.485	7.802	52.981	52.891	52.624	15.643	15.585	15.921
91.196	91.154	91.292	5.759	5.594	5.575	43.444	43.501	43.543	14.464	14.369	14.357
92.920	92.890	93.062	4.596	4.502	4.382	37.387	37.461	37.628	12.958	12.850	12.662
94.225	94.365	94.435	3.545	3.521	3.416	31.907	31.723	31.933	10.586	10.857	10.591
95.462	95.903	95.721	2.447	2.442	2.481	25.437	25.294	25.419	7.704	7.950	7.756
96.662	97.381	96.904	1.342	1.357	1.598	19.008	19.126	18.985	4.447	4.408	4.491
DEB% avg.	−0.130	−0.054		1.014	−1.955		0.060	−0.015		−0.503	−0.077
$T = 298$ K											
87.819	87.582	87.278	7.766	7.721	8.135	55.623	55.455	55.244	14.849	15.074	15.236
90.944	91.225	91.255	5.907	5.693	5.745	45.439	45.541	45.628	13.960	13.897	13.783
93.246	93.002	93.149	4.620	4.591	4.481	39.554	39.527	39.686	12.421	12.402	12.220
94.575	94.606	94.765	3.525	3.528	3.338	33.349	33.412	33.557	10.354	10.276	10.117
95.800	96.080	96.149	2.431	2.488	2.315	27.339	27.371	27.392	7.539	7.539	7.526
97.284	97.403	97.309	1.373	1.503	1.426	22.030	21.964	21.777	4.425	4.511	4.736
DEB% avg.	−0.037	−0.035		−1.171	1.204		0.023	0.044		−0.350	−0.714
$T = 313$ K											
86.661	86.587	86.270	8.202	8.092	8.527	59.442	59.291	59.060	14.156	14.403	14.591
90.988	90.830	90.867	6.028	5.870	5.920	48.628	48.595	48.684	13.530	13.533	13.404
92.759	92.793	92.946	4.814	4.699	4.574	42.130	42.202	42.382	12.245	12.153	11.938
94.525	94.521	94.684	3.599	3.583	3.370	35.586	35.694	35.856	10.233	10.086	9.899
96.010	96.055	96.116	2.452	2.520	2.326	29.334	29.345	29.372	7.421	7.411	7.393
96.867	97.386	97.266	1.381	1.539	1.453	23.855	23.752	23.534	4.289	4.476	4.736
DEB% avg.	−0.059	−0.051		−1.236	1.518		0.041	0.064		−0.634	−1.070

Table 3. Comparing Experimental and Predicted LLE Data for the Ternary System Water (1) + Acetic Acid (2) + Isophorone (3) (Where x = Molar Fraction)

aqueous phase						organic phase					
$100x_1$			$100x_2$			$100x_1$			$100x_2$		
exp	UNIQUAC	NRTL	exp	UNIQUAC	NRTL	exp	UNIQUAC	NRTL	exp	UNIQUAC	NRTL
$T = 283$ K											
93.663	93.675	93.519	5.928	5.835	5.778	31.760	31.812	31.816	20.384	20.348	20.316
94.923	94.909	94.826	4.729	4.706	4.622	35.889	35.802	35.803	18.526	18.587	18.592
96.065	95.847	95.810	3.783	3.837	3.737	39.141	39.220	39.213	16.815	16.822	16.839
96.839	96.933	96.931	2.866	2.819	2.712	42.583	42.541	42.530	14.210	14.143	14.161
97.893	97.904	97.913	1.887	1.899	1.802	45.151	45.099	45.091	10.860	10.947	10.955
98.793	98.864	98.857	0.993	0.981	0.918	48.092	48.136	48.139	6.706	6.662	6.661
DEB% avg.	0.008	0.057		0.468	3.905		0.000	0.006		0.021	−0.001
$T = 298$ K											
93.105	93.071	92.829	6.478	6.388	6.377	32.254	32.282	32.286	20.502	20.661	20.591
94.636	94.638	94.529	5.007	4.968	4.887	36.288	36.117	36.109	18.529	18.565	18.562
95.775	95.714	95.686	3.989	3.975	3.850	39.020	39.101	39.088	16.779	16.543	16.567
96.756	96.858	96.894	2.903	2.903	2.748	42.369	42.579	42.565	13.749	13.677	13.711
97.832	97.735	97.795	2.001	2.073	1.915	45.529	45.504	45.496	10.677	10.832	10.858
98.727	98.734	98.776	1.071	1.119	0.996	49.428	49.310	49.312	6.684	6.655	6.662
DEB% avg	0.014	0.058		−0.931	4.012		−0.004	0.011		−0.009	−0.073
$T = 313$ K											
93.528	93.320	93.198	6.124	6.101	5.996	32.590	32.790	32.786	19.585	19.567	19.567
94.405	94.523	94.450	5.091	5.013	4.902	36.984	36.811	36.825	18.052	17.906	17.923
95.571	95.626	95.584	4.037	4.000	3.893	40.267	40.072	40.078	15.908	15.892	15.905
96.728	96.688	96.659	2.963	3.012	2.920	43.075	43.101	43.096	13.201	13.394	13.392
97.699	97.669	97.665	2.023	2.061	1.998	45.772	45.929	45.916	10.146	10.315	10.303
98.719	98.778	98.723	1.065	1.035	1.014	48.738	48.714	48.698	6.168	5.984	5.983
DEB% avg.	0.009	0.066		0.345	2.811		−0.002	0.003		0.142	0.139

thermostat was 263 K to 373 K with a controller accuracy of ±0.1 K. The cell constituents were prepared by mass and stirred for not less than 4 h and allowed to settle for not less than 1 h. Longer mixing and settling periods did not result in any sensible change in the phase composition.

The concentrations of acetic acid and water in each phase were measured by titration.

The acid−base titration was performed using a Metrohm E 576 potentiometric titrator with 0.1 N NaOH; statistical measures of repeatability and uncertainty of acid mole values with gravimetrically prepared standard mixtures have given an error of ±0.15%.

Water content was measured by an Amel model 231 automatic Karl Fischer titrator using the Karl Fischer reagent. Water present in the organic phase was analyzed simply by titrating 0.5 mL of the organic solution. In contrast, water in the aqueous phase was analyzed after diluting 2.5 mL of the aqueous solution in 47.5 mL of

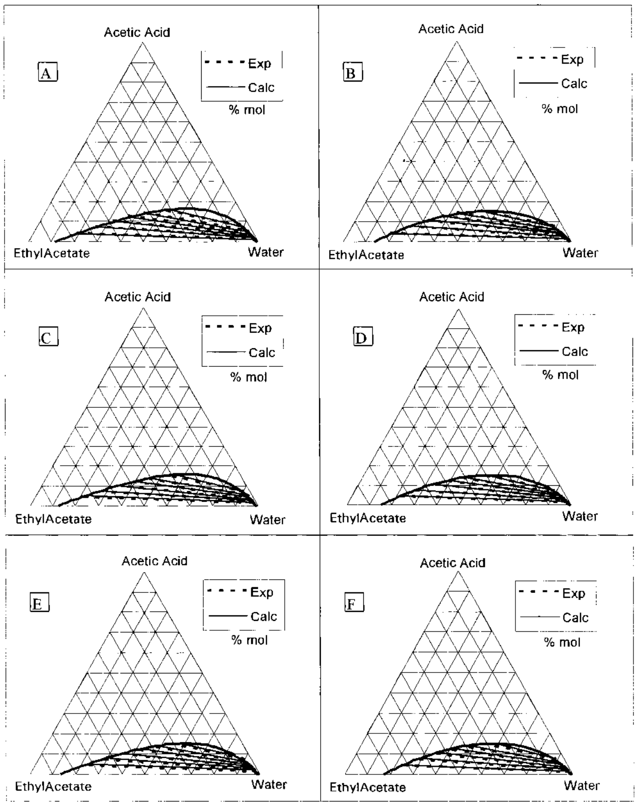

Figure 2. System ethyl acetate/acetic acid/water: (A) T = 283 K, model NRTL; (B) T = 283 K; Model UNIQUAC; (C) T = 298 K, model NRTL; (D) T = 298 K; Model UNIQUAC; (E) T = 313 K, model NRTL; (F) T = 313 K; Model UNIQUAC.

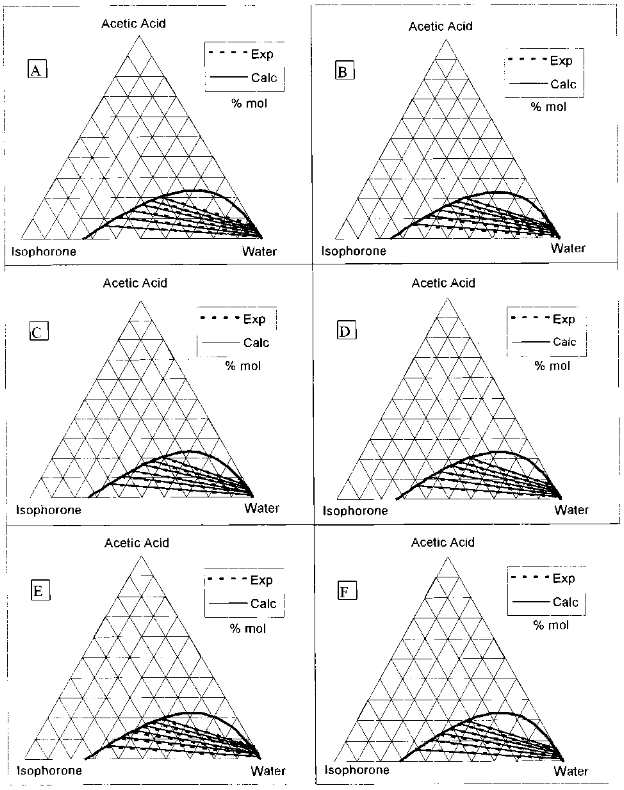

Figure 3. System isophorone/acetic acid/water: (A) T = 283 K, model NRTL; (B) T = 283 K, model UNIQUAC; (C) T = 298 K, model NRTL; (D) T = 298 K, model UNIQUAC; (E) T = 313 K, model NRTL; (F) T = 313 K, model UNIQUAC.

Table 4. Optimum Interaction Parameters According to the NRTL and UNIQUAC Models for the System Water + Acetic Acid + Ethyl Acetate at the Investigated Temperatures[a]

i	j	$a_{i,j}$ (K)	$a_{j,i}$ (K)
	UNIQUAC		
	T = 283 K		
H_2O	CH_3COOH	−98.167	−319.72
H_2O	EtOAc	131.08	342.71
CH_3COOH	EtOAc	−88.014	−507.89
	T = 298 K		
H_2O	CH_3COOH	35.762	−370.54
H_2O	EtOAc	178.43	295.72
CH_3COOH	EtOAc	−122.43	−430.69
	T = 313 K		
H_2O	CH_3COOH	26.209	−413.74
H_2O	EtOAc	202.65	281.7
CH_3COOH	EtOAc	−167.15	−468.53
	NRTL		
	T = 283 K		
H_2O	CH_3COOH	70.583	−142.66
H_2O	EtOAc	1146.8	201.02
CH_3COOH	EtOAc	−732.22	1223.1
	T = 298 K		
H_2O	CH_3COOH	−79.001	−153.38
H_2O	EtOAc	1287.5	150.63
CH_3COOH	EtOAc	−758.51	960.85
	T = 313 K		
H_2O	CH_3COOH	−185.65	−162.74
H_2O	EtOAc	1369.2	137.27
CH_3COOH	EtOAc	−804.59	979.74

[a] NRTL: $a_{i,j} = (g_{i,j} - g_{j,j})/R$ (K), α = 0.2. UNIQUAC: $a_{i,j} = (u_{i,j} - u_{j,j})/R$ (K).

Table 5. Optimum Interaction Parameters According to the NRTL and UNIQUAC Models for the System Water + Acetic Acid + Isophorone at the Investigated Temperatures[a]

i	j	$a_{i,j}$ (K)	$a_{j,i}$ (K)
	UNIQUAC		
	T = 283 K		
H_2O	CH_3COOH	169.3	−296.79
H_2O	isophorone	105.89	229.47
CH_3COOH	isophorone	−176.08	−164.57
	T = 298 K		
H_2O	CH_3COOH	214.25	−315.52
H_2O	isophorone	125.25	224.81
CH_3COOH	isophorone	−162.77	−159.87
	T = 313 K		
H_2O	CH_3COOH	143.8	−322.26
H_2O	isophorone	106.3	251.21
CH_3COOH	isophorone	−186.63	−190.63
	NRTL		
	T = 283 K		
H_2O	CH_3COOH	142.59	155.93
H_2O	isophorone	1818.8	−72.182
CH_3COOH	isophorone	−441.8	427.65
	T = 298 K		
H_2O	CH_3COOH	210.8	73.15
H_2O	isophorone	1926.9	−85.003
CH_3COOH	isophorone	−443.68	411.48
	T = 313 K		
H_2O	CH_3COOH	114.87	234.23
H_2O	isophorone	1992.1	−100.7
CH_3COOH	isophorone	−433.5	494.79

[a] NRTL: $a_{i,j} = (g_{i,j} - g_{j,j})/R$ (K), α = 0.2. UNIQUAC: $a_{i,j} = (u_{i,j} - u_{j,j})/R$ (K).

anhydrous methanol and then titrating 0.5 mL of this final solution. Also in this case, statistical measures of repeatability and uncertainty of final data were performed with gravimetrically prepared standard mixtures giving an error of ±0.16%.

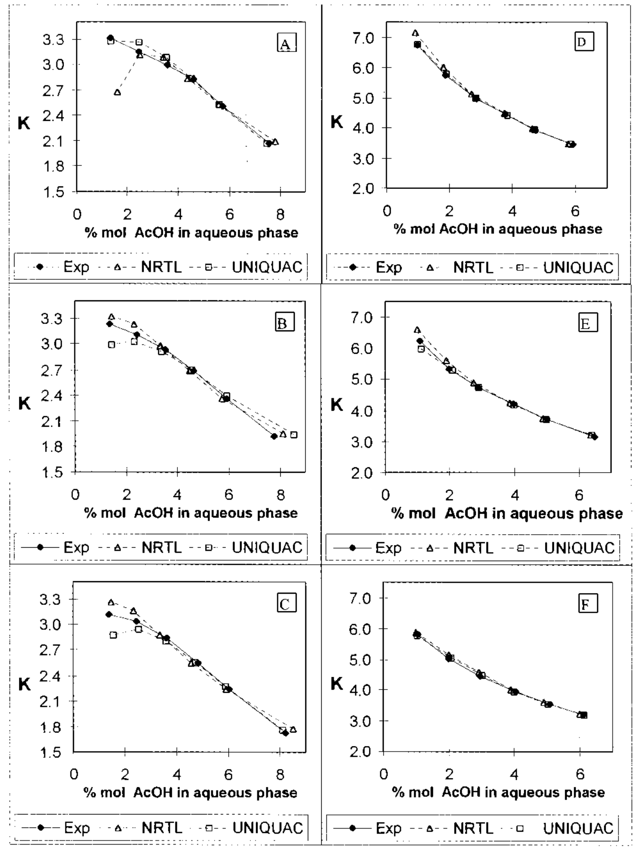

Figure 4. Distribution coefficient: (A) system ethyl acetate/acetic acid/water, T = 283 K; (B) system ethyl acetate/acetic acid/water, T = 298 K; (C) system ethyl acetate/acetic acid/water, T = 313 K; (D) system isophorone/acetic acid/water, T = 283 K; (E) system isophorone/acetic acid/water, T = 298 K; (F) system isophorone/acetic acid/water, T = 313 K.

The concentration of the organic solvent in each phase was calculated by material balance.

Models

If a liquid mixture of a given composition and at known temperature is separated into two phases (at equilibrium), the compositions of the two phases can be calculated using the following system of equations

$$\gamma_i^E x_i^E = \gamma_i^R x_i^R \tag{1}$$

where x_i^E and x_i^R are the moles fraction of component i in the extract (organic) phase and in the raffinate (aqueous) phase, respectively, and γ_i^E and γ_i^R are the corresponding activity coefficients of component i in the extract and raffinate phases, as calculated from the equilibrium model, i.e., NRTL or UNIQUAC. The interaction parameters between water, acetic acid, ethyl acetate, and isophorone are used to estimate the activity coefficients from NRTL and UNIQUAC equations. The r and q values for the UNIQUAC model, calculated using the UNIFAC group contribution method, are shown in Table 1 (Hansen et al., 1992).

Equation 1 is solved to calculate the mole fraction (x) for the component i in each liquid phase. This method of calculation gives a single tie line.

Results and Discussion

The measured equilibrium mole percents are shown in Tables 2 and 3. Figures 4 and 5 show the distribution coefficient (K), defined in eq 2, and the selectivity (β), defined in eq 3, for acetic acid at each temperature, respectively.

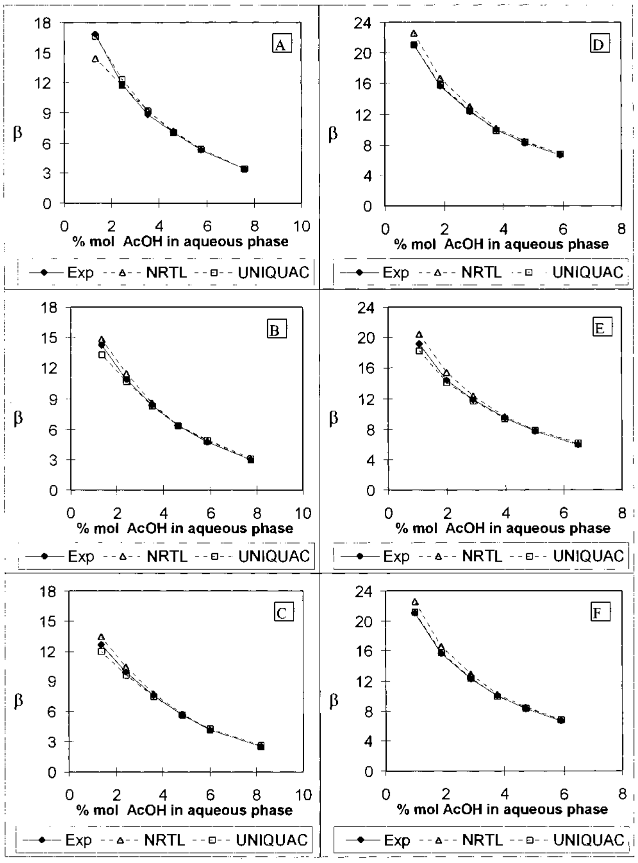

Figure 5. Selectivity: (A) system ethyl acetate/acetic acid/water, T = 283 K; (B) system ethyl acetate/acetic acid/water, T = 298 K; (C) system ethyl acetate/acetic acid/water, T = 313 K; (D) system isophorone/acetic acid/water, T = 283 K; (E) system isophorone/acetic acid/water, T = 298 K; (F) system isophorone/acetic acid/water, T = 313 K.

$$K = \frac{x_2^E}{x_2^R} \tag{2}$$

$$\beta = \frac{x_2^E \cdot x_3^R}{x_2^R \cdot x_3^E} \tag{3}$$

Component 2 is acetic acid, and component 3 is water.

The experimental data were used to calculate the optimum UNIQUAC and NRTL binary interaction parameters between the different constituents of the ternary systems. The NRTL and UNIQUAC equations were fitted to experimental data using an iterative computer program with the objective functions developed by Sørensen (1980). The NRTL model was fitted with fixed values of α (nonrandomness parameter) for each pair of compounds. A fixed value of 0.2 between each pair of compounds was used.

The values of the binary interaction parameters for the two equilibrium models for the three different temperatures are shown in Tables 4 and 5, and the corresponding calculated tie lines for the two models are shown in Tables 2 and 3. All the experimental data and calculations are also plotted on ternary diagrams (see Figures 2 and 3). The calculated K and β are shown in Figures 4 and 5.

Table 6. Optimum Interaction Parameters According to the NRTL and UNIQUAC Models. Global Set of Parameters[a]

i	j	$a_{i,j}$ (K)	$a_{j,i}$ (K)
Ethyl Acetate/Acetic Acid/Water System			
UNIQUAC			
H_2O	CH_3COOH	−621.56	−61.087
H_2O	EtOAc	298.33	170.66
CH_3COOH	EtOAc	−349.52	−135.59
NRTL			
H_2O	CH_3COOH	929.39	−713.04
H_2O	EtOAc	183.26	1237.8
CH_3COOH	EtOAc	260.65	−547.36
Isophorone/Acetic Acid/Water System			
UNIQUAC			
H_2O	CH_3COOH	−408.38	−289.23
H_2O	isophorone	171.19	197.62
CH_3COOH	isophorone	−385.93	−58.444
NRTL			
H_2O	CH_3COOH	549.98	−452.83
H_2O	isophorone	−79.494	1780.4
CH_3COOH	isophorone	251.34	146.29

[a] NRTL: $a_{i,j} = (g_{i,j} - g_{j,j})/R$ (K), $\alpha = 0.2$. UNIQUAC: $a_{i,j} = (u_{i,j} - u_{j,j})/R$ (K).

Table 7. DEB % Average Values for the Studied Models at Different Temperatures

	ethylacetate		isophorone	
T (K)	NRTL	UNIQUAC	NRTL	UNIQUAC
283	−0.525	0.110	0.992	−0.007
298	0.124	−0.384	1.002	−0.232
313	0.115	−0.472	0.755	0.123
avg.	−0.095	−0.249	0.916	−0.039
single set	0.699	−0.839	1.552	−0.402

A global set of parameters, temperature-independent, for UNIQUAC and NRTL was determined and reported in Table 6.

The percentage deviation from experimental basis (DEB%) was calculated from the difference between the experimental data and the predictions of each model at each temperature according to the following formula:

$$\mathrm{DEB\%} = \frac{(\exp - \mathrm{calc})}{\exp} \times 100 \qquad (4)$$

The UNIQUAC equation gave the lowest DEB% for isophorone systems with an average value of −0.039% and the NRTL model with an average value of −0.095% for ethyl acetate systems.

The comparisons between the two models are shown in Table 7. Isophorone resulted in a better extraction capacity for acetic acid with an higher distribution coefficient and selectivity, and in a lower miscibility with water.

Conclusions

The models NRTL and UNIQUAC were successfully used to regress the experimental equilibrium compositions of both studied systems. The two models were almost equally good in correlating the equilibrium composition with DEB% values lower than 1% in both the systems studied.

Isophorone, in comparison to ethyl acetate, experimentally resulted in a better extraction capacity for acetic acid, with an higher distribution coefficient and selectivity, and in a lower miscibility with water.

The models were calculated using single sets of parameters, one for each temperature, because they fitted the experimental results in a better way than the global set as reported in Table 7.

Acknowledgment

We are grateful to Chemical Engineering Department of Guido Donegani Institute, ENICHEM, Novara, Italy, for the support in correlating experimental data.

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Received for review December 9, 1997. Accepted September 22, 1998.

JE9702910