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Surface Tensions and the Gibbs Excess Surface Concentration of Binary Mixtures of the Ionic Liquid 1-Ethyl-3-methylimidazolium Bis[(trifluoromethyl)sulfonyl]imide with Tetrahydrofuran and Acetonitrile

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ABSTRACT: The surface tensions of binary mixtures containing the ionic liquid 1-ethyl-3-methyl-imidazolium bis[(trifluoromethylsulfonyl]imide ([EMIM][NTf$_2$]) and the aprotic solvents tetrahydrofuran (THF) or acetonitrile were measured at temperatures in the range from (293.15 to 313.15) K (or to 308.15 K for the system with THF) using the pendant drop method. On the basis of these experimental results and activity coefficients taken from vapor pressure measurements, the Gibbs excess surface concentrations for mixtures were calculated. The results and their relationship to electrolyte solutions are discussed.

INTRODUCTION

The large interest which room temperature ionic liquids (RTILs or ILs) have gained during last few years indicates their potential for application in many branches of chemistry and in industrial applications, for example, in catalysis, extraction, electrochemical processes, and others.[1−5] New ILs can be obtained by modifying their structure for tailoring desired solvent properties.[6] Therefore, it is of importance to have as many thermophysical properties available as possible, like densities, viscosities, surface tensions, or miscibilities with common solvents.

Surface properties are of a particular interest for two reasons. First, they are often considered as key properties to obtain valuable information about the transfer of mass and energy of dissolved molecules across the interface. For mixtures of ILs with other organic solvents they also provide new information about the aggregation behavior and drop formation of partly miscible mixtures revealing how these compounds participate as components in a mixed solvent system, used, for example, in extraction processes.

Second, data of surface tensions for mixtures in combination with the bulk activity coefficients allow us to obtain some information about the mixture composition in the surface which usually differs from the bulk composition.

Some surface tension data for pure ILs as well as for their binary mixtures can be found in the literature.[7−15] Besides the experimental data some of these works report also additional calculations concerning the thermodynamics of adsorption at interfaces.[16,17] However, Gibbs excess surface concentrations have not been widely discussed so far.

In this paper we report experimental values of surface tensions for binary mixtures of the IL 1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([EMIM][NTf$_2$]) and tetrahydrofuran (THF) or acetonitrile measured over a certain temperature range. From these data and from activities taken from vapor pressure data[18] Gibbs excess surface concentrations have been derived. Acetonitrile and THF were chosen as components in solution with ILs because of their good mutual solubility. It seems that such kinds of solutions may easily find practical applications.

EXPERIMENTAL SECTION

Chemicals. The characteristics of all chemicals used in this work including their water content (determined by a Karl Fischer titrator, Titroline KF Trace, Schott Instruments GmbH) are presented in Table 1.

[EMIM][NTf$_2$] has been dried and degassed under vacuum. THF and acetonitrile were used without any other purification after checking the water content and comparing their surface tensions with the literature values.[15,19−27] All solutions were degassed in an ultrasonic cleaner prior to use. Densities of the pure chemicals and their mixtures were reported and discussed in detail in a previous paper.[28]

Measurements. Surface tensions were measured with the DSA 10 Krüss tensiometer (with drop shape analysis software) using the pendant drop method covering the whole range of mixture concentrations of [EMIM][NTf$_2$] with THF at (293.15, 298.15, 303.15, and 308.15) K and also at 313.15 K with acetonitrile. Details of technique and experimental procedure have been described recently.[27,28] Each data point of the surface tension has been measured several times. The general uncertainty of the method is estimated to be ± 0.1 mN·m^{-1}.[27]

Experimental results in this work and literature data of surface tensions[15,19−27] of the pure substances at 298.15 K are

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Table 1. Source, Purity, and Surface Tensions, σ, at 298.15 K and the Amount of Water in Pure Compounds

compound	source and purity	amount of water	$\sigma/(\mathrm{mN \cdot m^{-1}})$ this work	$\sigma/(\mathrm{mN \cdot m^{-1}})$ lit.	methods used	AAD[a]/%
THF	Sigma-Aldrich, puriss. p.a.	107 ppm	26.68	26.59[b]	capillary rise[b]	0.91
				26.73[c]	drop volume[c]	
				27.04[d,e,f]	pendant drop[d]	
					drop volume[e]	
					drop volume[f]	
acetonitrile	HiPerSolv Chromanorm, for HPLC-isocratic grade	15 ppm	28.37	27.64[g]	stalagmometer[g]	1.45
				28.16[h]	maximum bubble pressure[h]	
				28.66[i]	capillary rise[i]	
$[EMIM][NTf_2]$	Io-li-tech, 99.9 %	25 ppm	35.90	35.43[j]	representative value after compilation[j]	0.9
				35.71[k]	pendant drop[k,l]	

[a] Absolute average deviation = $\sum_{i=1}^{n}|(\rho_{\exp} - \rho_{\mathrm{lit}})/\rho_{\exp}| \cdot (100/n)$. [b] Ref 19. [c] Ref 20. [d] Ref 21. [e] Ref 22. [f] Ref 23. [g] Ref 24. [h] Ref 25. [i] Ref 26. [j] Ref 15. [k] Ref 27. [l] The same measuring set.

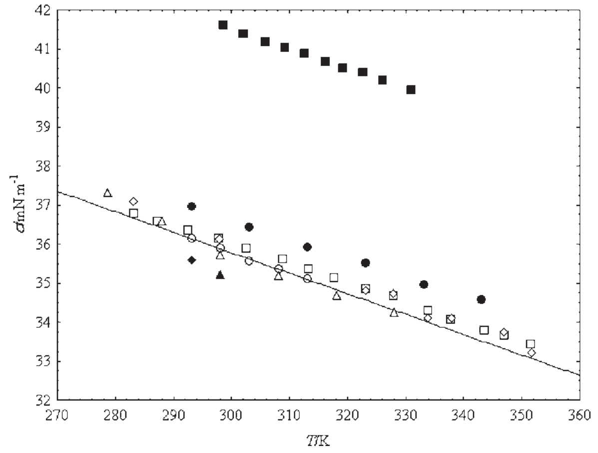

Figure 1. Experimental surface tensions of $[EMIM][NTf_2]$ at different temperatures: ○, this work (pendant drop method); □, ref 15 (Wilhelmy plate); ◇, ref 15 (Du Noüy ring); △, ref 27 (pendant drop method); ●, ref 29 (Pt/Ir Du Noüy ring); ■, ref 30 (Du Noüy ring); ◆, ref 9 (pendant drop method); ▲, ref 31 (capillary rise method; at room temperature); solid line, the linear fit of our results.

summarized in Table 1. The comparison of surface tensions of $[EMIM][NTf_2]$ at different temperatures of this work with literature data[9,15,27,29−31] is shown in Figure 1. It reveals that all surface tensions obtained by different methods are in a good agreement while one data set carried out with the Du Noüy method[30] deviates remarkably from the other results.

RESULTS

Surface tensions σ of binary mixtures of $[EMIM][NTf_2]$ and THF or acetonitrile determined with the pendant drop method are reported in Table 2 and in Figures 2 and 3. Each isothermal data set was described using the Connors and Wright polynomial:[32]

$$\sigma = \sigma_1 - [1 + bx_2/(1 - ax_2)] \cdot x_1(\sigma_1 - \sigma_2) \tag{1}$$

where σ, σ_1, and σ_2 are the surface tensions of the solutions and of the pure component 1 and 2, respectively, x_1 and x_2 are the mole fractions, and a and b are fitting constants.

Coefficients of eq 1 with their standard deviations and mean deviations from the regression lines are collected in Table 3.

Surface tensions of both mixtures investigated decrease with temperature and increase monotonically with the concentrations of $[EMIM][NTf_2]$ as shown in Figures 2 and 3.

The experimental results of the surface tensions have been evaluated to obtain Gibbs adsorption isotherms. Generally, the Gibbs adsorption $\Gamma_2^{(1)}$ or excess molar surface concentration is defined as the difference between the number of moles of component 2 (THF or acetonitrile in our case) in a surface phase of the unit area and the corresponding value in the bulk solution. To determine the excess molar surface concentration the surface tension gradient $(\partial\sigma/\partial a_2)_{T,p}$ has to be known:

$$\Gamma_2^{(1)} = -\frac{a_2}{RT}\left(\frac{\partial\sigma}{\partial a_2}\right)_{T,p} \tag{2}$$

where subscript 2 refers to THF or acetonitrile, a_2 is the activity of substance 2 in the bulk mixture with the IL, and superscript (1) means that there is no enrichment of substance 1 in the interface ($\Gamma_1 = 0$).

In the limiting case of an ideal liquid mixture eq 2 takes the simplified form:

$$\Gamma_2^{(1)} = -\frac{x_2}{RT}\left(\frac{\partial\sigma}{\partial x_2}\right)_{T,p} \tag{3}$$

This means that differences between eqs 2 and 3 arise from the nonideal behavior of the bulk mixtures. Activities a_2 of THF and acetonitrile in their mixtures with $[EMIM][NTf_2]$ were calculated from vapor pressure data taken from the literature[18] according to:

$$\ln a_2 = \ln\left(\frac{p_2}{p_2^*}\right) + \frac{(B_{22} - V_2^*) \cdot (p_2 - p_2^*)}{RT} \tag{4}$$

where p_2 is the partial pressure of the solvent, p_2^* is the pressure of the pure solvent, B_{22} is its second virial coefficient, and V_2^* is the molar volume of the pure liquid solvent. p_2 is identical to the total pressure of the mixtures since $[EMIM][NTf_2]$ has a negligible partial pressure. Second virial coefficients of THF and acetonitrile were taken directly from literature or were calculated on the basis of data presented in the literature.[33,34]

Table 2. Surface Tensions, σ, at Temperatures T for the Binary Systems [EMIM][NTf$_2$] (1) + THF (2) or + Acetonitrile (2)

x_1	$\sigma/(\mathrm{mN\cdot m^{-1}})$			
	[EMIM][NTf$_2$] (1) + THF (2)			
	T/K = 293.15	T/K = 298.15	T/K = 303.13	T/K = 308.15
0	27.31	26.68	26.04	25.38
0.1037	28.72	28.10	27.52	26.88
0.2024	29.94	29.42	28.84	28.33
0.3255	31.05	30.62	30.18	29.84
0.3841	31.62	31.18	30.82	30.52
0.4425	32.12	31.76	31.41	31.07
0.5469	32.98	32.63	32.39	32.08
0.6863	34.07	33.81	33.52	33.26
0.7697	34.55	34.38	34.15	33.92
0.9177	35.65	35.46	35.22	34.98
1	36.14	35.90	35.56	35.35

x_1	[EMIM][NTf$_2$] (1) + acetonitrile (2)				
	T/K = 293.15	T/K = 298.15	T/K = 303.13	T/K = 308.15	T/K = 313.15
0	28.95	28.37	27.66	27.03	26.43
0.0533	30.48	29.80	29.26	28.65	28.04
0.1886	32.72	32.10	31.63	31.16	30.69
0.3370	34.02	33.55	33.15	32.78	32.36
0.4724	34.77	34.42	33.99	33.61	33.28
0.6520	35.38	35.11	34.80	34.49	34.20
0.8245	35.83	35.60	35.29	34.99	34.75
0.9240	35.98	35.76	35.50	35.22	35.00
1	36.14	35.90	35.56	35.35	35.10

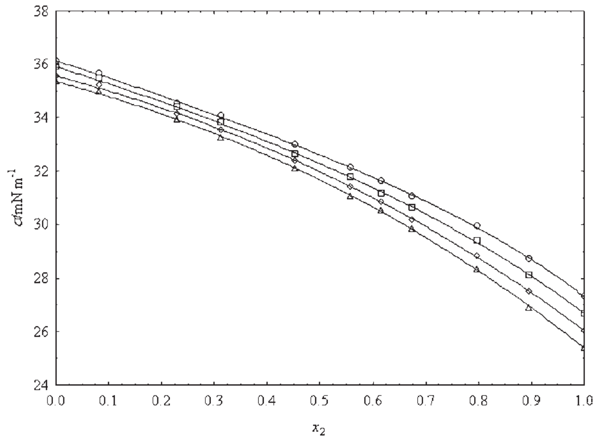

Figure 2. Surface tensions of binary mixtures of [EMIM][NTf$_2$] (1) + THF (2); points: ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; lines, polynomial (1).

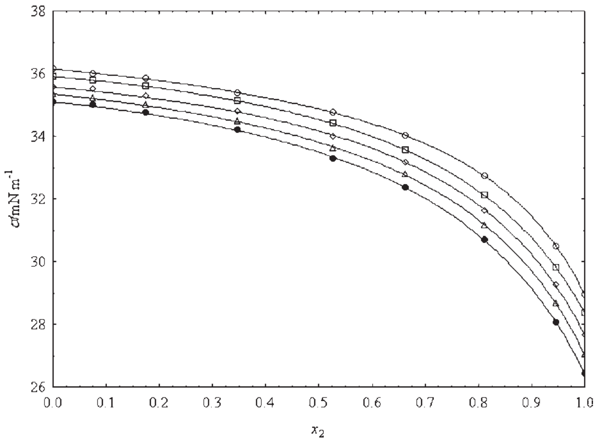

Figure 3. Surface tensions of binary mixtures of [EMIM][NTf$_2$] (1) + acetonitrile (2); points: ○, 293.15 K; □, 298.15 K; ◇, 303.15 K; △, 308.15 K; ●, 313.15 K; lines, polynomial (1).

The vapor pressures of THF or acetonitrile over pure solvents and over the solutions were measured at four temperatures: (283.15, 293.15, 303.15, and 313.15) K and for concentrations different from values in this work,[18] so it was necessary to fit these data using a suitable analytical function.

Activities a_2 of solvents determined from eq 4 were described as a function of mole fraction x_2, using the following polynomial expression:

$$a_2 = \sum_{i=0}^{n} b_i \cdot x_2^i \qquad (n \leq 4) \tag{5}$$

Adjusted coefficients of polynomials applied are reported in Table 4 at different temperatures. To find the activity coefficients required for the combination with surface tension at temperatures,

Table 3. Surface Tension Parameters *a* and *b* and Their Standard Deviations and Mean Deviation from Equation 1

	[EMIM][NTf$_2$] (1) + THF (2)			
	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15
a	−1.70 ± 0.31	−0.89 ± 0.23	−0.26 ± 0.12	−0.26 ± 0.11
b	−0.738 ± 0.055	−0.617 ± 0.046	−0.558 ± 0.030	−0.589 ± 0.028
$\delta/(\text{mN}\cdot\text{m}^{-1})$	0.029	0.033	0.026	0.032

	[EMIM][NTf$_2$] (1) + acetonitrile (2)				
	T/K = 293.15	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
a	−3.880 ± 0.082	−2.851 ± 0.064	−3.01 ± 0.19	−3.09 ± 0.12	−2.78 ± 0.11
b	−3.811 ± 0.046	−3.091 ± 0.036	−3.25 ± 0.11	−3.206 ± 0.065	−3.000 ± 0.061
$\delta/(\text{mN}\cdot\text{m}^{-1})$	0.007	0.011	0.031	0.020	0.018

Table 4. Parameters for Equation 5, Their Standard Deviations, and Correlation Coefficients for [EMIM][NTf$_2$] (1) + THF (2) or + Acetonitrile (2) Binary Mixtures

T/K	b_0	b_1	b_2	b_3	b_4	r
			[EMIM][NTf$_2$] (1) + THF (2)			
283.15	0.053 ± 0.012	−0.085 ± 0.088	2.02 ± 0.16	0	−0.952 ± 0.098	0.9996
293.15	0.0501 ± 0.0049	0	1.29 ± 0.16	1.39 ± 0.42	−1.73 ± 0.28	0.9998
303.15	0.0477 ± 0.0037	0	1.18 ± 0.13	1.52 ± 0.32	−1.75 ± 0.21	0.9999
313.15	0.0473 ± 0.0039	0	0.98 ± 0.13	1.90 ± 0.33	−1.94 ± 0.22	0.9999
			[EMIM][NTf$_2$] (1) + Acetonitrile (2)			
283.15	0.0467 ± 0.0065	0	1.144 ± 0.017	0	0	0.9985
293.15	0.0415 ± 0.0064	0	1.137 ± 0.016	0	0	0.9986
303.15	0.0363 ± 0.0061	0	1.125 ± 0.016	0	0	0.9987
313.15	0.0305 ± 0.0067	0	1.115 ± 0.017	0	0	0.9984

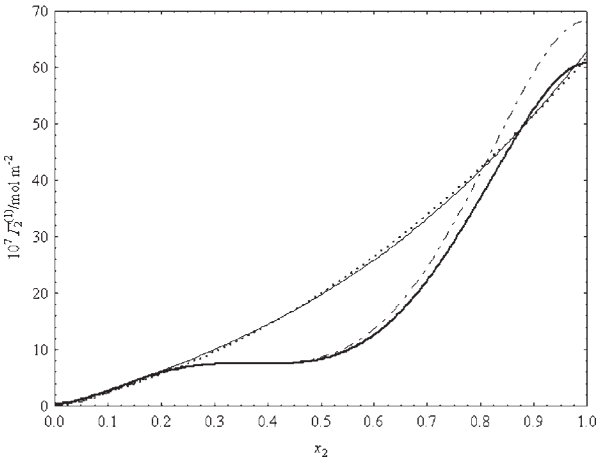

Figure 4. Gibbs excess surface isotherms $\Gamma_2^{(1)}$, of THF (2) in [EMIM][NTf$_2$] (1); obtained from eq 3 (ideal): solid line, at 293.15 K; dotted line, at 308.15 K; and from eq 6 (real): solid bold line, at 293.15 K; dashed line, at 308.15 K.

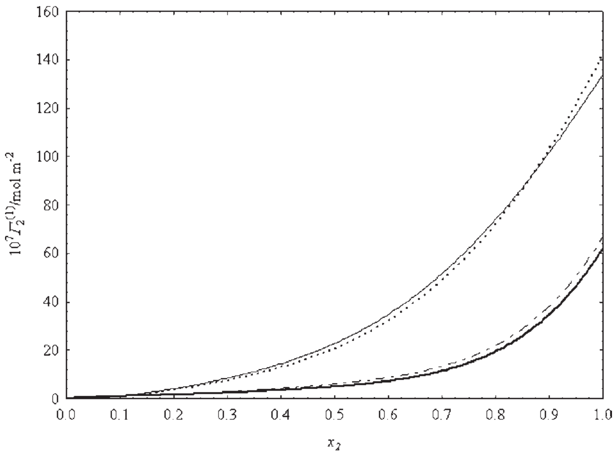

Figure 5. Gibbs excess surface isotherms $\Gamma_2^{(1)}$, of acetonitrile (2) in [EMIM][NTf$_2$] (1); obtained from eq 3 (ideal): solid line, at 293.15 K; dotted line, at 313.15 K; and from eq 6 (real): solid bold line, at 293.15 K; dashed line, at 313.15 K.

where the surface tension was measured, a linear interpolation between activity coefficients at given temperatures was carried out.

Using eqs 1 and 5, $\Gamma_2^{(1)}$ has to be calculated according to:

$$\Gamma_2^{(1)} = -\frac{1}{RT}\, a_2(x_2)\cdot\frac{\partial\sigma(x_2)}{\partial x_2}\cdot\left(\frac{\partial a_2(x_2)}{\partial x_2}\right)^{-1} \qquad (6)$$

For comparison $\Gamma_2^{(1)}$ was also calculated according to eq 3 which represents values for a hypothetical ideal liquid mixture.

Results for THF or acetonitrile in [EMIM][NTf$_2$] are shown in Figures 4 and 5. Figure 6 shows the Gibbs excess concentration isotherms for both systems at 298.15 K.

We presume that the uncertainty of determination of Gibbs excess surface concentrations may achieve (2 to 3) % due to

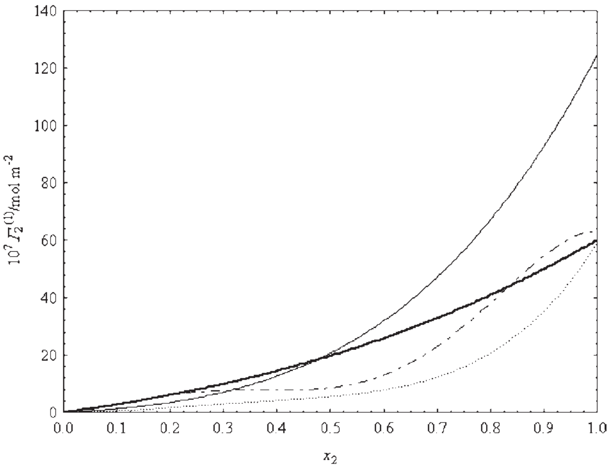

Figure 6. Gibbs excess surface isotherms $\Gamma_2^{(1)}$, of acetonitrile (2) or THF (2) in [EMIM][NTf$_2$] (1); obtained from eq 3 (ideal): solid bold line, with THF; solid line, with acetonitrile; and from eq 6 (real): dashed line, with THF; dotted line, with acetonitrile at 298.15 K.

experimental uncertainties and recalculations necessary to obtain $\Gamma_2^{(1)}$.

DISCUSSION AND CONCLUSIONS

This work presents the first time widely discussed data of the Gibbs excess surface concentration of liquid mixtures containing an IL. According to Onsagers's early theory of the surface tension σ, in solutions containing electrolytes[35] σ increases with increasing electrolyte concentration. A further consequence of this theory is that $\Gamma_2^{(1)}$ is positive indicating that there is an enrichment of solvent molecules in the surface layer compared to the bulk concentrations, that is, a formal repulsion of ions from the surface layer takes place. In nonelectrolyte solutions there is not such a unambiguous situation; in most cases the less polar component of the mixture is enriched in the surface layer. Our results indicate that ILs behave like usual electrolytes in this respect. The Coulombic forces present in IL solution obviously dominate the surface properties of IL + solvent mixtures and not the unpolar organic rest in the cation. It might be of interest for further research work to study the influence of an increasing size of the organic rest in the cation on $\Gamma_2^{(1)}$, for example, [HMIM]-[NTf$_2$] and [OMIM][NTf$_2$] solutions in the same solvents. It can be expected that there might be a crossover point where $\Gamma_2^{(1)}$ changes its sign as it is the case in ionic surfactant solutions where an enrichment of the cationic surfactant molecule is observed in the surface layer.[36]

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REFERENCES

(1) Chiappe, C.; Pieraccini, D. Ionic liquids: solvent properties and organic reactivity. *J. Phys. Org. Chem.* **2005**, *18*, 275–297.

(2) MacFarlane, D. R.; Pringle, J. M.; Howlett, P. C.; Forsyth, M. Ionic liquids and reactions at the electrochemical interface. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1659–1669.

(3) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH Verlags GmbH & Co. KgaA: Weinheim, Germany, 2008.

(4) Koel, M. *Ionic Liquids in Chemical Analysis*; CRC Press: Boca Raton, FL, 2009.

(5) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–629.

(6) Jork, C.; Kristen, C.; Pieraccini, D.; Stark, A.; Chiappe, C.; Beste, Y. A.; Arlt, W. Tailor-made ionic liquids. *J. Chem. Thermodyn.* **2005**, *37*, 537–558.

(7) Muhammad, A.; Abdul Mutalib, M. I.; Wilfred, C. D.; Murugesan, T.; Shafeeq, A. Thermophysical properties of 1-hexyl-3-methyl imidazolium based ionic liquids with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions. *J. Chem. Thermodyn.* **2008**, *40*, 1433–1438.

(8) Fernandez, A.; Garcia, J.; Torrecilla, J. S.; Oliet, M.; Rodriguez, F. Volumetric, Transport and Surface Properties of [bmim][MeSO$_4$] and [emim][EtSO$_4$] Ionic Liquids As a Function of Temperature. *J. Chem. Eng. Data* **2008**, *53*, 1518–1522.

(9) Fröba, A. P.; Kremer, H.; Leipertz, A. Density, Refractive Index, Interfacial Tension, and Viscosity of Ionic Liquids [EMIM][EtSO$_4$], [EMIM][NTf$_2$], [EMIM][N(CN)$_2$], and [OMA][NTf$_2$] in Dependence on Temperature at Atmospheric Pressure. *J. Phys. Chem. B* **2008**, *112*, 12420–12430.

(10) Torrecilla, J. S.; Palomar, J.; Garcia, J.; Rodriguez, F. Effect of Cationic and Anionic Chain Lengths on Volumetric, Transport, and Surface Properties of 1-Alkyl-3-methylimidazolium Alkylsulfate Ionic Liquids at (298.15 and 313.15) K. *J. Chem. Eng. Data* **2009**, *54*, 1297–1301.

(11) Domańska, U.; Pobudkowska, A.; Rogalski, M. Effect of temperature and composition on the surface tension and thermodynamic properties of binary mixtures of 1-butyl-3-methylimidazolium thiocyanate with alcohols. *J. Colloid Interface Sci.* **2008**, *322*, 342–350.

(12) Domańska, U.; Królikowska, M. Effect of temperature and composition on the surface tension and thermodynamic properties of binary mixtures of 1-butyl-3-methyl-imidazolium thiocyanate with alcohols. *J. Colloid Interface Sci.* **2010**, *348*, 661–667.

(13) Galan Sánchez, L.; Ribe Espel, J.; Onink, F.; Meindersma, G. W.; de Haan, A. B. Density, Viscosity, and Surface Tension of Synthesis Grade Imidazolium, Pyridinium, and Pyrrolidinium Based Room Temperature Ionic Liquids. *J. Chem. Eng. Data* **2009**, *54*, 2803–2812.

(14) Guan, W.; Tong, J.; Chen, S.-P.; Liu, Q.-S.; Gao, S.-L. Density and Surface Tension of Amino Acid Ionic Liquid 1-Alkyl-3-methylimidazolium Glutamate. *J. Chem. Eng. Data* **2010**, *55*, 4075–4079.

(15) Klomfar, J.; Souckova, M.; Patek, J. Surface tension measurements with validated accuracy for four 1-alkyl-3-methylimidazolium based ionic liquids. *J. Chem. Thermodyn.* **2010**, *42*, 323–329.

(16) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; John Wiley and Sons, Inc.: New York, 1997.

(17) Aratono, M.; Toyomasu, T.; Villeneuve, M.; Uchizono, Y.; Takiue, T.; Motomura, K.; Ikeda, N. Thermodynamic Study on the Surface Formation of the Mixture of Water and Ethanol. *J. Colloid Interface Sci.* **1997**, *191*, 146–153.

(18) Safarov, J.; Geppert-Rybczyńska, M.; Hassel, E.; Heintz, A. Vapor Pressures and Activity Coefficients of Binary Mixtures of 1-ethyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide with Acetonitrile and Tetrahydrofuran. *Fluid Phase Equilib.* **2010**, in press.

(19) Ramkumar, D. H. S.; Kudchadker, A. P. Mixture Properties of the Water + gamma-Butyrolactone + Tetrahydrofuran System. 2. Viscosities and Surface Tensions of gamma-Butyrolactone + Water at 303.15 - 343.15 K and gamma-Butyrolactone + Tetrahydrofuran at 278.15 - 298.15 K. *J. Chem. Eng. Data* **1989**, *34*, 463–465.

(20) Pineiro, A.; Brocos, P.; Amigo, A.; Pintos, M.; Bravo, R. Surface tensions and refractive indices of (tetrahydrofuran + *n*-alkanes) at *T* = 298.15 K. *J. Chem. Thermodyn.* **1999**, *31*, 931–942.

(21) Pan, C.; Ke, Q.; Ouyang, G.; Zhen, X.; Yang, Y.; Huang, Z. Excess Molar Volumes and Surface Tensions of Trimethylbenzene with

Tetrahydrofuran Tetrachloromethane and Dimethyl Sulfoxide at 298.15 K. *J. Chem. Eng. Data* **2004**, *49*, 1839–1842.

(22) Villares, A.; Giner, B.; Artigas, H.; Lafuente, C.; Roy, F. M. Study of the Surface Tensions of Cyclohexane or Methylcyclohexane with Some Cyclic Ethers. *J. Solution Chem.* **2005**, *34*, 185–198.

(23) Giner, B.; Bandres, I.; Artigas, H.; Cea, P.; Lafuente, C. Surface Tension of Mixtures of Tetrahydrofuran or Tetrahydropyran with Isomeric Chlorobutanes. *Int. J. Thermophys.* **2007**, *28*, 1188–1198.

(24) Kinart, C. M.; Kinart, W. J.; Kolasiński, A. Acetonitryle - water binary mixtures and their assumed internal structures. *Phys. Chem. Liq.* **1998**, *35*, 201–208.

(25) Kinart, C. M.; Kinart, W. J.; Kolasiński, A.; Ćwiklińska, A. Physicochemical Properties of Acetonitrile-Butan-1-ol and Acetonitrile-Butan-2-ol Mixtures. *Phys. Chem. Liq.* **2000**, *38*, 583–597.

(26) Teixeira, P. I. C.; Almeida, B. S.; Telo da Gama, M. M.; Rueda, J. A.; Rubio, R. G. Interfacial Properties of Mixtures of Molecular Fluids. Comparison between Theory and Experiment: $CH_3I + CCl_4$ and $CH_3CN + CCl_4$. *J. Phys. Chem.* **1992**, *96*, 8488–8497.

(27) Wandschneider, A.; Lehmann, J. K.; Heintz, A. Surface Tension and Density of Pure Ionic Liquids and Some Binary Mixtures with 1-Propanol and 1-Butanol. *J. Chem. Eng. Data* **2008**, *53*, 596–599.

(28) Geppert-Rybczyńska, M.; Heintz, A.; Lehmann, J. K.; Golus, A. Volumetric Properties of Binary Mixtures Containing Ionic Liquids and Some Aprotic Solvents. *J. Chem. Eng. Data* **2010**, *55*, 4114–4120.

(29) Carvalho, P. J.; Freire, M. G.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Surface Tensions for the 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) imide Ionic Liquids. *J. Chem. Eng. Data* **2008**, *53*, 1346–1350.

(30) Kilaru, P.; Baker, G. A.; Scovazzo, P. Density and Surface Tension Measurements of Imidazolium-, Quaternary Phosphonium-, and Ammonium-Based Room-Temperature Ionic Liquids: Data and Correlations. *J. Chem. Eng. Data* **2007**, *52*, 2306–2314.

(31) Martino, W.; Fernandez de la Mora, J.; Yoshida, Y.; Saito, G.; Wilkes, J. Surface tension measurements of highly conducting ionic liquids. *Green Chem.* **2006**, *8*, 390–397.

(32) Connors, K. A.; Wright, J. L. Dependence of surface tension on composition of binary aqueous-organic solutions. *Anal. Chem.* **1989**, *61*, 194–198.

(33) Hossenlopp, I. A.; Scott, D. W. Vapor heat capacities and enthalpies of vaporization of six organic compounds. *J. Chem. Thermodyn.* **1981**, *13*, 405–414.

(34) Nasirzadeh, K.; Neueder, R.; Kunz, W. Vapor pressures, osmotic and activity coefficients for (LiBr + acetonitrile) between the temperatures (298.15 and 343.15) K. *J. Chem. Thermodyn.* **2004**, *36*, 511–517.

(35) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Pergamon Press: Oxford, 1958.

(36) Heintz, A.; Lehmann, J. K.; Kozlova, S. A.; Balantseva, E. V.; Bazyleva, A. B.; Ondo, D. Micelle formation of alkylimidazolium ionic liquids in water and in ethylammonium nitrate ionic liquid: A calorimetric study. *Fluid Phase Equilib.* **2010**, *294*, 187–196.