



Efficient separation of phenolic compounds from model oils by dual-functionalized ionic liquids

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ABSTRACT

Four kinds of dual-functionalized ionic liquids (DFILs, [Et₂NEmim][Cl]₂, [Et₂NEmmor][Cl]₂, [Et₂NEmpyr][Cl]₂ and [Et₂NEmpic][Cl]₂) were synthesized and used to efficiently separate phenolic compounds from model oils. The effects of stirring time, temperature, mole ratio of DFIL to phenol and initial phenol content on the separation were investigated. The results indicate that at a DFIL:phenol mole ratio of 0.3, the content of phenol in the oil phase can reach the minimum value and the extraction efficiency of phenol is more than 96%. The minimum phenol content in the oil phase and the best phenol extraction efficiency were 5.9 g/m³ and 98.5%, respectively, when [Et₂NEmpyr][Cl]₂ was used. Compared with traditional ionic liquids, these DFILs not only reduce the dosage of extraction agents but also greatly decrease the content of Cl⁻ in the oil phase due to the double anion in the DFILs. The DFILs can be reused for 4 cycles without losses in phenol extraction efficiency and masses of the DFILs. The separation mechanism of extraction was studied using FT-IR. The result indicates that the two anions Cl⁻ on DFILs can form a hydrogen bond with phenol.

1. Introduction

Phenolic compounds are important industrial organic chemicals and chemical intermediates, which are used to produce engineering plastics, pharmaceuticals, preservatives and so on. Structural characteristics, special properties and broad application of phenolic compounds provide them with relatively high attention and considerable economic value at present [1,2]. Phenolic compounds mainly exist in coal liquefaction oil, coal-pyrolyzed oil and biomass-pyrolyzed oil [3,4]. For example, low-temperature coal-pyrolyzed oils contain 20–30% of phenolic compounds [5,6]. However, these phenolic compounds in oils are harmful to further refining of the oils. For instance, they can increase the consumption of H₂ during the hydrogen treating process of raw oils for the production of fuel oils [7,8]. As a result, it is of great importance to separate phenolic compounds from oils in advance.

Up to now, an alkali washing method using mineral alkaline and acidic aqueous solutions is the commercial way to separate phenolic compounds from oil mixtures. This traditional method is based on the acid-base neutralization. It not only uses large quantities of mineral alkaline aqueous solutions and mineral acid aqueous solutions to obtain phenolic compounds but also produces a large amount of wastewater containing phenols [2,9,10]. Therefore, this method results in high costs of separation and pollution control. It is necessary to find a new

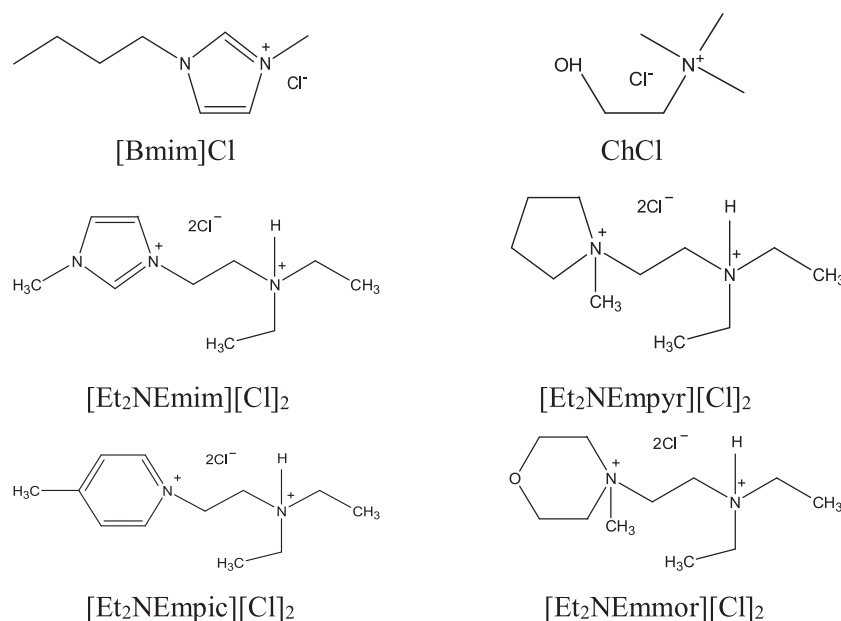
method to efficiently separate phenolic compounds and reduce the environmental pollution and the production cost. Hence, many research groups studied the separation of phenolic compounds from oils, and several methods were reported in the literature. For example, organic solvent extraction was investigated to separate phenolic compounds from oil mixtures [11–13]. However, the organic solvents are relatively volatile and easily issue to the atmosphere causing environmental pollution. Simultaneously, they have high solubility in oil, which can cross-contaminate the oil and complicate the extraction process.

In recent years, ionic liquids (ILs), which are regarded as a kind of green alternative solvents to normal organic solvents, have drawn much attention in various researches. One major property of ILs is structural designability, which makes them various and can satisfy various demands in the application. The other properties [14,15] like low vapor pressure, high chemical stability, non-flammability and high ionic conductivity make them a greener choice for a range of industrial applications, such as separation [16], catalysis [17], organic synthesis [18] and electrochemistry [19].

ILs have already been used in the separation of phenolic compounds from mixtures. Many researches have been carried out to separate phenolic compounds from aqueous solutions or oil mixtures using ILs. Fan et al. [20] used imidazolium-based hydrophobic ILs, 1-methyl-3-alkylimidazolium hexafluorophosphate [C_nmim][PF₆] (n = 4, 6, 8) and

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Scheme 1. Chemical structures of [Bmim]Cl, ChCl, [Et₂NEmim][Cl]₂, [Et₂NEmpr][Cl]₂, [Et₂NEmpic][Cl]₂ and [Et₂NEmmor][Cl]₂.

1-methyl-3-alkylimidazolium tetrafluoroborate [C_nmim][BF₄] (n = 6, 8), to separate phenolic compounds from aqueous solutions. The distribution ratio could reach 37.5 at pH < 7. Kristine et al. [21] studied the separation of phenol from aqueous solutions by 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆]. Li et al. [22] also used ILs 1-methyl-3-alkylimidazolium hexafluorophosphate [C_nmim][PF₆] (n = 4, 10) to separate phenol from aqueous solutions. Meng et al. [23] reported a complex process to extract phenol from model coal tar oil by ethanolanmonium based ILs. However, these ILs showed a relatively low ability to extract phenol, and the maximum extraction efficiency of phenol was about 94%. Moreover, the coexistent of toluene in the model oil had obvious influence on phenol extraction. When toluene content increased, an obvious decrease of phenol efficiency was observed. Our group [24] separated phenols from oils using imidazolium ILs, such as [Bmim]Cl and [Bmim]Br, and the phenol extraction efficiency could reach 99%. The study of the separation mechanism indicated that the formation of hydrogen bonding between –H on phenol and anion of ILs accounted for the separation.

Deep eutectic solvents (DESs) [25], which are proposed in recent years, have been widely used in many fields, such as separation of phenolic compounds from oil mixtures. For example, quaternary ammonium salts (QASs), such as choline chloride (ChCl) and tetraethylammonium chloride (TEAC), had been used to separate phenols from oils with high efficiency by forming DESs [26,27]. Moreover, the separation mechanism was also the formation of hydrogen bonding between –OH on phenols (called hydrogen bond donor, HBD) and Cl[–] of QASs (called hydrogen bond acceptor, HBA). Although these reported ILs and QASs can reach high phenol extraction efficiencies, there are still some disadvantages, such as the high solubility of ILs in oils [23] and large dosages of ILs or QASs consumed (almost equimolar to phenol).

To solve the problems mentioned above, we analyzed the existing extractants (like [Bmim]Cl and TEAC) in the literature. Although [Bmim]Cl has high phenol extraction efficiency, the solubility in the oil phase is high. So, if we modify it by introducing another anion, such as Cl[–] from TEAC structure, the solubility of IL in oils, such as toluene, can be considerably reduced due to the increase of polarity of the IL. Based on the separation mechanism of IL [Bmim]Cl and QAS TEAC, if both anions of the functionalized ILs can form hydrogen bonding with –OH on phenols to separate phenols from oil, the dosage of the ILs used may decrease. By modifying the structure of IL [Bmim]Cl further,

several kinds of dual-functionalized ionic liquids (DFILs) containing double Cl[–] were synthesized. The difference between DFILs and previously used ILs is that DFILs have high melting points than ILs, and they are solid at room temperature, which is similar to QASs. So, we wonder whether they can act as HBAs like QASs to form DES with phenol as HBA.

As we expected, DFILs synthesized in this work could act as HBA to separate phenol from oils via forming DES, and both anions (Cl[–]) could form hydrogen bonding with phenol to form DES. The experiment parameters, such as extraction time, temperature, mole ratio of DFILs:phenol and initial phenol content, were studied. Besides, the mechanism was also explored by using FT-IR to explain the formation of DES. Moreover, the recycle and reuse of DFILs were investigated. The experiment showed that all the DFILs had high extraction efficiencies of phenol from oil. Compared with previous ILs, both the dosage of the DFILs and the solubility of the DFILs in the oil phase were greatly decreased. Also, these DFILs had excellent repeatability and could repeatedly be used for many times.

2. Experimental

2.1. Chemical materials

Phenol (99%), 4-picoline (98%), *o*-nitrotoluene (99%) 4-methylmorpholine (99%), 1-methylpyrrolidine (98%), 1-methylimidazole (99%), 2-chloro-*N,N*-diethylethylamine hydrochloride (99%), ChCl (99%) and [Bmim]Cl (99%) were purchased from Aladdin Reagent, Co., Ltd., Shanghai, China. Toluene (98%) and diethyl ether (98%) were purchased from Beijing Chemicals Works, Beijing, China. Acetonitrile (98%) was purchased from Beijing Tongguang Fine Chemicals Co., Ltd., Beijing, China. All the chemical reagents in the experiments were analytical reagent grade and used without further purification. The water was distilled before used.

2.2. Preparation of DFILs

In this work, four kinds of DFILs, [Et₂NEmim][Cl]₂, [Et₂NEmmor][Cl]₂, [Et₂NEmpr][Cl]₂ and [Et₂NEmpic][Cl]₂, were synthesized and used as extraction agents to separate phenolic compounds from model oils. The structures of the four DFILs are shown in Scheme 1, and those of [Bmim]Cl and ChCl are also shown for comparison. The synthesis

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