

## Extraction of Naphthenic Acids from Liquid Hydrocarbon using Imidazolium Ionic Liquids

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**Abstract.** In the petroleum processing industry, the presence of carboxylic acids in the form of naphthenic acid could cause severe corrosion to the crude oil processing units, pipelines and storage tanks. This study investigates the potential of using ionic liquids as naphthenic acids extractor from a model hydrocarbon liquid i.e., dodecane. The ionic liquids *1-n-butyl-imidazolium* with three different anions namely thiocyanate [SCN], octylsulfate [OCS] and trifluoromethanesulfonate [OTF] are used to extract two types of carboxylic acids namely benzoic acid and n-hexanoic acid, from the hydrocarbon liquid. The results show that the ionic liquids exhibit high extraction efficiency for both carboxylic acids used. Using computational molecular simulation software i.e., COSMO-RS, the interaction mechanism is investigated based on surface polarization charge densities. From the simulation results, the extraction performance of the ionic liquids is predicted based on capacity and selectivity parameter. Comparison between the experimental results and the simulation prediction shows good agreement with each other.

**Keywords:** naphthenic acid, ionic liquids, deacidification process, liquid-liquid extraction

### 1. Introduction

Naphthenic acids is a term generally used in petroleum industry to refer to a collection of carboxylic acids with empirical formula of  $C_nH_{2n+z}O_2$  [1]. These compounds exist naturally in crude oil right from the reservoir. The crude oil with acid contents of more than 0.5mg KOH/g is considered to be a high acid crude oil by the industry [2]. The total acid content in crude oil is determined according to ASTM 664 method and is expressed in mg of KOH required to neutralize 1 g of oil [3]. Currently, most of the oil producing countries are beginning to produce heavy crude oil with high contents of naphthenic acids. The presence of naphthenic acids in crude oil could cause severe corrosion to refineries processing units especially those operating at temperature above 230°C [4]. The common industry practises to overcome the problem consist of blending with sweet crude or washing with caustic solution to lower the acid level, addition of corrosion inhibitor and utilisation of expensive corrosion resistant construction material for the processing unit. Lately, as the production of heavy crude oil continues to increase, these practises have become more unsuitable. A new class of solvents, namely the ionic liquids, have recently shown promising application for reducing the acid content in crude oil. The ionic liquids comprises of entirely free ions within a liquid state that exist over a wide temperature range. Besides reducing the acid content of the crude oil, several research works have also demonstrated the ability of some ionic liquids (Imidazolium based) to remove sulphur compounds. In another study, the same ionic liquids with different anion such as thiocyanate [SCN], octylsulfate [OCS] and trifluoromethane sulfonate [OTF] were also shown to be able to extract nitrogen and sulphur compounds [5-8].

Thus, the used of ionic liquids could be for a multitude of functions for upgrading the crude oil through removal of the undesirable impurities within a single processing step namely liquid-liquid extraction. In

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addition, features such as higher thermal stability with extremely low vapour pressure compared to the conventional solvents and coupled with the possibility of regeneration have given significant advantages to ionic liquids for replacing conventional solvents [5].

In designing and operating the liquid-liquid extraction process using ionic liquid, understanding the extraction mechanism is highly important. A reasonably large number of experimental work and analysis are required in order to obtain good overview on the extraction mechanism. Fortunately, preliminary mechanism could be explored using computational chemistry approach based on the quantum chemical continuum salvation model. For the purpose of the study, the Conductor-like Screening Model for Real Solvents (COSMO-RS) is used. The COSMO-RS generates sigma profiles for all the components that exist in the system studied from which the inter-component interactions (hydrogen bonding, Van der Waals forces or electrostatic interactions) can be identified and hence the form of extraction mechanism[9]. Performance data such as extraction selectivity versus capacity could also be predicted. There were several reported applications particularly in screening solvents for application in separation process [10-12]. Interestingly, the predicted simulation results are mostly found to be in good agreement with the experimental data [10][13].

In this paper, the capability of 1-*n*-butyl-3-methyl imidazolium ionic liquids with three different anions namely thiocyanate [SCN], octylsulfate [OCS] and trifluoromethane sulfonate [OTF] are employed to extract naphthenic acids from a model liquid hydrocarbon and their efficiencies are investigated. The results from the research work are expected to be useful in developing the design of extraction processes using ionic liquids for crude oil upgrading.

## 2. Experimental

### 2.1. Materials

The ionic liquids used comprised of 1-butyl-3-methylimidazolium thiocyanate[C<sub>4</sub>mim][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. Other main chemicals used are Cyclohexaneacetic Acid (Sigma Aldrich ≥ 98%), Benzoic Acid (Merck, Reag. Ph Eur), *n*-Hexanoic Acid (Sigma Aldrich, ≥ 98%), Toluene (Merck, ≥ 99.9%), 2-Propanol (Merck, ≥ 99.8%), *n*-Dodecane (Merck, ≥ 99.0%), Acetonitrile (Merck, ≥ 99.9%) and KOH solution in methanol, 0.1mol/L.

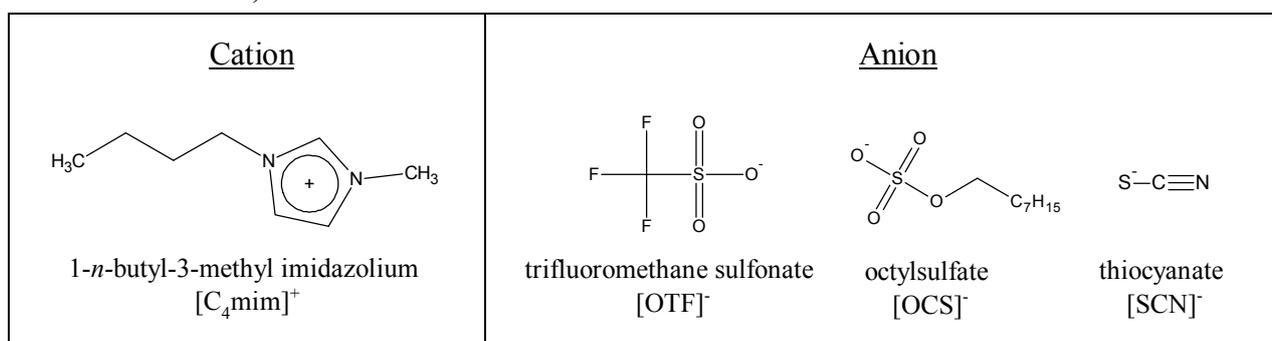


Figure 1: Structure and abbreviations for Imidazolium ionic liquid

### 2.2. Extraction Procedure

Two types of carboxylic acids namely benzoic acid (aromatic type) and *n*-hexanoic acid (aliphatic type) are selected to represent the “model” naphthenic acids. Dodecane, which is a stable hydrocarbon liquid is used as the “model” oil in which the carboxylic acids are dissolved into. Two batches of the model oil containing 2.45wt% of *n*-hexanoic acids and 0.5wt% of benzoic acids are prepared separately. The deacidification experiments are performed by mixing each of the selected ionic liquids with the two model oil 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 phase separation i.e., ionic liquids and oil phase, to take place under gravity for 3 hours. Each layer is then collected for TAN measurement. The Total Acid Number (TAN) is determined using potentiometric titration on each layer 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 the Equation 1 as below.

$$\text{Extraction Efficiency} = \frac{C_0 - C_1}{C_0} \times 100\% \quad (1)$$

Where,  $C_0$  is initial total acid number (TAN) in mg KOH/g,  $C_1$  is final total acid number (mg KOH/g). In addition, the infrared absorption spectra for the two layers 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 from  $4000\text{cm}^{-1}$  to  $650\text{cm}^{-1}$ .

### 2.3. COSMO-RS evaluation on the extraction process

The deacidification extraction efficiency could be predicted from the selectivity and capacity parameters determined from the COSMO-RS software. The two parameters are calculated from the ionic liquids activity coefficient determined using COSMOTherm. In addition, the sigma profile generated from the COSMO-RS could be used to identify the possible dominant interaction mechanism i.e., hydrogen bonding, Van der Waals forces or electrostatic interactions, which will mainly governs the extraction process.

All the COSMO-RS calculations are done using COSMOTherm software version C21\_0111 with the thermodynamics properties determined using BP\_TZVP\_C21\_0111 parameterization. The activity coefficients are calculated based on the equation below [14]:-

$$\gamma_{S^{Xi}} = \exp\left\{\frac{\mu_S^X - \mu_{Xi}^{Xi}}{RT}\right\} \times \frac{1}{2} \quad (2)$$

Where  $\gamma$  is the activity coefficient,  $\mu$  is the chemical potential,  $\mu_S^X$  is the chemical potential in the solvent,  $\mu_{Xi}^{Xi}$  is the chemical potential of pure compound. The capacity and selectivity parameters are calculated using the two equations below:

$$\text{Capacity at infinite dilution } (C^\infty) = \frac{1}{\gamma^\infty} \quad (3)$$

$$\text{Selectivity at infinite dilution } (S^\infty) = \left(\frac{\gamma_2^\infty}{\gamma_1^\infty}\right) \quad (4)$$

The capacity parameter,  $C^\infty$  reflects the amount of carboxylic acids that can be extracted by the ionic liquids. Higher value indicates lesser amount of ionic liquids needed for the extraction process. On the other hand, the selectivity parameter,  $S^\infty$  corresponds to the degree of preference on the type of carboxylic acid extracted by the ionic liquids [15]. Higher value indicates better separation due to low cross solubility between the ionic liquids and the oil phase.

## 3. Results and discussions

### 3.1. Extraction Efficiency

Using the ASTM 664 method, the lowest acid number that can be measured is 0.5mg KOH/g. The detection limit can be enhanced by diluting the titrant concentration to 0.01mol KOH/g. In this case, all the ionic liquids showed good extraction results as shown in Table 1. Almost complete removal of the two carboxylic acids was observed for all the ionic liquids used. The initial TAN values for the model oil containing hexanoic acid and benzoic acid are 10.978mg KOH/g and 2.165mg KOH/g respectively which exceed the TAN values for all types of crude oil known to authors. The deacidification of the model oil using imidazolium ionic liquids is capable to reduce the acidity level down to less than 0.1mg KOH/g. Another important observation from the results in Table 1 indicates that the affinity of the ionic liquids used was slightly more towards benzoic acid than n-hexanoic acid.

No	Ionic Liquids	Extraction Efficiency (%)	
		Extraction with model oil containing 2.5wt% hexanoic acid in dodecane	Extraction with model oil containing 0.5wt% benzoic acid in dodecane
1	[C <sub>4</sub> mim][SCN]	99.12	100.00
2	[C <sub>4</sub> mim][OCS]	99.55	100.00
3	[C <sub>4</sub> mim][OTF]	100.00	100.00

Table 1: Extraction efficiency of carboxylic acid removal from dodecane using ionic liquids

### 3.2. ATR-Infrared Analysis

The FTIR analysis is normally used to identify functional groups presence in any mixtures. Basically, the carboxylic acid exhibit strong carbonyl, C=O stretching band located between  $1710$  to  $1685\text{cm}^{-1}$  [16]. The C=O peak appears in [C<sub>4</sub>mim][SCN] phase after extraction process indicates the presence of hexanoic acid inside the ionic liquids. However, the intensity of the carbonyl peak appears to be really low due to the low concentration of hexanoic acid compared to the volume of the ionic liquids. To confirm the finding, another batch of pure [C<sub>4</sub>mim][SCN] was spiked directly with higher concentration of hexanoic acid before performing the ATR-IR measurement. The result shows that the carbonyl peak appears at the same wavelength hence confirming the presence of the hexanoic acid in the ionic liquids phase after extraction process. As for the other functional groups presence in the ionic liquids, the absorption peak representing them still appear at the same wavelength with similar intensity, indicating that the ionic liquid structure remained intact after the extraction process. Thus, it can be concluded that the extraction mechanism is based on physical extraction.

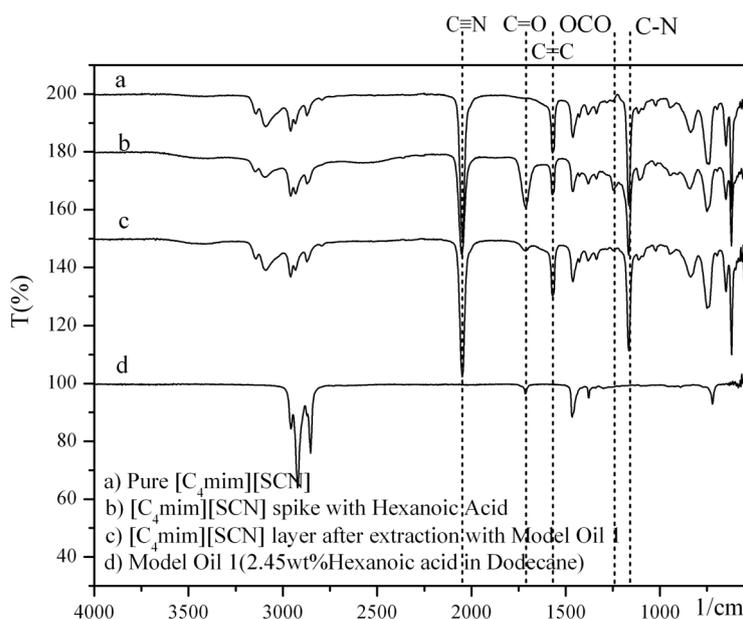


Figure 2: Absorption spectra for C=O functional groups in [C<sub>4</sub>mim][SCN] phase

### 3.3. COSMO-RS Evaluation

The extraction efficiency results presented in Table 1 is then used as a reference for evaluating the predicted same ionic liquids performance for the deacidification process using COSMO-RS simulation based on its capacity and selectivity parameters. The results on the two parameters are shown in Figure 3 and Figure 4, in the form of bar chart. Note that these parameters are determined using equation 3 and 4. The capacity of [C<sub>4</sub>mim][SCN] showed the highest value for benzoic acids. While for hexanoic acid, the [C<sub>4</sub>mim][OCS] showed the highest value. The capacity of 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].

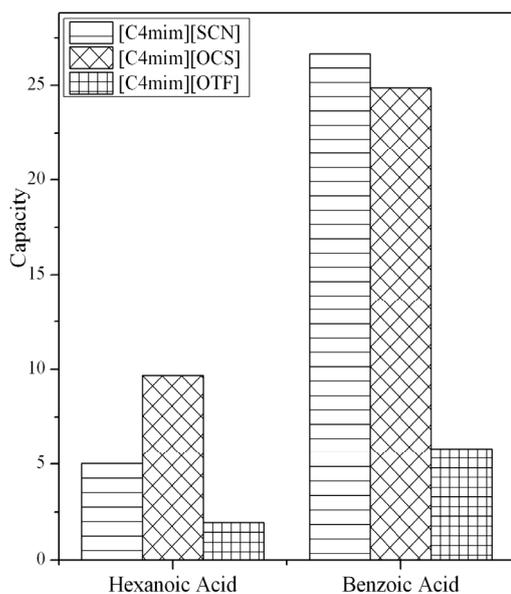


Figure 4: Ionic Liquids capacity for carboxylic acids

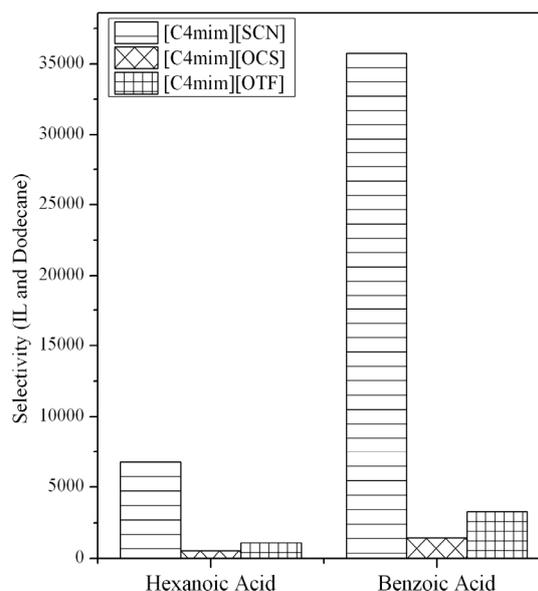
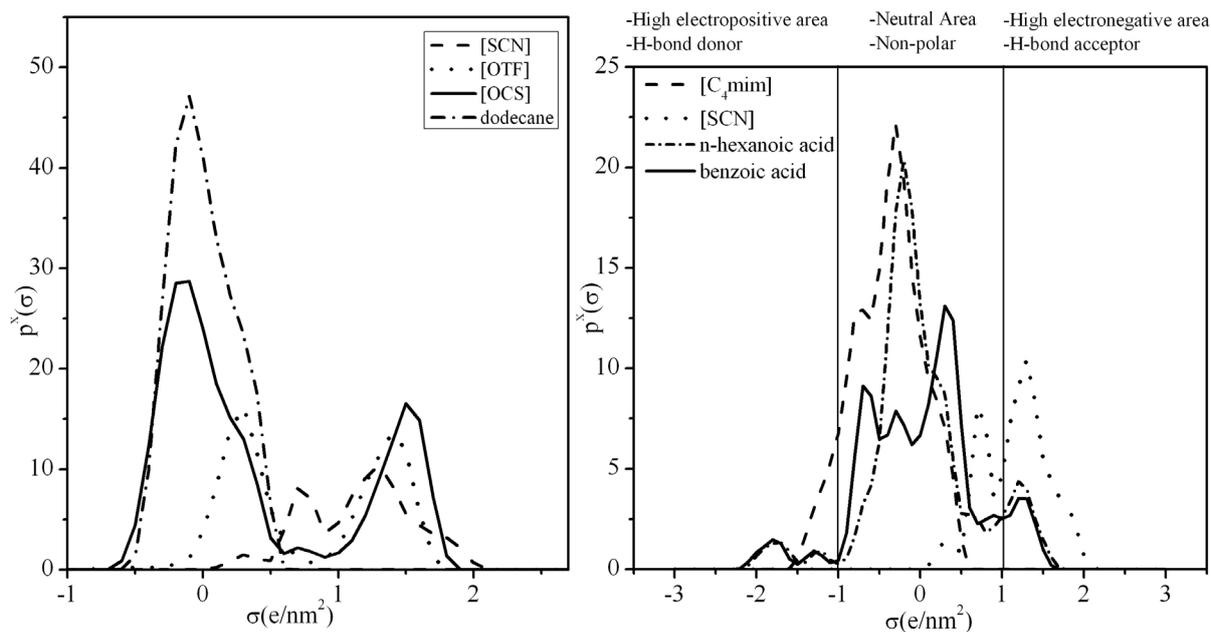


Figure 5: Selectivity of ionic liquids between carboxylic acids and dodecane

The results for the ionic liquids selectivity between hexanoic acid and dodecane are listed according to the following rank; [SCN] > [OTF] > [OCS]. For selectivity, [C<sub>4</sub>mim] [SCN] exhibit the highest selectivity towards the two acids compared to dodecane. This means that the ionic liquid could be easily separated from the hydrocarbon. On the other hand, both [C<sub>4</sub>mim] [OTF] and [C<sub>4</sub>mim] [OCS] show very low selectivity towards the two acids compared to dodecane thus signifying higher chances of dodecane to also be dissolved in the ionic liquids together with the acids. The effect was confirmed by the experiments conducted where the amount of model oil after the extraction process was found to decrease compared to the initial amount of the model oil used for the extraction. This condition is not favourable particularly in the refining industry where complex hydrocarbon mixtures such as crude oil are involved.

In COSMO-RS, the interaction energy of the surfaces are calculated and presented in a histogram  $\rho x(\sigma)$  plot [9]. These plots as shown in Figure 6 and 7 are also known as the sigma ( $\sigma$ ) profile. In the sigma profile, any peak observed at  $>1.0e/nm^2$  refers to the presence of negative lone pair atoms while any peak at  $<-1.0e/nm^2$  refers to the presence of positively polar surfaces. The peaks observed between  $<+1.0e/nm^2$  and  $>-1.0e/nm^2$  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 [9]. From Figure 6, it can be seen that polarization charge densities profile of the negative lone pair for [SCN] anion terminates at  $2.1e/nm^2$  which is largest among the ionic liquids anions followed by the [OTF] and the [OCS] anion which terminates at  $1.7e/nm^2$  and  $1.8e/nm^2$  respectively. Thus, the [SCN] anion could 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  $1.5e/nm^2$  representing the four oxygen atom of the polar sulphate area. Whereas the peak at  $-0.1e/nm^2$  shows the non polar hydrocarbon chain of the [OCS] anion. The negative molecular surfaces 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 signifying the ionic liquid is also extracting the dodecane in addition to the carboxylic acids during the deacidification process.

The same condition is observed for [OTF] anion. However for the [SCN] anion, the peak area of the anion has less overlap with the dodecane but more with the carboxylic acids. Thus it resulted in higher selectivity of the [SCN] ionic liquids towards the carboxylic acids.



## 4. Conclusions

In conclusion, the capability of three types of potential ionic liquids for extracting carboxylic acids from hydrocarbon phase 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 up to 99%. Based on computational molecular simulation, the capacity and selectivity of ionic liquids toward carboxylic acids were determined. The ionic liquids with [SCN] anion exhibits the highest capacity for benzoic acids and the highest selectivity for both benzoic and hexanoic acid. Using the sigma profile developed using COSMO-RS, the polarization charge density was used to explain the interaction between the anion and the carboxylic acids leading to the findings of the experimental work.

## 5. Acknowledgements

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## 6. References

- [1] J.S. Clemente, P.M. Fedorak, A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids, *Chemosphere*. 2005, 60:585-600.
- [2] G. Sartori, D.W. Savage, B.H. Ballinger, Process for neutralization of petroleum acids, in: *United States Patent*, Exxon Research and Engineering Company, 1997, pp. 1-4.
- [3] G. Sartori, D.W. Savage, M.L. Gorbaty, B.H. Ballinger, S.C. Blum, M.P. Anderson, T.A. Ramanarayanan, D.J. Martella, Process for decreasing the acid content and corrosivity of crudes, in: *United States Patent*, Exxon Research and Engineering Company, 2000, pp. 1-11.
- [4] H.M. Shalaby, Refining of Kuwait's heavy crude oil: Materials challenges, *Workshop on Corrosion and Protection of Metals*, Arab School for Science and Technology, December 3-7
- [5] Y. Nie, C. Li, A. Sun, H. Meng, Z. Wang, Extractive Desulfurization of Gasoline Using Imidazolium-Based Phosphoric Ionic Liquids, *Energy & Fuels*. 2006, 20:2083-2087.
- [6] A. Bosmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, P. Wasserscheid, Deep desulfurization of diesel fuel by

extraction with ionic liquids, *Chemical Communications*. 2001: 2494-2495.

- [7] A.R. Hansmeier, G.W. Meindersma, A.B. de Haan, Desulfurization and denitrogenation of gasoline and diesel fuels by means of ionic liquids, *Green Chem.* 2011, 13:1907-1913.
- [8] K. Kędra-Krolik, F. Mutelet, J.-C. Moïse, J.-N. Jaubert, Deep Fuels Desulfurization and Denitrogenation Using 1-Butyl-3-methylimidazolium Trifluoromethanesulfonate, *Energy & Fuels*. 2011, 25: 1559-1565.
- [9] A. Klamt, COSMO-RS from quantum chemistry to fluid phase thermodynamics and drug design, *Elsevier*, Amsterdam, The Netherlands, 2005.
- [10] B. Burghoff, E.L.V. Goetheer, A.B.d. Haan, COSMO-RS-Based Extractant Screening for Phenol Extraction As Model System, *Ind. Eng. Chem. Res.* 2008, 47: 4263-4269.
- [11] Spieß, Antje C., Werner Eberhard, Martina Peters, Marrit F. Eckstein, Lasse Greiner, and Jochen Büchs. Prediction of Partition Coefficients Using Cosmo-Rs: Solvent Screening for Maximum Conversion in Biocatalytic Two-Phase Reaction Systems, *Chemical Engineering and Processing* .2008, 47: 1034-41.
- [12] A.R. Hansmeier, M. Jongmans, G. Wytze Meindersma, A.B. de Haan, LLE data for the ionic liquid 3-methyl-N-butyl pyridinium dicyanamide with several aromatic and aliphatic hydrocarbons, *J. Chem. Thermodyn.* 2010, 42: 484-490
- [13] A.A.P. Kumar, T. Banerjee, Thiophene separation with ionic liquids for desulphurization: A quantum chemical approach, *Fluid Phase Equilib.* 2009, 278: 1-8.
- [14] M. Diedenhofen, A. Klamt, COSMO-RS as a tool for property prediction of IL mixtures--A review, *Fluid Phase Equilib.* . 2010, 294 :31-38
- [15] M. Krummen, P. Wasserscheid, J. Gmehling, Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique, *J. Chem. Eng. Data.* 2002, 47:1411-1417.
- [16] B. Smith, Infrared Spectral Interpretation; A Systematic Approach, *CRC Press LCC*, 1999.
- [17] M.G. Freire, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, Evaluation of COSMO-RS for the prediction of LLE and VLE of alcohols + ionic liquids, *Fluid Phase Equilib.* 2007, 255:167-178.