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Effect of an Ionic Liquid (IL) Cation on the Ternary System (IL + *p*-Xylene + Hexane) at $T = 298.15$ K[†]

Urszula Domańska,* Aneta Pobudkowska, and Zuzana Żołek-Tryznowska

Physical Chemistry Division, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3,
00-664 Warsaw, Poland

Liquid−liquid equilibrium data are presented for mixtures of {ionic liquid (butyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate, or hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate, or 1,3-dihexyloxymethylimidazolium tetrafluoroborate) + *p*-xylene + hexane} at 298.15 K. The alkyl chain length, hexyl vs butyl, has an influence on the separation process: the selectivities are statistically higher for the shorter alkyl chain. Unfortunately, polar 1,3-dihexyloxymethylimidazolium tetrafluoroborate is shown to have a very low selectivity. The nonrandom two liquid (NRTL) model was successfully used to correlate the experimental tie-lines and to calculate the phase compositions of the ternary systems. The average mean square deviation phase composition error is 0.018. The results are discussed in terms of the selectivity of separation of related systems. The data presented here indicate the usefulness of butyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate as a solvent for the separation of aromatic and aliphatic hydrocarbons using solvent extraction.

Introduction

A great number of industrial separation processes are concerned with liquid mixtures containing aromatics (benzene, toluene, *p*-xylene, alkylbenzenes) and saturated hydrocarbons (hexane, heptane, octane, decane). In liquid−liquid extraction processes, solvents such as sulfolane, *N*-methyl-2-pyrrolidinone (NMP) or NMP with water as cosolvent, furfuryl alcohol, and many other organic solvents have been used extensively.[1−3]

The design of a safe and environmentally benign separation process has an increasingly important role in the chemical industry. In recent years, there has been a surge of interest in using ionic liquids (ILs) as solvents. They show interesting properties that would allow them to replace classic organic solvents while improving performance and causing less damage to the environment. The separation of aromatic hydrocarbons (benzene, toluene, ethyl benzene, and xylenes) from aliphatic hydrocarbon mixtures is challenging because these hydrocarbons have similar boiling points and several combinations form azeotropes. The requirements of a suitable ionic liquid for the separation of aromatic and aliphatic hydrocarbons are the high solubility of aromatic hydrocarbons in the IL and the low solubility of aliphatic hydrocarbons in the IL. This is usually achieved by considering ILs which interact strongly with the aromatic hydrocarbon through $n-\pi$ or $\pi-\pi$ interactions. The experimental work concerning the liquid−liquid equilibria in ternary systems {IL + aromatic hydrocarbon + aliphatic hydrocarbon} using 1-ethyl-3-methylimidazolium bis{(trifluomethyl)sulfonyl}imide, [EMIM][NTf_2][4], is pertinent to the discussion here. The most soluble IL in toluene, found recently, was 4-methyl-*N*-butylpyridinium tetrafluoroborate, [MBPy][BF_4], which was more soluble than three other related ILs, 1,3-dimethylimidazolium methylsulfate, [MMIM][CH_3SO_4], 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM][$EtSO_4$], and 1-butyl-3-methylimidazolium methylsulfate, [BMIM][CH_3SO_4].[5] In this paper, it was stated that [MBPy][BF_4] was not only the best solvent of these four ILs for the aromatic/aliphatic separations but also better than sulfolane. Several ILs were discussed for this extraction by Meindersma et al.[6] In this work, the following values of selectivity were found: for [EMIM][I_3] (toluene/heptane, 48.6); for [MMIM][CH_3PO_4] (toluene/octane 48.0); for [EMIM][$EtSO_4$] (toluene/heptane, 43.0), in comparison with sulfolane (toluene/heptane, 30.9).[6]

From the activity coefficients at infinite dilution measurements, the best values were obtained for [EMIM][$EtSO_4$] (hexane/benzene, 40.8)[7]and 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate, [BMIM][$MDEGSO_4$] (hexane/benzene, 39.7),[8] at 298.15 K.

The nonvolatility of ILs in combination with their remarkable separation efficiency and selectivity enable new processes for the separation of azeotropic mixtures which, in comparison to conventional separation processes, might offer a potential for cost savings. Until now, it cannot be predicted which IL is the best one for certain applications. Some ILs such as [EMIM]-[NTf_2] or [EMIM][$EtSO_4$] are excellent entrainers for the separation of aliphatic from aromatic hydrocarbons by extractive distillation or extraction.[5−7]

The solubility of [$(C_6H_{13}OCH_2)_2$IM][BF_4] was measured previously in alcohols (hexan-1-ol, or octan-1-ol, or decan-1-ol) and water.[9] Solubilities of other dialkoxyimidazolium ILs, [$(C_4H_9OCH_2)_2$IM][BF_4], [$(C_8H_{17}OCH_2)_2$IM][NTf_2], and [$(C_{10}H_{21}OCH_2)_2$IM][NTf_2], were measured in a number of organic solvents.[10] For these salts, the solubility measurements in alcohols (ethanol, octan-1-ol) and in benzene were determined. The second alkoxy group in the molecule of IL causes the stronger interaction with the solvent. Only the [$(C_4H_9OCH_2)_2$IM][BF_4] salt exhibited a small miscibility gap in alcohols and a much lower solubility in benzene.[10] Complete miscibility in the liquid phase was observed for [$(C_8H_{17}OCH_2)_2$IM][Tf_2N] or [$(C_{10}H_{21}OCH_2)_2$IM][Tf_2N] in alcohols (ethanol, octan-1-ol) and in benzene.[10]

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* Corresponding author. Tel: +4822-6213115. E-mail: ula@ch.pw.edu.pl.

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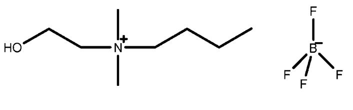
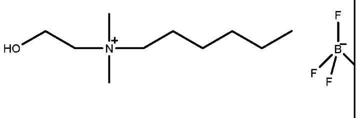
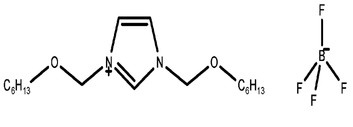
Table 1. List of Investigated Ionic Liquids, Names, Structure, and Abbreviations of Names

Butyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate		C_4BF_4
Hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate		C_6BF_4
1,3-dihexyloxymethylimidazolium tetrafluoroborate, $[(C_6H_{13}OCH_2)_2IM][BF_4]$		$[(C_6H_{13}OCH_2)_2IM][BF_4]$

Generally, the separation of the aromatic hydrocarbons/aliphatic hydrocarbons decreases with an increasing length of the alkyl chain at the imidazolium cation or anion of the salt. In this work, the separation properties of the low-cost ammonium ILs are compared to the separation properties of very polar and interactive alkoxy−IL salt with the same anion.

From the optimistic experimental data on activity coefficients at infinite dilution of $[BMIM][MDEGSO_4]$ (alkoxy group in the anion),[8] it can be deduced that the alkoxyimidazolium IL (alkoxy group in the cation) should show high selectivity for the aromatic/aliphatic separation.

In this work, we investigated the separation of *p*-xylene from hexane by extraction with two ammonium ionic liquids butyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate (C_4BF_4) and hexyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate (C_6BF_4) as well as one imidazolium ionic liquid, 1,3-dihexyloxymethylimidazolium tetrafluoroborate $[(C_6H_{13}OCH_2)_2IM][BF_4]$. Ternary liquid−liquid equilibrium data were measured experimentally at 298.15 K. The experimental technique is based on direct analysis of phases at equilibrium using ^1H NMR, which allows quantitative analysis of the three compounds.

Experimental Section

Materials. The origins of the chemicals (Chemical Abstract registry numbers, the manufactures reported, and mass percent purities are in parentheses) were as follows: hexane (110-54-3, Merck, 99 %), *p*-xylene (106-42-3, Aldrich, 99 %). Solvents were fractionally distilled over different drying reagents to the mass fraction purity ≥ 99.8 mass %. Solvents were stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The refractive indices for solvents were $n_D(298.15) = 1.493\ 21$ and 1.372 26 for *p*-xylene and hexane, respectively.

The ILs investigated here were synthesized as described in the Appendix. A list of investigated ionic liquids, names, structures, and abbreviations of names is presented in Table 1.

Procedures. For the experimental determination of the LLE tie-lines, the proton nuclear magnetic resonance spectroscopy (^1H NMR) was used as described in the Supporting Information. A description of the spectra is presented in Figure 1S of the Supporting Information. Water content was analyzed by Karl Fischer titration by the method presented in the Supporting Information.

Table 2. Compositions of the Conjugate Solutions, x_1^{II}, x_2^{II}, x_1^{I}, and x_2^{I}, Values of the Solute Distribution Ratio (β), and Selectivity (S) Together with the Tie-Line Composition for the Ternary Mixtures {Ionic Liquid (1) + *p*-Xylene (2) + Hexane (3)} at 298.15 K

ionic liquid-rich layer		hexane-rich layer			
x_1^{II}	x_2^{II}	x_1^{I}	x_2^{I}	β	S
		C_4BF_4			
1.00	0.00	0.00	0.00		
0.91	0.08	0.00	0.22	0.36	28.4
0.76	0.20	0.00	0.33	0.61	10.2
0.70	0.27	0.00	0.44	0.61	11.5
0.68	0.30	0.00	0.50	0.60	15.0
0.60	0.38	0.00	0.53	0.72	16.8
0.52	0.46	0.00	0.69	0.67	10.3
0.41	0.57	0.00	0.76	0.75	9.0
0.30	0.68	0.00	0.83	0.82	7.0
		C_6BF_4			
0.99	0.00	0.00	0.00		
0.97	0.02	0.00	0.31	0.11	4.5
0.94	0.05	0.00	0.45	0.21	6.1
0.87	0.12	0.00	0.56	0.46	9.4
0.70	0.29	0.00	0.63	0.72	17.0
0.45	0.51	0.00	0.71	0.79	5.2
0.36	0.60	0.00	0.76	0.06	4.7
		$[(C_6H_{13}OCH_2)_2IM][BF_4]$			
0.44	0.00	0.00	0.00		
0.40	0.14	0.00	0.20	0.68	1.2
0.37	0.25	0.00	0.34	0.74	1.3
0.34	0.33	0.00	0.41	0.80	1.4
0.34	0.34	0.00	0.44	0.77	1.4
0.34	0.35	0.00	0.45	0.78	1.0
0.31	0.43	0.00	0.55	0.78	1.4
0.29	0.47	0.00	0.60	0.78	1.3
0.27	0.50	0.00	0.63	0.79	1.3
0.20	0.63	0.00	0.74	0.85	1.4

Results and Discussion

The use of ILs as solvents for liquid extraction processes is one of their promising applications. The main purpose of this study was to produce a new IL for the LLE data on {IL + *p*-xylene + hexane} at 298.15 K and to correlate the data using the NRTL model. In this paper, the effect of the cation of the ionic liquid was examined with respect to the selectivity of *p*-xylene/hexane phase separation. Furthermore, the effect of the alkyl chain length of the ammonium ionic liquid on the phase properties of the ternary mixtures {IL + *p*-xylene + hexane} was investigated.

The measured compositions of the experimental tie-line ends of the ternary systems {IL + *p*-xylene (2) + hexane (3)} at 298.15 K are reported in Table 2.

The feasibility of using the IL as a solvent to perform the extraction of *p*-xylene from a mixture with hexane was evaluated by classic parameters such as the solute distribution ratio (β) and the selectivity (S), calculated from the experimental data.

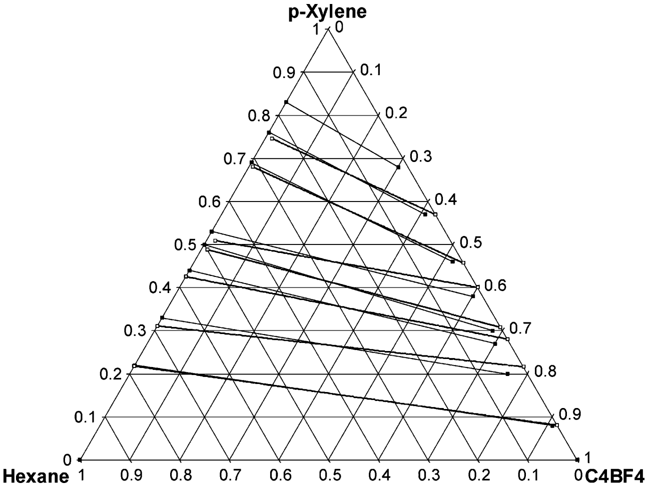


Figure 1. Experimental tie-lines (■, solid line) and NRTL correlation (α = 0.1) (□, dotted line) at 298.15 K and ambient pressure for the {C_4BF_4 + *p*-xylene (2) + hexane (3)} ternary system.

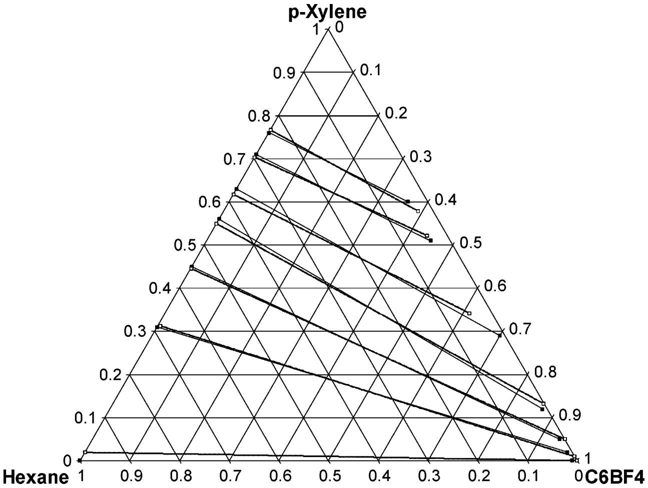


Figure 2. Experimental tie-lines (■, solid line) and NRTL correlation (α = 0.3) (□, dotted line) at 298.15 K and ambient pressure for the {C_6BF_4 + *p*-xylene (2) + hexane (3)} ternary system.

These parameters are defined by the following expressions

$$\beta = \frac{x_2^{II}}{x_2^{I}} \tag{1}$$

$$S = \frac{x_2^{II} \cdot x_3^{I}}{x_2^{I} \cdot x_3^{II}} \tag{2}$$

where x is the mole fraction; superscripts I and II refer to the hydrocarbon-rich phase and ionic liquid-rich phase, respectively; and subscripts 2 and 3 refer to *p*-xylene (solute) and hexane (inert, in our mixtures), respectively. The values of β and S are shown in Table 2, together with the experimental equilibrium data. The separation in the system *p*-xylene/hexane was to our knowledge never measured for other ILs, only with sulfolane. The selectivity value for the first tie-line was 17.3, and the values for the middle of the area of measures tie-lines were 7.7, 6.6, and 3.0 for {sulfolane + *p*-xylene + heptane} at 303.15 K.[1] Our solubility results for these ternary systems at 298.15 K (lower temperature, lower selectivities) are much better for C_4BF_4 than for C_6BF_4 and are fairly close to those previously

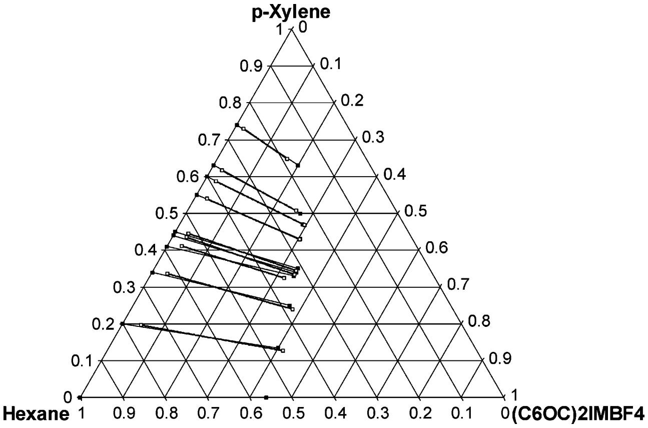


Figure 3. Experimental tie-lines (■, solid line) and NRTL correlation (α = 0.55) (□, dotted line) at 298.15 K and ambient pressure for the {$[(C_6H_{13}OCH_2)_2IM][BF_4]$ + *p*-xylene (2) + hexane (3)} ternary system.

published for sulfolane (see Table 2 and Figures 1 and 2). The results indicate that the increase in carbon number of the alkane from 4 to 6 in the cation of ammonium IL has a large effect. Thus, it appears that the separation of the aromatic hydrocarbons/aliphatic hydrocarbons decreases with an increasing length of the alkyl chain at the ammonium cation. This is most likely due to the higher solubility of hexane in the ionic liquids. The substitution of the hydroxyl group on the ammonium cation, as in C_4BF_4 and in C_6BF_4, increases the aromatic/aliphatic selectivity in comparison to methyl-tributylammonium methylsulfate, measured earlier in toluene/heptane separation processes.[6] The selectivities at 313.15 K were in the range of 7 to 9, which is much lower than that observed for our ionic liquids.

The distribution ratios of *p*-xylene with the two ammonium ionic liquids measured here were about the same value, being slightly lower for C_6BF_4. A much higher distribution ratio (double the value) was observed for hexyloxyimidazolium salt. The interaction of this ionic liquid with the aromatic *p*-xylene is most probably π-ionic in nature. Unfortunately, from the solubility measurements in the binary system, it can be seen that the hexyloxyimidazolium ionic liquid cannot be used for the separation of xylenes (*p*-, *m*-, and *o*-).[15]

One set of requirements for a suitable ionic liquid for the separation of aromatic and aliphatic hydrocarbons is a high solubility of aromatic hydrocarbons in the IL and a low solubility of aliphatic hydrocarbons in the IL. The first of these conditions—solubility of benzene, toluene, ethylbenzene, and xylenes—was unexpectedly large for the 1-hexyloxymethyl-3-methylimidazoliun bis{(trifluomethyl)sulfonyl}imide ionic liquid.[9,15] The same salt with a $[BF_4]^-$ anion has shown lower solubility of aromatic solvents than those in the IL salt with the $[NTf_2]^-$ anion but much higher than those observed for many other ILs.[15] These solubility results in binary systems have led us to measure the ternary system involving $[(C_6H_{13}OCH_2)_2IM][BF_4]$. The results are listed in Table 2 and are shown in Figure 3. Unfortunately, the selectivities are very low.

The slopes of the binodal curves for the IL + *p*-xylene mixture are similar. Figures 1 to 3 show that the area of the two-phase region increases in the order $[(C_6H_{13}OCH_2)_2IM][BF_4] < C_6BF_4 < C_4BF_4$. The relative solubility of *p*-xylene in hexane, or in IL, is evident from the tie-lines. The slopes of tie-lines presented in Figures 1 to 3 show that *p*-xylene is more soluble in hexane than in IL. It can be expected from the previous measurements with sulfolane that increasing the number of carbon atoms in hydrocarbon (heptane to dodecane) will increase the two-phase region.[15]

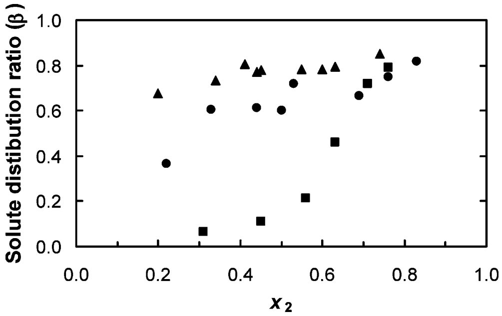


Figure 4. Solute distribution ratio at 298.15 K, as a function of the mole fraction of *p*-xylene in the hexane-rich phase, for the ternary systems: ●, {C_4BF_4 + *p*-xylene + hexane}; ■, {C_6BF_4 + *p*-xylene + hexane}; ▲, {[$(C_6H_{13}OCH_2)_2$IM][BF_4] + *p*-xylene + hexane}.

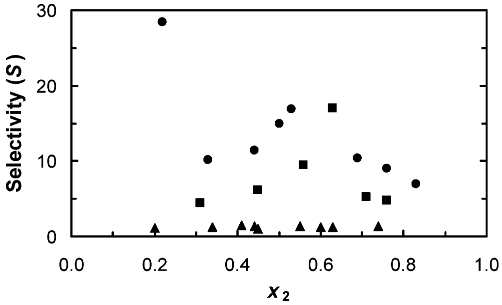


Figure 5. Selectivity at 298.15 K, as a function of the mole fraction of *p*-xylene in the hexane-rich phase, for the ternary systems: ●, {C_4BF_4 + *p*-xylene + hexane}; ■, {C_6BF_4 + *p*-xylene + hexane}; ▲, {[$(C_6H_{13}OCH_2)_2$IM][BF_4] + *p*-xylene + hexane}.

The graphical representation of the solute (*p*-xylene) distribution ratio as a function of the solute mole fraction in the hydrocarbon-rich phase is shown in Figure 4. It can be seen that the solute distribution ratios increase with an increase of the mole fraction of *p*-xylene to values of 0.8 to 0.9. These data are similar to sulfolane,[16] the most popular solvent used in industrial processes for the separation of aromatic and aliphatic hydrocarbons by liquid extraction. The opposite dependence but with a higher solute distribution ratio was found for [EMIM][NTf_2].[4]

Selectivity for our data increases as a function of the solute mole fraction for the systems with C_4BF_4 and C_6BF_4 from $x_2 = 0$ to $x_2 = 0.6$ and then decreases (Figure 5). The selectivity for sulfolane[16] and [EMIM][NTf_2][4] decreases regularly as the mole fraction of solute in the system increases. For [$(C_6H_{13}OCH_2)_2$IM][BF_4], the selectivities have a constant value.

Data Correlation

A thermodynamic model such as the nonrandom liquid equation (NRTL)[17] is used to correlate the experimental data for three ternary systems discussed here. The equations and algorithms used in the calculation of the compositions of liquid phases follow the method used by Walas.[18] The objective function $F(P)$ was used to minimize the difference between the experimental and calculated concentrations

$$F(P) = \sum_{i=1}^{n} [x_{2i}^{\text{Iexptl}} - x_{2i}^{\text{Icalcd}}(PT)]^2 + [x_{3i}^{\text{Iexptl}} - x_{3i}^{\text{Icalcd}}(PT)]^2 + [x_{2i}^{\text{IIexptl}} - x_{2i}^{\text{IIcalcd}}(PT)]^2 + [x_{3i}^{\text{IIexptl}} - x_{3i}^{\text{IIcalcd}}(PT)]^2 \quad (3)$$

where P is the set of parameters in the vector; n is the number of experimental points; x_{2i}^{Iexptl}, x_{3i}^{Iexptl} and $x_{2i}^{\text{Icalcd}}(PT)$, $x_{3i}^{\text{Icalcd}}(PT)$ are the experimental and calculated mole fractions of one phase; and x_{2i}^{IIexptl}, x_{3i}^{IIexptl} and $x_{2i}^{\text{IIcalcd}}(PT)$, $x_{3i}^{\text{IIcalcd}}(PT)$ are the experimental and calculated mole fractions of the second phase.

Table 3. Values of Parameters for the NRTL Equation for the Ternary Mixtures {Ionic Liquid (1) + *p*-Xylene (2) + Hexane (3)}[a]

i, *j*	$g_{ij} - g_{jj}$/J·mol^{-1}	$g_{ji} - g_{ii}$/J·mol^{-1}
	C_4BF_4 (0.015)[b]	
1, 2	1065.40	3731.81
1, 3	47889.08	36156.74
2, 3	10549.81	−5866.88
	C_6BF_4 (0.020)[c]	
1, 2	12738.53	1301.49
1, 3	10125.28	15963.59
2, 3	−4105.07	−4050.77
	[$(C_6H_{13}OCH_2)_2$IM][BF_4] (0.020)[d]	
1, 2	4067.13	7840.45
1, 3	3389.65	4581.79
2, 3	6389.23	415.80

[a] The rmsd values are given in parentheses. [b] Calculated with $\alpha_{ij} = 0.1$. [c] Calculated with $\alpha_{ij} = 0.3$. [d] Calculated with $\alpha_{ij} = 0.55$.

For the NRTL model, the third nonrandomness parameter, α_{ij}, was set at values of 0.1, 0.3, and 0.55 (see Table 3). The values of the starting parameters for the three binary systems were not known, thus the calculations were made by the correlation of the experimental points. The parameters and root-mean-square deviations (rmsd), calculated in this way, are included in Table 3. The rmsd values, which can be taken as a measure of the precision of the correlations, were calculated according the equation

$$\text{rmsd} = \left(\sum_i \sum_l \sum_m [x_{ilm}^{\text{exptl}} - x_{ilm}^{\text{calcd}}]^2/6k\right)^{1/2} \quad (4)$$

where x is the mole fraction and the subscripts i, l, and m designate the component, phase, and tie-line, respectively. As can be seen from Table 3 and Figures 1 to 3, the correlation obtained for the system {C_4BF_4 + *p*-xylene + hexane} was significantly better than that obtained for the two other systems.

Conclusions

Liquid−liquid equilibrium data for the three ternary systems {C_4BF_4 (or C_6BF_4 or [$(C_6H_{13}OCH_2)_2$IM][BF_4]) + *p*-xylene + hexane} were determined at 298.15 K. The separation of *p*-xylene from hexane by extraction with ionic liquid is feasible, especially with the C_4BF_4 compound, as can be concluded from the distribution ratios and selectivity data. The correlation based on the NRTL model showed the average rmsd equal to 0.018.

A comparison of the results obtained with C_4BF_4 or C_6BF_4 ionic liquids led to the conclusion that a shorter alkyl chain on the cation is more favorable for higher aromatic/aliphatic selectivities. Unfortunately, C_4BF_4 shows a lower distribution ratio than that observed for [$(C_6H_{13}OCH_2)_2$IM][BF_4].

Appendix

The IL alkyl(2-hydroxyethyl)dimethylammonium tetrafluoroborate was synthesized using *N*,*N*-dimethylethanolamine (Sigma-Aldrich, CAS number 108-01-0) and the appropriate haloalkanes: butyl bromide (Sigma-Aldrich, CAS number 109-65-9) and hexyl bromide (Sigma-Aldrich, CAS number 111-25-1). The substances were placed in a round-bottom flask and were mixed in 10 % excess of haloalkane. The intermediates were heated at 350 K for 30 min and stirred under reflux to form the reaction mixture. After that, the mixture was cooled down and the obtained solid product was dissolved in a mixture of 1-propanol (Sigma-Aldrich, CAS number 71-23-8) and methanol (Sigma-Aldrich, CAS number 67-56-1) at a ratio of 1:3. Subsequently, the mixture was heated at 303 K for 30 min under reflux. Later, the mixture was cooled down, and a very small portion of cyclohexane (Sigma-Aldrich, CAS number 110-82-7) was added to the mixture to form the solid powder. The solid phase was filtered through an S_4 filter, and that phase was collected. The salts were recrystallized from a mixture of 1-propanol and methanol and then rigorously dried under a vacuum for 48 h prior to use. The bromide salt was characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), mass spectroscopy, elemental analysis, differential scanning microscopy (DSC), and simultaneous thermogravimetry/differential thermal analysis (TG/DTA) and water content.[11] The synthesis of alkyl(2-hydroxyethyl)-dimethylammonium tetrafluoroborate has been performed via a metathesis reaction: 1 equiv of bromide salt reacts with 1 equiv of sodium tetrafluoroborate and $NaBF_4$ in water. The solvent was used in as small a quantity as possible to dissolve bromide salt. Reactions were performed in round-bottom flasks at 350 K under reflux with vigorous stirring for at least 24 h. After the reaction, the mixtures were transferred to the separator, and dichloromethane was added in equal volume to the reaction mixture. After shaking, the organic layer was collected and solvent was removed under a vacuum with a rotary evaporator. Washing by dichloromethane was repeated at least four times. After the last wash, the flask with the ionic liquid was placed under a high vacuum and was stirred at 340 K. After 24 h, water (Karl Fischer) content was measured. The physicochemical constants were presented earlier.[12] The imidazolium 1,3-dihexyloxymethylimidazolium tetrafluoroborate was obtained from 1,3-dihexyloxymethylimidazolium chloride.[13,14] The prepared IL was characterized by ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectra were recorded on a Varian model XL 300 spectrometer at 300 MHz with tetramethylsilane as the standard. The ^{13}C NMR spectra were recorded on the same instrument at 75 MHz to confirm the absence of any major impurities. The physicochemical constant and characteristics were presented earlier.

All ionic liquids were liquid at room temperature and were cleaned with activated carbon to remove traces of any colored compounds and dried under a vacuum at 300 K for 48 h to remove organic solvents and water. Analysis for the water contamination using the Karl Fischer technique for solvents and ILs showed that the impurity in each of the substances was $<$ 0.02 mol %.

Supporting Information Available:

Experimental ternary LLE procedure, NMR spectra, and water content measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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