



Efficient separation of phenol from model oils using environmentally benign quaternary ammonium-based zwitterions via forming deep eutectic solvents

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HIGHLIGHTS

- Environmentally benign quaternary ammonium-based zwitterions were designed to form DESs.
- Separation of phenol from oils via forming DES can avoid environmental pollution.
- The zwitterions are free from halogen anion, avoiding its corrosion to steel equipment.
- The maximum phenol extraction efficiency is 94.6% by using L-carnitine.
- The zwitterions can be regenerated and reused without losses in extraction efficiency and extractant mass.

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ABSTRACT

The separation of phenolic compounds from oil mixtures is widely used in the chemical industry. In this research, we found that two types of environmentally benign quaternary ammonium-based zwitterions, betaine and L-carnitine, could be used as new extractants for the separation of phenol from model oils by forming deep eutectic solvents (DESs). The effects of extraction time, temperature, mole ratio of zwitterion to phenol and initial phenol content on the efficiency of phenol separation were investigated. The results indicated that betaine and L-carnitine could form DESs with phenol, and the DESs were insoluble in model oils. Phenol in model oils could be extracted with extraction efficiencies up to 94.6% at an L-carnitine:phenol mole ratio of 0.4 (an L-carnitine:phenol mass ratio of 0.68) and 298.2 K. Phenol in DES could be recovered using an anti-solvent, and betaine and L-carnitine could be regenerated and reused for 4 cycles without obvious decreases in extraction efficiency and extractant mass, and they were not changed in their structures after reuse. The separation mechanism was investigated using FT-IR, which showed that betaine and L-carnitine formed DESs with phenol through hydrogen bonding.

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1. Introduction

Phenolic compounds, also called hydroxyl benzenes, are a group of aromatic organic compounds bonded directly with a hydroxyl group or more. The unique structural characteristics of phenolic compounds provide them with special properties, hence they are one of the major industrial organic chemicals and chemical intermediates, which are currently used in processes to produce synthetic fibers, engineering plastics, phenolic resins, alkylphenols, pesticides, pharmaceuticals, explosives, plasticizer, preservatives, spices, dye intermediates, and so on [1]. The major sources of

phenolic compounds include coal liquefaction oil, coal tar, petroleum and biomass pyrolysis oil [2,3]. For instance, low-temperature pyrolyzed coal tar oil typically consists of 20–30% of phenolic compounds. The existence of phenolic compounds affects the storage stability of the oil and increases hydrogen consumption in the following oil refining process. Therefore, the separation of phenolic compounds becomes increasingly important for the deep processing of oil mixtures [4–8].

The traditional method for separating phenolic compounds from coal tar oils or other oil mixtures containing phenolic compounds uses the principle of acid-base neutralization. In the method, strong alkaline aqueous solutions (such as NaOH) react with phenols to form phenolates that are dissolved in aqueous solution and separated from oil mixtures, then mineral acid (such

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as H_2SO_4 or H_2CO_3) is used to acidify the phenolates to recover the phenols [1,9,10]. The disadvantages of this method include (1) uses of large amounts of alkalis and acids, (2) the production of a large quantity of wastewater containing phenols, (3) serious equipment corrosion from strong alkaline and acidic aqueous solutions, increasing the costs of the separation process and environmental pollution.

In recent years, ionic liquids (ILs) have been successfully applied in a large diversity of separation processes. For instance, Hou et al. [11] separated phenols from model oils with high phenol extraction efficiency by using imidazolium-based ILs. However, there are disadvantages of using ILs to separate phenolic compounds from oil mixtures, such as high costs of ILs and difficulty to deal with the used or wasted ILs. At the same time, a new type of green solvents called deep eutectic solvents (DESs), which have similar properties to ILs and are also called ionic liquid analogues, has emerged and attracted more and more attention of researchers [12,13]. DESs are easily formed by simply mixing two compounds, hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA). In general, DESs are used in a liquid form. The advantages of DESs include low price, easy synthesis, no toxicity, chemical stability to water and biological degradation. DESs have recently been found to be efficient separation media cheaper than ILs [14–16]. Pang et al. [17] found that choline chloride reacted with phenols to form DESs that did not dissolve in the oil phase, making it an efficient method to separate phenols. Guo et al. [18] studied the phenol extraction efficiency of the homologous compounds of quaternary ammonium salts and explored the effects of different anions and cations on the extraction efficiency of phenol. The formation of these DESs results from the hydrogen bonding between $-\text{OH}$ and Cl^- . Although the phenol extraction efficiency is high, all these salts contain aqueous Cl^- . The aqueous Cl^- shows strong pitting corrosion to steel equipment and increases the costs of production and equipment in the industry [19,20]. Other researchers [21–23] found that the extractants, such as imidazole and nicotinamide, could separate phenol from model oils by forming DESs. However, these extractants have the disadvantage of large amounts of loss in reuse. For example, the recovery rate of imidazole is only 76%. Gao et al. used hexamethylenetetramine (HMT) and AlCl_3 to separate phenols from oils by acid–base adsorption. It not only needs a long extraction time (>1.5 h) but also operates at a very low phenol concentration (such as 1% phenol concentration in mass fraction), which leads to the limitation of its application [24]. Therefore, it is desired to find some alternative extraction agents with no Cl^- , no corrosion to the equipment, high phenol extraction efficiency, and high recovery rate.

The above research shows that quaternary ammonium-based halogen salts and imidazolium-based halogen salts (their typical molecular structures shown in Scheme 1) can effectively separate

phenolic compounds from oil mixtures. The reasons are that the hydrogen bond occurs between $-\text{OH}$ of phenolic compounds and halogen anion, and ionic compounds are immiscible with oil, resulting in phase separation. As we all know, quaternary ammonium-based zwitterion is also an ionic compound, such as betaine and L-carnitine (their molecular structures also shown in Scheme 1 for comparison), and the two zwitterions both contain quaternary ammonium group and carboxylic acid group. As can be seen, the oxygen on the carboxylic acid group also has the function of halogen anion, so they can react with $-\text{OH}$ on phenolic compounds to form hydrogen bonding. Since the quaternary ammonium-based zwitterions, betaine and L-carnitine, have the characteristics of quaternary ammonium halogen salts, the question is whether they can be used to separate phenolic compounds from oil. If it is feasible, the corrosion of halogen ions to the steel equipment can be avoided. Moreover, betaine and L-carnitine, which are nontoxic, environmentally benign, stable and biodegradable, can be obtained from plants and animals, and have wide applications in daily life, such as skin care products and medicines. Our study has found that betaine, L-carnitine and phenol can form DESs, which are insoluble with oil mixtures. Hence, it provides a new kind of extractants to separate phenolic compounds.

In this work, we used the two quaternary ammonium-based zwitterions as new extractants to separate phenol from model oils. The effect of the structure of the two extractants on phenols extraction efficiency was investigated. Additionally, the influence of experimental conditions, such as mole ratio of extractant to phenol, separation temperature, mixing time and the recycle of extractant, was studied. Finally, Fourier transform infrared (FT-IR) was used to study the mechanism of the separation. This work may provide important information to find new extraction reagents.

2. Experimental section

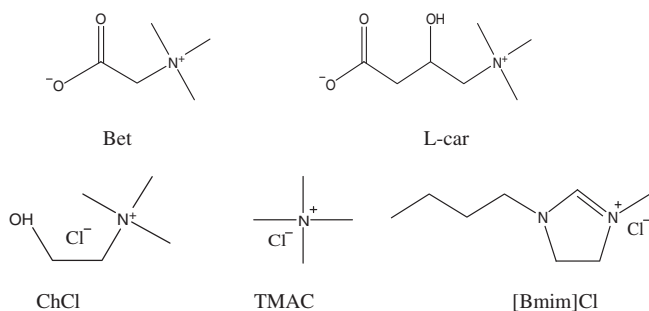
2.1. Chemical materials

Phenol with a purity of $>99\%$ was purchased from Aladdin Reagent, Co., Ltd., Shanghai, China. Toluene ($>99.5\%$) and diethyl ether ($>99\%$) were supplied from Beijing Chemical Factory, Beijing, China. Betaine ($>99\%$) and L-carnitine ($>98\%$) were made by Shanghai Yuanye Biological Technology Co., Ltd., China. All the chemicals in the experiments were used without further purification.

2.2. Separation procedures

In this experiment, the mixtures of phenol and toluene were used as model oils. The separation experiments were performed as follows. A certain amount of model oil and extractant with a specific mole ratio were charged in a graduated test tube. A magnetic stirrer was put into the tube. Then the tube was capped and partly immersed into a water bath, whose temperature was controlled by a controller within ± 0.1 K and the mixture in the tube was stirred for a desired time. After that, the tube was allowed to settle down until two phases were formed clearly. The lower phase was DES phase. The two phases were separated by a separating funnel, and the volume of the upper phase was carefully measured. A small amount of sample from the upper oil phase was taken and analyzed by GC to determine its composition.

To recycle the extractants, it is necessary to regenerate them from the eutectic mixture and recover phenol. In this work, we used diethyl ether as an anti-solvent to regenerate extractants and recover phenol from eutectic mixtures [21–23]. A certain amount of diethyl ether was added in the lower DES phase, and a white solid was re-crystallized quickly and precipitated at the bottom of the graduated test tube. The solid was washed with an



Scheme 1. Chemical structures of betaine (Bet), L-carnitine (L-car), choline chloride (ChCl), tetramethylammonium chloride (TMAC), and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl).

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