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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][$EtSO_4$]) and 1-ethyl-3-methylimidazolium acetate ([EMIM][CH_3COO]) 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][$EtSO_4$] and [EMIM][CH_3COO] 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][$EtSO_4$] and [EMIM][CH_3COO] 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][$EtSO_4$] and [EMIM][CH_3COO] based system, which are satisfactory considering that the method is *a priori*.

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 γ-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_2S 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_2-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
[$EtSO_4$]	Anion: ethyl sulphate
[CH_3COO]	Anion: acetate
[NtF_2]	Anion: bis-(trifluoromethanesuphonyl)-imide
TMAC	Trimethyl aluminium chloride
S	Selectivity
F	Objective function
RMSD	Root mean square deviation
a_{eff}	Effective segment surface area (Å^2)
c_{hb}	Misfit energy constant (kcal Å^4 mol^{-1} e^{-2})
$p_i(\sigma)$	Sigma profile of component *i*, i.e. probability of segment *i* having a charge density σ
R	Universal gas constant (J K^{-1} mol^{-1})
T	Temperature (K)
r_i	Normalized volume parameter for the Staverman–Guggenheim combinatorial term (Å^3)
q_i	Normalized surface area parameter for the Staverman–Guggenheim combinatorial term (Å^2)
r_{std}	Standard volume parameter, 79.53 Å^3
q_{std}	Standard surface area area parameter, 66.69 Å^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*

Greek letters

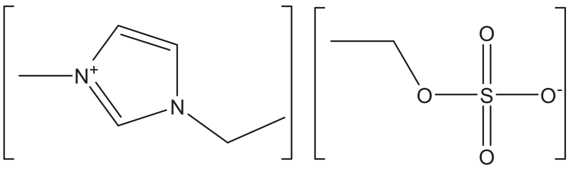
α'	Misfit energy constant (kcal Å^4 mol^{-1} e^{-2})
σ_{hb}	Hydrogen bonding cut-off value, 0.0084 e Å^{-2}
$\gamma_{i/S}$	Activity coefficient of solute *i* in solution *S*
Γ_S	Segment activity coefficient of segment σ_i in pure species
H_i	Peak area under NMR spectra of species *i*
β	Distribution coefficient
θ	Area fraction in UNIQUAC equation
τ	NRTL/UNIQUAC interaction parameter
Φ	Segment fraction in UNIQUAC equation
α	NRTL non-randomness parameter
$\gamma_{i/S}^{SG}$	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].

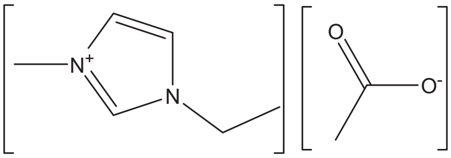
Ionic liquids, provides a suitable alternative to the conventional HDS process, due to their effectiveness in the removal of the otherwise refractory aromatic sulphur compounds. There are a number of favourable properties of ionic liquids that allow them to be competitive solvents. Ionic liquids are 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_4], [PF_6]. 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 posses 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_4] 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_2] 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_4 and PF_6 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 $AlCl_3$-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.

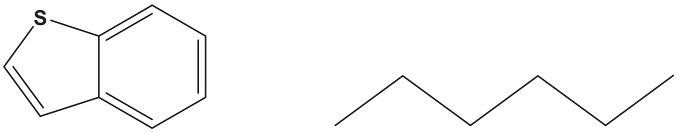
Predictive analysis of the selectivities of various ionic liquids for the extraction of thiophene at infinite dilution was done using the COSMO-RS model. The novelty of COSMO-RS model is that it is independent of experimental data and the only input required is the molecular structure [26–31]. It predicts 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.



1-Ethyl-3-Methylimidazolium ethylsulphate



1-Ethyl-3-Methylimidazolium acetate



Benzothiophene n-Hexane

Fig. 1. Chemical structure of studied ionic liquids, benzothiophene and *n*-hexane.

2. COSMO-RS model

The Conductor-like Screening Model (COSMO) is described by Klamt and Schüürmann [27]. In the extension termed as COSMO-RS, i.e. Real Solvents, individual molecules are treated as a collection of surface segments wherein the chemical potential of all the segments are added to get the non-ideal liquid phase activity coefficient [28]. In our work, the COSMO-RS model was used to predict the composition of ternary LLE systems containing ionic liquids, wherein the compositions of the extract and raffinate phase are calculated from the modified Rachford Rice algorithm [29]. In COSMO-RS, the interaction energies between the various segments are categorized into two types, namely, the misfit energy, E_{misfit} and the hydrogen bond energy, E_{hb}. The expressions and methodology for obtaining these parameters are given in details from our previous work [30–32]. The interaction energies are characterized by the COSMO-RS parameters, $a_{\text{eff}} = 6.25\,\text{Å}^2$ (surface area of a standard segment), $\alpha' = 8896\,\text{kcal}\,\text{Å}^4\,\text{mol}^{-1}\,\text{e}^{-2}$ (misfit energy constant) for misfit energy interaction, $c_{hb} = 54{,}874\,\text{kcal}\,\text{Å}^4\,\text{mol}^{-1}\,\text{e}^{-2}$ (hydrogen bonding energy constant) and $\sigma_{hb} = 0.0085\,\text{e}\,\text{Å}^{-2}$ (hydrogen bonding cutoff). These parameters are acquired from our earlier work [31].

2.1. Computational details

The sigma profiles of the individual molecules are the input for conducting the COSMO-RS predictions, and these are generated using GAUSSIAN 03 Quantum Chemistry package [33]. The equilibrium geometry of the cations and anions in the ideal gas phase are first obtained separately using the density functional theory (DFT) of PBV86 [34]. The triple zeta valence potential (TZVP) [35] basis set has been used in combination with the density fitting basis set DGA1 [36]. The COSMO file, which contains the ideal screening charges on the molecular surface are then computed using the same level of theory, PBV86 using the keyword *SCRF = COSMORS*. Prior to the generation of the COSMO file, the initial geometry and frequency optimization of the structure is done using the Hartree-Fock level of theory [37]. The geometry optimization of the molecule is done using the visualization software MOLDEN [38]. The structure prepared in MOLDEN is used by the Gaussian03 software to conduct the geometry optimization. The objective is to obtain true minimum energy geometry of the molecule. From the geometry and frequency optimization, the optimized structure for COSMO file generation is obtained.

In case of the ionic liquid, the COSMO file generation is essentially the same as described, except that here we do the optimization separately for the cation and the anion. For the cation, a stepping stone approach was used, starting with the imidazolium ring and adding successive carbons until the desired cation was constructed. We found a planar structure for the imidazolium cation which agrees well with the previous studies of Turner et al. [39]. Frequency optimization using the keyword *freq* was done at the same level on the optimal cation geometry in order to detect the presence of any imaginary or negative frequencies. The absence of negative vibrational frequencies implied the existence of a true minimum. A similar approach for the anion was followed with the exception of stepping stone approach.

2.2. Sigma profile of ionic liquid

From our previous work [40], it was found that the linear addition of sigma profiles of the cation and anion yielded excellent results. Additionally this approach can easily study various combination of ionic liquids from the same COSMO files of cations and anions which has to be generated once. Therefore, the same approach is adopted here, from which we obtain the sigma profile of the liquid as,

$$p_{ionic\quad liquid}(\sigma) = p_{cation}(\sigma) + p_{anion}(\sigma) \tag{1}$$

where $p_{cation}(\sigma)$ and $p_{anion}(\sigma)$ are the sigma profiles of the cation and anion respectively. Likewise, the COSMO volume and area [41] are also added linearly. The sigma profiles are then normalized so that it would appear as if it is the profile of a single molecule of the ionic liquid. The sigma profiles of the sulphur compound, benzothiophene and *n*-hexane are also obtained in a similar manner. The goodness of fit for prediction is usually gauged by root mean square deviation (RMSD), which is defined as:

$$RMSD\,(\text{in}\,\%) = 100 \times \left[\sum_{k=1}^{m} \sum_{i=1}^{c} \sum_{j=1}^{2} \frac{(x_{ik}^{j} - \hat{x}_{ik}^{j})^2}{2mc} \right]^{1/2} \tag{2}$$

where '*m*' refers to the number of tie lines, '*c*' the number of components and '2' is the number of phases.

3. Experimental

3.1. Chemicals and materials

The ionic liquids 1-ethyl-3-methylimidazolium ethyl sulphate of purity >95% and 1-ethyl-3-methylimidazolium acetate of purity >98%, were supplied by Sigma–Aldrich, Germany. Benzothiophene of 95% purity was supplied by Sigma–Aldrich, Germany. *n*-Hexane of 99.9% purity was supplied by Merck Specialities Private Limited, India. $CDCl_3$ of purity >99.8%, used for the NMR analysis of the extract and raffinate phase compositions was supplied by Sigma–Aldrich, Germany. All the chemicals were used without further purification. The comparisons of physical properties of the individual components have been reported in Table 1. Densities of the pure components were measured at atmospheric pressure with Anton Paar DSA-4500 MA digital vibrating U-tube densimeter. The uncertainty in the density measurement is $\pm 0.0011\,\text{g}\,\text{cm}^{-3}$. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air.

Table 1
Physical properties of components used in this work.

Component	CAS no.	M.W/g	ρ/g cm^{-3}	
			Present study	Literature
[EMIM][CH_3COO]	143314-17-4	206.26	1.0273	NA
[EMIM][$EtSO_4$]	342573-75-5	236.29	1.2421	1.2423 [42]
Benzothiophene	110-54-3	134.20	1.1604	NA
Hexane	95-15-8	86.18	0.6596	0.6551 [22]

3.2. Procedure

Feed mixtures of equimolar concentrations of the ionic liquid and *n*-hexane, with the benzothiophene concentrations varying from 5 to 50% were first prepared. All weighing was carried out in a Mettler Toledo AT 261 balance with an accuracy of $\pm 10^{-4}$ g. The total volume of all the feed mixtures was fixed at 8 ml. Capped glass bottles of a total capacity of 20 ml volume were used for holding the feed mixtures. The samples were properly sealed with parafilm tape to avoid any loss of the components due to evaporation. The bottles were then placed inside a water-shaker bath set at 308.15 K, and allowed to shake for not less than 6 h at 100 rpm in thermostatic shaker bath (Dailhan Lab, China). Spring clamps were used to hold the flasks on the tray. The temperature was accurate within an error of ±0.01 K, and was set to 308.15 K for all samples. The mixture was then allowed to settle for a minimum of 12 h so that equilibrium is attained. The LLE experiment was conducted at T = 308.15 K which is the melting point of benzothiophene. We selected this temperature since below this temperature benzothiophene is solid and the solubility of benzothiophene in IL or hexane is not known in literature. So in order to carry liquid–liquid equilibria we conducted the experiment at 308.15 K.

3.3. Compositional analysis

For doing compositional analysis, samples of each phase in equilibrium were taken using syringes. A drop of each phase was dissolved in 0.5 ml of $CDCl_3$ and placed inside NMR tubes (thrift Grade), which were properly sealed. The NMR spectrometer of 11.74 T (20 MHz response of ^1H) was used to conduct the ^1H NMR spectral analysis for the measurement of the peak areas of the hydrogen molecule of each component.

The aromatic sulphur compounds show a peak in the range of 7.5–7.8, the hydrocarbon (i.e. hexane) in the range of 1.1–1.3 for the $-CH_2-$ linkage, and below 1.1 for the $-CH_3$ group. The peaks of the ionic liquid are obtained in the range of 3–4, depending on the anion attached to the imidazolium ring. From these ranges, the peak areas of the individual hydrogen atoms belonging to the respective components were obtained by automatic integration of the NMR spectrogram. The equation used to calculate the concentration is given as follows,

$$x_i = \frac{H_i}{\sum_{i=1}^{3} H_i} \tag{3}$$

where x_i is the mole fraction of species i and H_i is the peak area of a single hydrogen atom in the component i. For checking the accuracy we prepared some known mixtures in the homogenous region close to the binodal curve and then obtained the ^1H NMR. The measured results were found to be in good agreement with the actual compositions. Calibration lines corresponding to standard deviations of <0.007 for each compound were obtained. The maximum absolute deviation was found to be 0.010 in mole fraction.

4. Results and discussions

4.1. Ternary tie-line data

Ternary LLE experiments were done for the systems 1-ethyl-3-methylimidazolium ethyl sulphate (1)-benzothiophene (2)-hexane (3) and 1-ethyl-3-methylimidazolium acetate (1)-benzothiophene (2)-hexane (3) at 308.15 K. These experiments were done so as to compare the potential of the individual ionic liquids on their performance in the extraction of benzothiophene from hexane.

The sample tie lines range from a feed concentration of 5–50% benzothiophene (mole basis). An equimolar ratio of ionic liquid over the hydrocarbon was considered for all the samples. The tie line compositions for these systems are reported in Tables 2 and 3. The selectivity and distribution coefficient for the corresponding tie line data are calculated from Eqs. (4) and (5) respectively.

$$S = \frac{x_{BT}^E}{x_{BT}^R} \times \frac{x_{HX}^R}{x_{HX}^E} \tag{4}$$

$$\beta = \frac{x_{BT}^E}{x_{BT}^R} \tag{5}$$

where x_{BT} and x_{HX} denote mole fraction of benzothiophene (BT) and hexane (HX) in extract phase, E and raffinate phase, R respectively. For both the systems, the values of selectivity and distribution coefficient decreased as the concentration of benzothiophene in the feed increased. The distribution coefficient and selectivity is especially higher for lower concentrations of benzothiophene in the feed. Since the quantity of sulphur compounds in the actual crude is in ppm level, these results are favourable for analyzing the

Table 2
Experimental tie lines for the system [EMIM][$EtSO_4$](1)–benzothiophene(2)–*n*-hexane(3) at 308.15 K.

Extract phase			Raffinate phase			S	β
(1)	(2)	(3)	(1)	(2)	(3)		
0.9287	0.0641	0.0072	0.0000	0.0350	0.9651	245.59	1.8365
0.8708	0.1203	0.0089	0.0000	0.0883	0.9117	139.57	1.3625
0.8100	0.1700	0.0200	0.0000	0.1496	0.8504	48.31	1.1362
0.7556	0.2112	0.0332	0.0000	0.2017	0.7983	25.15	1.0471
0.6986	0.2580	0.0434	0.0000	0.3429	0.6571	11.38	0.7523
0.6348	0.3171	0.0481	0.0000	0.4532	0.5468	7.95	0.6996
0.5885	0.3581	0.0534	0.0000	0.5125	0.4875	6.38	0.6988
0.5569	0.3938	0.0493	0.0000	0.5825	0.4175	5.73	0.6760

Table 3
Experimental tie lines and for the system [EMIM][CH_3COO](1)–benzothiophene(2)–*n*-hexane(3) at 308.15 K.

Extract phase			Raffinate phase			S	β_{BT}
(1)	(2)	(3)	(1)	(2)	(3)		
0.9054	0.0832	0.0114	0.0000	0.0346	0.9654	203.63	2.40
0.8542	0.1253	0.0205	0.0000	0.0672	0.9328	84.84	1.86
0.8133	0.1498	0.0369	0.0000	0.0959	0.9041	38.27	1.56
0.7077	0.2234	0.0689	0.0000	0.1671	0.8329	16.16	1.34
0.6542	0.2733	0.0725	0.0000	0.2278	0.7722	12.78	1.20
0.6040	0.3159	0.0801	0.0000	0.2851	0.7149	9.89	1.11
0.5288	0.3844	0.0868	0.0000	0.4250	0.5750	5.99	0.90
0.3824	0.4702	0.1474	0.0000	0.5495	0.4505	2.62	0.86

potential of these ionic liquids for aromatic sulphur extraction on an industrial scale.

From the analysis, it is observed that the concentration of hexane in extract phase was as high as 4.93% in [EMIM][$EtSO_4$] (Table 2) and 14.74% for [EMIM][CH_3COO] (Table 3). It should be noted that this concentration is obtained at the high concentration of benzothiophene in feed mixture. Since the quantity of benzothiophene in the actual crude is in ppm level, these results are favourable. This is of particular importance as this suggests that regeneration of the ionic liquid could be done with negligible loss of hydrocarbon at intermediate or lower concentration of benzothiophene. On the other hand, the corresponding concentration of IL in raffinate phase is zero for both ILs. Thus the ionic liquid does not remain as a impurity in the hydrocarbon or diesel rich phase. A comparison of the selectivity and distribution coefficients with the concentration of benzothiophene in the hydrocarbon-rich phase has been presented in Fig. 2.

The selectivity of [EMIM][$EtSO_4$] is higher than that for [EMIM][$COOCH_3$] for lower concentration of benzothiophene in the feed. The values of selectivity for [EMIM][$EtSO_4$] reached as high as 245.59, while that for [EMIM][$COOCH_3$] went up to 203.63, indicating the increased affinity for aromatic sulphur compounds towards ionic liquids, thereby supporting the well-known fact that as the aromaticity increases, the selectivity also increases. Values as high as 162.95 were achieved by Arce et al. [42] for the extraction of thiophene from hexane using [EMIM][$EtSO_4$]. Also, Zhang et al. [24] revealed a direct correspondence between the aromaticity of the sulphur compound and the affinity towards the ionic liquid.

4.2. NRTL and UNIQUAC correlations

According to the NRTL model [43], the non-ideal liquid phase activity coefficient (γ) of component i is given by the following equation.

$$\ln\gamma_i = \frac{\sum_{j=1}^{c}\tau_{ji}G_{ji}x_j}{\sum_{k=1}^{c}G_{ki}x_k} + \sum_{j=1}^{c}\left[\frac{G_{ij}x_j}{\sum_{k=1}^{c}G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_{i=1}^{c}\tau_{ij}G_{ij}x_i}{\sum_{k=1}^{c}G_{kj}x_k}\right)\right] \tag{6}$$

where

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{7}$$

The UNIQUAC model [44] gives the following equation for the non-ideal activity coefficient for component i.

$$\ln\gamma_i = \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2}q_i\ln\left(\frac{\theta_i}{\Phi_i}\right) + l_i - \frac{\Phi_i}{x_i}\sum_{j=1}^{c}x_j l_j + q_i\left(1 - \ln\sum_{j=1}^{c}\theta_j\tau_{ji} - \sum_{j=1}^{c}\frac{\theta_j\tau_{ij}}{\sum_{k=1}^{c}\theta_k\tau_{kj}}\right) \tag{8}$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{A_{ji}}{T} \tag{9}$$

$$\theta_i = \frac{q_i x_i}{q_T} \tag{10}$$

$$q_T = \sum_k q_k x_k \tag{11}$$

$$\Phi_i = \frac{r_i x_i}{r_T} \tag{12}$$

$$r_T = \sum_k r_k x_k \tag{13}$$

$$l_i = \frac{z}{2}(r_k - q_k) + 1 - r_k \tag{14}$$

In Eqs. (6)–(14), θ, τ and Φ represent the area fraction, interaction parameter and segment fraction, respectively. The pure-component surface area parameter and the pure-component volume parameter in the UNIQUAC model are represented by r and q, respectively. The mole fraction in the liquid phase is represented by x, and the coordination number is represented by $z(=10)$. We have used $\alpha_{ij} = \alpha_{ji} = 0.2$ in our calculations. In Eq. (9), g_{ji} represents the average interaction energy for the interaction of molecules of component j with molecules of component i, R represents the gas constant and T represents the temperature.

The binary interaction parameters were obtained from the experimental LLE data by minimizing the objective function, which was defined as the sum of the square of errors between the experimental and calculated compositions of all the components over the entire set of tie lines as per Eq. (15). The methodology, application and the details are presented in our earlier work [45]. We have taken the population size, *npop* = 100, and the number of generations, *ngen* = 200 for the GA program. As the GA toolbox [46] in

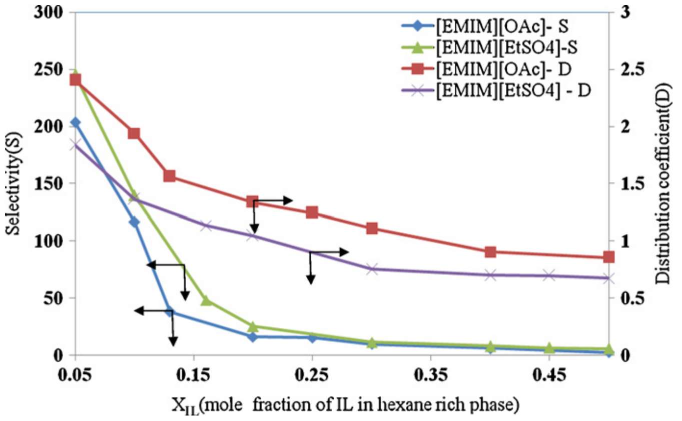


Fig. 2. Comparison of experimental selectivity and distribution coefficient vs. mole fraction of ionic liquid in *n*-hexane-rich phase for the ionic liquids: [EMIM][CH_3COO] and [EMIM][$EtSO_4$] (*S*: selectivity; *D*: distribution coefficient).

Table 4
UNIQUAC structural parameters for the different compounds in the LLE system.

Component	*r*	*q*
1-Ethyl-3-methylimidazolium ethyl sulphate[a]	8.3927	6.6260
1-Ethyl-3-methylimidazolium acetate[a]	8.7500	5.5600
Benzothiophene	5.3803	3.4200
Hexane	4.4998	3.8560

[a] Calculated via [47].

MATLAB is for maximization, the objective function (F) for minimizing the total error between the experimental and calculated mole fractions was defined as,

$$\text{maximize}: \quad F\begin{pmatrix} \text{with respect to } A_{ij} \\ \text{where } i,j=1,2,3 \\ \text{and } j\neq i \end{pmatrix}$$

$$= -\sum_{k=1}^{m}\sum_{l=I}^{II}\sum_{i=1}^{c} w_{ik}^{l}\left(x_{ik}^{l}-\hat{x}_{ik}^{l}\right)^{2}, \quad w_{ik}^{l}=1 \tag{15}$$

The goodness of the fit was measured by the root mean square deviation (RMSD) defined as,

$$RMSD\,(\text{in}\,\%) = \left(-\frac{F}{2mc}\right)^{1/2} = \left[\sum_{k=1}^{m}\sum_{i=1}^{c}\sum_{l=I}^{II}\frac{\left(x_{ik}^{l}-\hat{x}_{ik}^{l}\right)^{2}}{2mc}\right]^{1/2} \times 100 \tag{16}$$

where m refers to the number of tie lines and c refers to the number of components (viz. 3 for the present system). Here x_{ik}^{l} and $\hat{x}_{ik}^{l}$ are the experimental and predicted values of composition (mole fraction) for component i for the kth tie line in phase l, respectively. The modified Rachford–Rice algorithm [28] was used to compute the tie lines. For the UNIQUAC model, the structure parameters r and q of the components were predicted using the Polarizable Continuum Model (PCM) as outlined in our previous work [47]. The values of r and q for the components have been presented in Table 4.

The tie lines predicted by NRTL and UNIQUAC models are compared with the experimental tie lines in Figs. 3 and 4 and Figs. 5 and 6 for the [EMIM][EtSO$_4$] and [EMIM][CH$_3$COO] ternary systems respectively. The NRTL and UNIQUAC interaction parameters are presented in Table 5 The RMSD values of 0.48% and 0.83% were obtained for [EMIM][EtSO$_4$] and [EMIM][CH$_3$COO] respectively, when using the NRTL model, and the corresponding RMSD values when using the UNIQUAC model were 0.693% and 1.053%.

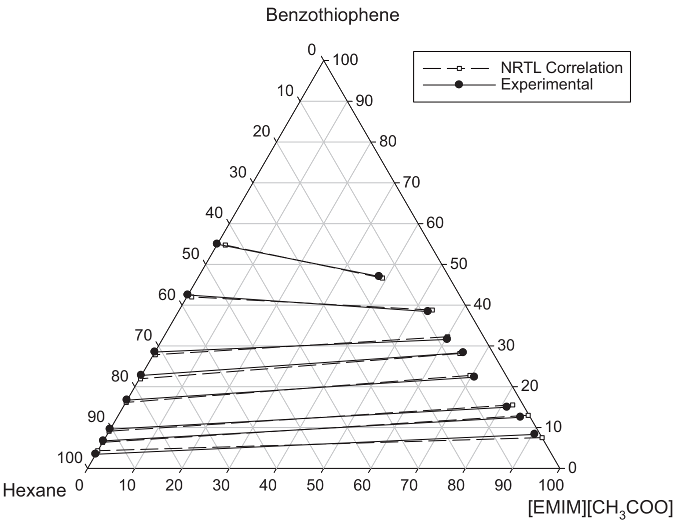


Fig. 4. Experimental vs. NRTL correlations for the composition tie lines of the system [EMIM][CH$_3$COO]–benzothiophene–*n*-hexane at 308.15 K.

4.3. COSMO-RS predictions

The equilibrium for ternary liquid–liquid system is defined by the equation:

$$\gamma_i^{I}x_i^{I} = \gamma_i^{II}x_i^{II} \quad i=1,2,3 \tag{17}$$

where γ_i, the activity coefficient of component i in a phase (I or II), is predicted using the COSMO-RS model. x_i^{I} and x_i^{II} represents the mole fraction of component i in phase I and II respectively. Most liquid–liquid equilibria are reached under adiabatic conditions, thus necessitating the consideration of an energy balance. However, if both feed F and solvent S enter the stage at identical temperatures, the only energy effect is the heat of mixing, which is often sufficiently small that only a very small temperature change occurs. Thus, we have assumed the process to occur isothermally and the compositions of the extract and raffinate phases are calculated using a flash algorithm as described by the modified

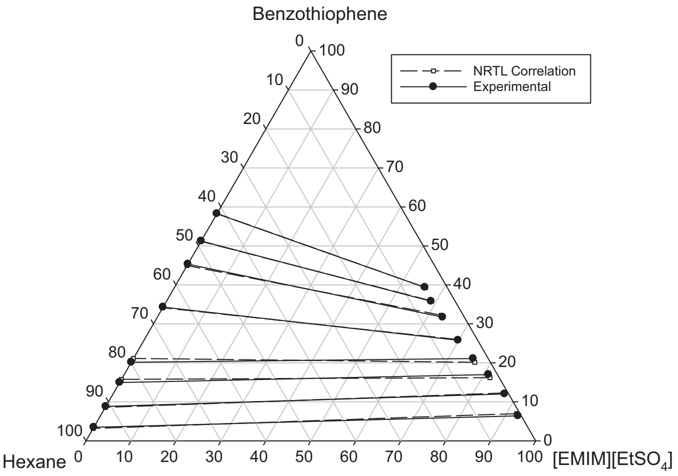


Fig. 3. Experimental vs. NRTL correlations for the composition tie lines of the system [EMIM][EtSO$_4$]–benzothiophene–*n*-hexane at 308.15 K.

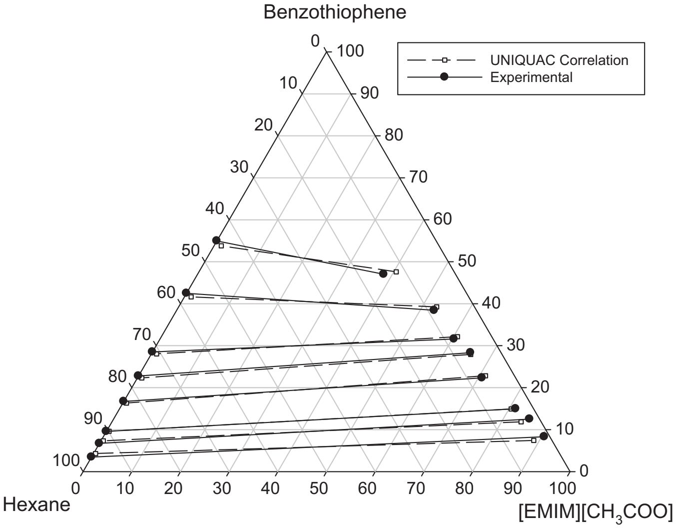


Fig. 5. Experimental vs. UNIQUAC correlations for the composition tie lines of the system [EMIM][CH$_3$COO]–benzothiophene–*n*-hexane at 308 K.

Table 5
NRTL and UNIQUAC interaction parameters for the two systems at $T = 308.15$ K.

$i-j$	NRTL model parameters				UNIQUAC model parameters			
	A_{ij}/K	A_{ij}/K	F^a	RMSD[b]	A_{ij}/K	A_{ij}/K	F^a	RMSD[b]
System: [EMIM][EtSO$_4$](1)–benzothiophene(2)–*n*-hexane(3)								
1–2	14.467	17.334			670.98	−150.01		
1–3	18.151	9.507	2.28×10^{-5}	0.48	358.05	156.55	2.3×10^{-3}	0.693
2–3	0.729	16.042			−9.0668	434.89		
System: [EMIM][CH$_3$COO](1)–benzothiophene(2)–*n*-hexane(3)								
1–2	19.238	2.662			−21.037	257.3		
1–3	19.469	12.870	3.31×10^{-3}	0.83	406.51	8.4471	5.32×10^{-3}	1.053
2–3	15.948	2.469			11.131	140.03		

[a] Calculated using Eq. (15).
[b] Calculated using Eq. (16).

Rashford–Rice Algorithm [28]. Also, the effect of pressure (P) on LLE calculations is assumed to be negligible. To start with, the feed concentration (z_i) is calculated using the following equation,

$$z_i = \frac{x_i^I + x_i^{II}}{2} \tag{18}$$

The feed rate has been assumed to be unity ($F = 1$). In the next step, the values of distribution coefficient (K_i, $i = 1, 2, 3$) are calculated using the equation:

$$K_i = \frac{x_i^{II}}{x_i^I} = \frac{\gamma_i^I}{\gamma_i^{II}} \tag{19}$$

Here γ_i^I and γ_i^{II} are predicted using the COSMO-RS model. With the values of K_i the isothermal flash equation is solved using Eq. (20),

$$f(\Psi) = \sum \frac{z_i(1 - K_i)}{1 + \Psi(K_i - 1)} = 0 \tag{20}$$

subject to,

$$Fz_i = L_1 x_i^I + L_2 x_i^{II} \tag{21}$$

and,

$$\Psi = \frac{L_1}{F} \tag{22}$$

Here L_1 and L_2 represents the flow rate of the extract and raffinate phases respectively. Eq. (20) which is non-linear in nature is first solved for ψ. Thereafter, the mole fractions in both phases are calculated via Eqs. (23) and (24).

$$x_i^I = \frac{z_i}{1 + \Psi(K_i - 1)} \tag{23}$$

$$x_i^{II} = K_i x_i^I \tag{24}$$

The experimental data obtained for both the ionic liquid systems were used to benchmark the COSMO-RS code that we compiled in the manner represented above to predict the tie line compositions. Similar tie line prediction has been done successfully in our earlier work on Ionic Liquid based ternary system [40]. The results of these predictions on the ternary systems for both the predicted and experimental tie lines have been presented in Figs. 7 and 8 for [EMIM][CH$_3$COO] and [EMIM][EtSO$_4$] based system respectively. We were able to successfully predict the result of the ternary equilibrium for the systems with fair amount of accuracy. RMSDs of 4.36% and 7.87% were obtained for the system containing the ionic liquids [EMIM][EtSO$_4$] and [EMIM][CH$_3$COO] respectively.

Thus, the COSMO-RS model based on the initial input of F, z_i, P, T can predict the tie lines for any system whose experimental data is not known or is not practically possible due to economic or technical constraints. For the LLE prediction of any unknown ternary system we first and foremost require the COSMO file of the components in the LLE system. Thereafter based on any random feed composition (z_i) one can generate the tie line data. The model will work only when Eq. (20) is solvable which in turn depends on the

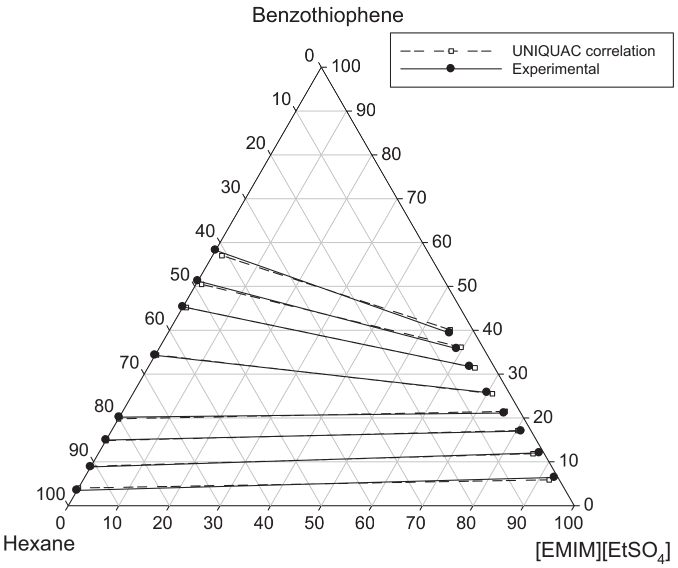


Fig. 6. Experimental vs. UNIQUAC correlations for the composition tie lines of the system [EMIM][EtSO$_4$]–benzothiophene–*n*-hexane at 308 K.

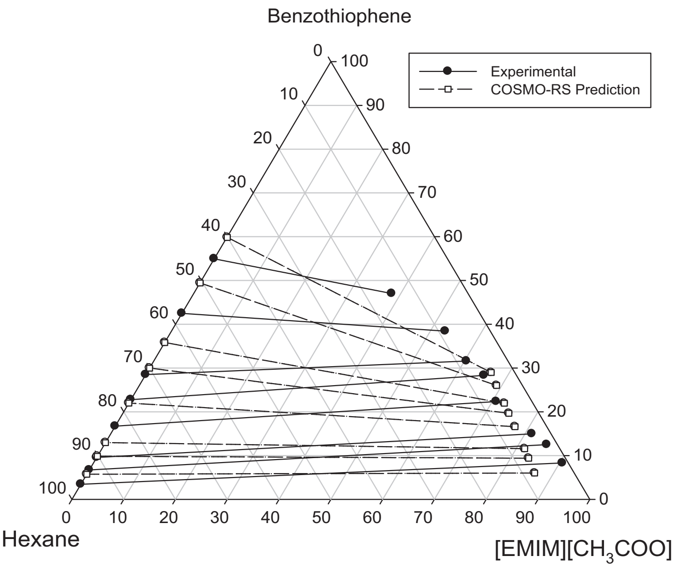


Fig. 7. Experimental vs. COSMO-RS predictions for the composition tie lines of the system [EMIM][CH$_3$COO]–benzothiophene–*n*-hexane at 308.15 K.

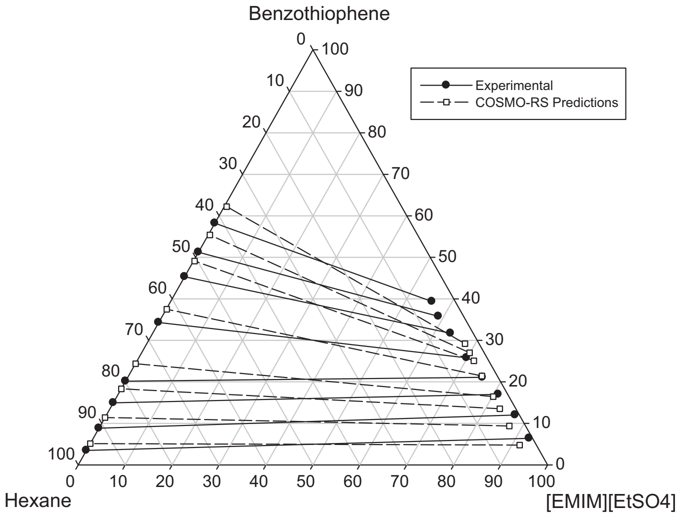


Fig. 8. Experimental vs. COSMO-RS predictions for the composition tie lines of the system [EMIM][$EtSO_4$]–benzothiophene–*n*-hexane at 308.15 K.

accuracy of predicting K_i (Eq. (20)). For a homogeneous phase, the flash algorithm will not converge, which gives an idea that the feed composition we have chosen lies outside the immiscible region. This can therefore be used as a check to help us choose feed points that lie within the immiscible zone. Moreover, this model is not just limited to binary or ternary systems. After making necessary adjustments, the same model can be utilized to predict the results containing more than three components. This has been discussed in the next section.

4.4. Single vs. mixed ionic liquids: COSMO-RS predictions

Using the COSMO-RS model that we implemented for ternary systems, higher selectivities were obtained for the $EtSO_4^-$ anion over the CH_3COO^- anion, though this difference was not really significant. On the other hand, the distribution coefficient was higher for the CH_3COO^- anion, again the difference being insignificant. Anantharaj and Banerjee [48] obtained the interaction of sulphur compounds with ionic liquids and linked the solvent power to the mode of interaction that is involved. The work was done for fluorinated anions in association with various cations, and their interaction with thiophene. It was observed that the affinity of the sulphur compounds for the anion in the ionic liquids depends on the electronegativity of the hetero atoms involved. In the case of acetate and ethyl sulphate, the difference in electronegativity is not large, which would explain the data on selectivity and distribution coefficient.

For imidazolium-based ionic liquids, the interactions between the ionic liquid and the sulphur compounds were found to mainly occur from the interactions between the –CH group in the imidazolium cation and the π-bond of the aromatic ring in the sulphur compound [49]. Going by this observation, in the case of imidazolium-based ionic liquids, the cation must have a larger effect on the selectivity than the anion. This could explain the insignificant difference in the selectivities irrespective of whether one uses the [$EtSO_4$] anion or the [CH_3COO] anion. Since the predictions and experiments done for single ionic liquids did not show any significant difference in the selectivity or distribution coefficient, we implemented the COSMO-RS model to analyze mixed ionic liquids. The primary objective of this analysis was to observe any changes in the selectivity and distribution coefficient when mixed ionic liquids are chosen for the extraction of benzothiophene. For this purpose, we benchmarked the COSMO-RS model using the feed mixture as obtained for the system [EMIM][$EtSO_4$](1)–benzothiophene(2)–*n*-hexane(3).

In order to obtain a mixture of ionic liquids, the two ionic liquids, [EMIM][$EtSO_4$] and [EMIM][CH_3COO], were added in different proportions. This was done by dividing the feed concentration of the experimental data between the two ionic liquids as given by,

$$z_f^{total} = z_f^{IL_1} + z_f^{IL_2} \tag{25}$$

where z_f^{total} is the total mole fraction of both the ionic liquids in the feed which is obtained from Eq. (20), $z_f^{IL_1}$ is the mole fraction of [EMIM][$EtSO_4$] and $z_f^{IL_2}$ is the mole fraction of [EMIM][CH_3COO]. The various mixtures of ionic liquids are obtained by varying the mole ratio of the same in the feed, or the ratio $z_f^{IL_1}/z_f^{IL_2}$ takes the values 1:4, 2:3, 1:1, 3:2 and 4:1 (i.e. 20, 40, 50, 60 and 80% respectively).

The selectivities and distribution coefficients for the various tie lines were calculated based on the equations as mentioned earlier. Figs. 9 and 10 present a comparison of selectivities and distribution

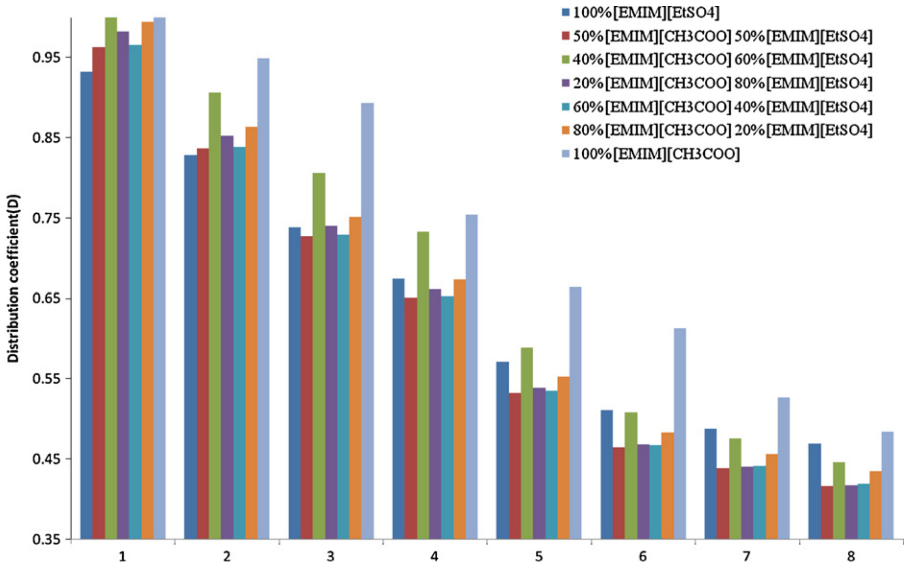


Fig. 9. Comparison of distribution coefficients of benzothiophene in mixed ionic liquids of varying ratios vs. the concentration of benzothiophene in the *n*-hexane rich phase at 308 K (*x*-axis corresponds to the feed concentration of benzothiophene: 1: 5%; 2: 10%; 3: 20%; 4: 25%; 5: 30%; 6: 35%; 7: 45%; 8: 50%).

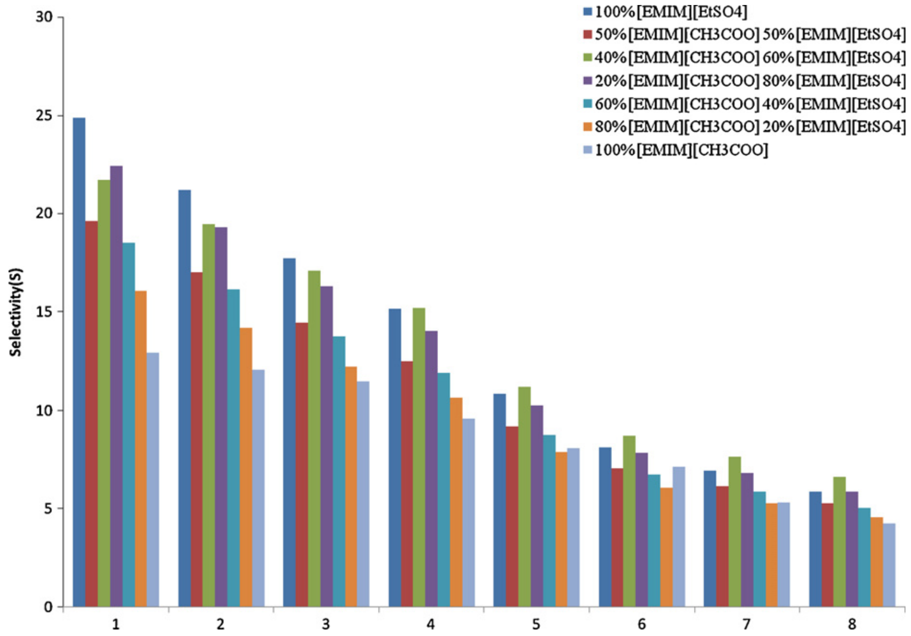


Fig. 10. Comparison of selectivities of benzothiophene in mixed ionic liquids of varying ratios vs. the concentration of benzothiophene in the *n*-hexane rich phase at 308 K (*x*-axis corresponds to the feed concentration of benzothiophene: 1: 5%; 2: 10%; 3: 20%; 4: 25%; 5: 30%; 6: 35%; 7: 45%; 8: 50%).

coefficients using the different ratios or %. From the charts, we can see that as long as [EMIM][$EtSO_4$] is the dominant ionic liquid, the selectivity is towards the higher side for all the benzothiophene feed concentrations, achieving maximum selectivity at 100% concentration of [EMIM][$EtSO_4$]. Whereas, when [EMIM][CH_3COO] is the dominant ionic liquid, the distribution coefficient is higher for all the feed concentrations of benzothiophene. For higher concentrations of benzothiophene in the raffinate, our model has predicted the selectivity to be the highest for a mixed composition of ionic liquids. Comparing Fig. 2 with Figs. 9 and 10, it is clear that the selectivity and distribution of mixed ionic liquids are very less as compared to single ionic liquid. Thus to have a better sulphur removal efficiency, it would be advisable to use a single ionic liquid. However, irrespective of the ionic liquid selected, the distribution coefficient and selectivity decreases with a rise in the feed concentration of benzothiophene. The importance of the findings is that using the COSMO-RS model, it is now possible to conduct a priori predictions for LLE systems containing mixed ionic liquids. In the present case, we have used two ionic liquids, benzothiophene and *n*-hexane as a quaternary system or pseudo ternary system. Thus using a similar approach, it is also possible to conduct predictions for systems containing any number of components. The only input required is the feed compositions and the sigma profiles of the individual components.

5. Conclusion

Very high selectivity values were achieved for the ternary experiments done on the systems, 1-ethyl-3-methylimidazolium ethyl sulphate–benzothiophene–*n*-hexane and 1-ethyl-3-methylimidazolium acetate–benzothiophene–*n*-hexane. The experimental results were correlated with the NRTL and UNIQUAC models, of which the NRTL model displayed superior accuracy in correlating the data. The experimental data so obtained was then used to benchmark the COSMO-RS predictions. The deviations were found to be satisfactorily low for both the systems.

From the experimental and predicted results, we conclude that the two ionic liquids, [EMIM][$EtSO_4$] and [EMIM][CH_3COO], are highly effective for the removal of benzothiophene from *n*-hexane. The studies also stand testimonial to the potential of imidazolium-based ionic liquids in general, for the extractive desulfurization of fuels. A high selectivity value with the absence of ionic liquid in the hydrocarbon-rich phase was obtained for both ILs. However the cross contamination of hexane in IL-rich phase was more pronounced in [EMIM][CH_3COO] based system. It was observed that the selectivity and distribution of mixed ionic liquids are very less as compared to single ionic liquid. Thus to have a better sulphur removal efficiency, it would be advisable to use a single ionic liquid.

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