Thermodynamic Properties of Mixtures Containing Ionic Liquids. 4. LLE of Binary Mixtures of $[C_2MIM][NTf_2]$ with Propan-1-ol, Butan-1-ol, and Pentan-1-ol and $[C_4MIM][NTf_2]$ with Cyclohexanol and 1,2-Hexanediol Including Studies of the Influence of Small Amounts of Water

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Experimental data are presented for liquid−liquid equilibria of mixtures of the room-temperature ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($[C_2MIM][NTf_2]$) with the three alcohols propan-1-ol, butan-1-ol, and pentan-1-ol and for the 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($[C_4MIM][NTf_2]$) with cyclohexanol and 1,2-hexanediol in the temperature range of 275 K to 345 K at ambient pressure. The synthetic method has been used. Cloud points at a given composition were observed by varying the temperature and using light scattering to detect the phase splitting. In addition, the influence of small amounts of water on the demixing temperatures of binary mixtures of $[C_2MIM][NTf_2]$ and propan-1-ol, butan-1-ol, and pentan-1-ol was investigated.

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1. Introduction

Ionic liquids (IL) represent an unusual class of solvents with many novel and promising properties. In contrast to common molten salts, ionic liquids exist in the liquid state at temperatures below 373 K and up to 730 K in most cases. Their extremely low vapor pressure and their miscibility and solubility behavior make them interesting for many applications in industry as well as in chemical synthesis.[1−4]

For the successful and large-scale use of ionic liquids, intensive and systematic investigations of their physicochemical properties are necessary. During the last few years, investigations of such properties have increased remarkably. Next to the fundamental thermodynamic properties (e.g., viscosity, density), the phase behavior (SLE, VLE, and LLE) of ionic liquids mixed with organic solvents and especially water has increasingly gained interest.[5−25] In this work, we present new results of liquid−liquid equilibria of the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($[C_2MIM][NTf_2]$) with propan-1-ol, butan-1-ol, and pentan-1-ol and, in addition, 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ($[C_4MIM][NTf_2]$) with cyclohexanol and 1,2-hexanediol. The chemical structure of the ionic liquids is shown in Figure 1.

As reported previously,[5,6] $[C_2MIM][NTf_2]$ shows partial miscibility with primary alcohols such as propan-1-ol, butan-1-ol, and pentan-1-ol. In this work, the ionic liquid was synthesized according to the same preparation method as reported previously,[5,6] and the LLE curves of mixtures with propan-1-ol, butan-1-ol, and pentan-1-ol have been redetermined with the purpose of studying carefully the influence of water on the results. Well-defined small amounts of water have been added to these mixtures, and the change in the LLE curves has been analyzed on a quantitative basis. These results are of special interest because it is well known that the purity of ionic liquids has a large influence on their properties.[12−14,26] Recently published results[12,13] have shown that water acts as a cosolvent. As a result, the demixing temperature of a binary mixture decreases with increasing water content, which has been confirmed by our studies.

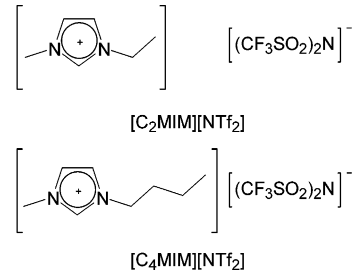

Figure 1. Structure of $[C_2MIM][NTf_2]$ and $[C_4MIM][NTf_2]$.

2. Experimental Section

Substances. The room-temperature ionic liquids $[C_2MIM][NTf_2]$ and $[C_4MIM][NTf_2]$ were synthesized according to previously described preparation methods.[5,6,27] All starting substances (except $LiNTf_2$) were purified by distillation prior to use.

The synthesis of $[C_2MIM][NTf_2]$ was carried out using the halogen-free route described previously.[5,6] The starting substances were *N*-methylimidazole and diethyl sulfate. After hydrolysis, the anion of the resulting ionic liquid was exchanged via a metathesis reaction with an aqueous solution of $LiNTf_2$.

For the preparation of $[C_4MIM][NTf_2]$, a different method was used. As starting materials, *N*-methylimidazole and butyl chloride were used. The precursor $[C_4MIM]Cl$ was treated with an aqueous solution of $LiNTf_2$. After phase separation, the halide was removed by intensively washing

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10.1021/je049564z CCC: \$30.25 © 2005 American Chemical Society
Published on Web 03/05/2005

Table 1. Water Content in the Organic Solvents

cyclohexanol	(165 ± 60) ppm
1,2-hexanediol	(215 ± 50) ppm
propan-1-ol	(100 ± 25) ppm
butan-1-ol	(70 ± 10) ppm
pentan-1-ol	(40 ± 10) ppm

the ionic liquid phase with water. The halide content was periodically checked by treating the water phase with acid $AgNO_3$.

To remove traces of volatile compounds from $[C_2MIM][NTf_2]$ and $[C_4MIM][NTf_2]$, we kept the substances under vacuum (about 10^{-6} bar) at 340 K for 24 h. The residue of the starting materials in the ionic liquid was tested by ^1H and ^{13}C NMR spectroscopy. The purity of the ionic liquids was ≥98% according to impurity peaks observed in the NMR spectrum. The water content was determined by Karl Fischer titration (DL35 Mettler Toledo) ((205 ± 10) ppm and (771 ± 10) ppm for $[C_2MIM][NTf_2]$; (160 ± 30) ppm and (480 ± 50) ppm for $[C_4MIM][NTf_2]$ in the first and second measurement runs, respectively). The substances were stored under an Ar atmosphere to avoid the absorption of water or air.

The solvents for the liquid−liquid equilibria measurements were supplied by Fluka, with purities of ≥97.0% for 1,2-hexanediol, ≥99.0% for cyclohexanol, ≥99.8% for propan-1-ol, and ≥99.0% for pentan-1-ol. Butan-1-ol was obtained from Merck with a purity of ≥99.8%. All solvents were dried over molecular sieves prior to use. The water content was determined by Karl Fischer titration and checked periodically. The residual water content for the solvents is summarized in Table 1.

Experimental Procedure. The experimental setup being used has been described in detail previously.[5,6] The special advantage of the apparatus is the small amount of sample (4 cm^3) needed to determine cloud point temperatures.

The composition was determined gravimetrically. The relative uncertainty of the mass fraction was estimated to be less than 2×10^{-4}. Cloud point temperatures have been determined with precisions of ±0.5 K and ±1.0 K depending on the quality of temperature control.

3. Results and Discussion

Miscibility Tests and Water Solubility. Prior to the measurements of liquid−liquid equilibria, a series of binary systems has been investigated with respect to a rough test of their miscibility properties. The results are presented in Table 2.

Because of the importance of water as an impurity in ionic liquids, the exact value of the maximum water content in the IL samples was determined. Samples have been saturated with water by shaking them with water for 40 h. The two-phase system stayed at rest for 8 h before water analysis was made by Karl Fischer titration. In the ionic liquid phase, (1.90 ± 0.06) mass % of water was found for $[C_2MIM][NTf_2]$, and (1.30 ± 0.01) mass % of water was found for $[C_4MIM][NTf_2]$ at 293 K. The results are in good agreement with results published by Crosthwaite et al.[15]

LLE of Mixtures Containing $[C_4MIM][NTf_2]$. In continuation of our previous work, we have investigated the phase behavior at atmospheric pressure of binary systems consisting of $[C_4MIM][NTf_2]$ + cyclohexanol and 1,2-hexanediol. The obtained phase diagrams are shown in Figure 2, and the demixing points are summarized in Tables 3 and 4.

Table 2. Qualitative Examination of the Miscibility of $[C_2MIM][NTf_2]$ and $[C_4MIM][NTf_2]$ (T = 278−358 K) with Different Solvents[a]

solvent	$[C_2MIM][NTf_2]$[b]	$[C_4MIM][NTf_2]$[b]
n-hexane	n.i.	im
1-hexene	n.i.	im
cyclohexane	n.i.	im
cyclohexene	n.i.	im
1,3-cyclohexadiene	n.i.	pm
benzene	pm[28]	pm
cyclohexanol	n.i.	pm
propan-1-ol	pm	mi
butan-1-ol	pm	pm
pentan-1-ol	pm	pm
hexan-1-ol	n.i.	pm
1,4-butanediol	pm	n.i.
1,2-hexanediol	n.i.	pm
1-hexanal	n.i.	mi
methyl caproate	n.i.	mi
2-hexanone	n.i.	mi
water	im	im

[a] mi − totally miscible; pm − partially miscible; im − immiscible; n.i. − not investigated. [b] 25 mass % < w_{IL} < 75 mass %.

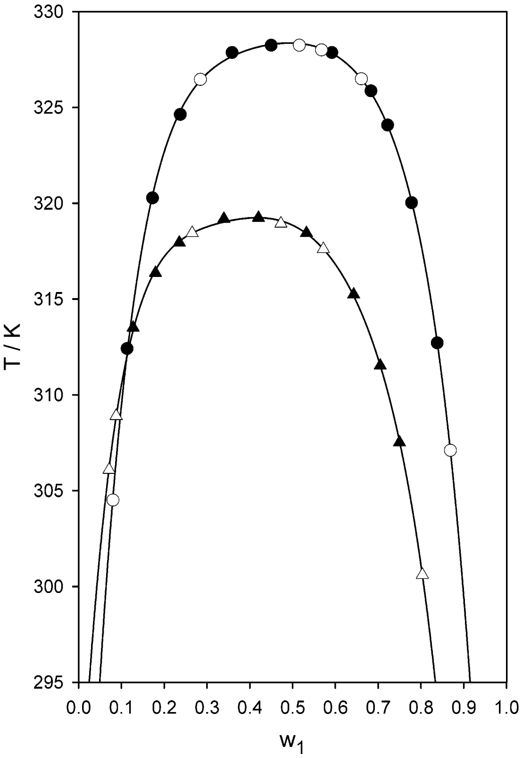

Figure 2. LLE coexistence curves for $[C_4MIM][NTf_2]$ (1) + solvents—▲, △, + cyclohexanol (2) and ●, ○, + 1,2-hexanediol (2)—as a function of mass fraction w_1. Filled symbols represent $w_{H_2O,1}$ = (160 ± 30) ppm, and empty symbols, $w_{H_2O,1}$ = (480 ± 50) ppm.

All binary systems exhibit an upper critical solution temperature (UCST), which is (319.2 ± 1.0) K for cyclohexanol and (328.2 ± 1.0) K for 1,2-hexanediol, respectively.

LLE of Mixtures Containing $[C_2MIM][NTf_2]$. Two years ago, demixing curves of binary systems containing $[C_2MIM][NTf_2]$, propan-1-ol, butan-1-ol, and pentan-1-ol were reported by our group.[5,6]

We have now remeasured the cloud points of selected mixtures using a new sample of the ionic liquid with a well-defined content of water. $[C_2MIM][NTf_2]$ was synthesized according to the same halogen-free preparation method. The experimental cloud point results for all three systems

Table 3. Experimental Cloud Points for [C$_4$MIM][NTf$_2$] (1) + Cyclohexanol (2) as a Function of Mass Fraction w_1[a]

w_1	T/K	w_1	T/K
first run		second run	
0.1274	313.5	0.0711	306.1
0.1796	316.4	0.0877	308.9
0.2352	318.0	0.2654	318.4
0.3395	319.2	0.4727	318.9
0.4201	319.2	0.5718	317.6
0.5324	318.4	0.8033	300.6
0.6428	315.2		
0.7048	311.5		
0.7499	307.5		

[a] Precision of temperature = ±1.0 K.

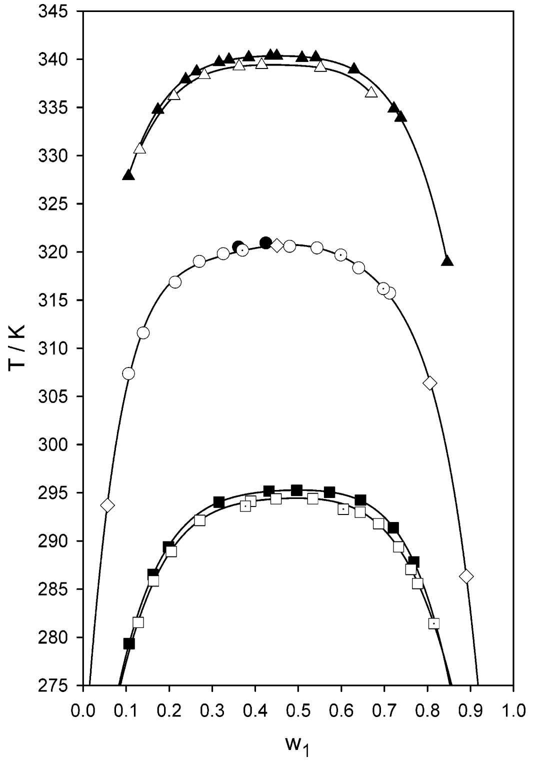

Figure 3. LLE coexistence curves for [C$_2$MIM][NTf$_2$] (1) + solvents—□, ■, ⊡, + propan-1-ol (2); ○, ●, ⊙, ◇, + butan-1-ol (2); and △, ▲, + pentan-1-ol (2)—as a function of mass fraction w_1. Filled symbols are for this work, and empty symbols, refs 5 and 6.

Table 4. Experimental Cloud Points for [C$_4$MIM][NTf$_2$] (1) + 1,2-Hexanediol (2) as a Function of Mass Fraction w_1[a]

w_1	T/K	w_1	T/K
first run		second run	
0.1131	312.4	0.0802	304.5
0.1726	320.3	0.2845	326.5
0.2376	324.6	0.5157	328.2
0.3584	327.9	0.5675	328.0
0.4500	328.2	0.6606	326.5
0.5916	327.9	0.8688	307.1
0.6830	325.9		
0.7221	324.1		
0.7781	320.0		
0.8380	312.7		

[a] Precision of temperature = ±1.0 K.

Table 5. Experimental Cloud Points for [C$_2$MIM][NTf$_2$] (1) + Propan-1-ol (2) as a Function of Mass Fraction w_1[a]

w_1	T/K
0.1070	279.3
0.1622	286.5
0.1983	289.4
0.3157	294.0
0.4319	295.2
0.4963	295.3
0.5724	295.1
0.6446	294.2
0.7210	291.4
0.7686	287.8

[a] $w_{H_2O,1}$ = (205 ± 10) ppm; $w_{H_2O,2}$ = (100 ± 25) ppm; precision of temperature = ±0.5 K.

Table 6. Experimental Cloud Points for [C$_2$MIM][NTf$_2$] (1) + Butan-1-ol (2) as a Function of Mass Fraction w_1[a]

w_1	T/K
0.4247	320.9
0.3608	320.5

[a] $w_{H_2O,1}$ = (771 ± 10) ppm; $w_{H_2O,2}$ = (70 ± 10) ppm, precision of temperature = ±0.5 K.

Table 7. Experimental Cloud Points for [C$_2$MIM][NTf$_2$] (1) + Pentan-1-ol (2) as a Function of Mass Fraction w_1[a]

w_1	T/K
0.1054	327.9
0.1738	334.8
0.2385	337.9
0.2639	338.7
0.3159	339.7
0.3390	340.0
0.3848	340.2
0.4354	340.4
0.4499	340.4
0.5087	340.1
0.5405	340.2
0.6295	338.9
0.7222	334.9
0.7380	333.9
0.8462	318.9

[a] $w_{H_2O,1}$ = (205 ± 10)ppm; $w_{H_2O,2}$ = (40 ± 10) ppm, precision of temperature = ±0.5 K

Table 8. Influence of Small Amounts of Water on the Cloud Point Temperatures for [C$_2$MIM][NTf$_2$] (1) + Propan-1-ol (2)[a]

w_1	T/K
$w_{H_2O,2}$ = (35 ± 10)ppm	
0.1731	287.3
0.3219	294.2
0.5183	295.3
0.6004	294.9
$w_{H_2O,2}$ = (235 ± 25)ppm	
0.5889	294.9

[a] $w_{H_2O,1}$ = (205 ± 10) ppm, precision of temperature = ±0.5 K.

are presented in Figure 3 in comparison to data published previously (Tables 5−7).

It is obvious that all demixing temperatures determined in the present work are shifted to higher temperatures. The deviations between the curves vary between 0.5 K and 1.5 K depending on the system and the composition of the mixture.

It is known from the literature that such deviations can be caused by varying amounts of impurities in the ionic liquid as well as in the organic solvent. Because it is very difficult to remove water or to avoid the absorption of water during sample preparation or storage, the water content seems to be the main reason for the observed deviations. Unfortunately, the water content of [C$_2$MIM][NTf$_2$] and the alcohols could not be measured two years ago, and a direct

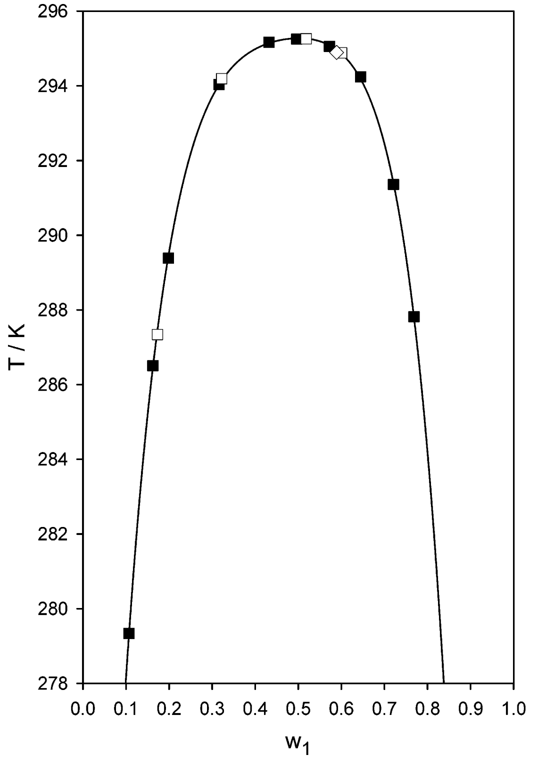

Figure 4. Influence of small amounts of water on the cloud point temperatures of the system [C_2MIM][NTf_2] (1) + propan-1-ol (2). ■, $w_{H_2O,2}$ = (100 ± 25) ppm; □, $w_{H_2O,2}$ = (35 ± 10) ppm; ◇, $w_{H_2O,2}$ = (235 ± 25) ppm.

comparison of the curves is not possible. Therefore, we have now started to investigate the influence of water on the demixing temperature in a systematic way. The water content of all original components used in the first series of measurements was determined by Karl Fischer titration (Table 1).

Table 9. Influence of Water on Cloud Point Temperatures[a]

$10^{-3}w_3$/ppm	T/K	$10^{-3}w_3$/ppm	T/K
[C_2MIM][NTf_2] (1) + Propan-1-ol(2)		[C_2MIM][NTf_2] (1) + Pentan-1-ol (2)	
$w_1 =$	0.7210	$w_1 =$	0.7222
0.18	291.4	0.16	334.9
1.06	290.3	1.06	334.0
1.97	289.3	2.04	333.1
2.92	288.3	3.00	332.2
6.27	284.6	5.05	330.2
7.94	282.8	7.06	328.2
[C_2MIM][NTf_2] (1) + Butan-1-ol (2)		[C_2MIM][NTf_2] (1) + Pentan-1-ol (2)	
$w_1 =$	0.3608	$w_1 =$	0.3159
0.32	320.5	0.09	339.7
2.44	318.8	1.53	338.6
3.56	317.8	4.06	336.5
4.58	316.9	5.64	335.2
6.46	315.4		

[a] Results for [C_2MIM][NTf_2] (1) + propan-1-ol (2), + butan-1-ol (2), or + pentan-1-ol (2) as a function of water content (3) in the mixtures (precision of temperature = ±0.5 K).

Influence of Small Amounts of Water on the Cloud Point Temperature. Measurements on three series of mixtures containing [C_2MIM][NTf_2] and propan-1-ol have been carried out. The distinction between the mixtures was small amounts of water in the propan-1-ol sample used for preparation ((35 ± 10) ppm, (100 ± 25) ppm, and (235 ± 25) ppm)). The compositions of the investigated mixtures and the measured demixing points are summarized in Table 8. A comparison of the cloud points with the coexistence curves (Figure 4) determined previously (Figure 3) shows that such small changes in water content have a negligible influence on the demixing temperatures. The deviations in temperature are within our experimental error of the method.

In addition to these measurements, the influence of water on the cloud point temperatures was investigated systematically by adding certain amounts of water (between 150 and 8000 ppm) to a binary mixture. For the mixture containing propan-1-ol as a solvent, the water

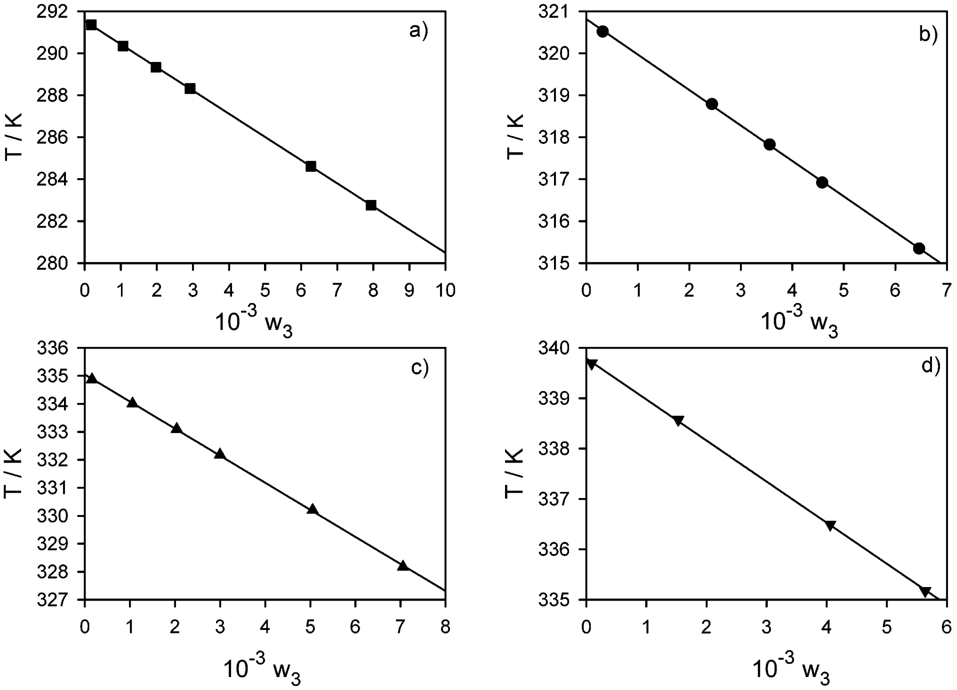

Figure 5. Influence of water content (3) on the cloud point temperatures of the system [C_2MIM][NTf_2] (1) + solvents (2): ■, + propan-1-ol (2), (a) w_1 = 0.7210; ●, + butan-1-ol (2), (b) w_1 = 0.3608; ▲, + pentan-1-ol (2), (c) w_1 = 0.7222; ▼, + pentan-1-ol (2), (d) w_1 = 0.3159.

content was analyzed by Karl Fischer titration after the measurement. The results of these investigations obtained with mixtures of [C_2MIM][NTf_2] + propan-1-ol, butan-1-ol, and pentan-1-ol are presented in Table 9 and illustrated in Figure 5, where the change in temperature is plotted versus the water content for four different compositions. The results show that in all cases a linear dependency is observed from which we conclude that LLE data of mixtures containing an ionic liquid and a nonaqueous solvent can be obtained from a systematic study of the influence of water on the demixing temperature and extrapolation to a water content of zero. Furthermore, the results indicate that a water content smaller than 0.02 mass % in the mixture will most probably provide data that represent the results of systems free of water within the experimental error limit.

Recently, we started to investigate the influence of water on the cloud point temperature for mixtures containing [C_4MIM][NTf_2] and 1,2-hexanediol. The first results showed that the system is less sensitive to water. The demixing temperature decreases only about 3 K per mass % of water. Details will be published in the future.

Literature Cited

(1) Hoffmann, M. M.; Heitz, M. P.; Carr, J. B.; Tubbs, J. D. Surfactants in Green Solvent Systems − Current and Future Research Directions. *J. Dispersion Sci. Technol.* **2003**, *24*, 155−171.

(2) Earle, M. J.; Seddon, K. R. Ionic Liquids. Green Solvents for the Future. *Pure Appl. Chem.* **2000**, *72*, 1391−1398.

(3) *Ionic Liquids: Industial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, D.C., 2002.

(4) *Ionic Liquids as Green Solvents: Progress and Prospects*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 856; American Chemical Society: Washington, D.C., 2003.

(5) Wertz, C. Diploma Thesis, University of Rostock, Rostock, Germany, 2002.

(6) Heintz, A.; Lehmann, J. K.; Wertz, C. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 3. Liquid−Liquid Equilibria of Binary Mixtures of 1-Ethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl)imide with Propan-1-ol, Butan-1-ol, and Pentan-1-ol. *J. Chem. Eng. Data*, **2003**, *48*, 472−474.

(7) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 1. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-*n*-butylpyridinium Tetrafluoroborate Using Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2001**, *46*, 1526−1529.

(8) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 2. Activity Coefficients at Infinite Dilution of Hydrocarbones and Polar Solutes in 1-Methyl-3-ethyl-imidazolium Bis(trifluoromethylsulfonyl) Amide and in 1,2-Dimethyl-3-ethyl-imidazolium Bis(trifluoromethylsulfonyl) Amide Using Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2002**, *47*, 894−899.

(9) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. Activity Coefficients at Infinite Dilution of Polar Solvents in 4-Methyl-N-butylpyridinium Tetrafluoroborate Using Gas−Liquid Chromatography. *J. Chem. Thermodyn.* **2002**, *34*, 1341−1347.

(10) Heintz, A.; Klasen, D.; Lehmann, J. K. Excess Molecular Volumes and Viscosities of Binary Mixtures of Methanol and the Ionic Liquid 4-Methyl-N-butyl-pyridinium Tetrafluoroborate at 25, 40, and 50 °C. *J. Solution Chem.* **2002**, *31*, 467−475.

(11) Wagner, M.; Stanga, O.; Schröer, W. Corresponding states analysis of the critical points in binary solutions of room-temperature ionic liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3943−3950.

(12) Najdanovic-Visak, V. N.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydlowski, J. Phase behaviour of room temperature ionic liquid solutions: an unusually large co-solvent effect in (water + ethanol). *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701−1703.

(13) Najdanovic-Visak, V. N.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydlowski, J. Pressure, Isotope, and Water Co-solvent Effects in Liquid−Liquid Equilibria of (Ionic Liquid + Alcohol) systems *J. Phys. Chem. B* **2003**, *107*, 12797−12807.

(14) Swatloski, R. P.; Visser, A. E.; Reichert, W. M.; Broker, G. A.; Farina, L. M.; Holbrey, J. D.; Rogers, R. D. On the solubilization of water with ethanol in hydrophobic hexafluorophosphate ionic liquids. *Green Chem.* **2002**, *4*, 81−87.

(15) Crosthwaite, J. M.; Aki, S. N. V. K.; Maginn, E. J.; Brennecke, J. F. Liquid-Phase Behavior of Imidazolium-Based Ionic Liquids with Alcohols. *J. Phys. Chem. B* **2004**, *108* (16), 5113−5119.

(16) Domańska, U.; Bogel-Lukasik, E.; Bogel-Lukasik, R. 1-Octanol/Water partition coefficients of 1-alkyl-3-methylimidazolium chloride. *Chem.−Eur. J.* **2003**, *9*, 3033−3041.

(17) Domańska, U.; Bogel-Lukasik, E.; Bogel-Lukasik, R. Solubility of 1-Dodecyl-3-methylimidazolium Chloride in Alcohols (C_2−C_{12}). *J. Phys. Chem. B* **2003**, *107*, 1858−1863.

(18) Domańska, U.; Marciniak, A. Solubility of 1-Alkyl-3-methylimidazolium Hexafluorophosphate in Hydrocarbons. *J. Chem. Eng. Data* **2003**, *48*, 451−456.

(19) Domańska, U.; Marciniak, A. Solubility of Ionic Liquid [emim]-[PF_6] in Alcohols *J. Phys. Chem. B* **2004**, *108*, 2376−2382.

(20) Anthony, J. L.; Maginn, E. J.; Brennecke J. F. Solution Thermodynamics of Imidazolium-Based Ionic Liquids and Water. *J. Phys. Chem. B* **2001**, *105*, 10942−10949.

(21) Anthony, J. L.; Maginn, E. J.; Brennecke J. F. Gas Solubility in 1-n-Butyl-3-methylimidazolium Hexafluorophosphate. In *Ionic Liquids: Industial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818: American Chemical Society: Washington, D.C., 2002; pp 260−296.

(22) Anthony, J. L.; Maginn, E. J.; Brennecke J. F. Solubilities and Thermodynamic Properties of Gases in the Ionic Liquid 1-*n*-Butyl-3-methylimidazolium Hexafluorophospate. *J. Phys. Chem. B* **2002**, *106*, 7315−7320.

(23) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why is CO_2 So Soluble in Imidazolium-Based Ionic Liquids? *J. Am. Chem. Soc.* **2004**, *126*, 5300−5308.

(24) Wu, C.-T.; Marsh, K. N.; Deev, A. V.; Boxall, J. A. Liquid−Liquid Equilibria of Room-Temperature Ionic Liquids and Butan-1-ol. *J. Chem. Eng. Data* **2003**, *48*, 486−491.

(25) Krummen, M.; Wasserscheid, P.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique. *J. Chem. Eng. Data* **2002**, *47*, 1411−1417.

(26) Seddon, K. R.; Stark, A.; Torres, M.-J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275−2287.

(27) Wasserscheid, P.; Van Hal, R.; Boesmann, A. New, Halogen-Free Ionic Liquids − Synthesis, Properties, and Application. *Electrochem. Soc. Proc.* **2002**, *19*, 146−154.

(28) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. Liquid clathrate formation in ionic liquid-aromatic mixtures. *Chem. Commun.* **2003**, 476−477.

Received for review December 9, 2004. Accepted February 2, 2005. We gratefully acknowledge financial support from the German Science Foundation (DFG).

JE049564Z