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Surface Tension Measurements for Four 1-Alkyl-3-methylimidazolium-Based Ionic Liquids with Hexafluorophosphate Anion

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Air−liquid interfacial surface tension measurements were performed on four 1-alkyl-3-methylimidazolium-based ([$C_n$mim], $n = 3, 4, 6, 8$) ionic liquids at 15 temperatures from (287 to 353) K at atmospheric pressure. To validate the accuracy of the results, the Wilhelmy plate method and the du Noüy ring method were employed in parallel using the Krűss K100MK2 tensiometer. At each temperature, from 33 to 55 Wilhelmy plate and from 10 to 30 du Noüy ring individual readings were taken in most cases. The surface tension average values at particular temperatures are presented with estimated overall standard uncertainty of 0.05 $\text{mN}\cdot\text{m}^{-1}$. An empirical surface tension−temperature equation has been developed describing the temperature dependence of each ionic liquid surface tension. To the 69 up-to-now published surface tension values of the above-mentioned four ionic liquids, the present study adds an additional 102 data points representing means calculated from about 3000 individual surface tension readings that altogether have been taken.

Introduction

It is now common knowledge that ionic liquids exhibit a unique combination of intrinsic physicochemical properties that make them highly promising in many applications. To exploit the possibility of designing properties of ionic liquids by choice of anion, cation, and substituent, knowledge is required of the dependence of the properties of ionic liquids on their structure. Predictive models for their thermophysical properties are necessary, such as the simple structure−property relationship (QSPR) models[1] or more sophisticated group contribution ones.[2] The development of effective predictive methods is conditional on a sufficiently large body of accurate experimental data. Despite the growing importance of ILs, the amount of available accurate experimental data on their physical and chemical properties is still limited. The data are often inconsistent and discrepant and in many cases are scarce or even absent. Also, surface tension is ranked among the properties of which knowledge is of importance not only in the process and product design but also, more generally, in the context of a wide range of problems in pure and applied science.

The aim of the present study was to obtain new reliable experimental data for air−liquid interfacial surface tension of selected ILs with accuracy validated by using two independent methods. Four imidazolium-based ionic liquids with hexafluorophosphate anion and different length of the alkyl chain ([PMIM][PF_6], 1-propyl-3-methylimidazolium hexafluorophosphate; [BMIM][PF_6], 1-butyl-3-methylimidazolium hexafluorophosphate; [HMIM][PF_6], 1-hexyl-3-methylimidazolium hexafluorophosphate; and [OMIM][PF_6], 1-octyl-3-methylimidazolium hexafluorophosphate), that is, [$C_n$mim][PF_6] with $n = 3$, 4, 6 and 8, were selected as fluids for which surface tension data are rather scarce. Table 1 gives an overview of the literature sources for experimental surface tension data for the ionic liquids of interest.

Experimental Section

In the present study, the surface tension measurements were performed by the Wilhelmy plate method and by the du Noüy ring method using the Krűss K100MK2 tensiometer equipped with a microbalance having a resolution of 10 μg. The du Noüy ring method was used as an independent second method to increase the credibility of the data obtained. The essential details of the apparatus and procedure are given elsewhere.[3]

The apparatus and the Wilhelmy plate measurement procedure were tested by measurement on water and methanol at temperatures from (279 to 333) K. For water, the maximum deviation of the results from the IAPWS correlation[4] is less than 0.05 $\text{mN}\cdot\text{m}^{-1}$ (root-mean-square deviation of 0.03 $\text{mN}\cdot\text{m}^{-1}$). The overall standard uncertainty of our surface tension data for methanol,[3] which follows from the comparison with the most reliable data obtained by the capillary rise method, is estimated to be ± 0.1 $\text{mN}\cdot\text{m}^{-1}$. The results for methanol appear to be somewhat less accurate than those obtained for water using the same apparatus and measuring procedure. It is most likely to be attributed to the influence of evaporation of the more volatile methanol after the sample vessel is open for the Wilhelmy plate to be immersed in the sample. This conjecture is supported by much less data dispersion observed for ionic liquids. The repeatability of the present surface tension and temperature measurements expressed in terms of experimental standard deviation of the values obtained within one experimental run is typically 0.05 $\text{mN}\cdot\text{m}^{-1}$ and 0.05 K, respectively.

In the evaluation of the surface tension force from the equivalent mass value given by the microbalance, the local value 9.81007 $\text{m}\cdot\text{s}^{-2}$ of the earth's gravitational acceleration from the Institute of Thermomechanics, Prague, Czech Republic, was used. Optically measured values of the geometrical parameters of the measuring bodies are given by the manufacturer with high accuracy. The wetted length of the used Wilhelmy plate amounts to 40.234 mm. The ring used in the present study is manufactured from a wire with a diameter of 0.368 mm and has a diameter of 18.758 mm. Therefore, the gravitational

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Table 1. Literature Sources for Experimental Surface Tension Data for the Ionic Liquids of Interest with the Sample Water Content Given As Water Mass Fraction, *w*

author(s)	year	temp range T/K	methods	no. of data	$100w$
1-Butyl-3-methylimidazolium Hexafluorophosphate [BMIM][PF_6]					
Huddleston et al.[8]	2001	298.15	du Noüy ring	1	0.0590
Law and Watson[9]	2001	336	du Noüy ring	1	n/a
Freire et al.[10]	2007	293.15 to 343.15	du Noüy ring	6	0.0610
Jiqin et al.[11]	2007	298.15	pendant drop	1	0.0430
Kilaru et al.[12]	2007	298.15 to 335.61	du Noüy ring	10	0.1920
Pereiro et al.[13]	2007	288.15 to 313.15	hanging drop	6	0.0300
Zhang et al.[14]	2007	298.15	du Noüy ring	1	n/a
Ghatee and Zolghadr[15]	2008	298 to 393	capillary rise	1	n/a
Yi et al.[16]	2008	298.15	n/a	1	n/a
this work	2008	287.6 to 352.8	Wilhelmy plate	14	0.1520
this work	2008	288.1 to 352.9	du Noüy ring	14	0.1520
1-Hexyl-3-methylimidazolium Hexafluorophosphate [HMIM][PF_6]					
Huddleston et al.[8]	2001	298.15	du Noüy ring	1	0.0472
Freire et al.[10]	2007	293.15 to 353.15	du Noüy ring	7	0.0021
Pereiro et al.[13]	2007	293.15 to 313.15	hanging drop	6	0.0300
Ghatee and Zolghadr[15]	2008	298 to 363	capillary rise	14	n/a
Yi et al.[16]	2008	298.15	n/a	1	n/a
Muhammad et al.[17]	2008	298.15 to 338.15	spinning drop	5	0.0456
this work	2008	284.3 to 353.7	Wilhelmy plate	15	0.1840
this work	2008	284.3 to 353.7	du Noüy ring	15	0.1840
1-Octyl-3-methylimidazolium Hexafluorophosphate [OMIM][PF_6]					
Huddleston et al.[8]	2001	298.15	du Noüy ring	1	0.0388
Law and Watson[9]	2001	336	du Noüy ring	1	n/a
Freire et al.[10]	2007	293.15 to 343.15	du Noüy ring	6	0.0018
Pereiro et al.[13]	2007	293.15 to 313.15	hanging drop	5	0.0300
this work	2008	283.9 to 353.5	Wilhelmy plate	15	0.1760
this work	2008	283.9 to 353.6	du Noüy ring	13	0.1760
1-Propyl-3-methylimidazolium Hexafluorophosphate [PMIM][PF_6]					
this work	2008	318.3 to 352.1	Wilhelmy plate	9	n/a
this work	2008	318.3 to 352.0	du Noüy ring	8	n/a

acceleration and the wetting length introduce no substantial additional uncertainty into the results. Contrary to the plate method, the ring method require a correction amounting up to (10 to 15) % of the obtained raw value of the surface tension. Owing to the high accuracy with which the values of the ring diameter, the ring wire diameter, and the sample density entering the correction can be given, the additional uncertainty introduced by the correction can be made to be negligible. In the present study, the most recent correction was used derived on the basis of a rigorous theory by Huh and Mason.[5] For the densities of ionic liquids necessary to evaluate the correction, the values given by the manufacturer were used.

Samples of ionic liquids supplied by Ionic Liquids Technologies GmbH & Co. (IoLiTec, Denzlingen, Germany) with specified minimum mass fraction purities of 99 % were used in the measurements. The sample water content is generally considered to be the major source of uncertainty in the measurements of the surface tension of ILs. Accordingly, all of the samples were dried by evaporation under vacuum at temperature 323 K for 7 h. No further drift was observed in the surface tension value after another drying period had been applied.

Another difficulty might arise from the adsorption of atmospheric moisture by hygroscopic ILs during surface tension measurement. After each 7 h period of measurements, the measuring vessel was placed in a vacuum chamber, where it was left for 17 h. The measurements were taken at only one temperature during each 7 h measurement period. No unidirectional drift in the surface tension value attributable to absorption of the air moisture by the sample was observed during particular measuring periods. The water content in our samples was determined after the measurements by Karl Fischer titration. The molar fraction of water in the samples is given in Table 1. The water content for the sample of [PMIM][PF_6] could not be determined because its melting point lies at 315 K.

Results and Discussion

For each IL sample, a total of about 530 individual Wilhelmy plate and about 220 du Nüoy ring readings were taken at 9 to 15 temperature points between (288 and 353) K. In most cases, three to five Wilhelmy plate runs were performed at each temperature, each containing 11 evaluated individual readings as a rule. One du Noüy ring run contains 10 readings of the surface tension force. Tables 2, 3, 4, and 5 give averages of the values of temperature and surface tension obtained at the individual temperature points together with the type A expanded uncertainty at the 95 % level of confidence. The results of the measurements at particular temperatures are given in the order in which they were performed. The sequence of temperatures was selected at random to suppress the influence of possible unidirectional effects proportional to the time elapsed on measurements.

The Guggenheim's empirical eq 1 with $n = 11/9$ derived for small-molecule liquids[6] is used[7,10,12] to estimate critical temperature, T_c, and the surface excess energy, γ_0, of the ionic liquid and to correlate experimental surface tension data

$$\gamma(T) = \gamma_0\left(1 - \frac{T}{T_c}\right)^n \qquad (1)$$

In Figures 1, 2, 3, and 4, deviations are plotted of the experimental data points from eq 1. Table 6 gives coefficients of eq 1 used to correlate the experimental data together with the standard uncertainty estimates of the equation parameters

Table 2. Present Experimental Data on the Dependence of the Surface Tension, γ, on Temperature, T, for 1-Butyl-3-methylimidazolium Hexafluorophosphate [BMIM][PF_6]

$(T \pm 2u)^a$ / K	$(\gamma \pm 2u)^a$ / $mN \cdot m^{-1}$	no. of data
	Wilhelmy Plate Method	
303.37 ± 0.01	43.51 ± 0.01	33
312.88 ± 0.01	42.90 ± 0.01	33
322.81 ± 0.02	42.21 ± 0.01	33
333.31 ± 0.01	41.63 ± 0.01	33
342.86 ± 0.02	41.05 ± 0.01	33
352.78 ± 0.01	40.47 ± 0.02	32
348.34 ± 0.01	40.80 ± 0.03	55
307.96 ± 0.01	43.24 ± 0.01	33
317.86 ± 0.01	42.58 ± 0.01	33
327.91 ± 0.01	41.94 ± 0.01	33
337.97 ± 0.03	41.37 ± 0.01	33
298.34 ± 0.01	43.82 ± 0.02	44
292.88 ± 0.01	44.11 ± 0.01	33
287.60 ± 0.01	44.41 ± 0.01	33
	du Noüy Ring Method	
288.14 ± 0.01	44.47 ± 0.01	10
292.99 ± 0.01	44.28 ± 0.01	20
297.86 ± 0.01	44.03 ± 0.01	20
303.33 ± 0.01	43.64 ± 0.01	30
308.21 ± 0.01	43.46 ± 0.01	60
312.44 ± 0.01	43.13 ± 0.01	30
318.23 ± 0.02	42.75 ± 0.01	30
322.98 ± 0.02	42.45 ± 0.01	20
327.89 ± 0.03	42.14 ± 0.01	29
332.84 ± 0.02	41.86 ± 0.02	20
337.59 ± 0.02	41.57 ± 0.01	20
343.06 ± 0.02	41.34 ± 0.01	20
348.16 ± 0.02	40.95 ± 0.03	20
352.99 ± 0.02	40.75 ± 0.04	20

[a] Estimations of the expanded uncertainty at the 95 % confidence level.

Table 3. Present Experimental Data on the Dependence of the Surface Tension, γ, on Temperature, T, for 1-Hexyl-3-methylimidazolium Hexafluorophosphate [HMIM][PF_6]

$(T \pm 2u)^a$ / K	$(\gamma \pm 2u)^a$ / $mN \cdot m^{-1}$	no. of data
	Wilhelmy Plate Method	
303.58 ± 0.01	37.99 ± 0.01	33
313.45 ± 0.01	37.26 ± 0.02	44
323.12 ± 0.01	36.67 ± 0.02	33
333.82 ± 0.01	35.99 ± 0.01	33
343.05 ± 0.01	35.48 ± 0.02	55
293.48 ± 0.01	38.60 ± 0.01	44
284.30 ± 0.01	39.12 ± 0.01	33
353.68 ± 0.02	34.70 ± 0.03	33
347.75 ± 0.01	35.09 ± 0.05	33
308.56 ± 0.01	37.61 ± 0.01	30
318.50 ± 0.01	36.94 ± 0.01	33
327.92 ± 0.01	36.29 ± 0.01	33
337.94 ± 0.01	35.74 ± 0.02	33
288.16 ± 0.01	38.86 ± 0.02	33
298.97 ± 0.01	38.25 ± 0.01	33
	du Noüy Ring Method	
284.36 ± 0.02	39.10 ± 0.01	10
288.25 ± 0.03	38.81 ± 0.01	10
293.56 ± 0.02	38.70 ± 0.01	12
299.02 ± 0.01	38.21 ± 0.01	10
303.67 ± 0.02	37.89 ± 0.01	10
308.58 ± 0.01	37.78 ± 0.01	10
313.53 ± 0.01	37.30 ± 0.01	10
318.45 ± 0.01	36.88 ± 0.01	10
323.16 ± 0.01	36.78 ± 0.01	10
327.89 ± 0.01	36.28 ± 0.01	10
333.78 ± 0.03	36.05 ± 0.02	10
337.92 ± 0.02	35.68 ± 0.01	10
343.09 ± 0.02	35.29 ± 0.01	10
347.67 ± 0.01	35.21 ± 0.03	10
353.76 ± 0.05	34.87 ± 0.04	10

[a] Estimations of the expanded uncertainty at the 95 % confidence level.

and the estimate of the standard uncertainty of surface tension values computed from the equation.

The criteria of minimizing of the sum of squared deviations (SSD) of the experimental data from the fitting function do not significantly discriminate among various values of the exponent n in eq 1. As a matter of fact, in a wide range of values of the exponent n, a temperature value, T_c, exists for each value of n, resulting in almost the same value of SSD.

The balance readings are the only source of the type A uncertainty, u_A, of the evaluated surface tension values. The microbalance, when used with the Wilhelmy plate, has a manufacturer's stated resolution equivalent to $\pm$ 0.001 $mN \cdot m^{-1}$. The estimated values of standard uncertainties, u_A, of the means given in Tables 2, 3, 4, and 5 are at least one order of magnitude greater. It should most likely be attributed to vibrations transmitted to the balance from external sources that did not turn out to be fully eliminable. Moreover, the standard deviation of the surface tension means from the fitting function (1), which is close to 0.05 $mN \cdot m^{-1}$ for all of the studied ILs, is also more then one order of magnitude greater than the resolution of the microbalance. This fact indicates that there exists a further source of uncertainty burdening the set of the readings taken at given temperatures as a whole.

Our results agree well with the results of Freire et al.,[10] especially for [BMIM][PF_6] (Figure S1 in the Supporting Information), and they are also roughly consistent with the values obtained by Pereiro et al.,[13] with the exception that the data for [OMIM][PF_6] shifted systematically compared with our data by more than 2 $mN \cdot m^{-1}$ (Figure 3).

The surface tension values obtained by Ghatee and Zolghadr[15] and by Kilaru et al.[12] for [BMIM][PF_6] and also the single points by Huddleston et al.[8] and Yi et al.[16] are shifted compared with ours by up to 4 $mN \cdot m^{-1}$ toward the higher values so that they roughly coincide with our results for [PMIM][PF_6] (Figure S1 in the Supporting Information). In a similar way, the result obtained by Ghatee and Zolghadr[15] for [HMIM][PF_6] roughly coincides with our experimental data for [BMIM][PF_6].

No surface tension data by other authors are available for [PMIM][PF_6]. It is noteworthy that in the case of [PMIM][PF_6], despite a number of attempts, we were not successful in obtaining surface tension values at temperatures near 335 K that did not markedly deviate from the linear course of the experimental values obtained at other temperatures (Figure 4). Moreover, the data seem to hint that a slight step change in surface entropy might occur near the temperature of 335 K.

In Figure 5, deviations of experimental data on the surface tension of [BMIM][PF_6] and [OMIM][PF_6] at 303.15 K by different authors are depicted versus the water content of the samples used in their measurements. The data by Huddleston et al.[8] and by Jiqin et al.[11] at 298.15 K have been shifted for this purpose to the temperature of 303.15 K by applying a slight correction calculated from the slope of our correlation function. In Figure 5, the results of Freire et al.[10] are also included for the dependence of the surface tension on the sample water content. The data show no apparent correlation with the water content, and their scatter markedly exceeds the effect of water. The observed differences seem to be more likely be due to differences in sample handling calibration and details of a measuring procedure. For example, our surface tension data for [BMIM][PF_6] coincide with the results of Freire et al.[10] obtained

Table 4. Present Experimental Data on the Dependence of the Surface Tension, γ, on Temperature, T, for 1-Octyl-3-methylimidazolium Hexafluorophosphate [OMIM][PF_6]

$(T \pm 2u)^a$ / K	$(\gamma \pm 2u)^a$ / $mN \cdot m^{-1}$	no. of data
	Wilhelmy Plate Method	
302.95 ± 0.01	33.56 ± 0.01	44
313.47 ± 0.01	32.98 ± 0.02	44
322.73 ± 0.01	32.52 ± 0.01	33
333.05 ± 0.01	31.93 ± 0.01	44
342.84 ± 0.01	31.46 ± 0.02	33
353.56 ± 0.01	30.94 ± 0.01	33
293.41 ± 0.01	34.14 ± 0.01	44
283.92 ± 0.01	34.62 ± 0.01	44
308.14 ± 0.01	33.32 ± 0.01	40
318.04 ± 0.01	32.80 ± 0.01	30
337.95 ± 0.01	31.68 ± 0.01	44
348.18 ± 0.01	31.15 ± 0.01	30
327.98 ± 0.01	32.25 ± 0.01	44
298.13 ± 0.01	33.95 ± 0.01	33
287.88 ± 0.01	34.48 ± 0.01	32
	du Noüy Ring Method	
303.00 ± 0.01	33.48 ± 0.01	10
313.51 ± 0.01	33.16 ± 0.01	10
322.79 ± 0.01	32.46 ± 0.01	10
332.98 ± 0.03	32.02 ± 0.01	10
343.00 ± 0.03	31.53 ± 0.01	10
353.62 ± 0.04	30.83 ± 0.01	10
293.42 ± 0.02	34.36 ± 0.01	10
283.91 ± 0.02	34.75 ± 0.01	9
308.10 ± 0.01	33.27 ± 0.01	10
318.02 ± 0.01	32.90 ± 0.01	10
337.93 ± 0.02	31.81 ± 0.01	10
348.12 ± 0.03	31.26 ± 0.01	10
327.97 ± 0.03	32.12 ± 0.01	10

[a] Estimations of the expanded uncertainty at the 95 % confidence level.

Table 5. Present Experimental Data on the Dependence of the Surface Tension, γ, on Temperature, T, for 1-Propyl-3-methylimidazolium Hexafluorophosphate [PMIM][PF_6]

$(T \pm 2u)^a$ / K	$(\gamma \pm 2u)^a$ / $mN \cdot m^{-1}$	no. of data
	Wilhelmy Plate Method	
318.33 ± 0.01	46.41 ± 0.01	66
352.08 ± 0.01	44.31 ± 0.02	44
332.63 ± 0.01	45.20 ± 0.01	55
343.25 ± 0.01	44.83 ± 0.01	44
323.12 ± 0.01	46.09 ± 0.01	44
348.08 ± 0.01	44.54 ± 0.01	44
333.28 ± 0.01	45.82 ± 0.01	22
338.21 ± 0.01	45.14 ± 0.02	44
328.13 ± 0.01	45.76 ± 0.01	44
	du Noüy Ring Method	
318.39 ± 0.02	46.75 ± 0.03	36
352.00 ± 0.02	44.38 ± 0.03	40
332.59 ± 0.01	45.52 ± 0.04	27
343.26 ± 0.01	44.86 ± 0.01	27
323.13 ± 0.01	46.33 ± 0.03	23
348.02 ± 0.01	44.66 ± 0.03	30
338.14 ± 0.03	45.65 ± 0.01	12
328.14 ± 0.01	45.93 ± 0.02	30

[a] Estimations of the expanded uncertainty at the 95 % confidence level.

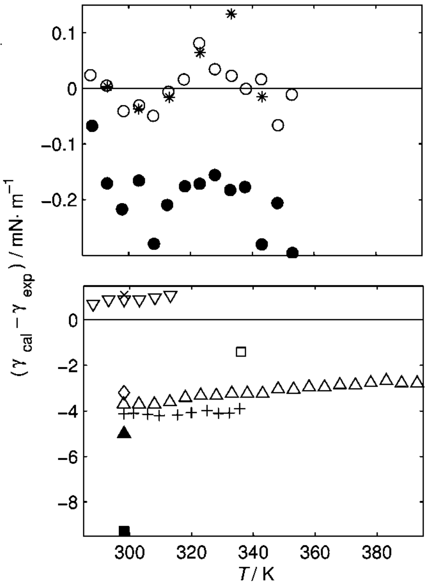

Figure 1. [BMIM][PF_6]: Deviations $\gamma_{calcd} - \gamma_{exptl}$ of experimental surface tension data, γ_{exptl}, by different authors from values, γ_{calcd}, calculated from eq 1 versus temperature, T: ▲, Huddleston et al.;[8] □, Law and Watson;[9] ∗, Freire et al.;[10] ■, Jiqin et al.;[11] +, Kilaru et al.;[12] ▽, Pereiro et al.;[13] ×, Zhang et al.;[14] △, Ghatee and Zolghadr;[15] ◇, Yi et al.;[16] ○, this work (Wilhelmy plate method); ●, this work (du Noüy ring method).

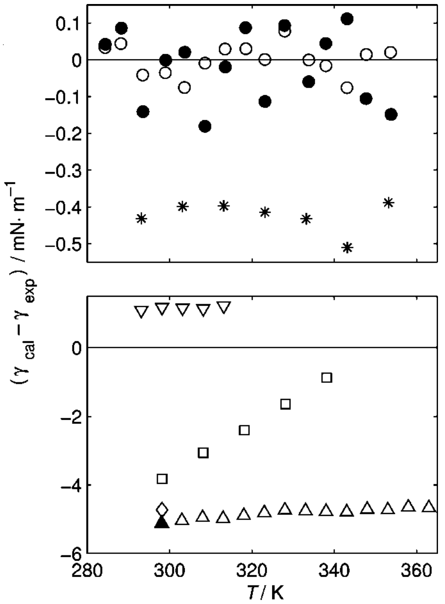

Figure 2. [HMIM][PF_6]: Deviations $\gamma_{calcd} - \gamma_{exptl}$ of experimental surface tension data, γ_{exptl}, by different authors from values, γ_{calcd}, calculated from eq 1 versus temperature, T: ▲, Huddleston et al.;[8] ∗, Freire et al.;[10] ▽, Pereiro et al.;[13] △, Ghatee and Zolghadr;[15] ◇, Yi et al.;[16] □, Muhammad et al.;[17] ○, this work (Wilhelmy plate method); ●, this work (du Noüy ring method).

for a sample of which the water content is less than half of that of our [BMIM][PF_6] sample. On the contrary, the surface tension values obtained by Kilaru et al.[12] for a sample with the water content comparable to that of our sample are shifted relative to our results by 4 $mN \cdot m^{-1}$ (i.e., by 9 %).

In Figure 6, the experimental points obtained by different authors at 303.15 K for the four ionic liquids of interest are depicted versus the length of the cation alkyl chain. The alkyl chain length dependence of the surface tension of the present four alkylimidazolium hexafluorophosphates seems to follow an inverse power law similar to that reported by Carvalho et al.[18] for the Tf_2N anion-based ILs.

Conclusions

In general, the experimental surface tension data for the four ionic liquids of interest available from literature are scarce and conflicting. The systematic differences among surface tension data by different authors reach values up to several millinewtons

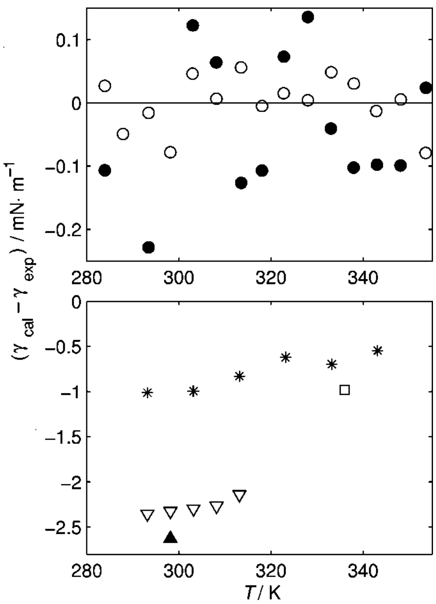

Figure 3. [OMIM][PF$_6$]: Deviations $\gamma_{\mathrm{calcd}} - \gamma_{\mathrm{exptl}}$ of experimental surface tension data, γ_{exptl}, by different authors from values, γ_{calcd}, calculated from eq 1 versus temperature, T: ▲, Huddleston et al.,[8] □, Law and Watson;[9] $*$, Freire et al.;[10] ▽, Pereiro et al.;[13] ○, this work (Wilhelmy plate method); ●, this work (du Noüy ring method).

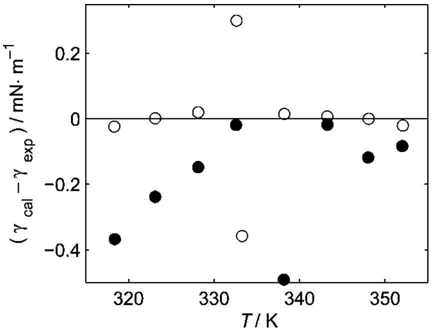

Figure 4. [PMIM][PF$_6$]: Deviations $\gamma_{\mathrm{calcd}} - \gamma_{\mathrm{exptl}}$ of the present experimental surface tension data, γ_{exptl}, from values, γ_{calcd}, obtained with the correlation eq 1 as a function of temperature, T: ○, this work (Wilhelmy plate method); ●, this work (du Noüy ring method).

Table 6. Coefficients γ_0 and T_c of Equation *1* and Estimates of Their Standard Uncertainties, u_{γ_0} and u_{T_c}, and the Standard Uncertainty, u_γ, of the Surface Tension Value Computed from Equation *1*

ionic liquid	$(\gamma_0 \pm u_{\gamma_0})$ mN·m^{-1}	$(T_c \pm u_{T_c})$ K	u_γ mN·m^{-1}
[PMIM][PF$_6$]	66.95 ± 0.22	1227.9 ± 7.4	0.050
[BMIM][PF$_6$]	62.72 ± 0.20	1171.4 ± 6.7	0.048
[HMIM][PF$_6$]	58.20 ± 0.21	1026.8 ± 6.6	0.056
[OMIM][PF$_6$]	50.81 ± 0.20	1056.0 ± 7.0	0.051

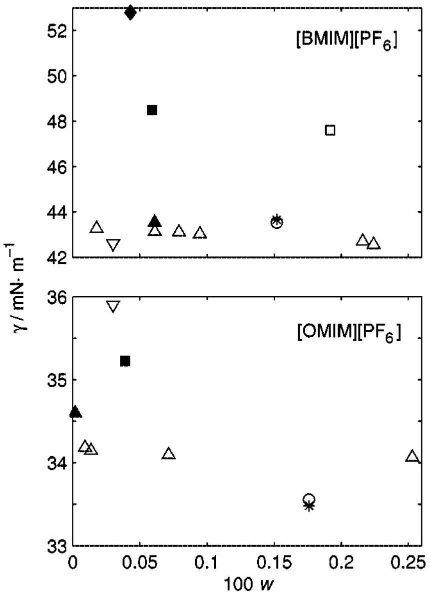

Figure 5. Surface tension values, γ, obtained by different authors at T = 303.15 K versus water mass fraction, w, in the sample: ■, Huddleston et al.;[8] ▲, Freire et al.;[10] △, Freire et al.[10] (water content dependence); ♦, Jiqin et al.;[11] □, Kilaru et al.;[12] ▽, Pereiro et al.;[13] ○, this work (Wilhelmy plate method); $*$, this work (du Noüy ring method).

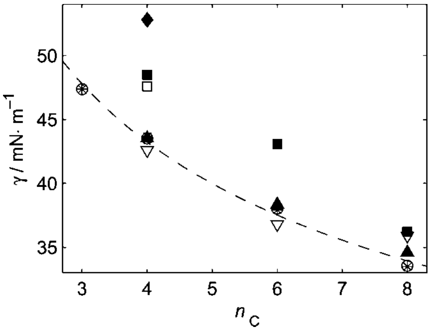

Figure 6. Alkyl chain length, n_{C}, dependence of the surface tension, γ, at T = 303.15 K for the ionic liquids of interest: ■, Huddleston et al.;[8] ▲, Freire et al.;[10] ♦, Jiqin et al.;[11] □, Kilaru et al.;[12] ▽, Pereiro et al.;[13] ○, this work (Wilhelmy plate method); $*$, this work (du Noüy ring method); − − −, power law approximation of the present data $\gamma = 70.1/n_{\mathrm{C}}^{0.349}$.

per meter. Therefore, the differences exceed the experimental uncertainties of the data declared by their authors by up to one order of magnitude for individual surface tension readings and by up to two orders of magnitude for their means. Our results seem to confirm the results of Freire et al.,[10] hinting that at low water mass fractions, for example, below w = 0.8 % for [BMIM][PF$_6$] or w = 0.4 % for [OMIM][PF$_6$], the surface tension of ionic liquids depends on the water content much less than for higher water concentrations in the sample. This observation corresponds to the fact that there exist two different regimes of interaction between water and ionic liquid. At low water contents, all water molecules are hydrogen bonded to the anions and cations, whereas above a certain water content, molecules that are not hydrogen bonded appear.

The experimental data points on the surface tension−temperature relations obtained in the present study using Wilhelmy plate method and du Noüy method are mutually highly consistent in both magnitude and slope. They differ from each other mostly by less than 0.2 mN·m^{-1}. The use of the two independent methods increases the credibility of the results. The present study adds 102 new experimental data points to the 69 surface tension values published so far of the above-mentioned four ionic liquids. These new surface tension values are means calculated from about 3000 individual surface tension readings, which have been taken altogether in the present study.

Supporting Information Available:

Temperature dependence of the surface tension of the four ILs of interest. Comparison of the experimental surface tension data obtained by various authors, including the present work. This material is available free of charge via the Internet at http://pubs.acs.org.

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