



## Experiments, correlations and COSMO-RS predictions for the extraction of benzothiophene from *n*-hexane using imidazolium-based ionic liquids

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### ABSTRACT

The extraction of benzothiophene from *n*-hexane was studied using 1-ethyl-3-methylimidazolium ethyl sulphate ([EMIM][EtSO<sub>4</sub>]) and 1-ethyl-3-methylimidazolium acetate ([EMIM][CH<sub>3</sub>COO]) at 308.15 K to analyze the performance of ionic liquids in the extractive desulphurization of aromatic sulphur compounds from petroleum fuels. A comparative study was done from the perspective of selectivity and distribution coefficient of the sulphur compounds. From the ternary LLE (liquid–liquid extraction) experiments, it was found that while the selectivity was higher for the ethyl sulphate-based ionic liquids, the distribution coefficient was higher for acetate-based ionic liquids. Selectivities as high as 245 and 203 were obtained for [EMIM][EtSO<sub>4</sub>] and [EMIM][CH<sub>3</sub>COO] with negligible loss of hydrocarbon. The experimental results were correlated using the NRTL and UNIQUAC models. The root mean square deviation (RMSD) values of 0.48% and 0.83% were obtained for [EMIM][EtSO<sub>4</sub>] and [EMIM][CH<sub>3</sub>COO] respectively, when using the NRTL model, and the corresponding RMSD values when using the UNIQUAC model were 0.693% and 1.053%. The quantum chemical based COnductor like Screening MOdel for Real Solvent (COSMO-RS) model was then used to predict the performance of single as well as mixed ionic liquids. RMSDs of 4.36% and 7.87% were achieved for [EMIM][EtSO<sub>4</sub>] and [EMIM][CH<sub>3</sub>COO] based system, which are satisfactory considering that the method is *a priori*.

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### 1. Introduction

The production of zero-emission diesel fuel is an area that is receiving considerable attention in the industry owing to the limit set by the federal agencies on sulphur levels in diesel. According to the standards adopted by the Environmental Protection Agency (EPA), the maximum allowable sulphur content in fuels is set at 15 ppm [1]. According to the emission standards adopted by the European Committee for Standardization (CEN), in their Euro 5/6 standards, these limits are set to a maximum of 10 ppm [2].

During conventional hydrodesulphurization (HDS) process hydrogen reacts with sulphur compounds in presence of catalyst at severe operating temperature and pressure. Transition metal sulphides modified by cobalt, and supported on  $\gamma$ -alumina are generally used as catalysts. The chief transition metals used are molybdenum, nickel and tungsten [3]. The major process variables that affect the HDS process are pressure and temperature. The typical conditions adopted are high temperatures of 350 °C and pressure greater than 30 bar. To achieve such extreme conditions, high energy consumption and investment cost for reactor, vessels and pumps become essential. Higher temperature also increases

the coke formation which acts detrimental to the life of the catalyst. When desulfurized at high pressure, various side reactions also occur, one of which is the saturation of olefins. Olefins make a significant contribution to the octane number, which make such side reactions undesirable [4,5]. Apart from pressure and temperature, other variables that are frequently used to describe the operating conditions are hydrogen purity and the gas/oil ratio [6]. Since the effluent stream from the hydrotreater consists of unreacted hydrogen, this needs to be further recycled. The recycled hydrogen contains impurities such as H<sub>2</sub>S and methane, which have to be separated [7].

The molecular structure and properties of the sulphur compounds present in the fuel play an important role in deciding the reactivity of such compounds during the HDS process. The aliphatic sulphur compounds like thiols (R-SH), thioethers (R-S-R), and disulphides (R-S<sub>2</sub>-R) are very reactive in the HDS process, and are completely removed from fuels without much difficulty. However, a class of sulphur compounds known as the refractory sulphur compounds are not easily removed during HDS due to its immunity to the HDS catalyst. These difficulties arise due to the various surface interactions and steric hindrance exhibited by these compounds. These compounds include thiophenes, benzothiophenes and their derivatives [8–12]. The removal of such aromatic sulphur compounds is now becoming not only a serious challenge to the HDS process, but also extremely essential because of the statu-

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### Nomenclature

[EMIM]	Cation: 1-ethyl-3-methylimidazolium
[OMIM]	Cation: 1-octyl-3-methylimidazolium
[EtSO <sub>4</sub> ]	Anion: ethyl sulphate
[CH <sub>3</sub> COO]	Anion: acetate
[NtF <sub>2</sub> ]	Anion: bis-(trifluoromethanesulphonyl)-imide
TMAC	Trimethyl aluminium chloride
S	Selectivity
F	Objective function
RMSD	Root mean square deviation
$a_{\text{eff}}$	Effective segment surface area ( $\text{\AA}^2$ )
$c_{\text{hb}}$	Misfit energy constant ( $\text{kcal}\text{\AA}^4\text{mol}^{-1}\text{e}^{-2}$ )
$p_i(\sigma)$	Sigma profile of component $i$ , i.e. probability of segment $i$ having a charge density $\sigma$
R	Universal gas constant ( $\text{J K}^{-1}\text{mol}^{-1}$ )
T	Temperature (K)
$r_i$	Normalized volume parameter for the Staverman–Guggenheim combinatorial term ( $\text{\AA}^3$ )
$q_i$	Normalized surface area parameter for the Staverman–Guggenheim combinatorial term ( $\text{\AA}^2$ )
$r_{\text{std}}$	Standard volume parameter, $79.53\text{\AA}^3$
$q_{\text{std}}$	Standard surface area area parameter, $66.69\text{\AA}^2$
$m$	Number of tie lines
$c$	Number of components in the LLE system
$x_i$	Mole fraction of component $i$ of either phase in the LLE system
$n_i$	Total number of segments on the surface of the molecular cavity
$H_i$	Peak area under NMR spectra of species $i$
$z$	Coordination number = 10
$l$	Staverman–Guggenheim combinatorial term parameter
$g_{ji}$	Average interaction energy for the interaction of molecules of component $j$ with molecules of component $i$
<b>Greek letters</b>	
$\alpha'$	Misfit energy constant ( $\text{kcal}\text{\AA}^4\text{mol}^{-1}\text{e}^{-2}$ )
$\sigma_{\text{hb}}$	Hydrogen bonding cut-off value, $0.0084\text{e}\text{\AA}^{-2}$
$\gamma_{i/S}$	Activity coefficient of solute $i$ in solution S
$\Gamma_S$	Segment activity coefficient of segment $\sigma_i$ in pure species
$H_i$	Peak area under NMR spectra of species $i$
$\beta$	Distribution coefficient
$\theta$	Area fraction in UNIQUAC equation
$\tau$	NRTL/UNIQUAC interaction parameter
$\Phi$	Segment fraction in UNIQUAC equation
$\alpha$	NRTL non-randomness parameter
$\gamma_{i/S}^{\text{SG}}$	Staverman–Guggenheim activity coefficient

tory regulatory norms. To meet these requirements, many new methods have been in study for the past few years. These include solvent extraction, reactive distillation, biodesulfurization, oxidative desulphurization, and adsorption [12,13]. Also, new advanced catalysts are being suggested to improve upon the present catalyst [14].

Ionic liquids, provides a suitable alternative to the conventional HDS process, due to their effectiveness in the removal of the otherwise refractory aromatic sulphur compounds. There are a number of favourable properties of ionic liquids that allow them to

be competitive solvents. Ionic liquids are environmentally benign, non-volatile, non-flammable, highly solvating and have a high thermal stability over a wide temperature range [15]. The most commonly studied ionic liquids are based on the imidazolium cation with fluorinated anions [BF<sub>4</sub>], [PF<sub>6</sub>]. However, the instability of such anions in the presence of water is drastic since the decomposition of these fluorinated anions leads to the formation of highly toxic and corrosive HF. On the other hand ionic liquids with anions such as alkyl sulphate are free from halogen and are known to be non-toxic. They are easy to synthesis and known to have excellent purity. Additionally they possess low viscosities and low melting points [16]. Moreover, their affinity for aromatic sulphur compounds is very high, and they are virtually immiscible with diesel, preventing cross-contamination. Post extraction, the sulphur compounds can be easily recovered by a simple heating process [17]. Moreover, due to the abundance of cations and anions, many combinations are possible, allowing one to fine tune the various physical and chemical properties depending on the extraction process.

Over the past few years, considerable amount of experimental and modeling work have been done using imidazolium-based ionic liquids with different alkyl groups substituted on the ring, which has yielded positive results for the extraction of the various aromatic sulphur compounds. Most of the research has been concentrated on the recovery of thiophene from model fuels like *n*-hexane, toluene, cyclohexane, etc. In a recent study, the potential of polysubstituted pyridinium-based ionic liquids for the extraction of thiophene from different model fuels was studied [18]. Pyridinium based ionic liquids also showed potential in removing sulphur with a high sulphur removal after multiple extraction cycles [19]. The ionic liquid [OMIM][BF<sub>4</sub>] used for extracting thiophene from *i*-octane yielded selectivities up to 27.62, and a high solubility of thiophene in the IL-phase, which establishes the high affinity of aromatic compounds for the ionic liquids [20,21]. In a separate study, the ionic liquid [OMIM][NtF<sub>2</sub>] was used to analyze the effect of the *n*-alkane on the extraction process [22]. Ionic liquids with an alkyl substituted imidazolium group as cation and different anions were used for the extraction of thiophene and its derivatives from model fuels [23]. A comprehensive analysis of the performance of alkylimidazolium-based ionic liquids with BF<sub>4</sub> and PF<sub>6</sub> as the anions was done by Zhang et al. [24], which showed an improvement in performance when the latter anion was used. This also illustrated the use of AlCl<sub>3</sub>-TMAC ionic liquid, which was lauded for its ease of preparation and highly effective sulphur removal, but at the cost of demerits like moisture sensitivity and colour formation. Domanska et al. [25] studied the LLE and SLE (solid–liquid equilibria) of binary systems which involved an ionic liquid and thiophene. An extensive study spanning ten ionic liquids was done in the study.

Predictive analysis of the selectivities of various ionic liquids for the extraction of thiophene at infinite dilution was done using the COSMO-RS model. The novelty of COSMO-RS model is that it is independent of experimental data and the only input required is the molecular structure [26–31]. It predicts the non-ideal liquid phase activity coefficient from which one can calculate phase equilibria such as LLE and SLE. From our earlier study, considerably high selectivities were achieved for acetate and ethyl sulphate based ionic liquids [26]. It was also found that a smaller cation led to a higher selectivity. Due to this we have chosen the cation as 1-ethyl-3-methylimidazolium ([EMIM]). In the present study, the effectiveness of imidazolium-based ionic liquids with the associated anions, acetate and ethyl sulphate is studied for the extraction of benzothiophene from a model fuel, *n*-hexane. The structure of the ionic liquid and benzothiophene are given in Fig. 1.

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