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Liquid−Liquid Equilibria for the Ternary System Methyl Isobutyl Ketone + Water + Hydroquinone

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Experimental liquid−liquid equilibria data of dilute hydroquinone concentration were determined for the ternary system methyl isobutyl ketone + water + hydroquinone at (25, 40, and 50) °C under atmospheric pressure. The experimental data were satisfactorily correlated with the UNIQUAC equation and the NRTL equation. The relative root-mean-square deviations and absolute mean deviations between the calculated and the experimental value are less than 1.2 %.

Introduction

Phenols are toxic organic pollutants. Hydroquinone is one of the main phenolic pollutants appearing in wastewater of many industrial processes, including petroleum refining, petrochemical manufacture, coking, coal gasification, and wood processing. Generally, the concentration of phenols in these wastewaters is in the range of (10 to 10^4) mg·L^{-1}. When the total phenolic pollutants in the wastewater exceed 1000 mg·L^{-1}, solvent extraction is a preferential technology used in the industries for recovery.[1−3] Methyl isobutyl ketone is the proposed solvent for the phenolic wastewater.[3] Fundamental liquid−liquid equilibria (LLE) data are very important in modeling and design of the extraction process. To provide fundamental data for the extraction process of hydroquinone removal from wastewater, the experimental LLE data of dilute hydroquinone concentration for the ternary system methyl isobutyl ketone + water + hydroquinone were determined at (25, 40, and 50) °C under atmospheric pressure. Furthermore, the experimental data were correlated with the UNIQUAC[4] equation and the NRTL[5] equation.

Experimental Section

Materials. Hydroquinone (ShanTou Guanghua Chemical Reagents Company, China, > 99.5 %) and methyl isobutyl ketone (MIBK, ShangHai Lingfeng Chemical Reagents Company, China, > 99 %) were used without further purification. The purity of these materials was checked and confirmed by gas chromatography. Distilled water was used in all experiments.

Procedure. A 100 mL glass-sealed cell surrounded by a thermostat water jacket was used to prepare LLE samples. The temperature of the cell was controlled and maintained with an accuracy of ± 0.1 °C. The ternary mixture was put into the sealed thermostatic cell and vigorously agitated by a magnetic stirrer for 2 h and then kept undisturbed for 12 h to ensure phase separation and equilibrium. The procedure was repeated, and a series of LLE samples were prepared by changing the compositions of the mixture.

Analysis. Both separated phases of water and methyl isobutyl ketone were sampled from the cell and analyzed using a gas chromatography (GC6820, Agilent Technologies, Inc., USA) equipped with a 30 m × 0.32 mm × 1 μm DB-1701 capillary column, a thermal conductivity detector (TCD), and a flame-ionization detector (FID). The organic phase samples were determined by TCD, while the aqueous phase samples were determined by FID. The compositions for each sample were determined by averaging over three samples. The measurement deviation in the composition analysis is less than 3 %.

Table 1. Experimental and Literature Values of Mutual Solubility of Methyl Isobutyl Ketone (1) + Water (2) as Mass Fraction *w*

	w_2 in organic phase		w_1 in aqueous phase	
t/°C	exptl	lit.	exptl	lit.
25	0.0194	0.019[a]	0.0171	0.017[a]
40	0.0244	0.025[b]	0.0148	0.0147[b]
50	0.0278	0.029[b]	0.0136	0.0138[b]

[a] From ref 6. [b] From ref 7.

Results and Discussion

Experimental Data. Mutual solubility data of the binary system methyl isobutyl ketone + water at (25, 40, and 50) °C along with literature values are listed in Table 1. The comparison indicates that the experimental method is reasonable and reliable. The experimental LLE data for the ternary system methyl isobutyl ketone + water + hydroquinone are shown in Table 2.

Data Correlation. Two widely used thermodynamic methods for strongly nonideal systems with limited miscibility, the UNIQUAC[4] equation and the NRTL[5] equation, were used to correlate the experimental data. Generally when a liquid mixture is separated into two phases and reaches equilibrium, the composition of the two phases can be determined by the following equations:

$$x_i'\gamma_i' = x_i''\gamma_i'' \tag{1}$$

$$\sum_i x_i' = 1 \tag{2}$$

$$\sum_i x_i'' = 1 \tag{3}$$

where x_i' and x_i'' are the mole fraction of component i in phases 1 and 2, γ_i' and γ_i'' are the corresponding activity coefficients of

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Table 2. Experimental Liquid−Liquid Equilibrium Data for the Ternary System of Methyl Isobutyl Ketone (1) + Water (2) + Hydroquinone (3) as Mass Fraction w

	organic phase			aqueous phase		
t/°C	w_1	w_2	w_3	w_1	w_2	w_3
25	0.9806	0.0194	0.0000	0.0172	0.9828	0.000000
	0.9782	0.0199	0.0019	0.0170	0.9829	0.000131
	0.9729	0.0205	0.0066	0.0169	0.9826	0.000499
	0.9622	0.0216	0.0162	0.0168	0.9819	0.001298
	0.9523	0.0232	0.0245	0.0166	0.9814	0.001974
	0.9321	0.0259	0.0420	0.0164	0.9798	0.003768
	0.9263	0.0264	0.0473	0.0161	0.9796	0.004311
	0.9092	0.0287	0.0621	0.0158	0.9781	0.006147
	0.8876	0.0326	0.0798	0.0155	0.9759	0.008606
	0.8597	0.0368	0.1035	0.0152	0.9723	0.012452
40	0.9756	0.0244	0.0000	0.0148	0.9852	0.000000
	0.9728	0.0251	0.0021	0.0148	0.9849	0.000249
	0.9675	0.0262	0.0063	0.0147	0.9846	0.000665
	0.9566	0.0274	0.0160	0.0146	0.9835	0.001917
	0.9493	0.0283	0.0224	0.0145	0.9828	0.002721
	0.9302	0.0305	0.0393	0.0144	0.9805	0.005056
	0.9259	0.0317	0.0424	0.0142	0.9799	0.005848
	0.9076	0.0347	0.0577	0.0140	0.9779	0.008060
	0.8857	0.0371	0.0772	0.0138	0.9749	0.011306
	0.8683	0.0394	0.0923	0.0136	0.9718	0.014582
50	0.9722	0.0278	0.0000	0.0136	0.9864	0.000000
	0.9697	0.0283	0.0020	0.0136	0.9861	0.000265
	0.9651	0.0292	0.0057	0.0135	0.9857	0.000839
	0.9554	0.0307	0.0139	0.0134	0.9845	0.002078
	0.9477	0.0328	0.0195	0.0133	0.9836	0.003105
	0.9320	0.0342	0.0338	0.0132	0.9810	0.005825
	0.9246	0.0358	0.0396	0.0131	0.9800	0.006935
	0.9097	0.0376	0.0527	0.0130	0.9777	0.009280
	0.8909	0.0395	0.0696	0.0129	0.9740	0.013104
	0.8701	0.0432	0.0867	0.0127	0.9702	0.017131

Table 3. NRTL and UNIQUAC Parameters g_{ij}/J·mol^{-1}, α_{ij}, and u_{ij}/J·mol^{-1} for the System Methyl Isobutyl Ketone + Water + Hydroquinone

t			UNIQUAC	NRTL	
°C	component i	component j	$u_{ij} - u_{jj}$	$g_{if} - g_{jj}$	α_{ij}
25	hydroquinone	MIBK	−2706.61	−4335.99	0.3
	MIBK	hydroquinone	2536.71	1095.82	
	hydroquinone	water	655.90	−6076.98	0.2
	water	hydroquinone	−1905.91	13097.6	
	MIBK	water	3830.54	1963.63	0.2
	water	MIBK	730.02	12738.15	
40	hydroquinone	MIBK	−1832.83	−3846.6	0.3
	MIBK	hydroquinone	937.4022	1079.36	
	hydroquinone	water	−1783.7	−5762.19	0.2
	water	hydroquinone	1411.525	12657.66	
	MIBK	water	3441.271	1456.55	0.2
	water	MIBK	980.0161	13015.25	
50	hydroquinone	MIBK	−2546.61	−4092.82	0.3
	MIBK	hydroquinone	1835.977	1010.26	
	hydroquinone	water	665.0442	−5794.04	0.2
	water	hydroquinone	−2616.26	11577.73	
	MIBK	water	3204.065	1300.20	0.2
	water	MIBK	1159.606	13184.85	

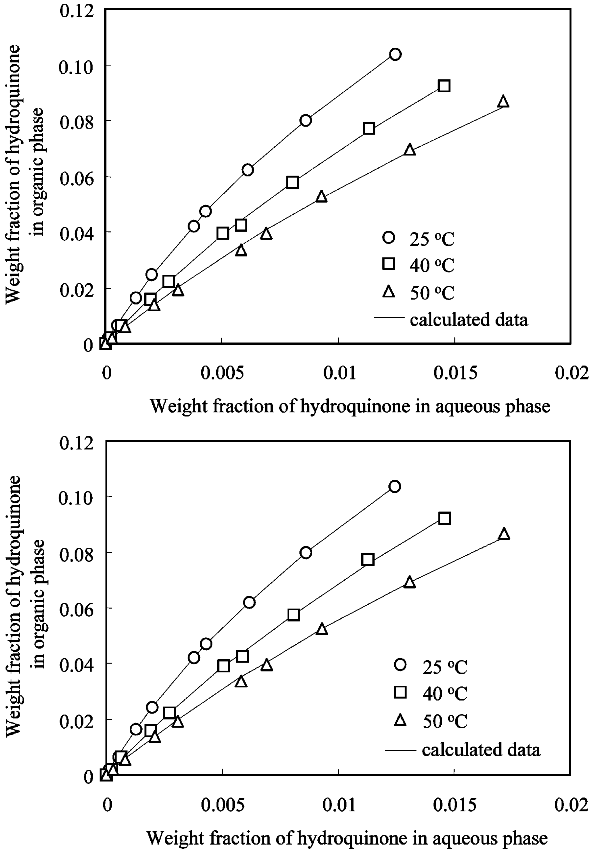

Figure 1. Comparison of experimental data and calculated data. (a) Calculated by UNIQUAC equation, (b) Calculated by NRTL equation

Table 4. Residual Deviations of Calculated Values from Experimental Values for the System Methyl Isobutyl Ketone + Water + Hydroquinone

t	UNIQUAC		NRTL	
°C	100RMD	100AMD	100RMD	100AMD
25	0.76	0.48	0.64	0.43
40	1.19	0.71	1.15	0.69
50	1.19	0.81	1.15	0.75

component i in phases 1 and 2 as calculated from the UNIQUAC equation or the NRTL equation. The interaction parameters between the components of the mixture are used to estimate the activity coefficients. These interaction parameters, ($u_{jf} - u_{ii}$) for the UNIQUAC equation and ($g_{jf} - g_{ii}$) for the NRTL equation can be regressed from the experimental LLE data.

The objective function (OF) was used to minimize the difference between the experimental and calculated mole fraction in the regression:

$$\mathrm{OF} = \sum_i \sum_j \sum_k (x_{ijk} - x_{ijk,\mathrm{cal}})^2 \tag{4}$$

where x_{ijk} is the measured mole fraction of component i in phase j on the k tie-line, and $x_{ijk,\mathrm{cal}}$ is the calculated value. The regressed results of the UNIQUAC group interaction parameters and the NRTL interaction parameters are shown in Table 3.

The comparisons of experimental data and calculated results for hydroquinone are shown in Figure 1. As shown, the calculated values are in good agreement with the experimental data either by the UNIQUAC equation or by the NRTL equation. Furthermore, it is found that the equilibrium distribution lines declined with the increase of temperature. This indicates that, at high temperature, the extraction performance of methyl isobutyl ketone for hydroquinone from water decreases.

The relative root-mean-square deviation (RMD) and relative absolute mean deviation (AMD) are calculated from the difference between the experimental data and the calculated data of each model according to the following equations:

$$\mathrm{RMD} = \sqrt{\frac{\sum\sum\sum\left(\frac{x_{ijk} - x_{ijk,\mathrm{cal}}}{x_{ijk}}\right)^2}{6n}} \tag{5}$$

$$\mathrm{AMD} = \frac{\sum\sum\sum\left(\frac{|x_{ijk} - x_{ijk,\mathrm{cal}}|}{x_{ijk}}\right)}{6n} \tag{6}$$

where n is the total number of tie line k, and if $x_{ijk} = 0$, then $(x_{ijk} - x_{ijk,\mathrm{cal}})/x_{ijk} = 0$. The results are shown in Table 4.

It is shown in Table 4 that the RMD and AMD between calculated and experimental data were all less than 1.2 %. This indicates that the LLE data of the ternary system methyl isobutyl ketone + water + hydroquinone are reasonably correlated by the UNIQUAC equation and the NRTL equation.

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