Fuel 215 (2018) 330–338

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Efficient extraction of indole from wash oil by quaternary ammonium salts *via* forming deep eutectic solvents

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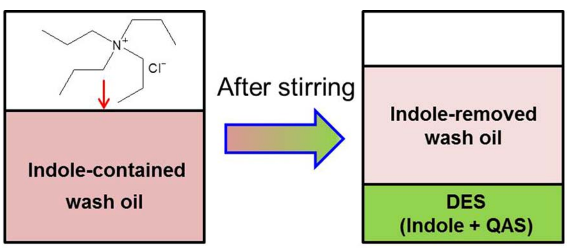
GRAPHICAL ABSTRACT



Quaternary ammonium salt (QAS) was used to extract indole from wash oil *via* forming deep eutectic solvent(DES) with high distribution coefficients, high extraction rates and no use of acid and alkali.

ARTICLE INFO

Keywords:
Indole
Wash oil
Deep eutectic solvent
Quaternary ammonium salt
Extraction

ABSTRACT

Indole plays a significant role in the production of products such as spices, medicines, and exogenous auxins. Deep eutectic solvents (DESs) formed by indole and quaternary ammonium salts (QASs, including tetraethylammonium chloride-TEAC, tetrapropylammonium chloride-TPAC, triethylmethyl-ammonium chloride-TEMAC) were found and proposed to efficiently extract indole from model wash oil. The effects of time, temperature, mole ratio of QAS to indole and initial indole concentration on the extraction of indole were studied. The results indicate that these QASs can extract indole from wash oil with efficiencies up to 96.7% (TPAC). The extraction process can be finished within 5 min. It is also found that the ultimate concentrations are almost identical for one kind of QAS although their initial concentrations are different, and the indole concentration in model wash oil can be reduced to a very low level of 1.3 g/dm^3 (TPAC). The maximum distribution coefficients of indole are 40.8 for TEAC, 91.9 for TPAC, and 29.5 for TEMAC at the studied conditions, and the extraction ability follows the order of TPAC > TEAC > TEMAC. Moreover, QASs in DESs can be reused without obvious reduction in extraction efficiency. The extraction mechanism was studied by FT-IR, and the results indicate that there is a hydrogen bond between QAS and indole. Finally, a comparison was made between this method and other methods to verify and demonstrate its desirable properties of efficiency and environmentally friendliness.

1. Introduction

To obtain indole, an important industrial chemical, two methods could be used: the first is extraction from wash oil, and second chemical synthesis [1,2]. For the first method, wash oil can be distilled from coal tar oil and contains more than 1% of indole [3]. Due to high contents of

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https://doi.org/10.1016/j.fuel.2017.10.057
Received 15 June 2017; Received in revised form 29 August 2017; Accepted 11 October 2017
0016-2361/

Nomenclature

DES	deep eutectic solvent
QAS	quaternary ammonium salt
TEAC	tetraethylammonium chloride
TPAC	tetrapropylammonium chloride
TEMAC	triethylmethyl-ammonium chloride
D	distribution coefficient
EE	extraction efficiency of indole
V_0	volume of initial model oil
C_0	initial concentration of indole
V_U	volume of the upper oil phase
V_L	volume of the lower DES phase
C_{In}	equilibrium concentration of indole
C_U	equilibrium concentrations of the components in the upper phase
C_L	equilibrium concentrations of the components in the lower phase
$C_{Initial}$	initial concentrations of the components of wash oil
RR	regeneration rate of QAS after each reuse step
m_{QAS}	mass of the regenerated QAS after each reuse step
m_0	initial mass of the QAS
K_C	equilibrium constant of Eq. (4), $K_C = C_{DES}/C_{In}$
C_{DES}	indole concentration in the DES phase

indole in wash oil and a large amount of wash oil produced, the extraction of indole from wash oil is potentially more economical than chemical synthesis. Additionally, a by-product of the extraction process is that the wash oil's washing ability increases.

Traditional methods to extract indole are alkali fusion and acid polymerization [1,4,5]. However, these methods use large amounts of aqueous alkaline solutions (such as aqueous NaOH) and mineral acids (such as aqueous H_2SO_4), and produce large quantity of wastewater. This complicates the process and reduces the extraction efficiency (less than 80%). Considering these disadvantages, methods such as supercritical fluid extraction [4,6] and inclusion with cyclodextrin [7], have been proposed. However, these extraction efficiencies are low with complex operations and harsh conditions. Therefore, alternative methods to extract indole from wash oil using a non-aqueous method are needed. Recently, Jiao et al. [3] achieved a relatively high extraction efficiency of indole using a series of ionic liquids (ILs) to extract indole from wash oil. They studied the influence of different experimental conditions, such as initial indole concentration, stirring time, extraction temperature, and volume ratio, on indole extraction. The effect of IL anion types was also studied. It was found that a long time and a large amount of IL were needed to extract indole, and that the distribution coefficient (D) of indole was low. In this work, we try to develop a more efficient and environmentally friendly method to extract indole from wash oil.

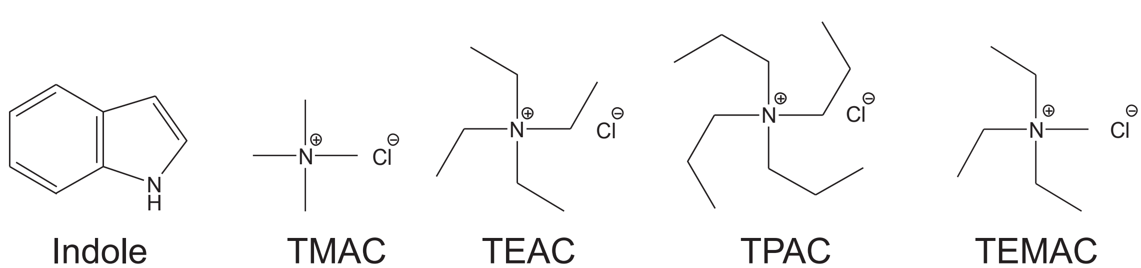
In 2003, Abbott et al. [8] reported that urea could form deep eutectic solvents (DESs) with quaternary ammonium salts (QASs). DES is composed of hydrogen bond acceptor and hydrogen bond donor, and the formed DES has a melting point much lower than either of the individual components [8,9]. Abbott et al. also found that DESs, which are usually formed from strong hydrogen bond interactions, could be formed between a series of carboxylic acids, including aromatic carboxylic acid, and QASs [10,11]. Afterwards, DESs were widely used in the preparation of metals, such as Ag, Cu, Cr, Sn and Zn, because of their good solubility [12,13]. In recent years, due to a series of advantages, such as non-toxicity, wide liquid range and biodegradation, DESs have been applied to the field of extraction. Shahbaz et al. synthesized three DESs using methyl triphenyl phosphunium bromide as salt and three different hydrogen-bond donors to remove all free glycerol from the palm-oil-based biodiesel [14]. Xu et al. synthesized four kinds of choline chloride (ChCl) based DESs to extract bovine serum albumin, and ChCl-glycerol DES was regarded as the most suitable extraction solvent [15]. Hayyan et al. proposed DESs formed by QASs and glycerol for extracting total glycerol from palm oil based biodiesel, and suggested a continuous extraction process for industrial scale application [16]. Wang et al. selectively extracted toluene from toluene/n-heptane mixtures using a series of DESs [17]. Jiao et al. separated phenolic compounds from coal tar *via* forming DESs by amide compounds [18], imidazole and its homolog compounds [19]. Our group found that QASs could extract phenolic compounds from oil mixtures *via* forming DES with phenolic compounds [20,21]. This DES method was proved to be a highly effective way to separate phenolic compounds with high extraction efficiencies. Due to their advantages of low vapor pressures and environmentally benign property, DESs have attracted widespread attention in separation applications [22–24], and continuous new achievements [25–28].

For indole, as shown in Scheme 1, the nitrogen atom is a strong electronegative atom, and thus the hydrogen in N—H is active. Therefore, QAS (hydrogen bond acceptor) containing ions with saturated electrons may share electrons with the hydrogen atom on indole (hydrogen bond donor) to form DES. In this article, three QASs containing Cl^-, including tetraethylammonium chloride (TEAC), tetrapropylammonium chloride (TPAC) and triethylmethyl-ammonium chloride (TEMAC), whose structural schemes are shown in Scheme 1, were studied and proposed to extract indole from wash oil of coal tar oil. The effects of stirring time, extraction temperature, QAS:indole mole ratio, and initial indole concentration on indole extraction were investigated, and the extraction mechanism was studied by FT-IR. It has been found that indole can be efficiently extracted from wash oil by the QASs with extraction efficiencies up to 96.7%, and there is a hydrogen bond between the QAS and indole. The results indicate that extraction of indole by QASs is an environmentally friendly and highly efficient method.

2. Experimental section

2.1. Chemical materials

The chemical materials used in this study include



Scheme 1. The structural schemes of indole, TMAC, TEAC, TPAC and TEMAC.