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Extraction and recovery of toxic acidic components from highly acidic oil using ionic liquids

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HIGHLIGHTS

- Highly toxic naphthenic acid was extracted from highly acidic model oil using ionic liquids.
- The extraction process required only very low amount of ionic liquids.
- Extracted naphthenic acid and the ionic liquids used were recovered by simple procedure.
- DFT calculations were performed to understand the mechanism of naphthenic acid extraction using ionic liquids.
- The ionic liquids can be used more than six times without losing its extraction efficiency.

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ABSTRACT

Naphthenic acid (NA) is a toxic compound that exists in the effluent discharged from highly acidic oil refineries. The amount of NA present in acidic crude oil can be as high as 4 wt%. The complicated structure of NA poses a challenge for oil refineries in their effort to extract NA from the heavy crude oil in an economical and environmental friendly manner. In the current study the extraction of NA from highly acidic model oil by ionic liquid (ILs) was performed using 1,8-diazobicycloundec-7-ene (DBU) based cation in combination with the thiocyanate anion. A detailed computer simulation study on the mechanism of NA extraction by the ILs was also performed. The extracted NA was completely recovered and the ILs used were regenerated by simple addition of water. It was found that increasing of the alkyl chain length increases the percent NA removal. Computer simulation suggests those thiocyanate anions are found to be playing a major role in the NA extraction process.

1. Introduction

The increase in the processing of acidic crude by refineries had raised significant environmental and operational concerns [1,2]. The major problem associated with the acidic crude oil is the presence of NA, which is considered as both toxic and corrosive. NA is generally described by the general formula $C_nH_{2n+z}O_2$, where n indicates the number of carbon atoms; z (negative integer or zero) indicates the deficiency of hydrogen because of the presence of cyclic or aromatic groups [3–5]. NA is highly toxic to aquatic organisms and is mostly present in the effluent discharge from different petrochemical industries processing acidic crude oil. Most of the studies focus on the NA toxicity in the effluent discharge. In order to avoid the toxic effect of NA acid on the aquatic system, a simple and efficient process for the extraction of NA from its source of origin (acidic crude oil) would be beneficial [6–8]. NA have higher solubility in water compared to hydrocarbons thus making it a major threat to aquatic environment [9]. The presence of NA can be as high as 4 wt% in heavy crude oil. The NA can also cause corrosion in the oil refineries and it can adversely affect the storage and combustion properties of the final product. On the other hand NA is an important raw material (2500–3500 USD/ton) having potential application in different areas such as production of paint and cross linking of rubber [10]. Hence, the removal and recovery of NA are

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highly advantageous to both the environment and to the industry. The presence of NA in crude oil is measured using the total acid number (TAN). TAN values greater than 0.5 mg KOH/g of crude oil are considered as potentially corrosive for refineries units [11].

The current method used in the industry for the extraction and recovery of NA is the soda wash method, which leads to the spillage of NA in the water reservoirs [10]. Adsorption using ion exchange and liquid–liquid extraction (LLE) using organic solvents are the methods that have been tested for the recovery of NA from crude oil at lab scale [12–14]. Decarboxylation is another alternative for acidity reduction of highly acidic crudes [15,16]. Esterification using SnO/Al_2O_3 had been used for diesel streams as well as for crude oil [17,18]. However, all these methods have certain operational difficulties such as harsh reaction conditions, higher operational costs and lack of environmental viability.

The restrictive factors in the current methods demands for a simple, environmental friendly and industrially viable process for the extraction of NA. Ionic liquids (ILs), solvents composed entirely of ions, have found application in energy, nuclear, catalysis, biomass, electrochemical and solar cells industries [19–26]. Although different ILs are used for extraction of NA, most of them are applicable only in the case of very low total acid number (<0.5 TAN). Moreover, most of them are using large amount of volatile organic solvents and the regeneration procedure of ILs and NA is quite complicated [27–31].

It has been shown that using anion with high pK_a can increase the extraction efficiency of NA [28,30]. This essentially suggests that the more basic the IL is, the higher extraction efficiency will become. However the effect of the basicity of the cation has not been tested. It has also been proposed that the mechanism of NA extraction using ILs occur through the formation of a cage-like structure of the IL species around the NA molecules [30]. However, no details study about the mechanism has been performed to date.

In this work, the extraction of NA using diazabicyclo undecane (DBU) based cation and thiocyanate anion is studied. The DBU based cation was selected for the extraction studies because conjugate acid of DBU is more basic than the conjugate acid of imidazole (>11 vs ~7) [34,35]. In theory the DBU-based cation should have higher extraction efficiency. The thiocyanate anion is incorporated because of the presence of two coordination site, which will lead to the enhanced interaction between ILs and NA. In addition, computational study is performed to understand the molecular level mechanism of the extraction process.

2. Experimental

2.1. General information

The chemicals used in this study were purchased from Sigma–Aldrich (Bornem, Belgium) and Acros Organics (Geel, Belgium). The synthesis and characterization of the ILs used in this study are performed using previously reported procedure [32]. The ILs used in this study are 1-hexyl-1,8-diazobicycloundec-7-ene thiocyanate, [DBU] [Hex], 1-octyl-1,8-diazobicycloundec-7-ene thiocyanate, [DBU] [Oct], 1-decyl-1,8-diazobicycloundec-7-ene thiocyanate, [DBU] [Dec]. The NMR spectra are recorded using Bruker Advance 500 spectrometer (operating at 500 MHz for ^1H and 125 MHz for ^{13}C). Number of scans is 16 and the pulse programme used is zg30.

2.2. Preparation of model acid oil

In the current study highly acidic oil is used for de-acidification. The total acid number of the acidic oil used in this study is 3.46 (±0.01) mg KOH/g of oil, which is calculated using Metler Toledo Auto titrator according to the ASTM D664 method. The acidic oil is prepared by adding commercial NA to dodecane. Dodecane is used in this study because of its closed proximity with kerosene, jet fuel oil and diesel. All these streams have the maximum concentration of naphthenic acid [33].

2.3. Deacidification process

The de-acidification of acidic oil is done by mixing model oil and ILs in a round bottom flask at constant stirring for one hour. The temperature is adjusted using silicon bath controlled by a hot plate and thermocouple. Once the reaction has completed, the reactants are transferred into a separating funnel. The two layers were easily separated because of the density difference. The de-acidified model oil is collected from the top of the separating funnel and its total acid number is analyzed. The percent NA is calculated using the formula given below:

$$\textit{Percent Naphthenic Acid Removal} = \left(1 - \frac{\mathrm{TAN}_f}{\mathrm{TAN}_i}\right) \times 100,$$

where TAN_f and TAN_i refer to final and initial TAN of the oil respectively.

2.4. Computational details

In order to understand the mechanism of the naphthenic acid extraction with DBU/SCN-based ILs, molecular dynamics simulation was performed on the [DBU-Hex] [SCN] system. To obtain reasonable statistics, the system is comprised of 1527 *n*-dodecane molecules, 86 [DBU-Hex] [SCN] ILs molecules, and 10 cyclohexyl acetic acid as the model NA. The simulation is performed using the AMBER [34] molecular dynamics package employing the GAFF-force field [35]. The charges were obtained using the RED Server Tools [36–39]. One modification was made to the angular force constant of the S—C—N. The modification was made due to the unmodified GAFF force constant causing the SCN molecule to be mostly in the bent form, while from our geometry optimization with *ab initio* method suggests that the SCN molecule is in linear form at equilibrium, and thus should be in the linear form most of the time. A molecular dynamics simulation on the pure [DBU-Hex] [SCN] system gives a density value of 1.0419 g/mL, which is in good agreement with the experimental density of 1.0564 g/mL obtained in our lab. The percent error is calculated to be 1.3726%.

The initial configuration of the system namely the topology as well as the input coordinate files required for the simulation are obtained using Avogadro [40], Packmol [41] and AmberTools 14 [42] software packages. The molecules are fitted into a cubic box using Packmol. The initial configuration of the system is minimized using the steepest decent method for 30,000 steps. Next, the system is equilibrated in the constant pressure-constant temperature ensemble (NPT) using Langevin dynamics with a time step of 0.5 fs, and collision frequency of 1.0 ps^{-1}. The temperature of the system is set to 300 K while the heat bath temperature coupling was set to 1.0 psi. The pressure of the system is set to 1 bar with isotropic position scaling while the pressure relaxation time was set to 1.0 psi.

Periodic boundary condition is used to account for the boundary effect. The Van der Waals cutoff and the direct space-inverted space Particle-Mesh Ewald cutoff are set to 10 Å. The equilibration step was performed for 150 ns. The system is set to have reached equilibrium by making sure that the density and the potential energy of the system were stable. The plots of the density and the potential energy of the system are shown in Figs. 1 and 2 in the supporting information.