



Efficient separation of phenolic compounds from model oil by the formation of choline derivative-based deep eutectic solvents



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ARTICLE INFO

Article history:

Received 9 November 2015
Received in revised form 7 March 2016
Accepted 7 March 2016
Available online 9 March 2016

Keywords:

Deep eutectic solvents
Phenolic compounds
Separation
Hydrogen bond
Far infrared spectroscopy

ABSTRACT

Phenolic compounds are an important class of compounds for organic chemical industry. In their traditional production processes, strong acid and base have to be used for the separation of phenolic compounds from oils, which often causes serious environmental problems. In this work, choline derivative salts $[N_{1,1,n}C_2OH]Cl$ ($n = 1, 4, 6, 8$) have been used as new extractants for the separation of 26 kinds of phenolic compounds from model oil (toluene) by forming deep eutectic solvents (DESs). It is found that only 16 kinds of phenolic compounds can be removed from toluene with single-step removal efficiency from 28.1% to 94.7%, strongly depending on the chemical structure of phenolic compounds. The nature, position and number of substituent groups in the phenolic compounds have a great effect on their removal efficiency. Far infrared spectroscopy and density functional theory calculations indicate that hydrogen bonds formed between $-OH$ of the phenolic compounds and anion of the choline derivative salts is the main driving force for such DES-based separation. The correlation observed experimentally between structure of phenolic compounds and their removal efficiencies has been discussed from hydrogen bonding in DESs, electrostatic interaction of cation and anion of the choline salts, and solvation of the phenolic compounds and choline salts in the oil.

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1. Introduction

Phenolic compounds are key precursors for building polycarbonates, epoxies, bakelite, nylon, detergents and numerous pharmaceutical drugs [1]. They are mainly obtained from coal liquefaction, coal tar, petroleum and hydrolysis of biomass resources [2] in the form of mixtures containing phenolic compounds and oils. Therefore, it is necessary to separate phenolic compounds from oils. The traditional method used for such a separation is using aqueous alkaline and H_2SO_4 solutions to extract phenolic compounds from oil [3,4]. This technology has disadvantages such as the use of large amounts of strong base and strong acids, and the production of high content of phenolic compounds waste water as well. An alternative approach for overcoming these drawbacks is the development of a non-aqueous technique to separate phenolic compounds from their oil mixtures.

Deep eutectic solvents (DESs) are composed of two or more compounds which can form a deep eutectic mixture with a melting point much lower than either of the individual components [5,6]. They share many characteristics and properties with ionic liquids (ILs) [7], and even have some advantages over ILs such as structural diversity, cheap and easily obtained raw materials, and green and simple synthetic procedures without using any organic solvents [7–11]. Thus, DESs have been widely acknowledged as greener replacements [11–14] for traditional volatile organic solvents in a variety of fields including chemical synthesis [15,16], catalytic chemistry [17,18], materials preparation [19–22], substance dissolution [23,24] and CO_2/SO_2 absorption [25–28].

In recent years, DESs have attracted great attention in the separation of azeotropic mixture [29,30], natural products [31–35], protein [36], isomers of benzene poly(carboxylic acid)s [37], glycerol from biodiesel [38,39], benzothiophene [40–42] and phenols from oils [43–46]. As far as separation of phenols from oil is concerned, the following excellent work has been reported. In the first work on the separation of phenol by DESs, Wu and co-workers [45,46] found that phenol could be separated by quaternary ammonium salts from model oil via formation of DESs, and the effect of structure of quaternary ammonium salts on the removal

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efficiencies of phenol was investigated in some details. They also used Fourier transform infrared spectroscopy (FT-IR) to investigate the interactions in the formation of DESs, and suggested that the formation of hydrogen bond between quaternary ammonium salt and phenol was the main driving force for the separation of phenol from oil. This method is simple, effective and practical, and provides a new technology for the separation of phenol from oils. Then, Qiu and co-workers [44] used choline-based DES as a new kind of green solvent for the efficient extraction of phenolic compounds from model oil. Zhang and co-workers [43] reported another example for the separation of phenols from model oil by the formation of DESs. To this end, imidazole and its homolog compounds were used to extract phenol, o-cresol, p-cresol and m-cresol, respectively, and the maximum removal efficiency could reach to 95%. However, it is noted that in the real mixtures containing phenolic compounds and oils, there are not only phenol but also many other different phenolic compounds. Thus, understanding the relationship between structure of phenolic compounds and their removal efficiencies is very important for the separation of phenolic compounds by DESs. In addition, although the formation of hydrogen bonds in DESs has been reported, direct evidence should be provided to support this point of view.

It is known that choline chloride is cheap, non-toxic, biodegradable and is always used as an essential nutrient in feed [47]. Also, choline chloride and phenolic compounds have been reported to form DESs that are immiscible with oil [47]. Therefore, in this work, choline chloride $[N_{1,1,1}C_2OH]Cl$ and choline derivative chlorides $[N_{1,1,n}C_2OH]Cl$ ($n = 4, 6, 8$) (see their structure in Fig. 1) have been used to separate phenolic compounds from model oil, toluene. In order to understand the relationship between chemical structure of the phenolic compounds and their separation efficiency, 26 kinds of phenolic compounds with different substituent groups are chosen for the DES-based separation investigations. Furthermore, Far infrared spectroscopy and density functional theory (DFT) calculation are used to characterize the hydrogen bonds present in some selected DESs formed by choline derivative chlorides and phenolic compounds. It is shown that the nature, position and number of substituent groups in the phenolic

compounds, alkyl chain length of choline derivative chlorides and solvation of phenolic compounds in oil have a great effect on the removal efficiency of the phenolic compounds. The formation of hydrogen bond between Cl^- anion of choline salts and H atom of $-OH$ group of the phenolic compounds is the main driving force for the separation of phenols from oil. Finally, the regeneration and reuse of the choline derivative salts have been examined in some details.

2. Materials and methods

2.1. Chemicals

2-Chlorophenol (99%), 3-chlorophenol (98%), 4-chlorophenol (99%), 2-bromophenol (99%), 3-bromophenol (98%), 4-bromophenol (98%), 2-methoxyphenol (99%), 3-methoxyphenol (97%), 4-methoxyphenol (99%), 4-methylphenol (99%), 4-ethylphenol (97%), 4-isopropylphenol (98%), 4-phenoxyphenol (98%), 4-iodophenol (98%), 4-fluorophenol (99%), 2-phenylphenol (98%), 2-tert-butylphenol (99%), 2-nitrophenol (98%), 2,4-dichlorophenol (99%), 2,5-dichlorophenol (98%), 3,5-dichlorophenol (98%), 2,6-dichlorophenol (99%), 4-chloro-3-methylphenol (99%), 4-methyl-2-nitrophenol (98%), pentachlorophenol (99%), 2,6-di-tert-butyl-4-methylphenol (99%), choline chloride (98%), N,N-dimethylethanolamine (98%), 1-chlorobutane (98%), 1-chlorohexane (98%) and 1-chlorooctane (99%) were purchased from Shanghai Aladdin Chem. Co., Ltd. Toluene (99.5%) and diethyl ether (99.7%) were obtained from Sinopharm Chem. Reagent Co., Ltd. These chemicals were used as received unless otherwise stated.

Choline derivative salts used in this work, $[N_{1,1,n}C_2OH]Cl$ ($n = 4, 6, 8$) were synthesized according to the procedures described in the literature [48]. These salts were analyzed by 1H NMR (Bruker, AV-400) to confirm the absence of any major impurities, and the purity of them is found to be greater than 99% in mass fraction. All of these salts were solid at the room temperature. Their 1H NMR spectra (Fig. S1–S3) and chemical shifts were given in Supporting Information, together with the elemental analysis results.

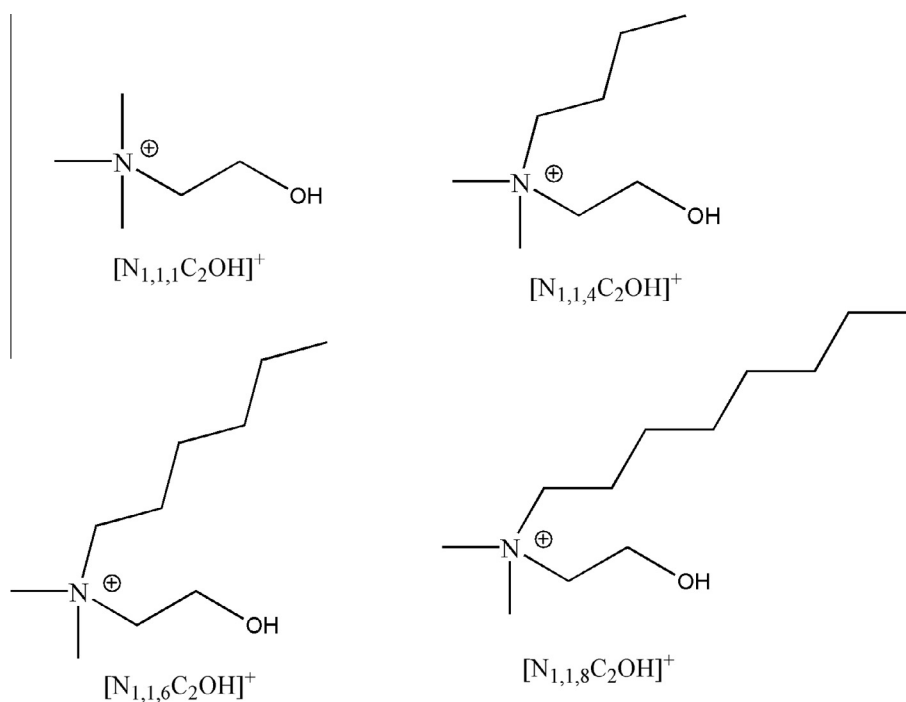


Fig. 1. Chemical structure of cation of choline derivative chlorides.

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