



# Thermodynamic modelling of liquid-liquid extraction of naphthenic acid from dodecane using imidazolium based phenolate ionic liquids



Syed Nasir Shah <sup>a,\*</sup>, M.I. Abdul Mutalib <sup>d</sup>, M. Farid Ismail <sup>b</sup>, Humbul Suleman <sup>d</sup>, Kallidanthiyil Chellesh <sup>a,c</sup>, Rashidah Binti Mohd Pilus <sup>e</sup>

<sup>a</sup> Centre of Research in Ionic Liquids, Universiti Teknologi Petronas, Bandar Seri Iskandar 32610, Perak, Malaysia

<sup>b</sup> Department of Chemistry, Universiti Putra Malaysia, 4330 Serdang, Malaysia

<sup>c</sup> Center for Biofuel and Biochemical Research, Universiti Teknologi Petronas, Bandar Seri Iskandar 32610, Perak, Malaysia

<sup>d</sup> Department of Chemical Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar 32610, Perak, Malaysia

<sup>e</sup> Department of Petroleum Engineering, Universiti Teknologi Petronas, Bandar Seri Iskandar 32610, Perak, Malaysia

## ARTICLE INFO

### Article history:

Received 14 September 2015

Accepted 18 March 2016

Available online xxxx

### Keywords:

Ionic liquids (ILs)

Naphthenic acid (NA)

Phenolate anion (Phe)

Alkyl methyl imidazole

Liquid-liquid equilibrium (LLE)

Non-random two liquid model (NRTL)

Universal Quasi Chemical (UNIQUAC)

## ABSTRACT

In this work, N-alkyl imidazolium based ionic liquids with phenolate anions have been used for the separation of naphthenic acid from model oil. The liquid-liquid equilibrium (LLE) data for the ternary mixture of [C<sub>7</sub>mim][Phe], dodecane and naphthenic acid were experimentally obtained at a constant temperature of 303.15 K and atmospheric pressure. The effect of chain length on the extraction capability was observed by calculating the distribution coefficient. The experimental tie line data was correlated using the non-random two liquid model (NRTL) and Universal Quasi Chemical (UNIQUAC) model and new interaction parameters for the ternary systems are reported. The experimental data provides a good correlation with the modelling data and a very low root mean square deviation (RMSD) value was observed for all the systems.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Ionic liquids (ILs) being designer solvents have found a large number of applications in academia as well as in the industry. The properties like negligible vapour pressure, high thermal and chemical stability, non-flammability; high heat capacity, high ionic conductivity etc. make them a greener choice for a range of industrial applications. In addition, ILs exhibit a very good solubility for organic compounds thus making them an excellent solvent for liquid-liquid extraction process [1,2]. These desirable properties make them suitable in numerous applications in which many conventional solvents are non-applicable and in-effective. Liquid-liquid extraction has found large applications in the separation industry because of the mild process conditions applied during the process i.e. low temperature and pressure. The solvent to be used in liquid-liquid extraction should have a high selectivity towards the solute. Moreover, it should be economical to produce, recyclable, and robust to withstand various processing environments. Most of the organic solvents are carcinogenic, highly volatile and their recyclability is very low. Contrarily, most of the ILs are greener, non-volatile and highly recyclable [3–6]. But the core issue that stands in the way of commercialisation is the high cost

of ILs. However, in one of the recent modelling and simulation studies on the ILs production process shows that ILs can be produced at lower cost (\$1.24 kg<sup>-1</sup>), which is in comparison with most of the organic solvents such as acetone or ethyl acetate with a cost of \$1.30–\$1.40 kg<sup>-1</sup> [7]. Similarly, in another study, the extraction of aromatic hydrocarbon from aliphatic hydrocarbon with 4-methyl-N-butylpyridinium tetrafluoroborate was modeled using ASPEN resulting in a positive margin of about € 20 million per year [8]. These results indicate that ILs are not necessarily expensive, and therefore large-scale ILs-based processes can become a commercial reality. Naphthenic acid removal from acidic crude is one of the major concerns of refiners all over the world. Naphthenic acid presence in heavy crude can cause corrosion in the refinery equipment and storage tanks. Additionally, it affects the combustion characteristic of the finished products [9,10]. Thus the removal of naphthenic acid from crude oil is highly desirable. On the other hand, naphthenic acids have a very complicated moieties and a wide variety of compounds lie in the definition of naphthenic acid. Naphthenic acids can be defined as a mixture of cyclic, aromatic and linear monocarboxylic acids present in the crude oil with the general formula C<sub>n</sub>H<sub>2n</sub> + zO<sub>2</sub>, where *n* indicates the number of carbon atoms, *z* indicates the deficiency of hydrogen because of the presence cyclic or aromatic groups. The value of *z* can be a negative integer or zero [11–14]. Commercial naphthenic acid is obtained from jet fuel, kerosene and diesel fractions by caustic wash followed by acidification of caustic stream with sulfuric

\* Corresponding author.

E-mail address: [nasir876@gmail.com](mailto:nasir876@gmail.com) (S.N. Shah).

acid. This process generates significant volume of sodium sulphate brine that is of the order of 10 L per kg of crude naphthenic acid. Moreover, it contains phenolic compounds that should be disposed in an environmental friendly way. In addition there is some carry-over of phenolic and sulphur compounds to the naphthenic acid streams affecting the properties of the final product [10]. There had been a lot of other lab scale methods for removal of naphthenic acid. The details of these methods can be found elsewhere [15–21]. Ionic liquids had also been used to remove naphthenic acid from crude oil. A lot of studies had been conducted to remove naphthenic acid from model oil and crude oil in which the ILs had been recycled for many times without compromising on their extraction efficiency and producing negligible waste [22–27]. In addition, negligible amount of ILs had been used to completely de-acidify crude oil having a very high acid number (4.74 ( $\pm$  0.01) mg of KOH/g) [26]. However, scarce published data is available for liquid-liquid equilibrium data of commercial naphthenic acid using ionic liquids. For instance, cyclohexane carboxylic acids (CCA) has been used as an analogy to naphthenic acid, but fails to address variety of naphthenic acids present in literature. Furthermore, the liquid-liquid equilibrium data have not been modelled previously using any thermodynamic models [28], creating a bottleneck in expansion of experimental data to modelling and simulation studies. Therefore, this work provides ample experimental data for the liquid-liquid equilibrium data for the discussed ternary system and their thermodynamic equilibrium. Subsequently, this extends our previous findings related to the aforementioned case [25].

In the current study four different ternary systems were used with dodecane as model oil, commercial naphthenic acid and  $[C_n\text{mim}][\text{Phe}]$ . The effect of chain length on the ionic liquids on separation efficiency was also studied. The distribution coefficient of the ionic liquids were calculated from the LLE data. The LLE data was correlated using NRTL and UNIQUAC model. New interaction parameters for both thermodynamic approaches are reported. Additionally, the volume parameter,  $R$  and the surface area parameter,  $Q$  for UNIQUAC model are determined using Density Functional Theory (DFT) and the FIXPVA method [29] for determining the cavity size as typically used in the Polarizable Continuum Model (PCM) method. The correlated results are in excellent agreement with experimental values.

## 2. Material and methods

The chemicals used for the synthesis of ILs were purchased from Acros Organics (Geel Belgium) and Sigma Aldrich (Bornem, Belgium). The synthesis of the ILs were carried out according to the already

reported procedure [30]. The properties and structures of all the synthesized ionic liquids are shown in Table 1.

### 2.1. UNIQUAC volume and surface area structural parameters

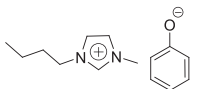
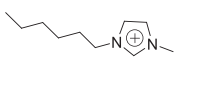
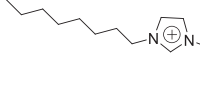
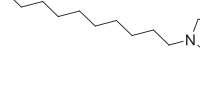
To get the surface and the volume parameters, the geometry of the cation and the anion of the ionic liquid is optimized using the density functional theory (DFT) method. The B3LYP functional with RIJCOSX SCF approximation, together with the minimally augmented ma-def2-TZVPP basis set [31,32] was used in the geometry optimization step using the ORCA quantum chemistry package [33,34]. The D3BJ dispersion-correction with Becke-Johnson damping [35, 36] was applied to account for the dispersion error of the DFT method. From the optimized geometry, the surface and volume values for the ILs had been calculated using the Fixed Points with Variable Areas (FIXPVA) method [29]. The FIXPVA method is a method used to calculate the cavity size for Polarizable Continuum Model (PCM) [37] as implemented in the GAMESS software package [38]. Similar method was used by Manohar et al. [39] to obtain the surface and volume parameters.

### 2.2. Liquid-liquid extraction experiments

The liquid-liquid equilibrium study for the four ternary systems was performed in 8 mL vials with airtight caps. The vials were weighted and known amount of dodecane, naphthenic acid and ionic liquids were added to the vials. After this the mixture were placed in a shaking incubator for 5 hours to attain thermodynamic equilibrium. The mixture was shaken at a constant speed of 700 RPM at a fixed temperature of 303.15 K ( $\pm$  0.1 K). To ensure the complete separation between the ionic liquids and hydrocarbon phase the vials were left overnight at a constant temperature of 303.15 K ( $\pm$  0.1 K). The structure of naphthenic acid is very complicated as already mentioned. This complicated structure of naphthenic acid makes it quite impossible to quantify via Gas chromatography or High Pressure liquid chromatography technique [11–14]. For this reason we had quantified the hydrocarbon layer by measuring refractive index. Refractive index had long been used to quantify the concentration of different solutes in aqueous as well as in organic solutions [40]. An ATAGO programmable digital refractometer (RX-5000 $\alpha$ ) was used with an uncertainty of  $\pm 4 \times 10^{-5}$  and temperature accuracy of  $\pm 0.05$  K. The mole fraction against refractive index graphs were drawn as shown in Figs. 1 and 2. All the concentrations of the hydrocarbon phase and IL phase was determined from these graphs.

To ensure no carryover of the ionic liquids to the hydrocarbon layer the  $^1\text{H}$  NMR of the hydrocarbon layer was performed using Bruker

**Table 1**  
Structures of synthesized ionic liquids plus water content and halide content.

ILs	Chemical structure	Water content (ppm)	Halide (ppm)
$[\text{C}_4\text{mim}][\text{Phe}]$		170	102
$[\text{C}_6\text{mim}][\text{Phe}]$		153	93
$[\text{C}_8\text{mim}][\text{Phe}]$		149	90
$[\text{C}_{10}\text{mim}][\text{Phe}]$		161	97

Download English Version:

<https://daneshyari.com/en/article/5410145>

Download Persian Version:

<https://daneshyari.com/article/5410145>

[Daneshyari.com](https://daneshyari.com)