Applying a QSPR correlation to the prediction of surface tensions of ionic liquids

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Abstract

Ionic liquids (ILs) have attracted large amount of interest due to their unique properties. Although large effort has been focused on the investigation of their potential application, characterization of ILs properties and structure–property relationships of ILs are poorly understood. Computer aided molecular design (CAMD) of ionic liquids (ILs) can only be carried if predictive computational methods for the ILs properties are available. The limited availability of experimental data and their quality have been preventing the development of such tools. Based on experimental surface tension data collected from the literature and measured at our laboratory, it is here shown how a quantitative structure–property relationship (QSPR) correlation for parachors can be used along with an estimation method for the densities to predict the surface tensions of ILs. It is shown that a good agreement with literature data is obtained. For circa 40 ionic liquids studied a mean percent deviation (MPD) of 5.75% with a maximum deviation inferior to 16% was observed. A correlation of the surface tensions with the molecular volumes of the ILs was developed for estimation of the surface tensions at room temperature. It is shown that it can describe the experimental data available within a 4.5% deviation. The correlations here developed can thus be used to evaluate the surface tension of ILs for use in process design or in the CAMD of new ionic liquids.
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1. Introduction

Ionic liquids (ILs) are a fascinating group of green chemicals with the potential to improve development in organic chemistry and chemical technology. Chemical engineers have been developing ILs to replace conventional volatile organic solvents that contribute to serious air pollution. The rapid growth in IL literature shows that they attract much attention as negligible vapour pressure alternatives to traditional organic solvents [1–4]. Currently, the interest in ionic liquids can be divided into two categories: the investigation of the usefulness and application of ILs in various fields, and the characterization of the ILs properties aiming at the development of structure–property relationships that may be used for their design. So far, most effort in ILs has been focused on the investigation of their potential applications, such as new media for chemical synthesis [5–9], biocatalysis [10,11], separation science [12,13], and nanomaterial technologies [14], and as solvent- free electrolytes for electrochemical devices and processes [15–18]. The most widely studied ILs are comprised of bulky, asymmetric N-containing organic cations (e.g., imidazole, pyrrole, pyridine, . . .) in combination with any wide variety of anions, ranging from simple inorganic ions (e.g., halides) to more complex organic species (e.g., triflate). Asymmetry of the ions is believed to be responsible for the low melting points of ionic liquids [19]. The nature of the anion is considered to be primarily responsible for many of the physical properties of ionic liquids, such as their miscibility with conventional solvents and hygroscopicity [20]. Changes in the cation and anion combinations or the nature of the moieties attached to each ion allow the physical properties of ionic liquids such as hydrophobicity, viscosity, density, coordinating ability, ion selectivity, and chemical and electrochemical stability, to be tailored for specific applications, as largely manifested by the task-specific ionic liquids (TSILs) [9].

The versatility of IL has driven increasing interest in using them in extraction and multiphasic homogeneous catalytic reactions [6,21–27] where one phase is chosen to dissolve the catalyst and be immiscible, and the second phase contains the reactant and products. Such processes occur at the interface between the IL and the overlying aqueous or organic phase, and are dependent on the access of the material to the surface and the transfer of material across the interface. A clearer understanding of the mechanisms behind these processes requires a more detailed examination of the surface properties of the ionic liquids.

The surface tension is an important property in the study of physics and chemistry at free surfaces. It affects the transfer rates of vapour absorption where a vapour–liquid interface exists. Such data are of importance to scientists, engineers, and practitioners in many fields such as chemical process and reactor engineering, flow and transport in porous media, materials selection and engineering, biomedical and biochemical engineering, electronic and electrical engineering, etc. The surface of a liquid is not only interesting for the fundamental aspect but also for its relevance in environmental problems, biological phenomena, and industrial applications [28,29].

Experimental data for surface tensions of ionic liquids are very scarce and limited to imidazolium based ionic liquids. When developing ionic liquids for a given purpose if experimentally measured surface tension data are not available, theoretical or empirical methods must be used to establish if the surface tensions are within acceptable limiting values defined in the design specifications. For this purpose prediction methods for surface tension of ILs are required.

While much work has been devoted to the wide range of applications of ILs, the basic understanding and study of their structure–property relationships is of equivalent importance but has lagged behind. Very few works have systematically studied the qualitative and/or quantitative relationships between the structures of ILs and their fundamental properties, such as melting point, viscosity, density, thermal and electrochemical stability, solvent properties, and surface tension [30–39]. To better understand the nature of ionic liquids and rationally expand their applications, knowledge of their physical properties is required. At present, however, data for many other physico-chemical properties of ionic liquids are in short supply, or too unreliable to allow similar structure–property relationship studies.

Recently, Deetlefs et al. [31] attempted, with limited success due to the lack of experimental data, to predict surface tension of ILs using parachors and densities. Having assembled a large database for surface tensions of ionic liquids, the QSPR (quantitative structure–property relationship) correlation of Knotts et al. [40] for surface tensions is here extended to ionic liquids. It will be shown that using parachors and densities predicted from QSPR methods, it is possible to obtain good predictions for surface tensions of ionic liquids.

2. QSPR correlation

A number of methods have been proposed to estimate the surface tension of liquids. One of the simplest methods is the empirical formula proposed by MacLeod [41]. It expresses the temperature-independent relationship between density, ρ, and surface tension, σ, Eq. (1).

$$\sigma^{1/4} = K \cdot \rho \tag{1}$$

where K is a constant which is independent of temperature. It is a characteristic of the compound under consideration. Shortly afterwards, Sugden [42] slightly modified MacLeod's original expression by multiplying each side of the expression with molecular weight, M_w, to give a constant $K \times M_w$, Eq. (2), which he called the parachor, P_{ch}, Eq. (3).

$$M_w \cdot \sigma^{1/4} = K \cdot M_w \cdot \rho \tag{2}$$

$$P_{ch} = K \cdot M_w = \frac{M_w \cdot \sigma^{1/4}}{\rho} \tag{3}$$

Sugden [42] showed that the parachor is an additive property and the parachor of a compound can be expressed as the sum of its parachor contributions. From the parachors it is possible to predict the surface tension of a compound from the knowledge of

its density and vice versa, provided of course, that the parachor itself can be calculated as the link for the estimations.

Mumford and Phillips [43], and Quayle [44] improved Sugden's parachor contribution values for neutral compounds. Recently, Knotts et al. [40] developed a QSPR correlation for the parachors using the vast amounts of physical data available for neutral organics in the DIPPR database. In their study, Knotts et al. [40] determined two individual parachor contribution data sets; the first obtained using a training set containing experimental surface tension values with an uncertainty less than 5% and the second, using surface tension data with uncertainties of less than 1%. Deviations for multifunctional compounds of 6.5 and 8.0%, respectively, were obtained with maximum deviations of 34%. No studies were attempted to develop QSPR correlations for ions.

Deetlefs et al. [31] attempted to use for ionic liquids the parachor correlations previously proposed by Knotts et al. [40]. They calculated parachors of ionic liquids using the neutral parachor contribution values and showed that the differences between the corresponding experimental and calculated parachor values were small. Although the data available in their study was very limited they postulated that the QSPR correlation based on neutral species could be used for ionic liquids.

Using data measured by ourselves for a number of ionic liquids along with a database of ionic liquids surface tensions obtained from the literature, the QSPR correlation of Knotts et al. will here be investigated for its ability to describe the surface tensions of ionic liquids and will be further extended to describe new compounds not available in the parameter table previously proposed. Using parachors, densities in $g\,cm^{-3}$ unit and molecular weight in $g\,mol^{-1}$ unit, the prediction of surface tension in $mN\,m^{-1}$ units for imidazolium based ionic liquids can be done using Eq. (4),

$$\sigma = \left(\frac{P_{ch} \cdot \rho}{M_w}\right)^4 \tag{4}$$

The parachors used are shown in Table 1 which are calculated from Knotts et al. [40] parachor QSPR correlation using the parameter table estimated from the second training set containing experimental surface tension values with an uncertainty less than 1%.

To make surface tension thoroughly predictive, by using Eq. (4), density data are required. Since density data is not always available, recently, we proposed an extension of the Ye and Shreeve method [45] for the estimation of ionic liquids densities [39] in a wide range of temperatures (273.15–393.15) K and pressures (0.10–100) MPa, according to Eq. (5) that can be used for the estimation of the surface tensions using Eq. (4) above.

$$\rho = \frac{M_w}{N_A \cdot V \cdot (a + b \cdot T + c \cdot P)} \tag{5}$$

where ρ is the density in $kg\,m^{-3}$, M_w is molecular weight in $kg\,mol^{-1}$, N_A is the Avogadro constant, V is the molecular volume in $Å^3$, T is the temperature in K and P is the pressure in MPa. The coefficients a, b and c were estimated by fitting Eq. (5) to our previously published experimental data [46,47]. A total amount of circa 800 density data points were used. The values of coefficient a, b and c obtained are $8.005 \times 10^{-1} \pm 2.333 \times 10^{-4}$, $6.652 \times 10^{-4} \pm 6.907 \times 10^{-7}\,K^{-1}$ and $-5.919 \times 10^{-4} \pm 2.410 \times 10^{-6}\,MPa^{-1}$, respectively, at 95% confidence level. The average percentage deviation of calculated densities from the experimental densities is 0.29%. The experimental density (Y), for the ILs used to obtain coefficient a, b and c of Eq. (5), is essentially identical to its calculated density (X): $Y = (0.9998 \pm 0.0003)X$ (correlation coefficient: $R^2 = 0.9989$, at 95% level of confidence). For the density calculation, volume parameters (V) of ions and groups were either directly taken from literature [45] or calculated following the Jenkins' procedure [48]. A number of groups not previously available for some anions are reported in reference [39]. Volume contributions for ions used are shown in Table 1.

3. Results and discussion

A database of experimental surface tension data available in the open literature or measured at our laboratory was collected and is reported in Table 2. Unfortunately only data for imidazolium based ionic liquids was available and thus only the applicability of the QSPR correlations studied to imidazolium based ionic liquids could be tested. A global number of 361 data points for 38 imidazolium based ILs containing $[BF_4]^-$, $[PF_6]^-$, $[Tf_2N]^-$ (bis(trifluoromethylsulfonyl)imide),

Table 1
Calculated parachor $((mN\,m^{-1})^{1/4}\,cm^3\,mol^{-1})$ and molecular volumes ($Å^3$) of imidazolium based ionic liquids

Cation	Calculated parachor	Molecular volume	Anion	Calculated parachor	Molecular volume
$[C_2mim]^+$	285.59	182	$[BF_4]^-$	108.11	73
$[C_3mim]^+$	325.49	210	$[PF_6]^-$	169.23	107
$[C_4mim]^+$	365.39	238	$[MeSO_4]^-$	190.21	116
$[C_4mmim]^+$	402.34	266	$[EtSO_4]^-$	230.11	144
$[C_5mim]^+$	405.29	266	$[TfO]^-$	189.84	129
$[C_6mim]^+$	445.19	294	$[Tf_2N]^-$	346.27	248
$[C_7mim]^+$	485.09	322	$[Cl]^-$	50.98	47
$[C_8mim]^+$	524.99	350	$[I]^-$	90.82	72
$[C_9mim]^+$	564.89	378	$[I_3]^-$	272.46	171
$[C_{10}mim]^+$	604.79	406	$[AlCl_4]^-$	278.89	175
			$[FeCl_4]^-$	261.47	170
			$[GaCl_4]^-$	276.97	174
			$[InCl_4]^-$	292.78	185

Table 2
Prediction of surface tensions of imidazolium based ionic liquids

Ionic liquid	M_w (g mol^{-1})	Calculated parachor ((mN m^{-1})$^{1/4}$ cm^3 mol^{-1})	Molecular volume (Å^3)	Temperature range (K)	Data points	Mean percent deviation (%)	Reference
[C$_4$mim][BF$_4$]	226.03	473.50	311	288.15–336	11	1.65	[49]
				298.15–323.15	6	4.56	[50]
				293.15–343.15	6	9.85	[51]
				293–360	4	9.61	[52]
				298.55	1	6.61	[31]
				298.15	1	7.77	[53]
				298.15	1	10.23	[54]
				298.15	1	11.89	[55]
[C$_5$mim][BF$_4$]	240.06	513.40	339	278.15–338.15	13	2.89	[56]
[C$_8$mim][BF$_4$]	282.13	633.10	423	293.15–343.15	6	13.96	[51]
[C$_4$mim][PF$_6$]	284.18	534.62	345	288.15–336	11	5.14	[49]
				300–390	10	6.20	[57]
				293.15–343.15	6	2.14	[51]
				288.15–313.15	6	2.45	[58]
				298	1	2.75	[59]
				298.15	1	3.19	[53]
				298.15	1	4.95	[60]
				298.15	1	9.71	[55]
[C$_5$mim][PF$_6$]	298.21	574.52	373	298.15	1	4.49	[60]
[C$_6$mim][PF$_6$]	312.24	614.42	401	293.15–353.15	7	6.38	[51]
				293.15–313.15	5	12.95	[58]
				298.15	1	0.15	[60]
				298.15	1	2.96	[55]
				299	1	12.36	[59]
[C$_7$mim][PF$_6$]	326.27	654.32	429	298.15	1	14.05	[60]
[C$_8$mim][PF$_6$]	340.29	694.22	457	293.15–313.15	5	11.93	[58]
				298.15	1	11.48	[55]
				298.15	1	14.85	[60]
[C$_9$mim][PF$_6$]	354.32	734.12	485	298.15	1	15.37	[60]
[C$_4$mmim][PF$_6$]	298.21	571.57	373	303.15–353.15	6	9.56	[51]
[C$_2$mim][EtSO$_4$]	236.29	515.7	326	288.15–313.15	6	1.55	[61]
				278.15–328.15	6	2.64	[62]
[C$_4$mim][MeSO$_4$]	250.32	555.60	354	283.15–313.15	7	6.41	[63]
[C$_4$mim][TfO]	288.29	555.23	367	293.15–343.15	6	10.46	[51]
[C$_8$mim][Cl]	230.78	575.97	397	298.15	1	0.16	[55]
[C$_4$mim][I]	266.13	456.21	279	298.15	1	0.13	[55]
[C$_6$mim][I]	294.17	536.01	366	298.45	1	12.69	[31]
[C$_4$mim][I$_3$]	519.92	637.85	409	298.35	1	12.85	[31]

Table 2 (*Continued*)

Ionic liquid	M_w (g mol^{-1})	Calculated parachor ((mN m^{-1})$^{1/4}$ cm^3 mol^{-1})	Molecular volume (Å^3)	Temperature range (K)	Data points	Mean percent deviation (%)	Reference
[C$_2$mim][Tf$_2$N]	391.32	631.86	430	293.15–343.15	6	5.33	[64]
				302	1	1.63	[59]
				298.15	1	9.58	[60]
[C$_3$mim][Tf$_2$N]	405.34	671.76	458	293.15–343.15	6	1.69	[64]
				298.15	1	7.53	[60]
[C$_4$mim][Tf$_2$N]	419.37	711.66	486	293.15–343.15	6	3.48	[51]
				298.25	1	5.80	[31]
				298.15	1	6.31	[55]
				298.15	1	6.10	[60]
				303	1	10.10	[59]
[C$_5$mim][Tf$_2$N]	433.40	751.56	514	293.15–343.15	6	4.97	[64]
				298.15	1	4.54	[60]
[C$_6$mim][Tf$_2$N]	447.42	791.46	542	293.15–343.15	6	6.59	[64]
				298.15	1	2.39	[60]
				304	1	11.79	[59]
[C$_7$mim][Tf$_2$N]	461.45	831.36	570	293.15–353.15	7	7.67	[64]
				298.15	1	9.93	[60]
[C$_8$mim][Tf$_2$N]	475.48	871.26	598	298.15	1	11.81	[60]
[C$_9$mim][Tf$_2$N]	489.51	911.16	626	298.15	1	13.20	[60]
[C$_{10}$mim][Tf$_2$N]	503.54	951.06	654	298.15	1	14.67	[60]
				306	1	15.01	[59]
[C$_4$mim][AlCl$_4$]	308.10	644.28	413	278.2–343.2	14	3.16	[65]
				303.15–393.15	10	8.77	[66]
[C$_5$mim][AlCl$_4$]	322.00	684.18	441	273.15–343.15	15	3.13	[67]
[C$_2$mim][FeCl$_4$]	308.89	547.06	352	293.15–343.15	11	2.98	[68]
[C$_4$mim][FeCl$_4$]	336.85	626.86	408	283.15–343.15	13	9.87	[69]
[C$_2$mim][GaCl$_4$]	322.70	562.56	356	288.15–343.15	12	8.58	[70]
[C$_4$mim][GaCl$_4$]	350.80	642.36	412	268.15–338.15	8	3.20	[71]
[C$_5$mim][GaCl$_4$]	364.80	682.26	440	273.15–343.15	15	2.70	[67]
[C$_6$mim][GaCl$_4$]	378.80	722.16	468	283.15–338.15	12	5.85	[72]
[C$_2$mim][InCl$_4$]	367.80	578.37	367	293.15–343.15	11	12.67	[73]
[C$_4$mim][InCl$_4$]	395.79	658.17	423	278.15–343.15	14	2.54	[74]
[C$_5$mim][InCl$_4$]	409.80	698.07	451	273.15–343.15	15	2.48	[67]
[C$_6$mim][InCl$_4$]	423.90	737.97	479	283.15–338.15	12	3.36	[75]
Total				268.15–393.15	361	5.75	

[TfO]$^-$ (trifluoromethanesulphonate), [MeSO$_4$]$^-$ (methylsul-phate), [EtSO$_4$]$^-$ (ethylsulphate), [Cl]$^-$, [I]$^-$, [I$_3$]$^-$, [AlCl$_4$]$^-$, [FeCl$_4$]$^-$, [GaCl$_4$]$^-$ and [InCl$_4$]$^-$ as anions [31,49–75] were used in this study. The mean percent deviation (MPD), defined as,

$$\text{MPD} (\%) = \frac{\sum_{i=1}^{N_p} |(\sigma_{\text{cal}} - \sigma_{\text{exp}})/\sigma_{\text{exp}}|_i}{N_p} \tag{6}$$

where N_p represents the number of data points that were esti-mated for each system and are reported in Table 2.

The predicted surface tensions (Y) of imidazolium based ILs using the QSPR correlations studied display a good agreement with the corresponding experimental surface tensions (X) from Eq. (4): $Y = (0.987 \pm 0.004)X$ (at 95% level of confidence). For the 38 ionic liquids studied the overall MPD is 5.75% with a maximum deviation inferior to 16%, which are much lower than the value reported by Knotts et al. [40] for multifunctional com-pounds in their study. From these 33.0% of the estimated surface tensions were within absolute deviation of 0.00–3.00%, 25.2% were within 3.001–6.00%, 24.1% were within 6.001–10.00%, 11.6% were within 10.001–13.00, and only 6.1% were within 13.001–15.58%. The deviations obtained were surprising since the QSPR correlation for the parachors was developed for neutral compounds and not for salts; it was thus developed with-out taking Columbic interactions into account. The maximum absolute deviation observed is comparable to the deviations between experimental data from various authors. The largest MPD observed in this study is of 15.58% for [C$_8$mim][BF$_4$] (1-octyl-3-methylimidazolium tetrafluoroborate) from Freire et al. [51] at 293.15 K, which is comparable to the deviations observed of 16.98% for [C$_6$mim][PF$_6$] (1-hexyl-3-methylimidazolium hexafluorophosphate) at 298.15 K from Pereiro et al. [58] and Huddleston et al. [55], 14.29% for [C$_4$mim][PF$_6$] (1-butyl-3-methylimidazolium hexafluorophosphate) at 298.15 K from Zhang et al. [53] and Huddleston et al. [55], 12.95% for [C$_4$mim][Tf$_2$N] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) at 298.15 K from Deetlefs et al. [31] and Huddleston et al. [55], and 12.10 and 11.18%, respectively, for [C$_5$mim][Tf$_2$N] (1-pentyl-3-methy-limidazolium bis(trifluoromethylsulfonyl)imide) and [C$_6$mim][Tf$_2$N] (1-hexyl-3-methylimidazolium bis(trifluoromethylsul-fonyl)imide) at 298.15 K from Carvalho et al. [64] and Dzyuba and Bartsch [60].

It is also shown in Fig. 1 that the experimental surface tensions of ILs containing imidazolium cations, display linear relationship with the corresponding predicted surface tensions in m Nm^{-1} units using density in g cm^{-3} unit and molecular weight in g mol^{-1} unit in Eq. (4).

To express the relationship between surface tension and tem-perature, Eötvös [76] suggested, in analogy with the gas law, $P \cdot V = R \cdot T$, using the equation

$$\sigma \cdot \left(\frac{M_w}{\rho}\right)^{2/3} = K \cdot (T_c - T) \tag{7}$$

where K is a constant, and ρ is density in g cm^{-3}, M_w is molecu-lar weight in g mol^{-1} and T_c is the critical temperature in K units.
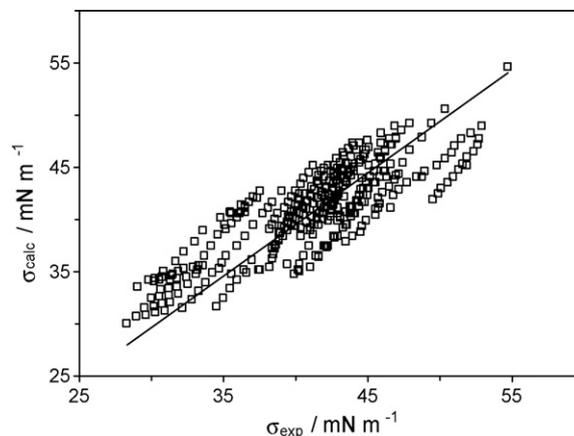

Fig. 1. Linear relationship between experimental and calculated surface tensions using Eq. (4) for imidazolium based ionic liquids.

Since the surface tension of a liquid decreases with increasing temperature and vanishes at the critical point, Guggenheim [77] suggested an alternate form for the temperature dependency of the surface tension

$$\sigma = \sigma_0 \cdot \left(1 - \frac{T}{T_c}\right)^{1+r} \tag{8}$$

where σ_0 is a constant and the value of r is 2/9.

The critical temperature values of ILs are not available and Eqs. (7) and (8) above could be a means to estimate them if sur-face tension data were available in a wide range of temperatures, that is not the case. Taking Eq. (7) and considering the fact that the surface enthalpy varies within a very narrow range for most of the available ionic liquids [51,64], a new equation relating the surface tension and the molar or molecular volume can be proposed

$$\sigma = \left(\frac{d}{V}\right)^{2/3} \tag{9}$$

where V is the molecular volume in Å^3 and its values can be obtained from the Ye and Shreeve's work [45] or calculated following Jenkins' procedure [48], and d is a constant fitted to experimental data using the modified Levenberg–Marquardt optimization with the following objective function (O.F.):

$$\text{O.F.} = \frac{\sum_{i=1}^{N_p} |(\sigma_{\text{cal}} - \sigma_{\text{exp}})/\sigma_{\text{exp}}|_i}{N_p} \tag{10}$$

where N_p refers to total number of experimental data points.

Experimental surface tension data available in literature at 298.15 K for the imidazolium based ionic liquids were correlated using Eq. (9). A value of $d = 2147.761 \pm 18.277$ (mN m^{-1}) Å^2 in Eq. (9), provides a mean percent deviation (MPD) of 4.50% for the surface tensions at 298.15 K of 47 data points of a total 22 imidazolium based ILs containing [BF$_4$]$^-$, [PF$_6$]$^-$, [Tf$_2$N]$^-$, [TfO]$^-$, [MeSO$_4$]$^-$, [EtSO$_4$]$^-$, [Cl]$^-$, and [I]$^-$ as anions [31,49,50,53–56,58–64]. The predicted surface tensions (Y) of imidazolium based ILs display good agreement with cor-responding experimental surface tensions (X) from Eq. (10): $Y = (0.987 \pm 0.008)X$ (at 95% level of confidence). 17.0% of
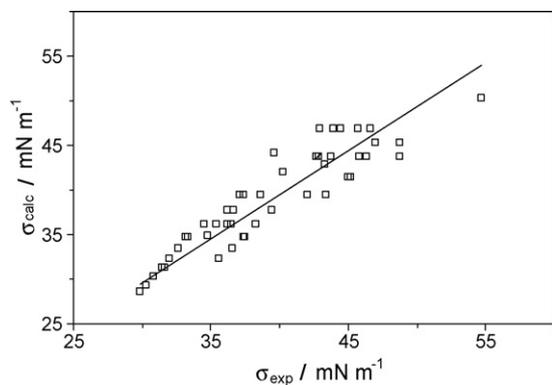
Fig. 2. Linear relationship between experimental and calculated surface tensions using Eq. (9) at 298.15 K for imidazolium based ionic liquids.

Fig. 3. Linear relationship between parachors and molecular volumes of imidazolium based ionic liquids.

the estimated surface tensions were within absolute deviation of 0.00–1.00%, 21.3% of the estimated surface tensions were within absolute deviation of 1.001–3.00%, 29.8% were within 3.001–6.00%, 23.4% were within 6.001–9.00%, and only 8.5% were within 9.001–11.56%. Maximum absolute deviation is 11.56 for [C$_5$mim][BF$_4$] (1-pentyl-3-methylimidazolium tetrafluoroborate) from Yang et al. [56] at 298.15 K. It is also shown in Fig. 2 that the predicted surface tensions of the ionic liquids studied display a linear relationship with the experimental surface tensions at 298.15 K using Eq. (9).

A comparison between the predicted surface tension values at 298.15 K using Eq. (9) and the QSPR correlation for the parachors in Eq. (4), for which more than one literature value available, is reported in Table 3.

From Eq. (3), it is clear that the parachor values are proportional to the molar or molecular volume. The plot of parachors calculated by the QSPR correlation from Knotts et al. [40] versus molecular volumes estimated by the Ye and Shreeve [45] method for imidazolium based ILs containing [BF$_4$]$^-$, [PF$_6$]$^-$, [Tf$_2$N]$^-$, [TfO]$^-$, [MeSO$_4$]$^-$, [EtSO$_4$]$^-$, [Cl]$^-$, and [I]$^-$ as anions, is shown in Fig. 3. For imidazolium based ILs, parachors (Y) show a very good linear relationship with molecular volume (X): $Y = (1.344 \pm 0.024)X + (67.386 \pm 10.646)$ (correlation coefficient: $R^2 = 0.993$, at 95% level of confidence). Using the
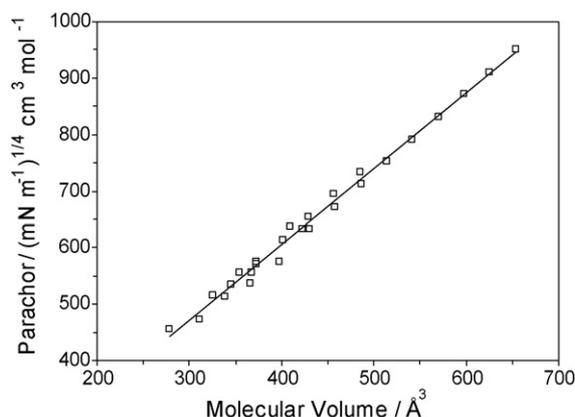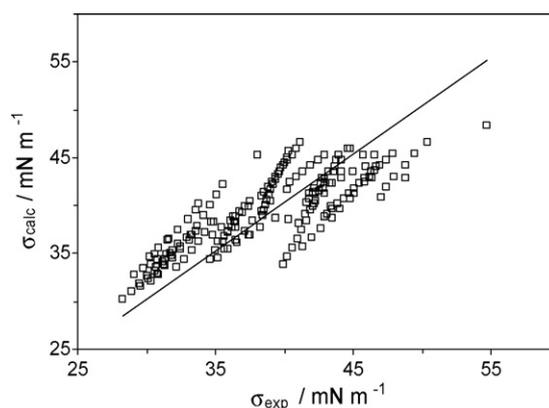

Fig. 4. Linear relationship between experimental and calculated surface tensions using estimated parachors in Eq. (4) at wide range of temperatures (278.15–390 K) for imidazolium based ionic liquids.

linear relation of parachor with molecular volume, we estimated the parachors and use them in Eq. (4) to predict surface tension data for imidazolium based ILs containing BF$_4$, PF$_6$, Tf$_2$N, TfO, MeSO$_4$, EtSO$_4$, Cl, and I as anions at 298.15 K, and also at wide range of temperatures (278.15–390 K) as shown in Fig. 4.

Table 3
Prediction of surface tensions of imidazolium based ionic liquids using Eq. (9) and using estimated parachor in Eq. (4) along with literature values (in range) at 298.15 K

Ionic liquid	Surface tension (mN m^{-1})		
	Predicted using Eq. (9)	Predicted using estimated parachors in Eq. (4)	Literature value (in range)[a]
[C$_4$mim][BF$_4$]	46.8	45.3	42.9 [50]–46.6 [55]
[C$_4$mim][PF$_6$]	43.7	42.9	42.7 [53]–48.8 [55]
[C$_6$mim][PF$_6$]	39.5	39.9	37.1 [58]–43.4 [55]
[C$_8$mim][PF$_6$]	36.2	37.8	35.43 [60]–36.5 [55]
[C$_2$mim][EtSO$_4$]	45.3	44.2	46.96 [61]–48.79 [62]
[C$_2$mim][Tf$_2$N]	37.7	38.7	36.67 [64]–39.40 [60]
[C$_3$mim][Tf$_2$N]	36.1	37.8	34.55 [64]–38.25 [60]
[C$_4$mim][Tf$_2$N]	34.7	36.9	33.20 [31]–37.5 [55]
[C$_5$mim][Tf$_2$N]	33.5	36.2	32.64 [64]–36.59 [60]
[C$_6$mim][Tf$_2$N]	32.3	35.5	32.02 [64]–35.60 [60]
[C$_7$mim][Tf$_2$N]	31.2	34.9	31.46 [60]–31.61 [64]

[a] Reference numbers are given in parenthesis.

The experimental surface tensions (Y) of the imidazolium based ILs studied display good agreement with the corresponding predicted surface tensions (X) at 298.15 K: $Y = (1.001 \pm 0.010)X$ (at 95% level of confidence). For 47 surface tension data points at 298.15 K of total 22 imidazolium based ILs, available in literature [31,49,50,53–56,58–64], the MPD is 6.03%; 23.4% of the estimated surface tensions were within absolute deviation of 0.00–2.00%, 25.5% of the estimated surface tensions were within absolute deviation of 2.001–6.00%, 21.3% were within 6.001–9.00%, 17.0% were within 9.001–11.00%, and only 12.8% were within 11.001–12.36%. Maximum absolute deviation is 12.36 for [C$_{10}$mim][Tf$_2$N] (1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) from Dzyuba and Bartsch [60] at 298.15 K. At wide range of temperatures (278.15–390 K), for 198 surface tension data points of total 25 imidazolium based ILs available in literature [31,49–64], $Y = (1.009 \pm 0.006)X$ (at 95% level of confidence) and the MPD is 7.18%; 14.6% of the estimated surface tensions were within absolute deviation of 0.00–2.00%, 26.3% of the estimated surface tensions were within absolute deviation of 2.001–6.00%, 25.3% were within 6.001–9.00%, 19.7% were within 9.001–12.00%, and only 14.1% were within 12.001–18.93%. Maximum absolute deviation is 18.93 for [C$_4$mim][BF$_4$] (1-butyl-3-methylimidazolium tetrafluoroborate) from Zhang et al. [53] at 298.15 K.

4. Conclusions

It is here shown that the QSPR correlation for parachors proposed by Knotts et al. [40] can be successfully extended to ionic liquids. This correlation, along with a density correlation previously proposed by us [39] allows the prediction of surface tension of ILs in wide ranges of temperature, 268.15–393.15 K. The validity of this correlation was evaluated by comparing the predictions against the experimental surface tensions collected from literature. For a database of 361 data points for 38 imidazolium based ILs, the mean percent deviation (MPD) observed was of only 5.75%. Predicted surface tensions are thus in good agreement with experimental literature data.

A new correlation is here proposed for the estimation of surface tension of ionic liquids at 298.15 K using only information on the molecular volumes. By using this correlation the MPD observed is of 4.50% for 47 surface tension data points available in literature at 298.15 K for a total of 22 imidazolium based ILs.

It is shown that parachors can also be correlated with molecular volumes and this correlation was used to estimate surface tensions at 298.15 K, and its validity evaluated by comparing its predictions against 47 experimental surface tension data points, for 22 imidazolium based ILs, with a MPD of 6.03%.

The three correlations here proposed show maximum absolute deviations for the predicted surface tensions that are inferior to those presented among literature values for same IL. Although only data for imidazolium based ionic liquids was available in the literature at this moment, the results obtained for a large number of anions makes us confidents that this method can be applied to other cations with confidence. Due to the lack of ionic liquid surface tension data in the literature, the use of predictive methods as illustrated in this work are invaluable for providing estimates for the ionic liquid surface tension values.

List of symbols

a, b, c	coefficients of density correlation
d	constant
K	constant
M_w	molecular weight (g mol^{-1})
N_A	Avogadro constant
N_p	number of data points
P_{ch}	parachor ((mN m^{-1})$^{1/4}$ cm^3 mol^{-1})
P	pressure (MPa)
R	gas constant
T	temperature (K)
T_c	critical temperature (K)
V	molecular volume (Å^3)

Greek letters

ρ	density (g cm^{-3})
σ	surface tension (m Nm^{-1})
σ_0	constant

Subscripts

cal	calculated property
exp	experimental property

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References

[1] P. Wasserscheid, T. Welton, Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2003.

[2] K.R. Seddon, R.D. Rogers, Ionic liquids IIIA: fundamentals, progress, challenges, and opportunities, in: ACS Symposium Series, vol. 901, American Chemical Society, Washington DC, 2005.

[3] K.R. Seddon, R.D. Rogers, Ionic liquids IIIB: fundamentals, progress, challenges, and opportunities-transformations and processes, in: ACS Symposium Series, vol. 902, American Chemical Society, Washington DC, 2005.

[4] ISI Essential Science Indicators, Special Topics: Ionic Liquids, URL: http://www.esi-topics.com/ionic-liquids, 2004.

[5] D. Holbrey, K.R. Seddon, Clean Prod. Process 1 (1999) 223–236.

[6] T. Welton, Chem. Rev. 99 (1999) 2071–2083.

[7] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. 39 (2000) 3772–3789.

[8] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667–3692.

[9] J.H. Davis Jr., Chem. Lett. 33 (2004) 1072–1077.

[10] R.A. Sheldon, R.M. Lau, M.J. Sorgedrager, F. van Rantwijk, K.R. Seddon, Green Chem. 4 (2002) 147–151.

[11] U. Kragel, M. Eckstein, N. Kaftzik, Curr. Opin. Biotechnol. 13 (2002) 565–571.

[12] C.C. Tzschucke, C. Markert, W. Bannwarth, S. Roller, A. Hebel, R. Haag, Angew. Chem. Int. Ed. 41 (2002) 3964–4000.

[13] C.F. Poole, J. Chromatogr. A 1037 (2004) 49–82.

[14] M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, Angew. Chem. Int. Ed. 43 (2004) 4988–4992.

[15] D.R. MacFarlane, M. Forsyth, Adv. Mater. 13 (2001) 957–966.

[16] M.C. Buzzeo, R.G. Evans, R.G. Compton, ChemPhysChem 5 (2004) 1106–1120.

[17] F. Endres, ChemPhysChem 3 (2002) 144–154.

[18] R. Hagiwara, Y. Ito, J. Fluorine Chem. 105 (2000) 221–227.

[19] K.R. Seddon, J. Chem. Technol. Biotechnol. 68 (1997) 351–356.

[20] P. Bonhote, A.-P. Dias, N. Papargeorgiou, K. Kalyanasundaram, M. Gratzel, Inorg. Chem. 35 (1996) 1168–1178.

[21] W.A. Herrmann, V.P.W. Bohm, J. Organomet. Chem. 572 (1999) 141–145.

[22] A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac, K.R. Seddon, Org. Lett. 1 (1999) 997–1000.

[23] H. Olivier, Y. Chauvin, Chem. Ind. 68 (1996) 249–263.

[24] Y. Chauvin, H. Olivier-Bourbigou, Chemtech 25 (1995) 26–30.

[25] S.G. Cull, J.D. Holbrey, V. Vargas-More, K.R. Seddon, G.J. Lye, Biotechnol. Bioeng. 69 (2000) 227–233.

[26] M. Erbeldinger, A.J. Mesiano, A.J. Russell, Biotechnol. Prog. 16 (2000) 1129–1131.

[27] R.M. Lau, F. van Rantwijk, K.R. Seddon, R.A. Sheldon, Org. Lett. 2 (2000) 4189–4191.

[28] I. Benjamin, Chem. Rev. 96 (1996) 1449–1475.

[29] I. Kuzmenko, H. Raraport, K. Kjaer, J. Als-Nielsen, I. Weissbuch, M. Lahav, L. Leiserowitz, Chem. Rev. 101 (2001) 1659–1696.

[30] A.R. Katritzky, V.R. Lobanov, M. Karelson, Chem. Soc. Rev. 24 (1995) 279–287.

[31] M. Deetlefs, K.R. Seddon, M. Shara, Phys. Chem. Chem. Phys. 8 (2006) 642–649.

[32] A.R. Katritzky, A. Lomaka, R. Petrukhin, R. Jain, M. Karelson, A.E. Visser, R.D. Rogers, J. Chem. Inf. Comput. Sci. 42 (2002) 71–74.

[33] D.M. Eike, J.F. Brennecke, E.J. Maginn, Green Chem. 5 (2003) 323–328.

[34] D.M. Eike, J.F. Brennecke, E.J. Maginn, Ind. Eng. Chem. Res. 43 (2004) 1039–1048.

[35] S. Trohalaki, R. Pachter, G.W. Drake, T. Hawkins, Energy Fuels 19 (2005) 279–284.

[36] K. Tamm, P. Burk, J. Mol. Model. 12 (2006) 417–421.

[37] N. Sun, X. He, K. Dong, X. Zhang, X. Lu, H. He, S. Zhang, Fluid Phase Equilib. 246 (2006) 137–142.

[38] M.H. Abraham, W.E. Acree, Green Chem. 8 (2006) 906–915.

[39] R.L. Gardas, J.A.P. Coutinho, Fluid Phase Equilib. 263 (2008) 26–32.

[40] T.A. Knotts, W.V. Wilding, J.L. Oscarson, R.L. Rowley, J. Chem. Eng. Data 46 (2001) 1007–1012.

[41] D.B. Macleod, Trans. Faraday Soc. 19 (1923) 38–41.

[42] S. Sugden, J. Chem. Soc. Trans. 125 (1924) 1167–1177.

[43] S.A. Mumford, J.W.C. Phillips, J. Chem. Soc. (1929) 2112–2133.

[44] O.R. Quayle, Chem. Rev. 53 (1953) 439–489.

[45] C. Ye, J.M. Shreeve, J. Phys. Chem. A 111 (2007) 1456–1461.

[46] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, J. Chem. Eng. Data 52 (2007) 80–88.

[47] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, J. Chem. Eng. Data 52 (2007) 1881–1888.

[48] H.D.B. Jenkins, H.K. Roobottom, J. Paasmore, L. Glasser, Inorg. Chem. 38 (1999) 3609–3620.

[49] G. Law, P.R. Watson, Langmuir 17 (2001) 6138–6141.

[50] K.S. Kim, D. Demberelnyamba, B.K. Shin, S.H. Yeon, S. Choi, J.H. Cha, H. Lee, C.S. Lee, J.J. Shim, Kor. J. Chem. Eng. 23 (2006) 113–116.

[51] M.G. Freire, P.J. Carvalho, A.M. Fernandes, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, J. Colloid Interface Sci. 314 (2007) 621–630.

[52] L.M.G. Sánchez, G.W. Meindersma, A.B. de Haan, Chem. Eng. Res. Des. 85 (2007) 31–39.

[53] Q. Zhang, Z. Li, J. Zhang, S. Zhang, L. Zhu, J. Yang, X. Zhang, Y. Deng, J. Phys. Chem. B 111 (2007) 2864–2872.

[54] W. Liu, T. Zhao, Y. Zhang, H. Wang, M. Yu, J. Solution Chem. 35 (2006) 1337–1346.

[55] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Green Chem. 3 (2001) 156–164.

[56] J.-Z. Yang, J. Tong, J.-B. Li, J.-G. Li, J. Tong, J. Colloid Interface Sci. 313 (2007) 374–377.

[57] V. Halka, R. Tsekov, W. Freyland, Phys. Chem. Chem. Phys. 7 (2005) 2038–2043.

[58] A.B. Pereiro, J.L. Legido, A. Rodriguez, J. Chem. Thermodyn. 39 (2007) 1168–1175.

[59] L.P.N. Rebelo, J.N.C. Lopes, J.M.S.S. Esperanca, E. Filipe, J. Phys. Chem. B 109 (2005) 6040–6043.

[60] S.V. Dzyuba, R.A. Bartsch, ChemPhysChem 3 (2002) 161–166.

[61] E. Gomez, B. Gonzalez, N. Calvar, E. Tojo, A. Dominguez, J. Chem. Eng. Data 51 (2006) 2096–2102.

[62] J.-Z. Yang, X.-M. Lu, J.-S. Gui, W.-G. Xu, Green Chem. 6 (2004) 541–543.

[63] A.B. Pereiro, P. Verdia, E. Tojo, A. Rodriguez, J. Chem. Eng. Data 52 (2007) 377–380.

[64] P.J. Carvalho, M.G. Freire, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, J. Chem. Eng. Data, submitted for review.

[65] J. Tong, Q.-G. Zhang, M. Hong, J.-Z. Yang, Acta Phys-Chim. Sin. 22 (2006) 71–75.

[66] V. Halka, R. Tsekov, W. Freyland, J. Phys.: Condens. Matter 17 (2005) S3325–S3331.

[67] J. Tong, M. Hong, W. Guan, J.-B. Li, J.-Z. Yang, J. Chem. Thermodyn. 38 (2006) 1416–1421.

[68] Q.-G. Zhang, W. Guang, J. Tong, Z.-X. Jin, Chem. J. Chin. Univ. 27 (2006) 925–929.

[69] Q.-G. Zhang, J.-Z. Yang, X.-M. Lu, J.-S. Gui, M. Huang, Fluid Phase Equilib. 226 (2004) 207–211.

[70] J.-Z. Yang, Q.-G. Zhang, F. Xue, J. Mol. Liq. 128 (2006) 81–84.

[71] W.-G. Xu, X.-M. Lu, Q.-G. Zhang, J.-S. Gui, J.-Z. Yang, Chin. J. Chem. 24 (2006) 331–335.

[72] J. Tong, Q.-S. Liu, W. Guan, J.-Z. Yang, J. Phys. Chem. B 111 (2007) 3197–3200.

[73] S.-L. Zanga, Q.-G. Zhang, M. Huanga, B. Wang, J.-Z. Yang, Fluid Phase Equilib. 230 (2005) 192–196.

[74] J.-Z. Yang, Q.-G. Zhang, M. Huang, F. Xue, S.-L. Zang, Chem. J. Chin. Univ. 26 (2005) 1873–1876.

[75] J. Tong, Q.-S. Liu, P. Zhang, J.-Z. Yang, J. Chem. Eng. Data 52 (2007) 1497–1500.

[76] J.L. Shereshefsky, J. Phys. Chem. 35 (1931) 1712–1720.

[77] E.A. Guggenheim, J. Chem. Phys. 13 (1945) 253–261.