Chemical Engineering Journal 284 (2016) 487–493

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Extraction of naphthenic acid from highly acidic oil using phenolate based ionic liquids

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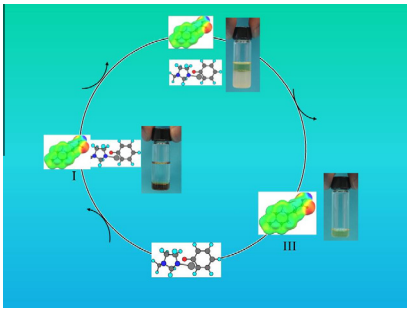
HIGHLIGHTS

- The extraction of naphthenic acid from highly acidic model oil was achieved.
- Very low ionic liquid/model oil ratio is necessary for the complete extraction of naphthenic acid.
- Phenolate based ionic liquids were reused three times without losing its activity significantly.
- COSMO-RS calculations were performed to get more insight into the extraction performance of phenolate based ionic liquids.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 3 September 2015
Accepted 7 September 2015
Available online 11 September 2015

Keywords:
Ionic liquids
Naphthenic acid
Phenolate anion
Alkyl methyl imidazole
Extraction
Heavy crude oil

ABSTRACT

In this study, N-alkyl imidazolium ionic liquids with highly alkaline phenolate anions were used for the removal of naphthenic acid from model acid oil. The effect of alkyl spacer length on the deacidification process was evaluated by attaching butyl, hexyl, octyl, decyl and dodecyl groups on imidazolium cation. It was found that increase in the alkyl chain length increases the percent naphthenic acid removal. Extremely low amount of ionic liquids were necessary for the complete deacidification of model oil with high TAN. The reusability of the phenolate ionic liquids was also investigated. COSMO-RS calculations were performed on phenolate ionic liquids to study their extraction efficiency, selectivity and solvent capacity.

1. Introduction

The world heavy crude oil demand is increasing because of the enhanced exploitation and utilization of oil resources in the world. The world's high-acidity crude oil production has increased by 0.3% per year during the recent years [1]. Naphthenic acid present in heavy crude oil is a major source of corrosion in most of the oil refineries around the world. The acidity of the crude oil is expressed in Total Acid Number (TAN), which is a measure of the amount of KOH in milligrams needed to neutralize one gram of crude oil.

Although several methods such as adsorption, solvent extraction, esterification, catalytic decarboxylation, and thermal decom-

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http://dx.doi.org/10.1016/j.cej.2015.09.017
1385-8947/

position were available for deacidification of crude oil, soda wash method is considered as the most economical and efficient method for treating the acid streams from refinery [2,3]. The liquid-liquid extraction (LLE) and adsorptive recovery using ion exchange is a widely used laboratory method for recovery of naphthenic acid from crude oil [4,5]. Acidity reduction for highly acidic crude is achieved using thermal and catalytic decarboxylation [6,7]. The catalytic esterification using SnO/Al_2O_3 had been used for crude oil as well as for the diesel streams [8,9]. The lack of process efficiency and loss of higher distillate streams restricts the use of this method. The ion exchange method can be applied only for low temperature lighter distillate fractions and the generation of organic solvent waste restrict the use of liquid–liquid extraction method. The higher temperature that leads to corrosion problems limits the use of decarboxylation process. In order to overcome all these problems, an environmentally friendly and industrially viable technique is required for the processing of high acidity streams.

Recently, Ionic liquids (ILs) has attracted significant attention due to their promising and unique properties such as almost zero volatility, mostly nonflammable, good thermal stability, wide electrochemical window, and wide liquid range. The area of application of ILs includes purification, electrochemistry, extractions, catalysis, etc. [10–14]. The application of ILs have also been reported for naphthenic acid extraction [15–17]. In this study a new class of phenolate anion based ionic liquids with imidazolium cation with varying chain length [$C_n$mim] had been employed for the deacidification of model oil. The phenolate anions were used because of their high basicity and the presence of π electrons, which can enhance the de acidification process. Binnemans et al. used phenolate anion with a *tert*-Butyl group at para position in combination with various cations for the development of a simple method for the synthesis of hydrophilic ionic liquids with very low halide content and highly base stable ammonium ionic liquids [18,19]. Phenolate ionic liquids with tetraalkylphosphonium cation has been used for CO_2 capture [20]. Recently, thermophysical properties of tetramethylguanidinium based ionic liquids with different substituents at para position of the phenol were reported [21]. However, to the best of our knowledge, there were no previous studies conducted on the use of imidazolium based phenolate ionic liquids for the extraction of naphthenic acid from model oil.

2. Experimental

2.1. General information

All the ILs used in this study were synthesized and characterized according to the previously reported literature procedure [22]. All the chemicals were purchased from Acros Organics (Geel, Belgium) or from Sigma–Aldrich (Bornem, Belgium) and were used as received, without further purification.

2.2. Preparation of model acid oil

The simulated acid oil (referred to as model oil) was prepared by adding a certain amount of naphthenic acid to dodecane. The Total acid number of 1.44 (±0.01) was attained and this value is considered as highly acidic based on the normal criteria used for crude oil. Most of the world commercial naphthenic acid is produced from kerosene and diesel fractions of the vacuum column. Dodecane is used as the representation of the kerosene and diesel fractions. The ASTM (American Society for Testing and Materials) D664 method, which is commonly used in the industry to calculate the Total Acid Number (TAN), was employed. Metler Toledo Auto titrator was used to calculate the total acid number according to the ASTM D664 method.

2.3. Deacidification process

The deacidification of model oil was performed by adding 10 g of dodecane and ionic liquid to a round bottom flask which is heated by a hot plate. A magnetic stirrer is used for stirring the mixture and a reflux condenser is attached at the top of the flask. The mixture was stirred at a constant temperature with a stirring rate of 500 rpm for a duration of one hour. The process temperature was optimized by applying different temperature settings. After one hour the reaction mixture was transferred to a separation funnel where it was kept for one hour to achieve a clear separation between the ionic liquid and the model oil. Deacidified oil was collected from the top of the separation funnel to compute the TAN. The percent naphthenic acid removal was calculated using the formula stated below:

$$\text{Percent Naphthenic Acid Removal} = (1 - \text{Tan}_f \div \text{Tan}_i) \times 100$$

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

2.4. Computational details

The computational details of the COSMO-RS are given as follows. For structural optimization of the cations and phenolate anion, TmoleX 3.1 (Turbomole Version 6.2) [23] quantum mechanics package was used. The structure of the phenolate anion, cations and naphthenic acids were drawn using COSMO build 1.5. The geometry optimization for naphthenic acids were performed at the density functional theory (DFT) level, utilizing the BP functional [24–26] with resolution of identity (RI) approximation and a triple-ξ valence polarized basis set (TZVP) [27,28]. For the prediction involving ionic liquids, electro neutral mixture approach was assumed. That is, cations and anions are treated separately in COSMO calculations by assuming equimolar composition of cations and anions. The geometry optimizations of the ionic liquids were performed using dispersion corrected DFT (DFT-dsp) methods as the interaction in ionic liquids are influenced significantly by dispersion forces [29]. COSMO-RS calculations were performed using the COSMOthermX programme (Version C21) with BP_TZVP_C21_0111.ctd parameterization. Activity coefficients at infinite dilutions of naphthenic acids and dodecane (model oil) were calculated at 298.15 k. The details about the COSMO-RS model along with the expression for activity coefficient in the liquid phase are described elsewhere [30]. The COSMO-RS theories for predictions have been extensively explained in the literature [31,32]. Selectivity and solvent capacity were calculated from the activity coefficient values.

3. Results and discussion

3.1. Effect of reagent/oil ratio

An overview of ILs used in this study is given in Fig. 1. Ionic liquids/oil ratio is one of the deciding factors in the de-acidification process. The effect of ionic liquid/model oil ratio on deacidification process was investigated. The percent naphthenic acid removal was calculated with different weight ratios. The extraction time was one hour, followed by a 1 h separation time. The effect of different reagent to oil ratio is given in Table 1 and Fig. 2.

As the ionic liquid/model oil ratio increases, there is a clear increase in the percent of naphthenic acid extraction for all types of ionic liquids. It was found that at room temperature, [C_{10}mim]