

Ternary Liquid–Liquid Equilibria for Mixtures of an Aromatic + an Aliphatic Hydrocarbon + 4-Methyl-*N*-butylpyridinium Tetrafluoroborate

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This research focused on a study of the ionic liquid 4-methyl-*N*-butylpyridinium tetrafluoroborate ([mebupy]-BF₄) as a solvent in liquid–liquid extraction. Liquid–liquid equilibrium data were obtained for mixtures of 4-methyl-*N*-butylpyridinium tetrafluoroborate + (benzene or ethylbenzene or *m*-xylene) + (*N*-hexane or *N*-octane) at $T = (313.2 \text{ and } 348.2) \text{ K}$ and $T = (313.2 \text{ and } 333.2) \text{ K}$ for the ternary mixture with benzene and $p = 0.1 \text{ MPa}$. The experimental data for the binary and ternary systems were well-correlated with the NRTL model. The aromatic/aliphatic selectivity values were comparable to those of toluene + *N*-heptane. The ionic liquid [mebupy]BF₄ is therefore a suitable solvent for an industrial extraction process for the separation of aromatic and aliphatic hydrocarbons.

Introduction

The separation of aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) from C₄ to C₁₀ aliphatic hydrocarbon mixtures is challenging since these hydrocarbons have boiling points in a close range and several combinations form azeotropes. The conventional processes for the separation of these aromatic and aliphatic hydrocarbon mixtures are liquid extraction, suitable for the range of (20 to 65) mass % aromatic content, extractive distillation for the range of (65 to 90) mass % aromatics, and azeotropic distillation for high aromatic content, >90 mass %.¹ This implies that there are no suitable separation processes available for process streams with an aromatic content below 20 mass %. Typical solvents used are polar components such as sulfolane,^{2–9} *N*-methyl pyrrolidone (NMP),⁸ *N*-formyl morpholine (NFM), ethylene glycols,^{9–11} and propylene carbonate.⁹ These solvents require additional distillation steps to separate the extraction solvent from both the extract and raffinate phases and to purify the solvent with, consequently, additional investments and energy consumption. Overviews of the use of extraction and extractive distillation for the separation of aromatic hydrocarbons from aliphatic hydrocarbons can be found elsewhere.^{12–15}

Replacement of volatile solvents in the separation of aromatic and aliphatic hydrocarbons by nonvolatile ionic liquids (ILs) can offer several advantages: less complex processes and a more simple regeneration of the solvent. To apply these ionic liquids in the chemical process industry, thermodynamic data need to be available for designing a proper separation process.

Liquid–liquid equilibrium (LLE) data are essential for the design of extraction equipment and/or for the calculation of the thermodynamic limit of a given separation. In the existing literature, hardly any data are found on LLE with ILs.^{16–29} There are only four references concerning LLE for an aromatic and an aliphatic hydrocarbon with ILs.^{16–19} Selvan et al.¹⁷ used the

ILs 1-ethyl-3-methylimidazolium triiodide ([emim]I₃) and 1-butyl-3-methylimidazolium triiodide ([bmim]I₃) for the extraction of toluene from a mixture of toluene and *N*-heptane. However, these ILs are very corrosive and, therefore, not suitable for industrial applications.²⁸ Letcher and Deenadayalu¹⁸ investigated ternary LLE for mixtures of 1-octyl-3-methylimidazolium chloride ([omim]Cl), benzene and an alkane at $T = 298.2 \text{ K}$. Letcher and Reddy¹⁹ investigated ternary LLE for mixtures of the ILs 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim]-BF₄) and 1-hexyl-3-methylimidazolium hexafluoroborate ([hmim]-PF₆), benzene, and an alkane with the goal to find an alternative for [hmim]PF₆, which decomposes in the presence of water and elevated temperatures to form HF. All benzene + heptane selectivities measured with these ILs have low values ($S < 10$), which are in general too low to be of industrial interest.

In an earlier paper,³⁰ we investigated several combinations of ILs and binary mixtures of toluene and *N*-heptane in order to determine thermodynamic data for the design of an extraction process suitable for separating aromatic and aliphatic hydrocarbons. The conclusion of our previous work is that the IL 4-methyl-*N*-butylpyridinium tetrafluoroborate ([mebupy]BF₄) is a suitable solvent for an industrial extraction process for the separation of aromatic and aliphatic hydrocarbons.

Since there are no thermodynamic data available for this IL, LLE data must be determined in order to evaluate the process performance. In this study, experimental LLE data over a wide composition range were gathered, and the phase compositions were correlated by using the non-random two-liquid (NRTL) model for the three IL systems: benzene + *N*-hexane + 4-methyl-*N*-butylpyridinium tetrafluoroborate at $T = (313.2 \text{ and } 333.2) \text{ K}$ and $p = 0.1 \text{ MPa}$; ethylbenzene + *N*-octane + 4-methyl-*N*-butylpyridinium tetrafluoroborate and *m*-xylene + *N*-octane + 4-methyl-*N*-butylpyridinium tetrafluoroborate at $T = (313.2 \text{ and } 348.2) \text{ K}$ and $p = 0.1 \text{ MPa}$.

Experimental Section

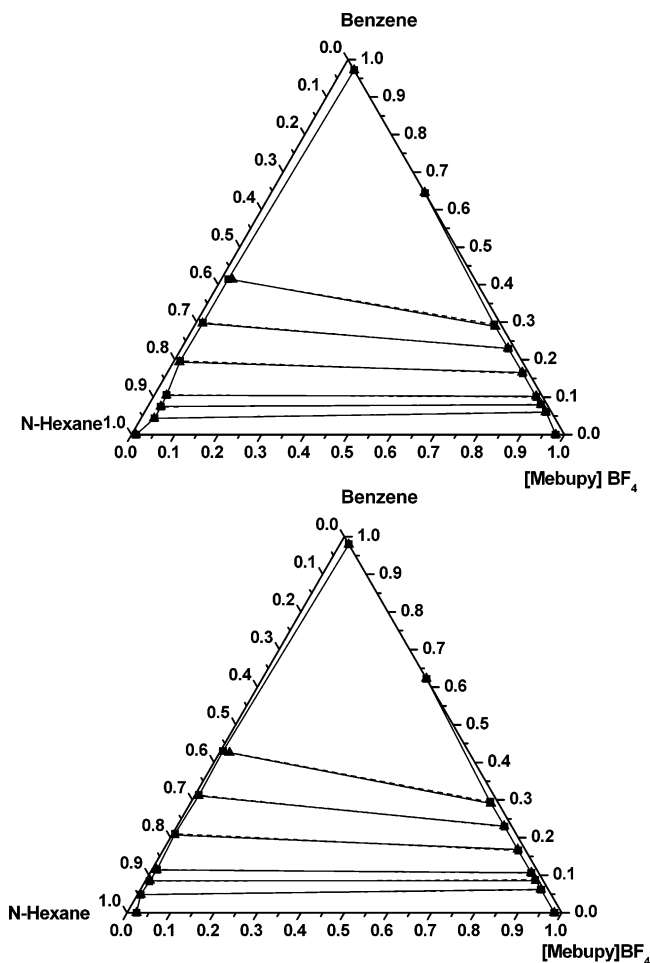
The IL [mebupy]BF₄ (> 97 %) was purchased from Fluka. Toluene (p.a., 99.9 %), *N*-heptane (p.a., > 99 %), benzene (p.a.,

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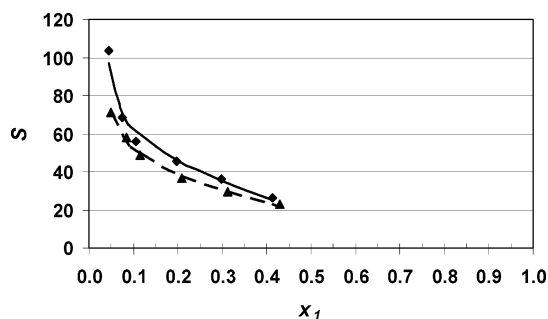
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Table 1. Experimental Tie Lines of the Benzene (1) + *N*-Hexane (2) + [mebupy]BF₄ (3) System at $p = 0.1$ MPa, Distribution Coefficients β of Benzene and *N*-Hexane, and the Benzene + *N*-Hexane Selectivity S

<i>N</i> -hexane-rich phase			[mebupy]BF ₄ -rich phase			β		S
x_1	x_2	x_3	x_1	x_2	x_3	benzene	<i>N</i> -hexane	exp.
$T = 313.2$ K								
0.000	0.990	0.010	0.000	0.020	0.980		0.020	
0.044	0.925	0.031	0.060	0.012	0.927	1.375	0.013	103.8
0.075	0.895	0.030	0.080	0.014	0.906	1.075	0.016	68.7
0.106	0.866	0.028	0.101	0.015	0.885	0.949	0.017	55.9
0.197	0.789	0.014	0.163	0.014	0.822	0.830	0.018	45.7
0.299	0.686	0.016	0.229	0.015	0.756	0.768	0.021	36.0
0.414	0.570	0.016	0.294	0.015	0.691	0.709	0.027	26.2
0.972	0.000	0.028	0.644	0.000	0.356	0.663		
$T = 333.2$ K								
0.000	0.978	0.022	0.000	0.017	0.983		0.017	
0.049	0.944	0.007	0.061	0.017	0.922	1.258	0.018	71.1
0.084	0.906	0.010	0.088	0.016	0.896	1.045	0.018	57.9
0.115	0.874	0.011	0.106	0.017	0.877	0.925	0.019	48.9
0.210	0.785	0.006	0.166	0.017	0.817	0.790	0.022	36.5
0.313	0.679	0.008	0.229	0.017	0.754	0.732	0.025	29.5
0.430	0.564	0.006	0.295	0.017	0.688	0.686	0.030	22.9
0.979	0.000	0.021	0.622	0.000	0.378	0.635		

**Figure 1.** Tie lines for ternary mixture of benzene + *N*-hexane + [mebupy]BF₄ at $T = 313.2$ K (top) and 333.2 K (bottom) and $p = 0.1$ MPa. Experiments: ■, dashed lines; calculated: ▲, solid lines.

99.7 %), ethylbenzene (> 99 %), *m*-xylene (> 99 %), *N*-octane (> 99 %), *N*-hexane (p.a., 99 %), *N*-pentane (> 99 %), and 1-butanol (p.a., > 99 %) were purchased from Merck. Acetone (p.a. > 99.5 %) was purchased from Acros, and acetone-*d*₆ (99.5 atom % D), for NMR analysis, was purchased from Aldrich.

**Figure 2.** Experimental and calculated selectivity S for benzene (1) + *N*-hexane (2) with [mebupy]BF₄. ◆, experiments at 313.2 K; —, calculated at 313.2 K; ▲, experiments at 348.2 K; ---, calculated at 348.2 K.

Our equilibrium experiments were carried out with the regenerated IL [mebupy]BF₄, except, of course, for the first experiment. Evaporating the organic compounds from the extract at $T = 348.2$ K under reduced pressure in a rotary evaporator could easily regenerate the IL used. Visible inspection of the NMR spectra of both the original IL and the regenerated product showed no differences between the two samples. The water content of the IL was about 0.1 mass %.

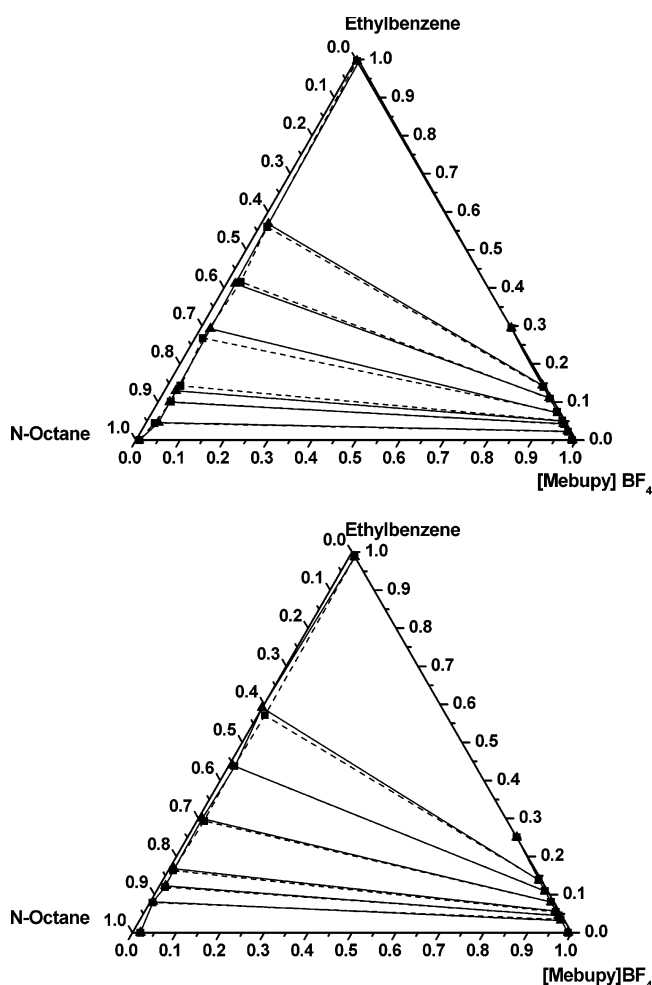
LLE experiments were carried out in jacketed vessels with a volume of approximately 70 mL. The top of a vessel was closed using a PVC cover, through which a stirrer shaft passed. Two stainless steel propellers, one in each phase, on the stirrer shaft were used with an electronic stirrer (Heidolph RZR 2051 control) to thoroughly mix both phases. The vessels were jacketed to circulate water from a water bath (Julabo F32-MW) in order to maintain the temperature inside the vessels at $T = (313.2, 333.2, \text{ or } 348.2)$ K.

For each experiment, 20 mL of the IL and 10 mL of an aromatic + aliphatic mixture were placed into the vessel. The temperature and the ratio of the aromatic hydrocarbon in the aliphatic hydrocarbon were varied. We established that equilibrium was reached within 5 min. This was done for one IL by taking samples after (5, 10, 15, 30, 65, and 120) min and analyzing them. To avoid this procedure for the other ternary mixtures, the extraction experiment was continued for 20 min. After being stirred, the two phases were allowed to settle for about 1 h.

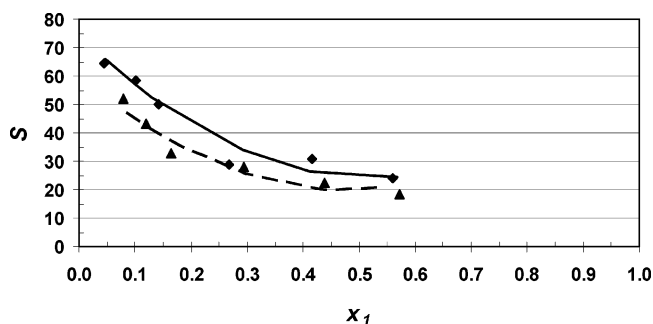
Samples (approximately 0.5 mL) were taken from both phases. 1-Butanol (0.5 mL) was added to each sample to avoid

Table 2. Experimental Tie Lines of the Ethylbenzene (1) + *N*-Octane (2) + [mebupy]BF₄ (3) System at $p = 0.1$ MPa, Distribution Coefficients β of Ethylbenzene and *N*-Octane, and the Ethylbenzene + *N*-Octane Selectivity S

<i>N</i> -octane-rich phase			[mebupy]BF ₄ -rich phase			β		S
x_1	x_2	x_3	x_1	x_2	x_3	ethylbenzene	<i>N</i> -octane	exp.
$T = 313.2$ K								
0.000	0.992	0.008	0.000	0.009	0.991		0.009	
0.045	0.935	0.020	0.023	0.007	0.970	0.502	0.008	64.3
0.101	0.870	0.029	0.042	0.006	0.952	0.416	0.007	58.3
0.143	0.827	0.030	0.051	0.006	0.943	0.356	0.007	49.9
0.268	0.714	0.018	0.074	0.007	0.919	0.276	0.010	29.0
0.416	0.554	0.030	0.109	0.005	0.886	0.263	0.008	31.0
0.560	0.422	0.018	0.140	0.004	0.856	0.250	0.010	23.9
0.996	0.000	0.004	0.294	0.000	0.706	0.295		
$T = 348.2$ K								
0.000	0.982	0.018	0.000	0.008	0.992		0.008	
0.079	0.914	0.007	0.035	0.008	0.958	0.437	0.008	51.9
0.121	0.866	0.014	0.045	0.008	0.948	0.373	0.009	43.1
0.164	0.825	0.011	0.055	0.008	0.937	0.334	0.010	32.8
0.294	0.690	0.016	0.081	0.007	0.912	0.275	0.010	27.9
0.437	0.550	0.013	0.110	0.006	0.884	0.251	0.011	22.3
0.572	0.413	0.016	0.139	0.005	0.856	0.242	0.013	18.5
0.987	0.000	0.013	0.250	0.000	0.750	0.253		

**Figure 3.** Tie lines for ternary mixture of ethylbenzene + *N*-octane + [mebupy]BF₄ at $T = 313.2$ K (top) and 348.2 K (bottom) and $p = 0.1$ MPa. Experiments: ■, dashed lines; calculated: ▲, solid lines.

phase splitting and to maintain a homogeneous mixture. *N*-Hexane was added to the samples as an internal standard for the GC analysis: 0.2 mL to the raffinate phase and 0.1 mL to the extract phase samples. For the analysis of *N*-hexane from the experiments with mixtures of benzene + *N*-hexane, acetone was used as the solvent instead of 1-butanol, and *N*-pentane was used as the internal standard.

**Figure 4.** Experimental and calculated selectivity S for ethylbenzene (1) + *N*-octane (2) with [mebupy]BF₄. ◆, experiments at 313.2 K; —, calculated at 313.2 K; ▲, experiments at 348.2 K; - - -, calculated at 348.2 K.

The compositions of benzene, ethylbenzene, *m*-xylene, *N*-hexane, and *N*-octane in the samples were analyzed by a Varian CP-3800 gas chromatograph with an Alltech Econo-Cap EC-Wax column (30 m × 0.32 mm × 0.25 μm) and with a Varian 8200 AutoSampler. Because the ionic liquid has no vapor pressure, it cannot be analyzed by GC. The IL is collected in a precolumn in order not to disrupt the analysis. In a ternary mixture, one has to analyze only two components; the third one, the IL, was determined by mass balance of the measured mole fractions of the aromatic and the aliphatic hydrocarbons.

Measurements were carried out in duplicate in order to exclude exceptions in the measurements that could lead to wrong conclusions. The deviance in the calibration curves of 1% and a possible contamination of the gas chromatograph can also cause a variance in the mole fractions (estimated on 1%). The averages of the two measurements were used in our results. The average deviation in the compositions is about 2.5% and in the temperature about 1 K.

Data Correlation

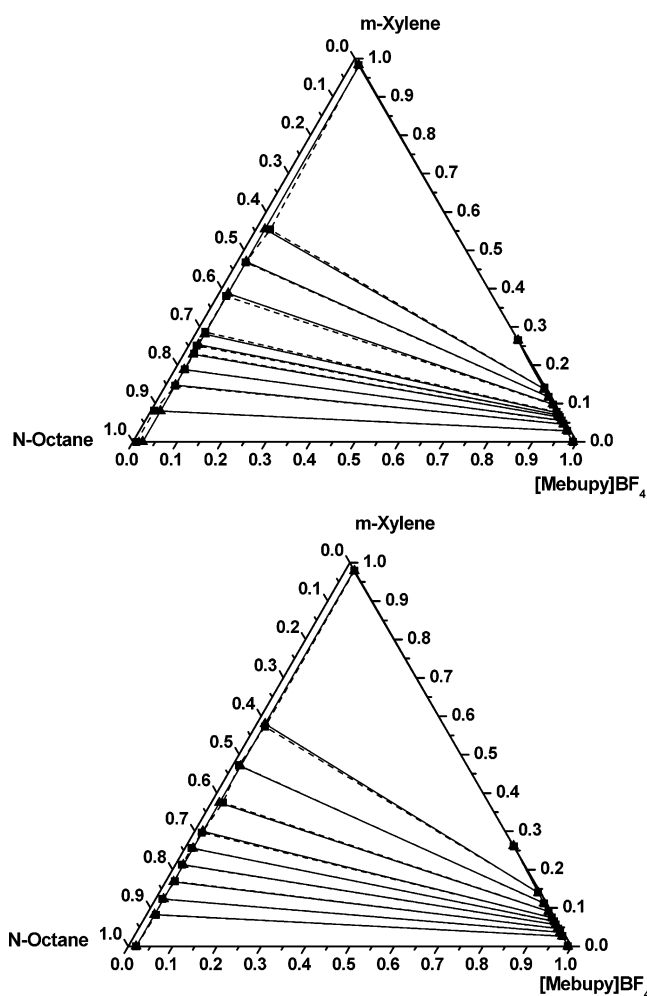
The phase equilibrium data for the described systems were correlated with the NRTL model. Several authors have used this model to describe their measurements of LLE and vapor-liquid equilibria (VLE) with ILs.^{17–29} The binary interactions were calculated using

$$\tau_{ij} = a_{ij} + b_{ij}/T \quad G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad \alpha_{ij} = \alpha_{ji} \quad (1)$$

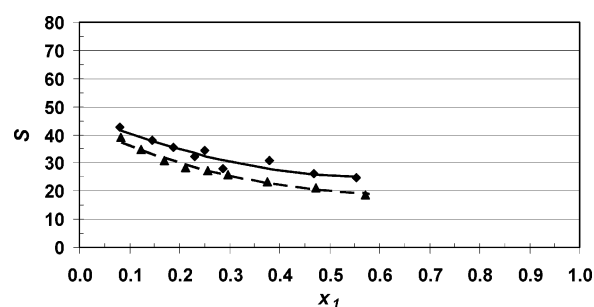
where τ_{ij} and G_{ij} are NRTL parameters, which are calculated

Table 3. Experimental Tie Lines of the *m*-Xylene (1) + *N*-Octane (2) + [mebupy]BF₄ (3) System at *p* = 0.1 MPa, Distribution Coefficients of *m*-Xylene and *N*-Octane, and the *m*-Xylene + *N*-Octane Selectivity *S*

N-octane-rich phase			[mebupy]BF ₄ -rich phase			β		<i>S</i>
<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>x</i> ₁	<i>x</i> ₂	<i>x</i> ₃	<i>m</i> -xylene	<i>N</i> -octane	exp.
<i>T</i> = 313.2 K								
0.000	0.992	0.008	0.000	0.009	0.991		0.009	
0.081	0.911	0.008	0.029	0.008	0.964	0.356	0.008	42.6
0.146	0.832	0.022	0.047	0.007	0.946	0.321	0.008	38.1
0.189	0.789	0.022	0.055	0.007	0.939	0.291	0.008	35.4
0.230	0.747	0.023	0.064	0.007	0.929	0.280	0.009	32.1
0.251	0.731	0.018	0.070	0.006	0.925	0.277	0.008	34.3
0.287	0.694	0.020	0.077	0.007	0.916	0.270	0.010	28.0
0.380	0.600	0.019	0.097	0.005	0.898	0.256	0.008	30.7
0.468	0.512	0.020	0.117	0.005	0.878	0.250	0.010	26.1
0.554	0.414	0.032	0.138	0.004	0.858	0.249	0.010	24.6
0.983	0.000	0.017	0.265	0.000	0.735	0.270		
<i>T</i> = 348.2 K								
0.000	0.982	0.018	0.000	0.008	0.992		0.008	
0.082	0.896	0.022	0.027	0.007	0.966	0.324	0.008	39.2
0.124	0.861	0.016	0.037	0.007	0.956	0.296	0.008	34.9
0.170	0.810	0.021	0.046	0.007	0.946	0.274	0.009	30.8
0.212	0.772	0.015	0.057	0.007	0.936	0.268	0.009	28.4
0.257	0.729	0.015	0.065	0.007	0.928	0.253	0.009	27.2
0.297	0.685	0.018	0.075	0.007	0.918	0.254	0.010	26.0
0.375	0.599	0.026	0.091	0.006	0.903	0.243	0.010	23.4
0.473	0.514	0.013	0.112	0.006	0.882	0.237	0.011	21.0
0.573	0.405	0.022	0.141	0.005	0.854	0.245	0.013	18.7
0.979	0.000	0.021	0.261	0.000	0.739	0.266		

**Figure 5.** Tie lines for the ternary mixture of *m*-xylene + *N*-octane + [mebupy]BF₄ at *T* = 313.2 K (top) and 348.2 K (bottom) and *p* = 0.1 MPa. Experiments: ■, dashed lines; calculated: ▲, solid lines.

via the non-randomness parameter α_{ij} and the parameters a_{ij} and b_{ij}/K . The model parameters of the NRTL equation

**Figure 6.** Experimental and calculated selectivity *S* for *m*-xylene + *N*-octane with [mebupy]BF₄. ◆, experiments at 313.2 K; —, calculated at 313.2 K; ▲, experiments at 348.2 K; ---, calculated at 348.2 K.

(α_{ij} , a_{ij} , a_{ji} , b_{ij}/K , and b_{ji}/K) were determined via data regression using ASPEN Plus 12.1.

Seiler et al.³¹ have also used ASPEN Plus to determine the model parameters for the NRTL equation for a VLE of ethanol + water + IL [emim]BF₄. In their work, the IL is treated as a non-dissociating component. Since the IL has no vapor pressure and its concentration in the vapor phase is close to zero, the parameter regression is not asked to fulfill the equation for the equality of the fugacity for the IL.

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

$$x_i^R = \gamma_i^E / \gamma_i^R \cdot x_i^E \quad (2)$$

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

For the component IL, this equation contains two values, which are close to zero: its composition in the raffinate phase (x_{IL}^R) and the value of $1/\gamma_{IL}^R$. The value of γ_{IL}^R is very large because the composition of the IL in the raffinate phase is very

Table 4. Regressed NRTL Interaction Parameters for the Description of the Aromatic (1) + Aliphatic (2) + [mebupy]BF₄ (3) System at $T = (313.2 \text{ to } 348.2) \text{ K}$

binary parameter	a_{ij}	a_{ji}	b_{ij}/K	b_{ji}/K	α_{ij}
benzene + <i>N</i> -hexane	2.888	0.578	264.9	1338	0.3
benzene + [mebupy]BF ₄	2.125	2.901	161.8	719.4	0.3024
<i>N</i> -hexane + [mebupy]BF ₄	1.535	1.565	1215	1090	0.4600
ethylbenzene + <i>N</i> -octane	2.413	30.671	-1256	-9852	0.3
ethylbenzene + [mebupy]BF ₄	9.699	-8.894	-3660	4264	0.380
<i>N</i> -octane + [mebupy]BF ₄	2.673	3.354	570.0	-2776	-0.185
<i>m</i> -xylene + <i>N</i> -octane	-2.930	4.470	675.9	-843.9	0.3
<i>m</i> -xylene + [mebupy]BF ₄	7.651	-2.135	-349.5	78.52	0.0983

Table 5. Value of the Root Mean Square Deviation for the Ternary Mixtures of an aromatic (1) + an Alkane (2) + [mebupy]BF₄ (3)

ternary system	T/K	rmsd
benzene + <i>N</i> -hexane + [mebupy]BF ₄	313.2	0.0025
	333.2	0.0035
ethylbenzene + <i>N</i> -octane + [mebupy]BF ₄	313.2	0.0044
	348.2	0.0019
<i>m</i> -xylene + <i>N</i> -octane + [mebupy]BF ₄	313.2	0.0019
	348.2	0.0016

small, and its composition in the extract phase is very large. Therefore, to circumvent numerical problems, the constraints for the IL for the parameter regression are left out, just as in the parameter regression carried out by Seiler et al.³¹ Also, where the compositions of the IL in the raffinate phase could not be detected, the compositions were set to 10^{-6} mole fraction in order to avoid numerical problems.

The value of the non-random parameter α_{ij} was set to 0.3 for the aromatic + aliphatic systems and was regressed for the combinations with the ILs, because the standard value gave erroneous results. For ionic systems, α_{ij} usually has another value rather than 0.3. Other authors who investigated LLE data with ILs also used other values for α_{ij} besides the standard value of 0.3.^{17–20} The binary interaction parameters for *N*-octane + [mebupy]BF₄ were determined by regression of two data sets of the ternary system *m*-xylene + *N*-octane + [mebupy]BF₄ at $T = (313.2 \text{ and } 348.2) \text{ K}$, because there were more experimental data points available for this ternary system than for the ethylbenzene + *N*-octane + [mebupy]BF₄ system. These interaction parameters were then used in the determination of the other interaction parameters of the ternary system ethylbenzene + *N*-octane + [mebupy]BF₄.

Results and Discussion

Ternary Mixtures with an Aromatic + an Aliphatic Hydrocarbon + [mebupy]BF₄. The experiments with benzene + *N*-hexane were carried out at $T = (313.2 \text{ and } 333.2) \text{ K}$ because of the low boiling point of *N*-hexane (342 K). The experiments with the two other mixtures were carried out at $T = (313.2 \text{ and } 348.2) \text{ K}$. The results can be found in the following tables and figures: (i) Benzene + *N*-hexane + [mebupy]BF₄ is in Table 1 and Figures 1 and 2. (ii) Ethylbenzene + *N*-octane + [mebupy]BF₄ is in Table 2 and Figures 3 and 4. (iii) *m*-Xylene + *N*-octane + [mebupy]BF₄ is in Table 3 and Figures 5 and 6.

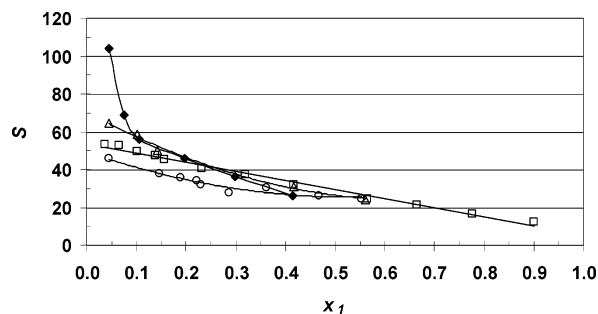
The distribution coefficient (β_i) of compound i was determined with

$$\beta_i = x_i^E/x_i^R \quad (3)$$

and the selectivity (S) of the IL was determined from

$$S = (x_1^E/x_2^E)/(x_1^R/x_2^R) \quad (4)$$

where x_1 and x_2 refer to the mole fractions of the aromatic hydrocarbon and the alkane, respectively; superscripts E and R

**Figure 7.** Selectivities S for aromatic + aliphatic mixtures with [mebupy]BF₄ at $T = 313.2 \text{ K}$. \blacklozenge , benzene + *N*-hexane; \square , toluene + *N*-heptane; \triangle , ethylbenzene + *N*-octane; \circ , *m*-xylene + *N*-octane. Data of selectivities S for toluene + *N*-heptane from ref 30.

refer to the extract (IL-rich) phase and to the raffinate (alkane-rich) phase, respectively.

Comparing the results of the three binary systems (1) + [mebupy]BF₄ (2), it can be seen that benzene (1) has the highest solubility in this IL, $x_1 = 0.63$. The solubility of ethylbenzene (1) and *m*-xylene (1) in [mebupy]BF₄ are $x_1 = 0.27$ and $x_1 = 0.26$, respectively. It can also be seen that *N*-hexane is more soluble in [mebupy]BF₄ than *N*-octane. The values are as follows: $x_{1,av} = 0.020$ and 0.017 for *N*-hexane (at $T = 313.2 \text{ K}$ and 333.2 K , respectively) and $x_{1,av} = 0.009$ and 0.008 for *N*-octane at $T = 313.2 \text{ K}$ and 348.2 K , respectively.

The distribution coefficients of the aromatic compounds increase with decreasing compositions of the aromatic compound in the raffinate phase, as can be seen in Tables 1 to 3. However, the distribution coefficients of the aliphatic compounds decrease slightly with decreasing compositions of the aromatic compound in the raffinate phase, as can be seen in Tables 1 to 3. Benzene has higher distribution coefficient than ethylbenzene or *m*-xylene, and *N*-hexane also showed higher distribution coefficients than *N*-octane. Since the distribution coefficients for the aliphatic hydrocarbons decrease and those for the aromatic compounds increase at decreasing aromatic composition in the raffinate phase, it follows that the aromatic + aliphatic selectivities increase at lower aromatic content in the raffinate. The highest aromatic + aliphatic selectivity was observed for the binary system benzene (1) + *N*-hexane (2), notably $S = 103.8$ at $x_1 = 0.044$ at $T = 313.2 \text{ K}$ due to the high solubility of benzene in [mebupy]BF₄. In Figure 7, the aromatic + aliphatic selectivities at $T = 313.2 \text{ K}$ for the three aromatic + aliphatic systems investigated here and the results of toluene + *N*-heptane from our previous work³⁰ are shown. From this figure, it is apparent that the benzene + *N*-hexane selectivity at low benzene compositions is significantly higher than the toluene + *N*-heptane, ethylbenzene + *N*-octane, or *m*-xylene + *N*-octane selectivities, as is also clear by comparing Figures 2, 4, and 6 and Tables 1 to 3.

Comparison of Experimental and Correlated Data. As can be seen from the results as depicted in Figures 1, 3, and 5, the experimental data are well-correlated with the NRTL equation.

The tie lines in the ternary diagrams coincide in many cases. Also, the experimental aromatic + aliphatic selectivity is very well-described with the calculated data, as can be seen in Figures 2, 4, and 6. In Table 4, all interaction parameters for the NRTL model are given.

The root mean square deviation (rmsd) is defined as:

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

where x is the mole fraction; the subscripts i , l , and m provide a designation for the component, phase, and the tie lines, respectively. The value k designates the number of tie lines. The values of the rmsd of the systems are listed in Table 5.

The values of rmsd in Table 5 provide a measure of the goodness of fit of the correlations. As can be inferred from these values, a good correlation of the experimental values with the NRTL model was obtained. Most of the rmsd values are below 0.0035.

Conclusions

Ternary data for the systems aromatic + aliphatic hydrocarbon + [mebupy]BF₄ were gathered for the aromatic + aliphatic combinations of benzene + *N*-hexane at $T = (313.2 \text{ and } 333.2)$ K and ethylbenzene + *N*-octane and *m*-xylene + *N*-octane at $T = (313.2 \text{ and } 348.2)$ K.

All experimental data can very well be correlated with the NRTL model. The rmsd values of the correlations are generally below 0.0035. The experimental and calculated aromatic + aliphatic selectivities are in good agreement with each other.

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