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Surface Tension and Density of Pure Ionic Liquids and Some Binary Mixtures with 1-Propanol and 1-Butanol

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The pendant drop method has been used for measuring the surface tension of the pure ionic liquids 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, butyltrimethylammonium bis(trifluoromethylsulfonyl)imide, methyltrioctylammonium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium ethylsulfate, and 1-butyl-3-methylimidazolium octylsulfate in the range of (278 to 333) K. In addition, densities and thermal expansion coefficients of these ionic liquids are presented. The values of surface tension lie between (25 and 48) $\text{mN}\cdot\text{m}^{-1}$ and decrease with temperature. Surface tension σ of the mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + 1-propanol and + 1-butanol have also been determined as a function of the mole fraction at 298 K. Since the pendant drop method requires precise density measurements of the mixtures, densities were also measured.

Introduction

Ionic liquids have attracted the attention of many research groups during the last years due to the large variety of applications of this new class of liquids in industry and applied chemistry. Due to the fact that most of the chemical and technological applications of ionic liquids take place in mixtures, the interest of an increasing number of research groups worldwide has been focused on properties such as liquid–liquid equilibria and vapor–liquid equilibria of mixtures containing ionic liquids. While the number of data concerning bulk mixture properties such as densities, activity coefficients, viscosities, and conductivities published in the literature has increased continuously, surface properties can rarely be found.[1–6] Recently, we published new data of liquid–liquid interface tension measurements of mixtures containing ionic liquids.[7]

In this work, we present new data of surface tension for six pure ionic liquids and for binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide with 1-propanol and 1-butanol. We also report the densities and thermal expansion coefficients for these systems and derive excess volumes.

Experimental section

Chemicals. The ionic liquids have been synthesized in the research group of Prof. Wasserscheid (University of Erlangen, Germany) with the exception of 1-ethyl-3-methylimidazolium ethylsulfate which was supplied by IoLiTec GmbH (Germany). All ionic liquids have been checked by NMR spectroscopy without indication of impurities. No Cl anions could be detected by adding $AgNO_3$. All samples have been dried under vacuum before using them, and their water mass fraction was determined by Karl Fischer titration with the following results: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2MIM][NTf_2]$) $< 2\cdot10^{-4}$, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4MIM][NTf_2]$) $< 2.15\cdot10^{-4}$, butyltrimethylammonium bis(trifluoromethylsulfonyl)imide ($[N_{4111}][NTf_2]$) $< 1.6\cdot10^{-4}$, methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($[N_{8881}][NTf_2]$) $< 1.5\cdot10^{-4}$, 1-ethyl-3-methylimidazolium ethylsulfate ($[C_2MIM][EtSO_4]$) $< 18\cdot10^{-4}$, and 1-butyl-3-methylimidazolium octylsulfate ($[C_4MIM]\ [OcSO_4]$) $< 18\cdot10^{-4}$, 1-propanol $< 0.7\cdot10^{-4}$, and 1-butanol $< 0.8\cdot10^{-4}$.

The alcohols were supplied by Fluka with purities higher than 99.9 %. They have been degassed and dried with molecular sieves before use.

Surface Tension Measurements. Surface tension has been measured using the pendant drop method.[8,9] The thermostatted cell of the apparatus was filled with dry argon. It contained a film of the liquid substance at the bottom to establish a saturated atmosphere in the cuvette. From a syringe, a drop was generated, pending on the outlet of the cannula. This drop was photographed by a CCD-camera, and from its digitalized shape the surface tension σ was determined solving Laplace's equation for curved interfaces exposed to a gravitational field

$$\frac{\partial\Phi}{\partial S} = \frac{2}{R} - \frac{\Delta\rho g z}{\sigma} - \frac{\sin\Phi}{z} \tag{1}$$

The meaning of the quantities in eq 1 are explained in Figure 1 showing schematically the shape of a drop (angle Φ, shape line S, and axis z). R is the radius of curvature at a point on the surface having the coordinates Φ and z; g is the earth's gravitational acceleration ($9.8144\ \text{m}\cdot\text{s}^{-2}$ for Rostock, Germany); and $\Delta\rho$ is the difference of the mass densities of the drop and argon. The surface tension σ can be evaluated by solving the differential equation (eq 1) numerically, where σ has to be adjusted to match the measured and the calculated shape of the drop. We estimate the uncertainty of σ to be $\pm\ 0.1\ \text{mN}\cdot\text{m}^{-1}$.

Density Measurements. For evaluating eq 1, accurate data of densities of the substances are required at different temperatures. The densities of all pure liquids and the corresponding mixtures were measured using a vibrating tube densimeter (Anton Paar DMA 512 P).

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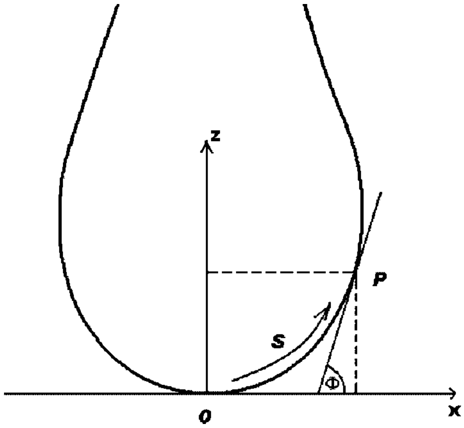

Figure 1. Schematic shape of a pendant drop (see text).

Table 1. Densities ρ of Pure Ionic Liquids ρ/g·cm^{-3}

T/K	[N_{4111}][NTf_2]	[N_{8881}][NTf_2]	[C_2MIM][NTf_2]
278.15	1.4123	1.1198	1.5391
288.15	1.4030	1.1122	1.5289
298.15	1.3940	1.1046	1.5187
308.15	1.3850	1.0972	1.5087
318.15	1.3761	1.0896	1.4986
328.15	1.3673	1.0821	1.4887

T/K	[C_4MIM][NTf_2]	[C_2MIM][$EtSO_4$]	[C_4MIM][$OcSO_4$]
278.15	1.4561	1.2551	1.0773
288.15	1.4462	1.2481	1.0704
298.15	1.4366	1.2411	1.0638
308.15	1.4270	1.2342	1.0571
318.15	1.4174	1.2273	1.0508
328.15	1.4079	1.2206	1.0443

Table 2. Thermal Expansion Coefficient α_p at 300 K

IL	α_p/K^{-1}
[C_2MIM][NTf_2]	$6.47 \cdot 10^{-4}$
[C_4MIM][NTf_2]	$6.84 \cdot 10^{-4}$
[N_{4111}][NTf_2]	$6.66 \cdot 10^{-4}$
[N_{8881}][NTf_2]	$6.73 \cdot 10^{-4}$
[C_2MIM][$EtSO_4$]	$5.58 \cdot 10^{-4}$
[C_4MIM][$OcSO_4$]	$6.21 \cdot 10^{-4}$

The DMA 512 P was calibrated at each temperature using liquid water, dry air, and *n*-hexane as calibration substances. The uncertainty of the density data are estimated to be $\pm 1 \cdot 10^{-4}$ g·cm^{-3}.

From these measurements, the thermal expansion coefficient was calculated according to eq 2 by using a quadratic function $\rho(T)$ (278 K < T < 348 K) fitted to the experimental data and calculating the derivative

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (2)$$

The molar excess volume V_m^E was calculated from the densities of binary mixtures ρ_{mix} and of the pure liquids ρ_1 and ρ_2 according to eq 3.

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{mix}} - x_1 \frac{M_1}{\rho_1} - x_2 \frac{M_2}{\rho_2} \qquad (3)$$

Results and Discussion

The experimental results of densities for pure ionic liquids are listed as a function of T in Table 1. Table 2 contains the thermal expansion coefficients α_p at 300 K calculated by eq 2. Data of surface tension of pure ionic liquids are presented in Table 3. As expected, densities and surface tension decrease almost linearly with increasing temperature in the observed temperature range. These results are shown in Figures 2 and 3. There exist data of [C_4MIM][NTf_2] for the surface tension in the literature[2] covering (293 to 343) K. These data have been obtained using the ring method and are systematically higher than our data by 1.5 %. The difference is outside the estimated experimental uncertainty of both methods and probably indicates that even very small impurities might influence sensitive surface tension data.

Table 3. Surface Tension σ of Pure Ionic Liquids σ/mN·m^{-1}

T/K	[N_{4111}][NTf_2]	[N_{8881}][NTf_2]	[C_2MIM][NTf_2]
278.75	33.31	29.65	37.31
288.15	33.04	28.92	36.58
298.15	32.46	27.93	35.71
308.15	32.00	27.02	35.17
318.15	31.21	26.56	34.68
328.15	30.64	26.03	34.25

T/K	[C_4MIM][NTf_2]	[C_2MIM][$EtSO_4$]	[C_4MIM][$OcSO_4$]
278.75	33.80	46.70	28.08
288.15	33.37	46.04	27.29
298.15	32.80	45.43	26.71
308.15	32.32	44.72	26.27
318.15	31.89	43.74	25.72
328.15	31.28	43.37	24.99

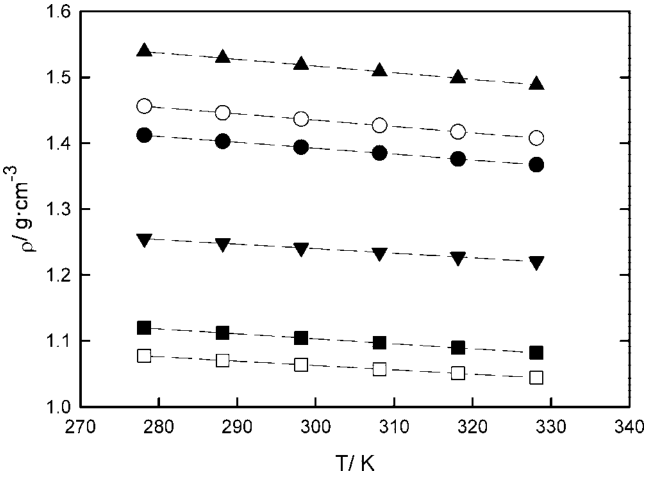

Figure 2. Densities ρ of the pure ionic liquids as a function of temperature: ▲, [C_2MIM][NTf_2]; ○, [C_4MIM][NTf_2]; •, [N_{4111}][NTf_2]; ■, [N_{8881}][NTf_2]; ▼, [C_2MIM][$EtSO_4$]; □, [C_4MIM][$OcSO_4$]; - - -, linear fit.

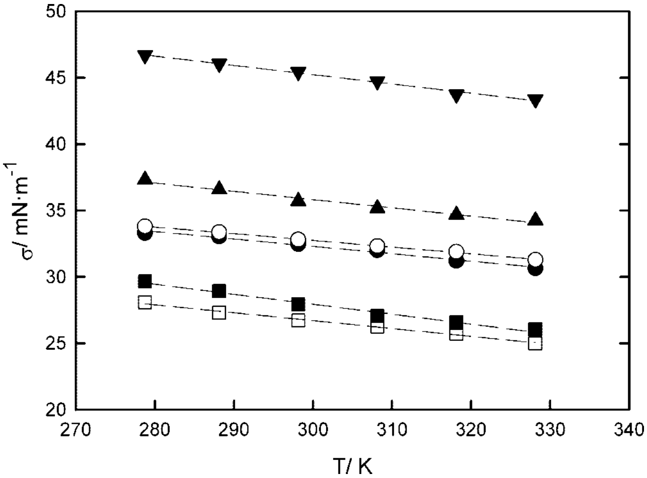

Figure 3. Surface tension σ of pure ionic liquids as a function of temperature: ▲, [C_2MIM][NTf_2]; ○, [C_4MIM][NTf_2]; •, [N_{4111}][NTf_2]; ■, [N_{8881}][NTf_2]; ▼, C_2MIM][$EtSO_4$]; □, [C_4MIM] [$OcSO_4$]; - - -, linear fit.

Table 4. Densities ρ, Surface Tensions σ, and Molar Excess Volumes V_m^E of [C$_4$MIM][NTf$_2$] + Alcohol Mixtures as a Function of x_{IL} at 298 K

1-butanol				1-propanol			
	ρ	σ	V_m^E		ρ	σ	V_m^E
x_{IL}	g·cm^{-3}	mN·m^{-1}	cm^3·mol^{-1}	x_{IL}	g·cm^{-3}	mN·m^{-1}	cm^3·mol^{-1}
0.0000	0.8053	23.96	0	0.000	0.7990	23.34	0
0.0941	0.9622	23.98	−0.074	0.035	0.8782	23.60	−0.096
0.2025	1.0871	23.88	0.026	0.131	1.0362	24.16	−0.154
0.2045	1.0890	23.80	−0.089	0.202	1.1165	24.73	−0.143
0.3060	1.1726	24.16	0.088	0.296	1.1941	25.77	−0.027
0.3064	1.1725	24.25	0.101	0.373	1.2435	26.47	0.007
0.3964	1.2305	25.17	0.134	0.517	1.3118	28.60	0.128
0.5002	1.2836	26.79	0.227	0.664	1.3619	29.89	0.177
0.5977	1.3235	28.32	0.405	0.685	1.3680	30.54	0.167
0.6848	1.3548	29.56	–	0.884	1.4220	32.49	–
0.8016	1.3886	30.96	0.404	1.000	1.4364	32.80	0
0.8986	1.4134	31.94	0.271				
1.0000	1.4364	32.80	0				

Surface tension data, densities, and molar excess volumes V_m^E of the mixtures [C$_4$MIM][NTf$_2$] + 1-propanol and + 1-butanol are listed as function of the mole fraction of the ionic liquid x_{IL} in Table 4. V_m^E has been obtained according to eq 3 using density data from Tables 1 and 4. The uncertainty of the V_m^E data is estimated to ± 0.025 cm^3. All results are shown in Figures 4 and 5.

Values of surface tension σ of pure ionic liquids shown in Table 3 and Figure 3 are lower than σ of water[10] 72.10 mN·m^{-1} and those of aqueous ionic solutions. This is a surprising result since surface tension of liquids containing ions is expected to have distinctly higher values; e.g., 1 mol·L^{-1} of NaCl solution[11] has a surface tension of 74.5 mN·m^{-1}. This result suggests that probably the alkyl groups of the ionic liquids are oriented toward the surface and are enriched there, while charged parts of the molecule are shifted into the bulk phase. This interpretation is also supported by the fact that the surface tension is lower the larger the organic residue is in either the cation or anion of the ionic liquid molecule. Surface tension σ (x_{IL}) of the mixtures indicates increasing values as a function of the mole fraction of the ionic liquid by a change in the curvature of the plot, represented in Figures 4 and 5. In the case of [C$_4$MIM][NTf$_2$] + 1-butanol, even a shallow minimum at x_{IL} = 0.2 is observed. Molar excess volumes V_m^E show S-shaped behavior with changing sign of their values. This has already been observed for other ionic liquid + solvent systems.[12]

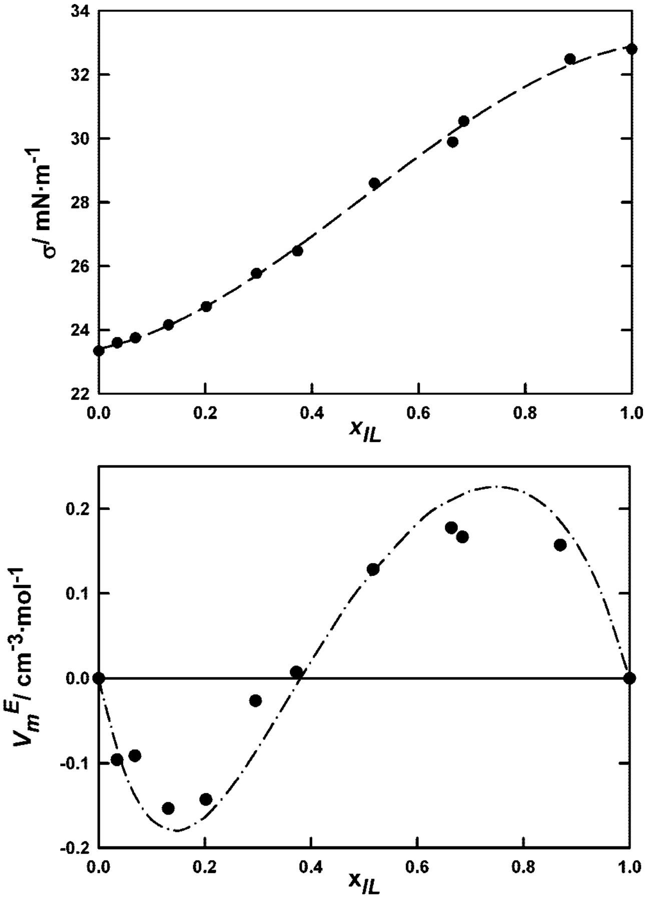

Figure 4. Surface tension σ and molar excess volume V_m^E vs mole fraction x_{IL} for the mixture [C$_4$MIM][NTf$_2$] + 1-propanol (1 − x_{IL}) at 298 K: •, experimental data; - - -, fitted with cubic polynomial; - • - Redlich–Kister polynomial $V_m^E = x_{IL}\cdot(1 - x_{IL})[0.4526 + 1.6538(x_{IL} - (1 - x_{IL})) - 0.7744(x_{IL} - (1 - x_{IL}))^2 + 0.9538(x_{IL} - (1 - x_{IL}))^3]$.

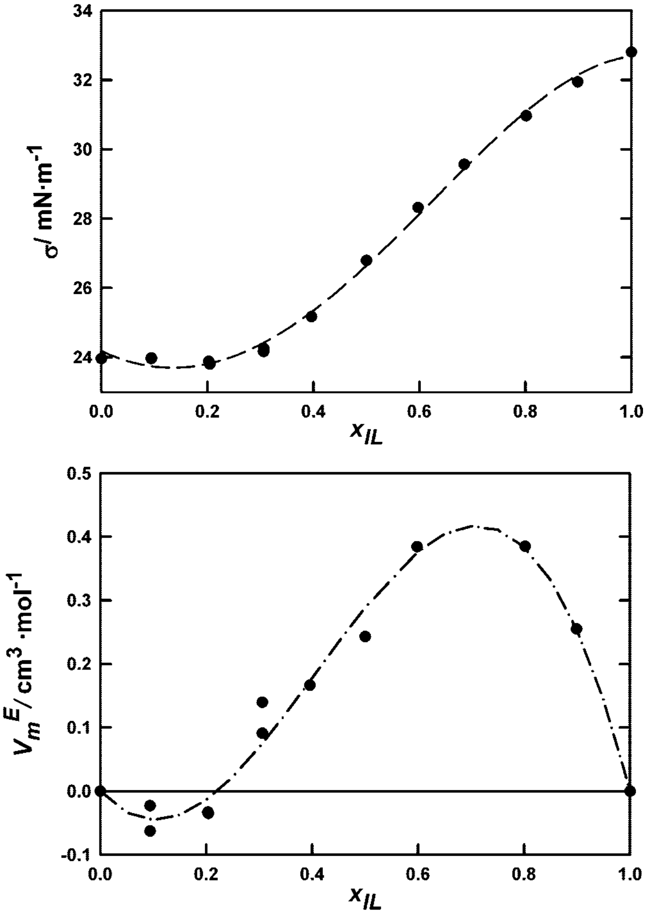

Figure 5. Surface tension σ and molar excess volume V_m^E vs mole fraction x_{IL} for the mixture [C$_4$MIM][NTf$_2$] (x_{IL}) + 1-butanol (1 − x_{IL}) at 298 K: •, experimental data; - - -, fitted with cubic polynomial; - • -, Redlich–Kister polynomial $V_m^E = x_{IL}\cdot(1 - x_{IL})[1.1555 + 2.0717(x_{IL} - (1 - x_{IL}))]$.

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