



## Research article

## Removal of the neutral oil entrained in deep eutectic solvents using an anti-extraction method

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## ABSTRACT

Forming deep eutectic solvents (DESs) by quaternary ammonium salts (QASs) and phenolic compounds to extract phenolic compounds from oil mixtures is effective. However, a small amount of neutral oil is entrained in the DESs. In this work, we proposed an anti-extraction method to remove the neutral oil entrained in DESs. Low-carbon alkanes (LCAs, including *n*-hexane, cyclohexane, and *n*-nonane) were added to model DESs to remove neutral oil. We found that the LCAs could effectively remove neutral oil entrained in the DESs. Of the three LCAs, *n*-hexane showed the best performance, and the removal rate of neutral oil could reach as high as 92.2%. The separation process could complete within 15 min, and the removal rate of neutral oil did not change significantly with temperature. In addition, *n*-hexane could effectively remove neutral oils in DESs formed by real coal tar and choline chloride. The neutral oil content in the phenolic compound product decreased to only 1.9 wt%, which greatly improves the purity of the phenolic compound product.

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## 1. Introduction

Phenolic compounds are mainly derived from coal liquefaction, coal tar and petroleum, and also from biomass via pyrolysis as reported in the literatures [1–3]. They are widely used in producing synthetic fibers, engineering plastics, pesticides, medicines, explosives, and so on [4]. Therefore, it is necessary to separate phenolic compounds from oil mixtures before further refinement or applications. The traditional method to separate phenol compounds from oil mixtures is chemical extraction [5]. This method uses sodium hydroxide solutions to react with phenolic compounds to form sodium phenolate aqueous solutions, which do not dissolve in oil mixtures. Then, strong acids are used to recover phenolic compounds from the aqueous solutions. The disadvantage of this process is the use of large amounts of both strong alkalis and acids, which may corrode devices. Additionally, the production of excessive amounts of wastewater containing phenols can be bad for the environment. In order to address these issues, it is necessary to use a new type of non-aqueous separation method.

In 2003, Abbott et al. [6] first reported that urea could form deep eutectic solvents (DESs) with quaternary ammonium salts (QASs). They also found that a DES could be formed between a series of carboxylic acids, including aromatic carboxylic acid, and QASs. The formation of these DESs resulted from the strong hydrogen bond interactions [7,8]. In recent years, because of DESs' many advantages, such as non-toxicity, non-water media and biodegradation, they have been applied to the

field of separation. Hayyan et al. [9] proposed DES formed by QASs and glycerine for extracting total glycerine from palm oil based biodiesel. They also suggested a continuous separation process for industrial scale application. Hadj-Kali et al. [10] used four DESs to extract sulfur-based compounds from *n*-heptane, and all the studied DESs showed good performance. Li et al. [11] used carboxylic acid-based DESs to separate organosulfur from oils. Hydrogen bonding between the sulfide and DES was found to be the main driving force of the extraction desulfurization process. Besides, DESs were also used in separation of biomass-based product mixtures [12,13]. Due to the advantages of extremely low vapor pressures of DESs, the applications of DESs in the field of organic synthesis, electrochemistry, separation, nano materials and biological chemistry have attracted widespread attention, and new achievements are continuously obtained [14–16]. DES has become a new research hotspot in the field of green chemistry and chemical engineering [17].

In 2012, our group [17,18] reported that phenol compounds could be separated from oil by QASs via forming DESs with phenolic compounds, which proved to be a highly effective way to separate phenolic compounds with a high removal efficiency. This process could be easily operated and not produce wastewater containing phenols, which is environmentally friendly.

However, in the process of removal, a small amount of neutral oil (such as toluene) is entrained into DES, which directly affects the purity of the product (phenolic compounds). In an experiment conducted by our group [19], choline chloride (ChCl) was used to separate phenol from model oil containing 200 g/dm<sup>3</sup> phenol via forming DES. Toluene was chosen as a neutral oil. It was found that the mass fraction of

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toluene in DES could reach as high as 15% at a ChCl:phenol mole ratio of 1:1. The mass ratio of toluene to phenol in DES was also as much as 30%. If not removed, the entrained toluene would make it hard to obtain high pure phenols. At the same time, it's a waste of toluene. These issues motivate the study on the removal of the neutral oil entrained in deep eutectic solvents.

Neutral components of coal tar are mainly a series of aromatic homologues, such as benzene, toluene, xylene, trimethylbenzene, naphthalene, etc. These neutral oil components have a similar structure of benzene ring to phenolic compounds, and these neutral oil components can form relatively strong  $\pi$ – $\pi$  bond with phenolic compounds.

It was reported that there was a very low content of *n*-hexane entrained in DES when the mixture of *n*-hexane and phenol was chosen as a model oil [20]. The phenol removal efficiency could reach as high as 99.2% and the purity of phenol product was 99.5%. As reported in the literatures [21–23], the solubility of toluene in *n*-hexane is very high. Therefore, it is possible that neutral oil can be removed by adding *n*-hexane to DES using an anti-extraction method.

In this work, we investigated the anti-extraction method to remove neutral oil entrained in DES formed by phenolic compounds and QASs, and a series of low carbon alkanes (LCAs, including *n*-hexane, cyclohexane and *n*-nonane) used as the extractants. The effects of LCA:DES volume ratio, extraction time, extraction temperature, QAS:phenol mole ratio, initial concentration of neutral oil and type of QASs (2-hydroxy-*N,N,N*-trimethyl-ethanaminium chloride, ChCl; *N,N,N*-trimethyl-methanaminium chloride, TMAC; and *N,N,N*-triethyl-ethanaminium chloride, TEAC) on the removal efficiency of neutral oil were studied. The structural schemes of ChCl, TMAC and TEAC are shown in Scheme 1. Meanwhile, *o*-xylene, *m*-xylene and *p*-xylene were chosen as model neutral oils to study the effect of different neutral oils on the removal efficiency. Lastly, we explored the effects of the addition of *n*-hexane on the removal of neutral oil in the DES formed by coal tar and ChCl. The results indicate that neutral oil in DESs can be removed efficiently.

## 2. Experimental section

### 2.1. Materials

The chemicals used in this study included *n*-hexane, *n*-nonane, cyclohexane, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, phenol, ChCl, TMAC, and TEAC. Their specifications are indicated in Table 1. All reagents were of analytical reagent grade and used without further purification. In addition, real coal tar, 453–503 K distillate fraction of coal liquefaction, with a content of phenolic compounds of 33.52 wt%, was supplied by Huanghua Coal Chemical Industry Co., Ltd., Hebei, China.

### 2.2. Preparation of model DESs

One example was shown to indicate how model DESs were prepared. An electrical balance with an accuracy of 0.1 mg (ME204E, Mettler Toledo) was used to weight samples. ChCl of 13.96 g, toluene of 6.27 g, and phenol of 18.82 g were added to a 200 cm<sup>3</sup> beaker equipped with a magnetic stirrer (524G, Shanghai Meiyongpu Instrument and Meter Manufacturing Co., Ltd., Shanghai, China). The mixture in the beaker was magnetically stirred for at least 30 min at room temperature until there was a distinctively clear solution formed, which

was called DES (the mole ratio of phenol to ChCl is 2.00, the mass ratio of phenol to toluene was 3.00). Similar procedure was adopted for the preparation of model DESs formed by TMAC or TEAC and phenol.

### 2.3. Experimental procedure

Model DESs and real DESs from coal tar were used in order to explain the removal process clearly. Both model DESs and DESs from coal tar contained neutral oils.

#### 2.3.1. Removal of neutral oil from model DESs

One example was shown how to remove the neutral oil from model DESs. A model DES of 10 cm<sup>3</sup> with a phenol:ChCl mole ratio of 2.00 was added to a graduated test tube. Then *n*-hexane of a volume 6.00 times to DES was charged into the graduated test tube by a liquid transfer tube. The system was placed in a constant temperature water bath with a magnetic stirrer that was equipped with a temperature controller, and was magnetically stirred for about 30 min. After the magnetic stirrer was turned off, in the test tube, two layers appeared clearly, of which the upper phase mainly consisted of *n*-hexane and neutral oil. The volumes of the upper phase and the lower phase were recorded as  $V_U$  and  $V_D$ , respectively. A sample of the upper phase was taken out and the concentration of neutral oil sample was analyzed using a gas chromatography (GC) (Meteorological chromatographic conditions: SHIMADZU GC-2014 gas chromatograph with chromatographic column of RTX-5 capillary column). Dichloromethane and 2-nitrotoluene were chosen as a solvent and an internal standard, respectively. The concentrations of neutral oil and phenol in the upper phase detected by GC were recorded as  $C_N$  and  $C_P$ , respectively. The lower phase was separated from the upper phase by a liquid separatory funnel. Removal efficiency, distribution coefficient, and selectivity of neutral oil were calculated through the following formulae.

$$RE = C_N \cdot V_U / m_N \cdot 100\% \quad (1)$$

$$EP = C_P \cdot V_U / m_P \cdot 100\% \quad (2)$$

$$D_N = C_N / [(m_N - C_N \cdot V_U) / V_D] \quad (3)$$

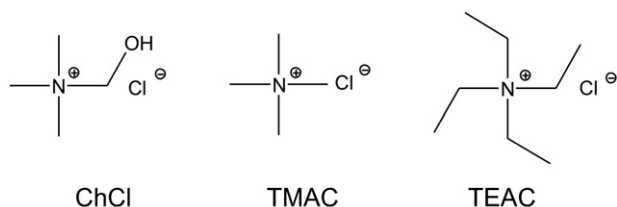
$$D_P = C_P / [(m_P - C_P \cdot V_U) / V_D] \quad (4)$$

$$S = D_N / D_P \quad (5)$$

where  $RE$  and  $EP$  represent the removal efficiency of neutral oil and entrained rate of phenol, respectively.  $D_N$  and  $D_P$  represent the distribution coefficients of neutral oil and phenol, in the upper phase and lower phase, respectively.  $m_N$  and  $m_P$  are the initial mass of neutral oil and phenol in the studied samples, respectively, g.  $S$  is selectivity of neutral oil against phenol.  $C_N$  and  $C_P$  are the equilibrium concentrations of neutral oil and entrained phenol, respectively, in the upper phase, g/dm<sup>3</sup>.

#### 2.3.2. Removal of neutral oil from real DESs

A certain amount of real coal tar was added to a 1000 cm<sup>3</sup> beaker. Then ChCl with a 0.6 time mole amount of phenols was added to the same beaker. The system was placed in a constant temperature water bath that was equipped with a magnetic stirrer and a temperature controller within  $\pm 0.1$  K and was magnetically stirred for about 30 min at 298.15 K. Then the magnetic stirrer was turned off and two layers, which lower phase was called real DES, appeared clearly. The real DES phase was separated from the upper phase by a liquid separatory funnel. The real DES was divided into two parts. One part of the real DES was extracted directly by ethyl acetate as an anti-solvent for comparison. The neutral oil fraction in product phenol was determined by China national standard method (GB/T 24200–2009, China) after rotary distillation. The other part of the real DES was firstly washed by an amount of *n*-hexane, and then the washed real DES was extracted by ethyl acetate as an anti-



Scheme 1. The structural schemes of ChCl, TMAC and TEAC.

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