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Liquid-liquid equilibria for methyl isobutyl ketone + cresols + water at 333.15 K, 343.15 K and 353.15 K: Experimental results and data correlation

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ABSTRACT

In this work, the liquid-liquid equilibrium (LLE) data for ternary systems, methyl isobutyl ketone + *o*, *m* or *p*-cresol + water were measured at 333.15 K, 343.15 K and 353.15 K under 101.3 kPa. The nonrandom (NRTL) and universal quasichemical (UNIQUAC) models were used to correlate the experimental data, and the results indicated that, both models predicted LLE data quite accurately, with root mean square deviations (RMSD) less than 2.5%. The binary interaction parameters calculated from these two models were also reported. Distribution coefficient and selectivity were calculated to assess the extraction performance of methyl isobutyl ketone.

1. Introduction

Coal gasification or distillation produces wastewater with highly concentrated phenols, which contains volatile phenols such as phenol and cresols, nonvolatile phenols such as hydroquinone and polyphenols, ammonia, organic acids and other substances. Among these pollutants, cresols are harmful to organism at concentration higher than 250 mg L^{-1} [1], and may bring long-term adverse effects to the aquatic environment. Cresols are extremely toxic, even more toxic than phenol: e.g. the LD50 (rats oral) of *o*-, *m*-, *p*-cresol and phenol are 121, 242, 207 and 317 mg/kg respectively. They also have higher bio-accumulation potential than phenol as indicated by the octanol-water partition coefficient: e.g. log Kow of *o*-, *m*-, *p*-cresol and phenol are 1.95, 1.96, 1.95 and 1.46 respectively [2]. Thus it is necessary to remove cresols from waste waters before discharging them [3].

Solvent extraction is a frequently used method to treat phenols containing waste water with a range of advantages such as ease of implement, high throughput, versatility and economical efficiency [4]. This method has being used in China [5], South Africa [1], United states [1,6], etc., for quite a few decades, and the process simulation, operation cost and industrial implementation has been studied thoroughly [7,8]. Liquid-liquid equilibria (LLE) data are essential for designing or optimizing an extraction process [9–11]. Some LLE data of the ternary solvent-cresol-water systems have been published in recent years. The experimental data for (toluene + *o*-, *m*-, *p*-cresol + water), (ethylbenzene + *o*-, *m*-, *p*-cresol + water), (heptane + *o*-, *m*-, *p*-cresol + water) and (octane + *o*-, *m*-, *p*-cresol + water) systems were measured by Martin et al. [12,13]. Kupatkin et al. [14] studied the ternary systems, (trimethylcarbinol + *o*-cresol + water) and (trimethylcarbinol + *m*-cresol + water) at 298.2 and 323.2 K. The system (methyl butyl ketone + *o*-, *m*-, *p*-cresol + water) at 298.2 and 313.2 K was investigated by Lv et al. [15]. The LLE data of the systems, (2-methoxy-2-methylpropane + *o*-, *m*-, *p*-cresol + water) at 298.15 and 313.15 K were reported by Luo et al. [16–18].

Methyl isobutyl ketone (MIBK) is considered to be an excellent extraction solvent to separate cresols from water with high distribution coefficients, and has been used to treat phenolic waste water in industry [5,7]. It also has attracted the interest of researchers, with tie line data for the systems, (methyl isobutyl ketone + *o*- or *p*-cresol + water), measured at 303.2 K by Telkikar et al. [19]. However, recovering phenols from waste water in industry are usually

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performed at temperatures above 333 K to avoid clogging the extraction installation by paraffin wax (melting point between 328.15 and 335.15 K) in the industrial efflux [20], while corresponding LLE data in such temperature range remain unknown. Hence it is critical to study solvent extraction of cresols with MIBK above 333 K for designing or optimizing wastewater treatment process in industry.

The LLE data of ternary systems, (methyl isobutyl ketone + *o*-, *m*-, *p*-cresol + water) at (333.15, 343.15 and 353.15) K under 101.3 kPa were measured in this work. The experimental data were correlated by NRTL [21] and UNIQUAC [22] activity coefficient to yield binary interaction parameters.

2. Experimental

2.1. Materials

The purity and source of chemical reagents in this work are listed in Table 1. These chemicals were used without further purification since their purity had been verified with analysis methods listed in Table 1. Distilled water was used throughout all experiments.

2.2. Apparatus and procedure

The experimental LLE data for the ternary systems, MIBK + *o*, *m* or *p*-cresol + water were measured at 333.15 K, 343.15 K and 353.15 K under 101.3 kPa. Certain amounts of MIBK, *o*, *m* or *p*-cresol, and water were loaded into a 100 mL glass equilibrium cell to form a ternary mixture. The mixture was agitated vigorously for more than 2 h and then was left to settle for over 20 h for the system to reach the phase equilibrium. The temperature of the mixtures in the cell was kept constant by using a thermostatic bath with a fluctuation of 0.1 K.

When the phase equilibrium was reached and the mixture was split into two layers, the samples of both layers were collected with a syringe, and were analyzed by a gas chromatography (GC 6820, Agilent Technologies) equipped with a flame ionization detector (FID, with a sensitivity of 10–100 ppb) and a DB-5MS capillary column (30 m × 0.32 mm × 0.25 μm). The oven initial temperature was held at 313.15 K for 2 min and then increased 443.15 K at a rate of 30 K min^{-1}. The detector and injector temperatures were held at 523.15 K and 533.15 K. The nitrogen was used as carrier gas with a rate of 30 ml min^{-1}. The solvent was methanol.

The composition of the sample was determined by an internal standard method, where *n*-butyl acetate was used as an internal standard for MIBK and 1, 3, 5-trimethylbenzene for cresols. The water' mole fraction was calculated from deducting those of the other two component (MIBK and cresols) from 1. The samples and internal standards were all weighed by an analytical balance (Shimadzu AUW220D) with an accuracy of ±0.1 mg. Each sample was measured for at least 3 times, with a standard deviation of less than 0.02%, thus the average value was reported in this work.

3. Results and discussion

3.1. Experimental LLE data

Tables 2–4 show the LLE data of ternary systems, MIBK + cresols + water at (333.15, 343.15 and 353.15) K under 101.3 kPa. All concentrations are expressed in mole fraction. The tie-lines data for the studied systems at were plotted in the triangular diagrams as shown in Figs. 1–3.

To estimate the capacity of MIBK to separate cresols from wastewater, the distribution coefficient (D) and separation factor (S) are calculated as follow

$$D = \frac{x_{21}}{x_{23}} \tag{1}$$

Table 2
Experimental LLE Data (mole fraction) for ternary system MIBK(1) + *o*-cresol(2) + water(3) at 333.15 K, 343.15 K and 353.15 K and 101.3 kPa.[a]

T/K	Organic phase			Aqueous phase			D	S
	x_1	x_2	x_3	x_1	x_2	x_3		
333.15	0.2521	0.3588	0.3891	0.0007	0.0008	0.9985	449	1152
	0.2869	0.3363	0.3769	0.0009	0.0007	0.9984	480	1272
	0.3197	0.3148	0.3655	0.0010	0.0006	0.9984	525	1434
	0.3682	0.2828	0.3490	0.0011	0.0005	0.9984	566	1619
	0.4135	0.2459	0.3406	0.0013	0.0004	0.9983	615	1803
	0.4750	0.2017	0.3233	0.0014	0.0003	0.9983	672	2075
	0.5230	0.1615	0.3155	0.0015	0.0002	0.9983	808	2557
	0.5599	0.1357	0.3045	0.0016	0.0001	0.9983	1357	4449
	0.6330	0.0967	0.2703	0.0017	0.0001	0.9982	967	3571
	0.8112	0.0000	0.1888	0.0023	0.0000	0.9977		
343.15	0.2341	0.3650	0.4008	0.0006	0.0009	0.9985	406	1011
	0.2653	0.3446	0.3900	0.0008	0.0008	0.9984	431	1103
	0.3008	0.3212	0.3781	0.0009	0.0007	0.9984	459	1212
	0.3566	0.2905	0.3529	0.0011	0.0006	0.9984	484	1369
	0.4054	0.2512	0.3434	0.0012	0.0004	0.9984	628	1826
	0.4677	0.2084	0.3238	0.0014	0.0003	0.9983	695	2143
	0.5233	0.1698	0.3069	0.0015	0.0002	0.9983	849	2762
	0.5667	0.1393	0.2939	0.0016	0.0001	0.9983	697	2368
	0.6145	0.1053	0.2803	0.0017	0.0001	0.9983	1053	3750
	0.7413	0.0000	0.2587	0.0022	0.0000	0.9978		
353.15	0.2175	0.3710	0.4115	0.0006	0.0010	0.9985	371	900
	0.2375	0.3519	0.4106	0.0007	0.0009	0.9985	391	951
	0.2787	0.3251	0.3962	0.0008	0.0008	0.9984	406	1023
	0.3169	0.2998	0.3832	0.0009	0.0006	0.9984	500	1303
	0.3745	0.2509	0.3746	0.0011	0.0005	0.9984	502	1338
	0.4190	0.2229	0.3581	0.0013	0.0004	0.9984	557	1553
	0.4752	0.1844	0.3404	0.0014	0.0003	0.9983	615	1804
	0.5347	0.1437	0.3215	0.0015	0.0002	0.9983	719	2233
	0.5794	0.1104	0.3102	0.0016	0.0001	0.9983	1104	3553
	0.6928	0.0000	0.3072	0.0019	0.0000	0.9981		

[a] Standard uncertainties u are $u(T) = 0.1$ K, $u(p) = 1$ kPa, $u(x) = 0.0002$.

Table 1
Source and purity of the materials studied.

Component	Source	Stated mass fraction purity	Purification method	Analysis method
Methanol	Xiya Reagent	≥0.99	None	GC[a]
2-Cresol	Xiya Reagent	≥0.99	None	GC[a]
3-Cresol	Xiya Reagent	≥0.99	None	GC[a]
4-Cresol	Xiya Reagent	≥0.99	None	GC[a]
1,3,5-Trimethylbenzene	Xiya Reagent	≥0.99	None	GC[a]
1-Octanol	Xiya Reagent	≥0.99	None	GC[a]
4-Methyl-2-pentanone	Xiya Reagent	≥0.99	None	GC[a]

[a] Gas chromatography.