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# Aromatic Extraction Using Mixed Ionic Liquids: Experiments and COSMO-RS Predictions

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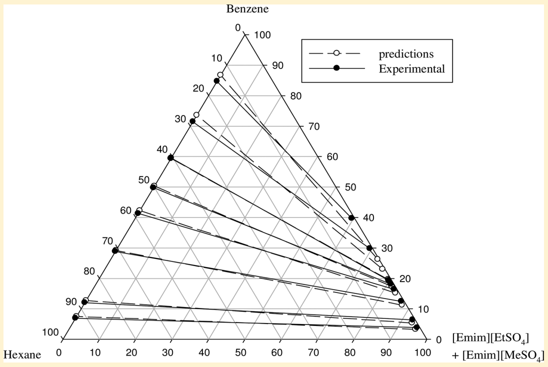
**ABSTRACT:** The use of mixed ionic liquids (ILs) as possible alternatives for the removal of aromatics has been studied here via experimentation and predictions. For the IL mixture, a predictive approach such as COSMO (COnductor like Screening MOdel) along with its extension to RS (real solvent) is used in this work. Initially the COSMO-RS model was benchmarked on three different LLE (liquid−liquid equilibria) systems. The binary LLE ([$C_2$mim][$NTf_2$] (1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide) + [$P_{66614}$][$NTf_2$] (trihexyl(tetradecyl)-phosphonium bis{(trifluoromethyl)sulfonyl}amide) gave a root-mean-square deviation (rmsd) of 7 %. Thereafter, ternary IL systems [EMIM]-[$ETSO_4$] + benzene + hexane and [EMIM][$MESO_4$] + benzene + hexane gave a rmsd of 1.68 and 1.86 %, respectively. Further the model was benchmarked on the quaternary IL based system: [BMIM][$BF_4$] + [OMIM][$BF_4$] + toluene + heptane, giving an rmsd of 5.25 %. For experimental benchmarking, the system [EMIM][$ETSO_4$] (1) + benzene (2) and hexane (3) was examined, which gave an rmsd equal to 4.13 % for the NMR technique and 6.32 % via the cloud point method. Further the LLE of the quaternary system [EMIM][$ETSO_4$] + [EMIM][$MESO_4$] + benzene + hexane at $T$ = 298.15 K was determined, and the average rmsd was around 5.25 % for eight tie lines, which is good considering our method to be a priori. Lesser values of selectivity and distribution ratio were obtained for the mixed IL used in this work as compared to a single IL.



## ■ INTRODUCTION

Aromatic species are the key chemicals in the petrochemical and chemical industry. Among all aromatics, benzene, toluene, xylene, and ethyl benzene are most important ones which act as basic raw material for many intermediates of commodity petrochemicals and valuable fine chemicals. Aromatics are extracted from the hydrocarbon feed stocks which are mainly a mixture of aromatic and aliphatic hydrocarbon. Therefore the extraction of aromatics from the hydrocarbon feed stocks, such as catalytic cracking feedstock, has potential for commercial importance in the oil industry.[1] The separation of aromatic hydrocarbons (benzene, toluene, xylene, and ethyl benzene) from the $C_4-C_{10}$ aliphatic hydrocarbon mixture is challenging since these compounds have a boiling point within a close range and several combinations form an azeotrope.[2,3] The conventional processes for the separation of these aromatic and aliphatic hydrocarbon mixture are liquid−liquid extraction (LLE), suitable for the range of (20 to 65) wt % aromatic content, extractive distillation, suitable for the range of (65 to 90) wt % aromatics and azeotropic distillation for high aromatic content, >90 wt %.[4] Liquid−liquid equilibrium (LLE) separation can be a useful separation process thereby reducing the energy consumption and the environmental impact. The LLE data provide important technical information in developing processes for the separation of desired products (extract) from mixtures of hydrocarbons.

There are several commercial solvents available for the selective separation of aromatics from the naphtha or gas condensate. Typical solvents used are polar components such as sulfolane,[5−7] *N*-methylpyrrolidone (NMP),[7] *N*-formylmorpholine, glycols,[8] and polypropylene carbonate.[9] Organic solvents are generally toxic and flammable, and the high volatility of these chemicals results in the loss of solvent to the atmosphere. On other hand, due to unfavorable capacity and selectivity of the organic solvents used, the extraction processes require high investments and exhibit large energy consumption due to the need of additional steps for the solvent recovery and purification of both product streams. The only way to improve the extraction technology at low aromatic content is the development of new solvent system that exhibits a dramatically higher aromatic distribution coefficient and/or a higher aromatic/aliphatic selectivity than sulfolane. Information from literature indicates that room temperature ionic liquids (RTILs) have the potential to fulfill these requirements.[10−15]

RTILs are salts that are liquid at room temperature.[15] They consist of an organic cation coupled with an inorganic/organic anion. RTILs are attractive solvents because of their negligible vapor pressure and subsequently their nonflammability. They also have a liquid range of more than 400 K. Ionic liquids (ILs) are called the “designer solvent” because fine-tuning of properties can be done by varying cation and anion selection. The use of ILs as media for liquid−liquid extraction is growing rapidly. Aromatic hydrocarbons have low activity coefficients at infinite dilution in several ILs, while aliphatic hydrocarbons

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show high activity coefficients in the same IL.[15] The vast majority of the studies reported so far are concentrated on the extraction properties displayed by various imidazolium or pyridinium ILs on mixtures of benzene or toluene and hydrocarbons (heptane, *n*-octane, and cyclohexane).[15] Recently Domanska et al.[16] studied the separation of aromatic hydrocarbons from alkanes using an ammonium IL.

However, in the domain of aromatic extraction, the study of using mixed and miscible ILs as solvents has not been attempted until now. Arce et al.[17] studied the phase behavior of mutually immiscible ILs. Arce et al.[18] also reported the use of a mutually immiscible IL system for the extraction of aromatic compounds from the aliphatic/aromatic mixture. It was shown that the mixing of two ILs may improve the extraction efficiency. It led to the formation of three phases and thus would definitely increase the complexity in separating the phases. Due to the formation of the third phase, contact between the IL (which is at bottom) with the aliphatic/aromatic mixture would be small. Therefore, chances of improving the separation are very less. They found that the two ILs are mutually immiscible if a structural difference exists (i.e., dissimilar cations) between them. From our earlier studies, a smaller cation has proven to give a higher extraction capability for aromatics.[19] Thus in this work two sets of IL mixtures having an imidazolium cation, namely, 1-ethyl-3-methylimidazolium [EMIM], was chosen. Further, for immiscible ILs the anions, namely, methylsulfate [$MESO_4$], ethylsulfate [$ETSO_4$], and methylsulfonate [$MESO_3$], have also been chosen. Thus the two IL binary mixtures (referred to as pseudosolvent), namely, [EMIM][$ETSO_4$] + [EMIM][$MESO_4$] and [EMIM][$ETSO_4$] + [EMIM][$MESO_3$], are used for the extraction of benzene from hexane.

Further to obtain the effective IL mixture, a predictive approach such as COSMO (COnductor like Screening MOdel)[20] along with its extension to RS (Real Solvent)[21−25] is used in this work. An important advantage of the COSMO-RS model is that it predicts a priori the liquid phase nonideal activity coefficient of any component in a mixture without using any experimental data. It uses the molecular structure of the solute/component as the only initial input.[21−27] Therefore, in this work we have used the COSMO-RS model for the a priori prediction of activity coefficients of aromatic and aliphatic components in various IL mixtures. We developed an algorithm based on the COSMO-RS model to predict the performance of a binary IL mixture.

## ■ COSMO-RS

In COSMO-RS, the molecules are regarded as a collection of surface segments, and the chemical potential of each segment is self-consistently determined from statistical mechanical calculation. The difference in segment activity coefficient between mixture and pure liquid gives the segment activity coefficients and activity coefficient of a molecule is obtained from the summation over the segment activity coefficients. In our original COSMO-RS reimplementation[22−24] model the activity coefficient $\gamma_{i/S}$ of solute i in the solution S is derived from,

$$\ln \gamma_{i/S} = \frac{\Delta G^{*res}_{i/S} - \Delta G^{*res}_{i/i}}{RT} + \ln \gamma^{SG}_{i/S} \qquad (1)$$

where $\Delta G^{*res}$ is the restoring solvation free energy and superscript SG denotes the Staverman−Guggenheim combinatorial term which is

$$\ln \gamma^{SG}_{i/S} = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \qquad (2)$$

where $\theta_i = (x_i q_i / \sum_j x_j q_j)$, $\phi_i = (x_i r_i / \sum_j x_j r_j)$, and $l_i = 1/2(r_i - q_i) - (r_i - 1)$.

Here, $x_i$ is the mole fraction of component *i*, and $r_i$ and $q_i$ are the normalized volume and surface parameters for *i*; *z* is the coordination number, usually taken to be 10, and the summation is over the species of the mixture. The activity coefficient is then calculated by:

$$\ln \gamma_{i/S} = n_i \sum_{\sigma_m} p_i(\sigma_m)[\ln \Gamma_S(\sigma_m) - \ln \Gamma_i(\sigma_m)] + \ln \gamma^{SG}_{i/S} \qquad (3)$$

Here $\Gamma_S(\sigma_m)$ and $\Gamma_i(\sigma_m)$ are the activity coefficient of the segment in the mixture and in the component *i*, respectively. The three-dimensional screening charge density distribution $p_i(\sigma_m)$ is quantified using a histogram known as the $\sigma$-profile which is the probability of finding a surface segment with screening charge density $\sigma$, that is, $p(\sigma) = (A_i(\sigma)/A_i)$, where $A_i(\sigma)$ is the surface area with a charge density of value $\sigma$ and $A_i$ is total surface area of species *i*. The details of the calculation and procedure[28−35] of COSMO-RS[21−27] can be found elsewhere.

From our previous work,[23] 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 combinations of ILs from the same COSMO files of cations and anions which have to be generated once. Therefore, the same approach is adopted here, from which we obtain the $\sigma$-profile (screening charge distribution) of the liquid as,

$$p_{IL}(\sigma) = p_{cation}(\sigma) + p_{anion}(\sigma) \qquad (4)$$

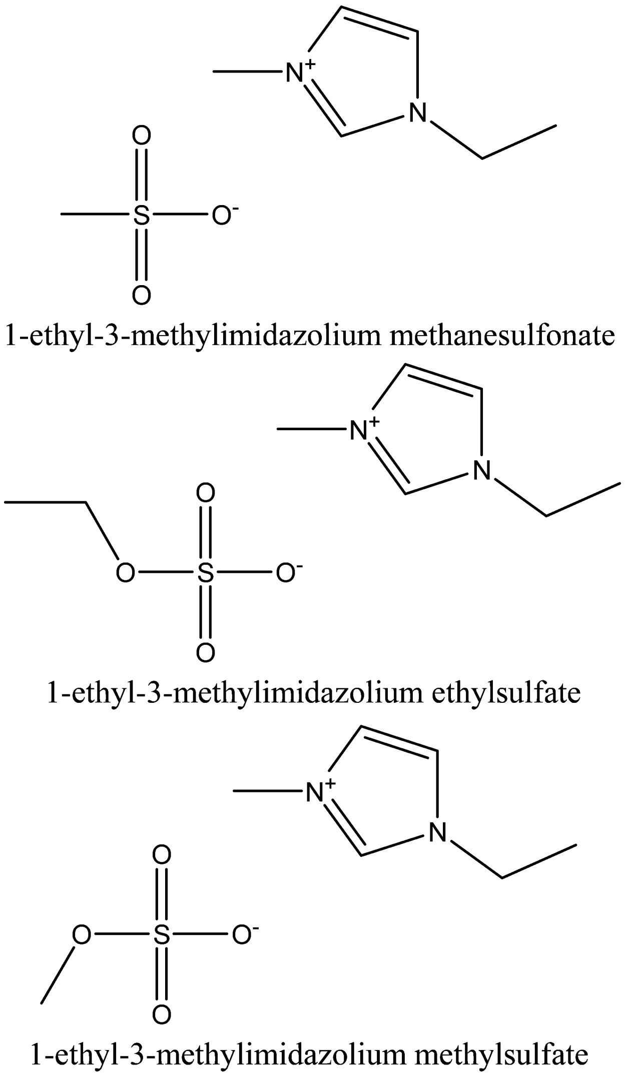
where $p_{cation}(\sigma)$ and $p_{anion}(\sigma)$ are the $\sigma$-profiles of the cation and anion, respectively. Likewise, the COSMO volume and area are also added linearly. The $\sigma$-profiles are then normalized so that it would appear as if it is the profile of a single molecule of the IL. The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

$$\text{rmsd (in \%)} = 100 \left[ \sum_{k=1}^{m} \sum_{i=1}^{c} \sum_{j=1}^{2} \frac{(x^j_{ik} - \hat{x}^j_{ik})^2}{2mc} \right]^{1/2} \qquad (5)$$

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

## ■ EXPERIMENTAL STUDIES

**Chemicals and Materials.** The ILs (Figure 1) 1-ethyl-3-methylimidazolium methanesulfonate ([EMIM][$MESO_3$]), 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][$ETSO_4$]), and 1-ethyl-3methyl-imidazolium methylsulfate ([EMIM][$MESO_4$]) were obtained from Sigma Aldrich with a reported purity of < 99 %. The water content of the three ILs as measured by a Karl Fisher titrator (KF 787, MetroOhm) are 280 ppm, 580 ppm, and 370 ppm, respectively. For reducing



1-ethyl-3-methylimidazolium methanesulfonate

1-ethyl-3-methylimidazolium ethylsulfate

1-ethyl-3-methylimidazolium methylsulfate

**Figure 1.** Structure of ILs used in this work.

the water content and volatile compounds to negligible values, vacuum (0.1 Pa) for at least 48 h was applied to all of the IL samples prior to the measurements. Benzene and extra pure *n*-hexane (≥ 99.7 %) was obtained from SISCO Research Laboratories Ltd., India. All of the chemicals were used without any further purification.

**Experimental Methodology.** To carry out the LLE experiments, mixtures of compounds with an overall composition lying in the region of immiscibility was prepared. The mixtures were placed in the glass cells which were closed by screw caps. To ensure a secure seal and to prevent humidity a Parafilm tape was used to seal the screw caps. The binary mixtures of known composition were prepared by mass on an analytical Sartorious BS224S balance with an accuracy of 0.1 mg. These flasks are placed in a thermostatic shaker bath (Dailhan Lab Made) which maintains the temperature to an accuracy of ± 0.01 K. The shaker bath was operated at 100 rpm. Spring clamps were used to hold the flasks on the tray. All of the mixtures were vigorously stirred for 5 h and then allowed to settle for not less than 12 h to ensure the equilibrium state. Then, samples of each phase in equilibrium were taken with the syringes for compositional analysis. A similar procedure was followed for quaternary LLE experiments.

## COMPOSITIONAL ANALYSIS

**Using $^1$H NMR Spectra.** The equilibrium compositions were measured using $^1$H NMR spectroscopy. A drop of each sample was dissolved in 0.5 mL of $CDCl_3$ (Aldrich, 99.8 % feuterated) and placed inside NMR tubes (thrift grade) which were properly sealed. The spectrometer of 11.74 T (400 MHz response of $^1$H) was used to measure the peaks. Peak areas proportional to hydrogen moles associated with the referred component are noted down. Thus, dividing the peak area by the number of hydrogen atoms we obtain an area proportional to the moles of the referred component. Finally, the molar fraction is obtained by dividing this area by the total sum of the areas of three components. The peak assignment for each compound is given in Table 1.

**Using the Cloud-Point Method.** The NMR technique has proved the absence of IL in the raffinate phase; hence to determine the equilibrium composition only one property is required. The detection limit for IL in NMR spectra was 3 mol %. Due to this the NMR analysis was used only for the extract phase, that is, the phase containing the IL. The best results were achieved using density instead of refractive index, according to a previous work.[36] The density was measured over the whole miscible region of the ternary system. The composition of the raffinate, formed by binary mixture (alkane + benzene), was determined by calibrating the density at various compositions using the DMA 4500 densitometer. The binodal solubility curve for the extract phase was determined by the cloud point method described by Letcher and Siswana.[37] It should be noted that the purity of benzene and hexane in Letcher and Siswana[37] is the same as reported in our work. Initially the extract phase coexistence curve is determined using the cloud point. Thereafter the intersection of the line connecting the raffinate phase composition and mixture point gives the exact extract phase composition.

## RESULTS AND DISCUSSION

**COSMO-RS Predictions for LLE.** The equilibrium relation for the ternary liquid–liquid system is defined by the equation:

$$\gamma_i^{\mathrm{I}} x_i^{\mathrm{I}} = \gamma_i^{\mathrm{II}} x_i^{\mathrm{II}} \qquad i = 1, 2, 3 \tag{6}$$

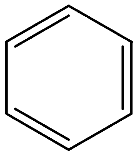
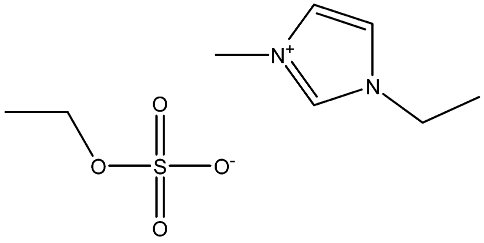
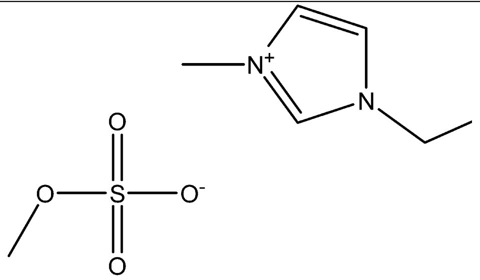
where $\gamma_i$, the activity coefficient of component $i$ in a phase (I or II), is predicted using the COSMO-RS model. $x_i^{\mathrm{I}}$ and $x_i^{\mathrm{II}}$ represents the mole fraction of component $i$ in phases I and II, respectively. Thus the selectivity and capacity follows the definition:

$$S = \frac{x_{\mathrm{benzene}}^{\mathrm{E}}}{x_{\mathrm{benzene}}^{\mathrm{R}}} \cdot \frac{x_{\mathrm{HX}}^{\mathrm{R}}}{x_{\mathrm{HX}}^{\mathrm{E}}} = \frac{\gamma_{\mathrm{benzene}}^{\mathrm{R}}}{\gamma_{\mathrm{benzene}}^{\mathrm{E}}} \cdot \frac{\gamma_{\mathrm{hexane}}^{\mathrm{E}}}{\gamma_{\mathrm{hexane}}^{\mathrm{R}}} \tag{7}$$

$$\beta = \frac{x_{\mathrm{benzene}}^{\mathrm{E}}}{x_{\mathrm{benzene}}^{\mathrm{R}}} = \frac{\gamma_{\mathrm{benzene}}^{\mathrm{R}}}{\gamma_{\mathrm{benzene}}^{\mathrm{E}}} \tag{8}$$

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 Rashford–Rice algorithm.[28] Also, the

Table 1. Molecular Structure of Compounds and Peak Assignment for Quantitative Analysis of the Mixtures

| Chemical Compound and Peak Type | Chemical Shifts in NMR Spectra (Relative to TMS) | Chemical Compound and Peak Type | Chemical Shifts in NMR Spectra (Relative to TMS) |
|---|---|---|---|
|  benzene | a1: ~ 7.2-7.4 (singlet,1H) |  1-ethyl 3-methylimidazolium ethyl sulphate | a: ~ 7.2-7.4 (doublet, 2H)<br>b: ~ 4.2-4.3 (triplet,2H)<br>c:~2.554 (singlet,3H) |
|  hexane | a2: 0.9-1.1(triplet,6H) |  1-ethyl-3-methylimidazolium methylsulphate | a: ~ 7.2-7.4 (doublet,2H)<br>b: ~ 4.2-4.3 (triplet,2H) |

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,

$$z_i = \frac{x_i^{\mathrm{I}} + x_i^{\mathrm{II}}}{2} \tag{9}$$

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:

$$K_i = \frac{x_i^{\mathrm{II}}}{x_i^{\mathrm{I}}} = \frac{\gamma_i^{\mathrm{I}}}{\gamma_i^{\mathrm{II}}} \tag{10}$$

Here $\gamma_i^{\mathrm{I}}$ and $\gamma_i^{\mathrm{II}}$ are predicted using the COSMO-RS model. With the values of $K_i$ the isothermal flash equation is solved using eq 11,

$$f(\Psi) = \sum \frac{z_i(1 - K_i)}{1 + \Psi(K_i - 1)} = 0 \tag{11}$$

subject to,

$$Fz_i = L_1x_i^{\mathrm{I}} + L_2x_i^{\mathrm{II}} \tag{12}$$

and

$$\Psi = L_1/F \tag{13}$$

Here $L_1$ and $L_2$ represents the flow rate of the extract and raffinate phases, respectively. Equation 11 which is nonlinear in nature is first solved for $\Psi$. Thereafter, the mole fractions in both phases are calculated using the following equations:

$$x_i^{\mathrm{I}} = \frac{z_i}{1 + \Psi(K_i - 1)} \tag{14}$$

$$x_i^{\mathrm{II}} = K_ix_i^{\mathrm{I}} \tag{15}$$

The experimental data obtained for both the IL systems were used to benchmark the COSMO-RS code that we compiled in the manner represented above to predict the tie-line compositions. A similar tie-line prediction has been done successfully in our earlier work on an IL based ternary system.[23] In our later sections we have benchmarked the code on IL containing binary, ternary, and quaternary systems.

Thus, the COSMO-RS model based on the initial input of $F$, $z_i$, $P$, and $T$ can predict the tie lines for any system whose experimental data are not known or not practically possible due to economic or technical constraints. For the LLE prediction of any unknown ternary system we require the COSMO file of the components in the LLE system which has to be obtained only once. Thereafter, based on any random feed composition ($Z_i$), one can generate the tie line data. The model will work only when eq 11 is solvable which in turn depends on the accuracy of predicting $K_i$ (eq 10). 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.

To obtain a mixture of ILs, the two ILs, [EMIM][ETSO$_4$] and [EMIM][MESO$_3$], were added in different proportions. This was done by dividing the feed concentration of the experimental data between the two ILs as given by,

$$z_{\mathrm{f}}^{\mathrm{total}} = z_{\mathrm{f}}^{\mathrm{IL_1}} + z_{\mathrm{f}}^{\mathrm{IL_2}} \tag{16}$$

where $z_{\mathrm{f}}^{\mathrm{total}}$ is the total mole fraction of both the ILs in the feed which is obtained from eq 16, $z_{\mathrm{f}}^{\mathrm{IL_1}}$ is the mole fraction of [EMIM][ETSO$_4$], and $z_{\mathrm{f}}^{\mathrm{IL_2}}$ is the mole fraction of [EMIM]-[MESO$_3$].

In our binary IL system as the solvent, we chose the ternary data of [EMIM][ETSO$_4$] + benzene + hexane.[38] In this data using eq 9 we got the initial feed concentration of IL($z_f^{IL}$). Thereafter we used eq 16 to create mixtures of ILs as a feed point, keeping the feed point of the other components, that is, benzene and hexane as obtained via eq 9. The various mixtures of ILs (i.e., [EMIM][MESO$_4$] + [EMIM][ETSO$_4$]) are obtained by varying the mole ratio of the same in the feed. Thus the ratio $((z_f^{[EMIM][ETSO_4]})/(z_f^{[EMIM][MESO_4]}))$ takes the values 1:4, 2:3, 1:1, 3:2, and 4:1 (i.e., 20 %, 40 %, 50 %, 60 %, and 80 % [EMIM][ETSO$_4$], respectively). Activity coefficients and the corresponding selectivity and capacity values obtained from eqs 7 and 8, respectively, were then plotted against the mole fraction of [EMIM][ETSO$_4$] in solvent (Figure 2). The point of intersection of these curves (~0.80 mole fraction) is taken as the best mole fraction of [EMIM][ETSO$_4$] for our experiments, since this point resembles a compromise in the selection of selectivity and capacity of the IL mixture.

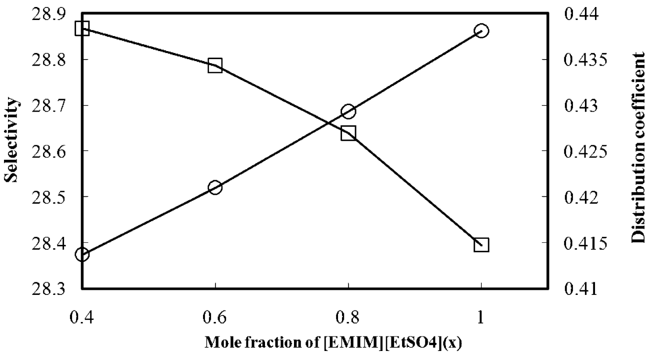


**Figure 2.** COSMO-RS prediction of the optimum mole fraction of [EMIM][EtSO$_4$] ($x$) + [EMIM][MESO$_4$] ($1 - x$) with respect to selectivity and distribution coefficient: □, distribution coefficient; ○, selectivity.

**LLE Predictions and Benchmarking.** We have earlier benchmarked and successfully used the COSMO-RS model to predict the LLE of binary and ternary IL systems. In our earlier work[23] the LLE prediction was done on 36 (aliphatic + aromatic + IL) ternary systems with an average rmsd of 9 %. Thus in this section we have benchmarked the COSMO-RS model on three tier predictions involving (a) binary LLE of ILs,[17] (b) ternary IL systems involving the ILs [EMIM][ETSO$_4$][38] and [BMIM][MESO$_4$],[39] and (c) the only quaternary IL based system available in literature, namely, [BMIM][BF$_4$] + [OMIM][BF$_4$] + toluene + heptane.[40]

**Binary System.** For benchmarking our predictions, we have compared our predictions with the reported mutual immiscible data as reported by Arce et al.[17] A rmsd of 7 % is achieved for the binary system of [C$_2$mim][NTf$_2$] (1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}-amide) + [P$_{66614}$][NTf$_2$] (trihexyl(tetradecyl)phosphonium bis{(trifluoromethyl)sulfonyl}amide) which is quite good considering our method to be a priori. Both ILs are liquid at room temperature and are hydrophobic in nature. For the predictions we have taken the cation and anion separately for both ILs as per eq 4. Figure 3 shows the comparison of predicted and experimental data.

**Ternary Systems.** Ternary plots in Figures 4 and 5 show the predicted and experimental tie lines for the systems: [EMIM][ETSO$_4$] + benzene + hexane and [BMIM][MESO$_4$] + benzene + hexane, respectively, at $T$ = 298.15 K. Excellent rmsd values of 1.68 % and 1.86 %, respectively, were obtained for the two systems.

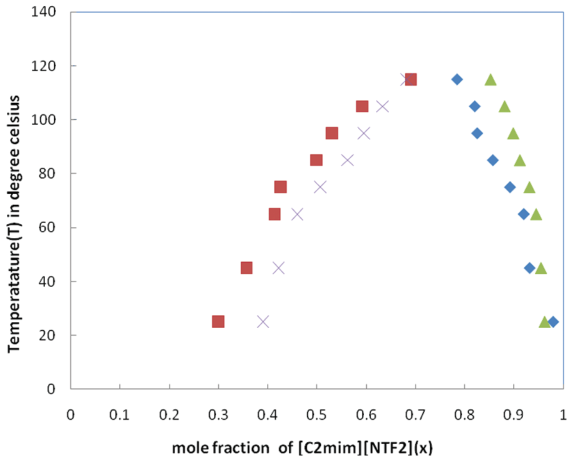


**Figure 3.** Predicted and experimental data[17] for [C$_2$mim][NTf$_2$] + [P$_{66614}$][NTf$_2$]: ◆, extract phase; ■, raffinate; ▲, estimated extract phase; ×, estimated raffinate phase.

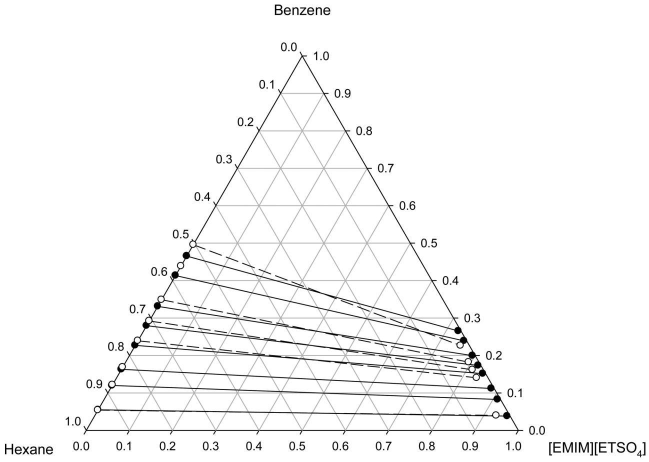


**Figure 4.** Experimental[38] and predicted tie lines for [EMIM][ETSO$_4$] + benzene + hexane at 298.15 K: ●, experimental; ○, COSMO-RS predicted.

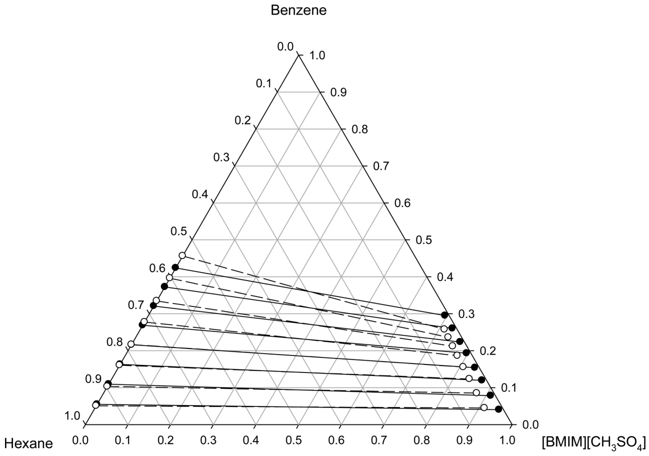


**Figure 5.** Experimental[39] and predicted tie lines for [BMIM]-[CH$_3$SO$_4$] + benzene + hexane at 298.15 K: ●, experimental; ○, COSMO-RS predicted.

Table 2. Experimental[40] and Predicted Mole Fractions for $[BMIM][BF_4]$ + $[OMIM][BF_4]$ + Toluene + Heptane at 313.15 K

| | Experimental Mole Fractions | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | IL-rich phase | | | | heptane-rich phase | | | |
| $[BMIM][BF_4]$ in solvent | heptane | toluene | $[BMIM][BF_4]$ | $[OMIM][BF_4]$ | heptane | toluene | $[BMIM][BF_4]$ | $[OMIM][BF_4]$ |
| 1 | 0.0055 | 0.0270 | 0.9675 | 0 | 0.9184 | 0.0816 | 0 | 0 |
| 0.8 | 0.0108 | 0.0323 | 0.7583 | 0.1986 | 0.9248 | 0.0752 | 0 | 0 |
| 0.6 | 0.0284 | 0.0367 | 0.5573 | 0.3776 | 0.9284 | 0.0716 | 0 | 0 |
| 0.4 | 0.0468 | 0.0411 | 0.3674 | 0.5447 | 0.9334 | 0.0666 | 0 | 0 |
| 0.2 | 0.0719 | 0.0448 | 0.1766 | 0.7066 | 0.9365 | 0.0635 | 0 | 0 |
| 0 | 0.1076 | 0.0478 | 0 | 0.8446 | 0.9396 | 0.0604 | 0 | 0 |
| | Predicted Mole Fractions | | | | | | | |
| 1 | 0.0051 | 0.0147 | 0.9802 | 0.0000 | 0.9245 | 0.0755 | 0 | 0 |
| 0.8 | 0.0120 | 0.0315 | 0.7608 | 0.1957 | 0.9362 | 0.0638 | 0 | 0 |
| 0.6 | 0.0276 | 0.0390 | 0.5745 | 0.3589 | 0.9368 | 0.0632 | 0 | 0 |
| 0.4 | 0.0490 | 0.0408 | 0.3605 | 0.5497 | 0.9452 | 0.0548 | 0 | 0 |
| 0.2 | 0.0738 | 0.0470 | 0.1801 | 0.6991 | 0.9562 | 0.0438 | 0 | 0 |
| 0 | 0.1023 | 0.0445 | 0.0000 | 0.8532 | 0.9602 | 0.0398 | 0 | 0 |

**Quaternary Systems.** In this prediction we have followed a similar procedure as used for binary or ternary LLE. To deal with the mixture of ILs, we have used the following equation for prediction:

$$p_{\text{mixedIL}}(\sigma) = \sum_{i=1}^{2} x_{\text{IL}i} p_{\text{IL}i}(\sigma) \qquad (17)$$

where $x_{\text{IL}i}$ and $p_{\text{IL}i}$ is the mole fraction and $\sigma$-profile of the $i$th IL in the mixture. For benchmarking, we compared the predicted results with the experimental results of García et al.[40] for the system: $[BMIM][BF_4]$ + $[OMIM][BF_4]$ + toluene + heptane. We benchmarked this system, since our work is related to the separation of aliphatic and aromatic compounds with the mixed IL. The experimental and predicted tie lines are compared and reported in Table 2 and illustrated in Figure 6. The rmsd is 5.25 % which is again very good considering our method to be a priori.

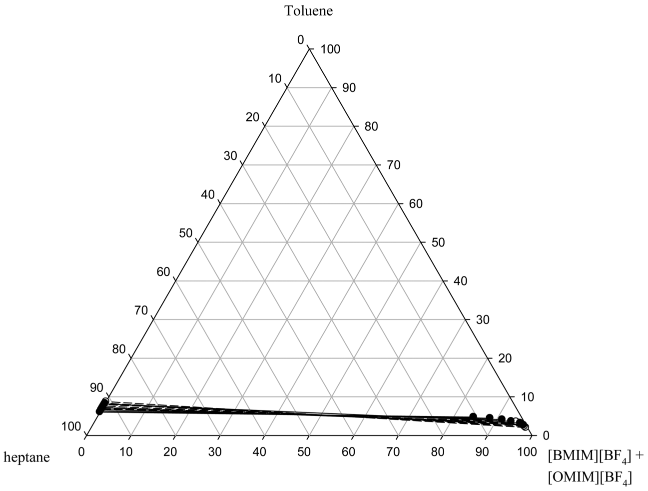


Figure 6. Experimental[40] and predicted tie lines for $[BMIM][BF_4]$ + $[OMIM][BF_4]$ + toluene + heptane at 313.15 K: --○--, predicted data; −●−, experimental data.

In our previous work[23] the LLE of 36 IL ternary systems gave a average rmsd deviation of ~9 %. It should be noted that the deviation varied with the anion of the IL. For example, ternary systems containing the ILs $[BMIM][CF_3SO_3]$ and $[HMIM][BF_4]$ gave rmsd's close to 10 %, whereas on the other hand the IL $[HMIM][PF_6]$ gave a rmsd of ~30 %. However systems with the ILs $[EMIM][EtSO_4]$ and $[MMIM][MESO_4]$ having the same anions as our work gave a lower rmsd of 2.3 % and 0.8 %, respectively. Similar lower rmsd's (~3 %) are observed in this work for the ternary and quaternary systems, namely, $[EMIM][ETSO_4]$ + benzene + hexane (Figure 4), $[BMIM][CH_3SO_4]$ + benzene + hexane (Figure 5), and ($[EMIM][ETSO_4]$ + $[EMIM][MESO_4]$) (1) + benzene (2) and hexane (3) (Figure 7).

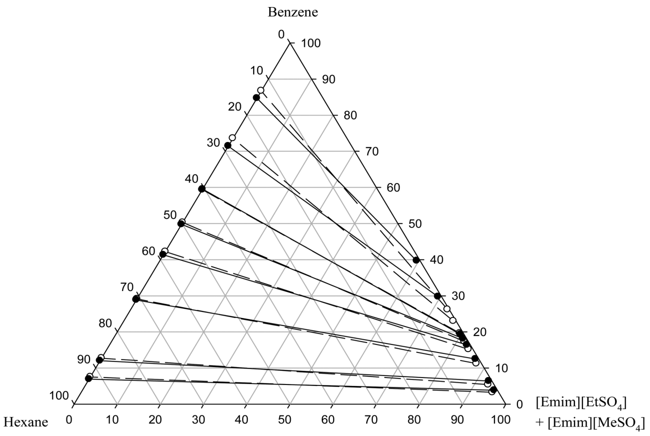


Figure 7. Experimental and predicted tie lines for the ternary system of mixed ILs: ($[EMIM][ETSO_4]$ + $[EMIM][MESO_4]$) (1) + benzene (2) and hexane (3) at 298.15 K: --○--, predictions; −●−, experiment.

**Experimental Benchmarking for Ternary Systems.** For benchmarking, we used the ternary system, namely, $[EMIM][ETSO_4]$ + benzene + hexane, as reported by García et al.[38] We benchmarked this system since we want to carry out a similar work related to the benzene−hexane separation using $[EMIM][ETSO_4]$. The experimental and predicted LLE data are reported in Table 3. Four single batch experiments for this system under the similar conditions are described by García et al.[38] Batch experiments were carried out corresponding to tie lines 2, 4, 6, and 8 of the reported LLE data. Overall feed compositions were taken corresponding to the midpoint of the tie lines. Samples from the raffinate and extract phases were

**Table 3. Comparison of Experimental and Reported[38] Tie Lines for the System [EMIM][ETSO$_4$] + Benzene + Hexane at 298.15 K**

| | | raffinate phase (mole fraction) | | | extract phase (mole fraction) | | |
|---|---|---|---|---|---|---|---|
| tie line | | [EMIM][ETSO$_4$] | benzene | hexane | [EMIM][ETSO$_4$] | benzene | hexane |
| 2 | reported[a] | 0.000 | 0.120 | 0.880 | 0.911 | 0.083 | 0.007 |
| | experimental[b] | 0.000 | 0.122 | 0.878 | 0.889 | 0.082 | 0.030 |
| 4 | reported[a] | 0.000 | 0.227 | 0.773 | 0.842 | 0.152 | 0.007 |
| | experimental[b] | 0.000 | 0.239 | 0.761 | 0.833 | 0.140 | 0.027 |
| 6 | reported[a] | 0.000 | 0.331 | 0.669 | 0.794 | 0.199 | 0.006 |
| | experimental[b] | 0.000 | 0.349 | 0.651 | 0.794 | 0.182 | 0.024 |
| 8 | reported[a] | 0.000 | 0.465 | 0.535 | 0.729 | 0.265 | 0.006 |
| | experimental[b] | 0.000 | 0.496 | 0.504 | 0.753 | 0.226 | 0.021 |

[a] Reference 38. [b] Results obtained via NMR.

**Table 4. Experimental Ternary LLE Data for the System ([EMIM][EtSO$_4$] + [EMIM][MeSO$_4$]) (1) + Benzene (2) and Hexane (3) at 298.15 K[a]**

| extract phase | | | raffinate phase | | | | |
|---|---|---|---|---|---|---|---|
| [EMIM][EtSO$_4$] + [EMIM][MeSO$_4$] | benzene | hexane | [EMIM][EtSO$_4$] + [EMIM][MeSO$_4$] | benzene | hexane | selectivity ($S$) | distribution ratio ($\beta$) |
| 0.954 | 0.0386 | 0.0074 | 0 | 0.0694 | 0.9306 | 69.94 | 0.5561 |
| 0.9286 | 0.064 | 0.0074 | 0 | 0.1202 | 0.8798 | 58.95 | 0.5324 |
| 0.8674 | 0.1249 | 0.0077 | 0 | 0.2886 | 0.7114 | 39.98 | 0.4327 |
| 0.8279 | 0.1642 | 0.0077 | 0 | 0.4133 | 0.5887 | 30.36 | 0.3972 |
| 0.8105 | 0.1814 | 0.0081 | 0 | 0.4978 | 0.5022 | 22.56 | 0.3612 |
| 0.7882 | 0.2037 | 0.0081 | 0 | 0.5954 | 0.4046 | 16.24 | 0.3421 |
| 0.6944 | 0.2976 | 0.008 | 0 | 0.7144 | 0.2856 | 14.89 | 0.4165 |
| 0.5953 | 0.397 | 0.0077 | 0 | 0.847 | 0.153 | 9.31 | 0.4687 |

[a] The composition of the IL mixture is taken as 80 mol % of [EMIM][EtSO$_4$].

collected at the end of the experiment as described in an earlier section. The experimental compositions were obtained both via cloud point as well as the NMR technique as described earlier. The percent rmsd was obtained to be equal to 4.13 % for the NMR technique and 6.32 % via the cloud point method.

**Mixed IL Performance.** There are only a few ILs which possess a simultaneously high distribution ratio and high selectivity. To minimize the cost of separation, a combination of high distribution coefficient and selectivity will serve the purpose. Using mixed conventional solvents for the extraction of aromatics is commonly practiced to balance between selectivity and the distribution ratio of different solvents.[41]

The experimental LLE data for a ternary system of mixed ILs ([EMIM][ETSO$_4$] + [EMIM][MESO$_3$]) (1) + benzene (2) and hexane (3) are shown in Table 4. Experimental and COSMO-RS predicted data are compared in Figure 7. The average rmsd is around 5.25 % for eight tie lines which is good considering our method to be a priori. It is clear from the slope of the tie line that benzene has more affinity toward the hexane-rich phase than the IL-rich phase. Thus the mixed IL is not recommended for aromatic extraction. It is interesting to note that the slope of the tie lines obtained are the opposite of what we have observed by using [EMIM][ETSO$_4$] (Figure 4) or [BMIM][MESO$_4$] (Figure 5) (the IL [BMIM][MESO$_4$] was chosen since data for [EMIM][MESO$_4$] were not available). Thus the selectivity and distribution ratio (eqs 7 and 8) of the mixture of IL are much less as compared to the single ILs. Smaller values of selectivity (Figure 8) and the distribution ratio (Figure 9) were obtained for the mixed IL as compared to the single IL.

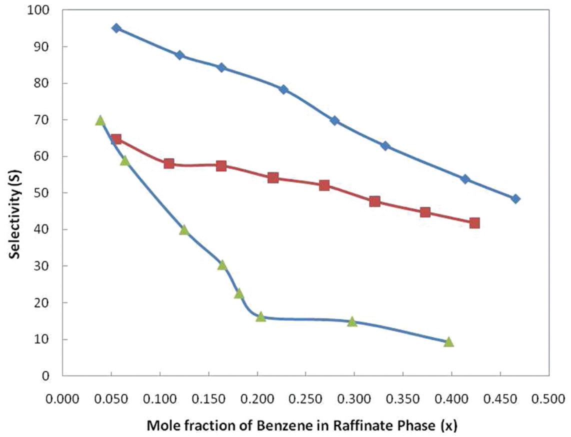


**Figure 8.** Comparison of selectivity (as per eq 7 and Table 4) in mixed and single IL performance: ◆, [EMIM][ETSO$_4$];[38] ■, [BMIM][MESO$_4$];[39] ▲, [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] (this work).

The results are quite contrary as compared to ternary systems. This implies that in our work [EMIM][EtSO$_4$] will give higher selectivity and capacity as compared to the mixture IL, that is, [EMIM][EtSO$_4$] + [EMIM][MESO$_4$]. It is true that both ILs are miscible in all proportions. So it is expected that the combined IL will have a higher extraction capacity; however, it does the opposite. This may be due to the reason that a combination of two IL results in less free volume as compared to a single IL. Due to this the benzene molecules are unable to penetrate the core of the pseudo IL compound. It should be noted that the COSMO-RS model only predicts the liquid-phase activity coefficients and is devoid of any three-dimensional information. For a complete understanding of these phenomena we need to consider the IL−IL interaction and the IL−IL−benzene interaction separately using ab initio or molecular dynamics simulations. The self-diffusivities and

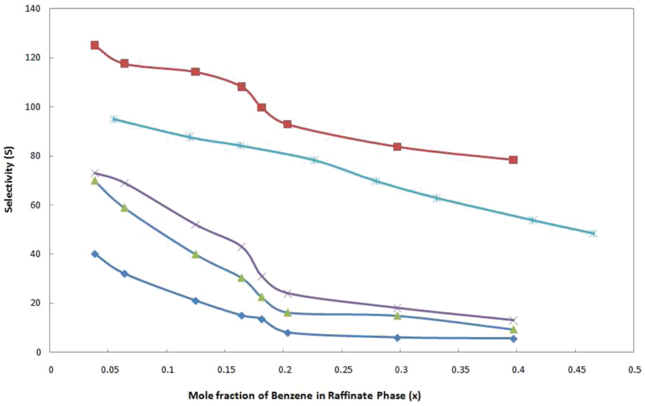


**Figure 9.** Comparison of COSMO-RS predicted selectivity in mixed and single ILs: ▲, [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] (this work); ◆, [BMIM][BF$_4$] + [OMIM][BF$_4$]; ■, [EPY][ETSO$_4$] + [EPY]-[MESO$_4$]; ×, [EMIM][BF$_4$] + [EMIM][PF$_6$]; ∗, [EMIM][ETSO$_4$].[38]

the partial charge analysis will give us an important idea regarding the decrease in solubility of benzene in the mixed IL.

The experimental phase equilibrium for a pseudoternary system of [EMIM][ETSO$_4$] (1) + [EMIM][MESO$_3$] (2) + benzene (3) + hexane (4) was also attempted. In the previous experiment we had used the cloud point method to find out the equilibrium composition. In this study the cloud point method was not used because [EMIM][ETSO$_4$] and [EMIM][MESO$_3$] formed a hazy mixture. Therefore we were not able to find out the cloud point with the addition of hexane. NMR also failed since the benzene peaks at 7.2 overlapped with the two IL peaks, that is, ~ 7.2 to 7.4 (doublet, 2H) .However to judge the effectiveness of the mixture we have used the criteria; that is, the benzene concentration should be minimum in the raffinate phase. The composition of the raffinate phase, formed by the binary mixture (alkane + benzene), was determined by the density composition curve of this binary mixture as obtained earlier. To compare the findings with ([EMIM][ETSO$_4$] + [EMIM][MESO$_4$], we chose the same feed point as that of the tie line of Table 5. The first tie line was chosen since this gives us an idea of the selectivity at infinite dilution, that is, when benzene concentration is near zero. Thereafter the mixture, that is, 80 % [EMIM][ETSO$_4$] + 20 % [EMIM][MESO$_3$], was chosen, and the experiment was repeated six times using the same amount of IL, benzene, and hexane as used for tie line 1 in Table 5. The experimental values of density of the raffinate phase and the corresponding equilibrium composition of benzene and hexane are reported in Table 5. On comparison it is seen that the mole fraction of benzene is higher in [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] as compared to [EMIM][ETSO$_4$] + [EMIM][MESO$_3$]. Thus [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] is a better solvent. However both mixtures fail in comparison to the single IL. It should be noted that the mixed IL indicates to this work only and does not indicate to any other mixture of IL(s) in literature.

**Table 5. Experimental Equilibrium Composition of Raffinate Phase of the Pseudoternary System [EMIM][ETSO$_4$] (1) + [EMIM][MESO$_3$](2) + Benzene (3) + Hexane (4) at 298.15 K**

| density of raffinate phase | | | | |
|---|---|---|---|---|
| gm·cm$^{-3}$ | benzene | hexane | benzene[a] | hexane[a] |
| 0.65330 | 0.0783 | 0.9216 | 0.0694 | 0.9306 |
| 0.65280 | 0.0751 | 0.9248 | | |
| 0.65443 | 0.0854 | 0.9145 | | |
| 0.65352 | 0.0797 | 0.9202 | | |
| 0.65388 | 0.0819 | 0.9180 | | |
| 0.65390 | 0.0821 | 0.9178 | | |

[a] Composition in the raffinate phase when [EMIM][EtSO$_4$] + [EMIM][MESO$_3$] is used as the solvent.

To evaluate the generality of our conclusion we have compared our IL mixture with three more IL combinations. The COSMO-RS model was then used to predict the selectivities within the mole fraction range of benzene in raffinate phase, that is, as per Figure 8. The three IL combinations taken are: (1) [OMIM][BF$_4$] + [BMIM][BF$_4$] (only mixed ILs available in literature[40]); (2) [EPY][EtSO$_4$] + [EPY][MESO$_4$] (effect of the ethylpyridinium [EPY] cation with the same anions as our work); and (3) [EMIM]-[PF$_6$] + [EMIM][BF$_4$] (commonly used anions, i.e., [PF$_6$] and[BF$_4$]). It can be seen that the mixture [EPY][EtSO$_4$] + [EPY][MESO$_4$] is the best IL mixture (Figure 9) among all of the IL mixtures studied. It is also surprising that the selectivities are higher than the single IL, that is, [EMIM][EtSO$_4$]. This also agrees well with the previous work as reported with the separation of aliphatic (octane) and aromatic compound (benzene) via ethylpyridinium cation by Gómez et al.[42] Although not confirmed by experiments it can be concluded that the judicious selection of mixed ILs may be a viable option for aromatic extraction. Thus a mixed IL may have a higher extraction capacity as compared to a single IL.

## ■ CONCLUSION

The COSMO-RS predictions for a binary IL LLE study has been done by comparing the results with those reported in the literature. The rmsd of 7 % is achieved for the binary system of [C$_2$mim]-[NTf$_2$] + [P$_{66614}$][NTf$_2$]. The COSMO-RS model was used to predict the performance of mixed IL as a solvent. An rmsd of 5.25 % was achieved for the extraction of benzene from hexane using a mixed IL: [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] which was also studied experimentally at $T$ = 298.15 K. It is clear from the slope of the tie line that benzene has more affinity toward the hexane-rich phase than the IL-rich phase. Thus the mixed IL, that is, [EMIM]-[ETSO$_4$] + [EMIM][MESO$_4$] is not recommended for the aromatic extraction of benzene from hexane. The extraction of benzene from hexane using the mixture of ILs: [EMIM] [ETSO$_4$] + [EMIM] [MESO$_3$] was also performed at $T$ = 298.15 K. On comparison it is seen that the mole fraction of benzene is higher in [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] as compared to [EMIM]-[ETSO$_4$] + [EMIM][MESO$_3$]. Thus [EMIM][ETSO$_4$] + [EMIM][MESO$_4$] is a better solvent. However both mixtures fail in comparison to a single IL, that is, [EMIM] [ETSO$_4$].

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### Notes

The authors declare no competing financial interest.

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