Ternary Liquid−Liquid Equilibria Measurement for Hexane and Benzene with the Ionic Liquid 1-Butyl-3-methylimidazolium Methylsulfate at $T = (298.2, 313.2, \text{and } 328.2)$ K

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This paper reports liquid−liquid equilibria (LLE) data for the ternary system based on hexane, benzene, and 1-butyl-3-methylimidazolium methylsulfate ([bmim]CH_3SO_4) at $T = (298.2, 313.2, \text{and } 328.2)$ K and atmospheric pressure. The degree of consistency of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation. For the extractive effectiveness of the ionic liquid [bmim]CH_3SO_4, the distribution ratio and separation factor curves were plotted and compared with those of sulfolane. In addition, the LLE data were successfully correlated with thermodynamic models such as UNIQUAC and NRTL.

Introduction

Recently, ionic liquids (ILs), due to their unique properties, have attracted increasing attention as replacements for conventional organic solvents in separation processes.[1−3] The application of ILs on the extraction of aromatics from their mixture with aliphatic hydrocarbons has previously been explored by experimental measurement of ternary LLE, and these results can be found elsewhere.[4−17] Most of these references describe separation processes using ILs which have so low values of selectivity and/or extractive capacity which prevent their possible use in industrial applications. Moreover, some of the tested ILs are highly expensive, potentially toxic, or corrosive. However, the alkylsulfate-based ILs, apart from their handling properties and their adequate performance in extractive applications, present low costs and are more environmentally friendly than other ILs.[18] Even more, to the best of our knowledge, availability of experimental LLE data for the ternary systems {aliphatic hydrocarbons + aromatic hydrocarbons + alkylsulfate-based ILs} is as yet scarce. Because of this, the objective of this work consists of measuring LLE for the ternary system {hexane + benzene + 1-butyl-3-methylimidazolium methylsulfate ([bmim]CH_3SO_4)} at $T = (298.2, 313.2, \text{and } 328.2)$ K and atmospheric pressure. These temperatures were set for the experiments because it is a common practice in the literature to determine the LLE of ternary systems at $T = 298$ K and also because this temperature range is that in which extraction at atmospheric pressure has a potential application. The extracting capacity and selectivity were calculated from the LLE data. The reliability of the experimentally measured LLE data was tested by the Othmer−Tobias correlation. Finally, the LLE data were correlated by nonrandom two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) models.

Experimental Section

Hexane ($w \geq 0.990$) and benzene ($w \geq 0.995$) were purchased from Fluka and used as received, without further purification. The [bmim]CH_3SO_4 IL ($w \geq 0.95$), produced by BASF, was obtained from Sigma-Aldrich. This was purified by heating in a vacuum (100 mbar, 353 K) for 24 h to remove any trace of volatile components including water. Analysis, using the Karl Fisher techniques,[19] showed that the water mass fraction in the IL was $3.2 \cdot 10^{-4}$. The thermophysical and volumetric properties of the IL were also determined and can be found elsewhere.[20,21]

The equilibrium experiments were carried out in a glass three-neck jacketed vessel with a volume of approximately 100 mL. Two necks were closed using septums, through which needles were passed to sample the lower and upper layers. The temperature was measured with a Pt100 sensor inserted through the third neck into the vessel with an uncertainty value of ± 0.1 K. The temperature in the jacket of the vessel was kept constant by circulating water from a thermostat bath (Julabo F30) capable of maintaining the temperature at a fixed value (within ± 0.1 K). Mixtures of known masses of hexane, benzene, and [bmim]CH_3SO_4 were introduced into the vessel, sealed, and magnetically stirred for at least 3 h and next left to settle overnight to ensure thermodynamic equilibrium and complete phase separation at a constant temperature.

Samples from the lower and upper layers were carefully taken with syringes and analyzed by a gas chromatograph (Varian GC, model 3800) equipped with a flame ionization detector (FID), a 30 m × 0.250 mm (film thickness = 0.25 μm) CP-Sil 8CB wall-coated open tubular column (Chrompack), and Varian Star Chromatography software, which enables instrument control and data handling on a Microsoft Windows-based platform. The oven temperature was fixed at 323 K. The injector port and detector temperature were held at 523 K. The flow rate of the carrier gas (helium) was kept at $1 \text{ mL} \cdot \text{min}^{-1}$. Because the IL has a negligible vapor pressure, it cannot be analyzed by gas chromatography. It was collected in a 5 m × 0.250 mm uncoated fused silica precolumn in order not to disrupt the analysis. Samples from the upper layer (hexane-rich phase) were assumed as totally free of IL as was demonstrated by observing visually the immiscibility of the IL in both pure hydrocarbons and confirmed afterward by ^{1}H NMR analysis of some hydrocarbon-rich phase samples. So, an area normalization method with a response factor was used to determine the molar fraction of both hydrocarbons in the upper layer. On the other hand, in the lower layer (IL-rich phase) the three components will be present. But, in a ternary mixture, one has to analyze only two components.

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Table 1. Experimental LLE Data in Mole Fraction, Solute Distribution Ratios (D_2), and Separation Factors ($\alpha_{2,1}$) for the Ternary System {Hexane (1) + Benzene (2) + [bmim]CH_3SO_4 (3)} at T = (298.2, 313.2, and 328.2) K

hexane-rich phase		IL-rich phase			
x_1^I	x_2^I	x_1^{II}	x_2^{II}	D_2	$\alpha_{2,1}$
		T = 298.2 K			
0.9451	0.0549	0.0107	0.0402	0.732	64.7
0.8908	0.1092	0.0110	0.0782	0.716	58.0
0.8370	0.1630	0.0107	0.1196	0.734	57.4
0.7838	0.2162	0.0103	0.1536	0.710	54.1
0.7311	0.2689	0.0101	0.1930	0.718	52.0
0.6790	0.3210	0.0099	0.2234	0.696	47.7
0.6273	0.3727	0.0098	0.2602	0.698	44.7
0.5762	0.4238	0.0096	0.2951	0.696	41.8
		T = 313.2 K			
0.9418	0.0582	0.0159	0.0490	0.842	49.9
0.8779	0.1221	0.0154	0.0993	0.813	46.4
0.8360	0.1640	0.0150	0.1273	0.776	43.3
0.7754	0.2246	0.0147	0.1631	0.726	38.3
0.7259	0.2741	0.0143	0.1877	0.685	34.8
0.6769	0.3231	0.0139	0.2273	0.703	34.3
0.6263	0.3737	0.0136	0.2494	0.667	30.7
0.5671	0.4329	0.0132	0.2853	0.659	28.3
		T = 328.2 K			
0.9294	0.0706	0.0191	0.0635	0.899	43.8
0.8811	0.1189	0.0187	0.1026	0.863	40.7
0.8296	0.1704	0.0181	0.1374	0.806	37.0
0.7711	0.2289	0.0176	0.1728	0.755	33.1
0.7175	0.2825	0.0173	0.2069	0.732	30.4
0.6686	0.3314	0.0167	0.2258	0.681	27.3
0.6120	0.3880	0.0165	0.2554	0.658	24.4
0.5498	0.4502	0.0162	0.2786	0.619	21.0

The third one, the IL, can be determined by mass balance of the measured molar fractions of the hydrocarbons. So, samples from the lower layer were analyzed following an internal standard method using heptane as the internal standard. Samples with known compositions were used to calibrate the instrument in the range of interest. All measurements were carried out in triplicate, and the averages are reported in our results. The estimated uncertainties in the determination of the hydrocarbon molar compositions in the upper and lower layers were less than $2 \cdot 10^{-4}$ and $4 \cdot 10^{-3}$, respectively.

Results and Discussion

The tie-line data for the ternary system {hexane + benzene + [bmim]CH_3SO_4} at T = (298.2, 313.2, and 328.2) K and atmospheric pressure are given in Table 1 and displayed on the triangular diagram shown in Figure 1. As can be seen, it was found that the two-phase region is rather unaffected with the increase in temperature. It is also clear from the data shown in Table 1 (and also in Figure 1) that the benzene has a much higher affinity toward hexane (upper layer) than [bmim]CH_3SO_4 (lower layer), while the lower layer has a low concentration of hexane. On the other hand, the upper layer (hexane-rich phase) is totally free of [bmim]CH_3SO_4.

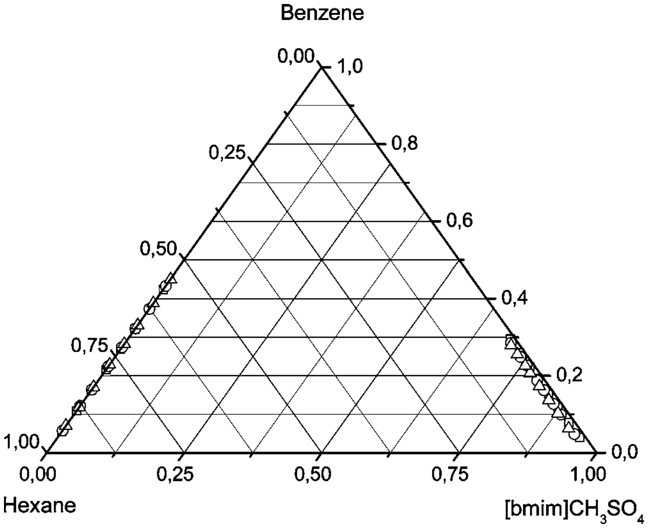

Figure 1. Experimental LLE data equilibrium molar compositions of the ternary system {hexane + benzene + [bmim]CH_3SO_4}: □, T = 298.2 K; ○, T = 313.2 K; △, T = 328.2 K.

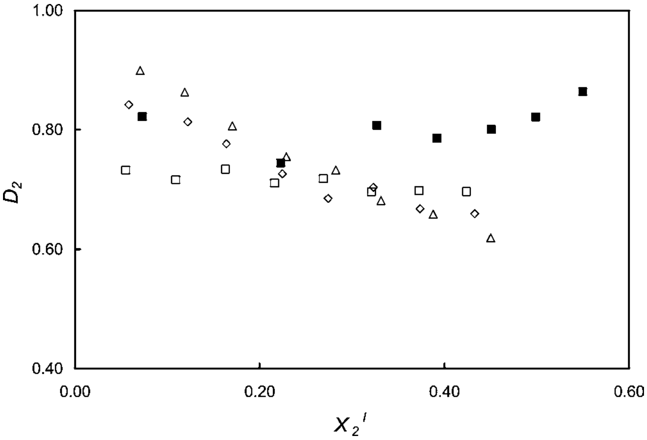

Figure 2. Distribution ratio of benzene for the ternary system {hexane + benzene + [bmim]CH_3SO_4} at (□, T = 298.2; ◇, T = 313.2; △, T = 328.2) K and {hexane + benzene + sulfolane} at ■, T = 298.2 K.[22]

The feasibility of using [bmim]CH_3SO_4 as a solvent to perform extraction of benzene from a mixture with hexane was evaluated by the benzene distribution ratio (D_2) and the separation factor ($\alpha_{2,1}$), calculated from the experimental data as follows

$$D_2 = \frac{x_2^{II}}{x_2^{I}} \tag{1}$$

$$\alpha_{2,1} = \frac{x_2^{II}x_1^{I}}{x_2^{I}x_1^{II}} \tag{2}$$

where x is the molar fraction; superscripts I and II refer to the hexane-rich and IL-rich phases; and subscripts 1 and 2 refer to hexane and benzene, respectively. The values of D_2 and $\alpha_{2,1}$ are shown in Table 1, together with the experimental equilibrium data.

The benzene distribution ratio and separation factor values for each temperature versus the benzene molar fraction in the hexane-rich phase are shown in Figures 2 and 3, respectively. As can be seen, the influence of temperature effect on both the distribution ratio and separation factor was found to be significant at the temperatures studied. A comparison with data in the literature for the ternary system {hexane + benzene + sulfolane} at a temperature of 298.2 K is also made.[22] At present, the sulfolane process licensed by UOP is the most important of all industrial extraction processes for aromatics. As can be seen from Figure 2, the distribution ratio values at a temperature of 298.2 K are slightly higher when using sulfolane, thus indicating a preference of the sulfolane for the benzene in the mixtures of hydrocarbons and also meaning an increase in the amount of solvent required to carry out the extraction with the IL of a given mixture. On the other hand, the separation factor values for the IL system are clearly higher than for the sulfolane system. So, high separation factor values will lead to fewer stages and better purity when the IL is used. Moreover,

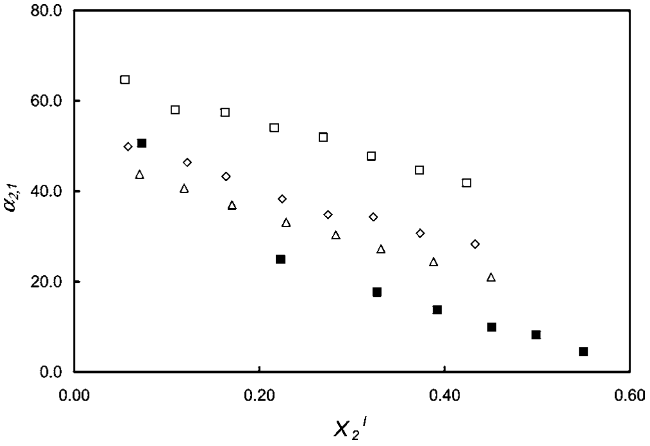

Figure 3. Separation factor for the ternary system {hexane + benzene + [bmim]CH_3SO_4} at (□, T = 298.2; ◇, T = 313.2; △, T = 328.2) K and {hexane + benzene + sulfolane} at ■, T = 298.2 K.[22]

Table 2. Constants of the Othmer−Tobias Correlation, Correlation Factors (R^2), and Standard Deviations (σ) for the {Hexane (1) + Benzene (2) + [bmim]CH_3SO_4 (3)} System As a Function of Temperature

T/K	a	b	R^2	σ
298.2	1.6431	0.8244	0.9996	0.0154
313.2	1.7419	0.7098	0.9987	0.0227
328.2	1.8847	0.6085	0.9956	0.0376

the IL is totally immiscible in the hexane-rich layer, unlike sulfolane. Thus, no IL will dissolve and become entrained in the raffinate stream if it is used as extracting solvent for the separation of aromatic and aliphatic hydrocarbons. Therefore, [bmim]CH_3SO_4 can be considered as a possible candidate for extraction of aromatic from aliphatic hydrocarbons.

The reliability of the experimentally measured tie-line data can be ascertained by applying the Othmer−Tobias correlation:[23]

$$\ln\left(\frac{1 - w_3^{\mathrm{II}}}{w_3^{\mathrm{II}}}\right) = a + b\ln\left(\frac{1 - w_1^{\mathrm{I}}}{w_1^{\mathrm{I}}}\right) \tag{3}$$

where w_3^{II} is the mass fraction of [bmim]CH_3SO_4 (3) in the lower layer (IL-rich phase); w_1^{I} is the mass fraction of hexane (1) in the upper layer (hexane-rich phase); and a and b are the fitting parameters of the Othmer−Tobias correlation. The linearity of the plot indicates the degree of consistency of the data. The parameters of the Othmer−Tobias correlation are given in Table 2. The regression coefficients (R^2) very close to unity and the very small values of the standard deviation (σ) presented in Table 2 indicate the degree of consistency of related data at T = (298.2, 313.2, and 328.2) K.

The experimental data of this work were also used to examine the LLE correlating capability of some liquid-phase models. The NRTL[24] and UNIQUAC[25] models were used to correlate the LLE data in the present work, as they have proven an adequately correlating capability to ternary and binary LLE data for systems that contain ILs.[26] In these models, the adjustable parameter was defined as follows for NRTL and UNIQUAC, respectively

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{4}$$

$$\tau_{ij} = \exp^{\left(a_{ij} + \frac{b_{ij}}{T}\right)} \tag{5}$$

Table 3. Values of the NRTL and UNIQUAC Binary Parameters Regressed from LLE Data for the {Hexane (1) + Benzene (2) + [bmim]CH_3SO_4 (3)} System at T = (298.2, 313.2, and 328.2) K

component $i-j$	a_{ij}	a_{ji}	b_{ij}/K	b_{ji}/K	α_{ij}
			NRTL parameters		
1−2	4.5037	4.9114	−963.09	−266.24	0.30
1−3	−3.5724	2.9759	−42.575	1744.7	0.03
2−3	1.8448	2.1575	304.78	−555.89	0.06
			UNIQUAC parameters		
1−2	−2.8028	−0.9622	862.15	256.78	
1−3	−0.1939	1.0990	−374.45	−351.89	
2−3	−2.5315	−1.7074	261.56	694.66	

Table 4. NRTL and UNIQUAC Models' Root Mean Square Deviation (rmsd) Values

	rmsd	
T/K	NRTL	UNIQUAC
298.2	0.0049	0.0014
313.2	0.0035	0.0033
328.2	0.0050	0.0011

The binary interaction parameters, a_{ij} and b_{ij}, for both equations were calculated using an ASPEN Plus Simulator. The regression method used in the ASPEN simulator was the generalized least-squares method based on the maximum likelihood principles. The Britt−Luecke algoritm[27] was employed to obtain the model parameters with the Deming initialization method. The regression convergence tolerance was set to 0.0001. The value of the nonrandomness parameter, α, in the NRTL equation was subject to optimization between 0 and 1. The IL structural parameters for UNIQUAC, r and q, were calculated using the method proposed by Banerjee et al.[28] based on computed pure component volume and surface parameters for ion-paired structures of ILs by COSMO-RS software. These values are 11.9 and 6.59, respectively. For hexane and benzene, r and q values in the ASPEN Plus Simulator Database were used.

Table 3 list the values of the binary interaction parameters over the corresponding range of temperatures for NRTL and UNIQUAC models, respectively. The values of the root-mean-square deviation (rmsd) of both models at each temperature are listed in Table 4. The rmsd is defined as

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

where x is the mole fraction and the subscripts i, l, and m provide a designation for the component, phase, and tie lines, respectively. The value k designates the number of tie lines.

Taking into account the rmsd shown in Table 4, both molecular models are adequate to correlate the LLE data. However, the major problem of both models is that they can not properly correlate the absence of IL in the hydrocarbon-rich phase.

Conclusions

In this work, liquid−liquid equilibria data for the system based on hexane, benzene, and [bmim]CH_3SO_4 were determined experimentally at T = (298.2, 313.2, and 328.2) K and at atmospheric pressure. The corresponding distribution ratio and separation factor values were calculated and compared with those for {hexane + benzene + sulfolane} at a temperature of 298.2 K. The degree of consistency of the experimental LLE data was ascertained by applying the Othmer−Tobias correlation.

The distribution ratio values for the aromatic extraction with the ionic liquid [bmim]CH_3SO_4 is slightly lower than using sulfolane which means that the amount of ionic liquid required to carry out the separation will be higher. However, the separation factor values for the ionic liquid system are clearly higher than for the sulfolane system. Thus, higher selectivity values will lead to fewer stages and better purity when the ionic liquid is used. In addition, [bmim]CH_3SO_4 is totally immiscible in the hydrocarbon phase which will make their recuperation and reuse easier and cheaper than when it is carried out using sulfolane. To recap, the ionic liquid [bmim]CH_3SO_4 could be considered as an alternative solvent to extract aromatic from aliphatic hydrocarbons.

Although, the NRTL and UNIQUAC models can satisfactorily correlate the experimental LLE data for the ternary system studied, they can not adequately describe the [bmim]CH_3SO_4 immiscibility in the hydrocarbon-rich phase.

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Literature Cited

(1) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. Room Temperature Ionic Liquids as Novel Media for 'Clean' Liquid-Liquid Extraction. *Chem. Commun.* **1998**, *16*, 1765–1766.

(2) Anjan, S. T. Ionic Liquid for Aromatic Extraction: Are They Ready? *Chem. Eng. Prog.* **2006**, *12*, 30–39.

(3) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Selection of Ionic Liquids for the Extraction of Aromatic Hydrocarbons from Aromatic/Aliphatic Mixtures. *Fuel Process. Technol.* **2005**, *87*, 59–70.

(4) Selvan, M. S.; McKinley, M. D.; Dubois, R. H.; Atwood, J. 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.

(5) Letcher, T. M.; Deenadayalu, N. Ternary Liquid-Liquid Equilibria for Mixtures of 1-Methyl-3-octyl-imidazolium Chloride + Benzene + an Alkane at T=298.2 K and 1 atm. *J. Chem. Thermodyn.* **2003**, *35*, 67–76.

(6) Letcher, T. M.; Reddy, P. Ternary (Liquid + Liquid) Equilibria for Mixtures of 1-Hexyl-3-methylimidazolium (Tetrafluoroborate or Hexafluorophosphate) + Benzene + an Alkane at T=298.2 K and p=0.1 MPa. *J. Chem. Thermodyn.* **2005**, *37*, 415–421.

(7) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary Liquid-Liquid Equilibria for Mixtures of Toluene + n-Heptane + an Ionic Liquid. *Fluid Phase Equilib.* **2006**, *247*, 158–168.

(8) Meindersma, G. W.; Podt, A. J. G.; de Haan, A. B. Ternary Liquid-Liquid Equilibria for Mixtures of an Aromatic + an Aliphatic Hydrocarbon + 4-Methyl-N-butylpyridinium Tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1814–1819.

(9) Deenadayalu, N.; Ngcongo, K. C.; Letcher, T. M.; Ramjugernath, D. Liquid-Liquid Equilibria for Ternary Mixtures (an Ionic Liquid + Benzene + Heptane or Hexadecane) at T = 298.2 K and Atmospheric Pressure. *J. Chem. Eng. Data* **2006**, *51*, 988–991.

(10) Domanska, U.; Pobudkowska, A.; Zolek-Tryznowska, Z. Effect of an Ionic Liquid (IL) Cation on the Ternary System (IL + p-Xylene + Hexane) at T = 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2345–2349.

(11) Wang, R.; Wang, J.; Meng, H.; Li, C.; Wang, Z. Liquid-Liquid Equilibria for Benzene + Cyclohexane + 1-Methyl-3-methylimidazolium Dimethylphosphate or + 1-Ethyl-3-methylimidazolium Diethylphosphate. *J. Chem. Eng. Data* **2008**, *53*, 1159–1162.

(12) Wang, R.; Wang, J.; Meng, H.; Li, C.; 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) 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.

(14) Domanska, U.; Pobudkowska, A.; Królikowski, M. Separation of Aromatic Hydrocarbons from Alkanes using Ammonium Ionic Liquid C_2NTf_2 at T = 298.15 K. *Fluid Phase Equilib.* **2007**, *259*, 173–179.

(15) Arce, A.; Early, M. J.; Rodríguez, H.; Seddon, K. R. Separation of Aromatic Hydrocarbons from Alkanes using the Ionic Liquid 1-Ethyl-3-methylimidazolium Bis{(trifluoromethyl) sulfonyl}amide. *Green Chem.* **2007**, *9*, 70–74.

(16) Arce, A.; Early, 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.

(17) 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.

(18) Wasserscheid, P.; van Hal, R.; Bösmann, A. 1-n-Butyl-3-methylimidazolium ([bmim]) Octylsulfate - An Even 'Greener' Ionic Liquid. *Green Chem.* **2002**, *4*, 400–404.

(19) Torrecilla, J. S.; Rafione, T.; García, J.; Rodríguez, F. Effect of Relative Humidity of Air on Density, Apparent Molar Volume, Viscosity, Surface Tension, and Water Content of 1-Ethyl-3-methylimidazolium Ethylsulfate Ionic Liquid. *J. Chem. Eng. Data* **2008**, *53*, 923–928.

(20) Fernández, A.; Torrecilla, J. S.; García, J.; Rodríguez, F. Thermophysical Properties of 1-Ethyl-3-methylimidazolium Ethylsulfate and 1-Butyl-3-methylimidazolium Methylsulfate Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 1979–1983.

(21) Fernández, A.; García, J.; Torrecilla, J. S.; Oliet, M.; Rodríguez, F. Volumetric, Transport and Surface Properties of [bmim][MeSO^4] and [emim][EtSO$_4$] Ionic Liquids As a Function of Temperatura. *J. Chem. Eng. Data* **2008**, *53*, 1518–1522.

(22) Chen, J.; Duan, L.; Mi, J.; Fei, W.; Li, Z. 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.

(23) Othmer, D. F.; Tobias, P. E. Toluene and Acetaldehyde Systems, Tie Line Correlation, Partial Pressures of Ternary Liquid Systems and the Prediction of Tie Lines. *Ind. Eng. Chem* **1942**, *34*, 693–696.

(24) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.

(25) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expession for the Excess Gibbs Energy of Partly or Completely miscible Systems. *AIChE J.* **1975**, *21*, 116–128.

(26) Simoni, L. D.; Lin, Y.; Brennecke, J. F.; Stadtherr, M. A. Modeling Liquid-Liquid Equilibrium of Ionic Liquid Systems with NRTL, electrolyte-NRTL, and UNIQUAC. *Ind. Eng. Chem. Res.* **2008**, *47*, 256–272.

(27) Britt, H. I.; Luecke, R. H. The Estimation of Parameters in Nonlinear, Implicit Models. *Technometrics* **1973**, *15*, 233–238.

(28) Banerjee, T.; Singh, M. K.; Sahoo, R. K.; Khanna, A. Volume, Ssurface and UNIQUAC Interaction Parameters for Imidazolium Based Ionic Liquids Via Polarizable Continuum Model. *Fluid Phase Equilib.* **2005**, *234*, 64–76.

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