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Liquid–Liquid Equilibria for the Ternary Systems Water + *n*-Pentanoic Acid with *n*-Heptane or Dichloromethane at 298.2 K

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The liquid–liquid equilibria for the water + *n*-pentanoic acid + *n*-heptane system and the water + *n*-pentanoic acid + dichloromethane system were determined at 298.2 K. The NRTL and UNIQUAC models were applied to both ternary systems. The interaction parameters obtained from the NRTL model correlated with the equilibrium compositions better than those from the UNIQUAC model.

1. Introduction

Pentanoic acid is produced industrially by the oxidation of amyl alcohol or by fermentation. It can be used as a base material in lubricants for CFC substitutes.[1] Because carboxylic acids are stable oxidation products, pentanoic acid also appears in the byproducts of industrial operations. Separation of *n*-pentanoic acid has been studied extensively in many applications such as selected extraction from mixed dibasic acids in the nylon production process,[2,3] extraction and back extraction of *n*-pentanoic acid in a fixed bed,[4] extractive ultrafiltration for the removal of pentanoic acid,[5] and reactive extraction for the recovery of carboxylic acids.[6] Liquid–liquid equilibrium data have been published for a number of ternary mixtures containing *n*-pentanoic acid and water with various solvents such as acetonitrile/cyclohexane,[7] butanenitrile,[8] benzonitrile,[9] cumene,[10] trioctylamine,[11] 1-octanol,[12,13] and chloroform.[14]

In this work, we studied the extraction of *n*-pentanoic acid from aqueous solution with solvents such as dichloromethane and *n*-heptane. Tie lines were measured for the ternary systems of water + *n*-pentanoic acid + dichloromethane and water + *n*-pentanoic acid + *n*-heptane. The results of the measurements were correlated by means of the NRTL model[15] and the UNIQUAC model.[16]

2. Experimental

Dichloromethane (99.5 %), *n*-heptane (99 %), 1,4-dioxane (99 %), and *n*-pentanoic acid (99 %) were purchased from Sigma-Aldrich Company and used without further purification. The chemical purity of each substance was confirmed to be over 99.0 % by gas chromatography. Water was purified by Direct-Q Tap-Fed water purification system (Millipore) with a resistivity of 18.2 MΩ·cm. The ternary mixtures were prepared by mass on a Mettler AG204 balance with a precision of 0.0001 g. The estimated uncertainty in the mole fraction was less than 10^{-4}. The experimental apparatus used for extraction consisted of a 50 mL glass cell equipped with a jacket to circulate water from a Julabo F33 water bath.[17] The jacket temperature was controlled within ± 0.1 K. The mixtures were stirred vigorously with a magnetic stir bar for an hour, and then left to settle for 12 h. Samples were collected by syringe through top and side PTFE/Silicone septum caps.

Table 1. Experimental LLE Data for the Water (1) + *n*-Pentanoic Acid (2) + *n*-Heptane (3) System

n-heptane-rich phase (mole fraction)		water-rich phase (mole fraction)			
x_1	x_2	x_1	x_2	K_D	S
0.0136	0.1520	0.9962	0.0038	40.19	2944
0.0229	0.2558	0.9959	0.0041	62.66	2725
0.0469	0.3725	0.9953	0.0047	79.56	1688
0.0597	0.4546	0.9950	0.0050	91.25	1521
0.0871	0.5147	0.9948	0.0052	99.32	1134
0.1015	0.5950	0.9945	0.0055	108.5	1063
0.1494	0.6243	0.9943	0.0057	109.9	731.2
0.2117	0.6202	0.9940	0.0060	103.7	486.8
0.2752	0.6165	0.9937	0.0063	98.14	354.4
0.3582	0.5838	0.9935	0.0065	90.06	249.8
0.4187	0.5586	0.9932	0.0068	82.36	195.4

Table 2. Experimental LLE Data for the Water (1) + *n*-Pentanoic Acid (2) + Dichloromethane (3) System

dichloromethane-rich phase (mole fraction)		water-rich phase (mole fraction)			
x_1	x_2	x_1	x_2	K_D	S
0.0579	0.2466	0.9948	0.0022	112.1	1926
0.0864	0.3415	0.9941	0.0029	117.8	1355
0.1910	0.4655	0.9939	0.0034	136.9	712.4
0.1350	0.4417	0.9940	0.0038	116.2	855.8
0.2466	0.4928	0.9935	0.0047	104.9	422.4
0.3602	0.5194	0.9944	0.0042	123.7	341.4
0.4296	0.5136	0.9947	0.0041	125.3	290.0

Quantitative analysis of *n*-pentanoic acid, dichloromethane, and *n*-heptane was performed with a 6890N gas chromatograph (Agilent Technologies) equipped with a 7863 series automatic injector, a flame ionization detector, and the HP ChemStation data system. The components were separated using an AT-1000 capillary column (15 m × 0.53 mm ID × 1.2 μm film thickness, Alltech). The oven temperature was maintained at 50 °C for the first 3 min and then increased to 250 at 10 °C·min^{-1}. 1,4-Dioxane was used as an internal standard in the quantitative analysis of *n*-pentanoic acid, dichloromethane, and *n*-heptane. The response factors for all components were measured under the same conditions as those used in the gas chromatograph measurement for the phase equilibrium data. Water concentrations were calculated to make the mole fraction equal to 1 and

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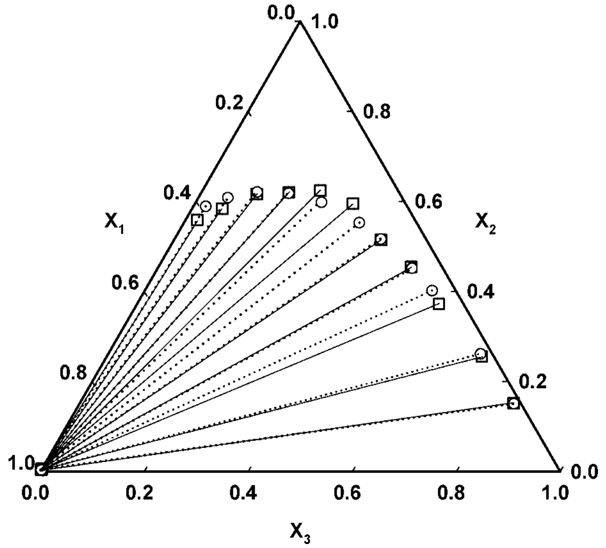

Figure 1. LLE of water (1) + *n*-pentanoic acid (2) + *n*-heptane (3) at 298.2 K: □—, experimental tie line data; ○. . ., NRTL.

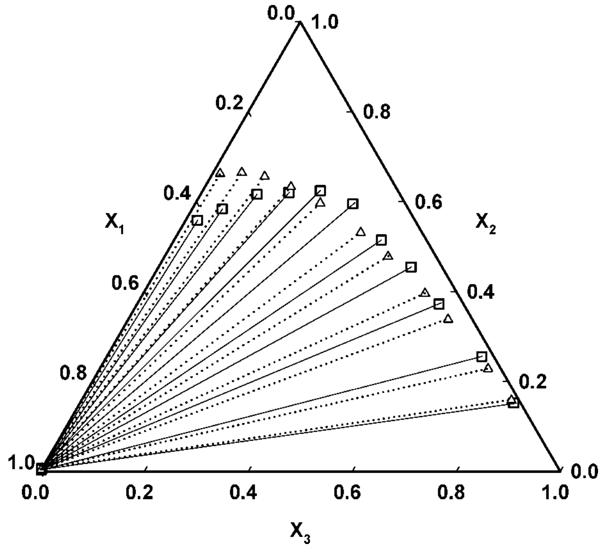

Figure 2. LLE of water (1) + *n*-pentanoic acid (2) + *n*-heptane (3) at 298.2 K: □—, experimental tie line data; △—, UNIQUAC.

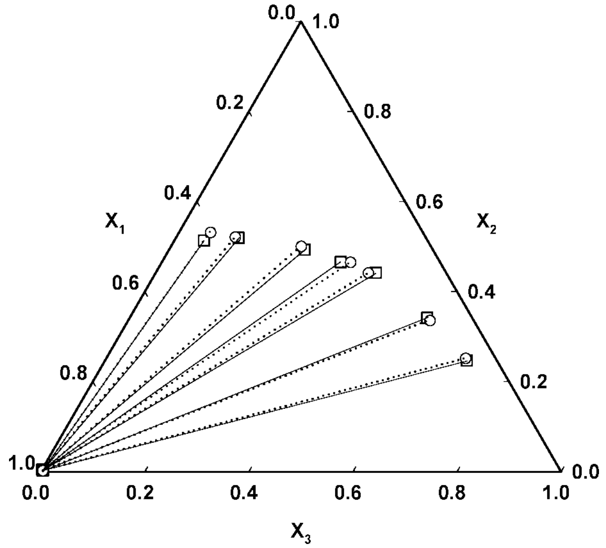

Figure 3. LLE of water (1) + *n*-pentanoic acid (2) + dichloromethane (3) at 298.2 K: □—, experimental tie line data; ○. . ., NRTL.

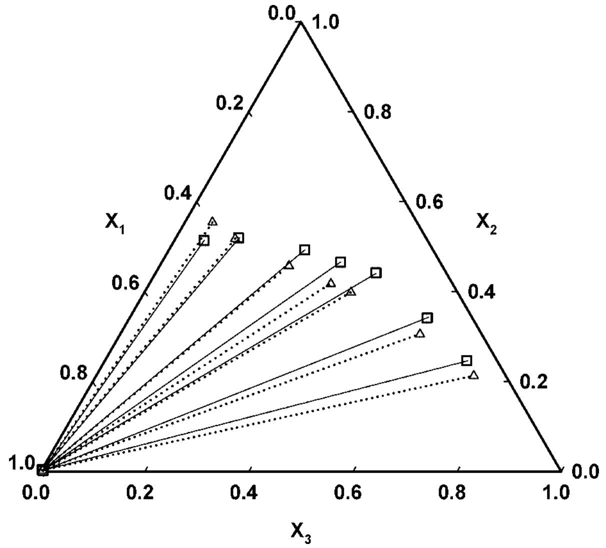

Figure 4. LLE of water (1) + *n*-pentanoic acid (2) + dichloromethane (3) at 298.2 K: □—, experimental tie line data; △—, UNIQUAC.

Table 3. Structure Parameters for the UNIQUAC Model

compound	van der Waals volume, *r*	van der Waals area, *q*
water	0.92	1.4
n-pentanoic acid	4.195	3.768
n-heptane	5.174	4.396
dichloromethane	2.206	1.98

were also checked with a Mettler Toledo DL31 Karl Fisher titrator to validate the chromatographic results.

3. Results and Discussion

The experimental tie line data of the water + *n*-pentanoic acid + *n*-heptane system and the water + *n*-pentanoic acid + dichloromethane system at 298.2 K are shown in Tables 1 and 2. The binodal curves in Figures 1 to 4 show that the water + *n*-pentanoic acid + *n*-heptane system exhibited a larger immiscibility region than the water + *n*-pentanoic acid + dichloromethane system.

The nonrandom two-liquid (NRTL) model and the UNIQUAC model were fitted to each experimental tie line data. The nonrandomness parameter α_{ij} for the NRTL model and the interaction parameters b_{ij} for the UNIQUAC model were estimated using the commercial simulator (Aspen Plus 2004.1). The calculated volume and the surface area parameters of the UNIQUAC model are presented in Table 3. The regressed NRTL binary parameters and UNIQUAC binary parameters of both ternary systems are listed in Tables 4 and 5 with the root-mean-square deviation (rmsd) values. The rmsd value is a measure of the agreement between the experimental data and the calculated values and is defined as follows[18]

$$\mathrm{rmsd} = \left(\sum_{k}^{M} \sum_{j}^{2} \sum_{i}^{3} \left(x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}} \right)^2 / 6M \right)^{\frac{1}{2}} \qquad (1)$$

where M is the number of tie lines; x^{exptl} is the experimental mole fraction; x^{calcd} is the calculated mole fraction; and the subscript i indexes the components, j the phases, and k the tie lines. The rmsd values for the water + *n*-pentanoic acid + *n*-heptane system were 0.0136 for the NRTL and 0.0336 for the UNIQUAC. The rmsd values for the water + *n*-pentanoic acid + dichloromethane system were 0.0070 for the NRTL and 0.0219 for the UNIQUAC. The correlation obtained with the

Table 4. Parameters of the UNIQUAC and NRTL Models for the Water (1) + *n*-Pentanoic Acid (2) + *n*-Heptane (3) System at 298.2 K and Their rmsd Values

model	b_{ij}/K and α_{ij}			rmsd
UNIQUAC	$b_{12} = -170.45$	$b_{13} = -325.42$	$b_{23} = -263.36$	0.0336
	$b_{21} = -173.27$	$b_{31} = -1318.0$	$b_{32} = 73.78$	
NRTL	$b_{12} = 1441.92$	$b_{13} = 2782.46$	$b_{23} = 384.85$	0.0136
	$b_{21} = 13.305$	$b_{31} = 1062.63$	$b_{32} = 3052.43$	
	$\alpha_{12} = 0.3$	$\alpha_{13} = 0.2$	$\alpha_{23} = 0.3$	

Table 5. Parameters of the UNIQUAC and NRTL Models for the Water (1) + *n*-Pentanoic Acid (2) + Dichloromethane (3) System at 298.2 K and Their rmsd Values

model	b_{ij}/K and α_{ij}			rmsd
UNIQUAC	$b_{12} = -265.3$	$b_{13} = -367.5$	$b_{23} = -795.1$	0.0219
	$b_{21} = -60.7$	$b_{31} = -3626.1$	$b_{32} = 201.4$	
	$b_{12} = 1498.4$	$b_{13} = -756.6$	$b_{23} = 724.7$	0.0070
NRTL	$b_{21} = 13.64$	$b_{31} = 2027.9$	$b_{32} = -310.78$	
	$\alpha_{12} = 0.3$	$\alpha_{13} = 0.2$	$\alpha_{23} = 0.3$	

NRTL is far better than that obtained with the UNIQUAC model. The phase diagrams for the water + *n*-pentanoic acid + *n*-heptane or dichloromethane ternary systems are presented in Figures 1 to 4.

The equilibrium distribution coefficients, K_D, and the separation factor of *n*-pentanoic acid, *S*, were obtained and are listed in Tables 1 and 2. The distribution coefficient of *n*-pentanoic acid is the ratio of the concentration of *n*-pentanoic acid in the organic layer to the concentration in the aqueous layer.

$$K_D = x_{23}/x_{21} \tag{2}$$

where x_{23} and x_{21} are the mole fractions of *n*-pentanoic acid (2) in the solvent-rich phase (3) and the aqueous-rich phase (1), respectively. The distribution coefficients in Figures 5 and 6 show that the NRTL model fits better than the UNIQUAC model for the water + *n*-pentanoic acid + dichloromethane system and the water + *n*-pentanoic acid + *n*-heptane system.

The NRTL model showed better correlation with the ternary system with other solvents for *n*-pentanoic acid such as the acetonitrile + *n*-pentanoic acid + cyclohexane system[7] and the water + *n*-pentanoic acid + butanenitrile system.[8] The rmsd for the water + *n*-pentanoic acid + butanenitrile system[8] was 0.019 for the NRTL compared with 0.284 for the UNIQUAC.[8] The NRTL model also showed better correlation with other ternary systems containing various carboxylic acids such as the water + acetic acid + 2-methyl-2-butanol system[19] and the water + propionic acid + methyl isoamyl ketone or diisobutyl ketone or ethyl isoamyl ketone systems.[20]

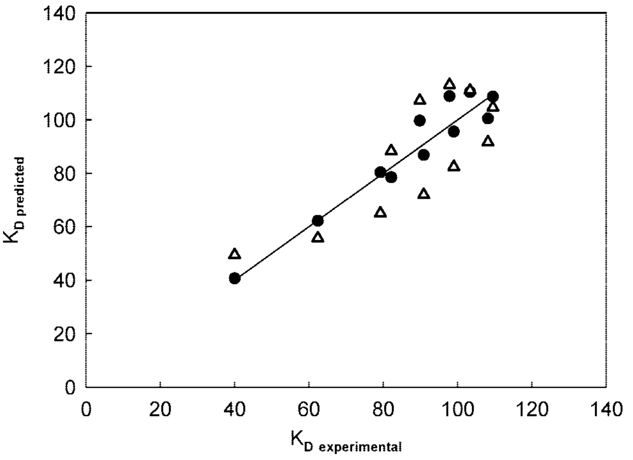

Figure 5. Predicted distribution coefficient for the water (1) + *n*-pentanoic acid (2) + *n*-heptane (3) system by ●, NRTL; and △, UNIQUAC.

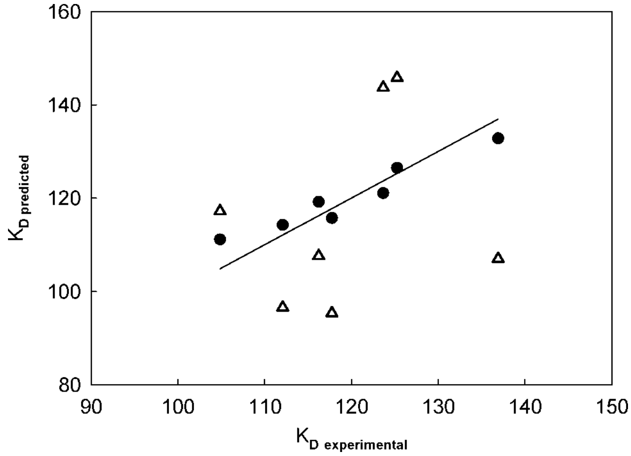

Figure 6. Predicted distribution coefficient for the water (1) + *n*-pentanoic acid (2) + dichloromethane (3) system by ●, NRTL; and △, UNIQUAC.

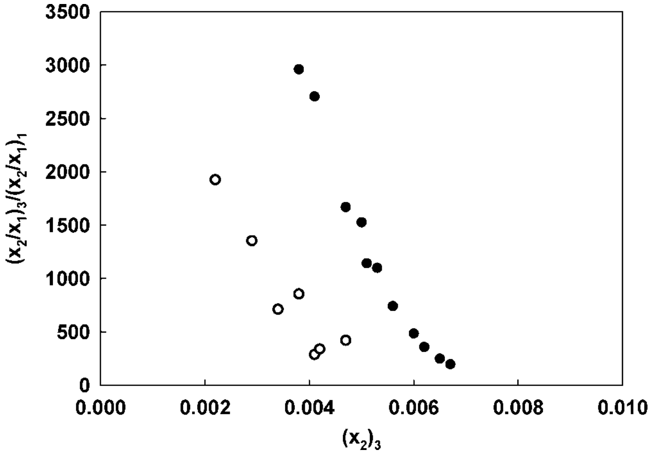

Figure 7. Relative separation for the systems at 298.2 K: ●, water (1) + *n*-pentanoic acid (2) + *n*-heptane (3); ○, water (1) *n*-pentanoic acid (2) + dichloromethane (3).

The relative separation factor or selectivity, *S*, between two components, water and solvent, can be described by the ratio of the two partition ratios as follows.

$$S = (x_2/x_1)_3/(x_2/x_1)_1 \tag{3}$$

where $(x_2/x_1)_3$ are the mole fractions of *n*-pentanoic acid (2) and water (1) in the solvent-rich phase (3) and $(x_2/x_1)_1$ are the mole fractions of *n*-pentanoic acid (2) and water (1) in the aqueous-rich phase (1).

The effectiveness of *n*-pentanoic acid extraction is given by its relative separation factor, which is an indication of the ability of the solvent to separate *n*-pentanoic acid from water. If this value is 1, no separation has been accomplished. Effective separation is accomplished when the separation factor is significantly different from unity. Figure 7 clearly shows that *n*-heptane is able to separate *n*-pentanoic acid from water better than dichloromethane. Aside from having a high separation factor, it is important to attain as high a K_D value as possible to minimize the needed solvent flow rate since the factor $K_D S/W$, where S/W is the mass flow ratio of solvent to water, should be greater than 1. As listed in Tables 1 and 2, the distribution coefficients are high enough for effective extraction. Moreover, *n*-heptane is also a green solvent with a low boiling point.

4. Conclusion

The extraction data for the water + *n*-pentanoic acid + *n*-heptane system and the water + *n*-pentanoic acid + dichloromethane system were obtained at 298.2 K. The *n*-pentanoic acid can be separated from water using solvents such as dichloromethane and *n*-heptane. The tie line correlation was fitted using the UNIQUAC and NRTL models, and the parameters for both models were calculated with the water + *n*-pentanoic acid + *n*-heptane system and the water + *n*-pentanoic acid + dichloromethane system. Better results were achieved with the NRTL model.

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