

# Liquid–Liquid Equilibria for the Three Ternary Systems (3-Methyl-*N*-butylpyridinium Dicyanamide + Toluene + Heptane), (1-Butyl-3-methylimidazolium Dicyanamide + Toluene + Heptane) and (1-Butyl-3-methylimidazolium Thiocyanate + Toluene + Heptane) at $T = (313.15$ and $348.15)$ K and $p = 0.1$ MPa

Antje R. Hansmeier,\* Meritxell Minoves Ruiz, G. Wytze Meindersma, and Andre B. de Haan

Process Systems Engineering (SPS), Technical University of Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Liquid–liquid equilibrium data for the ionic liquids 3-methyl-*N*-butylpyridinium dicyanamide ([3-Mebupy][DCA]), 1-butyl-3-methylimidazolium dicyanamide ([BMIM][DCA]), and 1-butyl-3-methylimidazolium thiocyanate ([BMIM][SCN]) with toluene and heptane were investigated at  $T = (303.15$  and  $328.15)$  K and atmospheric pressure. The experimental data were regressed and could be correlated adequately with the nonrandom two-liquid model. The results show that the extraction capacity of the three investigated ionic liquids is in the order of: [3-Mebupy][DCA] > [BMIM][DCA] > [BMIM][SCN].

## Introduction

The separation of aromatic and aliphatic hydrocarbons is complicated because of overlapping boiling points and azeotrope formation. Hence, the conventional processes for this type of separation are extraction or extractive distillation with polar, organic compounds. Industrially, most common processes use solvents including *N*-formylmorpholine (Uhde morphylane process), sulfolane (UOP/Shell sulfolane process), *N*-methylpyrrolidone, and ethylene glycols.<sup>1</sup>

Another class of solvents, which are considered promising to replace organic solvents in industrial processes,<sup>2</sup> are ionic liquids. Ionic liquids are liquid salts consisting of large, mostly organic, cations and a great variety of anions. Their positive properties are a wide liquid temperature range ( $\approx 300$  K), low vapor pressure, and the ability of tailoring. The latter provides the possibility to develop a special solvent for a specific application, for example, separation of aromatic and aliphatic hydrocarbons.

The criteria, which a suitable ionic liquid for the separation of aromatic and aliphatic hydrocarbons must meet, are the same as for conventional solvents.<sup>3–5</sup> In general, this means high solubility for the aromatic hydrocarbon in the solvent combined with a high selectivity through a low solubility of the aliphatic components.

In the open literature mostly imidazolium-based ionic liquids combined with anions like  $[\text{TF}_2\text{N}]^-$ ,  $[\text{CH}_3\text{SO}_4]^-$ , and  $[\text{BF}_4]^-$  are described as solvents for the extraction of aromatic hydrocarbons from aliphatic components<sup>6–13</sup> (Table 1). Moreover, hardly any data are available for ternary systems containing ionic liquids with pyridinium cations.<sup>2,5</sup>

MacFarlane et al.<sup>15</sup> showed that ionic liquids containing the anion dicyanamide have a significant lower viscosity than ionic liquids combined with other anions. Since low viscosity is a favorable property of a solvent, in this work liquid–liquid equilibrium (LLE) data for pyridinium and imidazolium-based ionic liquids combined with the anions dicyanamide,  $[\text{DCA}]^-$ ,

**Table 1. Capacity and Selectivity of Different Ionic Liquids for Toluene + Heptane at  $T = 313$  K**

ionic liquid	components	aromatic capacity		
		[mol/mol]	selectivity	lit.
[EMIM][ $\text{TF}_2\text{N}$ ]	toluene + heptane <sup>a</sup>	0.55	22.2	9
[BMIM][ $\text{TF}_2\text{N}$ ]	toluene + heptane <sup>a</sup>	0.80	15.4	9
[MMIM][ $\text{CH}_3\text{SO}_4$ ]	toluene <sup>a</sup>	0.06		14
[BMIM][ $\text{BF}_4$ ]	toluene <sup>a,b</sup>	0.24		10
[OMIM][ $\text{BF}_4$ ]	toluene <sup>a,b</sup>	0.57		10
[Mebupy][ $\text{BF}_4$ ]	toluene + heptane <sup>c</sup>	0.44	53	5
[Mebupy][ $\text{BF}_4$ ]	toluene <sup>a</sup>	0.38		2

<sup>a</sup> At infinite dilution. <sup>b</sup> At  $T = 323$  K. <sup>c</sup> Toluene fraction  $\Phi = 10$  %.

**Table 2. Viscosities of the Investigated Ionic Liquids at  $T = 298.15$  K**

ionic liquid	$\eta$	
	[mPa·s]	lit.
[BMIM][DCA]	37	17
[BMIM][SCN]	51.7	18
[3-Mebupy][DCA]	37.8	19

and thiocyanate,  $[\text{SCN}]^-$ , are studied. The ionic liquids [3-methyl-*N*-butylpyridinium][dicyanamide], [1-butyl-3-methylimidazolium][dicyanamide], and [1-butyl-3-methylimidazolium][thiocyanate] are low viscosity ionic liquids with a considerably high capacity and selectivity for aromatic hydrocarbons.<sup>16</sup> The viscosities of the ionic liquids are shown in Table 2.

The binary mixture toluene + heptane has been chosen to simulate a simplified naphtha feed, since during the processing of naphtha aromatic/aliphatic separation is an important part of the process. Experimental LLE data for the examined ionic liquids were measured over a wide composition range and at two different temperatures commonly used in industry. The experimental phase compositions were correlated with the nonrandom two-liquid (NRTL) activity coefficient model for the ternary systems (3-methyl-*N*-butylpyridinium dicyanamide + toluene + heptane), (1-butyl-3-methylimidazolium dicyanamide + toluene + heptane), and (1-butyl-3-methylimidazolium thiocyanate + toluene + heptane) at  $T = (313.15$  and  $348.15)$  K and  $p = 0.1$  MPa.

\* Corresponding author. E-mail: a.hansmeier@tue.nl.

## Experimental Section

**Materials and Methods.** The ionic liquid 3-methyl-*N*-butylpyridinium dicyanamide, [3-Mebupy][DCA], was purchased from Merck; the ionic liquids 1-butyl-3-methylimidazolium dicyanamide, [BMIM][DCA], and 1-butyl-3-methylimidazolium thiocyanate, [BMIM][SCN], were purchased from Iolitec. Toluene (p.a., 99.9 %), heptane (p.a., > 99 %), and ethylbenzene (> 99 %) were purchased from Merck. Acetone (p.a. > 99 %) was purchased from Fluka. Prior to the experiments, the ionic liquids have been dried in a rotary evaporator (Büchi Rotavapor R-200) at 100 °C and under reduced pressure. Subsequently, the water content of the ionic liquids has been determined by means of Karl Fischer titration and was found to be 900 ppm for [3-Mebupy][DCA], 500 ppm for [BMIM][DCA], and 1400 ppm for [BMIM][SCN] before the experiments.

**Equipment and Experimental Procedure.** Liquid–liquid extraction experiments were carried out in jacketed glass vessels with a volume of about 70 mL. The vessels were closed with a PVC cover through which a stirrer shaft was led. For each experiment 10 mL of the feed (toluene + heptane) and 20 mL ionic liquid have been added, and the mixture was stirred (1200 rpm) for 15 min to reach equilibrium. In previous work Meindersma et al. reported that a mixing time of 5 min is sufficient to reach equilibrium.<sup>5</sup> Nevertheless, to make sure that the phase equilibrium is reached in every case the extraction experiment has been continued for 15 min. After stirring, the two phases were allowed to settle for about 1 h. This has been done according to the procedure described by Meindersma et al.<sup>5</sup> For phase mixing two stainless steel propellers, one in the bottom phase and one at the phase interface, with an electronic stirrer (Ika Eurostar) were used. Constant temperature ( $\pm 0.1$  °C) was maintained by means of a water bath (Julabo F32-MW).

**Analysis.** After equilibrium was reached, a sample of 0.5 mL of each phase was taken and analyzed by gas chromatography (GC; Varian CP-3800). Acetone was added to the samples to avoid phase splitting and to maintain a homogeneous mixture. Ethylbenzene (0.2 mL for the raffinate samples and 0.1 mL for the extract phase samples) was used as internal standard for the GC analysis. The compositions of toluene and heptane in the samples were analyzed by a Varian CP-3800 gas chromatograph with an WCOT fused silica CP-SIL 5CB column (50 m  $\times$  0.32 mm; DF = 1.2) and a Varian 8200 AutoSampler. Since ionic liquids have no vapor pressure and they cannot be analyzed by GC, only the hydrocarbons of the feed were analyzed, and the amount of ionic liquid was calculated by means of a mass balance. For a ternary mixture, only two components need to be analyzed; the third one, the ionic liquid, was determined by a mass balance of the measured mass fractions of toluene and heptane. To avoid inaccuracy of the analysis caused by fouling of the GC by the ionic liquid, a linear and a precolumn have been used. Furthermore, measurements were carried out in duplicate to increase accuracy.

The deviation in the calibration curves of 1 % and a possible contamination of the gas chromatograph can cause a variance in the mole fractions (estimated on 1 %). The averages of the two measurements were used in our results. The relative average deviation in the compositions is about 2.5 %.

## Results and Discussion

**LLE Data Correlation.** The phase equilibrium data for the described systems were correlated with the NRTL model.<sup>20</sup> It was shown earlier that this model is a good approach for the

**Table 3. Binary Interaction Parameters for the Correlation of the Experimental LLE Data by Means of the NRTL Model**

binary parameter	$a_{ij}$	$a_{ji}$	$b_{ij}/\text{K}$	$b_{ji}/\text{K}$	$\alpha$
[BMIM][DCA] and [BMIM][SCN]					
toluene + heptane	-4.597	-1.734	4414.8	900.5	0.3
toluene + [BMIM][DCA]	-32.272	21.430	15000	-9944.9	0.0148
heptane + [BMIM][DCA]	11.470	-5.775	-5157.3	4299.3	-0.0618
toluene + [BMIM][SCN]	-5.276	5.621	11000	-9476.7	-0.0034
heptane + [BMIM][SCN]	1.022	-5.214	-4124	8065.8	0.0200
[3-Mebupy][DCA]					
toluene + heptane	-3.162	-3.507	1702.8	1009.5	0.3
toluene + [3-Mebupy][DCA]	2.403	-2.134	510.8	484.9	0.2111
heptane + [3-Mebupy][DCA]	3.635	-2.008	832	-1111.6	-0.0695

description of LLE and vapor–liquid equilibrium for systems containing ionic liquids.<sup>21–23</sup>

The objective function for the regression of the NRTL parameters is the equality of the activity for each component in both phases. With the assumption of equilibrium in the liquid phase, the referring equation is:

$$x_i^R = \gamma_i^E / \gamma_i^R \cdot x_i^E \quad (1)$$

where  $x_i^R$  is the composition of component  $i$  in the raffinate phase,  $x_i^E$  the composition of component  $i$  in the extract phase,  $\gamma_i^E$  the activity coefficient of component  $i$  in the extract phase, and  $\gamma_i^R$  the activity coefficient of component  $i$  in raffinate phase.

The activity coefficients were determined by means of excess Gibbs energy. Hence, the required parameters for the binary interactions were calculated according to:

$$\tau_{ij} = a_{ij} + b_{ij}/T \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \alpha_{ij} = \alpha_{ji} \quad (2)$$

whereas  $\tau_{ij}$  and  $G_{ij}$  are NRTL parameters, which are calculated via the nonrandomness parameter,  $\alpha_{ij}$ , and the parameters  $a_{ij}$  and  $b_{ij}/\text{K}$ . The model parameters of the NRTL equation ( $a_{ij}$ ,  $a_{ji}$ ,  $b_{ij}/\text{K}$ , and  $b_{ji}/\text{K}$ ) were determined via data regression using ASPEN Plus 12.1. The values of the nonrandomness parameter,  $\alpha$ , were assigned to 0.3 for the interaction of toluene/heptane and regressed for the interaction toluene/IL and heptane/IL; see Table 3. Because of obviously different interactions of toluene and heptane with the pyridinium cation and imidazolium cation, on the basis of their different chemical structure, it was not possible to describe all three systems with one set of parameters. Therefore, two sets of parameters for the toluene/heptane interaction have been used.

Since the concentration of the ionic liquid in the raffinate phase is very low, while it is very large in the extract phase, the constraints for the ionic liquids in the data properties were left out to avoid numerical problems. This has been done according to Seiler et al.,<sup>24</sup> who suggest treating the IL as a nondissociating solvent. The negligible vapor pressure for the ionic liquids was represented by means of the Antoine equation and, to be able to fulfill the equation for the equality of fugacity and to circumvent numerical problems, calculated to be  $< 10^{-2}$  Pa. The values for the regressed binary parameters are given in Table 3.

## Experimental Data

The experimental LLE data for the ternary systems (toluene + heptane + [BMIM][DCA]), (toluene + heptane + [BMIM][SCN]), and (toluene + heptane + [3-Mebupy][DCA]) at  $T = (303.15 \text{ and } 328.15) \text{ K}$  and  $p = 0.1 \text{ MPa}$  are reported in Tables 4, 5, and 6. The value of the ionic liquid mole fraction in the raffinate phase is very small and has therefore been set to 0.001.

**Table 4. Phase Composition, Solute Distribution Ratio ( $\beta$ ), and Selectivity ( $S$ ) for (Toluene (1) + Heptane (2) + [3-Mebupy][DCA] (3)) at  $p = 0.1$  MPa and  $T = (303.15$  and  $328.15)$  K**

heptane-rich phase			[3-Mebupy][DCA]-rich phase			$\beta$		$S$
$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$	toluene	heptane	exp.
$T = 303.15$ K								
0.000	0.999	0.001	0.000	0.018	0.976	0.0180		
0.064	0.935	0.001	0.055	0.018	0.925	0.859	0.0192	44.7
0.133	0.866	0.001	0.101	0.017	0.882	0.759	0.0196	38.7
0.275	0.724	0.001	0.184	0.014	0.802	0.669	0.0193	34.6
0.425	0.574	0.001	0.294	0.018	0.688	0.692	0.0313	22.1
0.708	0.291	0.001	0.413	0.019	0.576	0.583	0.0651	9.0
0.999	0.000	0.001	0.475	0.000	0.525	0.475		
$T = 328.15$ K								
0.000	0.999	0.001	0.000	0.022	0.978		0.0220	
0.071	0.928	0.001	0.051	0.022	0.922	0.718	0.0237	30.3
0.141	0.858	0.001	0.093	0.021	0.887	0.660	0.0244	27.0
0.291	0.708	0.001	0.177	0.021	0.802	0.608	0.0296	20.5
0.445	0.554	0.001	0.280	0.019	0.701	0.629	0.0342	18.4
0.734	0.265	0.001	0.406	0.019	0.582	0.553	0.0714	7.7
0.999	0.000	0.001	0.637	0.000	0.363	0.637		

**Table 5. Phase Composition, Solute Distribution Ratio ( $\beta$ ), and Selectivity ( $S$ ) for (Toluene (1) + Heptane (2) + [BMIM][DCA] (4)) at  $p = 0.1$  MPa and  $T = (303.15$  and  $328.15)$  K**

heptane-rich phase			[BMIM][DCA]-rich phase			$\beta$		$S$
$x_1$	$x_2$	$x_4$	$x_1$	$x_2$	$x_4$	toluene	heptane	exp.
$T = 303.15$ K								
0.000	0.999	0.001	0.000	0.014	0.970		0.0140	
0.065	0.934	0.001	0.041	0.010	0.948	0.631	0.0107	59.0
0.155	0.844	0.001	0.084	0.009	0.907	0.542	0.0104	52.1
0.305	0.694	0.001	0.150	0.008	0.843	0.492	0.0107	46.0
0.472	0.527	0.001	0.208	0.006	0.787	0.441	0.0113	39.0
0.681	0.318	0.001	0.294	0.004	0.702	0.432	0.0125	34.6
0.999	0.000	0.001	0.473	0.000	0.527	0.473		
$T = 328.15$ K								
0.000	0.999	0.001	0.000	0.019	0.981		0.0190	
0.070	0.929	0.001	0.039	0.017	0.944	0.557	0.0183	30.4
0.163	0.836	0.001	0.084	0.015	0.903	0.515	0.0179	28.8
0.318	0.681	0.001	0.150	0.012	0.838	0.472	0.0176	26.8
0.492	0.507	0.001	0.213	0.009	0.778	0.433	0.0177	24.5
0.705	0.294	0.001	0.295	0.007	0.699	0.418	0.0237	17.6
0.999	0.000	0.001	0.467	0.000	0.533	0.467		

**Table 6. Phase Composition, Solute Distribution Ratio ( $\beta$ ), and Selectivity ( $S$ ) for the (Toluene (1) + Heptane (2) + [BMIM][SCN] (5)) at  $p = 0.1$  MPa and  $T = (303.15$  and  $328.15)$  K**

heptane-rich phase			[BMIM][SCN]-rich phase			$\beta$		$S$
$x_1$	$x_2$	$x_5$	$x_1$	$x_2$	$x_5$	toluene	heptane	exp.
$T = 303.15$ K								
0.000	0.999	0.001	0.000	0.008	0.986		0.0080	
0.074	0.925	0.001	0.037	0.007	0.956	0.500	0.0076	65.8
0.149	0.850	0.001	0.062	0.008	0.930	0.416	0.0094	44.3
0.321	0.678	0.001	0.126	0.008	0.866	0.393	0.0118	33.3
0.524	0.475	0.001	0.190	0.007	0.804	0.363	0.0147	24.7
0.728	0.271	0.001	0.256	0.004	0.740	0.352	0.0147	23.9
0.999	0.000	0.001	0.398	0.000	0.602	0.398		
$T = 328.15$ K								
0.000	0.999	0.001	0.000	0.009	0.985		0.0090	
0.077	0.922	0.001	0.035	0.012	0.953	0.455	0.0130	35.0
0.153	0.846	0.001	0.059	0.009	0.931	0.386	0.0106	36.4
0.335	0.664	0.001	0.122	0.010	0.868	0.364	0.0150	24.3
0.548	0.451	0.001	0.183	0.007	0.809	0.334	0.0155	21.5
0.747	0.252	0.001	0.251	0.005	0.744	0.336	0.0198	17.0
0.999	0.000	0.001	0.378	0.000	0.622	0.378		

Together with the LLE data, Tables 4 to 6 include the corresponding values for the solute distribution ratio ( $\beta_i$ ) and the selectivity ( $S$ ), which are widely used parameters to characterize the suitability of a solvent in liquid–liquid extraction. The distribution coefficients,  $\beta_i$ , are directly calculated from the mole fractions in extract and raffinate phase.  $\beta_i$  is defined

as the ratio of the mole fractions of the component in the extract phase (ionic liquid) and in the raffinate phase (organic phase). Their calculation is easily made from the experimental compositions of the tie-line ends, according to the following expressions:

$$\beta_1 = x_1^{\text{IL}}/x_1^{\text{org}} \quad (3)$$

$$\beta_2 = x_2^{\text{IL}}/x_2^{\text{org}} \quad (4)$$

The selectivity  $S$  is derived from the ratio of the distribution coefficients, according to:

$$S = \beta_1/\beta_2 \quad (5)$$

As described above, the deviation for the mole fractions is 1 % and therewith for the distribution coefficient is 2 %. Consequently, the deviation for the selectivity is 5 %.

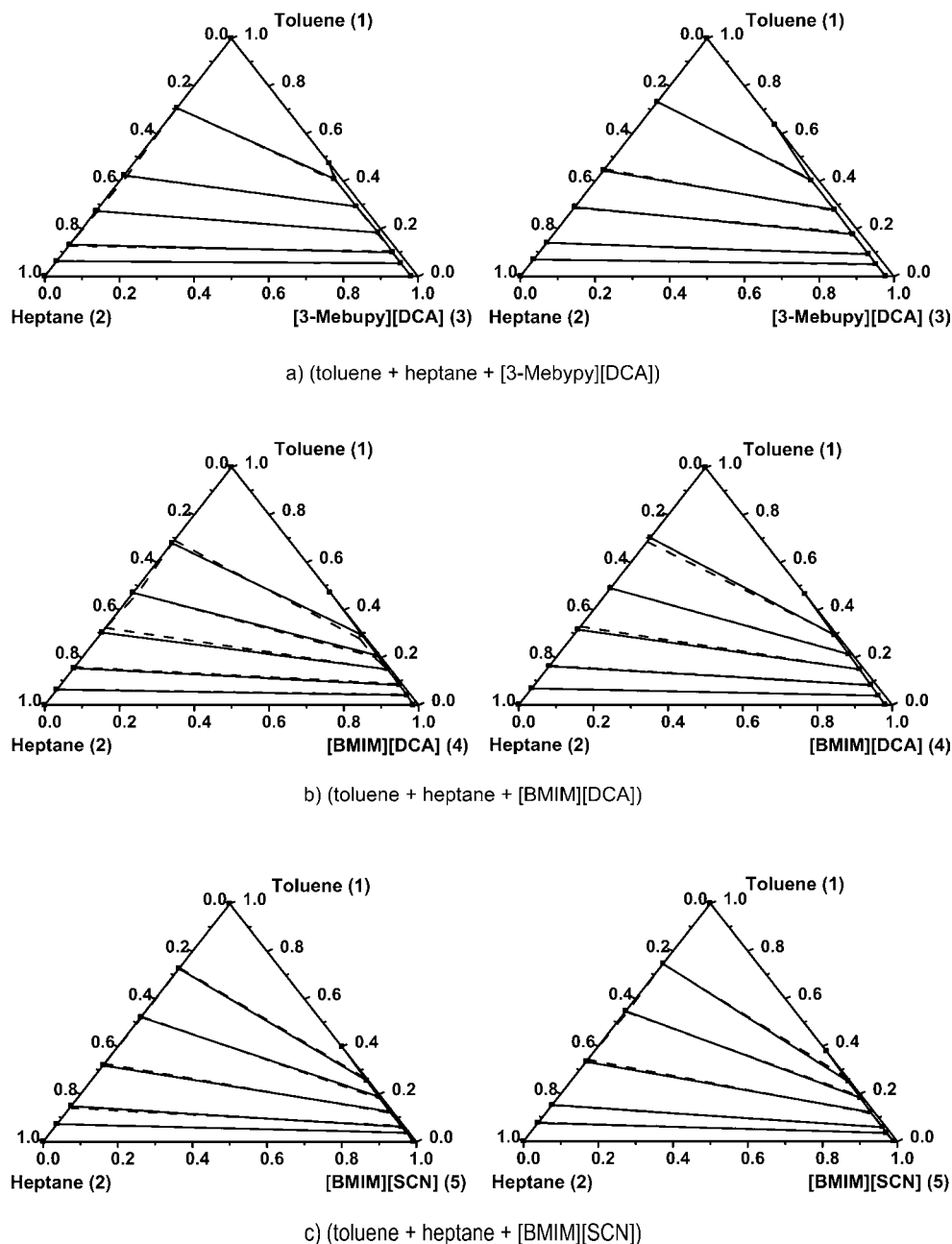
The ternary diagrams for all three systems at both temperatures are depicted in Figure 1.

The binodal curves in Figure 1 indicate that toluene is partially soluble in all of the three tested ionic liquids. Solubility limits for the binary systems toluene + IL and heptane + IL are presented in Tables 4 to 6. By comparing the different ternary diagrams, it is apparent that the solubility of toluene in the three investigated ionic liquids is in the order of [3-Mebupy][DCA] > [BMIM][DCA] > [BMIM][SCN], with  $x_{1,3} = 0.475$ ,  $x_{1,4} = 0.473$ , and  $x_{1,5} = 0.398$  at  $T = 303$  K. However, the solubility of heptane in the tested ionic liquids is much lower than for toluene and in the order of [3-Mebupy][DCA] > [BMIM][DCA] > [BMIM][SCN]. The maximum solubility for heptane in the ionic liquids is  $x_{2,3} = 0.0180$ ,  $x_{2,4} = 0.0140$ , and  $x_{2,5} = 0.0080$  at  $T = 303$  K.

**Distribution Coefficient.** As illustrated by Figure 2, the toluene distribution coefficient decreases with increasing toluene mole fraction, whereas the aliphatic distribution coefficient increases with increasing aromatic mole fraction. Holbrey et al. showed that ionic liquids and aromatic solutes organize in a sandwich structure, where the ionic liquid cations and the aromatic solutes interact in an alternating structure through  $\pi$ – $\pi$  interactions with the ionic liquid anions arranged around this complex.<sup>25</sup> With increasing toluene content the molecular grid expands, resulting in a larger spherical distance between aromatic solutes and cations, reducing the strength of interaction and thereby the distribution coefficient. Additionally, the increased aromatics content of the ionic liquid increases the heptane distribution coefficient by enabling the heptane molecules to arrange themselves between the toluene and the ionic liquid molecules.

With respect to temperature, it is visible in Figure 2 that the toluene distribution coefficient,  $\beta_{\text{toluene}}$ , decreases with increasing temperature, while the heptane distribution coefficient increases with increasing temperature. Increasing temperature causes increased molecular movements, which breaks down the ordered sandwich-like structure within the ionic liquid. As a consequence, the solubility due to the specific toluene–ionic liquid  $\pi$ – $\pi$  interactions is reduced, while at the same time the thermal expansion enables more toluene molecules to arrange themselves between the ions. In this case the  $\pi$ – $\pi$  interaction between the toluene and the ionic liquid is the dominating force which causes the visible decrease of the distribution coefficient. For heptane the breakdown of the ordered structure within the ionic liquid is the dominating effect, resulting in a higher heptane solubility at higher temperatures.

**Selectivity of an Ionic Liquid ( $S$ ).** In line with the effects of toluene concentration and temperature on the distribution coefficients is the influence of these effects on the toluene/



**Figure 1.** Ternary diagrams of the systems: (a) (toluene + heptane + [3-Mebupy][DCA]), (b) (toluene + heptane + [BMIM][DCA]), and (c) (toluene + heptane + [BMIM][SCN]) at  $T = (303.15$  (left) and  $328.15$  (right) K, (experiments: ■, solid lines; calculated: dashed lines).

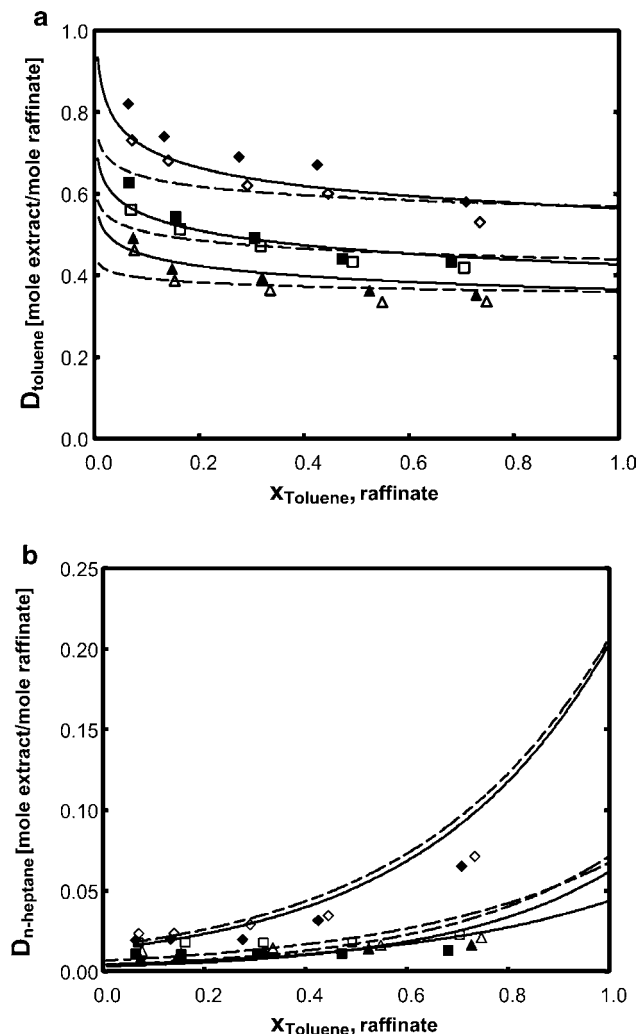
heptane selectivity. The decrease of  $\beta_{\text{toluene}}$  and increase of  $\beta_{\text{heptane}}$  is expressed by a decrease in selectivity as it is apparent from Figure 3. The toluene selectivity of the investigated ionic liquids for  $x_{\text{toluene}} < 0.15$  is in the order of [3-Mebupy][DCA] < [BMIM][DCA] < [BMIM][SCN]. For  $x_{\text{toluene}} > 0.15$ , the order is [3-Mebupy][DCA] < [BMIM][SCN] < [BMIM][DCA]. This is mainly due to the heptane distribution coefficient,  $\beta_{\text{heptane}}$ , which increases significantly more for the ionic liquid [BMIM][SCN] than for [BMIM][DCA] at  $T = 303.15$  K.

For the ionic liquid [BMIM][SCN] Domanska and Laskowska determined the activity coefficients at infinite dilution of several aromatic and aliphatic solutes.<sup>26</sup> The selectivity that can be calculated from the infinite dilution activity coefficients provides an indication for the experimental values of this work at low toluene concentrations. The selectivity of 70.4 at 308.15 K reported by Domanska et al. is in good agreement with the

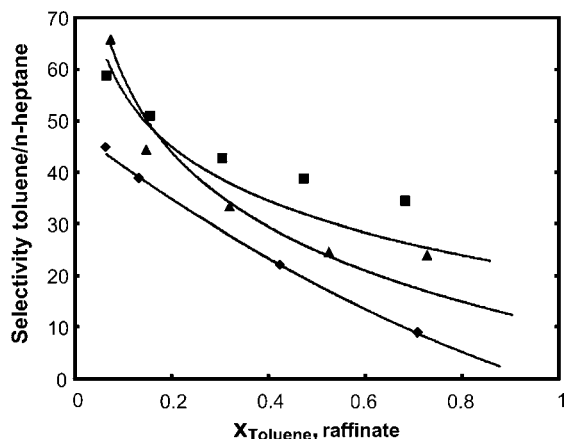
selectivity value of 65.8 for the toluene/heptane selectivity in [BMIM][SCN] at 303.15 K of this work. However, the selectivity at 328.15 K reported by Domanska and Laskowska is with 51.8 significantly higher than the selectivity of 35.0 determined by us for toluene/heptane in [BMIM][SCN]. This observation can be explained from the effect that, in comparison to Domanska et al.,  $\beta_{\text{heptane}}$  in this work increases more with increasing temperature than the infinite activity coefficient reported by Domanska et al. decreases with increasing temperature. Nevertheless, Domanska and Laskowska observed, with a decreasing  $\gamma_{\text{heptane}}^{\infty}$  and increasing  $\gamma_{\text{toluene}}^{\infty}$  with increasing temperature, the same trends as for the distribution coefficients reported in this work.

**Comparison of Experimental and Correlated Data.** As it is visible in Figure 1, the experimental data are well-correlated by the NRTL equation. Hence, there is a good agreement





**Figure 2.** (a) Toluene distribution coefficient dependent on the toluene concentration in the raffinate phase (◆, [3-Mebupy][DCA]; ■, [BMIM][DCA]; ▲, [BMIM][SCN]; ◆, ▲, ■, 303.15 K; ◇, △, □, 328.15 K; solid line, calculated at 302.15 K; dashed line, calculated at 328.15 K). (b) Heptane distribution coefficient dependent on the toluene concentration in the raffinate phase (◆, [3-Mebupy][DCA]; ■, [BMIM][DCA]; ▲, [BMIM][SCN]; ◆, ▲, ■, 303.15 K; ◇, △, □, 328.15 K; solid line, calculated at 302.15 K; dashed line, calculated at 328.15 K).



**Figure 3.** Toluene/heptane selectivity dependent on the toluene concentration in the raffinate phase at  $T = 303.15$  K (◆, [3-mebupy][DCA]; ■, [BMIM][DCA]; ▲, [BMIM][SCN]; solid line, calculated).

between experimental and calculated data, which becomes apparent by the coinciding tie lines in the ternary diagrams.

**Table 7.** Root-Mean-Square Deviation (rmsd) for the Ternary Mixtures

ternary system	rmsd	
	303.15 K	328.15 K
toluene + heptane + [3-Mebupy][DCA]	0.0040	0.0041
toluene + heptane + [BMIM][DCA]	0.0076	0.0051
toluene + heptane + [BMIM][SCN]	0.0050	0.0052

The validity of the model has been verified by means of the root-mean-square deviation (rmsd):

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

where  $x$  is the mole fraction; 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. The values of the rmsd of the systems are shown in Table 7. From these values it can be inferred that a good correlation of the experimental values with the NRTL model was obtained (rmsd < 0.076). The small deviations that arise are mainly due to the poor predictions of the low mole fractions for the ionic liquid mole fraction in the raffinate phase and the heptane mole fraction in the extract phase.

Experimental and calculated values of the selectivities of the three measured ternary diagrams are compared in Figure 3. It is apparent that for all measured ternary systems the values are in good agreement.

## Conclusion

Liquid–liquid experimental data were determined for the ternary systems (toluene + heptane + [3-Mebupy][DCA]), (toluene + heptane + [BMIM][DCA]), and (toluene + heptane + [BMIM][SCN]) at  $T = (303.15$  and  $328.15)$  K. The ionic liquid [3-Mebupy][DCA] has the highest extraction capacity for toluene, whereas [BMIM][SCN] provides the highest selectivity. All experimental data can be adequately correlated with the NRTL model. The rmsd values of the correlations are generally below 0.076. The experimental and calculated toluene/heptane selectivities are in good agreement with each other.

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