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Liquid−Liquid Equilibrium Data for {Heptane + Aromatic + 1-(2-Hydroxyethyl)-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ([hemim][NTf$_2$])} Ternary Systems

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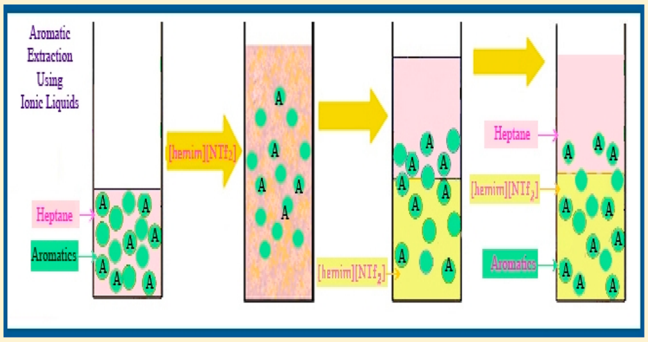

ABSTRACT: 1-(2-Hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid ([hemim][NTf$_2$]) was synthesized as a new functionalized ionic liquid to study the effect of addition of the hydroxyl group to the imidazolium cation on aliphatic/aromatic separations. For this purpose, liquid−liquid equilibrium (LLE) data for {heptane + toluene or benzene + 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hemim][NTf$_2$])} systems were measured at 313.2 K and atmospheric pressure. The measured LLE data were correlated using three basically distinct thermodynamic models; that is, nonrandom two-liquid (NRTL), Othmer−Tobias, and Hand correlations. Results show that there is good agreement between correlated and experimental data. Our experimental results indicate that the addition of the hydroxyl group to imidazolium cation significantly enhances the performance of the ionic liquid in terms of selectivity.

1. INTRODUCTION

The application of aromatic hydrocarbons such as benzene, toluene, and xylene as raw materials in the production of various valuable petrochemicals has increased their importance in the petrochemical industry. The extraction of aromatics from refinery cuts such as naphtha, kerosene, and jet fuels has a potential of commercial importance in the oil refining industry.[1] High demands for aromatics in the chemical industries and the increasing legal restrictions on the aromatic content in gasoline and other fuels have caused the separation of these compounds from mixtures containing saturated hydrocarbons to be a subject of keen interest.[2]

The separation of aromatics from their mixtures using aliphatic hydrocarbons, namely, C_4−C_{10} compounds, is still a challenging task owing to some restrictions. For instance, azeotrope formations have been reported for several aliphatic/aromatic combinations. On the other hand, similarities in the structures and boiling points of the components of such mixtures have restricted the efficiency of conventional separation processes.[3−7] Considering the aromatic content of the aforementioned mixtures, some applicable and conventional processes for separation of aromatic compounds include liquid−liquid extraction for aromatic content weight percent of 20 to 65, extractive distillation for 65 to 90, and azeotropic distillation for over 90 %.[8]

Typical polar solvents such as sulfolane,[9] *N*-methyl pyrrolidone (NMP),[10] *N*-formyl morpholine (NFM), ethylene glycols,[11] *N*-methylimidazole, or *N*-ethylimidazole,[12] propylene carbonate,[13] or combinations of solvents to balance the selectivity and ability are used in liquid extraction.[14] However, the loss of solvents due to their high volatility (vapor pressure), flammability, and toxicity are deficiencies associated with these solvents.[1] Furthermore, solvent recovery is expected to impose an increase in investments and operational costs.[15]

Over about the last two decades, ionic liquids (ILs) have been suggested as a novel alternative for traditional organic solvents in liquid−liquid extractions.[16] Given the advantages of ionic liquids such as negligible vapor pressure, high performance, and meeting the environmental regulations, their applications as extractive solvents and alternatives for classic organic solvents have been industrially approved.[17] Although the preparation costs of ionic liquids may be relatively high, they can be easily recovered, making operational costs dramatically decrease.[18] The application of ILs in extraction processes is promising because a simple flash distillation is required for solvent recovery.

Much work has already been carried out on the separation of aromatic and aliphatic compounds using ionic liquids. For example, selectivity for the ternary system {heptane + toluene + 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Rmim][NTf$_2$])}, where R refers to methyl, ethyl, butyl, or hexyl groups} has been studied at 313.2 K. The ranges of selectivity for 1-methyl-, 1-ethyl-, 1-butyl-, and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides are 10

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Table 1. Specifications for Chemicals Used

chemical name	source	initial mole fraction purity	purification method	final mole fraction purity	analysis method
heptane	Aldrich	0.99	none		
toluene	Aldrich	0.998	none		
[hemim][NTf$_2$]	Synthesis	0.99	none		^{1}H NMR
benzene	Aldrich	0.998	none		
1-methylimidazole	Aldrich	0.99	distillation	0.998	GC
KOH	Aldrich	0.90	none		
2-chloroethanol	Aldrich	0.99	none		
ethyl acetate	Aldrich	0.998	none		
LiNTF$_2$	Acros Organics	0.99	none		
acetonitrile	Aldrich	0.998	none		
methanol	Aldrich	0.998	none		
chloroform	Aldrich	0.99	none		

to 38, 8 to 30, 5 to 20, and 2 to 12, respectively.[19] As one can observe, longer alkyl chains cause reductions in selectivity, which shows the inverse proportionality of alkyl chain length with selectivity. Furthermore, LLE data have been reported for the ternary systems consisting of heptane, toluene, and 1-methyl-3-propylimidazolium or 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids with selectivity ranges of 5 to 25 and 6 to 29, respectively.[20] Some other ternary systems studied in this regard consist of heptane, toluene, and 1-alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids ([Rdmim][NTf$_2$]), where R refers to ethyl, propyl, or butyl} at 313.2 K. The ranges of selectivity for 1-ethyl-, 1-propyl-, and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide are 5 to 29, 6 to 25, and 2 to 12, respectively.[21] In addition, LLE data for ternary systems consisting of benzene, hexane, and 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Rmim]-[NTf$_2$]), where R refers to ethyl, butyl, octyl, decyl, and dodecyl, have been obtained, and the effect of the alkyl chain substituent in [Rmim][NTf$_2$] on the separation of mixtures of hexane and benzene has also been reported. The ranges of selectivity for 1-butyl-, 1-octyl-, 1-decyl-, and 1-dodecyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides are 3 to 17, 2 to 7, 1 to 5, and 1 to 3, respectively.[22] Finally, the suitability of [hemim][NTf$_2$] for the separation of hydrocarbons of the C$_7$ and C$_8$ fractions at 298 K has been shown.[22]

The aim of the present work was to enhance selectivity by using functionalized ionic liquids to increase the solubility of aromatic compounds and thereby selectivity. The addition of polar hydroxyl group into the imidazolium cation enhances the polarity of the ionic liquid and thus increases the tendency of absorption of aromatic compounds by ionic liquids and their selectivities. In fact, selectivities in the 13.9 to 73.5 range were observed in this work. LLE data for ternary systems consisting of heptane + benzene or toluene +1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([hemim][NTf$_2$]), also abbreviated as [HEMIM][Tf$_2$N], [HOmim][NTf$_2$], [hoemim][Tf$_2$N], and [Hemim][NTf$_2$], have been measured at 313.2 K and atmospheric pressure to investigate the effect of the hydroxyl functional group.

In this work, solutions of benzene and toluene in heptane have been used as models in the separation of aromatic compounds from heptane. The presence of a methyl group in the aromatic ring of toluene molecule increases the steric hindrance of the ring and thus lowers the solubility of the aromatic compound in the ionic liquid and thereby the selectivity.[23] The degree of quality of the experimental LLE data was ascertained by applying the Othmer–Tobias and Hand correlations.

2. METHODOLOGY

To verify the reliability of the experimental LLE data, the Othmer–Tobias (eq 1)[24] and Hand correlations (eq 2) were applied:[25]

$$\ln\left(\frac{1 - w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) = a + b\ln\left(\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \quad (1)$$

$$\ln\left(\frac{1 - w_2^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) = c + d\ln\left(\frac{1 - w_2^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) \quad (2)$$

where w_3^{II} is the mass fraction of ionic liquid (IL) (3) in the IL-rich phase (lower layer), w_1^{I} is the mass fraction of heptane (1) in the heptane-rich phase (upper layer), a and b are the fitting parameters of the Othmer–Tobias correlation, and c and d are the fitting parameters of the Hand correlations.

The performance of the synthesized ([hemim][NTf$_2$]) in the separation of aromatics, namely, toluene and benzene from heptane, was evaluated through the determination of the solute distribution ratios D_1 and D_2 and the selectivity, S.

These parameters were calculated following equations below:

$$D_1 = \frac{x_1^{\mathrm{II}}}{x_1^{\mathrm{I}}} \quad (3)$$

$$D_2 = \frac{x_2^{\mathrm{II}}}{x_2^{\mathrm{I}}} \quad (4)$$

$$S = \frac{D_2}{D_1} \quad (5)$$

where x is the mole fraction, superscripts 1 and 2 refer to heptane and aromatic (solute), and subscripts I and II refer to the heptane-rich phase and IL-rich phase, respectively.

The calculated values of D_1, D_2, and S for the studied ternary mixtures at 313.2 K are listed in Table 1. In this table, D_1 increases with the increase in the aromatic content of the ternary systems, while D_2 decreases. On the other hand, S decreases with the increase of the aromatic content.

A comparison of measured LLE data with those reported for heptane + toluene + [emim][NTf$_2$][19] and heptane + toluene + sulfolane[22] ternary systems has been made. Finally, the LLE data have been correlated by the nonrandom two-liquid (NRTL) model.

3. EXPERIMENTAL SECTION

3.1. Chemicals and Apparatus. All chemicals were used without any further purification, except for 1-methylimidazole. This compound was purified by refluxing over KOH pellets at reduced pressure. The specifications for chemicals used are shown in Table 1.

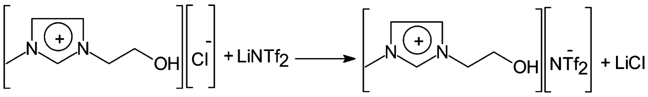
GC analyses were carried out using a 6890 Agilent gas chromatograph equipped with an HP-5 capillary column. A Milestone MICROSYNTH laboratory microwave oven was used in the synthesis of 1-(2-hydroxyethyl)-3-methylimidazolium chloride [hemim][Cl].

To protect ionic liquids from moisture, they were kept in tightly closed bottles in desiccators. Prior to using ionic liquids, they were always subjected to vacuum (P = 0.3 Pa) and a moderate temperature (373.15 K) for seven hours to remove possible traces of moisture.

^{1}H NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer. The solvents used were $CDCl_3$ and D_2O (99.95 atom % D), supplied by Acros Chemical Co. GC analyses were performed using an Agilent gas chromatograph equipped with a capillary column

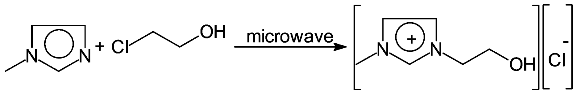
Water contents were measured using ASTM D1533 by a 787 Karl Fischer Titrino instrument and were all found to be less below 100 ppm. Chloride ion contents in the ionic liquids prepared were measured using the Vollhard procedure as a wet chemical method and were all found to be below 1 ppm. Weights were measured using a Sartorius balance with a precision of ± 0.001 %. Mixings were performed using an IKA WERKE heater-stirrer equipped with a contact thermometer to control the mixing temperature. The uncertainties of temperature measurement were ± 0.1 K and set at 313.2 K.

3.2. Syntheses. 1-(2-Hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl) imide ([hemim][NTf_2]) ionic liquid was prepared in two steps. 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([hemim][Cl]) ionic liquid was first prepared as an intermediate, which was used to synthesize



1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl) imide.

3.2.1. Synthesis of 1-(2-Hydroxyethyl)-3-methylimidazolium Chloride [hemim][Cl] Ionic Liquid. This compound was synthesized by modification of a known literature procedure.[27]



To 2-chloroethanol (4.9 g, 61 mmol) was added 1-methylimidazole (5 g, 61 mmol) in a TFM (the highest density and thermally resistant form of PTFE available) vessel of a Milestone MICROSYNTH laboratory microwave oven. The resulting mixture thus obtained was exposed to microwave (MW) irradiation (200 W) at a temperature of 383 K and pressure of 10 bar for half an hour. The oily product was washed with refluxing ethyl acetate (353 K) in order to remove any traces of unreacted starting materials and the pure product was then heated for 7 h under vacuum at 363 K to yield 6.6 g (66.6%) of the product.

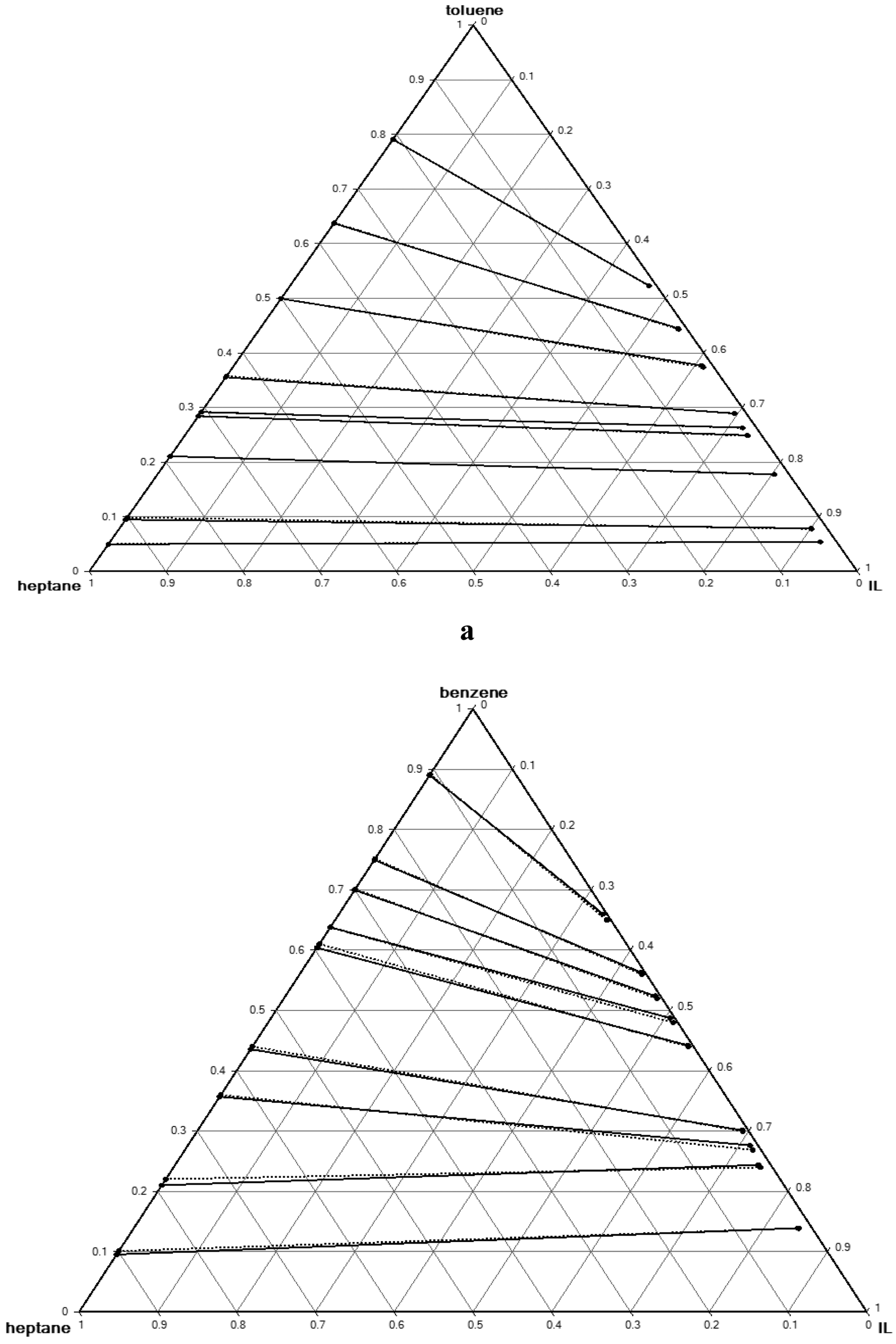
^{1}H NMR (500 MHz, D_2O, 298 K): δ (ppm) = 3.87 (3H, S, NCH_3), 3.89 (2H, t, $N\underline{CH_2}CH_2OH$), 4.28 (2H, t, $NCH_2\underline{CH_2}OH$), 7.42 (1H, d, H- 4), 7.47 (1H, d, H-5), and 8.71 (1H, S, H-2)).

3.2.2. Synthesis of 1-(2-Hydroxyethyl)-3-methylimidazolium Bis(trifluoromethanesulfonyl) imide [hemim][NTf_2]

Table 2. Experimental (Liquid−Liquid) Equilibrium Data in Mole Fraction for Ternary Systems of {Heptane (1) + Toluene and Benzene (2) + [hemim][NTf_2]} at T = 313.2 K and p = 0.1 MPa, Solute Distribution Ratio (D), and Selectivity (S) Values[a]

heptane-rich phase (upper layer)		IL-rich phase (lower phase)					
x_1^{I}	x_1^{II}	x_2^{I}	x_2^{II}	x_3^{II}	D_1	D_2	S
			{Heptane (1) + toluene (2) + [hemim][NTf_2] (3)}				
0.9501	0.0211	0.0499	0.0541	0.9240	0.0222	1.0841	48.8
0.9050	0.0209	0.0950	0.0789	0.9002	0.0230	0.8305	35.9
0.7890	0.0194	0.2110	0.1778	0.8028	0.0245	0.8426	34.2
0.7157	0.0185	0.2843	0.2494	0.7321	0.0258	0.8772	33.9
0.7082	0.0182	0.2918	0.2632	0.7186	0.0256	0.9019	35.1
0.6445	0.0153	0.3555	0.2893	0.6954	0.0237	0.8137	34.2
0.5006	0.0139	0.4994	0.3770	0.6091	0.0277	0.7549	27.2
0.3628	0.0110	0.6372	0.4452	0.5438	0.0303	0.6986	23.0
0.2091	0.0099	0.7909	0.5234	0.4667	0.0473	0.6617	13.9
			{Heptane (1) + Benzene (2) + [hemim][NTf_2] (3)}				
0.9045	0.0179	0.0955	0.1390	0.8431	0.0197	1.4554	73.5
0.7899	0.0157	0.2101	0.2437	0.7406	0.0198	1.1599	58.3
0.6429	0.0101	0.3571	0.2762	0.7137	0.0157	0.7734	49.2
0.5642	0.0075	0.4358	0.3012	0.6913	0.0132	0.6911	51.9
0.3960	0.0064	0.6040	0.4422	0.5514	0.0161	0.7321	45.3
0.3620	0.0059	0.6380	0.4873	0.5068	0.0162	0.7637	46.8
0.2505	0.0052	0.7495	0.5630	0.4318	0.0207	0.7511	36.2
0.3002	0.0064	0.6998	0.5239	0.4697	0.0213	0.7486	35.1
0.1099	0.0049	0.8901	0.6598	0.3353	0.0445	0.7412	16.6

[a] The standard uncertainties u for the temperature and mole fraction are $u(T)$ = 0.1 K and $u(x)$ = 0.001. x_1^{I} = heptane mole fraction in heptane-rich phase. x_2^{I} = heptane mole fraction in IL-rich phase. x_1^{II} = aromatic mole fraction in heptane-rich phase. x_2^{II} = aromatic mole fraction in IL-rich phase. D_1 = solute distribution ratio of heptane. D_2 = solute distribution ratio of aromatic. S = selectivity.



a

b

Figure 1. Experimental LLE of the ternary systems: (a) {heptane (1) + toluene (2) + [hemim][NTf$_2$]}, (b) {heptane (1) + benzene (2) + [hemim][NTf$_2$]} at T = 313.2 K and atmospheric pressure. Solid lines indicate experimental and dashed lines indicate data by the NRTL model.

Ionic Liquid. This compound was synthesized using 1-(2-hydroxyethyl)-3-methylimidazolium chloride [hemim][Cl] ionic liquid as the starting material (see part 3.2.2 below) by modification of a known literature procedure.[26]

A solution of lithium bis(trifluoromethanesulfonimide) (8.83 g, 31 mmol) in deionized water (10 mL) and acetonitrile (10 mL) and 1-(2-hydroxyethyl)-3-methylimidazolium chloride (5.0 g, 31 mmol) were mixed. The resulting two-phase mixture was magnetically stirred for 24 h at ambient temperature. After the reaction was complete, deionized water and acetonitrile were separated under vacuum, and the ionic liquid product was removed from LiCl by extraction in dry methanol (17 mL) and chloroform (3 mL). The suspension was then filtered and chloroform (3 × 7 mL) and diethyl ether (3 × 7 mL) were used to wash the filtrate and remove impurities and unreacted starting materials. The product obtained was then heated for 7 h under vacuum at 343 K to remove the residual water and yield 7.84 g (62.6 %) of the ionic liquid. The purity of the ionic liquid was ascertained using ^{1}H NMR spectroscopy.

^{1}H NMR (500 MHz, D_2O, 298 K): δ (ppm) = 3.87 (3H, S, NCH_3), 3.90 (2H, t, $N\underline{CH_2}CH_2OH$), 4.28 (2H, t, $NCH_2\underline{CH_2}OH$), 7.42 (1H, d, H- 4), 7.47 (1H, d, H-5), and 8.69 (1H, S, H-2).

3.3. General Procedure for Extraction. The LLE experiments were performed in glass cells with screw caps providing tight sealing. In each experiment, after weighing the glass cell, 1 g of a toluene + (or benzene +) *n*-heptane solution was poured into the glass cell, followed by addition of 1 g of ionic liquid. The contents of the glass cell were vigorously agitated for 5 h at 800 rpm. Finally, the glass cell was left overnight in a dry constant-temperature bath of 313.2 K to ensure complete phase separation. The samples from the upper (heptane-rich phase) and lower (ionic liquid-rich phase) layers were analyzed using ^{1}H NMR spectroscopy.[28]

4. RESULTS AND DISCUSSION

4.1. Experimental LLE Data. The experimental LLE data for the (heptane + aromatic + ([hemim][NTf_2]) ternary systems at 313.2 K and atmospheric pressure are given in Table 2 and plotted in Figure 1. According to the ^{1}H NMR spectra of the samples from the heptane rich phase, no detectable signals associated with the IL are shown; thus, the IL mole fraction in the heptane rich phase appears to be negligible. Therefore, this will decrease the number of extractions needed to purify the raffinate phase for recovering the solvent.

The parameters of the Othmer−Tobias and Hand correlations are given in Table 2. The regression coefficients (R^2) presented in Table 3, also shown in Figure 2, are very close to unity indicating a high degree of quality of the experimental LLE data.

Table 3. Othmer−Tobias and Hand Equation Parameters, together with the Correlation Factor, at T = 313.2 K for Both Ternary Systems[a]

Othmer−Tobias equation		
a	*b*	R^2
{Heptane (1) + Toluene (2) + [hemim][NTf_2] (3)}		
0.645	−1.962	0.975
{Heptane (1) + Benzene (2) + [hemim][NTf_2] (3)}		
0.567	−1.948	0.944
Hand equation		
c	*d*	R^2
{Heptane (1) + Toluene (2) + [hemim][NTf_2] (3)}		
2.640	1.332	0.968
{Heptane (1) + Benzene (2) + [EMpy][$EtSO_4$] (3)}		
3.190	1.601	0.953

[a] R^2 = regression coefficients. The standard uncertainty *u* for the temperature is *u*(*T*) = 0.1 K.

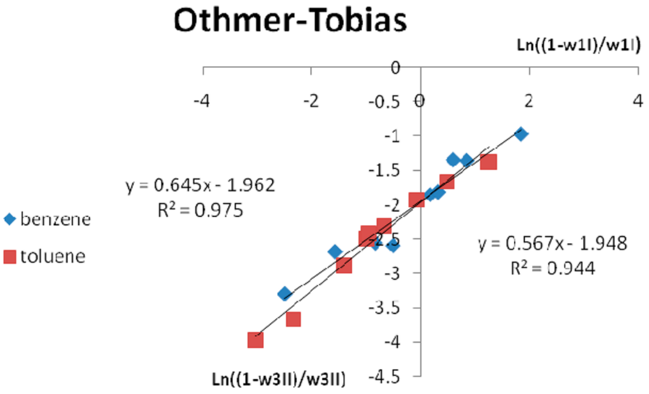


Figure 2. Othmer−Tobias plot for the systems: red ■, {heptane (1) + toluene (2) + [hemim][NTf_2] (3)}; blue ◆, {heptane (1) + benzene (2) + [hemim][NTf_2] (3)}.

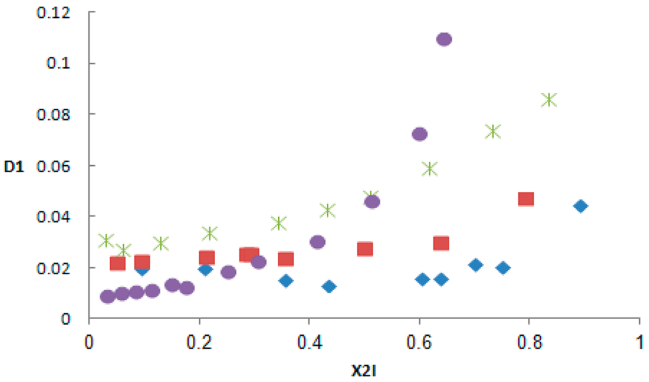


Figure 3. Heptane distribution ratio for the ternary systems at T = 313.2 K: red ■, {heptane (1) + toluene (2) + [hemim][NTf_2] (3)}; blue ◆, {heptane (1) + benzene (2) + [hemim][NTf_2] (3)}; green ∗, {heptane (1) + toluene (2) + [emim][NTf_2] (3)} (from ref 24); purple ●, heptane + toluene + sulfolane (from ref 33).

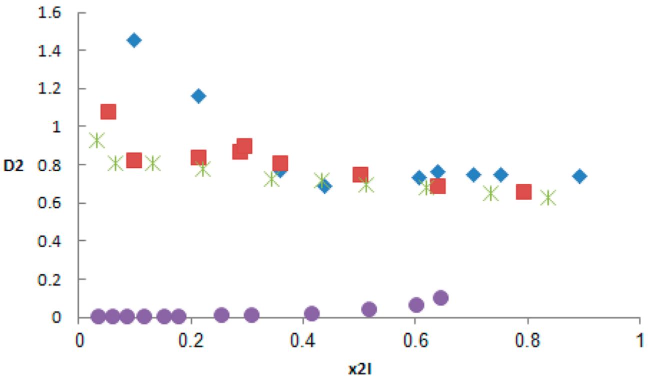


Figure 4. Aromatic distribution ratio for the ternary systems at T = 313.2 K: red ■, {heptane (1) + toluene (2) + [hemim][NTf_2] (3)}; blue ◆, {heptane (1) + benzene (2) + [hemim][NTf_2] (3)}; green ∗, {heptane (1) + toluene (2) + [emim][NTf_2] (3)} (from ref 24); purple ●, heptane + toluene + sulfolane (from ref 33).

4.2. Distribution Ratio and Selectivity. The calculated values of *D* and *S* for the studied ternary mixtures at 313.2 K are listed in Table 1. In this table, *D* values decrease with an increase in the aromatic contents of the ternary systems. On the other hand, *S* values decrease by increasing aromatic content. In Figures 3 and 4, the D_1, D_2 and *S* of ternary mixtures are presented as a function of the aromatic mole fraction in the heptane rich phase. The values for the analogous heptane + aromatic + [emim][NTf_2] system[21] and sulfolane[24] at 313.2 K obtained from the literature are also plotted.

To compare [hemim][NTf_2], [emim][NTf_2], and sulfolane solvents, the solvent must have a higher aromatic distribution coefficient (D_2); that is, the aromatic concentration in solvent rich phase should be greater than that in the lean phase. Furthermore, the solvent must have a lower aliphatic distribution coefficient (D_1); that is, the aliphatic concentration in the lean phase should be more than that in the solvent phase. As a result, the selectivity of the solvent for aromatic compounds ought to be as high as possible.[29] As shown in Figure 3, the amount of extraction in [hemim][NTf$_2$] ionic liquid rich phase for mole percentages of over 0.4 is much less than that under similar conditions in [emim][NTf$_2$] and sulfolane. Figure 4 indicates that the aromatic distribution coefficient of sulfolane is lower than that of [hemim][NTf$_2$] ionic liquid. Also, the aromatic distribution coefficient of [hemim][NTf$_2$] is close to that of [emim][NTf$_2$]. If [hemim][NTf$_2$] is used as the solvent, the amount of solvent consumption will decrease. As depicted in Figure 5, the selectivity coefficient of [hemim][NTf$_2$] system is greater than those of the [emim][NTf$_2$] and sulfolane systems because the presence of hydroxyl function in the imidazolium cation increases the polarity of the ionic liquid and thus the efficiency of extraction of the aromatic compounds will increase.

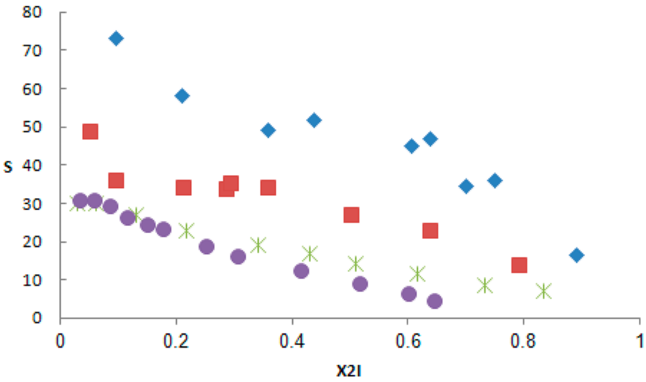


Figure 5. Selectivity for the ternary systems at T = 313.2 K: red ■, {heptane (1) + toluene (2) + [hemim][NTf$_2$](3)}; blue ◆, {heptane (1) + benzene (2) + [hemim][NTf$_2$] (3)}; green ∗, {heptane (1) + toluene (2) + [emim][NTf$_2$] (3)} (from ref 24); purple ●, heptane + toluene + sulfolane (from ref 33).

4.3. Recyclability of the Ionic Liquid. 1-(2-Hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [hemim][NTf$_2$] ionic liquid was completely capable of being recovered following each experiment and could be used again in the LLE experiments. To reuse the ionic liquid, first, the lower phase (IL rich) containing ionic liquid, benzene or toluene, and some heptane was extracted in toluene or benzene. The solvent was then separated using a rotary evaporator at reduced pressure. The purity of the recovered sample was ascertained using ^{1}H NMR. The pure ionic liquid thus recovered was used for the extraction of aromatic compounds up to six times without any appreciable loss of selectivity as shown in Table 4.

Table 4. Recyclability of [hemim][NTf$_2$] Ionic Liquid in the Extraction of Toluene in {Heptane (1) + Toluene (2) + [hemim][NTf$_2$] (3)} Ternary System[a]

extraction no.	x_1^{I}	x_2^{I}
1	0.914	0.086
2	0.911	0.089
3	0.910	0.090
4	0.910	0.090
5	0.899	0.101
6	0.899	0.101

[a] The standard uncertainty u for mole fraction is $u(x)$ = 0.001.

4.4. Thermodynamic Correlation. The NRTL equation[30] was used to correlate the experimental LLE data. The NRTL model has been successfully implemented for the prediction of the phase behavior of several systems containing ionic liquid by several authors.[31−34]

The parameters were adjusted to minimize the difference between the experimental and the calculated mole fractions defined as:

$$\mathrm{O.F} = \sum_{i=1}^{n} [(x_{1i}^{\mathrm{I}}(\mathrm{exp}) - x_{1i}^{\mathrm{I}}(\mathrm{calc}))^2 + (x_{2i}^{\mathrm{I}}(\mathrm{exp}) - x_{2i}^{\mathrm{I}}(\mathrm{calc}))^2 \cdot \sum_{i-1}^{n} [(x_{1i}^{\mathrm{II}}(\mathrm{exp}) - x_{1i}^{\mathrm{II}}(\mathrm{calc}))^2 + (x_{2i}^{\mathrm{II}}(\mathrm{exp}) - x_{2i}^{\mathrm{II}}(\mathrm{calc}))^2] \qquad (6)$$

where, x_{1i}^{I}, x_{2i}^{I}, x_{1i}^{II}, x_{2i}^{II} are the experimental mole fractions and $x_{1i}^{\mathrm{I}}(\mathrm{calc})$, $x_{2i}^{\mathrm{I}}(\mathrm{calc})$, $x_{1i}^{\mathrm{II}}(\mathrm{calc})$, $x_{2i}^{\mathrm{II}}(\mathrm{calc})$ are the calculated mole fractions. The value of the nonrandomness parameter, α_{ij}, in the NRTL model was subject to optimization between 0 and 1. The exact values for α_{ij} are shown in Table 5. Table 4 summarizes the fitting parameters associated with the estimation deviations, which were calculated by applying the following expression:

$$\mathrm{rmsd} = \left\{ \frac{\sum_i \sum_l \sum_m (x_{ilm}^{\mathrm{exp}} - x_{ilm}^{\mathrm{cal}})^2}{6k} \right\}^{1/2} \qquad (7)$$

where x is the mole fraction and the subscripts i, l, and m designate the number of the component phase and tie lines, respectively. The value of k designates the number of tie lines. It can be concluded from rmsd values that the NRTL model satisfactorily correlates the experimental LLE data of the two studied ternary systems.

Table 5. Values of the NRTL Parameters Obtained from LLE Data by Regression at T = 313.2 K[a]

	NRTL parameters			
component (i−j)	$\Delta g_{ij}/R$ (K)	$\Delta g_{ji}/R$ (K)	α_{ij}	rmsd
{Heptane (1) + Toluene (2) + [hemim][NTf$_2$] (3)}				
1−2	840.32	492.72	0.278	
1−3	3998.12	799.32	0.378	0.0046
2−3	1450.32	28.67	0.208	
{Heptane (1) + Benzene (2) + [hemim][NTf$_2$] (3)}				
1−2	638.87	232.95	0.354	
1−3	2780.15	589.32	0.401	0.0025
2−3	570.12	20.34	0.256	

[a] g_{ij} = energy parameter characteristic of the i−j interaction. R = gas constant. The standard uncertainty u for the temperature is $u(T)$ = 0.1 K.

5. CONCLUSION

The goal of this work was to introduce a new class of functionalized ionic liquid based on 1-(2-hydroxyethyl)-3-methylimidazolium cation in aromatic/aliphatic separations to obtain LLE data for {heptane (1) + toluene (2) + [hemim][NTf_2] (3)} and {heptane (1) + benzene (2) + [hemim][NTf_2] (3)} ternary systems at 313.2 K and atmospheric pressure.

Based on the calculated selectivity and distribution ratios, the miscible region of the studied systems is greater for benzene compared with toluene. In addition, the experimental results indicate that the addition of a hoydroxyl group into the imidazolium cation enhances the solubility of both aromatic and aliphatic compounds in the ionic liquid. In terms of aromatic selectivity, the performance of the functionalized ionic liquid is much better than sulfolane and the corresponding ionic liquid with an identical anion (NTf_2).

The consistency of the LLE data was ascertained by applying the Othmer–Tobias and Hand correlations, and the experimental LLE data were satisfactorily correlated by the NRTL model.

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Notes

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■ REFERENCES

(1) Hombourger, T.; Gouzien, L.; Mikitenko, P.; Bofils, P. *Solvent Extraction in the Oil Industry*; Technip: Paris, 2000.

(2) Weissermei, K.; Arpe, H. J. *Industrial Organic Chemistry*; Wiley-VCH: Weinheim, 2003.

(3) Arce, A.; Early, M. J.; Rodríguez, H.; Seddon, K. R.; Soto, A. 1-Ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide as solvent for the separation of aromatic and aliphatic hydrocarbons by liquid extraction-extension to C_7 and C_8 fractions. *Green Chem.* **2008**, *10*, 1294–1300.

(4) Meindersma, G. W.; Podt, A.; de Haan, A. B. Selection of ionic liquids for the extraction of aromatic/aliphatic mixtures. *Fuel Process. Technol.* **2005**, *87*, 59–70.

(5) Letcher, T. M.; Reddy, P. Ternary liquid–liquid equilibria for mixtures of 1-hexyl-3-methylimidozolium (tetrafluoroborate or hexafluorophosphate) + ethanol + an alkene at T = 298.2 K. *Fluid Phase Equilib.* **2004**, *219*, 107–112.

(6) Maduro, R. M.; Aznar, M. Liquid–liquid equilibrium of ternary systems 1-butyl-3-methylimidazolium hexafluorophosphate + aromatic + aliphatic. *Fluid Phase Equilib.* **2008**, *265*, 129–138.

(7) Weissermel, K.; Arpe, H. J. *Industrial Organic Chemistry*, 4th completely revised ed.; Wiley-VCH: Weinheim, 2003; pp 313–336.

(8) Tripathi, R. P.; Ram, A. R.; Rao, P. B. J. Liquid-liquid equilibriums in ternary system toluene-n-heptane-sulfolane. *Chem. Eng. Data* **1975**, *20*, 261–336.

(9) Al-Jimaz, A. S.; Fandary, M. S.; Alkhaldi, K. H. A. E.; Al-Kandary, J. A.; Fahim, M. A. Extraction of Aromatics from Middle Distillate Using N-Methyl-2-pyrrolidone: Experiment, Modeling, and Optimization. *Ind. Eng. Chem. Res.* **2007**, *46*, 5686–5696.

(10) Chen, D. C.; Ye, H. Q.; Wu, H. Liquid–Liquid Equilibria for Aromatics Extraction Systems with Tetraethylene Glycol. *J. Chem. Eng. Data* **2007**, *52*, 1297–1301.

(11) Wang, W.; Gou, Z. M.; Zhu, S. L. Liquid-Liquid equilibria for aromatics extraction systems with tetraethylene glycol. *J. Chem. Eng. Data* **1998**, *43*, 81–83.

(12) Wang, R.; Li, C.; Meng, H.; Wang, J.; Wang, Z. Ternary Liquid–Liquid Equilibria Measurement for Benzene + Cyclohexane + N-Methylimidazole, or N-Ethylimidazole, or N-Methylimidazolium Dibutylphosphate at 298.2 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2008**, *53*, 2170–2174.

(13) Ali, S. H.; Lababidi, H. M. S.; Merchant, S. Q.; Fahim, M. A. Extraction of aromatics from naphtha reformate using propylene carbonate. *Fluid Phase Equilib.* **2003**, *214*, 25–38.

(14) Mohsen-Nia, M.; Paikar, I. (Liquid + liquid) equilibria of ternary and quaternary systems containing n-hexane, toluene, m-xylene, propanol, sulfolane, and water at T = 303.15 K. *J. Chem. Thermodyn.* **2007**, *39*, 1085–1089.

(15) Schneider, D. F. Avoid sulfolane regeneration problems. *Chem. Eng. Prog.* **2004**, *100*, 34–39.

(16) Abu-Eishah, S. I.; Dowaidar, A. M. Liquid–Liquid Equilibrium of Ternary Systems of Cyclohexane + (Benzene, + Toluene, + Ethylbenzene, or + o-Xylene) + 4-Methyl-N-butyl Pyridinium Tetrafluoroborate Ionic Liquid at 303.15 K. *J. Chem. Eng. Data* **2008**, *53*, 1708–1712.

(17) Seddon, K. R.; Plechkova, N. V. Applications of Ionic Liquids in the Chemical Industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.

(18) Abu-Eishah, S. I. *Ionic Liquids Recycling for Reuse in Ionic Liquids–Classes and Properties*; InTech: Croatia, 2011; pp 239–272.

(19) Garcia, S.; Larriba, M.; Garcia, J.; Torrecilla, J. S.; Rodriguez, F. Liquid–liquid extraction of toluene from heptane using 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids. *J. Chem. Eng. Data* **2011**, *56*, 113–118.

(20) Garcia, S.; Larriba, M. J.; Garcia, J. S.; Torrecilla, F.; Rodriguez, J. (Liquid + liquid) equilibrium for the ternary systems {heptane + toluene + 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide} and {heptane + toluene + 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide} ionic liquids. *J. Chem. Thermodyn.* **2011**, *43*, 1641–1645.

(21) Garcia, S.; Larriba, M. J.; Garcia, J. S.; Torrecilla, F.; Rodriguez, J. 1-Alkyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids for the liquid–liquid extraction of toluene from heptane. *J. Chem. Eng. Data* **2011**, *56*, 3468–3474.

(22) Arce, A.; Earle, M. J.; Rodríguez, H.; Seddon, K. R. Separation of benzene and hexane by solvent extraction with 1-alkyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ionic liquids: effect of the alkyl substituent length. *J. Phys. Chem. B* **2007**, *111*, 4732–4736.

(23) Cassol, C. C.; Umpierre, A. P.; Ebeling, G.; Ferrera, B.; Chiaro, S. S. X.; Dupo, J. On the Extraction of Aromatic Compounds from Hydrocarbons by Imidazolium Ionic Liquids. *Int. J. Mol. Sci.* **2007**, *8*, 593–605.

(24) Othmer, D. F.; Tobias, P. E. Liquid-liquid extraction data-The line correlation. *Ind. Eng. Chem.* **1942**, *34*, 693–696.

(25) Hand, D. B. Dineric Distribution. *J. Phys. Chem.* **1930**, *34*, 1961–2000.

(26) Dubreuil, J. F.; Bazureau, J. P. Efficient combination of task-specific ionic liquid and microwave dielectric heating applied to one-pot three component synthesis of a small library of 4-thiazolidinones. *Tetrahedron* **2003**, *59*, 6121–6130.

(27) Yeon, S. H.; Kim, K. S.; Choi, S.; Lee, H. Physical and electrochemical properties of 1-(2-hydroxyethyl)-3-methyl imidazolium and N-(2-hydroxyethyl)-N-methyl morpholinium ionic liquids. *Electrochim. Acta* **2005**, *50*, 5399–5407.

(28) Jacobsen, N. E. *NMR Spectroscopy Explained* [S.I.]; John Wiley & Sons: New York, 2007.

(29) Hansmeier, A. R. *Ionic Liquids as Alternative Solvents for Aromatics Extraction*; Gildeprint Drukkerijen: Enschede, the Netherlands, 2010.

(30) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.

(31) Selvan, M. S.; Mckinley, M. D.; Dubois, R. H.; Atwood, H. L. Liquid−liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide. *J. Chem. Eng. Data* **2000**, *45*, 841−845.

(32) Alonso, L.; Arce, A.; Francisco, M.; Soto, A. Thiophene separation from aliphatic hydrocarbons using the 1-ethyl-3-methylimidazolium ethylsulfate ionic liquid. *Fluid Phase Equilib.* **2008**, *270*, 97−102.

(33) Chen, J.; Duan, L. P.; Mi, J. G.; Fei, W. Y.; Li, Z. C. Liquid−liquid equilibria of multi-component systems including n-hexane, n-octane, benzene, toluene, xylene and sulfolane at 298.15 K and atmospheric pressure. *Fluid Phase Equilib.* **2000**, *173*, 109−119.

(34) Atik, Z.; Kritli, A. Liquid-Liquid Equilibrium for 2,2,2-Trifluoroethanol + Ethanol + Cyclohexane from (288.15 to 308.15) K. *J. Chem. Eng. Data* **2008**, *53*, 1146−1150.