



Determination and modeling of liquid-liquid equilibrium for ternary mixtures of methyl isopropyl ketone, cresol isomers and water



Yun Chen^{*}, Ran Lv, Furong Wang, Libo Li

Key Laboratory of Heat Transfer Enhancement and Energy Conservation of Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, PR China

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ABSTRACT

Ternary liquid-liquid phase equilibria data for three systems, (methyl isopropyl ketone + *o*-cresol + water), (methyl isopropyl ketone + *m*-cresol + water) and (methyl isopropyl ketone + *p*-cresol + water), were determined at 298.2 and 313.2 K and 101.3 kPa. The ternary phase diagrams composed of liquid-liquid equilibrium (LLE) data were presented graphically. The performance of methyl isopropyl ketone (MIPK) in extracting cresols was evaluated by distribution coefficients and separation factors. It could be concluded from the high distribution coefficients of cresols and separation factors that MIPK is an adequate extractant to extract cresols from its dilute aqueous solutions. The experimental data were correlated by the NRTL and UNIQUAC activity coefficient models. And the deviations between the experimental data and the calculated data from the NRTL and UNIQUAC models are very small, thus the two models both could represent the studied systems well.

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1. Introduction

Cresols, including *o*-cresol, *m*-cresol and *p*-cresol, as derivatives of phenol, are very important raw materials widely used in the manufacture of various chemicals [1,2]. However, cresols are also major pollutants existing in wastewater from various kinds of chemical industry, such as oil refineries, petrochemicals, coal conversion plants, coal tar distillation, phenol production industries and pharmaceuticals [3,4]. Cresols in the wastewater are highly toxic even at low concentration, and they could cause severe harms to human and the environment [3,5]. If such industrial wastewater containing cresols could not be adequately treated, it will cause serious water pollution, which could pose great threat to human health and the ecological system as water is the source of life.

For the abatement of organic pollutants in industrial wastewater, there have been many technologies investigated, including non destructive methods such as distillation, adsorption, and extraction, and destructive method such as chemical oxidation, catalytic oxidation, and biochemical degradation [6]. Among these investigated methods, solvent extraction is one of the more promising methods for treating cresols wastewater, as it has several

advantages, including high through put, ease of automatic operation and of scale up, handling highly concentrated phenols very well [7–9]. In addition, when solvent extraction method is adopted to handle wastewater, cresols in the wastewater could be recovered and reused as valuable materials. There have been commercial applications of treating wastewater with solvent extraction by a range of companies or plants, such as Chem-Pro Equipment Corp. [10], the Great Plains Gasification Plant in USA [11], the Sasol coal to liquids facility in South Africa [11], Inner Mongolia Tuke Coal-fertilizer project of China National Coal Group Corp. [11], China Datang Coal-based Natural Gas Project in Inner Mongolia and Liaoning [11], China Harbin Coal-chemicals Inc. [12,13], and Ordos Coal-chemicals Inc. in China [14], etc.

The flow diagram of industrial extraction process for phenolic wastewater treatment, especially in the coal chemical industry, is given in Fig. S1 in the Supplementary materials [12,13]. The industrial extraction process of phenolic wastewater treatment usually consists of three steps: extraction, solvent recovery, and stripping [12,13]. Firstly, the wastewater was sent into an extraction column and had a countercurrent contact with the extraction solvent at each stage of the column, after which the concentration of phenolic compounds in the wastewater could be reduced to below 300 mg/L, suitable for following biochemical treatment. Second, the extraction phase from the top of the extraction column was sent to a solvent recovery (distillation) column to separate phenolic

^{*} Corresponding author.

E-mail address: yunchen@scut.edu.cn (Y. Chen).

compounds from the solvent and to recover the solvent. At the same time, the extracted wastewater from the bottom of the extraction column was sent to a stripping column to recover the solvent dissolved in the wastewater, after which the concentration of solvent in the wastewater could be reduced to below 10 mg/L.

Thus in this paper, solvent extraction method was researched to remove cresols from aqueous solution. The key to solvent extraction is the selection of extraction agent. Desirable physicochemical properties, such as low toxicity, good stability, low cost and so on, are primary requirements for a suitable extractant [15], and high distribution coefficients and separation factors could guarantee the extractant's good efficiency in the extraction process. Previously, only a few solvents for extracting cresols from aqueous solution have been reported: e.g. toluene (temperature range, 298.15–323.15 K) [16], heptane (298.15–323.15 K) [17], 2-methoxy-2-methylpropane (MTBE, 298.15–313.15 K) [18–20], methyl butyl ketone (MBK, 298.2–313.2 K) [21], and methyl isobutyl ketone (MIBK, 333.15–353.15 K) [22]. Therefore, to investigate more promising solvent for extracting cresols is still primary consideration.

In this work, a new extraction solvent, methyl isopropyl ketone (MIPK), was considered for extracting cresols from aqueous solution. Precise liquid-liquid equilibrium (LLE) data are necessary for experimental studying and designing or optimizing solvent extraction process involved in wastewater treatment [23–27]. Consequently, in this work, the LLE data for the ternary systems, (MIPK + *o*-cresol, *m*-cresol, or *p*-cresol + water), were measured at 298.2 K and 313.2 K and 101.3 kPa, which haven't been found in any previous references to data. The reason of choosing these two temperatures, 298.2 K and 313.2 K, for LLE data measurement in this work is given below. On the one hand, LLE data and distribution coefficients of phenolic compounds extraction with different solvents are usually reported at temperature ranges of about 298.2–313.2 K [24,28–32], thus we measured LLE data at 298.2 K and 313.2 K to compare the distribution coefficient, and further the efficiency of MIPK with the solvents in literature directly. On the other hand, extraction process research was usually performed at moderate temperature range, e.g. at about 298.2 K [7,10], or at higher temperature of about 313.2 K [12,13], in laboratory or at industrial level, therefore, the measurement of LLE data in this work could provide fundamental data for the further research of extraction process. The distribution coefficients and separation factors for the studied systems were calculated. The nonrandom two-liquid (NRTL) [33] and universal quasi-chemical (UNIQUAC) [34] equations were used to correlate the experimental LLE data, and the binary interaction parameters were obtained.

2. Experimental

2.1. Chemicals

Chemical analytically pure reagents were brought from Xiya Regent Co., Ltd. with a declared mass purity of no less than 0.99. The purity (mass fraction) of these chemicals was confirmed by gas chromatography (GC) and no appreciable peaks of impurity were detected. Thus, all chemicals were used as received from supplier without further purification. Distilled water was used throughout this work. The details for source, purity and UNIQUAC parameters of chemicals used in this work are listed in Table 1.

2.2. Apparatus and procedure

The LLE measurements for the three studied ternary systems, (MIPK + *o*-cresol, *m*-cresol, or *p*-cresol + water), were carried out at 298.2 and 313.2 K and 101.3 kPa. The apparatus and procedure

adopted for the measurements of LLE in this work are similar with those reported in our previous work [21]. The apparatus for LLE establishment mainly consisted of a 100 cm³ glass equilibrium cell, a thermostat water bath, and a magnetic stirrer. In order to establish equilibrium, a certain amount of MIPK, cresol and water were added in a glass equilibrium cell, in which the temperature was kept at a constant (i.e. at 298.2 K, or at 313.2 K) by a thermostat water bath. And the prepared mixture was then agitated vigorously for 2 h and left to settle for at least 20 h to reach liquid-liquid phase equilibrium. The samples of the lower phase and the upper phase were carefully collected with a syringe when the equilibrium was reached.

2.3. Analysis

The compositions of the samples were analyzed by a gas chromatography (Agilent Technologies, GC 6820). A 30 m long DB-5MS column (320 μm diameter with a 0.25 μm film thickness) was used, and the temperature of column was controlled by a temperature-rising program: initially at 313.2 K (2 min), from (313.2–463.2) K at 30 K min⁻¹, finally at 463.2 K (2 min), while the temperature of the injector port was set at 523.2 K. The GC analysis was accomplished by a flame ionization detector (FID) installed on the GC, and the temperature of the detector was kept at 543.2 K. In addition, the carrier gas was nitrogen, with a flow rate of 30 cm³ min⁻¹. An internal standard method was used to quantify the mass fractions of MIPK (internal standard: *n*-propyl acetate) and cresols (internal standard: 1,3,5-trimethylbenzene), and the samples as well as the internal standards were all carefully weighed by an analytical balance (Shimadzu, AUW220D) accurate to within 0.0001 g. The mass fraction of water in each sample was obtained by mass balance. Each sample was analyzed for at least three times and the average result was reported.

2.4. Uncertainty calculation

The uncertainty of the experimental LLE data in this work was calculated according to the GUM and NIST guidelines [35,36]. The corresponding equations are given as follows.

$$u(w_i) = \left[\frac{1}{n(n-1)} \sum_{k=1}^n (w_{i,k} - \bar{w}_i)^2 \right]^{1/2} \quad (1)$$

$$\bar{w}_i = \frac{1}{n} \sum_{k=1}^n w_{i,k} \quad (2)$$

where n is the number of independent observations, $w_{i,k}$ is the input quantity obtained under the same measurement condition and $k = 1, 2, \dots, n$.

3. Results and discussion

3.1. Experimental LLE data

The experimental LLE data in mass fraction for the ternary mixtures (MIPK + *o*-cresol, *m*-cresol or *p*-cresol + water) at 298.2 and 313.2 K are listed in Tables 2–4. And also the LLE data for these three systems at temperature of only 298.15 K are presented in the triangle phase diagrams in Figs. 1–3. The influence of temperature on the size of two-phase region in the phase diagrams is very small among the studied temperature range (from 298.2 K to 313.2 K), causing the phase diagrams for LLE data at 298.2 and 313.2 K to be very much alike, thus phase diagrams with only temperature of

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