(Liquid + Liquid) Equilibria of (Cyclohexane + Dimethyl Sulfoxide + Cyclohexanone) and (Cyclohexane + Dimethyl Sulfoxide + Cyclohexanol) at $T = 303.2$ K

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Phase diagrams of mixtures consisting of (cyclohexane + cyclohexanone + dimethyl sulfoxide) and (cyclohexane + cyclohexanol + dimethyl sulfoxide) were obtained at a temperature of 303.2 K. Nonrandom two-liquid and UNIQUAC models applied to both ternary systems produced interaction parameters that were well-correlated with the equilibrium compositions. These parameters enable the prediction of (liquid + liquid) equilibrium mixtures with either cyclohexanone or cyclohexanol.

1. Introduction

Cyclohexanone and cyclohexanol are typically synthesized by the catalytic oxidation of cyclohexane.[1] Their main purpose is as precursors for caprolactam, the monomer for nylon 6, and adipic acid, the intermediate chemical for nylon 66 and polyurethane resins.[1] The ratio of cyclohexanone to cyclohexanol can be controlled by adjusting the production parameters. A high mass fraction of cyclohexane is preferred for caprolactam production, while high cyclohexanol mass fraction is preferred for adipic acid production. Studies of the equilibrium of (cyclohexane + cyclohexene + water + cyclohexanol) and (cyclohexane + cyclohexene + water + cyclohexanol + methanoic acid + cyclohexyl ester) have been reported in the literature.[2,3] However, cyclohexanone and cyclohexanol were found to act as solvents in most of the (liquid + liquid) equilibrium data. (Liquid + liquid) equilibrium studies have been performed using an aqueous solution of methanoic acid, propionic acid, 2-hydroxypropanoic acid, 3-methylbutanoic acid, 4-oxopentanoic acid, tetrahydrofurfuryl alcohol, and phosphoric acid with 1-hexanol in the cyclohexanone solvent system.[4−10] Systems containing cyclohexanol with an aqueous solution of 1,4-butanediol, 1-propanol, 2-propanol, nitromethane, pyridine, and 2-ethyl-2-hydroxymethyl-1,3-propandiol have also been discussed.[11−16]

In this work, the (liquid + liquid) equilibria of {cyclohexane + cyclohexanone + dimethyl sulfoxide (DMSO)} and (cyclohexane + cyclohexanol + DMSO) were studied the mixture. Tie lines were measured for both ternary mixtures, (cyclohexane + cyclohexanone + DMSO) and (cyclohexane + cyclohexanol + DMSO). The results of the measurements were correlated using the nonrandom two-liquid (NRTL) model and the UNIQUAC model.[17,18]

2. Experimental Section

Cyclohexane (suppliers cited mole fraction purity of 0.99), cyclohexanone (suppliers cited mole fraction purity of 0.99), cyclohexanol (suppliers cited mole fraction purity of 0.99), DMSO (suppliers cited mole fraction purity of 0.999), and 1,4-dioxane (suppliers cited mole fraction purity of 0.995) were obtained from Sigma-Aldrich Company. All mole fraction purities were confirmed by gas chromatography to be greater than 0.996 and were therefore used without further purification. The experimental tie line data were measured using 50 cm^3 glass cells, each equipped with a jacket to circulate water from a Julabo F30C water bath.[19] The jacket temperature was controlled within ± 0.1 K. The ternary mixtures were prepared by weighing with a Mettler AB304S balance with an uncertainty of ± 0.0001 g. The estimated uncertainty of the mole fractions was less than $\pm\ 10^{-4}$. Each mixture was stirred with a magnetic stir bar vigorously for a time of 1 h and then left to separate into two phases for at time of at least 6 h. Samples of the upper cyclohexane-rich phase and lower DMSO-rich phase were collected by syringe through top and side PTFE/silicone septum caps, respectively.

Quantitative analysis of cyclohexane, cyclohexanone, cyclohexanol, and DMSO were performed using 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 (30 m × 0.53 mm ID × 1.2 μm film thickness, Alltech). The oven temperature was maintained at 80 °C for the first 600 s and then increased to 200 °C at a rate of $1/6\ {}^\circ\text{C}\cdot\text{s}^{-1}$. 1,4-Dioxane was used as an internal standard for quantitative analysis of each chemical. The response factors of all components were measured under the same conditions used for the gas chromatography measurements.

3. Results and Discussion

Experimental tie-line data of (cyclohexane + cyclohexanone + DMSO) and (cyclohexane + cyclohexanol + DMSO) were obtained at $T = 303.2$ K and are listed in Tables 1 and 2, respectively. The bimodal curves, shown in Figures 1 and 2, show that (cyclohexane + cyclohexanone + DMSO) exhibits larger immiscibility than (cyclohexane + cyclohexanol + DMSO). The NRTL model and the UNIQUAC model were fitted to experimental tie-line data. The interaction

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Table 1. Experimental (Liquid + Liquid) Equilibrium Data for Cyclohexane (1) + Cyclohexanone (2) + DMSO (3)

cyclohexane-rich phase (mole fraction)		DMSO-rich phase (mole fraction)			
x_1	x_2	x_1	x_2	K_D	S
0.9628	0.0244	0.0542	0.0541	2.42	42.9
0.9021	0.0692	0.0807	0.1312	1.90	21.2
0.8450	0.1069	0.1110	0.1834	1.72	13.1
0.7795	0.1468	0.1554	0.2263	1.54	7.7
0.6705	0.2025	0.2129	0.2589	1.28	4.0
0.5632	0.2355	0.2799	0.2751	1.17	2.4
0.5175	0.2475	0.3450	0.2722	1.10	1.6

Table 2. Experimental (Liquid + Liquid) Equilibrium Data for the Cyclohexane (1) + Cyclohexanol (2) + DMSO (3)

cyclohexane-rich phase (mole fraction)		DMSO-rich phase (mole fraction)			
x_1	x_2	x_1	x_2	K_D	S
0.9856	0.0024	0.0658	0.0249	10.38	155.4
0.9742	0.0077	0.0838	0.0639	8.30	96.5
0.9667	0.0128	0.1034	0.0998	7.80	72.9
0.9490	0.0217	0.1342	0.1360	6.27	44.3
0.9280	0.0317	0.1671	0.1655	5.22	29.0
0.8961	0.0463	0.2150	0.1919	4.14	17.3
0.8346	0.0728	0.2795	0.2124	2.92	8.7

parameter for the NRTL and UNIQUAC models, b_{ij}, was regressed using the commercial simulator (Aspen Plus 2004). The binary parameters, b_{ij}, are $(g_{ij} - g_{ji})/R$ in Kelvin, where R is the universal gas constant and g_{ij} is the energy parameter. The nonrandomness parameter, α_{ij}, for the NRTL model was fixed to be 0.3 for nonassociated liquids and 0.2 for immiscible liquids. For {cyclohexane (1) + cyclohexanol (2) + DMSO (3)}, the nonrandomness parameter, α_{12}, for the NRTL model was considered as a decision variable[2,3] and obtained by regression of the experimental data because of the high tendency of cyclohexanol to self-associate.[20,21] The calculated volume parameter and surface area parameter 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 along 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:

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

where M is the number of tie lines, x^{exp} is the experimental mole fraction, x^{calc} is the calculated mole fraction, and the subscript i indexes the components, j the phases, and k the tie lines. The rmsd values for (cyclohexane + cyclohexanone + DMSO) were 0.0115 for the NRTL model and 0.0111 for the UNIQUAC model. The rmsd values for (cyclohexane + cyclohexanol + DMSO) were 0.0077 for the NRTL model and 0.0225 for the UNIQUAC model. The correlation obtained with the NRTL model is better than that obtained with the UNIQUAC model for (cyclohexane + cyclohexanol + DMSO). The reliability of the experimentally measured tie-line data was assessed by the Othmer−Tobias equation in Figure 3.[22] The linearity of these plots indicates the degree of consistency of the related data.

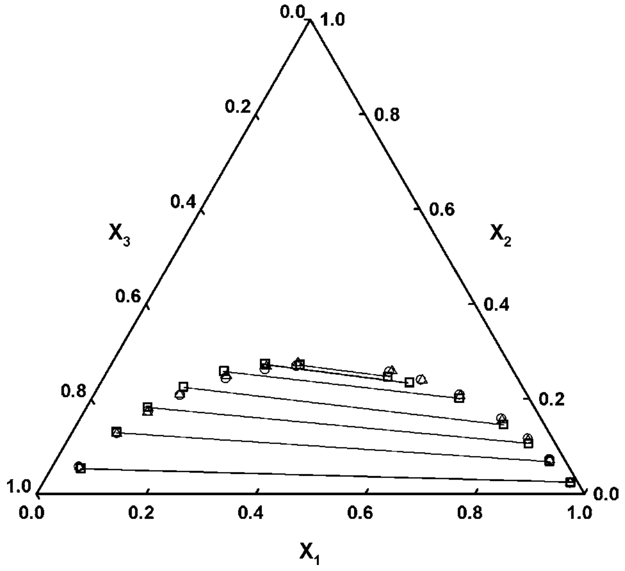

Figure 1. (Liquid + liquid) equilibrium of cyclohexane (1) + cyclohexanone (2) + DMSO (3) at T = 303.2 K: □, experimental tie-line data; ○, NRTL; Δ, UNIQUAC.

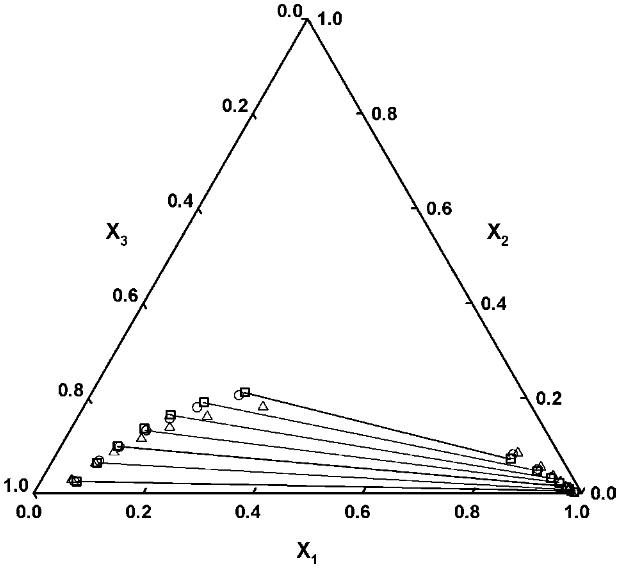

Figure 2. (Liquid + liquid) equilibrium of cyclohexane (1) + cyclohexanol (2) + DMSO (3) at 303.2 K: □, experimental tie-line data; ○, NRTL; Δ, UNIQUAC.

Table 3. Parameters for the UNIQUAC Equation

compound	van der Waals volume, r	van der Waals area, q
cyclohexane	4.046	3.24
DMSO	2.827	2.472
cyclohexanone	4.114	3.34
cyclohexanol	4.274	3.284

Table 4. Parameters of the NRTL (b_{ij} and α_{ij}) and UNIQUAC (b_{ij}) Models for the Cyclohexane (1) + Cyclohexanone (2) + DMSO (3) at a Temperature of 303.2 K and Their RMSD Values

model	b_{ij}/K and α_{ij}			rmsd
NRTL	$b_{12} = -329.25$	$b_{13} = 1020.63$	$b_{23} = -472.17$	
	$b_{21} = -19.17$	$b_{31} = 585.90$	$b_{32} = 37.72$	0.0115
	$\alpha_{12} = 0.3$	$\alpha_{13} = 0.2$	$\alpha_{23} = 0.3$	
UNIQUAC	$b_{12} = 8.91$	$b_{13} = -516.18$	$b_{23} = 167.69$	0.0111
	$b_{21} = 41.70$	$b_{31} = -93.82$	$b_{32} = -68.05$	

Table 5. Parameters of the NRTL (b_{ij} and α_{ij}) and UNIQUAC (b_{ij}) Models for the Cyclohexane (1) + Cyclohexanol (2) + DMSO (3) at a Temperature of 303.2 K and Their RMSD Values

model	b_{ij}/K and α_{ij}			rmsd
NRTL	$b_{12} = 98.74$	$b_{13} = 1034.09$	$b_{23} = 324.36$	
	$b_{21} = -53.01$	$b_{31} = 473.06$	$b_{32} = -1163.63$	0.0077
	$\alpha_{12} = 5.33$	$\alpha_{13} = 0.2$	$\alpha_{23} = 0.3$	
UNIQUAC	$b_{12} = -238.50$	$b_{13} = -449.74$	$b_{23} = 354.32$	0.0225
	$b_{21} = 175.21$	$b_{31} = -91.61$	$b_{32} = -389.76$	

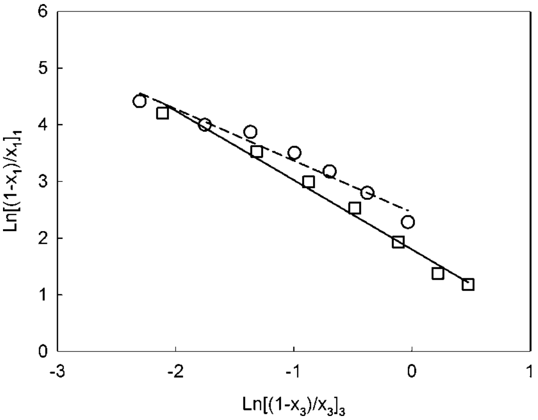

Figure 3. Othermer−Tobias plot: □, solid line, (cyclohexane + cyclohexanone + DMSO ($R^2 = 0.99$)); ○, dotted line, cyclohexane + cyclohexanol + DMSO ($R^2 = 0.96$).

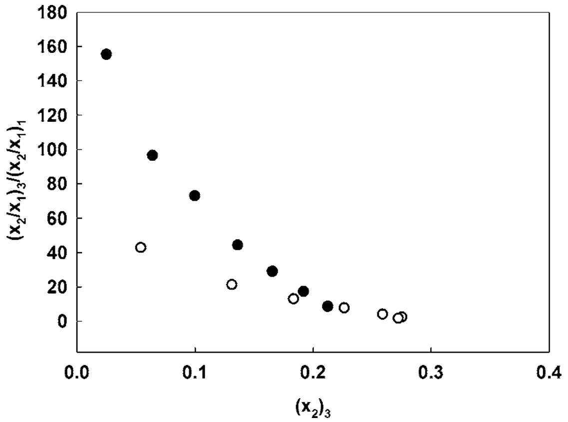

Figure 4. Relative separation for the mixtures studied at $T = 303.2$ K: ○, cyclohexane + cyclohexanone + DMSO; ●, cyclohexane + cyclohexanol + DMSO.

The equilibrium distribution coefficient of cyclohexanone is the ratio of the concentration of cyclohexanone or cyclohexanol in the DMSO layer to the concentration in the cyclohexane layer.

$$K_D = x_{23}/x_{21}$$

where x_{23} and x_{21} are the mole fractions of cyclohexanone or cyclohexanol (2) in the DMSO-rich phase (3) and the cyclohexane-rich phase (1), respectively, and are listed in Table 1 and 2.

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.

$$S = (x_2/x_1)_3/(x_2/x_1)_1 \qquad (2)$$

where $(x_2/x_1)_3$ is the mole fraction of cyclohexanone or cyclohexanol (2) and cyclohexane (1) in the DMSO-rich phase (3) and $(x_2/x_1)_1$ is the mole fraction of cyclohexanone or cyclohexanol (2) and cyclohexane (1) in the cyclohexane-rich phase (1).

The effectiveness of cyclohexanone or cyclohexanol extraction is given by its relative separation factor, which is an indication of the ability of the solvent to separate cyclohexanone or cyclohexanol from cyclohexane. If this value is 1, no separation has occurred. An effective separation is accomplished when the separation factor is significantly different from unity. Figure 4 clearly shows that DMSO is able to separate cyclohexanol from cyclohexane better than cyclohexanone from cyclohexane. Besides having such a high separation factor, the highest possible K_D value should be attained to minimize the needed solvent flow rate. This is because the factor K_DS/W, where S/W is the mass flow ratio of solvent to that of water, should be greater than 1. As listed in the Tables 1 and 2, the distribution coefficients are high enough for effective extraction.

4. Conclusion

The (liquid + liquid) equilibrium data for (cyclohexane + cyclohexanone + DMSO) and (cyclohexane + cyclohexanol + DMSO) were obtained at $T = 303.2$ K. The tie-line correlation data was fitted using the NRTL and UNIQUAC models, and the parameters for both models were calculated for (cyclohexane + cyclohexanone + DMSO) and (cyclohexane + cyclohexanol + DMSO). The relative separation factor diagram indicated that the mixtures containing cyclohexanol were higher than those with cyclohexanone.

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