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Surface Tension of Binary Mixtures of 1-Alkyl-3-Methyl-Imidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids with Alcohols

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Abstract New experimental surface tension data have been provided at 283.15, 298.15, 313.15 K and atmospheric pressure for binary mixtures of 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide and 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids with the alcohols: methanol, ethanol, 1-propanol, 2-propanol, l-butanol and 1-pentanol. The experimental results show that the surface tensions of these mixtures depend systematically on the alkyl chain length of the ionic liquid and alcohol, composition and temperature. Surface tension changes on mixing have been calculated and adequately fitted by the Redlich–Kister polynomial equation. The adjustable parameters and the standard deviations between experimental and calculated values are reported.

Keywords Surface tension · [$C_n$mim][NTf_2] · Alcohols

1 Introduction

In recent years, ionic liquids (ILs) have attracted much attention from the scientific community due to their large variety of applications in industry and applied chemistry [1]. The ionic nature of these compounds results in a unique combination of properties [2, 3]. Of these, negligible vapour pressure may be the most attractive from the environmental point of view and it also implies a high potential for recycling. Most ILs exhibit other interesting properties such as wide liquid range, chemical and physical stability, non-flammability, high thermal conductivity, and the ability to dissolve a broad range of compounds. Moreover, tunable

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physical, chemical and biological properties obtained by combination of the cation and anion of an ionic liquid generates a huge number of applications for these salts.

To design any process involving ILs on an industrial scale, it is necessary to know a range of physical properties, including density, viscosity, surface tension, etc. The surface tension of a liquid mixture plays an important role in affecting the mass and heat transfer at the interface. It is needed in many industrial applications such as liquid–liquid extraction, gas absorption, distillation, condensation and so on. These data are needed not only for process and product design but also for development of correlation and prediction models. A key factor in evaluating simulation and design programs is the reliability of predicted thermophysical properties and phase equilibria. Unfortunately, these data are limited and in several cases contradictory.

Moreover, the surface tension reveals information about the structure and energetics of the surface region between two phases. Variation in surface energy depends on variation in molecular forces and of the density of packing or molecular size. For this reason, the determination of this property for liquid mixtures lets us study interactions among the components. In the literature, there are few works collecting surface tension data for mixtures of ILs and alcohols. Furthermore, interactions follow very different patterns. Aggregation appears in several cases [4, 5] and strong intermolecular interactions which lead to continuous variations occur in several other systems [6, 7].

This work reports experimental measurements of surface tension for 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C_4mim][NTf_2]) or 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C_8mim][NTf_2]) IL and alcohol (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, or 1-pentanol) binary mixtures at 283.15, 298.15, 313.15 K and atmospheric pressure. Surface tension changes of mixing are calculated and fitted by Redlich–Kister polynomial equation.

2 Experimental

2.1 Materials

The source and purity of the methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 1-pentanol are shown in Table 1. No further purification of these products was carried out. The 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C_4mim][NTf_2]) and 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([C_8mim][NTf_2]), were synthesized in our laboratory by reaction of 1-methylimidazole (Aldrich, >99 mass%, GC) with an excess of 1-bromobutane (Merck, >98 mass%) and with an excess of 1-chlorooctane (Aldrich, 99 mass%) to produce [C_4mim][Br] and [C_8mim][Cl], respectively. These bromide and chloride salts were mixed with lithium bis(trifluoromethanesulfonyl) imide, Li[NTf_2] (Solvionic, >99 mass%) in deionized water, to obtain [C_4min][NTf_2] and [C_8min][NTf_2], respectively, by ion metathesis. After washing, the purification of the ILs was completed by heating them under high vacuum for at least 48 h (1 mbar, 353.15 K). More details about the experimental procedure can be found in earlier publications [8]. No bromide concentration was detected by means of capillary electrophoresis in the [C_4min][NTf_2] while the chloride concentration detected in the [C_8min][NTf_2] by the same technique was 14.2 ppm. The ILs were analyzed by ^{1}H and ^{13}C NMR to confirm the absence of any major impurities. Estimated purity is >99.5 mass% for both ILs.

Table 1 Physical properties of the pure components

Component	CAS	Source, purity (mass%)	$10^{-6}\omega$ (H_2O)	ρ/g·cm^{-3} T = 298.15 K		σ/mN·m^{-1} T = 283.15 K		σ/mN·m^{-1} T = 298.15 K		σ/mN·m^{-1} T = 313.15 K	
				This Work	Literature	This Work	Literature	This Work	Literature	This Work	Literature
Methanol	67-56-1	Fluka 99.8	75	0.78663	0.78637 [9]	23.23	23.39 [10]	22.14	22.09 [6] 22.22 [10] 22.51 [11]	–	21.13 [11]
Ethanol	64-17-5	Merck >99.9	347	0.78514	0.78493 [9]	23.13	23.32 [10]	22.04	21.55 [6] 22.10 [10] 21.82 [11]	20.84	20.83 [10] 20.62 [11]
1-propanol	71-23-8	Riedel de Haën 99.9	100	0.79958	0.79960 [9]	24.31	24.57 [10]	23.45	23.34 [7] 23.40 [10] 23.28 [11]	22.13	22.22 [10] 22.1 [11]
2-propanol	67-63-0	Sigma–Aldrich 99.5	175	0.78088	0.78126 [9]	21.98	22.15 [10]	21.24	21.01 [10] 21.22 [11]	19.87	19.84 [10] 19.71 [11]
1-butanol	71-36-3	Sigma–Aldrich 99.8	100	0.80581	0.8024 [9]	25.22	25.65 [10]	24.33	23.67 [6] 23.96 [7] 24.37 [10]	23.07	23.09 [10]
1-pentanol	71-41-0	Fluka >99.0	153	0.81097	0.81080 [9]	26.15	26.59 [10]	25.17	24.74 [9] 25.30 [10] 25.36 [12] 24.97 [13]	23.84	24.01 [10]

Table 1 continued

Component	CAS	Source, purity (mass%)	$10^{-6}\omega$ (H_2O)	ρ/g·cm^{-3} T = 298.15 K		σ/mN·m^{-1} T = 283.15 K		σ/mN·m^{-1} T = 298.15 K		σ/mN·m^{-1} T = 313.15 K	
				This Work	Literature	This Work	Literature	This Work	Literature	This Work	Literature
[C_4mim] [NTf_2]	174899-83-3	Our laboratory	46.33	1.436579	1.4366 [7] 1.43 [14] 1.437 [15]	33.58	33.58 [7][*] 33.5 [24][a]	32.62	32.80 [7] 37.00 [16] 37.50 [17] 33.20 [18] 33.15 [19] 33 [25] 30.7 [26] 38.4 [27] 35.4 [28] 46.3 [29] 33.04 [24][c]	31.77	32.1 [7][*] 32.50 [22, 31] 31.9 [30][b] 31.97 [24][d]
[C_8mim] [NTf_2]	178631-04-4	Our laboratory	35.93	1.32059	1.32 [15] 1.32076 [20] 1.32 [21]	32.07	Not found	30.90	31.44 [19] 31.61 [22][*] 30.63 [23] 29.5 [26]	29.74	30.57 [22] 29.2 [30]

[*] Interpolated value

[a] 284 K

[b] 313.3 K

[c] 298.41 K

[d] 313.93 K

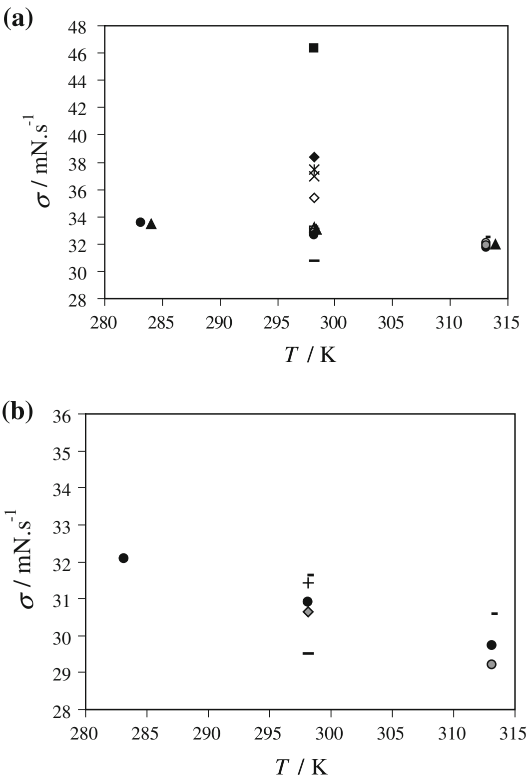


Fig. 1 Comparison of experimental surface tension available in the literature of **a** [C_4mim][NTf_2] and **b** [C_8mim] [NTf_2]: *filled circle* this work; *open circle* [7]; *filled triangle* [24]; *times* [16]; *asterisk* [17]; *open triangle* [18]; *plus* [19]; *open square* [25]; *minus* [26]; *filled diamond* [27]; *open diamond* [28]; *filled square* [29]; *hyphen* [22, 31]; *filled grey circle* [30]; *filled grey diamond* [23]

Table 1 shows a comparison between experimental and literature [6, 7, 9–31] density data at 298.15 K and surface tension data at 283.15, 298.15, 313.15 K and atmospheric pressure. The water content of pure components, also reported in this table, was determined by means of a Karl Fisher titration method carried out in a Metrohm 737 KF.

Figure 1 shows a comparison of the surface tension determined here for the ILs [C_4min] [NTf_2] and [C_8min][NTf_2] at 283.15, 298.15, 313.15 K with data available in the literature [7, 16–19, 22–31]. In spite of the fact that trace amounts of impurities have dramatic effects on the physical properties of ILs, it can be seen that our data are in good agreement with previously measured values. In the case of the measurements at 298.15 K, many data have been published and some of them are clearly dispersed.

Figure 2 illustrates the influence of the anion on the surface tension at 298.15 K of ILs with [C_4mim] or [C_8mim] cations [6, 7, 17, 18, 25–27, 32–40]. It can be seen that the influence of the anion is greater for the shorter alkyl substituent on the imidazolium cation. A detailed analysis of the influence of each specific anion can be found in the interesting review of Tariq et al. [39].

2.2 Experimental Apparatus and Procedure

Densities of the pure components were measured using an Anton Paar DMA 5000 densimeter. This instrument, calibrated by air and water, automatically corrects for the effect of viscosity on the density measurement over the whole viscosity range. The uncertainty in the density and the temperature measurements are $\pm 3 \times 10^{-5}$ g·cm^{-3} and ± 0.01 K, respectively.

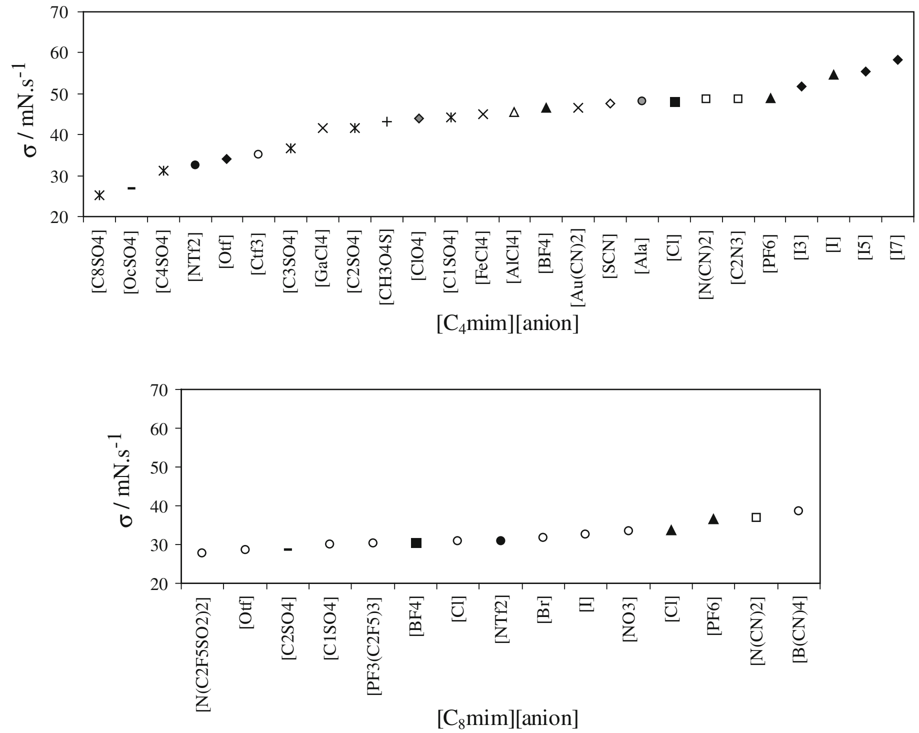


Fig. 2 Experimental surface tension at 298.15 K for different anions in [C_4mim] and [C_8mim] cations available in the literature. **a** [C_4mim]: *filled circle* this work; *open circle* [25]; *filled triangle* [17]; *open triangle* [32]; *asterisk* [33]; *filled square* [34]; *plus* [35]; *open square* [36] at 293.15 K; *minus* [7]; *filled diamond* [18]; *open diamond* [6]; *times* [37]; *filled grey circle* [38] at 293 K; *filled grey diamond* [39] at 293 K. **b** [C_8mim]: *filled circle* this work; *open circle* [26]; *filled triangle* [17]; *filled square* [34]; *open square* [27] at 293 K; *dash* [40]

Mixtures were prepared by mass with a Mettler Toledo AT 261 balance (repeatability $\pm 1 \times 10^{-4}$ g), and the deviation in the mole fraction was estimated to be ±0.0002.

The Wilhelmy plate method was used for the measurement of the surface tensions. All measurements were carried out in a Krüss K11 tensiometer, equipped with an specially adapted platinum plate of cylindrical shape (Krüss accessory reference PL 22; dimensions: 10 mm height × 20 mm base perimeter × 0.1 mm width), suitable for the production of reliable measurements with lower amounts of sample than a conventional plate. The temperature inside the sample vessels (cylindrical open-top glass vessels with a diameter of 30 mm) was kept constant by means of an oil bath controlled by a circulating water bath connected to a Julabo F12 cryogenic thermostat. The uncertainty in the temperature measurement is ±0.1 K. Each value of surface tension reported in this work is the average of ten consecutive immersion measurements, after two initial immersion measurements that were systematically disregarded. The method described has an estimated uncertainty of $\pm 0.1\ \mathrm{mN{\cdot}m^{-1}}$.

3 Results and Discussion

Experimental results of surface tension, σ, and surface tension changes of mixing, $\Delta\sigma$, were measured for [C_4mim][NTf_2] or [C_8mim][NTf_2] and alcohols (methanol, ethanol,

Table 2 Experimental surface tension (σ) and surface tension changes of mixing ($\Delta\sigma$) of [C_4mim][NTf_2] with methanol, ethanol, 1-propanol, 2-propanol, and 1-butanol at different temperatures

	283.15 K		298.15 K		313.15 K	
x	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}
{x [C_4mim][NTf_2] + (1 − x) Methanol}						
0.1049	26.41	2.095	25.52	2.281		
0.2076	28.14	2.761	27.43	3.114		
0.3025	29.40	3.039	28.61	3.300		
0.4087	30.61	3.150	29.79	3.367		
0.5037	31.21	2.770	30.52	3.102		
0.5994	31.79	2.356	31.09	2.668		
0.7168	32.62	1.972	31.78	2.128		
0.7523	32.87	1.853	32.03	2.006		
0.8215	33.14	1.408	32.18	1.431		
0.8649	33.35	1.168	32.40	1.196		
0.9164	33.42	0.706	32.50	0.757		
0.9577	33.44	0.298	32.52	0.344		
{x [C_4mim][NTf_2] + (1 − x) Ethanol}						
0.0999	24.63	0.456	23.77	0.673	22.66	0.728
0.1949	26.05	0.883	25.25	1.148	24.18	1.210
0.2962	27.40	1.174	26.50	1.326	25.60	1.522
0.4001	28.69	1.379	27.79	1.517	26.89	1.677
0.5069	29.83	1.403	29.18	1.777	28.24	1.859
0.6376	31.15	1.357	30.45	1.664	29.63	1.816
0.7183	31.93	1.294	31.22	1.580	30.45	1.759
0.7764	32.46	1.217	31.68	1.426	30.87	1.544
0.8126	32.76	1.139	31.92	1.283	31.09	1.369
0.8615	32.96	0.827	32.06	0.905	31.31	1.053
0.9245	33.33	0.539	32.43	0.604	31.57	0.625
0.9601	33.42	0.257	32.51	0.312	31.66	0.326
{x [C_4mim][NTf_2] + (1 − x) 1-Propanol}						
0.1041	25.12	−0.155	24.35	−0.055	23.11	−0.024
0.2052	25.95	−0.263	25.14	−0.192	23.99	−0.119
0.2969	26.83	−0.233	26.01	−0.163	24.93	−0.063
0.3736	27.66	−0.113	26.87	−0.006	25.92	0.188
0.4946	29.08	0.185	28.41	0.425	27.48	0.582
0.6132	30.45	0.456	29.87	0.797	29.02	0.979
0.7079	31.57	0.698	30.93	0.989	30.03	1.076
0.8031	32.39	0.636	31.59	0.776	30.78	0.908
0.9018	33.04	0.370	32.30	0.580	31.50	0.676
0.9333	33.23	0.268	32.45	0.442	31.65	0.523
{x [C_4mim][NTf_2] + (1 − x) 2-Propanol}						
0.1006	22.68	−0.467	21.95	−0.435	20.77	−0.298
0.1975	23.57	−0.702	22.82	−0.668	21.63	−0.591
0.2878	24.72	−0.598	24.06	−0.455	22.88	−0.415

Table 2 continued

	283.15 K		298.15 K		313.15 K	
x	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}
0.3871	26.11	−0.361	25.58	−0.066	24.45	−0.027
0.4810	27.63	0.070	26.94	0.226	26.05	0.456
0.5517	28.78	0.400	28.02	0.501	27.21	0.774
0.6311	29.86	0.560	29.11	0.688	28.30	0.920
0.7059	30.80	0.631	30.08	0.806	29.22	0.949
0.8232	31.94	0.411	31.28	0.672	30.53	0.864
0.8961	32.62	0.245	31.83	0.392	31.13	0.596
0.9772	33.34	0.024	32.43	0.069	31.65	0.151
{x [C$_4$mim][NTf$_2$] + (1 − x) 1-Butanol}						
0.1048			24.68	−0.518	23.52	−0.461
0.1989			25.07	−0.909	24.09	−0.710
0.3045			25.65	−1.204	24.67	−1.049
0.3940			26.43	−1.167	25.58	−0.918
0.5099	28.47	−1.012	27.82	−0.737	26.99	−0.516
0.6154	29.88	−0.485	29.27	−0.162	28.45	0.026
0.6974	30.86	−0.190	30.12	0.008	29.45	0.313
0.8081	32.15	0.174	31.43	0.401	30.68	0.579
0.9065	33.00	0.202	32.34	0.495	31.60	0.644
0.9563	33.36	0.145	32.54	0.282	31.71	0.320

1-propanol, 2-propanol, 1-butanol, 1-pentanol) binary systems at 283.15, 298.15, and 313.15 K and are summarized in Tables 2 and 3, respectively. Measurements for mixtures of ILs and methanol were not carried out at 313.15 K since the proximity to the methanol boiling point caused problems of evaporation, preventing accurate measurements. The [C$_4$mim][NTf$_2$] system with 1-butanol is partially miscible at 283.15 K and with 1-pentanol is immiscible at all the temperatures.

The surface tension changes of mixing, $\Delta\sigma$, were calculated as:

$$\Delta\sigma/(\mathrm{mN{\cdot}m^{-1}}) = \sigma_M - \sum_i x_i\sigma_i \tag{1}$$

where σ_M and σ_i are the surface tension of the mixture and pure component, respectively.

The surface tension deviations, $\Delta\sigma$, were fitted with composition data by using the Redlich–Kister polynomial equation [41], which for binary mixtures is:

$$\Delta\sigma_{ij} = x_i x_j \sum_k A_k \left(x_i - x_j\right)^k \tag{2}$$

where, x_i is the mole fraction of component i, A_k is the polynomial coefficient, and k is the number of the polynomial coefficient.

The Redlich–Kister coefficients for the binary systems and the standard deviations obtained in the correlations are listed in Table 4 for all temperatures studied. In each case, the coefficients were obtained by fitting Eq. 2 by least-squares regression. Fisher's F-test was used to define the polynomial degree.

Table 3 Experimental surface tension (σ) and surface tension changes of mixing ($\Delta\sigma$) of $[C_8mim][NTf_2]$ with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 1-pentanol at different temperatures

	283.15 K		298.15 K		313.15 K	
x	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}
$\{x\ [C_8mim][NTf_2] + (1 - x)$ Methanol$\}$						
0.0978	25.93	1.835	25.05	2.053		
0.1821	27.46	2.620	26.81	3.075		
0.2826	28.51	2.782	27.87	3.254		
0.3885	29.38	2.716	28.56	3.017		
0.5129	30.10	2.336	29.31	2.677		
0.6131	30.59	1.941	29.73	2.220		
0.7002	31.02	1.601	30.04	1.767		
0.8036	31.09	0.757	30.06	0.881		
0.8449	31.21	0.511	30.22	0.679		
0.9368	31.62	0.108	30.62	0.273		
$\{x\ [C_8mim][NTf_2] + (1 - x)$ Ethanol$\}$						
0.1042	24.81	0.748	24.04	1.076	22.93	1.162
0.1872	26.18	1.377	25.31	1.612	24.23	1.719
0.2691	27.27	1.734	26.35	1.926	25.32	2.085
0.3961	28.64	1.969	27.75	2.201	26.93	2.565
0.4723	29.40	2.047	28.54	2.315	27.76	2.716
0.5549	30.00	1.909	29.25	2.294	28.38	2.601
0.6223	30.31	1.616	29.55	1.996	28.78	2.401
0.7248	30.83	1.220	30.01	1.548	29.22	1.929
0.7632	31.00	1.047	30.12	1.318	29.30	1.667
0.8252	31.26	0.753	30.23	0.879	29.35	1.161
0.8560	31.36	0.577	30.24	0.616	29.35	0.891
0.9136	31.60	0.302	30.49	0.356	29.42	0.449
0.9784	31.96	0.083	30.81	0.101	29.64	0.092
$\{x\ [C_8mim][NTf_2] + (1 - x)$ 1-Propanol$\}$						
0.0974	25.32	0.254	24.49	0.315	23.28	0.409
0.1935	26.24	0.429	25.47	0.579	24.28	0.678
0.2894	27.11	0.554	26.30	0.694	25.23	0.898
0.3793	27.84	0.587	27.03	0.755	26.07	1.054
0.4688	28.53	0.582	27.70	0.757	26.79	1.092
0.5552	29.17	0.552	28.25	0.664	27.42	1.065
0.5967	29.46	0.519	28.47	0.574	27.65	0.979
0.6916	30.08	0.403	29.07	0.468	28.23	0.837
0.7790	30.62	0.265	29.61	0.356	28.66	0.602
0.8556	31.14	0.190	30.07	0.246	28.94	0.299
0.9461	31.72	0.068	30.58	0.082	29.46	0.125
$\{x\ [C_8mim][NTf_2] + (1 - x)$ 2-Propanol$\}$						
0.1006	23.08	0.085	22.39	0.178	21.25	0.387
0.1910	24.21	0.302	23.53	0.444	22.56	0.804
0.3141	25.87	0.720	25.13	0.855	24.27	1.299

Table 3 continued

x	283.15 K		298.15 K		313.15 K	
	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}	σ/mN·m^{-1}	$\Delta\sigma$/mN·m^{-1}
0.4209	27.47	1.244	26.66	1.355	25.74	1.716
0.5131	28.65	1.492	27.81	1.613	26.89	1.955
0.5878	29.54	1.629	28.63	1.712	27.85	2.178
0.6857	30.28	1.382	29.43	1.566	28.54	1.902
0.7940	30.93	0.938	30.00	1.090	28.84	1.133
0.8899	31.29	0.330	30.28	0.443	29.14	0.486
0.9343	31.52	0.113	30.46	0.195	29.24	0.149
{x [C$_8$mim][NTf$_2$] + (1 − x) 1-Butanol}						
0.1161	25.61	−0.406	24.86	−0.233	23.70	−0.145
0.2051	26.09	−0.535	25.38	−0.297	24.28	−0.158
0.3127	26.81	−0.552	26.06	−0.324	25.07	−0.085
0.4123	27.65	−0.394	27.00	−0.039	26.03	0.210
0.5216	28.55	−0.243	27.86	0.103	27.07	0.521
0.6175	29.37	−0.080	28.66	0.273	27.71	0.521
0.7401	30.24	−0.050	29.40	0.207	28.44	0.433
0.8254	30.83	−0.044	29.90	0.147	28.83	0.249
0.8794	31.23	−0.019	30.23	0.122	29.12	0.184
{x [C$_8$mim][NTf$_2$] + (1 − x) 1-Pentanol}						
0.1008	26.42	−0.327	25.52	−0.227	24.28	−0.155
0.2042	26.72	−0.639	25.88	−0.460	24.76	−0.285
0.2977	27.11	−0.802	26.34	−0.536	25.21	−0.386
0.4024	27.61	−0.922	26.85	−0.625	25.82	−0.394
0.4977	28.08	−1.016	27.31	−0.712	26.37	−0.407
0.5917	28.74	−0.913	27.91	−0.650	27.00	−0.331
0.7053	29.52	−0.805	28.65	−0.561	27.78	−0.221
0.7968	30.22	−0.647	29.28	−0.456	28.42	−0.121
0.9040	31.01	−0.492	30.06	−0.290	29.12	−0.054

Figure 3 shows, as function of the IL mole fraction, the surface tensions for the binary mixtures of [C$_4$min][NTf$_2$] + alcohol and [C$_8$min][NTf$_2$] + alcohol at 283.15, 298.15 and 313.15 K.

In the case of [C$_4$min][NTf$_2$], Fig. 3a shows that, at any temperature, when methanol or ethanol is added to the IL, the surface tension increases from that of the alcohol to that of the IL. The graph becomes flat at high concentrations of the IL ($x_{IL} > 0.8$). In the case of the other alcohols, there is a change in the curvature of the plots. The initial slopes of curves are low (tensions near the alcohol value). The property increases and, similar to alcohols of lower molecular weight, plots are flat near the pure IL. The same qualitative behavior is found for [C$_8$min][NTf$_2$] (Fig. 3b). In this case, the curves corresponding to mixtures with 1-pentanol are flat at low concentrations of IL, but increase practically linearly up to the alcohol surface tension.

Figure 4 shows, as function of the IL mole fraction, the surface tension changes of mixing for the binary mixtures of [C$_4$min][NTf$_2$] + alcohol and [C$_8$min][NTf$_2$] + alcohol at 283.15, 298.15 and 313.15 K.

Table 4 Redlich-Kister coefficients and standard deviations (S) of Eq. 1 for $\Delta\sigma$ for the investigated systems at 283.15, 298.15 and 313.15 K

T/K	A_0	A_1	A_2	A_3	S
{x [C_4mim][NTf_2] + (1 − x) Methanol}					
283.15	11.179	−6.6776	6.5836	–	0.081
298.15	12.332	−7.5623	6.6046	–	0.078
{x [C_4mim][NTf_2] + (1 − x) Ethanol}					
283.15	5.9671	1.2495	–	–	0.056
298.15	7.1291	1.2128	–	–	0.074
313.15	7.7774	1.3085	–	–	0.071
{x [C_4mim][NTf_2] + (1 − x) 1-Propanol}					
283.15	0.9457	4.7008	–	–	0.053
298.15	1.8874	5.7129	–	–	0.080
313.15	2.5392	5.9220	–	–	0.069
{x [C_4mim][NTf_2] + (1 − x) 2-Propanol}					
283.15	0.6161	8.2434	−3.3124	−5.5719	0.024
298.15	1.3216	6.8189	−2.8800	–	0.045
313.15	1.9808	7.5823	−2.0320	–	0.071
{x [C_4mim][NTf_2] + (1 − x) 1-Butanol}					
298.15	−3.2114	7.2382	4.4363	–	0.062
313.15	−2.2817	7.5247	4.9535	–	0.057
{x [C_8mim][NTf_2] + (1 − x) Methanol}					
283.15	9.6736	−6.4380	3.3724	−8.2417	0.046
298.15	10.912	−8.1547	5.0394	−6.9313	0.070
{x [C_8mim][NTf_2] + (1 − x) Ethanol}					
283.15	7.5581	−3.0287	–	–	0.077
298.15	8.8837	−3.2260	–	–	0.097
313.15	10.742	−2.1819	−2.6541		0.073
{x [C_8mim][NTf_2] + (1 − x) 1-Propanol}					
283.15	2.2659	−0.9694	–	–	0.013
298.15	2.8163	−1.3920	–	–	0.019
313.15	4.1591	−0.9781			0.051
{x [C_8mim][NTf_2] + (1 − x) 2-Propanol}					
283.15	5.9650	2.9338	−6.4679	–	0.081
298.15	6.4225	3.0242	−5.2579	–	0.081
313.15	8.0338	4.8406	−5.4774	−8.2424	0.047
{x [C_8mim][NTf_2] + (1 − x) 1-Butanol}					
283.15	−1.3717	2.6216	–	–	0.062
298.15	0.0051	2.6347	–	–	0.075
313.15	1.6165	2.7252	−3.1433	–	0.058
{x [C_8mim][NTf_2] + (1 − x) 1-Pentanol}					
283.15	−3.9305	−0.2912	–	–	0.046
298.15	−2.6850	−0.1758	−0.2540	–	0.021
313.15	−1.5612	0.8320	0.7396	–	0.011

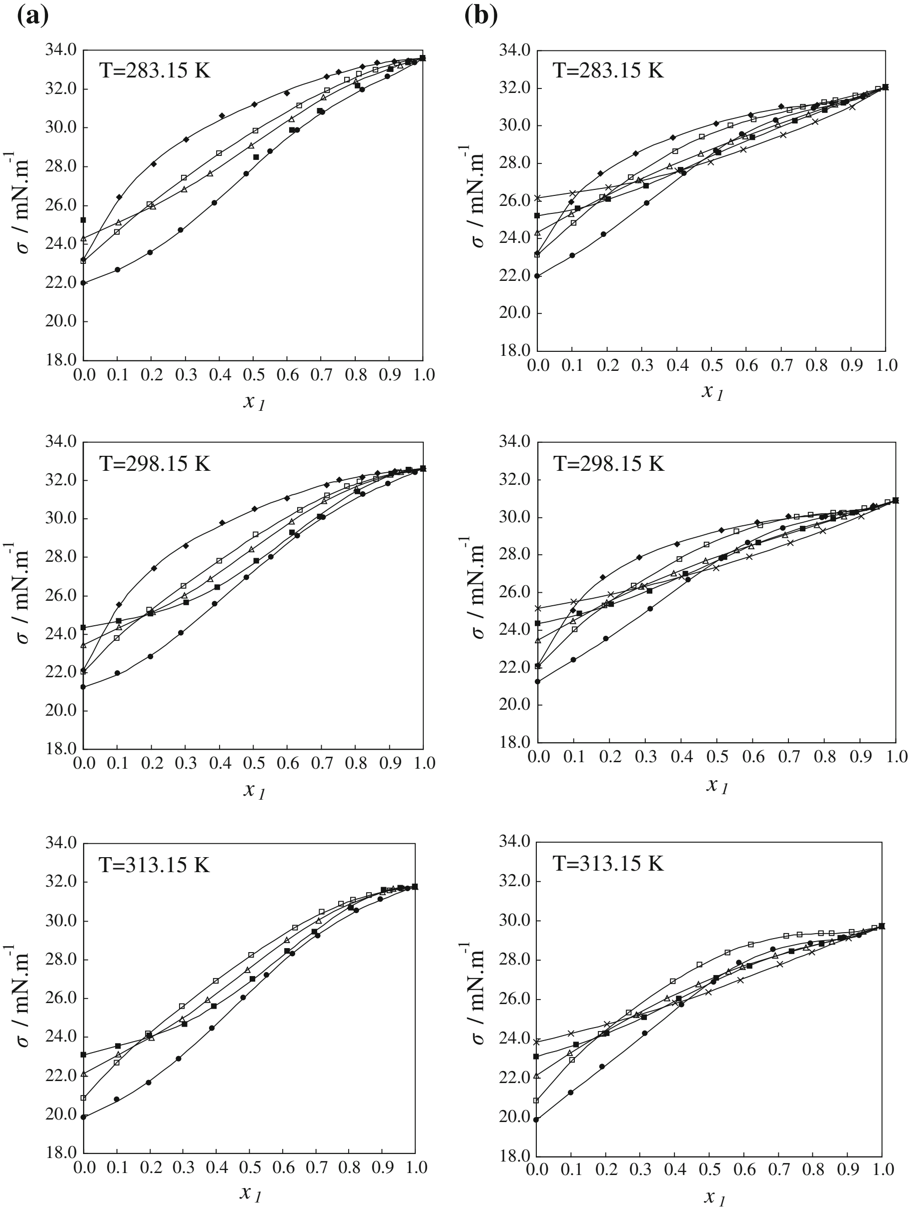


Fig. 3 Plots of σ against mole fraction of [C_4mim][NTf_2] (**a**) and [C_8mim][NTf_2] (**b**) at 283.15, 298.15 and 313.15 K for IL + methanol (*filled diamond*), ethanol (*open square*),1-propanol (*open triangle*), 2-propanol (*filled circle*), 1-butanol (*filled square*), and 1-pentanol (x) binary systems; the *points* are experimental points and the *lines* are calculated from Eq. 2 using the parameters listed in Table 4

In terms of surface tension changes of mixing, Fig. 4a shows that mixtures of [C_4min][NTf_2] with methanol or ethanol have positive surface tensions of mixing at all IL compositions and temperatures studied in this work. The maximum is displaced to low concentrations of IL in the case of methanol. Systems with other alcohols show an *s*-shaped

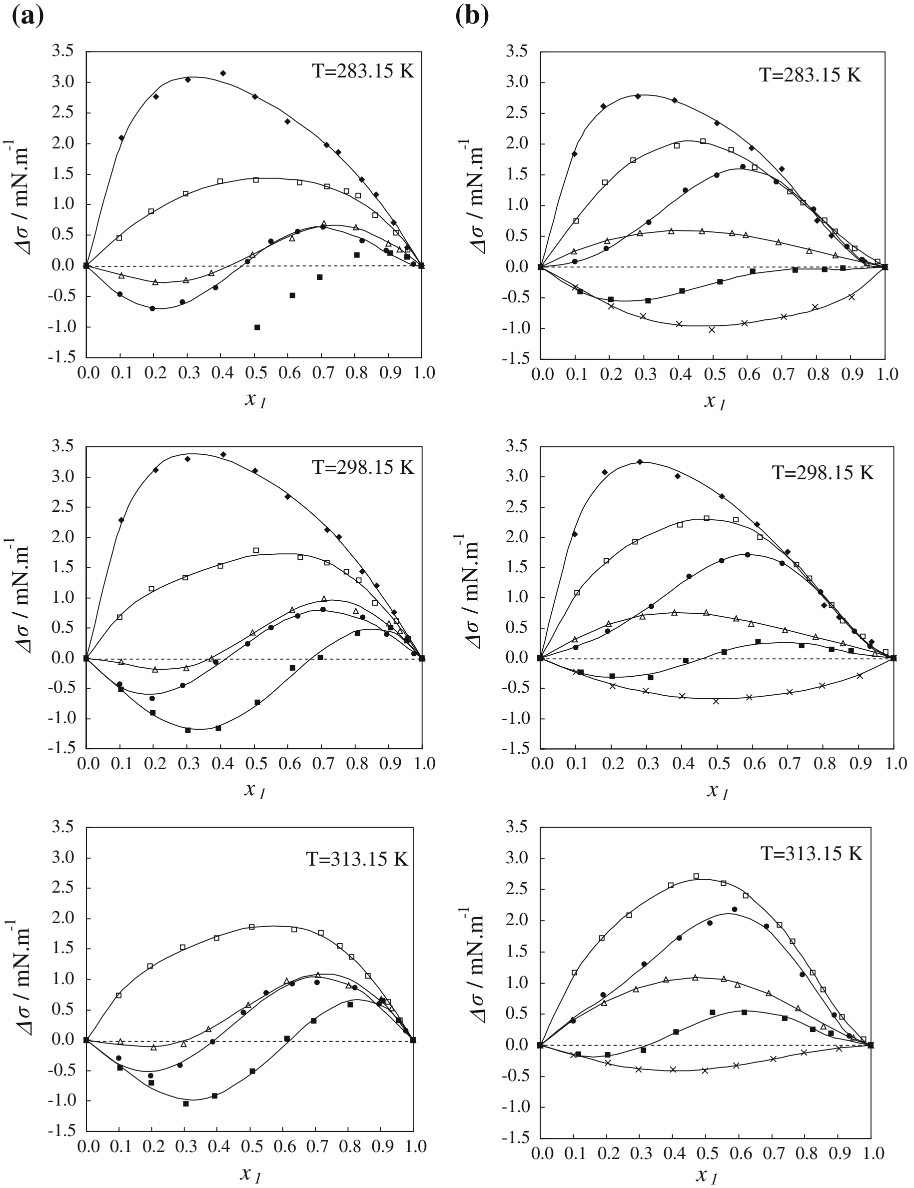
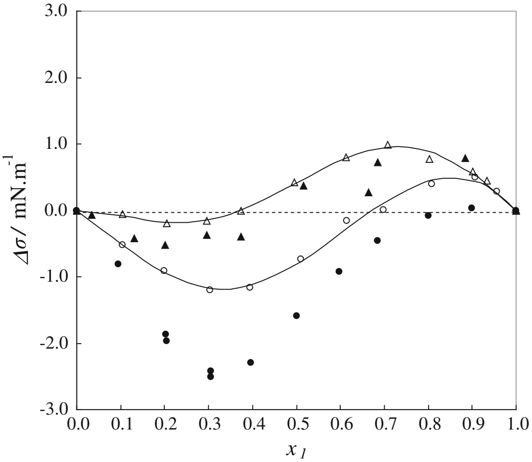


Fig. 4 Plot of Δσ against mole fraction of $[C_4mim][NTf_2]$ (**a**) and $[C_8mim][NTf_2]$ (**b**) at 283.15, 298.15 and 313.15 K for IL + methanol (*filled diamond*), ethanol (*open square*),1-propanol (*open triangle*), 2-propanol (*filled circle*), 1-butanol (*filled sqaure*), and 1-pentanol (x) binary systems; the *points* are experimental points and the *lines* are calculated from Eq. 2 using the parameters listed in Table 4

dependence on composition, whereas $\Delta\sigma$ is negative at high alcohol mole fractions; positive values are found at high IL concentrations.

Figure 5 shows a comparison between surface tension data measured in this work for $[C_4min][NTf_2]$ + 1-propanol and $[C_4min][NTf_2]$ + 1-butanol with data reported in the

Fig. 5 Comparison between surface tension changes of mixing data from this work (*open triangle* {[C_4mim][NTf_2] + 1-propanol}; *open circle* {[C_4mim][NTf_2] + 1-butanol}) and from the literature Ref. [7] (*filled triangle*, *filled circle*, respectively) at 298.15 K; the *lines* are Redlich–Kister correlations



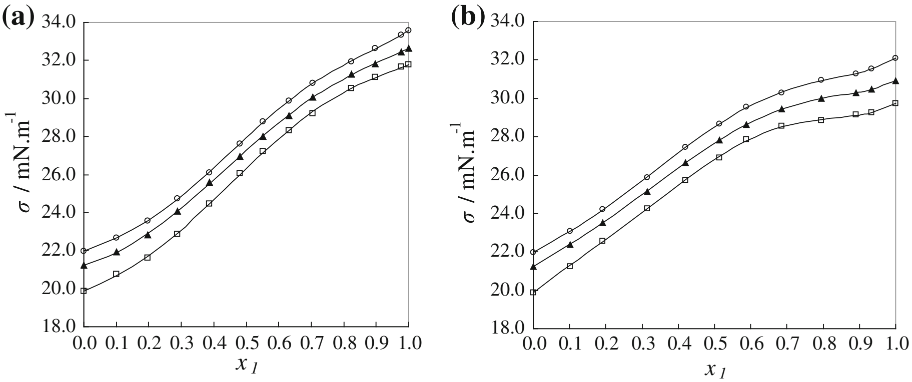


Fig. 6 Effect of temperature on surface tension, σ, for [C_4mim][NTf_2] + 2-propanol (**a**) and [C_8mim][NTf_2] + 2-propanol (**b**) binary systems at (*open circle*) 283.15, (*filled triangle*) 298.15, (*open square*) 313.15 K; the *symbols* are experimental points and the *lines* are calculated from Eq. 2 using the parameters listed in Table 4

literature at 298.15 K [7]. Data series are in relatively good agreement for the [C_4min][NTf_2] + 1-propanol binary system. However, surface tension changes of mixing determined in this work for [C_4min][NTf_2] + 1-butanol binary system are higher than those published by Wandschneider et al. [7] This can be justified since, as discussed previously, trace amounts of impurities can have dramatic effects on physical properties of ILs and their mixtures. No other comparable data were found in the literature.

As it can be seen from Fig. 4b, in the case of [C_8min][NTf_2], surface tension changes of mixing are positive for systems with methanol, ethanol, 1-propanol, and 2-propanol for all compositions and temperatures. [C_8min][NTf_2] + 1-butanol shifts from negative values of the property at 283.15 K to an s-shaped dependence on composition at higher temperatures. $\Delta\sigma$ for systems with 1-pentanol are negative for all compositions and temperatures. No comparable data were found in the surveyed literature for [C_8min][NTf_2] + alcohol systems.

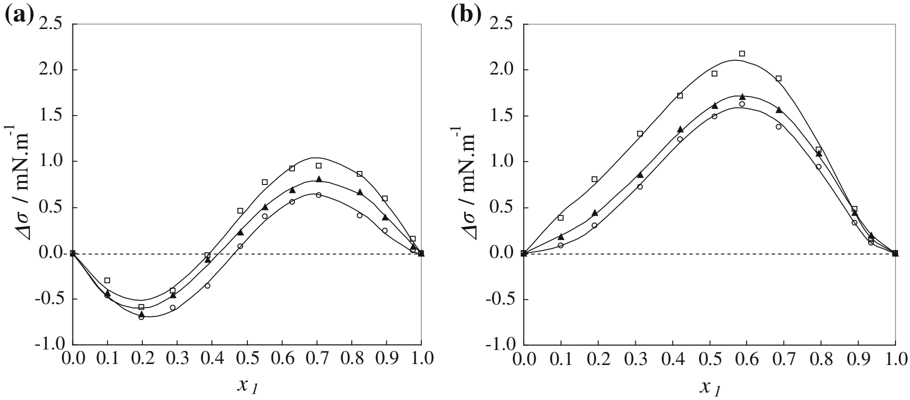


Fig. 7 Effect of temperature on surface tension changes of mixing, $\Delta\sigma$, for [C$_4$mim][NTf$_2$] + 2-propanol (**a**) and [C$_8$mim][NTf$_2$] + 2-propanol (**b**) binary systems at (*open circle*) 283.15, (*filled triangle*) 298.15, (*open square*) 313.15 K; the *symbols* are experimental points and the *lines* are calculated from Eq. 2 using the parameters listed in Table 4

Figure 6 shows the effect of temperature on the surface tensions of [C$_4$min][NTf$_2$] + 2-propanol and [C$_8$min][NTf$_2$] + 2-propanol. Figure 7 shows the effect of temperature on the surface tension changes of mixing for these systems. The surface tension decreases with temperature as is typical for organic solvents. Surface tension changes of mixing increase with temperature. This effect is found for the two binary systems studied.

For the pure ILs, the surface tension decreases with increasing alkyl chain length, as was showed previously [22, 42]. Consequently, the same behavior is found for the mixtures with an alcohol, with lower values of this property in the case of mixtures with [C$_8$min][NTf$_2$]. For a system with an alcohol at one temperature, values of surface tension changes of mixing become more positive in going from [C$_4$min][NTf$_2$] to [C$_8$min][NTf$_2$] except in the case of methanol where the values of $\Delta\sigma$ are slightly lower.

4 Conclusions

In this study new experimental data for the [C$_4$min][NTf$_2$] or [C$_8$min][NTf$_2$] + alcohol systems at 283.15, 298.15 and 313.15 K have been measured. The results show that the surface tension of these mixtures depends systematically on alkyl chain length of the ionic liquid and alcohol, composition and temperature. It was observed that alcohols with small hydrocarbon backbones, such as methanol and ethanol, show positive surface tension changes of mixing. With increasing number of carbon atoms in their hydrocarbon chain, this becomes negative at high alcohol concentrations and positive at higher IL concentrations; it becomes completely negative for systems with [C$_4$min][NTf$_2$] and 1-pentanol. The calculated surface tension changes of mixing were adequately correlated by means of the Redlich–Kister equation.

A large amount of experimental work and computational simulations are needed to establish a clear correlation among the surface tension and the molecular structure of the ionic liquids.

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