



# Mass transfer dynamics in the separation of phenol from model oil with quaternary ammonium salts via forming deep eutectic solvents



Yucui Hou<sup>a,b</sup>, Jie Kong<sup>b</sup>, Yuehong Ren<sup>a</sup>, Shuhang Ren<sup>b</sup>, Weize Wu<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry, Taiyuan Normal University, Taiyuan 030031, China

<sup>b</sup> State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

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## ABSTRACT

The separation of phenols from oil mixtures with quaternary ammonium salts (QASs) via forming deep eutectic solvents (DESs) is efficient, which avoids using alkali and acid and producing phenol-contained wastewater. In order to understand deeply the extraction process, the extraction kinetics of phenol in a model oil/DES system was studied using a constant-interface Lewis cell technique. The mass transfer coefficients and extraction rates of phenol were determined and the effects of stirring rate, temperature, specific area and QASs on the extraction were investigated. The results show that when using choline chloride as extractant, the extraction rate and mass transfer coefficient of phenol increase with increases of stirring rate and temperature. In the extraction process, the apparent active energy is  $8.85 \text{ kJ mol}^{-1}$ . The mass transfer of phenol is controlled by diffusion, and the phenol diffusion in the DES phase is the slow extraction rate-determining step.

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## 1. Introduction

Phenolic compounds are important chemicals in the industry and widely used to produce engineering plastics, pesticides, medicines, synthetic fibers, explosives, preservatives, and so on [1]. They are mainly obtained from coal tar, coal liquefaction, petroleum and biomass-pyrolyzed oil [2]. The separation of phenolic compounds from oil mixtures can avoid the corrosion of phenolic compounds to equipment and decrease the consumption of hydrogen in further hydrogenation processes, and can promote the added value of the oil mixtures. The current method to separate oil mixtures is chemical extraction of phenolic compounds using NaOH aqueous solutions to yield sodium phenolates and then recovery of the phenolic compounds using mineral acids (like  $\text{H}_2\text{SO}_4$ ). The shortcomings of the method are not only consuming inorganic alkalis and acids, but also producing phenols-contained waste water. Therefore, it is necessary to develop an environmentally friendly method to separate the oil mixtures.

Recently, deep eutectic solvents (DESs) are considered as an environmentally friendly solvents and have drawn broad attention all over the world [3–6]. DESs can be formed by hydrogen bond acceptors (HBAs, such as choline chloride) and hydrogen bond donors (HBDs, such as phenol, ethyl glycerol), and the formation

of DESs results from strong hydrogen bond interactions between HBA and HBD [7]. In 2003 and 2004, Abbott et al. [3,8] synthesized a series of DESs using quaternary ammonium salts (QASs) as HBAs, and alcohols, acids and amines as HBDs, and measured the properties of the synthesized DESs. They found that the DESs had unusual solvent properties, which are similar to those of ionic liquids, another environmentally friendly solvents. In 2007, the same group used DESs to separate glycerol from biodiesel based on rapeseed and soybeans [9]. In 2010, Heyyan et al. [10] employed a DES to extract efficiently glycerol from palm-oil-based biodiesel.

In our previous work [11], it was found that choline chloride (ChCl) could interact with phenol in oil mixtures at room temperatures to form DES quickly, which was not miscible with the oil mixture, resulting in separating phenol from oil mixtures and leaving no residues of ChCl in the oil phase. A variety of QASs were investigated to separate phenol from oil mixtures, and the results indicated that QASs could efficiently separate phenolic compounds from oil mixtures. For instance, when tetramethylammonium chloride (TMAC) as HBA was added to toluene model oil with equimolar phenol, the extraction rate of phenol was 96% and TMAC in DES was regenerated completely by butyl ether or diethyl ether as an anti-solvent and phenol was recovered in the anti-solvent solution [12]. Recently, imidazole and its homolog compounds were used as HBAs to extract phenolic compounds from model oil and coal tar via DES formation [13,14]. As indicated above, the advantages of the DES method can avoid the production of wastewater

\* Corresponding author.

E-mail address: [wzwu@mail.buct.edu.cn](mailto:wzwu@mail.buct.edu.cn) (W. Wu).

containing phenolic compounds and the use of inorganic acids and alkalis. Moreover, the physical properties of a variety of DESs formed by ChCl and typical phenolic compounds were studied, and the results indicated that the mole ratio of ChCl to phenolic compounds influenced greatly the physical properties of DES, like melting point, viscosity, conductivity and density [15].

During the separation of phenolic compounds from oil mixtures, phenolic compounds are transferred from the oil mixture phase to the DES phase. As we know, mass transfer dynamics is important for the application of the process in a large scale. However, up to now, there is no report on the mass transfer dynamics in the separation of phenolic compounds from oil mixtures via forming DESs.

Mass transfer dynamics for liquid-liquid extraction were studied broadly with Lewis cell technique after Lewis' report [16]. Lewis cell or modified ones were reported to determine accurately mass transfer coefficients of solutes through the interface between two phases [17–21]. It was demonstrated that the Lewis cell technique has the advantages to study mass transfer dynamics of liquid-liquid extraction, for example, composition uniformity in each phase by sufficiently mixing, well-defined interface area with adjustable area sizes, independently controlled stirring rate in each phase with a stable interface, easily mounted configurations, interface stability, and observability during the operation [17].

In this work, a modified Lewis cell was used to study the mass transfer dynamics in the separation of phenols from model oil via forming deep eutectic solvents. The mass transfer coefficients and extraction rate of phenol were determined and the effects of stirring speed, temperature, specific area and QASs on the extraction were investigated.

## 2. Experimental

### 2.1. Materials

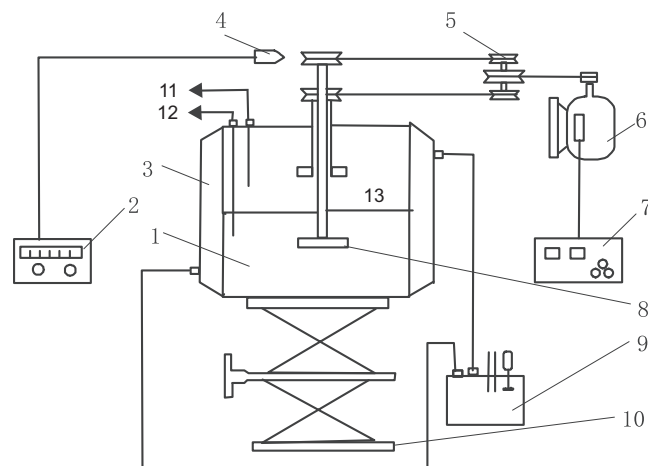
ChCl (>98.0%), TMAC (99%) and phenol (99%) were purchased from Aladdin Chemicals Co., Ltd., Shanghai, China. Toluene ( $\geq 99.5\%$ ), dichloromethane (99%) and petroleum ether (99%, 333–363 K) were supplied from Tongguang Fine Chemicals Co., Ltd., Beijing, China. *n*-Hexane ( $\geq 97.0\%$ ), diethyl ether ( $\geq 99.0\%$ ), and other organic solvents were A.R. grade and produced by Beijing Chemical Reagent Plant, Beijing, China. Pyridine-free Karl Fischer reagent was purchased from Tianjin Concord Technology Co., Ltd., Tianjin, China.

### 2.2. Synthesis of DESs

In this work, DESs were synthesized by mixing phenol and QAS (such as ChCl, TMAC) with a mole ratio of 1.5. The DESs with 1.5 mol ratio of phenol to QAS has the power to extract phenol from oil mixture and exist in a liquid state [12]. Typically, a 500 cm<sup>3</sup> jacketed glass vessel with a mechanical stirrer was used to mix phenol and ChCl with a mole ratio of 1.5 at 40 rpm and 353.2 K until a homogeneous liquid appeared. The water contents of synthesized DESs, detected by a Karl-Fischer titration (ZDJ-400S, Beijing Xianqu Weifeng Technology Development Co., Ltd., China), were less than 0.5% in mass fraction.

### 2.3. Apparatus and procedure

The schematic diagram of the apparatus used in this work is shown in Fig. 1. It consisted of a double-jacket Lewis cell with an interfacial Teflon plate and stirring rakes, a constant temperature water bath, a rotational speed controller, a constant temperature



**Fig. 1.** Schematic diagram of the apparatus of Lewis cell technique used in this work: 1, double jacket Lewis cell; 2, rotational speed controller; 3, constant temperature jacket; 4, rotational speed detector; 5, transmission gear; 6, electric motor; 7, rotational speed controller; 8, stirring rake; 9, constant temperature water bath and temperature controller; 10, lifting platform; 11, sampling for the oil phase; 12, sampling for the DES phase; 13, interfacial Teflon plate.

controller, a lifting platform, and sampling tubes from oil phase and DES phase.

The Lewis cell consisted of a cylindrical double-layered glass vessel, which was mounted with two double-bladed paddles in each phase. Each paddle had 6 blades. Each phase in the Lewis cell could be equally or independently mixed without disturbing the interface. The volumes of the DES phase and oil phase both could be changed up to 400 cm<sup>3</sup>.

The two phases were separated by the interfacial Teflon plate, which had 6 holes with a same diameter, where the interface between the two liquids was located. The diameter and thickness of the interfacial Teflon plate were 100.0 mm and 6.0 mm, respectively. The interfacial area could be changed by changing the diameter size of the 6 holes on the interfacial Teflon plate. The constant-temperature water bath was controlled by a temperature controller (HX101, Beijing Changliu Scientific Instrument Co., Ltd., China) with a temperature accuracy of  $\pm 0.1$  K.

In a typical experiment, 400 cm<sup>3</sup> of DES and 400 cm<sup>3</sup> of model oil were charged into the Lewis cell. Then the two phases were stirred with the double-blade paddle in each phase, and the temperature of Lewis cell was controlled by the water bath. The system could reach equilibrium state for at least 6 h. About 10 g phenol was added into oil phase. There were two Teflon capillary tubes inserted in the oil phase and the DES phases, which were used to take aliquot samples (about 0.5 g) from the oil phase and the DES phase separately at a desired time interval. It should be noted that samples were taken without interrupting the interface between the two phases.

The samples were analyzed with GC (GC-2014, Shimadzu, Japan) for their composition, as reported in our previous work [12]. For GC analysis, the carrier gas was nitrogen and the column was a capillary column (RTX-5, Restek, USA), and a FID (flame ionization detector) was used for the quantification of the components.

## 3. Results and discussion

### 3.1. Calculation of mass transfer rate and mass transfer coefficient

In this work, mass transfer rate and mass transfer coefficient of phenol between the two phases were calculated based on the modified equations for Lewis cell [22]. At a temperature, the mass of

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