Synthesis of a deep eutectic solvent triethylamine/salicylic acid and its use for extractive denitrogenation

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Abstract. In this study, a novel deep eutectic solvent (DES) triethylamine/salicylic acid was synthesized and was used for the extractive denitrogenation of model oil. The structure of the DES was analyzed by Fourier transform infrared spectrometry and the factors that influence nitrogen removal efficiency were investigated. Under the conditions of 20 min time, 30 ℃ temperature, 800 rpm stirring speed, 1:1 mass ratio of DES to oil, nitrogen removal efficiency reached more than 95%. After two extraction stages the nitrogen content of model oil could be reduced to less than 10 ppm. Therefore, the novel DES triethylamine/salicylic acid will became a promising extractant for fuel oil denitrogenation.

1. Introduction
The combustion of nitrogen compounds in fuel oil can emit a lot of nitrogen oxide and result in the air pollution. Furthermore, the nitrogen compound in fuel oil has a significant hindering influence on the hydrodesulfurization process [1, 2]. Therefore, it is of great importance to remove nitrogen compounds from fuel oil. The traditional method for nitrogen removal from fuel oil is hydrodenitrogenation (HDN). However, HDN can’t meet the increasingly stringent requirements of nitrogen content in fuel oil because of its inability in removing some heterocyclic nitrogen compounds. Furthermore, HDN needs severe reaction conditions such as high temperature and high pressure. Thus, some new denitrogenation methods have been developed as an alternative to HDN such as extraction [3, 4], adsorption [5], oxidation [6], and biodenitrogenation [7]. Among them, extractive denitrogenation seems more competitive due to its mild reaction conditions.

Deep eutectic solvent (DES), ionic liquid analogues, has attracted a large amount of attentions as a new type of solvent recently. A DES is generally a eutectic mixture which consists of two or more compounds by hydrogen bond [8, 9]. DESs not only share the properties of ionic liquids such as chemical stability, low vapor pressure and designability, but also enjoy many advantages which the traditional ionic liquids do not have, such as (1) cheap raw materials, (2) easy to store because most of DESs are chemically inert with water, (3) simple synthesis process because DESs can be synthesized through simply mixing two or more compounds without purification and waste disposal encountered with traditional ionic liquids and (4) greenness because DESs are biodegradable, biocompatible and...
non-toxic [10]. Thanks to these advantages, DESs have been widely used instead of traditional ionic liquids in catalysis, synthesis, electrochemistry, extraction, etc.[11,12] However, in comparison with traditional ionic liquids, DESs have been seldom used in the extractive denitrogenation of fuel oil up to now.

In this work, triethylamine (TEA) was chosen as hydrogen bond acceptor (HBA) and salicylic acid (SA) was chosen as hydrogen bond donor (HBD), from which a novel DES was synthesized and was used for the extractive denitrogenation of fuel oil. The structure of the DES was analyzed by fourier transform infrared spectrometry (FTIR) and the factors that influence nitrogen removal efficiency were investigated.

2. Experimental section

2.1. Materials
Model fuel oil with nitrogen contents of 500 ppm was prepared by dissolving quinoline in n-octane. TEA (99%), SA (AR) and n-octane (≥ 98%) were supplied by Shanghai Macklin Biochemical Co. Ltd. Quinoline was supplied by Shanghai Aladdin Reagent Co. Ltd.

2.2. Synthesis of DESs
TEA was chosen as HBA and SA was chosen as HBD. HBA and HBD with a molar ratio of 1:2 were added into a round bottomed flask and was stirred vigorously for an hour at 90 °C. Then, a homogeneous yellow liquid was obtained.

2.3. Extraction experiment
A typical extraction experiment was carried out in a round bottomed flask. Model fuel oil and DESs were added into the reactor and were stirred vigorously under a certain temperature for a while. After the reaction, the reaction mixture was separated into two phases after standing for a minute. The upper oil phase was used for nitrogen content analysis. Nitrogen removal efficiency was calculated by the following formula (1),

\[
\text{Nitrogen removal efficiency (wt%) = } \frac{\text{TN}_1 - \text{TN}_2}{\text{TN}_1} \times 100\%
\]

where TN\textsubscript{1} is the nitrogen content in the original model oil and TN\textsubscript{2} is the nitrogen content in the treated model oil.

2.4. Analytical Methods
The nitrogen content in model fuel oil after denitrogenation was determined by gas chromatography-flame ionization detector (GC-FID, 9790II, Fuli) equipped with a SE-54 capillary column. Analysis conditions were as follows. Both the injector and detector temperature were set at 280 °C, the column temperature program started 80 °C, then increased to 280 °C at 15 °C/min (held for 2 min). The structure of DES was analyzed by FTIR (Nicolet 6700).

3. Results and Discussion

3.1. Characterization of DES
Figure 1 showed the FTIR spectrum of TEA/SA. The absorption peaks at 3017 cm\textsuperscript{-1} and 2978 cm\textsuperscript{-1} should correspond to the stretching vibration of C-H on TEA. 1175 cm\textsuperscript{-1} and 1039 cm\textsuperscript{-1} should correspond to the stretching vibration of C-N on TEA. 767 cm\textsuperscript{-1} should correspond to the deformation vibration of C-H on SA. Therefore, all the absorption peaks confirm the structure of TEA/SA. In addition, the absorption peak of the C=O stretching vibration on SA should be in the range of 1650-1670 cm\textsuperscript{-1}, while that on TEA/SA moved to 1701 cm\textsuperscript{-1}. Namely, a blue shift took place, which indicated that a hydrogen bond formed between TEA and SA. Therefore, hydrogen bond is responsible for synthesizing TEA/SA.
3.2. Effect of reaction conditions on nitrogen removal efficiency

3.2.1 Extraction time. Figure 2(a) showed the effect of extraction time on nitrogen removal efficiency. Nitrogen removal efficiency remained almost constant when extraction time increases from 10 min to 30 min. It means that the extraction equilibrium can be reached in 10 min. In order to ensure complete extraction, 20 min is selected in the following experiments.

3.2.2 Extraction temperature. Figure 2(b) showed the effect of extraction temperature on nitrogen removal efficiency. Nitrogen removal efficiency increased slightly at the initial stage of reaction, and then decreased with the increase of extraction temperature. The reason is possibly that: on one hand, the temperature ($T$) has a significant influence on the viscosity ($\eta$) of DESs. According to the previous report [13], the relationship between the viscosity of DESs and temperature can be expressed by the equation $\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT}$, where $\eta_0$ is a constant and $E_\eta$ is the activation energy of viscous flow. Therefore, the viscosity of DESs decreases with the increasing of temperature. The decrease of viscosity is conducive to the mass transfer in reaction system, accordingly increasing nitrogen removal efficiency. On the other hand, too high temperature is unfavourable to the extraction process because of its exothermic characteristic. The maximum value of nitrogen removal efficiency of 95.6% was obtained when extraction temperature was 40 ℃. From saving energy point of view, 30 ℃ is selected in the other experiments.

3.2.3 Stirring speed. Figure 2(c) showed the effect of stirring speed on nitrogen removal efficiency. Nitrogen removal efficiency increased initially, and then decreased with the increase of stirring speed. The possible reason is that the increase of stirring speed is conducive to the mass transfer in reaction system initially, accordingly increasing nitrogen removal efficiency. However, too high stirring speed will break the combination of DESs and organic nitrogen compounds in model oil, which will decrease nitrogen removal efficiency. The maximum value of nitrogen removal efficiency was obtained when stirring speed is 800 rpm.

3.2.4 Mass ratio of DES to oil ($M_{\text{DES/oil}}$). Figure 2(d) showed the effect of $M_{\text{DES/oil}}$ on nitrogen removal efficiency. Nitrogen removal efficiency increased rapidly with the increasing of $M_{\text{DES/oil}}$ at the initial stage of reaction, and then reaches its maximum value. e.g., nitrogen removal efficiency is only 86.7% when $M_{\text{DES/oil}}$ was 0.5:1, whereas that soars to 97.1% when $M_{\text{DES/oil}}$ was 1.5:1. However, the maximum
value of nitrogen removal efficiency remained almost stable when the $M_{\text{DES/oil}}$ increases from 1.5:1 to 2.5:1. From economical point of view, the $M_{\text{DES/oil}}$ of 1:1 is selected in the other experiments.

![Graph](image)

Figure 2 Effect of reaction conditions on nitrogen removal efficiency. (a) extraction time (30 ℃, 800 rpm, 1:1 $M_{\text{DES/oil}}$); (b) temperature (20min, 800 rpm, 1:1 $M_{\text{DES/oil}}$); (c) stirring speed (20min, 30 ℃, 1:1 $M_{\text{DES/oil}}$); (d) $M_{\text{DES/oil}}$ (20min, 30 ℃, 800 rpm).

### 3.3. Multistage extraction
In order to realize deep denitrogenation, multistage extraction is necessary for an industrial process. In this work, a model oil sample is treated with fresh DESs many stages. The effect of extraction stages on nitrogen removal efficiency was examined. As shown in Figure 3, residual nitrogen content decreased with the increasing of extraction stages. After two extraction stages the nitrogen content of model oil could be reduced to less than 10 ppm. Namely, the deep denitrogenation of model oil could be realized.

### 4. Conclusions
In this work a novel DES was synthesized using TEA as HBA and SA as HBD and was used for the extractive denitrogenation of model oil. The structure of the DES was analyzed by FTIR and the result indicated that hydrogen bond was responsible for synthesizing TEA/SA. The factors that influence nitrogen removal efficiency were investigated. Under the conditions of 20 min time, 30 ℃ temperature, 800 rpm stirring speed, 1:1 $M_{\text{DES/oil}}$, nitrogen removal efficiency reached more than 95%. After two extraction stages the nitrogen content of model oil could be reduced to less than 10 ppm. In summary,
the novel DES TEA/SA will become a promising extractant for fuel oil denitrogenation. Further study should focus on the regeneration and recycling of the DES.

![Figure 3 Multistage extraction (20min, 30 ℃, 800 rpm, 1:1 MDES/oil).](image)

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