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Liquid−Liquid Equilibrium for the System Water + Cyclohexene + Cyclohexanol over the Temperature Range of (303.2 to 403.2) K

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Liquid−liquid equilibrium (LLE) data for the ternary system water + cyclohexene + cyclohexanol were determined at atmospheric pressure and at high pressure over the temperature range of (303.2 to 403.2) K. The accuracy of the high pressure apparatus was verified by duplicating the literature data. The measured LLE data were compared with the values correlated by the nonrandom two-liquid (NRTL) model. The NRTL model was successfully fitted to the new experimental data.

Introduction

Cyclohexanol is being synthesized on an industrial scale today as an intermediate in the production of adipic acid and caprolactam. These in turn are intermediates for the production of nylon 6,6 and nylon 6. Since nylon is a bulk polymer, the world production of cyclohexanol had already reached 1.1 million tons per year in the beginning of the 1980s.[1]

Currently there are three commercial routes to produce cyclohexanol: the oxidation of cyclohexane, the hydrogenation of phenol, and the direct hydration of cyclohexene. Of these, the cyclohexane oxidation route is still by far the largest. However, the process has drawbacks. It suffers from a high safety risk associated with the formation of explosive mixtures when mixing cyclohexane and air for oxidation. It also has a fairly low selectivity, even at very low conversions, and is very energy-consuming because of the high hydrogen consumption in the production of cyclohexane from benzene. Phenol hydration mainly suffers from high phenol prices as compared to benzene.[2] In recent years, the direct hydration of cyclohexene was an important research direction.

We proposed a new route for the preparation of cyclohexanol by catalytic hydration of cyclohexene in a reactive distillation column using a cosolvent, and it seemed to offer a solution for those problems of former technologies. To investigate the phase separation on the reaction process, a complete set of thermodynamic data valid for the whole range of reaction conditions within such a column is necessary. Some data on the liquid−liquid equilibrium (LLE)[3,4] exist but are far from being complete. Liquid−liquid equilibria at ambient temperature in the ternary system cyclohexene + cyclohexanol + water were measured.[5] More LLE data was necessary to investigate the liquid−liquid phase splitting behavior. Because the hydration of cyclohexene is conducted at high temperatures, the LLE data for the ternary system at high temperature are also important. The boiling point of the cyclohexene is very low, so the LLE data at high temperatures should be measured in the high pressure autoclave. In particular, we notably found a sufficiently large and reliable set of data to fit parameters for an activity coefficient model such as the nonrandom two-liquid (NRTL) model for the ternary system of water + cyclohexene + cyclohexanol.

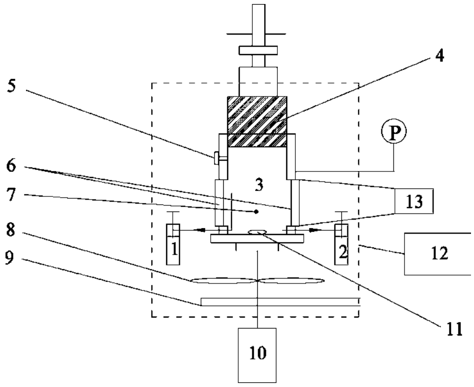

Figure 1. Experimental apparatus for determining LLE at high pressure. 1, sampling tube at upper layer; 2, sampling tube at lower layer; 3, autoclave; 4, piston; 5, inlet; 6, viewport; 7, temperature measurement point; 8, fan; 9, heating rod; 10, motor; 11, magnetic stir bar; 12, temperature controller; 13, light source.

Experimental Section

Materials. Cyclohexene ($w > 0.98$, chemical grade) and cyclohexanol ($w > 0.98$, chemical grade) were both purchased from Sino Pharm and purified to 99.5 mass fraction by batch distillation. The purity of these materials was checked by gas chromatography (GC) and used without further purification. Distilled water was prepared in our laboratory.

Apparatus and Procedures. LLE data for the ternary system at atmospheric pressure were measured by an apparatus of a 30 mL glass cell which is the same as those already described.[6]

The equipment used for the high-pressure LLE measurements was schematically shown in Figure 1. It included an autoclave, a magnetically driven stirrer, two sampling tubes, and a heating rod. The autoclave's volume was 100 cm^3. Heating of the autoclaves was achieved by outside electrical heating elements. There were thermal insulations surrounding the autoclave. The two sampling tubes were both placed into the temperature insulation layer to minimize the temperature variations during sampling. The temperature was controlled by a regulator with a precision of better than 0.1 K. The pressure was controlled by the piston. The pressure variations due to temperature variations and the pressure drop during sampling can be minimized by adjusting the position of the piston.

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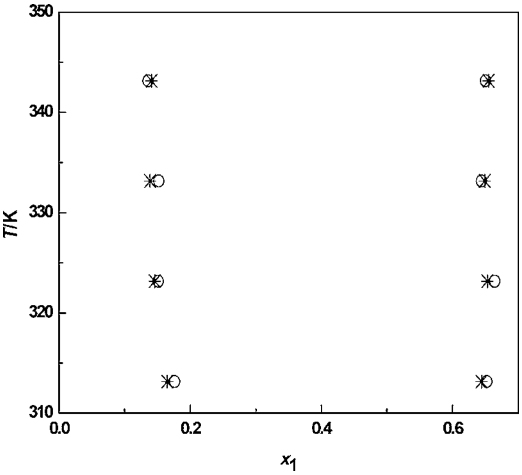

Figure 2. $T-x$ diagram for the 2-butanol (1) + water (2) system at 10 MPa.

The prepared mixtures were introduced into the equilibrium cell, and the equilibrium cell was totally filled with liquid. The pressure was adjusted to 4.0 MPa to avoid boiling and kept constant for the whole equilibrium procedure. After reaching the preset temperature, the sampling began following agitation for 2 h and then settled to 3 h for complete phase separation. From the viewport, we can see the phase separation was good.

The samples of two equilibrium liquid phases were carefully taken from the autoclave into the sampling tubes through the sample pipes. The sucked samples were diluted quantitatively by ethanol immediately to prevent the samples from splitting into two phases.

Analysis. The cyclohexene and cyclohexanol components in both the organic phase and the aqueous phase were determined using a Varian CP-3900 GC equipped with a hydrogen flame ionization detector (FID). A 25 m long capillary column (0.32 mm diameter with a 0.25 μm film thickness) was used with a temperature-programmed analysis illustrated as follows: column temperature of 353 K, hold for 1 min, 20 K·min^{-1} heating for 3.5 min, hold for 1 min, 20 K·min^{-1} heating for 5 min, at 523 K, hold for 1 min. The injection mode was a split ratio 50/1, the injector temperature 523 K, detector temperature 573 K, carrier gas 1.0 mL·min^{-1} nitrogen, and injected volume 0.2 μL of liquid sample. The FID's response was calibrated with methylbenzene as an internal standard. The calibration samples were prepared by weighing with an analytical balance accurate to within ± 0.0001 g. The calibration equations were used to convert the area fraction into mass fraction. Calibration coefficients were obtained by fitting a straight line to the calibration results for each composition range. The accuracy of the measurements was within ± 0.0001 in mass fraction.

The water in the organic phase was determined by the Metrohm 756KF coulometer (measure error $\leq$ 0.3 %). The water in the aqueous phase was calculated by the fraction summation equation. Samples with known compositions were used to calibrate the instrument in the composition range of interest. Three or four analyses were performed for each sample to obtain a mean mass fraction value with a repeatability better than 1 %.

Calibration of Apparatus. The reproducibility and accuracy of the experimental technique were verified by duplicating the data of Moriyoshi et al.[7] for the 2-butanol–water binary system at 10 MPa. Figure 2 showed a good agreement between our measurements and the literature values. All compositions are in weight fraction.

Table 1. LLE Data for the Ternary System of Water (1) + Cyclohexanol (2) + Cyclohexene (3)

T	organic phase (I)			aqueous phase (II)		
K	x_1	x_2	x_3	x_1	x_2	x_3
303.2	0.4204	0.5796	0	0.9933	0.0067	0
	0.3386	0.5943	0.0671	0.9914	0.0085	$1.4 \cdot 10^{-5}$
	0.3027	0.5825	0.1148	0.9940	0.0060	$1.5 \cdot 10^{-5}$
	0.2687	0.5578	0.1735	0.9943	0.0056	$1.7 \cdot 10^{-5}$
	0.2195	0.5193	0.2612	0.9945	0.0055	$2.0 \cdot 10^{-5}$
	0.1482	0.4460	0.4058	0.9952	0.0047	$2.8 \cdot 10^{-5}$
	0.1189	0.3673	0.5138	0.9960	0.0040	$1.9 \cdot 10^{-5}$
	0.0778	0.3027	0.6195	0.9964	0.0036	$1.3 \cdot 10^{-5}$
	0.0417	0.2336	0.7247	0.9964	0.0036	$2.1 \cdot 10^{-5}$
	0.0137	0.1048	0.8815	0.9971	0.0028	$4.7 \cdot 10^{-5}$
	0.0028	0	0.9972	1.0000	0	$3.3 \cdot 10^{-5}$
323.2	0.4045	0.5955	0	0.9943	0.0057	0
	0.3429	0.5923	0.0648	0.9950	0.0050	$1.4 \cdot 10^{-5}$
	0.2922	0.5866	0.1212	0.9943	0.0057	$1.1 \cdot 10^{-5}$
	0.2584	0.5906	0.1510	0.9949	0.0051	$1.5 \cdot 10^{-5}$
	0.2447	0.5750	0.1803	0.9960	0.0040	$4.6 \cdot 10^{-5}$
	0.2294	0.5529	0.2177	0.9950	0.0049	$6.0 \cdot 10^{-5}$
	0.1886	0.5206	0.2908	0.9961	0.0038	$6.4 \cdot 10^{-5}$
	0.1333	0.4453	0.4214	0.9958	0.0042	$2.3 \cdot 10^{-5}$
	0.1156	0.3885	0.4959	0.9966	0.0034	$1.9 \cdot 10^{-5}$
	0.0783	0.3102	0.6115	0.9965	0.0034	$6.4 \cdot 10^{-5}$
	0.0374	0.2286	0.7340	0.9971	0.0029	$7.5 \cdot 10^{-5}$
	0.0240	0.1368	0.8391	0.9979	0.0020	$3.5 \cdot 10^{-5}$
	0.0055	0	0.9945	1.0000	0	$2.7 \cdot 10^{-5}$
383.2	0.4856	0.5144	0	0.9926	0.0074	0
	0.4334	0.4599	0.1067	0.9939	0.0061	$2.8 \cdot 10^{-5}$
	0.3313	0.4345	0.2342	0.9942	0.0058	$4.0 \cdot 10^{-5}$
	0.2384	0.3578	0.4038	0.9955	0.0045	$4.4 \cdot 10^{-5}$
	0.1486	0.2984	0.5530	0.9962	0.0038	$4.8 \cdot 10^{-5}$
	0.0760	0.2163	0.7077	0.9965	0.0035	$6.1 \cdot 10^{-5}$
	0.0493	0.1014	0.8493	0.9981	0.0018	$6.2 \cdot 10^{-5}$
	0.0159	0	0.9841	0.9999	0	$8.0 \cdot 10^{-5}$
403.2	0.5668	0.4332	0	0.9906	0.0094	0
	0.4337	0.4655	0.1008	0.9924	0.0076	$3.8 \cdot 10^{-5}$
	0.3515	0.4620	0.1865	0.9926	0.0074	$4.5 \cdot 10^{-5}$
	0.2398	0.3875	0.3727	0.9949	0.0050	$4.0 \cdot 10^{-5}$
	0.1967	0.3510	0.4523	0.9952	0.0048	$7.3 \cdot 10^{-5}$
	0.1444	0.2603	0.5953	0.9967	0.0033	$6.8 \cdot 10^{-5}$
	0.0481	0.1246	0.8273	0.9975	0.0024	$7.0 \cdot 10^{-5}$
	0.0306	0	0.9694	0.9987	0	$1.3 \cdot 10^{-3}$

Results and Discussion

The LLE compositions for the water + cyclohexene + cyclohexanol system at (303.2, 323.2, 383.2, and 403.2) K are listed in Table 1, and the experimental data of the ternary system

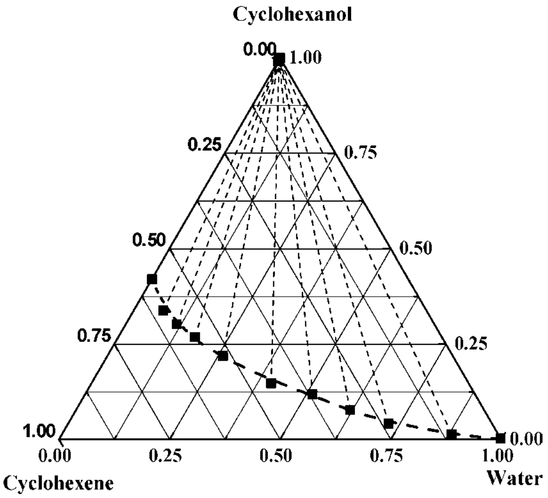

Figure 3. LLE phase diagram for water (1) + cyclohexanol (2) + cyclohexene (3) at 303.2 K: ■, experimental data in this work; dashed line indicates calculated curves by the NRTL model.

at $T = 303.2$ K are plotted in Figure 3. All compositions are in mole fraction. The experimental pressure at (383.2 and 403.2) K is 4.0 MPa.

From the experimental data, it was easily found that the two-phase region became smaller with the temperature increasing from (323.2 to 383.2) K. In other words, increasing temperature can improve the solubility of the organic phase and aqueous phase. But, when the temperature was increasing from (383.2 to 403.2) K, the increase is not obvious.

Correlation of the Data. Our experimental data were correlated with the NRTL model of Renon and Prausnitz.[8] For the NRTL model, a value of nonrandomness parameter $\alpha = 0.24319$, 0.26904, and 0.79362 was separately used for the water−cyclohexene pair,[5] the water−cyclohexanol pair, and the cyclohexene−cyclohexanol pair.

The NRTL model was fitted to experimental data using an iterative computer program, based on particle swarm optimization, developed by Kennedy and Eberhart.[9,10] The objective function OF[11] used in this case was

$$\mathrm{OF} = \sum_{k=1}^{N}\sum_{i=1}^{3}\left(\frac{K_{\mathrm{ik}}^{\mathrm{exp}} - K_{\mathrm{ik}}^{\mathrm{cal}}}{K_{\mathrm{ik}}^{\mathrm{exp}}}\right)^2 / 3N$$

$$= \sum_{k-1}^{N}\sum_{i=1}^{3}\left(\frac{\left(\dfrac{x_{\mathrm{ik}}^{\mathrm{I}}}{x_{\mathrm{ik}}^{\mathrm{II}}}\right)\Big/\left(\dfrac{y_{\mathrm{ik}}^{\mathrm{II}}}{y_{\mathrm{ik}}^{\mathrm{I}}}\right)}{\left(\dfrac{x_{\mathrm{ik}}^{\mathrm{I}}}{x_{\mathrm{ik}}^{\mathrm{II}}}\right)}\right)^2 / 3N \qquad (1)$$

where K_{ik}, γ_{ik}, and x_{ik} are the distribution coefficient, activity coefficient, and mole fractions, respectively. The superscripts I and II denote the organic phase and aqueous phase, respectively. The subscripts i and k denote the component and tie-line, respectively. N is the number of tie-lines.

The optimization results were judged by calculating the corresponding root-mean-square deviation (rmsd %)[12] values using the following equation;

$$\mathrm{rmsd}\,\% = 100\sqrt{\sum_{k=1}^{N}\sum_{j=1}^{2}\sum_{i=1}^{3}\frac{(x_{\mathrm{ijk}}^{\mathrm{exp}} - x_{\mathrm{ijk}}^{\mathrm{cal}})^2}{6N}} \qquad (2)$$

where the subscript j denotes different phases.

The values of the interaction parameters for the NRTL model at different temperatures are shown in Table 2. These parameters are used to calculate LLE tie lines for the present system. Figure 3 also compares the calculated curves from the NRTL model with the experimental results. As seen from Table 2, good agreements have been obtained for the ternary system.

Table 2. Correlated Results from the NRTL Model for the Water (1) + Cyclohexanol (2) + Cyclohexene (3)

T/K	$i-j$	Δg_{ij}/J·mol^{-1}	Δg_{ji}/J·mol^{-1}	rmsd %
303.2	1−2	50007.9	−1873754.8	1.881
	1−3	72117.6	73856.1	
	2−3	−1873524.5	−1874730.0	
323.2	1−2	65418.3	−1996974.1	1.927
	1−3	57251.9	69147.0	
	2−3	−1997190.2	−1997522.1	
383.2	1−2	69478.7	−2369239.8	1.410
	1−3	87436.3	64896.6	
	2−3	−2369827.8	−2369910.0	
403.2	1−2	72510.7	−2493259.1	0.775
	1−3	89603.1	88259.0	
	2−3	−2493715.2	−2493050.2	

Conclusion

An experimental investigation of the equilibrium behavior of the system composed of water + cyclohexene + cyclohexanol was carried out at different temperatures of (303.2, 323.2, 383.2, and 403.2) K. The NRTL model was used to correlate the experimental LLE data. The optimum NRTL parameters were determined using the experimental liquid−liquid data. It was found that the NRTL method fitted satisfactorily to the experimental data.

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