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Liquid−Liquid Equilibrium for the 1-Pentanol + Tris(hydroxymethyl)propane + Water and 1-Hexanol + Tris(hydroxymethyl)propane + Water Systems at 293.15 and 313.15 K

Jaehoon Choe,[†] **In-Won Kim,**[‡] **and Kwang Ho Song***[,†]

LG Chemical Ltd./Research Park, 104-1 Moonji-dong, Yusong-gu, Taejon 305-380, Korea, and Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Kwangjin-gu, Seoul 143-701, Korea

The liquid−liquid equilibrium for the 1-pentanol + tris(hydroxymethyl)propane + water and 1-hexanol + tris(hydroxymethyl)propane + water systems were determined at 293.15 and 313.15 K. The NRTL and UNIQUAC models were applied to both ternary systems. The interaction parameters obtained from both models successfully correlated the equilibrium compositions.

Introduction

Tris(hydroxymethyl)propane is used mainly as a raw material for the production of various resinous materials such as paint resin or urethane resin. It can be produced by the reaction of butyraldehyde, formaldehyde, and sodium hydroxide in aqueous medium.[1] Solvent extraction has been used to isolate the tris(hydroxymethyl)propane from the aqueous reaction mixture.[1] The ternary equilibrium data have been published for cyclohexanol[2] and methyl isobutyl ketone[3] as a solvent. Other solvents such as acetone,[1] ethyl acetate,[4] isobutanol and xylene,[5] and methyl *tert*-butyl ether[6] have been used to extract tris(hydroxymethyl)propane.

In this work, 1-pentanol and 1-hexanol were tested as a solvent for tris(hydroxymethyl)propane extraction. Tie lines and solubility curves were obtained at two different temperatures. Results of the measurement were correlated by means of the UNIQUAC model[7] and the NRTL model.[8]

Experimental Section

Chemicals. Tris(hydroxymethyl)propane (Aldrich, 99.0%), 1-hexanol (Aldrich, 99.0%), 1-pentanol (Aldrich, 99.0%), methanol (Aldrich, 99.93%), and 1,4-dioxane (Merck, 99.98%) were used without further purification. Water was purified by a Milli Q-UV system equipped with a Mili RO5 Plus (Millipore) with a resistivity of 18.2 MΩ cm. Karl Fischer reagents, Hydranal-composite-5 and Hydranal-methanol dry, were purchased from Riedel-de Haën.

Procedures. The ternary mixtures were prepared at the immiscibility region by mass with a precision of 0.0001 g on a Mettler AG204 balance. The estimated uncertainty in mole fraction was $<10^{-4}$. The extraction cell was placed in a temperature-controlled water bath (±0.1 K). It is similar to that used by Tamura et al.;[9] however, it has two orifices on the top and side for sampling. The mixtures were stirred for 30 min in this cell (100 mL) at a given temperature. After complete mixing, the cells were placed in a temperature-controlled oven (±0.1 K) for a day. After equilibrium was reached, each of the liquid phases was sampled by syringe through the lateral and top orifices. Analysis of 1-pentanol, 1-hexanol, and tris(hydroxymethyl)propane was performed using a Hewlett-Packard gas chromatograph equipped with a flame ionization detector. The components were separated using an HP-5 column (30 m × 0.32 mm × 0.25 μm film thickness, cross-linked 5% PHME Siloxane, Hewlett-Packard). After 0.5 min of operation at 50 °C, the oven temperature was programmed to reach 270 °C at the rate of 20 °C/min. The injection port temperature and the detector temperature were held at 260

Table 1. LLE Composition of the System 1-Pentanol (1) + Tris(hydroxymethyl)propane (2) + Water (3)

	organic phase (mole fraction)		aqueous phase (mole fraction)	
T/K	x_1	x_2	x_1	x_2
293.15	0.5287	0.0178	0.0038	0.0073
	0.5070	0.0359	0.0046	0.0153
	0.4603	0.0533	0.0059	0.0242
	0.3845	0.0743	0.0064	0.0344
	0.3237	0.0798	0.0077	0.0388
313.15	0.5456	0.0210	0.0031	0.0061
	0.4760	0.0427	0.0048	0.0162
	0.4251	0.0558	0.0052	0.0236
	0.3365	0.0761	0.0066	0.0339
	0.3217	0.0738	0.0096	0.0417

Table 2. LLE Composition of the System 1-Hexanol (1) + Tris(hydroxymethyl)propane (2) + Water (3)

	organic phase (mole fraction)		aqueous phase (mole fraction)	
T/K	x_1	x_2	x_1	x_2
293.15	0.6501	0.0155	0.0010	0.0074
	0.6083	0.0338	0.0012	0.0156
	0.5184	0.0680	0.0019	0.0346
	0.3917	0.1015	0.0028	0.0572
	0.3059	0.1194	0.0049	0.0728
	0.1990	0.1298	0.0132	0.0904
313.15	0.6318	0.0179	0.0011	0.0074
	0.5811	0.0381	0.0013	0.0153
	0.4787	0.0699	0.0018	0.0345
	0.3446	0.0977	0.0037	0.0587
	0.2439	0.1135	0.0060	0.0725

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* Author to whom correspondence should be addressed (e-mail khsong@lgchem.co.kr).

[†] LG Chemical Ltd.

[‡] Konkuk University.

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Table 3. Compositions of Experimental Solubility Curve Data

	1-hexanol (1) + tris(hydroxymethyl)propane (2) + water (3) system (mole fraction)		1-pentanol (1) + tris(hydroxymethyl)propane (2) + water (3) system (mole fraction)	
T/K	x_1	x_2	x_1	x_2
293.15	0.0006	0.0130	0.0038	0.0073
	0.0019	0.0346	0.0042	0.0140
	0.0028	0.0572	0.0062	0.0269
	0.0046	0.0769	0.0077	0.0388
	0.0287	0.0975	0.0421	0.0645
	0.0874	0.1165	0.0694	0.0690
	0.1865	0.1271	0.1190	0.0756
	0.2857	0.1217	0.1663	0.0772
	0.4391	0.0905	0.3781	0.0755
	0.5437	0.0542	0.5090	0.0753
313.15	0.0011	0.0056	0.0037	0.0139
	0.0014	0.0189	0.0071	0.0325
	0.0019	0.0358	0.0193	0.0478
	0.0039	0.0608	0.0414	0.0589
	0.0430	0.0937	0.0799	0.0694
	0.1442	0.1132	0.1334	0.0787
	0.2405	0.1154	0.2219	0.0844
	0.3824	0.0944	0.3292	0.0756
	0.5744	0.0464	0.5099	0.0368

Table 4. Parameters of the NRTL and UNIQUAC Model for the 1-Pentanol (1) + Tris(hydroxymethyl)propane (2) + Water (3) System and Their RMSD Values

model	T/K	parameter/K		RMSD
NRTL	293.15	$b_{12} = 359.744$	$b_{21} = -388.097$	
$\alpha_{ij} = 0.3$		$b_{13} = 101.620$	$b_{31} = 1708.173$	0.0036
		$b_{23} = -407.580$	$b_{32} = 282.288$	
	313.15	$b_{12} = -936.771$	$b_{21} = -457.836$	
		$b_{13} = 114.771$	$b_{31} = 1793.953$	0.0019
		$b_{23} = -521.473$	$b_{32} = -948.119$	
UNIQUAC	293.15	$b_{12} = -250.460$	$b_{21} = 137.828$	
		$b_{13} = 27.660$	$b_{31} = -425.707$	0.0032
		$b_{23} = 308.784$	$b_{32} = -511.803$	
	313.15	$b_{12} = 211.415$	$b_{21} = 93.989$	
		$b_{13} = 18.112$	$b_{31} = -443.111$	0.0018
		$b_{23} = -213.596$	$b_{32} = 602.558$	

Table 5. Parameters of the NRTL and UNIQUAC Model for the 1-Hexanol (1) + Tris(hydroxymethyl)propane (2) + Water (3) System and Their RMSD Values

model	T/K	parameter/K		RMSD
NRTL	293.15	$b_{12} = -26.160$	$b_{21} = -595.541$	
$\alpha_{12} = 0.2$		$b_{13} = 2.508$	$b_{31} = 2945.455$	0.0028
$\alpha_{13} = 0.3$		$b_{23} = -675.130$	$b_{32} = -236.348$	
$\alpha_{23} = 0.3$	313.15	$b_{12} = -2474.950$	$b_{21} = -735.683$	
		$b_{13} = -37.920$	$b_{31} = 3024.748$	0.0022
		$b_{23} = -784.873$	$b_{32} = -2784.650$	
UNIQUAC	293.15	$b_{12} = -92.445$	$b_{21} = 120.635$	
		$b_{13} = 6.883$	$b_{31} = -650.166$	0.0027
		$b_{23} = -148.944$	$b_{32} = 323.486$	
	313.15	$b_{12} = 14.659$	$b_{21} = 157.222$	
		$b_{13} = 7.043$	$b_{31} = -650.727$	0.0024
		$b_{23} = -142.944$	$b_{32} = 494.509$	

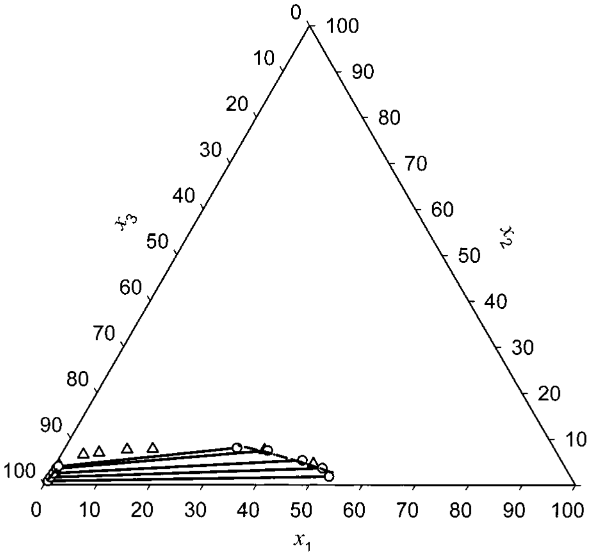

Figure 1. LLE of 1-pentanol (1) + tris(hydroxymethyl)propane (2) + water (3) at 293.15 K: ○, experimental tie-line data; △, experimental solubility data; ···, NRTL model; - - -, UNIQUAC model.

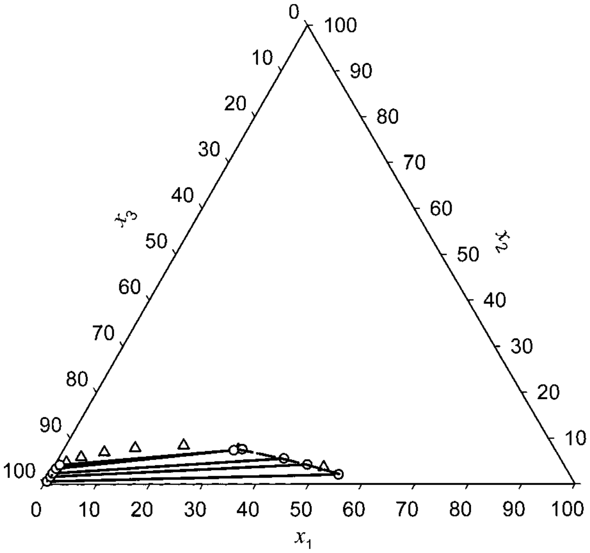

Figure 2. LLE of 1-pentanol (1) + tris(hydroxymethyl)propane (2) + water (3) at 313.15 K: ○, experimental tie-line data; △, experimental solubility data; ···, NRTL model; - - -, UNIQUAC model.

°C and 270 °C, respectively. The internal standard method was employed for quantitative analysis of mixtures, and 1,4-dioxane was chosen as an internal standard.[10] Water concentration was determined according to the Karl Fischer method by means of a Metrohm 701KF model. The experimental solubility data for the ternary system were determined by the cloud-point method.[11] Known compositions of binary mixtures of water and tris(hydroxymethyl) propane or solvent and tris(hydroxymethyl) propane were stirred in a cell (50 mL) equipped with a jacket for circulating water from a constant-temperature water bath. The other component, solvent or water, was then added by mass until a transition point was reached.

Results and Discussion

Experimental Results. The liquid−liquid equilibrium data for the two ternary systems, 1-pentanol + tris(hydroxymethyl)propane + water and 1-hexanol + tris(hydroxymethyl)propane + water, at 293.15 K and 313.15 K are listed in Tables 1 and 2, respectively. The experimental data for the solubility curve of the two ternary systems at two different temperatures are listed in Table 3.

Models and Predictions. The NRTL model was applied to correlate tie-line data from experimental results. Values

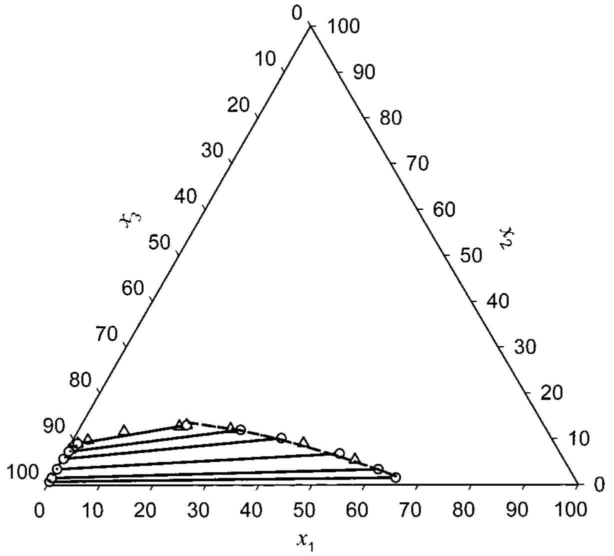

Figure 3. LLE of 1-hexanol(1) + tris(hydroxymethyl)propane (2) + water (3) at 293.15 K: ○, experimental tie-line data; △, experimental solubility data; · · ·, NRTL model; - - -, UNIQUAC model.

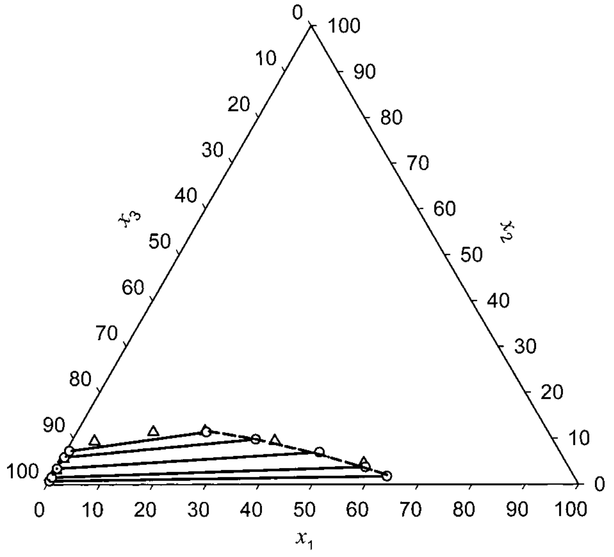

Figure 4. LLE of 1-hexanol (1) + tris(hydroxymethyl)propane (2) + water (3) at 313.15 K: ○, experimental tie-line data; △, experimental solubility data; · · ·, NRTL model; - - -, UNIQUAC model.

of the randomness parameter α_{ij} for the NRTL model[12] are shown in Table 4 for the 1-pentanol + tris(hydroxymethyl)-propane + water system and in Table 5 for the 1-hexanol + tris(hydroxymethyl)propane + water system. The NRTL binary parameters of both ternary systems correlated at different temperatures are listed in Tables 4 and 5 with the root-mean-square deviation (RMSD) values defined as[13]

$$\mathrm{RMSD} = \left(\sum_k^M \sum_j^2 \sum_i^3 (x_{ijk}^{\mathrm{exptl}} - x_{ijk}^{\mathrm{calcd}})^2/6M\right)^{1/2} \qquad (1)$$

where M is the number of tie lines, x^{exptl} is the experimental mole fraction, x^{calcd} indicates the calculated mole fraction, and the subscripts i, j, and k index the components, the phase, and the tie lines, respectively.

The UNIQUAC model was also used to calculate the liquid activity coefficients. Tables 4 and 5 show the interaction parameters, b_{ij}, for both ternary systems.

The liquid−liquid equilibrium data of the two ternary systems are shown in Figures 1−4. The NRTL and UNIQUAC models are found to describe the experimental data well. The b_{ij} and RMSD values of both ternary systems are shown in Tables 4 and 5. Tris(hydroxymethyl)propane is more soluble in pentanol than in hexanol, and the pentanol + tris(hydroxymethyl)propane + water system shows a smaller area of the two-phase immiscible region than the hexanol system. The slope of the tie lines represents, in all cases, that the tris(hydroxymethyl)propane is more soluble in the pentanol- and hexanol-rich phase than in the water-rich phase. Figures 1−4 show that the effect of temperature on the size of the immiscible region is insignificant.

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