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Liquid–Liquid Equilibria of the Ternary System Water + Acrylic Acid + 4-Methyl-2-pentanone at 298.15 K

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In this work, experimental liquid–liquid equilibrium data for the ternary system water + acrylic acid + 4-methyl-2-pentanone were determined at 298.15 K and atmospheric pressure. The experimental data were also compared with the values correlated by the NRTL and UNIQUAC models. Good quantitative agreement was obtained with these models. In general, the average deviations from the NRTL model are slightly greater than those from the UNIQUAC model. The reliability of the experimental tie-line data was confirmed by using the Othmer−Tobias correlation. Distribution coefficients and selectivity were evaluated for the immiscibility region.

Introduction

The use of renewable feedstock, such as carbohydrates, is a key issue in the development of sustainable large-scale production processes. Several processes for conventional products already exist, such as bioethanol (13 million tons per year), glutamate, and citric acid (each at 0.8 million tons per year). Nowadays, several global consortia of agro and bulk chemical producers have joined forces to develop "green" processes for bulk chemicals, essentially targeted at monomers for renewable polymer production (1,3-propanediol, polylactic acid, and polyhydroxyalkanoate).[1,2]

It can be expected that for many other commodity chemicals, fermentation production processes will be developed in the next decades. An industrially relevant chemical that is an interesting target is acrylic acid.[1,2] Biomass derived sugars provide opportunities for new and potentially low-cost routes for chemical intermediates. One example is the transformation of glucose to acrylic acid.

The recovery of organic acids from aqueous dilute solutions resulting from fermentation processes is the most important purification stage. In the case of acrylic acid production, if distillation is used, the energy consumed in the purification stage is very high, since it is present in considerable dilution in the mixture;[3,4] moreover, the acrylic acid is thermally unstable. So, the liquid–liquid extraction process appears as a potential alternative, and many solvents have been tried to improve the recovery.[5–8] The phase behavior of this kind of mixture plays an important role in the research of critical phenomena and wetting transitions.[9–18] In this work, the ternary system water + acrylic acid + 4-methyl-2-pentanone has been investigated because of its possible application in industrial processes.

The solvent selection is of prime importance for successful separation by liquid–liquid extraction, and much of the process research is directed toward the evaluation of potential solvents. Among several solvent selection criteria, the distribution coefficient and selectivity are of considerable value since they measure the separating power of a solvent. 4-Methyl-2-pentanone (methyl isobutyl ketone) was investigated because it has been employed in the extraction of phenol and its derivatives from aqueous solutions.[19–22]

Liquid–liquid equilibrium (LLE) data are required to evaluate extraction processes. Activity coefficient models, such as the NRTL (nonrandom two-liquid) model[23] and the UNIQUAC (universal quasichemical) model,[24] have been successfully applied to correlate the LLE data.

The UNIFAC (universal functional-group activity coefficient) method[21,25] has been applied to predict liquid–liquid equilibrium data. The UNIFAC method is particularly useful for predicting the phase equilibrium for other systems that have not yet been studied experimentally but which contain the same functional groups, whereas the NRTL and UNIQUAC models depend on experimentally optimized interaction parameters.

In this work, experimental liquid–liquid equilibrium data of the ternary system (water + acrylic acid + 4-methyl-2-pentanone) were determined at 298.15 K and 1 atm. The capabilities of the NRTL and UNIQUAC activity coefficient models to correlate these data were tested. The calculated compositions showed a good agreement with the experimental data.

Experimental Section

Chemicals. Acrylic acid and 4-methyl-2-pentanone (99 %) were supplied by Merck. Water was purified by a Milli-Q system with resistivity lesser than 18 $\text{m}\Omega\cdot\text{cm}$.

Apparatus and Procedure. An isothermal, water-jacketed equilibrium cell, with a volume of about 43 cm^3, was used. The cell was equipped with a magnetic stirrer, and the temperature was controlled within 0.05 K. Before the experiment, water, acrylic acid, and 4-methyl-2-pentanone were added into the cell by mass at certain controlled ratios; the mixture points appear in Table 1. The mixtures were stirred for 2 h and left for about 12 h, allowing phase separation and equilibrium establishment. The upper, 4-methyl-2-pentanone-rich layer and the lower, water-rich layer were sampled with different syringes. The samples were immediately quantitatively diluted in methanol for acrylic acid analyses (1.000 g of each layer to 25.00 mL of methanol), following a dilution of 1.00 mL of the first

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Table 1. Mass Fraction (*w*) for the Ternary System Water (1) + Acrylic Acid (2) + 4-Methyl-2-pentanone (3) at 298.15 K and 1 atm

w_1	w_2	w_3
0.2306	0.3203	0.4491
0.4899	0.2297	0.2804
0.2871	0.1978	0.5151
0.3901	0.3299	0.2800
0.3865	0.2176	0.3959
0.5740	0.2378	0.1882
0.2105	0.2610	0.5285
0.4005	0.3105	0.2890
0.4013	0.3607	0.2380
0.2498	0.0510	0.6992

Table 2. Experimental LLE of the Ternary System Water (1) + Acrylic Acid (2) + 4-Methyl-2-pentanone (3) at 298.15 K and 1 atm

aqueous-rich layer			organic-rich layer		
w'_1	w'_2	w'_3	w''_1	w''_2	w''_3
0.8289	0.1334	0.0377	0.1487	0.3351	0.5162
0.8450	0.1245	0.0305	0.1370	0.3156	0.5474
0.9014	0.0807	0.0179	0.0931	0.2172	0.6897
0.7544	0.2005	0.0451	0.2065	0.3932	0.4003
0.8700	0.1036	0.0264	0.1147	0.2901	0.5952
0.8000	0.1606	0.0394	0.1674	0.3694	0.4632
0.8719	0.1002	0.0279	0.1151	0.2958	0.5891
0.7950	0.1705	0.0345	0.1575	0.3706	0.4719
0.7159	0.2357	0.0484	0.2218	0.4318	0.3464
0.9700	0.0074	0.0226	0.0340	0.0572	0.9085

solution to 100.00 mL of water. The diluted samples were analyzed by high-performance liquid chromatography (HPLC) for acrylic acid, while a volumetric Karl Fisher titrator was used for water. The third component was obtained by mass balance.

The HPLC analysis and quantification of acrylic acid were carried out with a Waters liquid chromatography system equipped with a 600E pump, a dual λ absorbance detector 2487, and the Millennium^{32} chromatography manager software version 3.20 (Waters). A reverse-phase column Nova-Pak 60 Å (150 × 3.9 mm, 4 μm) was used. The mobile phase was a mixture of acetonitrile and water having a volume ratio of 3/97 (pH = 3, adjusted with phosphoric acid). The flow rate was 1.0 $\text{mL}\cdot\text{min}^{-1}$, and the wavelength was 210 nm, at room temperature.

To determine the concentration, several standards of acrylic acid were made with the same solvents (methanol and water) at concentrations of (0.0100, 0.0200, 0.0500, 0.1000, 0.2000, and 0.2500) $\text{mg}\cdot\text{mL}^{-1}$. The quantity of each component was then determined by comparison of the chromatograms of both sample and standard solutions. The accuracy of this analysis was ± 0.01 % of acrylic acid.

The water content in the aqueous and organic phase was determined with a Karl Fischer titration Mettler Toledo DL31. The accuracy of the analysis depends on the amount of water that is contained in the sample. In this case, the accuracy in the mass fraction was found to be ± 0.0001.

Results

Experimental and calculated compositions of the equilibrium phases of the ternary system water + acrylic acid + 4-methyl-2-pentanone at 298.15 K and 1 atm are listed in Table 2. Figure 1 shows the corresponding triangular phase diagram.

A simple distribution curve of acrylic acid between water and 4-methyl-2-pentanone can be obtained by plotting the concentration of acrylic acid in the water-rich phase (w'_2) against its concentration in the 4-methyl-2-pentanone-rich phase (w''_2). This curve is presented in Figure 2. The acrylic acid distributes preferentially in the 4-methyl-2-pentanone-rich layer; consequently, this solvent can be recommended for extracting acrylic acid from aqueous solutions.

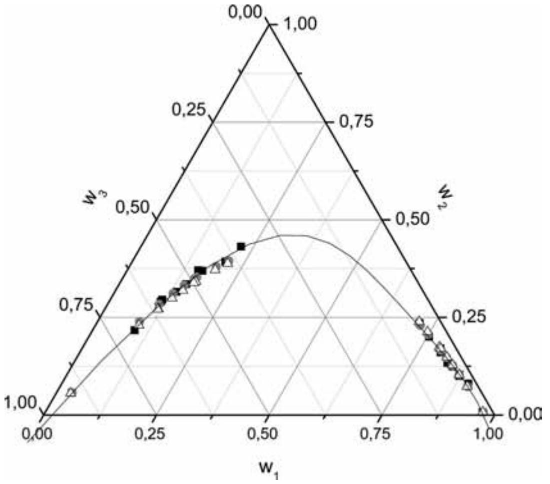

Figure 1. Ternary diagram for LLE of water (1) + acrylic acid (2) + 4-methyl-2-pentanone (3) at 298.15 K. □, experimental data; Δ, UNIQUAC data; •, NRTL data; solid line, best fit representing the binodal curve.

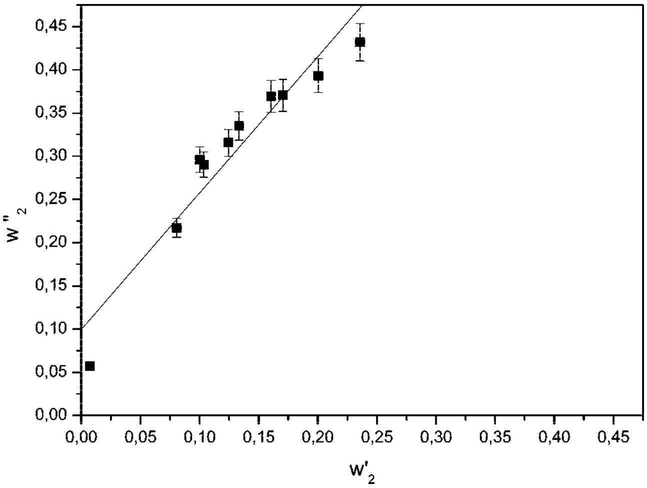

Figure 2. Distribution (*K*) of acrylic acid (2) between 4-methyl-2-pentanone (3) and water (1) (*K* = 1.58, angular coefficient), where: w''_2 = mass fraction of acrylic acid in the organic solvent; w'_2 = mass fraction of acrylic acid in water; □, experimental data; solid line, best linear fit (linear fit: $y = A + Bx$, $A = 0.09973$, $B = 1.58$, $r = 0.9573$).

Table 3. Selectivity, *S*, of 4-Methyl-2-pentanone to Extract Acrylic Acid from its Aqueous Solutions in Relation to the Water Mass Fraction in the Aqueous-Rich Layer

water content (w'_1)	*S*
0.7159	3.206
0.7544	3.268
0.7950	3.792
0.8000	4.315
0.8289	4.372
0.8450	6.303
0.8700	8.450
0.8719	9.029
0.9014	12.23
0.9700	30.02

The selectivity, *S*, of 4-methyl-2-pentanone to extract acrylic acid from aqueous solutions is $S = (w''_2\cdot w''_1/w'_2\cdot w'_3)$. Selectivity increases considerably with increasing composition of water in the aqueous layer (Table 3). This will impact directly the extraction process.[12,15,26,27]

Othmer−Tobias and Hand Correlations. The reliability of experimentally measured tie-line data can be ascertained by

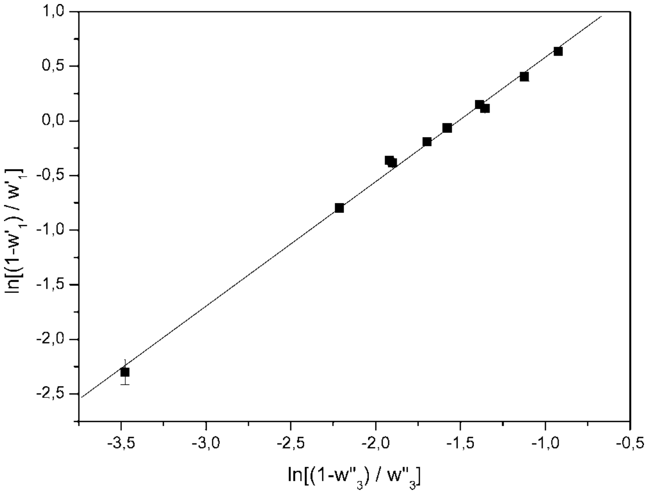

Figure 3. Othmer−Tobias correlation of LLE data for water (1) + acrylic acid (2) + 4-methyl-2-pentanone (3) at $T = 298.15$ K (linear fit: $y = A_1 + B_1x$, $A_1 = 1.723$, $B_1 = 1.140$, $r = 0.9979$).

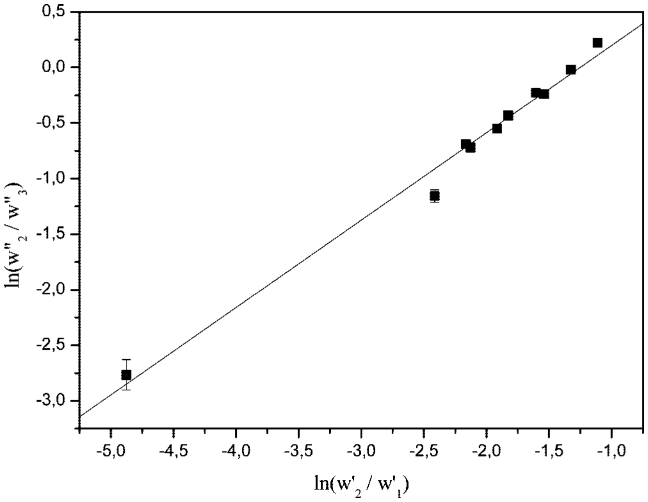

Figure 4. Hand correlation of LLE data for water (1) + acrylic acid (2) + 4-methyl-2-pentanone (3) at $T = 298.15$ K (linear fit: $y = A_2 + B_2x$, $A_2 = 0.9854$, $B_2 = 0.7860$, $r = 0.9932$).

Table 4. Estimated NRTL Parameters

i/*j*	A_{ij}	A_{ji}	B_{ij}/K	B_{ji}/K	α_{ij}
water + acrylic acid	0.0	0.0	1351.92	−407.76	0.30
water + 4-methyl-2-pentanone	1.2587	282.13	−712.56	−2773.62	0.20
acrylic acid + 4-methyl-2-pentanone	0.0	0.0	2072.88	−549.86	0.30

applying Othmer−Tobias and Hand equations[28,29] given by eqs 1 and 2, respectively:

$$\ln\left(\frac{1-w''_3}{w''_3}\right) = A_1 + B_1 \ln\left(\frac{1-w'_1}{w'_1}\right) \tag{1}$$

$$\ln\left(\frac{w''_2}{w''_3}\right) = A_2 + B_2 \ln\left(\frac{w'_2}{w'_1}\right) \tag{2}$$

The correlations are shown in Figures 3 and 4. The correlation coefficients and correlation factor (r) values were determined by the least-squares method and are given in the figure legends. A correlation factor close to 1 suggests a high degree of consistency of the related data.

The experimental data were used to estimate binary energy interaction parameters for the UNIQUAC and NRTL models.

Table 5. Estimated UNIQUAC Parameters

i/*j*	A_{ij}	A_{ji}	B_{ij}/K	B_{ji}/K
water + acrylic acid	0.12	0.0	−78.99	104.24
water + 4-methyl-2-pentanone	−17.29	−134.05	1068.27	5680.19
acrylic acid + 4-methyl-2-pentanone	0.0	0.0	−300.34	386.96

Table 6. Root Mean Square Error (rmse)[a]

water + acrylic acid + 4-methyl-2-pentanone at 298.15 K		100 rmse NRTL	100 rmse UNIQUAC
water-rich layer	water	1.06	0.79
	acrylic acid	6.51	11.00
	4-methyl-2-pentanone	10.55	18.46
organic-rich layer	water	7.08	4.08
	acrylic acid	8.12	10.20
	4-methyl-2-pentanone	7.51	5.23

[a] rmse $= \sqrt{1/N \sum_i (w_i^{\text{exptl}} - w_i^{\text{pred}})^2}$.

In a general way, binary interaction parameters predicted from ternary data must be carefully evaluated since they can led to poor results; however, there are no binary data available in the literature for the studied systems. The estimation procedure was carried out by minimization of the Maximum-Likelihood objective function, by using a modified New Britt Luecke algorithm.[30]

The estimated parameters are shown in Tables 4 and 5. The root-mean-square errors (rmse) between calculated (predicted) and experimental results are presented in Table 6.

Conclusions

The experimental investigation of liquid–liquid equilibrium of the ternary system water + acrylic acid + 4-methyl-2-pentanone was carried out at 298.15 K. The data show that 4-methyl-2-pentanone is a good solvent for extracting acrylic acid from aqueous solutions.

The experimental data were correlated using NRTL and UNIQUAC models. Both of them show a good fit to the experimental data. Root mean square errors (rmse) are between (1.06 and 10.55) % for the NRTL model and (0.79 and 18.46) % for the UNIQUAC model.

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