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Measurements and thermodynamic modeling of liquid–liquid equilibria in ternary system 2-methoxy-2-methylpropane + *p*-cresol + water☆

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ABSTRACT

Liquid–liquid equilibrium (LLE) data for the ternary system 2-methoxy-2-methylpropane (methyl *tert*-butyl ether) + *p*-cresol + water was measured at atmospheric pressure and temperatures of 298.15 K and 313.15 K. From the distribution coefficients and selectivity, it was found that 2-methoxy-2-methylpropane is an efficient solvent to extract *p*-cresol from wastewater. The consistency of the experimental tie-line data was verified with the Hand and Bachman equations. These data were also correlated with the non-random two liquid (NRTL) and universal quasi-chemical correlation activity coefficient (UNIQUAC) models to yield binary interaction parameters for *p*-cresol extraction process evaluation. Both models agreed with experiments very well, yet the NRTL model showed even smaller average deviation than the UNIQUAC model.

1. Introduction

Liquid–liquid extraction plays an important role in removing phenolic compounds from wastewater. Phenolic compounds, such as *p*-cresol, are major toxic pollutants usually detected in the effluent of various industries. Some solvents including ether, ketone, ester and alcohol can be used to extract phenols from wastewater, because phenols show much higher solubility in these solvents than in water. Liquid–liquid equilibria (LLE) data are essential for proper understanding and simulating the solvent extraction processes [1,2]. There have been a lot of liquid–liquid equilibrium studies about ternary systems of water + phenolic compound + extraction solvent, such as 2-methoxy-2-methylpropane + phenol or hydroquinone + water [3,4] and methyl butyl ketone + phenol or hydroquinone + water [5].

p-Cresol is widely used as antioxidants, herbicides, surfactants, pigments and dyes [6,7]. Waste water from relevant industries usually contains such compound with high concentration, whose water solubility is above 24.4 $\mathrm{g\cdot L^{-1}}$ at 298.15 K [8]. *p*-Cresol is highly toxic, potentially carcinogenic, and can bring negative effect to the nervous, cardiovascular and respiration systems even at very low concentrations [9,10]. For such reason, *p*-cresol is classified as a pollutant of Group C (possible human carcinogens) and is listed as a priority pollutant by USA-EPA [11,12]. Therefore, we studied 2-methoxy-2-methylpropane as an organic solvent to extract *p*-cresol from water. 2-Methoxy-2-methylpropane is chosen as the solvent due to its high distribution coefficients [13] and low energy consumption in phenol recovery process.

In this work, the LLE data for the ternary system, 2-methoxy-2-methylpropane + *p*-cresol + water, were measured at 298.15 K and 313.15 K under atmospheric pressure. Also, this system's phase behavior was studied. The reliability of these tie-line data was assessed by the Hand [14] and Bachman [15] equations. They were also correlated by the NRTL [16] and UNIQUAC [17] models, which both yield LLE data in good agreement with experimental results. To the best of our knowledge, no similar LLE data has been reported for the 2-methoxy-2-methylpropane + *p*-cresol + water ternary system.

2. Experimental

2.1. Chemicals

Commercial analytical grade chemicals were used in this work. 2-Methoxy-2-methylpropane was supplied by Sinpharm Chemical Reagent Co., Ltd. *p*-Cresol and 1,3,5-trimethylbenze were obtained from Xiya Reagent Research Center. Methanol was purchased from ShangHai LingFeng Chemical Reagent Co., Ltd, and *n*-butanol from JiangSu Qiangsheng Functional Chemistry Co., Ltd. Distilled water was prepared in our laboratory and used throughout all experiments in this work. The

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purity of these chemicals was verified before use by gas chromatography and by comparing their densities with reported values [18,19]. The purities and densities of these chemicals are shown in Table 1.

2.2. Procedure

In this work, all chemicals' densities were measured by a digital vibrating glass tube densitometer (Anton Paar, DMA 4500 M, Austria) to verify their purities. This densitometer was automatically calibrated with distilled water and dry air. Its temperature was set at 293.15 K with an uncertainty of ±0.03 K. According to the user manual, the uncertainty of measured density was 5×10^{-5} g·cm^{-3} in the density range of 0–3 g·cm^{-3}. Please refer to other literatures [20,21] for the details of density measurement.

In LLE experiments, a 100 ml glass-sealed cell surrounded by a thermostat water jacket was used to prepare the samples. The cell temperature was controlled by a thermostatic bath, whose fluctuation was less than 0.1 K. An ~55 ml 2-methoxy-2-methylpropane + *p*-cresol + water ternary mixture which contained ~5 ml 2-methoxy-2-methylpropane, ~10 ml *p*-cresol and ~40 ml water was fed into this glass cell, followed by a more than 2-hour vigorous agitation with a magnetic stirrer, then was left to stand for 18 h or more until the phase equilibrium was reached and the ternary mixture formed two liquid phases. Samples of both phases were collected by syringes, and were analyzed by a gas chromatography (GC6820, Agilent Technologies) equipped with a flame ionization detector (FID) and a DB-5MS capillary column (30 m × 0.32 mm × 0.25 μm). After GC analysis, we added 3– 5 ml of 2-methoxy-2-methylpropane into the glass cell and repeated the above procedures to get a new tie-line data. In GC analysis, the injection volume for the organic phase was 0.5 μl while that for the aqueous phase was 1 μl, so the split ratio was 20:1. The sample's composition was determined by an internal standard method, where an internal standard was added into the LLE sample, collected by syringes from the LLE system, before GC analysis. All chemicals in GC analysis were weighed by an analytical balance (Shimadzu, AUW220D) whose accuracy was 0.1 mg. In the experiments, 1, 3, 5-trimethylbenze and methanol were used as internal standards for *p*-cresol and 2-methoxy-2-methylpropane, respectively. *n*-Butanol was used as solvent to dissolve GC analysis samples with internal standards. The mass fraction of water was calculated from the mass balance equation: the total mass fraction of the extractants, *p*-cresol and water is 1. In GC analysis, the initial temperature of the oven was kept at 313.15 K for 2 min, then was increased to 473.15 K at a rate of 30-K·min^{-1}. The carrier gas was nitrogen, with a flow rate of 30 ml·min^{-1}. The temperatures of the injector and the detector were set at 523.15 K and 543.15 K respectively. Each sample was measured at least 3 times and the standard deviation was less than 0.5%, so the average value was reported in this work.

Table 1
Purities, densities and UNIQUAC parameters of the components used in this work

Component	GC analysis (by mass)/%	ρ/g·cm^{-3} at 298.15 K		UNIQUAC volume and area parameters①	
		Exp.	Lit. value	r	q
2-Methoxy-2-methylpropane	≥99	0.73780	0.74050②	4.0678	3.6320
p-Cresol	99	1.03445	1.0347③	4.8180	3.6480
1,3,5-Trimethylbenze	99.5	0.86403	0.86111③,④	–	–
Methanol	≥99.9	0.79100	0.78700②	–	–
n-Butanol	≥99.5	0.80796	0.80570②	–	–
Water	≥99.9	0.99715	0.99710②	0.9200	1.4000

① Ref. [22] and [23].
② Ref. [18].
③ Ref. [19].
④ At 293.15 K.

Table 2
Experimental LLE data for ternary system 2-methoxy-2-methylpropane(1) + *p*-Cresol(2) + Water(3) at $T = 298.15$ K and $T = 313.15$ K①

T/K	Organic Phase			Aqueous phase			D	S
	w_1	w_2	w_3	w_1	w_2	w_3		
298.15	0.53968	0.41176	0.04856	0.01353	0.00238	0.98409	173.03	3506.83
	0.57512	0.38185	0.04303	0.01450	0.00220	0.98330	173.95	3975.00
	0.61625	0.34577	0.03799	0.01541	0.00193	0.98266	179.57	4645.36
	0.67806	0.29075	0.03119	0.01720	0.00152	0.98129	191.75	6033.25
	0.71712	0.25450	0.02837	0.01798	0.00132	0.98070	193.01	6672.00
	0.75535	0.21855	0.02610	0.01872	0.00108	0.98020	202.12	7590.67
	0.78871	0.18909	0.02220	0.01969	0.00093	0.97938	204.32	9013.31
	0.81855	0.16142	0.02003	0.02048	0.00073	0.97879	219.68	10,732.39
	0.84724	0.13424	0.01852	0.02132	0.00060	0.97807	223.26	11,790.74
	0.90173	0.08187	0.01640	0.02287	0.00036	0.97677	229.37	13,662.93
	0.98831	0.00000	0.01169	0.03680	0.00000	0.96320		
313.15	0.33552	0.60979	0.05468	0.00307	0.00597	0.99097	102.19	1851.91
	0.39238	0.56001	0.04761	0.00467	0.00438	0.99095	127.94	2662.82
	0.51274	0.44822	0.03905	0.00890	0.00228	0.98882	196.72	4981.90
	0.59079	0.37605	0.03316	0.01183	0.00148	0.98669	254.15	7562.38
	0.64464	0.32527	0.03008	0.01400	0.00105	0.98495	308.47	10,099.71
	0.69840	0.27369	0.02791	0.01573	0.00080	0.98347	341.89	12,045.28
	0.72675	0.24690	0.02635	0.01663	0.00068	0.98269	365.14	13,617.56
	0.75714	0.21828	0.02458	0.01751	0.00057	0.98193	383.43	15,315.04
	0.78868	0.18848	0.02285	0.01840	0.00047	0.98113	403.20	17,316.03
	0.82479	0.15478	0.02043	0.02026	0.00036	0.97938	431.20	20,672.12
	0.98530	0.00000	0.01470	0.02500	0.00000	0.97500		

① Standard uncertainties u are $u(T) = 0.1$ K, $u(w) < 0.0019$ for $w > 0.1$, $u(\mathrm{w}) < 0.0001$ for $w < 0.1$.