Extraction of Carboxylic Acids from Hydrocarbon Mixture Using Imidazolium Ionic Liquids

Hasiah Kamarudin, M. I. Abdul Mutalib, and Zakaria Man

Abstract—This study focuses on the extraction performance of selected Imidazolium type ionic liquids on two different carboxylic acids namely benzoic (aromatic) and n-hexanoic (aliphatic) acids from a hydrocarbon bulk liquid. Three types of ionic liquids were used in the liquid-liquid extraction study which comprise of 1-n-butyl-3-methylimidazolium as the cation, coupled with three different anions namely thiocyanate [SCN], octylsulfate [OCS] and trifluoromethanesulfonate [OTF]. The liquid-liquid extraction study was conducted using experimental approach and the finding on its performance is compared against the prediction calculated using molecular simulation approach based on conductor like screening MOdel for Real Solvents (COSMO-RS) method. The comparison between the two shows good agreement in the ranking of the extraction performance of the three ionic liquids as well as the trend observed from the experimental results. In addition, the understanding developed from the molecular simulation was found to be useful in explaining the results observed from the experimental work.

Index Terms—Ionic liquids, COSMO-RS, liquid-liquid extraction, carboxylic acids

I. INTRODUCTION

Ionic Liquid is a chemical compound that composed entirely of ions. These ionic salts appear as liquid over a wide range of temperature [1]. The various possible combinations of different inorganic anion and organic cation of ionic liquids offer opportunities to produce numerous types of ionic liquids [2]. Ionic Liquids that melts at temperature below 100°C is known as Room-Temperature Ionic Liquids (RTIL). These compounds possessed interesting and attractive characteristics’ such as negligible vapor pressure, non-combustible, high thermal decomposition temperature etc [2], [3]. The major difference of ionic liquids compared to the conventional salts is the structure arrangements of the molecule. Conventional salts such as sodium chloride exists in the form of solid at room temperature due to the close packing of all its molecules in a structured symmetrical arrangements thus producing stronger bonding between them. In contrast, ionic liquids composed of unsymmetrical anion [2] and cation with poor molecular arrangement hence weakening the forces that hold them together leading to much lower melting temperature.

The application of ionic liquids in hydrocarbon related industry such as petroleum processing has seen growing application potential. A number of published research have demonstrated the ability of several ionic liquids particularly Imidazolium type in removing sulphur compounds [3], [4] from hydrocarbon liquid. In another study, the same ionic liquids but with different anions such as thiocyanate [SCN], octylsulfate [OCS] and trifluoromethane sulfonate [OTF] were also shown to extract nitrogen in addition to the sulphur compounds [5]-[8]. Given the significant presence of various acids, some of which could potentially cause severe corrosion problems, it makes sense to commission a study to investigate the ability of the above mentioned ionic liquids for acids removal.

Carboxylic acid having a chemical compounds empirical formula of C_{n}H_{2n+1}O_{2}, occurs naturally in crude oil right from the reservoir [9]. Crude oil with a high content of carboxylic acid is generally known as High Acid Crude (HAC) Oil or High Total Acid Number crude oil. The Total Acid Number (TAN) is expressed as the weight in milligram of potassium hydroxide required to neutralize 1gram of oil [10]. The minimum allowable for crude acidity is 0.5mgKOH/g [11]. The presence of carboxylic acids in the crude oil is known to cause severe corrosion problems to refineries especially for the equipment operating at temperature above 230°C [12]. Outside the usage of ionic liquids in petroleum industry, there are already considerable published works discussing on the capability of ionic liquids in extracting carboxylic acids. Matsumoto etal [13] investigated the potential of Imidazolium ionic liquids as extractants for in situ extractive fermentation process. Similar work was conducted by Jan Martak and co-workers, where lactic acid was extracted using phosphonium based ionic liquids [14]. Their valuable findings reveal the significant potential of ionic liquids to be used as acid extractants.

The present study employs three types of Imidazolium ionic liquids namely 1-butyl-3-methylimidazolium thiocyanate [C_{4}mim][SCN], 1-butyl-3-methylimidazolium octylsulfate [C_{4}mim][OCS] and 1-butyl-3-methylimidazolium trifluoromethane sulfonate [C_{4}mim][OTF].

II. METHODOLOGY

A. Chemicals

The main chemicals used in this study are
1-butyl-3-methylimidazolium thiocyanate[CN][SCN] (Merck, ≥ 95%), 1-butyl-3-methylimidazolium octylsulfate [OCS] (Merck, ≥ 98%) and 1-butyl-3-methylimidazolium trifluoromethane sulfonate [OTF] (Merck, ≥ 99%). The ionic liquids molecular structures and abbreviations are presented in Figure 1. Carboxylic acids such as Cyclohexaneacetic Acid (Sigma Aldrich ≥ 98%), Benzoic Acid (Merck, Reag. Ph Eur) and n-Hexanoic Acid (Sigma Aldrich, ≥ 98%) are used as model carboxylic acids. Other than that are the chemicals for acidity determination experiment such as Toluene (Merck, ≥ 99.9%), 2-Propanol (Merck, ≥ 99.8%), Acetonitrile (Merck, ≥ 99.9%) and KOH solution in methanol, 0.1mol/L. To represent the hydrocarbon based liquid, n-Dodecane (Merck, ≥ 99.0%) is selected.

**Extraction Efficiency** is calculated using Equation 1.

\[
\text{Extraction Efficiency} = \frac{C_0 - C_x}{C_0} \times 100\%
\]  

where \(C_0\) is the initial total acid number (TAN) in mg KOH/g and \(C_x\) is the final total acid number (mg KOH/g). In addition, the infrared absorption spectra for the two phases are also captured and recorded using 8400S Spectrophotometer (Shimadzu, Japan) equipped with ATR Miracle A, and ZnSe prism. These spectra are collected for wavelength ranging between 4000cm\(^{-1}\) to 650cm\(^{-1}\). Analysis on the chemical structure of the two phases is performed using Nuclear Magnetic Resonance Analysis (Bruker 500MHz Avance III Nuclear Magnetic Resonance) by collecting the data of \(^1\)H (proton) spectra.

**C. COSMO-RS Evaluation**

COSMO-RS calculations are performed using the COSMOTHERM program version C21_0111. For the determination of thermodynamic properties, the BP_TZVP_C21_0111 parameterization is used. The activity coefficient for the respective compounds in the mixture can be determined using the equation below:

\[
\gamma_i = \exp\left(\frac{\mu_i - \mu_{i}^{\text{pure}}}{RT}\right)
\]  

where \(\gamma\) is the activity coefficient, \(\mu\) is the chemical potential, \(\mu_{i}^{\text{pure}}\) is the chemical potential of the pure compound. The activity coefficient for ionic liquids can then be calculated using Eq. 3 below:

\[
\gamma_i^{\text{binary}} = \frac{1}{2}\gamma_i^{\text{ternary}}
\]  

This activity coefficient is used to calculate the capacity and selectivity parameters as presented in the two equations below:

\[
\text{Capacity at infinite dilution (C)} = \frac{1}{\gamma}
\]  

\[
\text{Selectivity at infinite dilution (S)} = \left(\frac{\gamma_1}{\gamma_2}\right)
\]  

where subscript 1 refers to the carboxylic acids and subscript 2 refers to the ionic liquids. The Capacity parameter indicates the amount of ionic liquids required for the extraction process. Higher capacity value means lesser amount of ionic liquids is needed for the extraction and vice versa. On the other hand, the Selectivity parameter reflects the efficiency of the separation process through the preference of the ionic liquid in extracting the target compound which in this case is the two carboxylic acids. High selectivity value indicates better affinity of the ionic liquids to the carboxylic acids as compared to the dodecane resulting in lesser hydrocarbon losses to the ionic liquids phase and also number of stages required for the extraction process.

**B. Extraction Experiment**

Two types of carboxylic acids namely benzoic acid (aromatic type) and n-hexanoic acid (aliphatic type) are selected to represent the “model” acids. Dodecane, which is a stable hydrocarbon liquid is used as the bulk hydrocarbon liquid in which the carboxylic acids are dissolved into. Two batches of the hydrocarbon liquid containing 2.45wt% of n-hexanoic acids (A) and 0.5wt% of benzoic acids (B) in dodecane are prepared separately. The deacidification experiments are performed by mixing each of the selected ionic liquids with the two hydrocarbon liquid using a ratio of 1:1 in a closed container. The mixtures are stirred at 700 rpm for 30 minutes with temperature setting of 25°C before they were left for 3 hours to allow for phase separation i.e., ionic liquids and hydrocarbon phase. Samples from each phase are then collected for TAN measurement. The Total Acid Number (TAN) is determined using potentiometric titration according to the ASTM 664 standard. In this method, 0.1 mol KOH in methanol is used as the titrant and all the samples are dissolved in a phenolic solution prior to titration. The extraction efficiency is calculated using Equation 1.

![Fig. 1. Structure and abbreviations for Imidazolium ionic liquid](image-url)
III. RESULTS AND DISCUSSIONS

A. Extraction Efficiencies

The initial concentrations of the two prepared hydrocarbon liquid are tabulated in Table I:

<table>
<thead>
<tr>
<th>Hydrocarbon Liquid</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mgKOH/g)</td>
<td>10.978</td>
<td>2.165</td>
</tr>
</tbody>
</table>

This initial acid number is found to be relatively high but all three Imidazolium ionic liquids was observed to have extracted up to 90% of the carboxylic acids from the hydrocarbon liquid. Three replicates are made for hydrocarbon liquid A and B and the results of the carboxylic acids removal are listed in the tables below.

<table>
<thead>
<tr>
<th>Ionic Liquids</th>
<th>Extraction Efficiency (%)</th>
<th>Distribution Ratio (K_d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₄mim][SCN]</td>
<td>99.21±0.1284</td>
<td>140.85</td>
</tr>
<tr>
<td>[C₄mim][OCS]</td>
<td>99.52±0.0305</td>
<td>182.52</td>
</tr>
<tr>
<td>[C₄mim][OTF]</td>
<td>100.00±0.0000</td>
<td>∞</td>
</tr>
</tbody>
</table>

From Table II, the extraction efficiency of the ionic liquids on hexanoic acid can be ranked as follow: [C₄mim][OTF] > [C₄mim][OCS] > [C₄mim][SCN]. However, the extraction efficiency of the same Imidazolium ionic liquids toward benzoic acid are ranked as follow: [C₄mim][OTF], [C₄mim][SCN] > [C₄mim][OCS]. Here, it can be seen that [C₄mim][OTF] can extract the aliphatic type carboxylic acids more than the aromatic type. While, the performance of [C₄mim][SCN] and [C₄mim][OCS] are in contrary to the [C₄mim][OTF]. These two ionic liquids are a good extractant for aromatic type carboxylic acids. Nevertheless, all of the three ionic liquids achieved outstanding carboxylic acid removal signifying their high affinity toward the solute. The distribution ratios (K_d) are high for all studied ionic liquids.

B. ATR-Infrared Analysis

ATR-IR analysis is capable in identifying the important functional groups present in any chemical compound. Basically, carboxylic acid exhibit strong C=O stretching band between 1710 to 1685 cm⁻¹[15]. The ATR-IR spectra of fresh [C₄mim][OTF], [C₄mim][OTF] after extraction, [C₄mim][OTF] spiked with hexanoic acid and hydrocarbon liquid A containing hexanoic acids is displayed in Fig. 2. The C=O peak appears in the spectra for [C₄mim][OTF] after extraction which indicates that the ionic liquid has managed to extract the hexanoic acid from the hydrocarbon liquid A. Originally the hexanoic acid is presence in the hydrocarbon liquid A as indicated by the C=O stretching peak observed in the spectra for the hydrocarbon liquid A. The intensity of the C=O peak appear to be relatively low due to the small amount of hexanoic acid extracted compared to the volume of the ionic liquids used. For confirmation, the analysis was also conducted on a fresh batch of [C₄mim][OTF] spiked directly with higher concentration of hexanoic acid. The carbonyl peak was again observed at the same wavelength but with higher intensity confirming the C=O stretching peak as previously seen in the [C₄mim][OTF] after extraction. As for the other chemical functional group presence in the ionic liquid, consistent spectrum representing them all were observed in all the ionic liquids samples. This indicates that they had remained intact during the extraction process. The Infrared absorbance wavenumber for the other functional groups presence in [C₄mim][OTF] are tabulated in Table IV.

![Fig. 2. Absorption spectra for C=O functional groups in [C₄mim][OTF] phase.](image)

![Fig. 3. NMR spectra for pure [C₄mim][SCN], [C₄mim][SCN] phase after the extraction and pure n-hexanoic acid.](image)

C. Nuclear Magnetic Resonance Analysis

Nuclear Magnetic Resonance is a powerful tool used for determining the structure, dynamics, reaction state and chemical environment of molecules [16]. In this study, the analysis is used to confirm the structure of the ionic liquids
for each experimental stage involved. A collection of proton (¹H) spectrum for pure [C₄mim][SCN], [C₄mim][SCN] after extraction and pure n-hexanoic acid are shown in Figure 3.

The integration value of the [C₄mim][SCN] peak appearing in each spectra reveals that the structure of the ionic liquids remained the same. In addition, the extracted hexanoic acid may also be visualized in the spectra with the presence of small peaks as indicated in the second spectra of Figure 3. ¹H NMR for alkyl CH₂ at the Imidazolium cation with sextet splitting (~1.3ppm) [16] overlaps with one of the ¹H NMR for the extracted n-hexanoic acid. As a consequence, the integration value has increased. Nevertheless, the remaining peaks showed the same integration and even appear at the same location of chemical shift. Hence conclusion can be made suggesting that the carboxylic acids are physically extracted by the ionic liquids. The ionic liquids [C₄mim] [OTF] and [C₄mim][OCS] were also found to exhibit the same trends. Hence, the NMR analysis shows a consistent result in agreement with the ATR-IR analysis.

Fig. 4 represents briefly the mechanism of the extraction process. During the liquid-liquid extraction, the carboxylic acids travel from the hydrocarbon liquid phase to the ionic liquid phase due to its strong affinity towards the chemical compounds of the ionic liquids.

D. COSMO-RS Evaluation

The trend observed in the extraction efficiency results presented earlier in Table I is then used for comparison against the predicted performance of the same ionic liquids obtained from COSMO-RS simulation based on its capacity and selectivity parameters. The results on the two parameters obtained from the COSMO-RS simulation are shown in Figure 5 and Figure 6, in the form of bar chart. Note that these parameters are determined using equation (4) and (5). The capacity of [C₄mim][SCN] showed the highest value for benzoic acids. While for hexanoic acid, the [C₄mim][OCS] showed the highest value. The capacity of the ionic liquids for benzoic acid can be ranked as follow; [SCN] > [OCS] > [OTF], while the capacity ranking for hexanoic acid follows the order of [OCS] > [SCN] > [OTF].

The results for the ionic liquids selectivity between hexanoic acid and dodecane can be listed according to the following rank; [SCN] > [OTF] > [OCS]. For selectivity, [C₄mim][SCN] shows the highest selectivity towards the two acids compared to dodecane. This means that the ionic liquid could be easily separated from the hydrocarbon after extraction. On the other hand, both [C₄mim] [OTF] and [C₄mim] [OCS] show very low selectivity towards the two acids compared to dodecane thus signifying greater chances of dodecane to also dissolve in the ionic liquids together with the acids. The effect was confirmed by the experiments conducted where the amount of hydrocarbon liquid after the extraction process was found to decrease compared to its initial amount used for the extraction. This condition is not favorable particularly in the refining industry where complex hydrocarbon liquid mixtures such as crude oil are involved.

In COSMO-RS, the interaction energy of the surfaces are calculated and presented in a histogram px(σ) plot [17]. These plots, as shown in Fig. 7 and 8, are also known as the sigma (σ) profile. In the sigma profile, any peak observed at >1.0e/nm² refers to the presence of negative lone pair atoms while any peak at <-1.0e/nm² refers to the presence of positively polar surfaces. The peaks observed between ±1.0e/nm² represents the non-polar atoms. Basically, an atom with a negatively polar lone pair electron
could form hydrogen bonding with a positively polar hydrogen atom [17]. From Fig. 7, it can be seen that polarization charge densities profile of the negative lone pair for [SCN] anion terminates at 2.1e/nm² which is largest among the ionic liquids anions followed by the [OTF] and the [OCS] anion which terminates at 1.7e/nm² and 1.8e/nm² respectively. Thus, the [SCN] anion is expected to naturally form the strongest hydrogen bond with polar hydrogen. Using the sigma profile it is easy to determine which atoms in the structure that will dominate the interaction. Another criterion to be considered is the peak area for the sigma profile. Overlapping of the peak area between the compounds indicates possible miscibility of the compounds with each other. The [OCS] anion structure comprises of two major groups of molecules with difference polarity. The highest sigma profile peak is at 1.5e/nm² representing the four oxygen atom of the polar sulphate area. Whereas the peak at -0.1e/nm² shows the non polar hydrocarbon chain of the [OCS] anion. The negative molecular surface form hydrogen bonding with the polar hydrogen in the carboxylic acids and at the same time, the hydrocarbon tail structure forms interaction with the non polar molecules such as the hydrocarbon compounds. In this simulation, the sigma profiles reveal that the non polar hydrocarbon chain of [OCS] anion is actually interacting with the dodecane resulting in hydrocarbon losses from the cross solubility between the ionic liquids and the hydrocarbon. This causes the selectivity to be low, showing the ionic liquid is also extracting the dodecane together with the carboxylic acids during the extraction process. The same trend was observed for [OTF] anion and hence similar argument. However, for the [SCN] anion, the peak area of the anion has less overlap with the dodecane but more with the carboxylic acids. This resulted in higher selectivity of the [SCN] ionic liquids towards the carboxylic acids.

IV. CONCLUSIONS

In conclusion, the capability of three types of potential imidazolium ionic liquids for extracting carboxylic acids from hydrocarbon liquid has been evaluated through experimental and molecular simulation software. The 1-n-butyl-3-methyl Imidazolium ionic liquid with anions namely octylsulfate [OCS], trifluoromethanesulfonate [OTF] and thiocyanate [SCN] showed carboxylic acid removal of up to 99%. Using the computational molecular simulation based on COSMO-RS method, the trends on the capacity and selectivity of the ionic liquids for extracting carboxylic acids were theoretically predicted and compared against the observed experimental data. The results show a good agreement between the two. Also, using the sigma (σ) profile obtained from the simulation work, the explanation for the observed experimental results could be developed. Analysis conducted on the ionic liquids before and after extraction reveals that the mechanism was most likely based on physical means. However, further investigation need to be conducted to confirm the findings.

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