



Effect of water on the separation of phenol from model oil with choline chloride via forming deep eutectic solvent



Shu-Hang Ren^a, Ying Xiao^a, Yi-Ming Wang^b, Jie Kong^a, Yu-Cui Hou^c, Wei-Ze Wu^{a,*}

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

^b School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

^c Department of Chemistry, Taiyuan Normal University, Taiyuan 030031, China

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ABSTRACT

Choline chloride (ChCl) was demonstrated to efficiently separate phenols from model oils by forming deep eutectic solvents (DESs). The DES way is a non-aqueous process that avoids the use of mineral alkalis and acids, and prevents the production of wastewater containing phenol. However, real oils, such as coal tar oil and liquefaction oil, consist of a small amount of water, and ChCl is a strong hygroscopic compound, which may influence the removal of phenol in real oil. In this work, the effect of water in mixtures of phenol and toluene (defined as model oils) on the separation of phenol by forming DES with ChCl was studied. The results indicated that water could interact with ChCl to form DES and the interaction between water and ChCl was stronger than that between phenol and ChCl. In the presence of water in model oils, the amount of ChCl should be increased to get the same phenol removal as that without water. Moreover, with water in model oils, the influence of temperature on the phenol removal was more negative. After the reuse of ChCl for four cycles with the presence of water, ChCl accumulated about 23% water and the removal efficiency of phenol decreased from 92% to 87%. To reduce the effect of water on phenol separation, an air drying method could be used to remove water in regenerated ChCl.

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1. Introduction

Phenols, which are widely used in chemical industry, are important materials for producing phenolic resins, dyes, pesticides, insecticides, and other preservatives [1]. Phenolic compounds have many kinds of phenols, which are mainly derived from coal tar, coal liquefaction oil, petroleum, and biomass via pyrolysis as documented in recent reports [2, 3]. Phenols are of high value but are difficult to be hydrogenated. It is therefore necessary to separate phenols from oils for further application.

The current method employed in industry to separate phenols from oil mixtures is as follows: extraction of phenols with aqueous alkaline solutions (such as NaOH), then recovery by using mineral acids (such as H₂SO₄). However, this process uses large amounts of strong alkalis and acids, producing wastewater containing phenols. Due to the above disadvantages, it is necessary to develop a new method to separate phenols from oil mixtures using a non-aqueous and oil-immiscible extractant.

Deep eutectic solvents (DESs) are composed of a mixture of organic compounds, hydrogen bond donors and hydrogen bond accepters, named so due to its melting point being far below that of either individual component, which are usually solid at room temperature. They have

physical properties similar to those of room temperature ionic liquids: low melting point, negligible vapor pressure, wide liquid range, non-flammability, and high thermal and chemical stabilities [4]. As a result, DES is widely used as a green solvent. For example, DES was used to extract and analyze natural products, such as phenolic metabolites, as well as to recover compounds from extracts, such as glycerol from palm oil-based biodiesel [5–7].

In our previous work [8], we demonstrated that choline chloride (ChCl) interacted with phenol from oils at room temperature forming DES, which separates phenol from oils with higher than 90% removal efficiency quickly, leaving no residues of ChCl left in the oil phase. We also studied the physical properties of a variety of DESs which were synthesized by mixing ChCl with different hydrogen bond donors (phenol, o-cresol, and 2,3-xyleneol), and the results showed that the mole ratio and hydrogen bond donor had strong effects on the physical properties of DES [9]. Recently, a variety of quaternary ammonium salts, including tetramethylammonium chloride (TMAC), tetramethylammonium bromide tetraethylammonium chloride, tetraethylammonium bromide, tetrapropylammonium chloride, tetrabutylammonium chloride, and choline bromide, could also form DES with phenol. Quaternary ammonium salts, which are composed of cations with appropriate chain lengths, high symmetry and anions with high electronegativity, were favorable to separate phenol from model oil. For example, phenol removal efficiency could reach 96% with 1:1 mole ratio of TMAC to phenol,

* Corresponding author. Tel./fax: +86 10 64427603.
E-mail address: wzwu@mail.buct.edu.cn (W.-Z. Wu).

and TMAC in DES was recovered completely by butyl ether or diethyl ether as an anti-solvent [10].

It was reported that water in DESs or in the extracts had a significant effect on the separation processes [6,11]. As we know, real oils, such as coal tar, coal liquefaction oil, and petroleum, are always processed in the presence of water [12]. In our work, when ChCl was used to separate phenols from real coal oils, there was a large decrease in phenol removal efficiency from that of model oil (from 93% to 85%). On the one hand, oil can dissolve water. For instance, the solubility of water in n-hexane is 9×10^{-4} mole fraction at 300 K and in benzene 3×10^{-3} mole fraction [13]. On the other hand, although the solubility of water in oil like n-hexane or benzene is very low, phenols in oil can increase the solubility of water. Hence, real oils consist of a small amount of water, such as 2 wt.% of moisture in coal tar oil [12]. Quaternary ammonium salts like ChCl are strong hygroscopic compounds. During the separation of model oil, we found that almost all the water in oil was transferred to DES. It is possible that when ChCl is added to oil containing water, ChCl may interact with water and influence the phenol removal.

The effect of water on the separation of phenol from oil by forming DES with ChCl has not been studied to the best of our knowledge. In this work, the solubility of water in model oils was investigated and the presence of water in model oils was studied for its effect on phenol removal and the reuse of ChCl.

2. Material and methods

2.1. Materials

ChCl (AR, >98.0%) and phenol (AR) were purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Toluene ($\geq 99.5\%$), n-hexane ($\geq 97.0\%$), diethyl ether ($\geq 99.0\%$), and other organic solvents were AR grade and produced from Beijing Chemical Reagent Plant (Beijing, China). Pyridine-free Karl Fischer reagent was purchased from Tianjin Concord Technology Co., Ltd. (Tianjin, China).

2.2. Apparatus and procedures

In this experiment, model oils with different contents of phenol were prepared by mixing toluene (or n-hexane) and phenol. The weight of phenol was measured by an electrical balance (CPA1003S, Sartorius) with an accuracy of 1 mg. For example, to prepare model oil with a phenol content of $116.3 \text{ g} \cdot \text{L}^{-1}$, 58.150 g of phenol was measured in a beaker, dissolved with a little amount of toluene, poured into a 500 mL volumetric flask, and made up to volume with toluene.

To measure the solubility of water in model oils with different contents of phenol, water was added into model oil until a small water phase appeared, and then the solubility of water in model oil was analyzed. For instance, to measure the solubility of water in model oil of $245.3 \text{ g} \cdot \text{L}^{-1}$ phenol at 298.15 K, the model oil (15 cm^3) and a magnetic stirrer were charged in a test tube of 25 mL with a cover. The test tube was put in a water bath, controlled by a temperature controller (A2, Beijing Changliu Scientific Instrument Company, China) with an accuracy of 0.1 K. After stirring for 20 min, water was dropped slowly into the model oil until a new phase appeared. The mixture was magnetically stirred for 30 min and settled for 10 min. Then the content of water in the upper oil phase was measured by Karl Fischer titration (ZDJ-400S, Multifunctional Titrator, Beijing Xianqu Weifeng Co. Ltd., Beijing, China). The expanded uncertainty of water mass fraction is $\pm 1\%$.

The phenol-separation process is as follows. Model oil of 15 cm^3 volume, containing a certain mass fraction of water, was added into a glass tube (25 cm^3) with some ChCl (according to the mole ratio of phenol and ChCl) in a water bath, whose temperature was maintained with an accuracy of 0.1 K. The mixture was magnetically stirred for 30 min and settled for 10 min. Two phases appeared in the glass tube and a small amount of sample from the upper oil phase was taken and analyzed by GC (GC-2014, Shimadzu, Japan) to determine its composition,

as reported in the literature [10]. For GC analysis, the carrier gas was nitrogen and the column was a capillary column (RTX-5, Restek, USA). A FID (Flame Ionization Detector) was used for the quantification of the products.

To investigate ChCl reuse in the presence of water, we run three drying cycles with four regeneration cycles nested in each of the three parent cycles. The model oil with 2% water and $121.0 \text{ g} \cdot \text{L}^{-1}$ phenol content was used. ChCl was added to the model oil at a mole ratio of 1:1 with phenol. After separation, the upper oil phase was removed, leaving the DES phase. Then 20 cm^3 of diethyl ether (DEE) was added as an anti-solvent to the DES phase. This mixture was shaken for 20 min at 298.2 K, and then ChCl was re-crystallized and precipitated to the bottom of the separator glass tube, completing the first nested cycle. The regenerated ChCl was then used again three times. After that, the regenerated ChCl was further dried under air at 373.2 K for 3 h to remove moisture, which completes the first parent cycle, to be repeated twice.

3. Results and discussion

3.1. Solubility of water in oil

The solubility of water in model oils with different phenol contents at different temperatures was studied. We initially chose two kinds of model oils: n-hexane and phenol, and toluene and phenol, but for this experiment we only chose that with toluene due to the extremely low solubility of water in the model oil of n-hexane and phenol. The reasons are: (1) the phenol solubility in n-hexane is not more than $36 \text{ g} \cdot \text{L}^{-1}$,

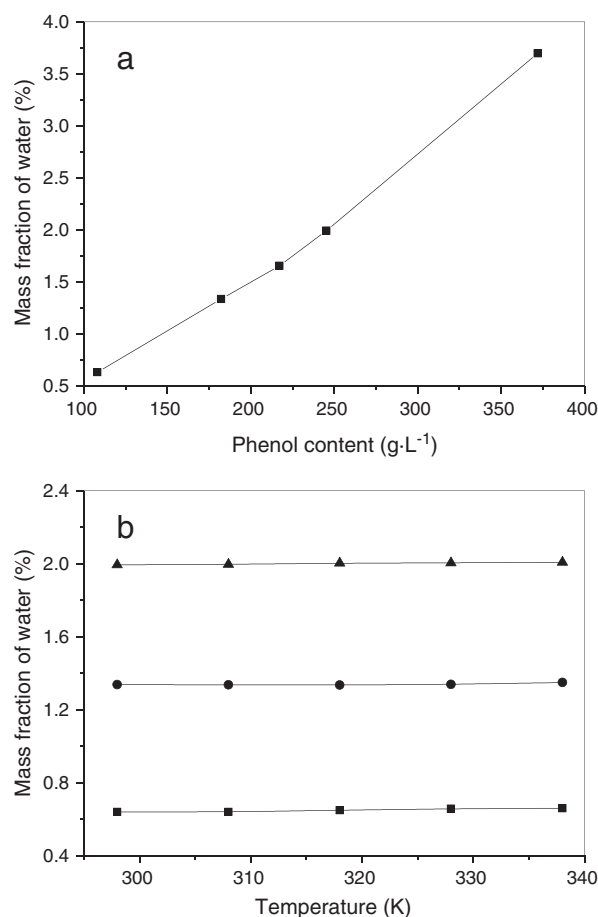


Fig. 1. (a) Solubility of water ($w_{\text{H}_2\text{O}}$ in mass fraction) in the model oil with different phenol contents at 298.2 K. (b) Effect of temperature on the solubility of water in the model oil with different phenol contents: (■), $108.1 \text{ g} \cdot \text{L}^{-1}$; (●), $217.3 \text{ g} \cdot \text{L}^{-1}$; and (▲), $245.3 \text{ g} \cdot \text{L}^{-1}$.

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