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Liquid-liquid equilibrium for ternary systems, methyl isobutyl ketone + (catechol, resorcinol and hydroquinone) + water at 333.15 K, 343.15 K and 353.15 K

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A B S T R A C T

Liquid-liquid equilibrium (LLE) data are vital to extraction process design and optimization. To provide fundamental data for the extracting process of dihydric phenol from wastewater, experimental liquid equilibrium data for ternary systems {methyl isobutyl ketone + catechol + water}, {methyl isobutyl ketone + resorcinol + water} and {methyl isobutyl ketone + hydroquinone + water} were determined at 333.15 K, 343.15 K and 353.15 K under atmospheric pressure. The NRTL and UNIQUAC models were used to correlate the experimental data and relevant binary interaction parameters were yielded. The experimental data were successfully correlated with the two models, and the root mean square deviations (RMSD) between the calculated and experimental values were less than 2%. Moreover, NRTL model performed slightly better than UNIQUAC model since the RMSD was smaller. Distribution coefficient and selectivity were employed to assess methyl isobutyl ketone's extraction capacity, which indicate that, methyl isobutyl ketone is a desirable extractant with extraction performance and physiochemical properties outperforming other extractants.

1. Introduction

Gasification and low temperature distillation process for low quality coal produce wastewater with high concentration of phenol and ammonia, which contains organic pollutants such as volatile phenols (e.g. phenol, cresols), non-volatile phenols (e.g. dihydric phenols and trihydric phenols), etc [1]. Non-volatile phenols such as catechol, resorcinol and hydroquinone are highly toxic, and the lethality (intra-abdominal injection, 100% death in 2 h) of dihydric phenols for *Dicentrarchus labrax* is 5.8 mg/100 g [2]. It is because of all these undesirable ecological effects of phenols that, strict regulations have been placed on their concentration in surface water around many countries (e.g. less than 0.5 ppm) [3] and there has been long standing effort to remove phenols from industrial wastewaters before discharging them to the environment.

Solvent extraction is the most common method to treat high concentration phenol and ammonia wastewater in chemical industries, which mainly includes following steps: firstly, removing coal tar and sludge from wastewater; secondly, senting high concentration phenol and ammonia wastewater to a stripper with side-draw to remove ammonia and sour gas simultaneously [4]; thirdly, after exchanging with the hot feeding stream and cooling with circulating water, sewage effluent from stripper bottom will flow into an extraction tower and countercurrent extract with extracting agent [5,6]. After extraction, solvent recovered from the extraction or the raffinate phase are sent back to the extraction column for recycling. Most LLE or solvent extraction study of phenols were carried out below 328 K, since the industrial treatment of phenolic wastewater have normally been performed in this temperature range. This usually lead to a severe problem that, the paraffin wax (melting point range between 328 K and 335 K) in the wastewater would clog the extraction device [7]. Such problem is critical for treating wastewater in the coal gasification or distillation industry [1], which forces some commercial plants (e.g. Harbin Coal Chemical Industry Co. Ltd. in China [4,6]) elevate the extraction temperature to above 333 K with ketones as the extractant. Therefore, to study the liquid-liquid equilibrium of ketone-phenols-water systems above 333 K is of great significance for industrial wastewater treatment [8].

Liquid-liquid equilibria (LLE) data are essential for designing or

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optimizing an extraction process [9–11]. LLE data of some ternary solvent-dihydric phenols-water systems have been published in recent years. Lei et al. [12] measurement the LLE data of the quaternary system, {2-methoxy-2-methylpropane + phenol + hydroquinone + water}, at 313.15 K. Xu et al. [13] studied the quaternary system of {water + isopropyl ether + phenol + hydroquinone} at 319.15 K. Lv et al. [14] reported the LLE data of the systems {MIPK + hydroquinone + water} and {MIPK + resorcinol + water} 298.15 K, 313.15 K and 323.15 K. However, these solvents have some shortcomings when they are used to extract phenols in industry, especially at moderate temperatures. The extraction efficiency (e.g. distribution coefficient or selectivity) of 2-methoxy-2-methylpropane (boiling point 328.15 K) and isopropyl ether (boiling point 341.15 K) for dihydric phenols are quite low (distribution coefficient are less than 10). Additionally, they are not suitable for extraction at moderate temperatures due to their low boiling points. Methyl isobutyl ketone (MIBK, boiling point 389.15 K) is a desirable solvent because of its desirable physical properties and high extraction efficiency for dihydric phenols. The LLE data of the ternary systems, {methyl isobutyl ketone + 1,2-benzenediol + water}, {methyl isobutyl ketone + m-Benzenediol + water} at 298.15 K, 308.15 K and 318.15 K, {methyl isobutyl ketone + hydroquinone + water} at 298.15 K, 303.15 K and 323.15 K, and the quaternary system, {methyl isobutyl ketone + phenol + hydroquinone + water}, have been reported by Yang et al. [15–18]. Wang et al. studied the systems {methyl isobutyl ketone + *m*-, *o*-, *p*-cresol + water} at 333.15 K, 343.15 K, 353.15 K and system {methyl isobutyl ketone + phenol + water} at 333.15 K, 343.15 K, 353.15 K [19,7]. However, those of the ternary systems, {methyl isobutyl ketone + catechol, resorcinol and hydroquinone + water}, above 333.15 K have not been published yet.

In this work, liquid-liquid equilibrium data for ternary systems, {MIBK + catechol + water}, {MIBK + resorcinol + water} and {MIBK + hydroquinone + water}, were measured at 333.15 K, 343.15 K and 353.15 K under atmospheric pressure. These LLE data were used to calculate binary interaction parameters with the NRTL [20] and UNIQUAC [21] models.

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

A 100 mL glass equilibrium cell, a thermostatically controlled bath, a magnetic agitator, an analytical balance and gas chromatography were used in this work to measure the LLE data for the ternary systems, {MIBK + catechol + water}, {MIBK + resorcinol + water} and {MIBK + hydroquinone + water} at (333.15, 343.15 and 353.15) K under atmospheric pressure. The mixture of MIBK, catechol, resorcinol or hydroquinone and water was loaded into a glass equilibrium cell and was agitated vigorously for more than 2 h to mix thoroughly, then was left to settle for at least 20 h to reach the phase equilibrium. The temperature of the mixture in the cell was kept constant by using a thermostatic bath with a fluctuation of 0.1 K.

After the ternary mixture formed two phases, a sample was taken from each phase using a syringe and was 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 initial oven temperature was held at 313.15 K for 2 min and then increased to 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, respectively. The nitrogen was used as the carrier gas with a rate of 30 ml min^{-1}. The solvent used in the GC analysis was methanol to dilute the samples.

The composition of the sample was determined by an internal standard method, where *n*-butyl acetate was used as the internal standard for MIBK and n-octanol for catechol, resorcinol and hydroquione. The mole fraction of water was calculated from deducting those of the other two components (MIBK and dihydric phenols) from 1. The samples and internal standards were weighed by an analytical balance (Shimadzu AUW220D) with an accuracy of 0.1 mg. Each sample was GC analyzed for at least 3 times, with a standard deviation of less than 0.2%, thus the average value was reported.

3. Results and discussion

The experimental tie line data for the studied systems, {MIBK + catechol + water}, {MIBK + resorcinol + water} and {MIBK + hydroquinone + water}, were determined at (333.15, 343.15 and 353.15) K under atmospheric pressure. The extraction efficiency of MIBK for catechol, resorcinol and hydroquinone is assessed by distribution coefficient (D) and separation factor (S), defined as follows:

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

$$S = D\frac{x_{33}}{x_{31}} \tag{2}$$

where x_{21} and x_{23} are diphenols mole fraction in the organic and the aqueous phases, respectively, x_{31} and x_{33} are water mole fraction in the organic and the aqueous phases, respectively. Tables 2–4 summarize the LLE data (expressed in mole fraction), distribution

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]
catechol	Xiya Reagent	≥0.99	None	GC[a]
resorcinol	Xiya Reagent	≥0.99	None	GC[a]
hydroquinone	Xiya Reagent	≥0.99	None	GC[a]
n-butyl acetate	Xiya Reagent	≥0.99	None	GC[a]
n-octanol	Xiya Reagent	≥0.99	None	GC[a]
methyl isobutyl ketone	Xiya Reagent	≥0.99	None	GC[a]

[a] Gas chromatography