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# Thermophysical Properties of Ionic Liquids

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David Rooney, Johan Jacquemin, and Ramesh Gardas

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**Abstract** Low melting point salts which are often classified as ionic liquids have received significant attention from research groups and industry for a range of novel applications. Many of these require a thorough knowledge of the thermophysical properties of the pure fluids and their mixtures. Despite this need, the necessary experimental data for many properties is scarce and often inconsistent between the various sources. By using accurate data, predictive physical models can be developed which are highly useful and some would consider essential if ionic liquids are to realize their full potential. This is particularly true if one can use them to design new ionic liquids which maximize key desired attributes. Therefore there is a growing interest in the ability to predict the physical properties and behavior of ionic liquids from simple structural information either by using group contribution methods or directly from computer simulations where recent advances in computational techniques are providing insight into physical processes within these fluids. Given the importance of these properties this review will discuss the recent advances in our understanding, prediction and correlation of selected ionic liquid physical properties.

## Contents

- 1 Introduction
  - 1.1 Liquidus Range
  - 1.2 Other Critical Properties
  - 1.3 Density
  - 1.4 Viscosity

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D. Rooney et al.

- 1.5 Surface Tension
  - 1.6 Specific Heat Capacity
  - 1.7 Thermal Conductivity
  - 1.8 Conclusions
- References

## 18 Nomenclature

19	Anions
20	[NTf <sub>2</sub> ] <sup>-</sup> Bis(trifluoromethylsulfonyl)imide
21	[OTf] <sup>-</sup> Trifluoromethanesulphonate
22	[C <sub>1</sub> SO <sub>4</sub> ] <sup>-</sup> Methylsulphate
23	[C <sub>2</sub> SO <sub>4</sub> ] <sup>-</sup> Ethylsulphate
24	[PF <sub>6</sub> ] <sup>-</sup> Hexafluorophosphate
25	[BF <sub>4</sub> ] <sup>-</sup> Tetrafluoroborate
26	[Methide] <sup>-</sup> Tris(trifluoromethylsulfonyl)methide
27	[DCA] <sup>-</sup> Dicyanamide
28	[FAP] <sup>-</sup> Tris(perfluoroalkyl)trifluorophosphate
29	For cations, <i>n</i> represents the carbon number of the alkyl chain, i.e.,
30	ethyl = 2, butyl = 4, etc.
31	[C <sub><i>n</i></sub> mim] <sup>+</sup> 1-Alkyl-3-methylimidazolium
32	[C <sub><i>n</i></sub> mpy] <sup>+</sup> Alkyl-1-methylpyridinium
33	[C <sub><i>n</i></sub> mpyr] <sup>+</sup> 1-Alkyl-1-methylpyrrolidinium
34	[P <sub>66614</sub> ] <sup>+</sup> Trihexyl-(tetradecyl)phosphonium
35	[CNpy] <sup>+</sup> 1-Cyanomethylpyridinium
36	[CNmpyr] <sup>+</sup> 1-Cyanomethyl-1-methylpyrrolidinium

## 37 1 Introduction

[Au1]

38 Over the last few years there has been a dramatic increase in research relating to the  
 39 use of ionic liquids as potential replacements for organic solvents in chemical proc-  
 40 esses [1–4]. More recently specialized areas such as lubricants [5], heat transfer  
 41 fluids [6] and analytical applications [7] have been investigated. These materials are  
 42 generally organic salts which have a relatively low melting point when compared  
 43 to inorganic salts. For example, many are fluid at temperatures below 298 K and  
 44 these are often described as room temperature ionic liquids (RTILs). However, the  
 45 term ionic liquid does not exclude those salts which have higher melting points and  
 46 although this description is associated with salts which melt below 373 K, in reality  
 47 there is no clear distinction between the term molten salt (often used for high  
 48 temperature liquids) and the term ionic liquid. The expanding range of applications  
 49 is not surprising given that approximately 10<sup>18</sup> anion–cation combinations exist  
 50 which could generate ionic liquids [8] and thus these liquids could be classified as  
 51 true designer materials, particularly since many of these designs include in-built  
 52 functionality. Therefore given the potential range available it is possible for them to  
 53 have properties suited to a particular application or, if desired, contradict some of





## Thermophysical Properties of Ionic Liquids

the earlier perceived advantages of dealing with fluids consisting of only ionic species. 54  
For example, ionic liquids are generally regarded as having negligible vapor pressure 55  
yet recently there have been reports of volatile ionic liquids [9] and the distillation 56  
of ionic liquids has been demonstrated [10]. Their biodegradability and toxicity has 57  
been questioned yet nutritional or pharmacological ionic liquids are feasible [11]. 58  
Similarly while some ionic liquids could be used as flame retardants, others are 59  
combustible and energetic ionic liquids are a reality [12]. 60

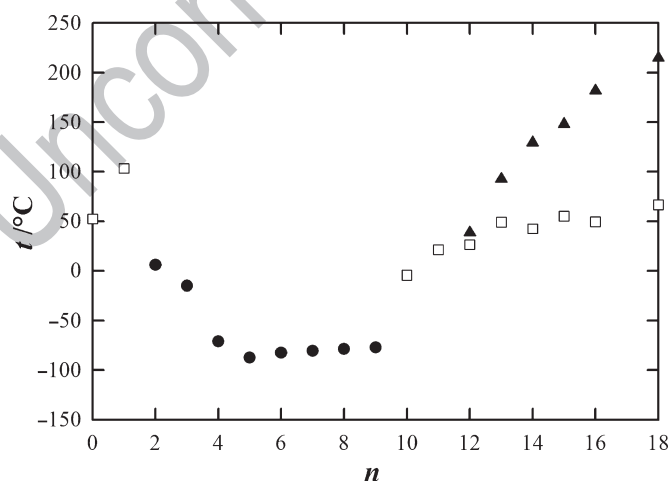
In each of the potential applications listed above, the ionic liquids often display 61  
at least one key advantage over molecular fluids. This may be simply that ionic 62  
liquids tend to have much greater liquidus temperature range [13] at atmospheric 63  
pressure than common molecular solvents, allowing for greater flexibility in 64  
processing conditions, or it could be that the chemistry within an ionic environ- 65  
ment is sufficiently different to cause an increase in yield or selectivity. Such 66  
chemical effects have been reported for some ionic liquid facilitated reactions 67  
[14] although in other cases normal solvent effects can be used to describe the 68  
system behavior [15]. For applications such as lubricants, heat transfer fluids, 69  
and in general when considering any scale-up or process design, knowledge of 70  
thermophysical properties and in particular transport properties is important. 71  
The IUPAC ionic liquid database (IL Thermo) [16], which has been operating 72  
for approximately 3 years, has collected a significant amount of such data 73  
including chemical and physical properties as well as measurement methods, 74  
etc. Importantly it also contains information with regard to sample purity and 75  
the uncertainty of quoted property values and thus this database serves as an 76  
important tool in addressing the need to find reliable physical property data. In 77  
particular, experimental data is reported for a large range of properties with 78  
density and viscosity being the most widely examined. An additional advantage 79  
of such a repository is that it facilitates research into the development of predictive 80  
tools to generate group contribution parameters for these important physical 81  
properties which overall increases our basic understanding of structure–property 82  
relationships of these novel fluids. Currently very few works have systematically 83  
studied the qualitative and/or quantitative relationships between the structures 84  
of ILs and their fundamental properties [17–21] such as melting point, viscosity, 85  
density, surface tension, thermal and electrochemical conductivity, solvent 86  
properties and speed of sound. At present, data for many other important 87  
physico-chemical properties of ionic liquids are in short supply, or are currently 88  
too unreliable to allow for similar structure-property relationship studies. 89  
Group contribution models (GCMs) are commonly used as predictive tools by 90  
engineers and physical scientists in process design, and many have become an 91  
integral part of process simulation software packages, due to their wide appli- 92  
cability, ease of use and relative accuracy. The basic assumptions of GCMs are 93  
that the physical properties of a component are dependent on the functional 94  
groups which make up its structure and each functional group provides a fixed 95  
contribution towards the physical properties, irrespective of the species involved 96  
[22]. Herein we will examine a number of key ionic liquid thermophysical 97  
properties including those for density, viscosity, heat capacity, surface tension, 98  
melting point, and the critical properties and discuss current strategies to model 99  
them. 100



## 101 1.1 Liquidus Range

102 The liquidus range relates to the temperature range where the ionic liquid is in  
 103 liquid form; in general this is the difference between the melting point and the  
 104 decomposition temperature. However it could also represent the temperature differ-  
 105 ence between glass transition point and boiling point, etc. Accurate values for melting  
 106 points for ionic liquids are scarce as, like in the case of inorganic salts, melting  
 107 point and glass transition temperatures can be strongly affected by the presence of  
 108 impurities. For example, reported glass transition temperatures for  $[C_4mim][PF_6]$   
 109 vary between 196 and 212 K [23, 24]. Van Valkenburg et al. [25] studied the  
 110 freezing–melting behavior of some ionic liquids when contaminated with water and  
 111 identified that  $[C_2mim][BF_4]$  has two freezing exotherms at 237 and 214 K, respec-  
 112 tively. Here they observed that contamination with water substantially extended the  
 113 lower temperature limit. In this study they also noted that chloride impurities had  
 114 little effect on the freezing–melting behavior of the studied liquids.

115 Ngo et al. [26] identified that larger more asymmetric cations tend to yield ionic  
 116 liquids with lower melting points and the highest melting points are associated with  
 117 more symmetric cations. It was also shown that branched alkyl chains such as *iso*-  
 118 propyl displayed higher melting points than those containing straight chains. In general  
 119 the melting point of an ionic liquid is a function of both the cation and the anion.  
 120 Figure 1 shows the melting points for the  $[C_nmim][BF_4]$  series, where it can be  
 121 observed that the melting point is initially high and then decreases as the chain  
 122 length increases, i.e., decreases with increasing asymmetry in agreement with Ngo  
 123 et al. [26].



**Fig. 1** Phase transition temperature as a function of chain length,  $n$ , for the  $[C_nmim][BF_4]$  series where  $n = 0\text{--}16, 18$  [123]. *open squares*, melting point; *filled circles*, glass transition; *filled triangles*, clearing transition



## Thermophysical Properties of Ionic Liquids

At chain lengths greater than around nine, the melting point increases again and liquid crystalline regions are observed to form at higher chain lengths; such materials are of interest in areas relating to catalysis and solar cells [27, 28], etc. A similar trend has also been reported for the  $[C_n\text{mim}][PF_6]$  series [29].

In order to investigate ionic liquid structural features which could lead to low melting point salts, Katritzky et al. employed quantitative structure–property relationship (QSPR) methods with reasonable success [8, 17]. In this study, correlations with  $R^2$  values between 0.70 and 0.90 were reported. The premise of this method is that all physical properties of a compound can be directly related to its chemical structure through the use of molecular descriptors. While not all molecular descriptors will be relevant to all properties the correct choice of descriptor can be used to develop a relationship between it and the property under study. Eike et al. [30] used this approach to correlate and predict the melting points of organic salts based on quaternary ammonium and pyridinium cations and validated the method using the previously reported bromides. For example the correlation represented by (1) gave an  $R^2$  value of 0.79 using five-descriptors for a series of N-pyridinium bromides:

$$T_m / ^\circ\text{C} = 125.85 + 0.58[D_1] - 2273.22[D_2] - 104.03[D_3] + 254.70[D_4] - 74.37[D_5] \quad (1)$$

Here,  $D_1$ – $D_5$  are molecular descriptors for the total charge weighted negative surface area, atomic charge weighted fractional negative surface area, bonding information content, relative negative charge and the relative positive charge surface area respectively. Those with negative multipliers, such as the bonding information content ( $D_3$ ), indicate that the larger the value of the descriptor the lower the melting point; in this case that melting point decreases with increasing asymmetry. By extending the range of molecular descriptors used it is possible to improve the accuracy of the correlation. For example, Carrera and Aires-de Sousa [31] generated regression trees as a method for determining the most significant descriptors and used this for estimating the melting points of a range of pyridinium bromides from their molecular structure. In this study 126 pyridinium cations were analyzed using 1,085 molecular descriptors including those for molecular geometry, charge indices, connectivity between molecules, counts of specific functional groups and atomic weight, etc. Using this approach a reasonably good correlation was obtained between the experimental and calculated values with a reported  $R^2 = 0.933$  and a root-mean-square (rms) error = 12.6 K. Importantly this method was able to estimate the melting point of nine new pyridinium bromides. While this error may seem to be reasonably large, Charton and Charton [32] reported an rms error of 16.4 K for a range of 303 normal and branched substituted alkanes using an 11 term QSPR function. For other data sets Eike et al. [30] found that additional descriptors should be used; for example, tetraalkyl-ammonium bromides and (*n*-hydroxyalkyl)-trialkyl-ammonium bromides necessitated descriptors including the valence-modified connectivity for two bond paths, or three atoms in a row and the complementary information content. Similarly, Trohalaki et al. [33] developed QSPR relationships for the melting points and densities for a range of energetic ionic liquids such as the 1-substituted 4-amino-1,2,4-triazolium bromide and nitrate



D. Rooney et al.

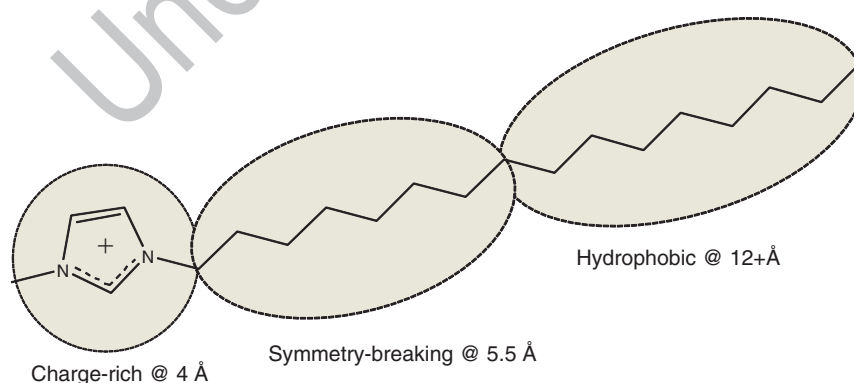
166 salts. A good correlation ( $R^2 > 0.85$ ) with the experimental melting point data was  
167 found using the following three parameter equation for the bromide salts:

$$168 \quad T_m / ^\circ \text{C} = -262.00 - 6.91 \times 10^5 [D_6] + 47.40 [D_7] - 136.00 [D_8]^{-1}, \quad (2)$$

169 where  $D_6$ – $D_8$  are descriptors for the nucleophilic reactivity index for the amine  
170 nitrogen, the area weighted surface charge of the hydrogen-bond acceptor atoms  
171 and the energy of the lowest unoccupied molecular orbital. A similar three param-  
172 eter equation was derived for the nitride salts, in this case using two descriptors for  
173 the hydrogen bond donating ability of the cation and the minimum nucleophilic  
174 reactivity index for a carbon atom.

175 Despite the fact that the QSPR approach was successful in each of the above  
176 studies, every class of ionic liquid generated its own descriptor function and thus the  
177 technique cannot easily be extended to the entire family of potential ionic liquids.  
178 More recently, López-Martin et al. [34] treated the cations and anions separately and  
179 calculated 1,500 descriptors for each ion, thereby generating 3,000 for each ionic  
180 liquid. Importantly this was the first report covering the anion influence on the ionic  
181 liquid melting point discussed previously. Here the authors optimized the cation and  
182 anion geometries using semi-empirical QM calculations before deriving, ranking by  
183 variable importance analysis, and classifying the descriptors into three categories,  
184 relating to anion size, anion symmetry and charged surface areas. For the imidazolium  
185 based ionic liquids three regions were identified which influence the melting point.  
186 These are: the charge-rich region, which is localized on the ring and responsible for  
187 ionic interaction; the symmetry-breaking region, which exists in the range of 5.5 until  
188 12 Å; and the hydrophobic region, which increases melting point due to increased  
189 Van der Waals forces. These regions are shown schematically in Fig. 2.

190 Alternative approaches to the study of melting points of ionic liquids include  
191 molecular dynamics simulations such as that conducted by Alavi and Thompson  
192 [35]. Here simulations of  $[\text{C}_2\text{mim}][\text{PF}_6]$  over a wide temperature range, which



**Fig. 2** Structural regions important in determining the melting point of the 1-alkyl imidazolium based cations; adapted from López-Martin et al. [34]





## Thermophysical Properties of Ionic Liquids

included the known melting point, predicted a value approximately 40 K higher than that given in the literature. Similar atomistic simulations by Jayaraman and Maginn [36] estimated the melting point of the orthorhombic [C<sub>4</sub>mim][Cl] at 365 ± 6 K which is some 26 K higher than the literature value.

Krossing et al. [37] assessed the Gibbs free energy of fusion as a predictor of the melting point using a Born–Fajans–Haber cycle which was closed by the lattice and solvation Gibbs energies of the constituent ions in the molten salt. These were calculated using a combination of volume based thermodynamics and quantum chemical calculations for the lattice free energies and the COSMO solvation model and experimental dielectric constants for the free energy of solvation. For the range of 14 different ionic liquids studied, which included a variety of anion and cation combinations, the Gibbs free energy of fusion was found to be negative for all the ionic liquids studied indicating that the liquid state was thermodynamically favorable. It was also shown from this study that it is possible to predict the melting point of an ionic liquid using the dielectric constant.

One of the most publicized advantages of ionic liquids has been their insignificant vapor pressures. On one hand this can reduce fire hazards when employed as solvents in chemical processes or equally it can cause difficulties in the recovery of high boiling point products which would have normally been purified by distillation of the solvent. In reality ionic liquids will exert some degree of vapor pressure although for most aprotic ionic liquids these pressures will be significantly lower than commonly used organic solvents particularly at room temperature. At higher temperatures the ionic liquids may undergo thermal decomposition to a range of undesired products such as water, carbon dioxide and hydrocarbons [38] or could simply revert back to the original components. The latter is generally encountered when using protic ionic liquids such as 1-methylimidazolium chloride ([C<sub>0</sub>mim]Cl) generated in the BASIL process [39] which can be reverted back to methylimidazole and hydrochloric acid. Thus all ionic liquids have a maximum operating temperature in order to avoid volatilizing or decomposing of the liquid. The temperature at which this happens represents the other limit of the liquidus range. Table 1 shows the reported liquidus range of a number of different ionic liquids. The onset temperature ( $T_{\text{onset}}$ ) is defined as the intersection of the baseline weight

**Table 1** Melting points and thermal decomposition temperatures for a range of selected 1-alkyl-imidazolium ionic liquids. All temperatures in Kelvin, data taken from Fredlake et al. [123] except for superscript a values which are from Wilkes et al. [25]

	Ionic liquid	Melting point (°C)	Glass transition (°C)	$T_{\text{onset}}$ (°C)	$T_{\text{start}}$ (°C)
[Au2]	[C <sub>4</sub> mim]Cl	314	204	537	423
	[C <sub>4</sub> mim]Br	–	223	546	488
	[C <sub>2</sub> mim][BF <sub>4</sub> ]	287 <sup>a</sup>	–	718 <sup>a</sup>	–
	[C <sub>4</sub> mim][BF <sub>4</sub> ]	–	188	634/696 <sup>a</sup>	563
	[C <sub>4</sub> mim][NTf <sub>2</sub> ]	271	187	695	603
	[C <sub>4</sub> mim][OTf]	286	–	665	613
	[C <sub>4</sub> mim][Methide]	–	208	686	633
	[C <sub>4</sub> mim][DCA]	–	183	573	513







D. Rooney et al.

225 and the tangent of the weight vs temperature curve obtained from TGA analysis as  
226 decomposition occurs, while the start temperature ( $T_{\text{start}}$ ) is the temperature at which  
227 the decomposition of the sample begins. As such  $T_{\text{start}}$  is lower than  $T_{\text{onset}}$ .

228 For some of the reported ionic liquids in Table 1, the range is significant. For  
229 example it is 332 K in the case of  $[\text{C}_4\text{mim}][\text{NTf}_2]$ , whereas for others this range is  
230 relatively small, as in the case of  $[\text{C}_4\text{mim}]\text{Cl}$ . These examples have used the  
231 temperature difference between the melting point and the starting temperature for  
232 thermal decomposition ( $T_{\text{start}}$ ). From this it can be observed that even the relatively  
233 poor range of  $[\text{C}_4\text{mim}]\text{Cl}$  is greater than that of water when operating at atmospheric  
234 pressure. The large liquidus range of certain ionic liquids was exploited by Rodríguez  
235 et al. [40] in thermometer applications using the ionic liquids tris(2-hydroxyethyl)  
236 methylammonium methylsulfate ( $[\text{TEMA}][\text{C}_1\text{SO}_4]$ ) and  $[\text{P}_{66614}][\text{NTf}_2]$ .

237 It can be seen in Table 1 that a significant difference in the  $T_{\text{onset}}$  values has been  
238 reported between groups for  $[\text{C}_4\text{mim}][\text{BF}_4]$ . Kosmulski et al. [41] observed that the  
239 scan rate, mass of the ionic liquid, moisture content and addition of silica all influ-  
240 enced the thermal decomposition. This latter observation agrees with that of Ngo  
241 et al. [26] where it was found that the pan construction material was important for  
242 certain ionic liquids, most notably the  $[\text{PF}_6]^-$  salts. It was also observed by  
243 Kosmulski et al. [41] that, while the thermal decomposition temperatures are high,  
244 slow degradation occurred for a range of  $[\text{C}_n\text{mim}][\text{PF}_6]$  ionic liquids at a temperature  
245 of 473 K which is more than 100 K lower than the  $T_{\text{onset}}$  value found. Awada et al.  
246 [38] studied the thermal decomposition of a number of ionic liquids and reported  
247 that both the chain length and counter ion have an effect on the thermal stability of  
248 the imidazolium salts. In this study it was found that  $[\text{PF}_6]^-$ ,  $[\text{NTf}_2]^-$  and  $[\text{BF}_4]^-$  anions  
249 were more thermally stable than the equivalent halide salts and that the stability was  
250 inversely proportional to the length of the alkyl chain. It was also shown that the  
251 atmosphere has an effect on the thermal stability of the  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  salts  
252 where both the onset and decomposition temperatures were significantly reduced  
253 when run under air as compared to those under an  $\text{N}_2$  atmosphere. Kamavaram and  
254 Reddy [42] investigated the long term thermal stability of  $[\text{C}_n\text{mim}]\text{Cl}$  ( $n = 4, 6$ )  
255 using isothermal TGA at various temperatures ranging from 423 to 473 K over an  
256 extended period under an argon purge. For both liquids it was found that the weight  
257 loss was approximately 5% at 423 K increasing to >90% at 473 K over 15 h. The  
258 authors fitted the data to a pseudo-first order rate expression and determined the  
259 activation energies for the decomposition as 121 and 117  $\text{kJ mol}^{-1}$  for  $n = 4$  and 6,  
260 respectively. From the above investigations it would appear that it is difficult to  
261 predict accurately the thermal decomposition point for ionic liquids as a number of  
262 factors can influence the observed temperatures.

263 Under a combination of high temperatures and low pressures ionic liquids have  
264 been shown to evaporate, albeit at very low rates [10]. For example at 573 K and  
265 0.1 mbar the evaporation rate was calculated as  $0.12 \text{ g h}^{-1}$  for  $[\text{C}_2\text{mim}][\text{NTf}_2]$   
266 decreasing to  $2.40 \times 10^{-3} \text{ g h}^{-1}$  when the alkyl chain length was increased to 16.  
267 Similarly  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ( $n = 10, 12$ ) were shown by Rebelo et al. [43] to evaporate  
268 at 450 K and a lower pressure of 0.01 mbar. This study was also the first to estimate  
269 the critical properties of the ionic liquids using literature correlations based on the





## Thermophysical Properties of Ionic Liquids

relationship between the critical temperature and the temperature dependence of the surface tension and liquid density. A further generalization that the boiling point is approximately 60% of the critical temperature allowed for a crude estimation of this value. Based on these calculations the estimated boiling points for [C<sub>n</sub>mim][NTf<sub>2</sub>] ionic liquids decreased from around 625 K for  $n = 2$  to 479 K when  $n = 10$ . It was noted in this paper that the vapor pressure at different temperatures is significantly affected by the vaporization enthalpy ( $\Delta_{\text{vap}}H$ ) where it was shown, for example, that the vapor pressure drops by one order of magnitude for each 15 K decrease in temperature when using a  $\Delta_{\text{vap}}H$  of 300 kJ mol<sup>-1</sup>. Since this initial work a number of groups have investigated the boiling point and  $\Delta_{\text{vap}}H$  of ionic liquids using a variety of approaches as shown in **Table 2**.

Zaitsau et al. [44] measured the vapor pressure of a series of [C<sub>n</sub>mim][NTf<sub>2</sub>] ionic liquids using the integral effusion Knudsen method and correlated the  $\Delta_{\text{vap}}H$  with the molar volumes and the surface tensions of the compounds. What is clear from this study is that the values for  $\Delta_{\text{vap}}H$  are approximately half that used in Rebelo's initial estimate and further indicated that the Eotvos–Guggenheim correlations which are suitable for molecular solvents do not apply for ionic liquids.

In what is essentially a temperature programmed desorption (TPD) technique, Armstrong et al. [45] evaporated eight imidazolium based ionic liquids using an ultra-high vacuum and analyzed the vapors by line of sight mass spectrometry. Not only was this approach used to determine the  $\Delta_{\text{vap}}H$  values of the ionic liquids but equally importantly it was able to show that the ionic liquids evaporated as ion pairs. Furthermore an electrostatic model was developed, which in principal related the  $\Delta_{\text{vap}}H$  to the molar volumes of the ionic liquids which can in turn, as will be shown later, be estimated using group contribution models with reasonable accuracy. The values determined using this technique agree well with those determined by Zaitsau et al. [44] except for the [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> salts where contamination of the ionic liquids during the surface tension measurements was suggested as the probable cause for the discrepancy. Verevkin [46] modified the approach of Emel'yanenko et al. [47] which uses a combination of calorimetry and high-level ab initio calculations. Despite the time involved in the combustion and calculation measurements this technique is shown to agree well with that of the TPD results,

**Table 2** Estimated values of enthalpies of vaporization ( $\Delta_{\text{vap}}H_{298}$  in kJ mol<sup>-1</sup>) for ionic liquids obtained using various methods

Ionic liquid	Surface tension [46]	Microcalorimetry		MD calculations	
	TPD [47]	[48]	TGA[50]	[51]	
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	136.1	134	132.9	120.6	159
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	134.6	134	137.9	118.5	174
[C <sub>6</sub> mim][NTf <sub>2</sub> ]	141.6	139	142.9	124.1	184
[C <sub>8</sub> mim][NTf <sub>2</sub> ]	149.0	149	147.9	132.3	201
[C <sub>10</sub> mim][NTf <sub>2</sub> ]	155.5	–	–	134.0	–
[C <sub>8</sub> mim][BF <sub>4</sub> ]	122.0	162	160.4	–	–
[C <sub>8</sub> mim][PF <sub>6</sub> ]	144.3	169	168.9	–	–





D. Rooney et al.

302 further suggesting that the problems with the  $[\text{BF}_4]^-$  and  $[\text{PF}_6]^-$  salts are due to  
303 errors in the surface tension measurements. Recently Luo et al. [48] demonstrated  
304 an isothermogravimetric technique (TGA) where  $\Delta_{\text{vap}}H$  is estimated using a combi-  
305 nation of the Langmuir and Clausius–Clapeyron expressions using the assumption  
306 that the enthalpy of vaporization is independent of temperature. As can be seen in  
307 Table 2, the values reported using this technique are lower than those determined  
308 using alternative methods although they follow a similar trend to those found using  
309 the surface tension technique. Molecular dynamics approaches have also been used  
310 to estimate the  $\Delta_{\text{vap}}H$  of the  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ionic liquids, as shown in Table 2, which  
311 agree well with literature values [49]. Other purely computational methods include  
312 that proposed by Diedenhofen et al. [50] in which the vapor pressures of a range of  
313 ionic liquids were estimated using two separate approaches based on the  
314 COSMO-RS method and quantum chemical gas phase calculations. It was shown  
315 that the  $\Delta_{\text{vap}}H$  values are predicted with reasonable accuracy using both strategies,  
316 indicating that the enthalpic interactions are correctly described in the proposed  
317 models. Recently Ludwig [51] reported that a number of thermodynamic properties  
318 including vapor pressures, enthalpies of vaporization, boiling points and entropies  
319 of vaporization can be predicted from purely theoretical methods using ab initio  
320 cluster calculations in combination with statistical thermodynamics. Together these  
321 recent papers demonstrate that computational techniques for the determination of  
322 these properties have advanced considerably in the last few years.



## 323 1.2 Other Critical Properties



324 Recently, Valderrama and Robles developed and applied the modified Lydersen–  
325 Joback–Reid group contribution model for the determination of normal boiling  
326 points, acentric factors and critical properties of ionic liquids [52, 53]. Although  
327 they were unable to validate this directly, due to the lack of experimental data on  
328 ionic liquid boiling points or critical properties, they used the values obtained in a  
329 model for the prediction of densities with reasonable accuracy. The developed  
330 group contribution model is also highly flexible as the groups are relatively small  
331 allowing for an estimation of these properties for a large range of cations and ions.

## 332 1.3 Density

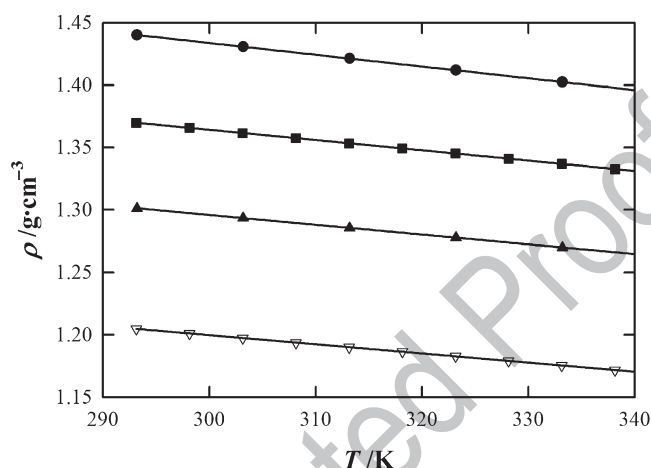
333 A considerable amount of experimental data has been measured for the density as  
334 a function of the temperature for a range of imidazolium, pyridinium, ammonium,  
335 phosphonium and pyrrolidinium based ionic liquids. For pure ILs, the values vary  
336 depending on the choice of anion and cation. Typical values range from 1.05 to 1.64  
337  $\text{g cm}^{-3}$  at 293 K which decrease with temperature to between 1.01 and 1.57  $\text{g cm}^{-3}$   
338 at 363 K. As with molecular solvents the densities are closely related to the molar



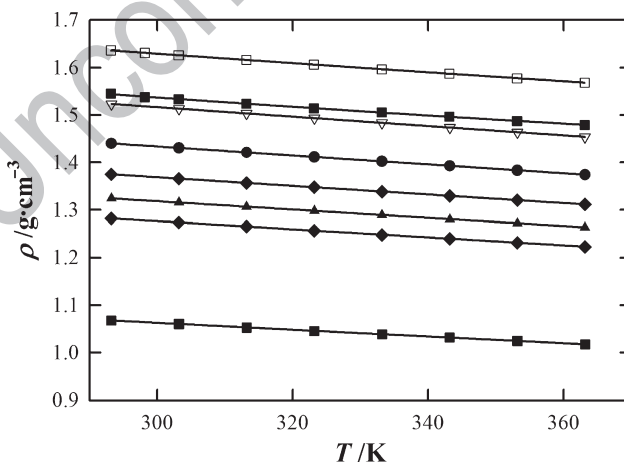


## Thermophysical Properties of Ionic Liquids

mass of the liquid with ILs containing heavy atoms found to be most dense. Figures 339  
 3 and 4 show a range of measured densities of dried ionic liquids as a function of 340  
 temperature at 0.1 MPa where it can be observed that the density is found to be a 341  
 strong function of anion type and decreases with increasing alkyl chain length. 342



**Fig. 3** Effect of the anion on the densities of  $[C_4mim]^+$  based ionic liquids: *filled circles*,  $[NTf_2]^-$ ; *filled squares*,  $[PF_6]^-$ ; *filled triangles*,  $[OTf]^-$ ; *inverted open triangles*,  $[BF_4]^-$  [61]



**Fig. 4** Effect of the cation on the densities of  $[NTf_2]^-$  based ionic liquids: *filled circles*,  $[C_2mim]^+$ ; *filled diamonds*,  $[C_4mim]^+$ ; *filled triangles*,  $[C_6mim]^+$ ; *filled diamonds*,  $[C_8mim]^+$ ; *filled diamonds*,  $[C_{10}mim]^+$ ; *filled squares*,  $[CNpy]^+$ ; *open squares*,  $[CNmpyr]^+$ ; *inverted open triangles*,  $[P_{66614}]^+$  [61]





D. Rooney et al.

The most widely used method for ionic liquid density measurement is the vibrating-tube densitometer method which relies on a calibration as a function of temperature and pressure using appropriate reference fluids [54, 55]. For many reported ionic liquids this is not routinely performed and corrections for the case of viscous fluids (i.e.,  $>100$  mPa s) are often ignored [56–58]. Despite these factors the densities of ionic liquids measured with vibrating tube densitometers have a standard uncertainty to within 0.1%. Alternative methods include the calculation of density through speed of sound measurements [59] or piezometric methods [54]. Both approaches are relatively complex technically but present the advantage of providing extra thermodynamic property data. Pycnometric methods or hydrostatic weighing techniques are also used extensively; however, the use of pycnometers requires a large sample of fluid and extensive volume calibration procedures with a reference fluid to obtain very accurate values of the density.

As with other physical properties impurities can have a significant effect. Jacquemin et al. [60] studied six hydrophobic and hydrophilic ILs including five imidazolium and one ammonium based ionic liquid as a function of temperature up to 393 K and at atmospheric pressure and found that the densities of the water-saturated IL samples were lower when compared with dried samples. This difference was relatively small at around 1–2% for hydrophobic ionic liquids samples containing a mole fraction of water close to 30%. More recently Jacquemin et al. [61] reported experimental densities for a range of selected ionic liquids contaminated by a mass fraction of water ( $w_w$ ) of  $1 \times 10^{-3}$  at 298.15 K and 0.1 MPa, shown here in Table 3. It can be observed from this data that while the variation on the overall density is small, the change in the calculated molar volume ( $\Delta V_m$ ) is significantly larger given the relative difference in the molecular weights between ionic liquid and water. Here the water mole fraction is given by the  $x_w$  value.

Similarly it has been reported that increasing halide (such as chloride and bromide) contamination also tends to decrease the density over a wide range of values [62].

A number of models which can estimate density at atmospheric pressure have recently been reported. For example, Rebelo et al. [63, 64] defined the effective molar volumes of ions at 298.15 K and used the assumption of “ideal behavior” for the determination of the molar volume of ionic liquids. Yang et al. [65] used a theory based on the “interstice model” which correlated the density and the surface tension of the ionic liquid. Group contribution models have been reported by Kim et al. [66, 67] for the calculation of the density and CO<sub>2</sub> gas solubility for 1-alkyl-3-methylimidazolium based ionic liquids as a function of the temperature and CO<sub>2</sub> gas pressure with reasonable accuracy over a 50 K temperature range; however, the

**Table 3** Impact of water impurities on the calculated molar volume of ionic liquids

Ionic liquid	$\rho$ g cm <sup>-3</sup>	$V_m$ (cm <sup>3</sup> mol <sup>-1</sup> )	$10^2 \times x_w$	$\Delta V_m$ (%)
[C <sub>2</sub> mim][NTf <sub>2</sub> ]	1.5150	258.29	2.13	-2.0
[C <sub>4</sub> mim][NTf <sub>2</sub> ]	1.4351	292.22	2.27	-2.2
[C <sub>10</sub> mim][NTf <sub>2</sub> ]	1.2755	394.77	2.72	-2.6
[P <sub>6614</sub> ][NTf <sub>2</sub> ]	1.0601	720.70	4.07	-4.0





## Thermophysical Properties of Ionic Liquids

effect of the anion was not studied. In their work, Ye and Shreeve [68] observed a linear relationship between the density in solid and liquid states of ionic liquids and used a group contribution model for the calculation of the density in solid state coupled with linear regression to estimate the liquid density. Recently, Gardas and Coutinho [69] extended the Ye and Shreeve group contribution method for the estimation of the density over a wide range of temperatures and pressures with a determined uncertainty of 0.6%. As in the original work, the calculation of ionic liquid density was determined from a prior knowledge of their mechanical coefficients thus limiting the general applicability of this methodology. Alternative strategies to the GCM include that of Deetlefs et al. [18] which studied the determination of refractive index, surface tension and density at 298 K for a range of ionic liquids using a parachor function defined by Knotts et al. [70].

Recently Jacquemin et al. [61, 71] extended the concept proposed by Rebelo et al. In this method the effective molar volume of an ionic liquid and hence density can be determined by assuming that the volumes of the ions behave as an “ideal” mixture. This strategy was used to calculate the effective molar volumes of a wide range of ions using a large set of previously reported data as a function of the temperature difference at 0.1 MPa and a reference temperature of 298.15 K using the following equation:

$$V_{\text{ion}}^*(\delta T) = \sum_{i=0}^2 (C_i \times \delta T^i). \quad (3)$$

The coefficients ( $C_i$ ) were obtained for 44 anions and 102 cations which achieved a high degree of accuracy when using more than 2150 data points. This approach was further extended to include pressure [72] by applying the commonly used Tait equation. In this case the effective molar volumes are estimated using the following equation:

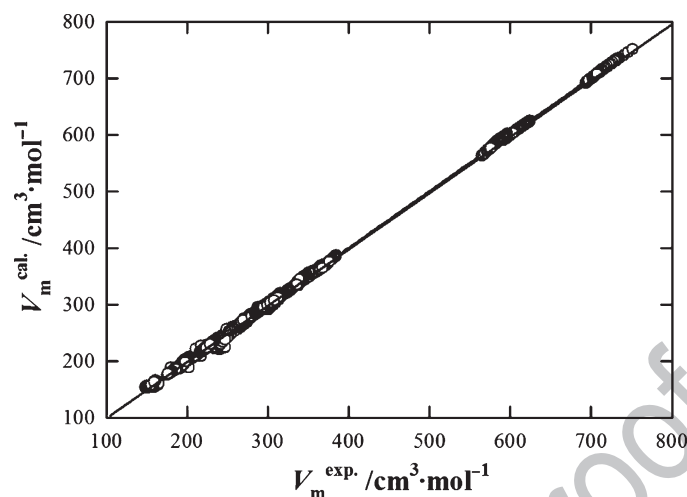
$$V_{\alpha}^*(\delta T, p, G, H) = \frac{V_{\alpha}^*(\delta T, p_{\text{ref}})}{1 - G \ln \left( \frac{\sum_{i=0}^2 (H_i \cdot \delta T^i) + p}{\sum_{i=0}^2 (H_i \cdot \delta T^i) + p_{\text{ref}}} \right)}. \quad (4)$$

Here  $\alpha$  can represent the cation or anion constituting an IL or an extra  $-\text{CH}_2-$  group in the alkyl chain length of an 1-alkyl-3-methylimidazolium based ionic liquid and  $V_{\alpha}^*(\delta T, p_{\text{ref}})$  is the effective molar volume obtained using the reference pressure ( $p_{\text{ref}} = 0.1$  MPa). The coefficients ( $G$  and  $H_i$ ) were obtained by fitting literature data and, as can be seen in Fig. 5, the approach was successful in estimating the densities over a wide temperature and pressure range yielding 0.36% error for 5,080 experimental data points.





D. Rooney et al.



**Fig. 5** Predicted vs experimental molar volumes for a range of ionic liquids at varying temperature and pressure using the group contribution method proposed by Jacquemin et al. [72]

#### 413 **1.4 Viscosity**

414 Viscosity relates to the internal friction within the fluid which is caused by  
 415 intermolecular interactions and is therefore important in all physical processes  
 416 which involve the movement of the fluid or components dissolved within it.  
 417 Therefore the design of liquid-liquid extractors, distillation columns, heat-transfer  
 418 equipment, process piping, reactors, and other units found in various chemical and  
 419 pharmaceutical industries requires the knowledge of the viscosity of fluids and their  
 420 mixtures.

421 Viscosity is arguably the most important physical property when considering  
 422 any scale-up of ionic liquid applications. In general a low viscosity is desired for  
 423 solvent applications in order to minimize pumping costs and increase mass transfer  
 424 rates while higher viscosities may be favorable for other applications such as lubri-  
 425 cation or use in supported membrane separation processes. It is known that the  
 426 viscosity of ionic liquids vary widely depending on the type of cation and anion and  
 427 are relatively high when compared to those of common organic solvents.

428 Organic solvents typically have room temperature viscosities ranging from 0.2  
 429 to 10 cP [73] whereas ionic liquids display, generally, a broad range of room  
 430 temperature viscosities, from 10 to 726 cP [74] and significantly higher (Fig. 6).  
 431 It can be seen in Fig. 6 that the viscosity increases with alkyl chain length of  
 432 imidazolium cation. For example, in the series of  $[C_n\text{mim}][\text{PF}_6]$  with  $n = 2, 4-8$ ,  
 433 the viscosity at 298.15 K increases monotonously from 172.3 to 677.4 cP.  
 434 Viscosities for the series of  $[C_n\text{mpy}][\text{NTf}_2]$  ionic liquids are slightly higher than  
 435 those of  $[C_n\text{mim}][\text{NTf}_2]$  ionic liquids. The increment with the alkyl chain length  
 436 of imidazolium cation is more pronounced in case of ionic liquids containing the





## Thermophysical Properties of Ionic Liquids

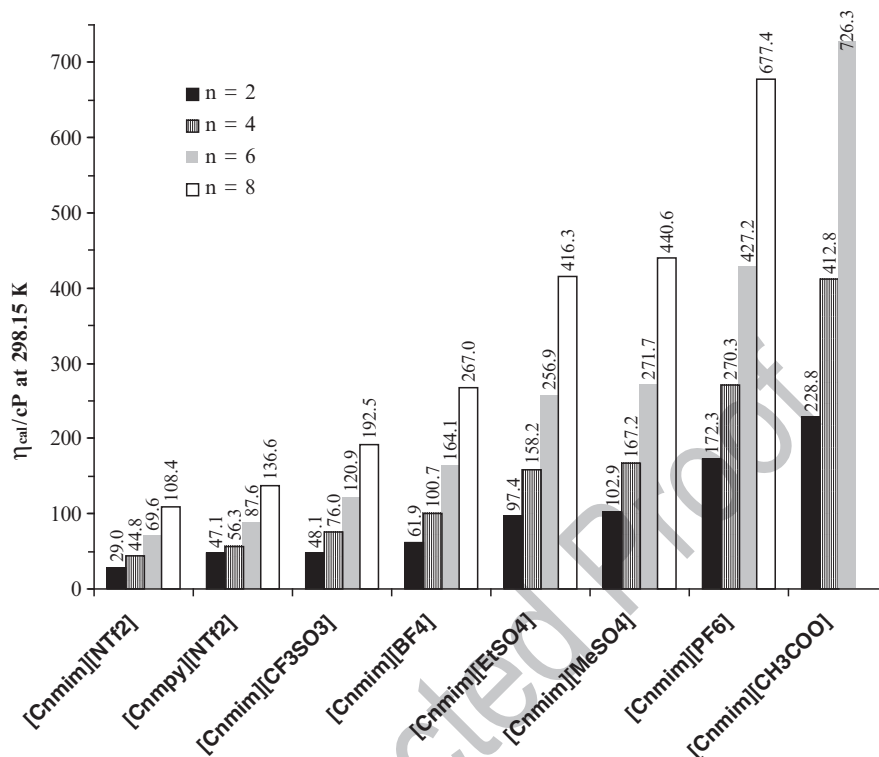


Fig. 6 Viscosity at 298 K of some common ionic liquids as a function of chain length,  $n$

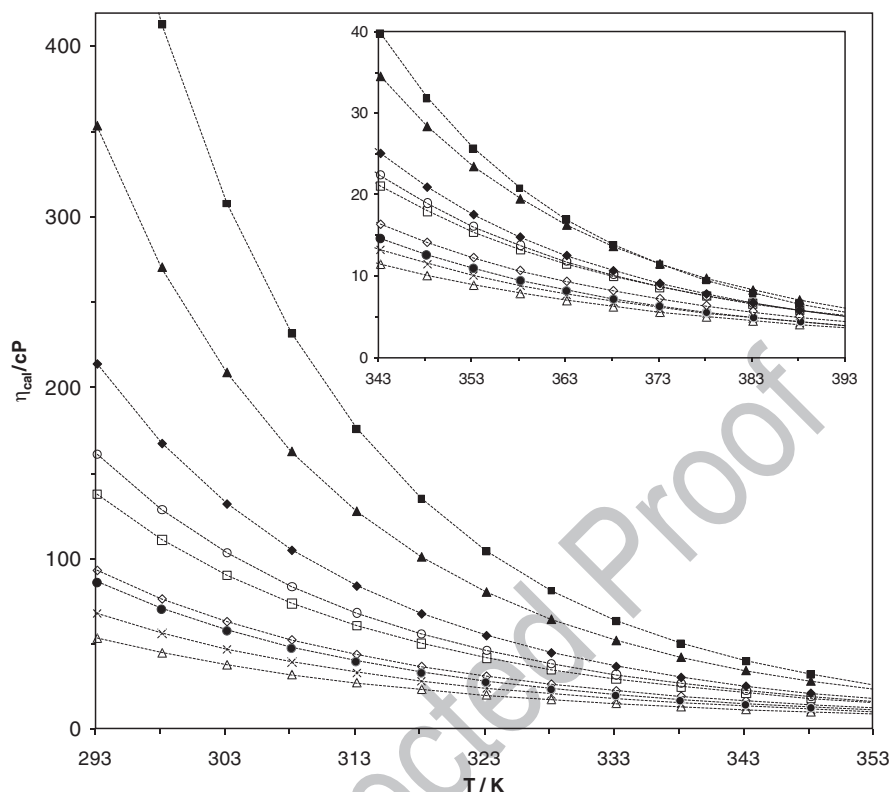
$\text{Cl}^-$  anion, and seems to decrease with the symmetry of anion, showing the trend  $\text{Cl}^- > [\text{CH}_3\text{COO}]^- > [\text{PF}_6]^- > [\text{C}_4\text{SO}_4]^- > [\text{C}_2\text{SO}_4]^- > [\text{BF}_4]^- > [\text{OTf}]^- > [\text{NTf}_2]^-$ . In general ionic liquids having highly symmetric or almost spherical anions are more viscous and viscosity decreases with increasing anion asymmetry. For ionic liquids having a common anion and a similar alkyl chain length on the cation, it is observed that the viscosity increases with cations following the order imidazolium < pyridinium < pyrrolidinium. This is in agreement with the results of Crosthwaite et al. [75] which shows that pyridinium salts are generally more viscous than the equivalent imidazolium salts.

More exhaustive and theoretically based studies are required to rationalize the different trends and care is recommended when comparing or using viscosity data for ionic liquids as differences among the results of several authors may be important since, as it is well known, the presence of small amounts of water or other impurities such as chloride seem to have a remarkable effect on the viscosity [76–81].

These studies show that small changes in the structure of the ionic liquid can produce considerable differences in viscosity. From studies where a series of imidazolium based salts with various alkyl substituents and different anions was characterized in terms of viscosity in order to establish a relationship between



D. Rooney et al.



**Fig. 7** Viscosities of ionic liquids calculated according to Gardas and Coutinho method [101]. *filled squares*, [C<sub>4</sub>mim][CH<sub>3</sub>COO]; *filled triangles*, [C<sub>4</sub>mim][PF<sub>6</sub>]; *filled diamonds*, [C<sub>4</sub>mim][C<sub>1</sub>SO<sub>3</sub>]; *filled circles*, [C<sub>4</sub>mpyr][NTf<sub>2</sub>]; *open diamonds*, [C<sub>4</sub>mim][OTf]; *multiplication signs*, [C<sub>4</sub>mpy][NTf<sub>2</sub>]; *open triangles*, [C<sub>4</sub>mim][NTf<sub>2</sub>]; *open circles*, [C<sub>4</sub>mpy][BF<sub>4</sub>]; *open squares*, [C<sub>4</sub>mim][BF<sub>4</sub>]

chemical structure and physical properties [60, 74, 82–87], it was suggested that the viscosity of ionic liquids is mainly controlled by hydrogen bonding, Van der Waal forces, molecular weight and mobility.

Like many viscous fluids the viscosity can decrease markedly with increasing temperature (Fig. 7). For example, [C<sub>4</sub>mim][PF<sub>6</sub>] has a viscosity of 270.3 cP at 298 K, which decreases to 80.4 cP at 323 K and 23.5 cP at 353 K.

Viscosity is a difficult property to predict and flexible predictive models will require further experimental data in order to obtain a better understanding of this property. Many prediction methods are available in literature for the viscosity of pure component and their mixtures [88]; most of these are generally based on group contributions (e.g., the Orrick–Erbar method [89], the Sastry–Rao method [90], and the UNIFAC–VISCO method [91]), the corresponding states concept (e.g., Przedzicki and Sridhar [92], Chatterjee and Vasant [93], Teja and Rice [94, 95],





and Queimada et al. [96, 97]) or the corresponding-states group-contribution (CSGC) method (e.g., Yinghua et al. [98]). Group contribution methods for the estimation of liquid viscosity usually use some variation of temperature dependence proposed by de Guzman [99], known as the Andrade equation [100]. Gardas and Coutinho [101] developed a group contribution method for the viscosity of ionic liquids using an Orrick–Erbar-type approach [102], and for 498 data points of 29 imidazolium, pyridinium, and pyrrolidinium based ionic liquids containing  $[\text{PF}_6]^-$ ,  $[\text{BF}_4]^-$ ,  $[\text{NTf}_2]^-$ ,  $\text{Cl}^-$ ,  $[\text{CH}_3\text{COO}]^-$ ,  $[\text{C}_1\text{SO}_4]^-$ ,  $[\text{C}_2\text{SO}_4]^-$ , and  $[\text{OTf}]^-$  anions, observed a maximum deviation of less than 28%. The largest deviations observed in predicted viscosities were mainly due to the discrepancies in viscosity values reported in literature, which may be related to water content, halogen and other impurities present in the samples, or the experimental method adopted. The Orrick–Erbar method [89] requires density data for the prediction of viscosity. To overcome this limitation and to attempt the development of an improved viscosity model with lower deviations in estimated viscosities of ionic liquids, a new correlation model based on the Vogel–Tammann–Fulcher (VTF) equation was recently proposed by Gardas and Coutinho [103]. This model was successful as demonstrated in Fig. 7.

## 1.5 Surface Tension

The versatility of ILs has driven increasing interest in using them in extraction and multiphasic homogeneous catalytic reactions [104] where one phase is chosen to dissolve the catalyst and be immiscible with the second phase which 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.

Surface tension is an important property in the study of physics and chemistry at free surfaces as it affects the transfer rates of vapor absorption at the vapor–liquid interface. 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 aspects but also for its relevance in environmental problems, biological phenomena, and industrial applications.

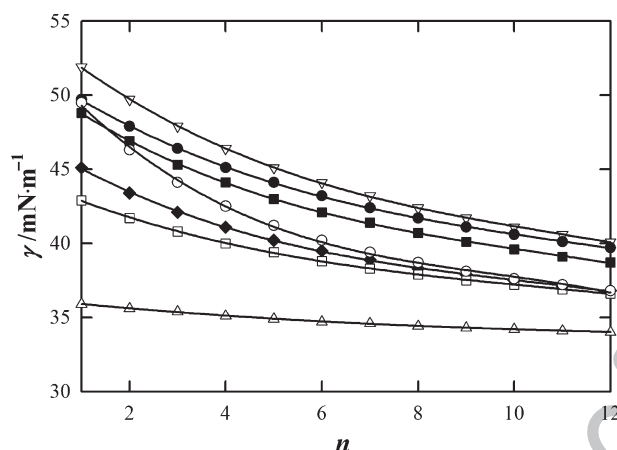
Experimental data for surface tensions of ionic liquids is very scarce and currently limited to imidazolium based ionic liquids. Typical values for surface tension are shown in Fig. 8 which shows that these ionic liquids have a lower surface tension than water ( $71.97 \text{ mN m}^{-1}$  at 298 K) but higher than many organics.

For the ILs having similar anion, the surface tension decreases with an increase in alkyl chain length of imidazolium cation and as is observed with organic solvents the decreases with increasing temperature.





D. Rooney et al.



**Fig. 8** Surface tension ( $\square$ ) at 298 K as a function of chain length,  $n$ , for a series of imidazolium based ionic liquids constituted with the following anion: *inverted open triangles*,  $[\text{C}_1\text{SO}_4]^-$ ; *filled circles*,  $[\text{C}_2\text{SO}_4]^-$ ; *filled squares*,  $[\text{PF}_6]^-$ ; *open circles*,  $[\text{CH}_3\text{COO}]^-$ ; *filled diamonds*,  $[\text{BF}_4]^-$ ; *open squares*,  $[\text{OTf}]^-$ ; *open triangles*,  $[\text{NTf}_2]^-$  [Au4]

509 When developing ionic liquids for a given purpose, if experimentally measured  
 510 surface tension data are not available, theoretical or empirical methods must be  
 511 used to establish if the surface tensions are within acceptable limiting values  
 512 defined in the design specifications. For this purpose prediction methods for surface  
 513 tension of ionic liquids are required.

514 Recently, Deetlefs et al. [18] attempted to predict the surface tension of ionic  
 515 liquids using parachors and available densities. More recently Gardas and Coutinho  
 516 [105] have shown that the QSPR correlation of Knotts et al. [106] can be extended  
 517 to ionic liquids for the estimation of surface tension. By applying this technique it  
 518 was possible to obtain good predictions for 361 literature data points for 38 imida-  
 519 zolium based ionic liquids containing  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ ,  $[\text{NTf}_2]^-$ ,  $[\text{OTf}]^-$ ,  $[\text{C}_1\text{SO}_4]^-$ ,  
 520  $[\text{C}_2\text{SO}_4]^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$ ,  $[\text{I}_3]^-$ ,  $[\text{AlCl}_4]^-$ ,  $[\text{FeCl}_4]^-$ ,  $[\text{GaCl}_4]^-$  and  $[\text{InCl}_4]^-$  as anions; the over-  
 521 all mean percentage deviation was 5.75% with a maximum deviation less than 16%.  
 522 The deviations obtained were surprising since the QSPR correlation for the parachors  
 523 was developed for neutral compounds and not for salts; it was thus developed without  
 524 taking Coulombic interactions into account.

## 525 1.6 Specific Heat Capacity

526 Heat capacity represents the relationship between energy and temperature for a specified  
 527 quantity of material. In general this value relates to the kinetic energy stored within  
 528 the vibrations of the molecule of interest and can be correlated to such. For example,  
 529 Strechan et al. [107] reported a predictive method for determining heat capacities



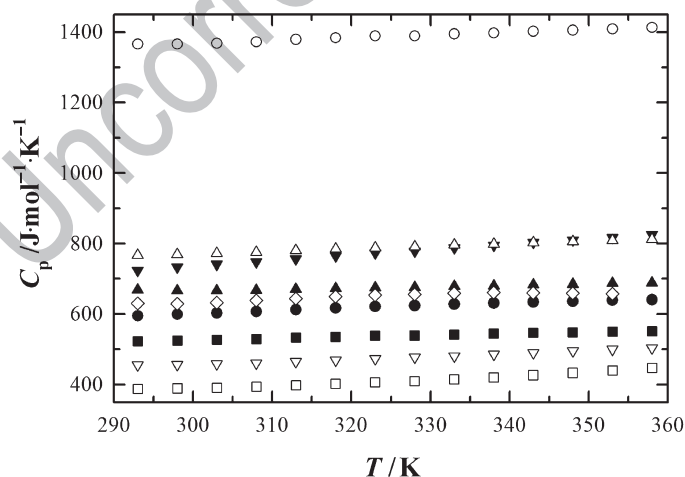


## Thermophysical Properties of Ionic Liquids

of six different ionic liquids by correlating this property with the intramolecular vibrational contribution where they reported a relative deviation of 0.9%.

The fact that these fluids are ionic should not have a significant effect on the specific heat capacity of ionic liquids and indeed reported values are in line with those one would expect for organic molecules. For example the heat capacity for chlorobenzene is  $152.1 \text{ J mol}^{-1} \text{ K}^{-1}$  or  $1.36 \text{ kJ kg}^{-1} \text{ K}^{-1}$  when written in terms of weight, is similar to that reported for  $[\text{C}_2\text{mim}][\text{NTf}_2]$ , i.e.,  $525 \text{ J mol}^{-1} \text{ K}^{-1}$  or  $1.34 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . When written in a molar basis the heat capacities of ionic liquids are generally higher than typical organic solvents which is expected given their relatively large molecular weights, for example, at 298 K the heat capacities of water, ethanol, nitromethane, benzene are between 75 and  $292 \text{ J mol}^{-1} \text{ K}^{-1}$  [108, 109].

Figure 9 shows an example of a number of ionic liquid heat capacities as a function of temperature. Here it is observed that an approximately linear relationship is obtained and a secondary relationship between the chain length of the  $[\text{C}_n\text{mim}][\text{NTf}_2]$  ionic liquids and heat capacity is also apparent. From the results of Ge et al. [110], each additional “ $-\text{CH}_2-$ ” group increases the heat capacity by approximately  $35 \text{ J mol}^{-1} \text{ K}^{-1}$  at 298 K which is similar to the observations made by Holbrey et al. [111] Archer et al. [112] and Paulechka et al. [113] who reported incremental increases in  $C_p$  of 40, 30 and  $31 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. Ge et al. [110] also reported measurements on the influence of impurities on the heat capacity where it was found that the heat capacity was lowered with increasing water or chloride and that this followed a linear relationship. Overall it was reported that for small chloride or water mass fraction contents, i.e., up to  $1 \times 10^{-3}$ , a decrease in the heat capacity of  $\approx 0.15\%$  or  $\approx 1.3\%$  on average when compared with the halide free or dried IL respectively was observed.



**Fig. 9** Heat capacities of ionic liquids as a function of temperature. *filled squares*,  $[\text{C}_2\text{mim}][\text{NTf}_2]$ ; *filled circles*,  $[\text{C}_4\text{mim}][\text{NTf}_2]$ ; *filled triangles*,  $[\text{C}_6\text{mim}][\text{NTf}_2]$ ; *inverted filled triangles*,  $[\text{C}_8\text{mim}][\text{NTf}_2]$ ; *open circles*,  $[\text{P}_{66614}][\text{NTf}_2]$ ; *open diamonds*,  $[\text{C}_4\text{mPyrr}][\text{NTf}_2]$ ; *open triangles*,  $[\text{C}_4\text{mPyrr}][\text{FAP}]$ ; *inverted open triangles*,  $[\text{C}_4\text{mim}][\text{OTf}]$ ; *open squares*,  $[\text{C}_2\text{mim}][\text{EtSO}_4]$  [110]





D. Rooney et al.

As expected, the larger the molecular weight of the ionic liquid, the larger the heat capacity. For example the heat capacity of  $[P_{66614}][NTf_2]$  has been reported as 1,366 J mol<sup>-1</sup> K<sup>-1</sup>, compared with 525 J mol<sup>-1</sup> K<sup>-1</sup> for  $[C_2mim][NTf_2]$  at 298 K. Similarly the choice of anion significantly changes the heat capacity for example  $[C_4mim][OTf] < [C_4mim][NTf_2]$  and  $[C_4mpyr][NTf_2] < [C_4mpyr][FAP]$  demonstrating again that the heat capacity increases with anion size. As found for other properties, such as density and viscosity [60], the anion type has a greater impact than the cation on the heat capacity.

Furthermore, Ge et al. [110] reported an extension to the Joback [114] and Benson [115] group contribution method, a model often used for the estimation of organic materials, by developing new contributions for the “-SO<sub>2</sub>-”, “P” and “B” groups which are commonly found in these liquids. This was tested against the heat capacities for a range of ionic liquids including measured values determined using a heat flux differential scanning calorimeter technique as described by Diedrichs and Gmehling [116]. As stated above, the Joback method is widely used to predict the ideal gas heat capacities of molecular compounds through application of following equation:

$$C_p^o(T) = \left[ \sum_{i=1}^k n_i A_{C_{pi}} - 37.93 \right] + \left[ \sum_{i=1}^k n_i B_{C_{pi}} + 0.210 \right] T + \left[ \sum_{i=1}^k n_i C_{C_{pi}} - 3.91 \times 10^{-4} \right] T^2 + \left[ \sum_{i=1}^k n_i C_{C_{pi}} - 2.06 \times 10^{-7} \right] T^3, \quad (5)$$

where  $A_{C_{pk}}$ ,  $B_{C_{pk}}$ ,  $C_{C_{pk}}$  and  $D_{C_{pk}}$  are group contribution parameters,  $n_i$  is the number of groups of type  $i$  in the molecule and  $T$  is the temperature in K. However, in order for Ge et al. [110] to apply this equation to ionic liquids, the principle of corresponding states (6) was required [115]:

$$\frac{C_p^r}{R} = \frac{C_p - C_p^o}{R} = 1.586 + \frac{0.49}{1 - T_r} + \omega \left[ 4.2775 + \frac{6.3(1 - T_r)^{\frac{1}{8}}}{T_r} + \frac{0.4355}{1 - T_r} \right]. \quad (6)$$

Equation (6) requires knowledge of the critical properties of the ionic liquids which have been discussed previously thereby making this approach more complex than other potential techniques. However despite the number of equations used a relative absolute deviation of 2.9% was observed when testing the model against 961 data points from 53 different ionic liquids reported. Overall this is highly versatile approach given the range of ionic liquids which can be generated using the groups available.

An alternative approach to that of Ge et al. [110] was adopted by Gardas and Coutinho [117]. In this study 2,396 data points for 19 ILs consisting of combinations of imidazolium, pyridinium and pyrrolidinium cations with a range of anions including  $[PF_6]^-$ ,  $[BF_4]^-$ ,  $[NTf_2]^-$ ,  $Br^-$ , and  $[OTf]^-$  anions, over a wide temperature range from 196.36 to 663.10 K was modeled using the method proposed by





## Thermophysical Properties of Ionic Liquids

Ruzicka and Domalski [118, 119]. The group contribution equation used in this study was

$$C_{pL} = R \left[ \sum_{i=1}^k n_i a_i + \sum_{i=1}^k n_i b_i \left( \frac{T}{100} \right) + \sum_{i=1}^k n_i d_i \left( \frac{T}{100} \right)^2 \right], \quad (7)$$

where  $R$  is the gas constant,  $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $T$  is the absolute temperature. Again  $n_i$  represents the number of groups of type  $i$ ,  $k$  the total number of different groups. The parameters  $a_i$ ,  $b_i$ , and  $d_i$  were reported for three cations, six anions as well as the  $-\text{CH}_2-$ ,  $-\text{CH}_3$  and dimethyl ammonium groups. Overall, a mean percent deviation of 0.36% and a maximum deviation of  $< 2.5\%$  was reported. Therefore this approach gives a slightly higher accuracy than that proposed by Ge et al. [110] although the range of ionic liquids which can be generated from the groups is significantly lower.

## 1.7 Thermal Conductivity

At present there are limited data available on the thermal conductivities of ionic liquids. Of those which have been reported, two main methods have been used for the measurement of this property, namely the transient hot wire method and the transient grating technique. In the former the measurements are made by heating a probe (containing a heating element and a thermoresistor) within the sample while simultaneously monitoring the temperature change of the probe. The latter technique does not directly measure the thermal conductivity but instead estimates this value from the measured thermal diffusivity and previously reported values for heat capacity and density. This difference in methods can lead to significant differences in the calculated thermal conductivities. For example, Frez et al. [120] calculated a value for the thermal conductivity of  $[\text{C}_4\text{mim}][\text{BF}_4]$  which was 15% lower when using the transient gradient approach than that reported by Van Valkenburg et al. [25] where the transient hot wire was used. It is expected that, as the transient grating technique requires additional properties, this method is more prone to errors and thus the transient hot wire method appears to be more accurate.

Reported values for ionic liquids using this technique indicate that ionic liquid thermal conductivities are similar to those of commonly used organic solvents. For example, Tomida et al. [121] determined the thermal conductivity for a series of  $[\text{C}_n\text{mim}][\text{PF}_6]$  salts and reported values for  $[\text{C}_4\text{mim}][\text{PF}_6]$  which compared well with those of benzene,  $0.145$  and  $0.16 \text{ W m}^{-1} \text{ K}^{-1}$ , respectively. In their study they also concluded that the thermal conductivity was not a strong function of temperature, pressure or chain length.

Ge et al. [122] used a similar technique for the measurement of 11 ionic liquids over the temperature range  $293\text{--}353 \text{ K}$ . In this study the thermal conductivities were found to be between  $0.1$  and  $0.2 \text{ W m}^{-1} \text{ K}^{-1}$ . Here a slight negative and linear relationship with temperature was observed. Similar to that reported by Tomida et al. [121], there







D. Rooney et al.

was no significant effect on the thermal conductivity by varying the alkyl chain length,  $n$ , of the  $[C_n\text{mim}]$  cation family. From these studies it appears that, while the chain length of a particular cation series does not appear to alter significantly the thermal conductivity, the choice of both cation and anion do have an effect. For example, when using the same  $[\text{NTf}_2]^-$  anion at 298 K the thermal conductivity of  $[\text{P}_{66614}]^+ > [\text{C}_4\text{mim}]^+ > [\text{C}_4\text{mpyr}]^+$ , 0.144, 0.128 and 0.125  $\text{W m}^{-1} \text{K}^{-1}$ , respectively. Whereas while keeping the cation as  $[\text{C}_4\text{mim}]^+$  the thermal conductivity of  $[\text{OTf}]^- \approx [\text{PF}_6]^- > [\text{NTf}_2]^-$ , 0.146, 0.145 and 0.128  $\text{W m}^{-1} \text{K}^{-1}$ , respectively. The fact that the  $[\text{P}_{66614}]^+$  ionic liquids have similar thermal conductivities to those of the 1-alkyl-3-methylimidazolium based liquids highlights that this property is independent of viscosity. These studies also indicate that the highest thermal conductivity is associated with  $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4]$ , 0.181  $\text{W m}^{-1} \text{K}^{-1}$  at 298 K, while the lowest is the  $[\text{C}_4\text{mpyr}][\text{FAP}]$  liquid, 0.106  $\text{W m}^{-1} \text{K}^{-1}$  at 298 K.

Ge et al. [122] also investigated the impact of both water and halide impurities where it was found that, in the case of small quantities, i.e., up to a mass fraction of 0.01 for water and 0.05 for halide (chloride), no significant effect on thermal conductivity was observed. Above this the thermal conductivity of the mixture could be modeled using the Jamieson correlation:

$$\lambda_m = w_1\lambda_1 + w_2\lambda_2 - \alpha(\lambda_2 - \lambda_1)(1 - w_2^{0.5})w_2, \quad \lambda_2 > \lambda_1, \quad (8)$$

where  $w_1$  and  $w_2$  are mass fractions and the adjustable parameter  $\alpha$  varied depending on the system and impurity chosen. For example, values of 0.42, 0.70 and 1.39 were obtained for the binary mixtures  $[\text{C}_2\text{mim}][\text{OTf}] + \text{water}$ ,  $[\text{C}_2\text{mim}][\text{C}_2\text{SO}_4] + \text{water}$  and  $[\text{C}_6\text{mim}][\text{NTf}_2] + [\text{C}_6\text{mim}]\text{Cl}$ , respectively.

The use of thermal conductivity, heat capacity and rheological properties for  $[\text{C}_2\text{mim}][\text{NTf}_2]$  was also shown by Chen et al. [123] to correlate with Shah's equation for forced convective heat transfer in the laminar flow regime, indicating that knowledge of these parameters can successfully be used to model heat transfer behavior of ionic liquid systems at the larger scale.

## 1.8 Conclusions

The topic of ionic liquids has grown significantly over the last number of years with the vast majority of this research focusing on their use as solvents for a wide range of chemical reactions. However none of these reactions would ever be industrially exploited without some knowledge of the physical properties of these materials. In an effort to address this problem the ionic liquid thermodynamic property database (IL Thermo) was developed and has grown considerably over recent years to contain a variety of important physical properties such as densities, viscosities, etc. This database shows that ionic liquids can have a wide range of properties depending on the choice of anion and cation. Many of these are intuitively what one would expect. For example, ionic liquids containing heavy inorganic anions will be denser





## Thermophysical Properties of Ionic Liquids

than those containing lighter organic anions. However, other properties such as melting points and viscosity are more difficult to predict from simple structural information. This review has focused on a number of key ionic liquid properties including those that define the liquid range, density, viscosity and surface tension as well as the main thermal properties of heat capacity and thermal conductivity. In each of these we have attempted to provide typical values as well as show the important factors which influence the observed trends. We have also discussed techniques by several groups which can be used to estimate these properties from simple structural information including methods such as group contributions, molecular descriptors and molecular dynamics approaches. Over the coming years as new data becomes available our understanding of the relationship between ionic liquid formulation and its physical properties will increase allowing us to design ionic liquids which maximize key desired attributes for any desired application.

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D. Rooney et al.

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# Author Queries

Chapter No.: 128\_TCC\_Ch32

Queries	Details Required	Author's Response
AU1	Kindly provide keywords.	
AU2	Please add a Tablenote to explain the meaning of the superscript a.	
AU3	There are two 'filled diamonds' in this caption. I assume one should be 'open diamond' - please change one of them.	
AU4	I think this is a corrupted symbol and not 'opensquares' (which is used later in the caption). Please insert correct symbol.	
AU5	Please either enter a valid range or just use the one page number (11296) if the reference is just a single page.	
AU6	Please enter a valid page range (with a lower number first and a higher number second).	
AU7	Kindly update reference 103.	



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