



Research article

Highly efficient extraction of phenolic compounds from oil mixtures by trimethylamine-based dicationic ionic liquids via forming deep eutectic solvents

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ABSTRACT

In this article, dicationic ionic liquids (DILs), including *N,N,N,N',N',N'*-hexaethyl-ethane-1,2-diammonium dibromide (HEDBr), *N,N,N,N',N',N'*-hexaethyl-propane-1,3-diammonium dibromide (HPDBr) and *N,N,N,N',N',N'*-hexaethyl-butane-1,4-diammonium dibromide (HBDBr), were designed and used to extract phenolic compounds from model oil and coal tar oil. The effects of stirring time, temperature, DIL:phenol mole ratio, and initial phenol concentration on the extraction of phenol were studied. It is found that the DIL:phenol mole ratio is only around 0.3 when the highest extraction efficiency of phenol is obtained. The extraction process completes within 5 min at room temperature, and the extraction efficiency is not dependent on temperature. Also, the ultimate phenol concentration remains constant despite the difference in initial phenol concentrations. Of these DILs, HPDBr shows the lowest ultimate phenol concentration of 3.9 g/dm³, and the extraction efficiency of phenol can reach as high as 97.0%. These DILs can be regenerated by anti-solvent method and reused several times without significant reduction in extraction efficiency. In addition, HPDBr was demonstrated to extract phenolic compounds from real coal tar oil, and its extraction efficiency of phenolic compounds is 92.7%. The mechanism, analyzed by FT-IR, shows that there is a hydrogen bond between phenol and DIL.

1. Introduction

Phenolic compounds are those that one or more hydrogen atoms on the benzene ring of aromatic hydrocarbons are replaced by hydroxyl. Typical phenolic compounds are phenol, cresol, and xylenol. They are widely applied in producing synthetic fibers, engineering plastics, pesticides, medicines, explosives, and so on [1–3]. Phenolic compounds are mainly derived from the oil mixtures of coal liquefaction, coal pyrolysis, and biomass pyrolysis as reported in the literatures [4,5]. The extraction of phenolic compounds from these oil mixtures has been considered as an important step for further refining or applications. The widely used method in industry to separate phenolic compounds from oil mixtures is chemical extraction [6–8], which requires a large amount of sodium hydroxide solution to form sodium phenolate solution with phenolic compounds. Then, inorganic acids are used to react with the sodium phenolate solution to recover phenolic compounds. There are many disadvantages to this process. First, the use of large amounts of both strong alkalis and acids increases the cost of the extraction, and leads to the corrosion of devices. Second, phenolic compounds dissolve in water, creating large amounts of wastewater.

Therefore, we seek to develop a new type of extraction method not using aqueous phase, and alkalis or acids.

Much research has been done to try to solve the problems mentioned above. The first approach uses ionic liquids (ILs) to extract phenolic compounds from oil mixtures. ILs have been paid much attention in the applications of synthesis [9,10], catalysis [11,12], electrochemistry [13], and extraction [14] in the past few years due to their unique properties, such as wide liquid range, excellent solvent power, and low vapor pressure. Also, some work has been done in the field of phenolic compounds extraction. Meng et al. [15] developed six protonated ILs to extract phenolic compounds from oil mixtures. These ILs showed excellent extraction performance. Xiong et al. [16] synthesized poly ILs to adsorb phenol from coal tar oil. The poly ILs showed good thermal stability, but the mass transfer for phenol was poor. Meanwhile, Hou et al. [17] synthesized several imidazolium-based ILs, and found that their extraction performance of phenol was excellent. Of the synthesized ILs, 1-butyl-3-methyl-imidazolium chloride ([Bmim]Cl) showed the highest extraction efficiency.

The second approach uses deep eutectic solvents (DES) to extract phenolic compounds from oil mixtures. In 2003, Abbott et al. [18] first

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reported that urea could form DESs with quaternary ammonium salts (QASs). Since then, much research has been done on DESs [19–22]. In recent years, the extraction of phenolic compounds via forming DESs has also attracted much attention. Jiao et al. designed imidazole homolog compounds that form deep eutectic solvents with phenolic compounds to extract phenolic compounds from coal tar oil [23]. The extraction efficiencies could reach more than 90%. Jiao et al. also used amide compounds to extract phenolic compounds [24]. Moreover, our group extracted phenolic compounds from model oils with QASs via forming DESs [25,26]. In addition, there are some other papers focused on phenolic compounds extraction [27–30]. These new discoveries proved to separate phenolic compounds effectively with high removal efficiencies.

However, some extractants are poor in thermal stability, and, most importantly, extractants are highly soluble in oil mixtures. Gao et al. [31] found that imidazole homolog compounds were partially oil-soluble, and thus contaminated the oil phase. Meng et al. [15] revealed that some IL extractants could dissolve in oil and anti-solvents up to 1000 ppm, which may complicate the extraction process. [Bmim]Cl, which was considered as one of the best extractants, with a maximum extraction efficiency of 99.9% for phenol [17], was found to be unstable at 150 °C [32]. In addition, Meng et al. [15] reported that the decomposition temperatures of the ILs used in the experiment mostly ranged from 140 to 180 °C. The high solubility of extractants in oil mixtures and anti-solvents may pollute the oil mixtures, consume extractants, and make the extraction process complicated. The low thermal stability of extractants may also limit their applications.

Our work therefore seeks to design extractants with high thermal stability and low concentrations in oil mixtures. It is reported that dicationic ionic liquids (DILs), which consist of one dicationic and two mono anions, usually have higher thermal stability (thermal decomposition temperature ranges from 330 °C to 400 °C) than mono-cationic ILs (thermal decomposition temperature ranges from 145 °C to 185 °C) [33–35]. Due to the excellent extraction performance of tetraethylammonium chloride (TEAC) for phenol [26], DILs that have the similar structure to TEAC may both have high thermal stability and high extraction efficiency like TEAC. In addition, since DILs contain hydrophilic Br[−] and symmetrically doubly charged structure [34,36], they may have low solubility in oil mixtures and anti-solvents used in regeneration process of extractants, which can decrease the loss of extractants and protect oil mixtures from being polluted. Considering the above information, trimethylamine-based DILs were designed and studied to extract phenolic compounds from oil mixtures. In this work, three DILs, including *N,N,N,N',N',N'*-hexaethyl-ethane-1,2-diammonium dibromide (HEDBr), *N,N,N,N',N',N'*-hexaethyl-propane-1,3-diammonium dibromide (HPDBr), *N,N,N,N',N',N'*-hexaethyl-butane-1,4-diammonium dibromide (HBDBr), were synthesized, and the structural schemes of the three DILs are shown in Scheme 1. Although all these DILs are solid at room temperature, interestingly, all the DILs can form DESs with phenol during extraction. The three DILs were used to extract phenolic compounds from model oils and real coal tar oil via forming DES. The effects of temperature, stirring time, and DIL:phenol mole ratio on extraction efficiency were investigated. These DILs could be reused without significant change in extraction efficiency. In addition, the extraction of phenolic compounds from real coal tar oil was also demonstrated. Lastly, the extraction mechanism was studied by FT-IR, and a comparison was made against other methods.

2. Experimental

2.1. Materials

The chemicals used in this work include 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane, triethylamine, *n*-hexane, acetonitrile, phenol and toluene, and their specifications are listed in Table 1. All reagents were of analytical reagent grade and used without further purification. In addition, real coal tar oil, 180–230 °C distillate fraction of coal liquefaction, was supplied by Huanghua Coal Chemical Industry Co., Ltd., Hebei, China.

2.2. Preparations of DILs

The three DILs were synthesized through quaternization reaction and characterized following the previous report [34]. In a typical experiment, a mixture of dibromo alkane (0.100 mol) and trimethylamine (0.240 mol) was introduced to a 250.0 cm³ round-bottomed flask. The system was placed in an oil bath (DF-101S, Zhengzhou Great Wall Industry and Trade Co., Ltd., China) that was set to a constant temperature of 90.0 °C, and refluxed in acetonitrile solvent for 8 h. Enough diethyl ether was used to remove the unreacted reactants and the solvent. These DILs were dried under a vacuum at 80 °C until weight was constant. Then, these DILs were stored in a desiccator due to their hydrophilic property. The obtained DILs were confirmed by ¹H NMR (Bruker, AVANCE III, Germany, 400 MHz, D₂O).

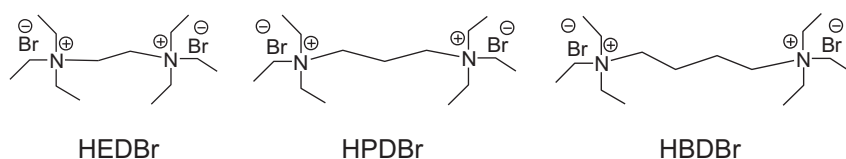
2.3. Preparation of model oils

Because of the complexity of real oil mixtures, phenol was chosen to represent the phenolic compounds, and toluene or *n*-hexane was chosen to represent the oil mixtures. One example was shown how to prepare model oils. Firstly, phenol of 50.0 g was added to a 500.0 cm³ beaker. Then, 300 cm³ of toluene was also added to the beaker. The beaker was magnetically stirred for 15 min until all phenol dissolved in toluene. Then the phenol-toluene solution was transferred to a 500.0 cm³ volumetric flask. Finally, toluene was added to the volumetric flask to the calibration volume scale at room temperature. Similar procedures were adopted for the preparation of other model oils used in this experiment.

2.4. Extraction procedure and analysis method

In a typical experiment, 10 cm³ (*V*₀) of model oil, with an initial phenol concentration of *C*₀ g/dm³, was added to a graduated test tube. A certain amount of DIL was then added to the graduated test tube. The tube was placed in a constant temperature water bath equipped with a magnetic stirrer and a temperature controller within ± 0.1 °C. The mixture in the tube was magnetically stirred for about 30 min. After the mixture was settled down, two phases appeared clearly. The volume of the upper phase (oil phase) and the lower phase (DIL phase) can be recorded as *V*_U and *V*_L, respectively. A certain amount of sample of the upper phase was taken out to analyze its composition.

For the model oil formed by toluene and phenol, the phenol concentration was determined by gas chromatography (GC, Shimadzu GC-2014, Japan). The GC was equipped with RTX-5 capillary column. Dichloromethane and 2-nitrotoluene were chosen as solvent and internal standard, respectively. The conditions are listed as follows: column, RTX-5 capillary column (30 m × 0.25 mm × 0.25 μm);



Scheme 1. The structural schemes of HEDBr, HPDBr, and HBDBr.

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