11 Physicochemical Properties of Ionic Liquids

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ABSTRACT

This chapter discusses the key relationships of the physicochemical properties of ionic liquids, particularly melting point, density, viscosity, and surface tension, including an assessment of the current situation and identifying trends for ionic liquids in the future.

11.1 INTRODUCTION

Today, scientific developments occur at the intersection, penetration, and integration of multiple disciplines: from here new research areas are opened up and new growth points for these disciplines are born. It is exactly this background that has led to the emergence of ionic liquids, which have provided new opportunities for the development of chemical technology. A significant amount of research on ionic liquids has been performed, from fundamental studies to application, due to their unique characteristics, such as non-volatility, excellent catalytic performance, and good solubility for many materials. These unique physical and chemical properties depend on the special microstructure and the complex interactions within the ionic liquid systems. However, there are thought to be at least a million types of possible ionic liquids and a trillion (10^{18}) types of mixed-liquid systems [1]. Therefore, it is very challenging to

screen and design functional ionic liquids for specific applications from the countless possible combinations of cations and anions. Anyone developing ionic liquids for technological applications must face this challenge, and there is always the danger that a competitor will chance upon a better choice. Hope lies in the major efforts now being made to model and predict the properties of ionic liquids [2], although such predictive methods will take much time to develop, and sometimes they are applicable only to several ionic liquids. So, currently, research on the physicochemical properties of ionic liquids has been closely combined with development of their applications.

Along with the continuing emergence of new research on ionic liquids, producing huge amounts of data describing their properties, easy access to the exponentially increasing number of publications on ionic liquids during the past decade necessitates a comprehensive data collection of as many properties as possible. However, a large amount of data is dispersed in various journals, reports, books, patents, and so on. Some scientific research associations or companies have established databases of ionic liquid physicochemical properties in order to aid systematic evaluation and analysis, such as ILThermo [3], Institute of Process Engineering (IPE) (Chinese Academy of Sciences, Beijing) [4], Merck (Germany) [5], DDBST [6], and DelphIL [7]. According to incomplete statistics, there are more than 2000 different ionic liquids that have been synthesised during the last 20 years [4]. From Figure 11.1, imidazolium ionic liquids are the most popular ionic liquids extensively investigated by both academia and industry: the structures of other common cations are shown in Table 11.1, which account for 800, or about one-third of total number of ionic liquids. These ionic liquid databases provide access to the scientific data needed to refine universal property relationships, reveal the inner relationship between microscopic structure and macroscopic properties, design new ionic liquids effectively, and develop applications for ionic liquids.

In the following sections, we will discuss the key relationships of the physicochemical properties of ionic liquids, especially melting point, density,
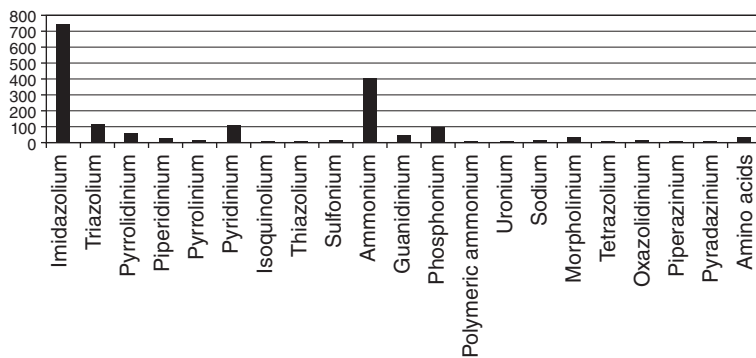

Figure 11.1   The distribution of different types of ionic liquids [4].

TABLE 11.1 The Structures of Common Cations found in Ionic Liquids

Entry	Name of Cations	Structure	Entry	Name of Cations	Structure
1	1-Alkylimidazolium		14	Phosphonium	
2	1,3-Dialkylimidazolium		15	Sodium[a]	Na$^+$
3	Trialkylimidazolium		16	Morpholinium	
4	Tetraalkylimidazolium		17	Tetrazolium	
5	Pentaalkylimidazolium		18	Oxazolidinium	
6	Double imidazolium		19	Amino acids	
7	Triazolium		20	Isoquinolinium	

(*Continued*)

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TABLE 11.1 (Continued)

Entry	Name of Cations	Structure	Entry	Name of Cations	Structure
8	Pyrrolidinium		21	Sulfonium	
9	Piperidinium		22	Uronium	
10	Pyrrolinium		23	Piperazinium	
11	Pyridinium		24	Pyridazinium	
12	Ammonium		25	Polymeric ammonium	
13	Guanidinium				

[a] The anions Na$^+$ salts are [M(TiW$_{11}$O$_{39}$)$_2$]$_{13}^-$ (M = La, Ce, Pr, Sm, Gd, Dy, Er, Tm, Yb) and [MTiW$_{11}$O$_{39}$]$_5^-$ (M = Cr, Mn, Fe, Zn).

TABLE 11.2   The Properties and Data Points for Ionic Liquids

Entry	Physicochemical Properties	Data Points
1	Melting point	1473
2	Glass transition temperature	755
3	Crystallisation temperature	27
4	Decomposition temperature	910
5	Solid–solid transition temperature	55
6	Freezing point	85

viscosity, and surface tension, including an assessment of the current situation and identifying trends for ionic liquids in the future.

11.2   MELTING POINT

Melting point is one of most important properties of ionic liquids, and also one of the most reported phenomena. However, up to now, the collected data of melting points are only around 1400 (see Table 11.2); but many ionic liquids have no melting points, instead exhibiting a glass transition temperature. To complicate matters further, many room-temperature ionic liquids also exist as supercooled liquids, occasionally for extended periods of time (days or even weeks). For example, $[C_2mim][BF_4]$ exists as a supercooled liquid below the melting point [8]. As a result, melting point determinations are not always straightforward and some compounds may be incorrectly considered to be liquids if care is not taken during the course of the investigation [9]. Accurate values for melting points for ionic liquids are scarce as, like in the case of inorganic salts, melting point and glass transition temperatures can be strongly affected by the presence of impurities [10]. The presence of water, organic solvents (hexane, ethanenitrile, benzene, etc.), and halide impurities, even in small concentrations, has been long understood to alter the physical properties of ionic liquids [11–15]. Wilkes and coworkers investigated the freezing–melting behaviour of $[C_2mim][BF_4]$, $[C_4mim][BF_4]$, and $[C_3C_1mim][NTf_2]$. Contamination of ionic liquids by water and metal cations has variable impact on their freezing exotherms. But chloride impurities had little effect on the freezing–melting behaviour of the studied ionic liquids [16]. So, in our database, $[C_2mim][BF_4]$ has eight different melting points, ranging from 279.15 to 288.15 K, and $[C_2mim][NTf_2]$ has even 10 different melting points ranging from 252.15 to 270.15 K [4].

Figure 11.2 shows the melting points range of different series of ionic liquids. Up to now, it is known that the melting point of trialkylimidazolium ionic liquids is highest, with the melting point of 1,3-dimethyl-2-phenylimidazolium bromide at 556.15 K [17]. $[N_{1\ 8\ 8\ 8}][Me_3CC(O)CHC(O)(CF_2)_2CF_3]$ has the lowest melting point at 177.15 K [18].
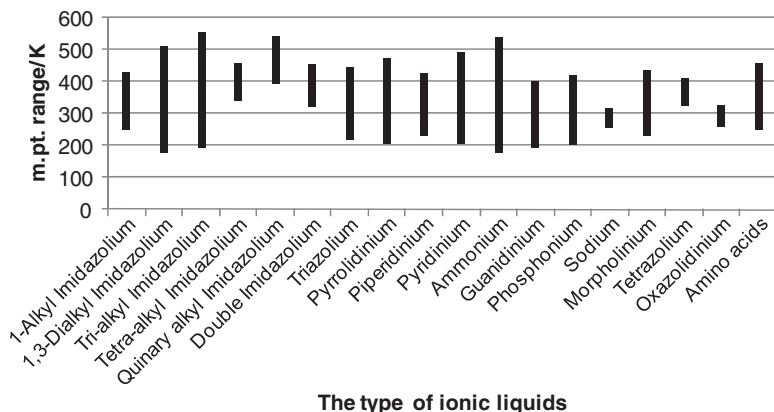
Figure 11.2   The melting point ranges of typical series of ionic liquids.

The melting point (T_{m}) of an organic molecular compound is determined by the strength of its crystal lattice, which is controlled by three main factors: molecular symmetry, intermolecular forces, and conformational degrees of freedom of the molecule; this principle is also applicable to ionic liquids. Qualitatively, reducing ion symmetry, increasing the ion conformational degrees of freedom (e.g., utilising flexible substituents), and improving the charge distribution of the cation and/or anion are effective approaches for reducing the lattice energy of the salts, thus resulting in low melting materials [19]. This principle can be used in various types of ionic liquids. Detailed descriptions can be found in a large number of papers [20–25].

Up to now, the most popular family of ionic liquids are those ionic liquids based on the imidazolium cations. The modern resurrection of ionic liquid chemistry, in general, is largely due to the unusually low melting point of many imidazolium salts, and can be traced to the seminal report of Wilkes and Zaworotko [26]. As a result, an enormous number of different alkyl groups and anions have been explored. So, the melting point principle of imidazolium-based ionic liquids is more detailed than the other ionic liquids.

Several significant papers have discussed the melting point trend of alkyl substitution on methylimidazole [9, 24, 25], so the subject requires little detailed repetition. The smallest alkyl groups (methyl, ethyl, or propyl) result in salts having higher melting points, often being solids at room temperature. As can be seen in Figure 11.3, when the alkyl chain becomes longer (butyl to octyl), the melting point decreases and usually reaches a minimum somewhere in the range from butyl to octyl. Beyond this point, the melting point again increases until, with a much longer alkyl group (tetradecyl and higher), liquid crystalline compounds are often obtained. The most accepted explanation is that longer alkyl chains decrease the symmetry of the imidazolium cation and thereby interfere in efficient crystal packing: Coulombic forces are responsible for
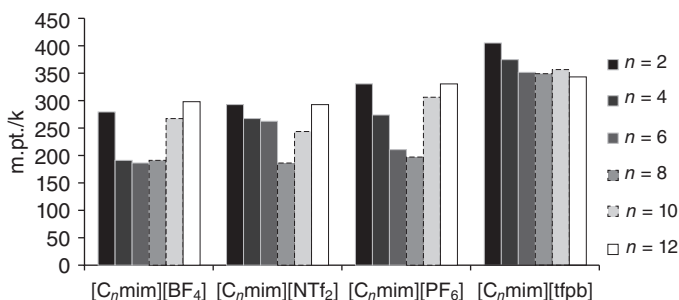
Figure 11.3 The effect of alkyl chain length on the melting points of 1-alkyl-3-methylimidazolium ionic liquids.

TABLE 11.3 The Melting Points of Ionic Liquids, [A][X]

Entry	Cation (A)	Anion (X)	m.pt./K	Reference
1	Hmim	Cl	345.15	27
2	C_1mim	Cl	398.15	28
3	C_1C_1mim	Cl	462.15	29
4	Hmim	Br	314.15	27
5	C_1mim	Br	382.65	30
6	C_2im	Cl	331.15	27
7	C_2mim	Cl	362.15	21
8	C_2C_1mim	Cl	461.15	21
9	Hmim	NTf_2	282.15	27
10	C_1mim	NTf_2	295.15	31
11	C_2mim	NTf_2	270	31
12	C_2C_1mim	NTf_2	293	31

much of the attractive forces in shorter alkyl group ionic liquids, and van der Waals forces are responsible for much of the attractive forces in the longer alkyl group ionic liquids. Anything that interferes in packing should decrease the melting point. When the alkyl chains are sufficiently long to become a significant component, the attractive van der Waals forces will lead to a steady increase in melting point.

Usually, an increase in molecular weight and the accumulation of charge causes an increase in the melting point. From Table 11.3, we can see that the addition of one methyl group may increase the melting point of an ionic liquid by 20–100 K. For example, the melting point of $[C_2C_1mim][NTf_2]$ is 23 K greater than that of $[C_2mim][NTf_2]$, and the melting points of $[Hmim]Cl$, $[C_1mim]Cl$, and $[C_1C_1mim]Cl$ are 345.15, 398.15, and 462.15 K, respectively.

The increased branching of the alkyl group results in melting points higher than the linear analogues. An isopropyl group instead of an *n*-propyl group increases the melting point by 82 °C. Thus, [$^iC_4$mim][PF$_6$] (432.85 K) and [$^iC_3$mim][PF$_6$] (375.15 K) have higher melting points than [$^sC_4$mim][PF$_6$] (356.45 K) and [C$_3$mim][PF$_6$] (322.15 K), while [$^sC_4$mim][PF$_6$] (356.45 K) in turn has a higher melting point than simple [C$_4$mim][PF$_6$] (265.15 K) [3].

These principles are also applicable to other types of ionic liquids, such as pyridinium-based ionic liquids, ammonium-based ionic liquids, and phosphonium-based ionic liquids. Beyond simple alkyl groups, an increasing number of functionalised side chains have been reported: partially fluorinated alkyl groups have the tendency to increase the melting point slightly over their non-fluorinated counterparts. The ester, nitrile, amide, ether, or hydroxyl modified ionic liquids have melting points that are little different from those of the simple alkyl ionic liquids with similar molecular weight. As a result, there is not a clear correlation between the functionalisation of an ionic liquid and its melting point.

Explaining the anion effect is more difficult, owing to the presence of water and its interactions with the cation and anion. As is shown in Figure 11.4, imidazoles neutralised with HCl, HNO$_3$, or HBr gave relatively high values of T_m. In contrast, salts neutralised with bis{(trifluoromethyl)sulfonyl}amidic acid (HNTf$_2$) and bis{(pentafluoroethyl)sulfonyl}amidic acid (HNPf$_2$) were obtained as liquids [27]. For ionic liquids containing structurally similar anions
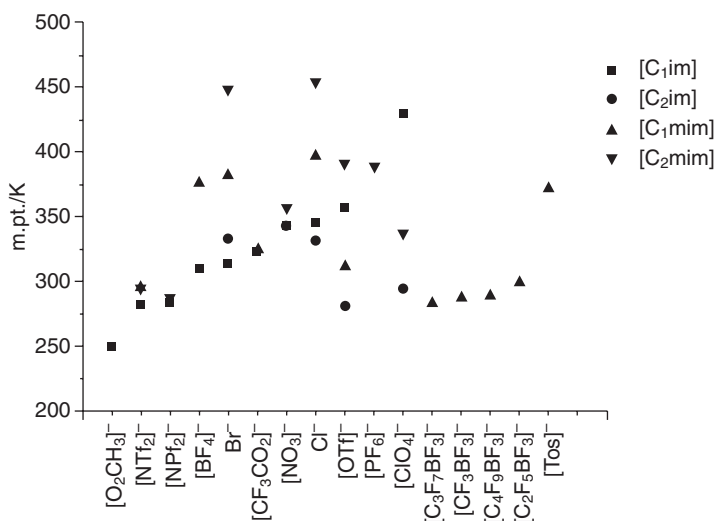

Figure 11.4 The melting points of imidazolium-based ionic liquids.

such as triflate ($[OTf]^-$) and $[NTf_2]^-$, the lower melting point of the $[NTf_2]^-$ salt could be attributed to electron delocalisation and the anion's inability to hydrogen-bond. In a similar manner, differences between $[C_2mim][CF_3CO_2]$ and $[C_2mim][C_1CO_2]$, besides the former having a melting point of 31 °C lower than the latter, can undoubtedly be attributed to the presence of fluorine atoms on that anion and their interaction with other anions and the cation. The melting point for $[C_2mim][NO_2]$ is 17 °C higher than that for $[C_2mim][NO_3]$, suggesting that anion structure also contributes to the thermal properties [26].

In order to investigate ionic liquid structural features that could lead to low melting point salts, several methods have been used in attempts to make quantitative predictions of their melting points, such as quantitative structure–property relationships (QSAR) [32–34], molecular mechanics (MM) simulations, as well as modifying "hole theory" or the "Parachor" [35–39]. However, these methods all have significant drawbacks, which limit their application for predicting the properties of unknown salts. These include the need for large experimental data sets to derive correlations, time-consuming computational methods, or the need for at least some experimental data from the ionic liquid under study [40]. Recently, Krossing and coworkers showed that the relatively low melting points of ionic liquids can be understood by a simple thermodynamic cycle based on lattice and solvation energies [41]. They 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 [40, 42]. These were calculated using a combination of volume-based thermodynamics and quantum chemical calculations for the lattice free energies and the COSMO-RS (**CO**nductor-like**S**creening**MO**del for Real Solvents) solvation model. The two methods, the volume-based model (only ion volumes, σ, and τ as input) and the augmented method (using ion volumes, σ, τ, and COSMO-RS output), were tested on several sets of ionic liquids, and a combination of all sets (67 ionic liquids) that span an experimental melting temperature range of 337 °C. The average error of the simpler, volume-based model is 36.4 °C and that of the augmented method is 24.5 °C. This method has no need for experimental input or tedious simulations, but relies on simple calculations feasible with standard quantum chemical program codes, and may further be augmented by COSMO-RS.

11.3 DENSITY

Density is an important physicochemical and crucial for the design of many technological processes, especially for the simulation of heat and mass transfer, and hydrodynamics calculations. Up to now, the total level of density data in ILThermo from IUPAC [3] and other databases [4] are 28.8% and 24.2%, respectively. In addition to some ionic liquids with cations of imidazolium,
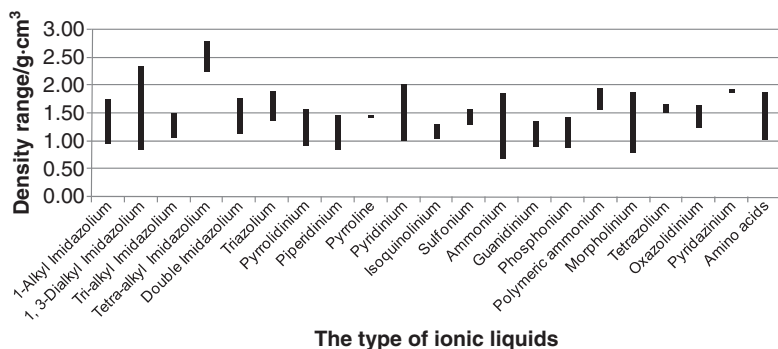
Figure 11.5 The density range of different types of ionic liquids [4].

pyrrolidinium, piperidinium, quaternary ammonium, guanidinium, quaternary phosphonium, and morpholinium, which densities lie in the range of 0.6–0.97 g cm^{-3}, almost all ionic liquids possess a density greater than 1 g cm^{-3}, some being close to, or more than, 2 g cm^{-3} at 298.15 K (see Figure 11.5). This means that they can fully play a role as separation media in two-phase applications.

In terms of the designability of ionic liquids, the density is relatively easy to modulate and is influenced little by temperature shifts or impurities, such as halide, water, or solvent from the synthetic process. For pure ionic liquids, the values of density vary depending on the choice of cation and anion. Table 11.4 has listed several conventional ionic liquids, which are easy to analyse; these data reveal that the cationic structure influences the densities significantly. Generally, when connected with the same anion, the densities decrease progressively with increasing alkyl chain length of the cation, for example, for [C$_n$mim]X (X = [BF$_4$], [PF$_6$], or [NTf$_2$]). Figure 11.6 shows that the densities of the ionic liquids tend to approach those of linear alkanes, suggesting that the densities of those tail chains are promoted as n increases. This may be because elongating the alkyl chain length increases the free volume within the ionic liquid, accordingly lowering its density. And this principle applies not only to imidazolium ionic liquids but also to pyridinium and quaternary ammonium ionic liquids.

The anion has a more remarkable influence to the density of ionic liquids. For the ionic liquids with cation [C$_4$mim]$^+$, the densities increase in the order

$$[C(CN)_3]^-, [O_2CMe]^-, [N(CN)_2]^-, [O_3SOC_8]^- < Cl^- < [NO_3]^-$$
$$< [BF_4]^-, [O_3SOC_2]^-, [CF_3CO_2]^- < [O_3SOC_1]^- < [AlCl_4]^-$$
$$< [OTf]^- < Br^- < [C_3F_7CO_2]^- < [PF_6]^- < [FeCl_4]^- < [NTf_2]^-,$$
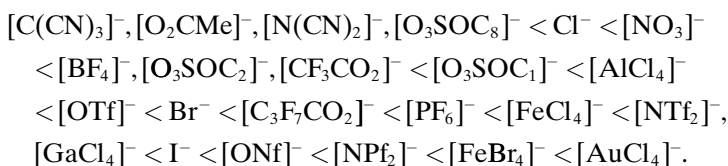$$[GaCl_4]^- < I^- < [ONf]^- < [NPf_2]^- < [FeBr_4]^- < [AuCl_4]^-.$$

TABLE 11.4 The Densities of Conventional Ionic Liquids at 298.15 K

Ionic liquid	ρ/g·cm^{-3}	Reference	Ionic liquid	ρ/g·cm^{-3}	Reference
[C$_1$mim][BF$_4$]	1.373	31	[C$_1$mim][NTf$_2$]	1.559	56
[C$_2$mim][BF$_4$]	1.28	8		1.570	37
	1.279	43		1.580	31
	1.280	37	[C$_2$mim][NTf$_2$]	1.51	80
	1.27	44		1.518	43
[C$_3$mim][BF$_4$]	1.24	8, 37, 45		1.519	37, 61
[C$_4$mim][BF$_4$]	1.19	46		1.515	52
	1.21	8		1.523 (293 K)	43
	1.17	47	[C$_3$mim][NTf$_2$]	1.475	61
	1.21105	48		1.473	81
	1.2012	49	[C$_4$mim][NTf$_2$]	1.43	20, 47
	1.208	50		1.436	52, 61, 68, 73
	1.19735	51		1.437	37, 82
	1.199	52		1.433	31
[C$_6$mim][BF$_4$]	1.16	45		1.429	56
	1.177	31		1.44 (293 K)	83
	1.1453	53		1.439 (293 K)	84
	1.101	54	[C$_5$mim][NTf$_2$]	1.403	61
[C$_8$mim][BF$_4$]	1.08	55		1.412	85
	1.11	50, 56, 57	[C$_6$mim][NTf$_2$]	1.372	61
	1.092	54		1.304	56
	1.10	58		1.378	31
	1.1019	49		1.364	54
[C$_{10}$mim][BF$_4$]	1.04	55, 59	[C$_7$mim][NTf$_2$]	1.357	73
	1.072	56		1.377	57
[C$_4$mim][PF$_6$]	1.35	20, 60	[C$_8$mim][NTf$_2$]	1.344	61
	1.368	61, 62		1.32	61
	1.3674	63		1.317	68
	1.36657	64		1.319	52
	1.35876	51		1.321	37, 73, 86
	1.36	58, 65		1.337	31

(Continued)

TABLE 11.4 (*Continued*)

Ionic liquid	$\rho/\text{g·cm}^{-3}$	Reference
[C$_6$mim][PF$_6$]	1.29	20
	1.292	52, 61
	1.2937	66
	1.2941	67
	1.302	68
[C$_7$mim][PF$_6$]	1.262	61
	1.274	69
[C$_8$mim][PF$_6$]	1.22	37
	1.234	52
	1.2357	66
	1.237	61, 69
[C$_9$mim][PF$_6$]	1.212	61
[C$_{10}$mim][PF$_6$]	1.14	59
[C$_4$mim]Cl	1.08	20, 60
	1.10	56, 58
[C$_4$mim]Br	1.32	58
[C$_4$mim]I	1.44	20, 60
[C$_4$mim][O$_3$SOC$_1$]	1.2	56
	1.2074	70
	1.2057	71
	1.211	52
[C$_4$mim][O$_3$SOC$_2$]	1.19893	72
[C$_4$mim][O$_3$SOC$_8$]	1.072	73
	1.0676	49
[C$_4$mim][AlCl$_4$]	1.2380	74, 75
	1.24	56
[C$_4$mim][FeCl$_4$]	1.3651	76
	1.38	37
[C$_4$mim][GaCl$_4$]	1.43	77
[C$_4$mim][AuCl$_4$]	2.146	78, 79
	2.350	78, 79
[C$_4$mim][FeBr$_4$]	1.98	37, 77

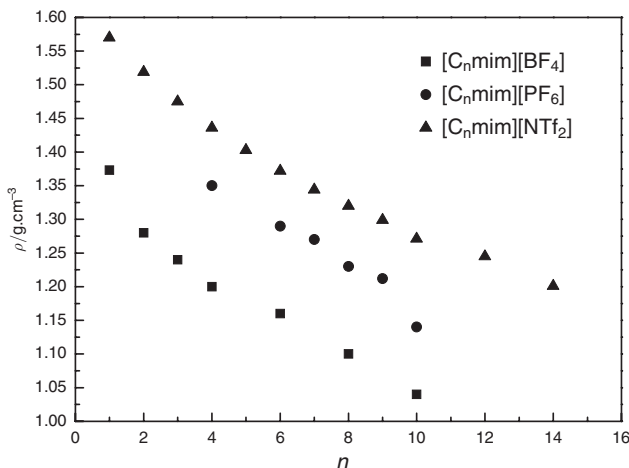| Ionic liquid	$\rho/\text{g·cm}^{-3}$	Reference
[C$_9$mim][NTf$_2$]	1.299	61
[C$_{10}$mim][NTf$_2$]	1.271	61, 81
	1.279	73
	1.278	52
	1.245	52
[C$_{12}$mim][NTf$_2$]	1.131	54
[C$_{14}$mim][NTf$_2$]	1.201	52
[^{i}C$_4$mim][NTf$_2$]	1.428 (293 K)	87
[C$_2$F$_3$mim][NTf$_2$]	1.656 (293 K)	37, 87
[C$_4$mim][C(CN)$_3$]	1.0473	88
[C$_4$mim][N(CN)$_2$]	1.06	56
[C$_4$mim][NO$_3$]	1.058	54
	1.059	73
	1.159	54
	1.1565	89
[C$_4$mim][NPf$_2$]	1.514	37
[C$_4$mim][OTf]	1.29	56, 57
	1.296	68
	1.2976	53
	1.299	52
	1.3	54
[C$_4$mim][ONf]	1.473	56
[C$_4$mim][O$_2$CMe]	1.06	56
	1.053	52
[C$_4$mim][CF$_3$CO$_2$]	1.198	31
	1.209	57
	1.068	73
	1.217	90
[C$_4$mim][C$_3$F$_7$CO$_2$]	1.333	91, 92

Figure 11.6   The densities of the ionic liquids vs. the chain length of cations.

The densities of ionic liquids with halides increase in the order of increasing volume, that is, $Cl^- < Br^- < I^-$, and $[FeCl_4]^- < [FeBr_4]^-$. However, for $[O_3SOC_n]^-$, which exhibits similar volume increases, the trend is the other way round, and the densities increase in the order $[O_3SOC_8]^- < [O_3SOC_2]^- < [O_3SOC_1]^-$. This result suggests that increasing the number of the carbon chain unit in anion decreases the densities of ionic liquids. This is the same trend observed for the cations. The results for the anions with similar structure, for example, $[AlCl_4]^-$, $[FeCl_4]^-$, $[GaCl_4]^-$, and $[AuCl_4]^-$, are caused by the difference in the mass of the central atom. It is generally believed that the densities of those ionic liquids with large volume, weak anions are relatively high, and that this trend has nothing to do with the cation. Therefore, when designing ionic liquids with different densities, the first selection should be an appropriate anion to determine the approximate density range, and then fine-tune this value through the choice cation.

Krossing and coworkers noticed a strong relationship between the molecular volumes V_m of ionic liquids and their fundamental physical properties: density, viscosity, and conductivity [40]. The molar concentration of ionic liquids is related to V_m by a power series, which leads to the relationship between V_m and the density, Equation (11.1),

$$\rho = MgV_m^{-h}, \tag{11.1}$$

where M is the molar mass, and g and h are empirical constants of best fit. This correlation is applicable to a wide variety of ionic liquids. However, the molar concentrations of the nitrile-functionalised ionic liquids do not fit with the data for the other salts. It is likely that functionalisation significantly changes the

intermolecular interactions in the ionic liquid, and that this strongly affects the density changes that occur in the ionic liquids with temperature change, and during phase transitions [40].

Generally, it can be readily observed that an increase in temperature causes density to decrease, with a basically linear relationship, a trend almost universally observed. For example, Jacquemin et al. used this to calculate the density of ionic liquids at different temperatures, Equation (11.2) [93],

$$\rho = a + b(T - 273.15), \tag{11.2}$$

where T is temperature (°C), a is a coefficient, and b is the density coefficient (in g cm^{-3} K^{-1}). There are also some workers who used quadratic equations to fit the variation with temperature [94–97],

$$\rho = \sum_{i=0}^{2} a_i T^i. \tag{11.3}$$

Gardas and Coutinho [99] proposed an extension, Equation (11.4), to the Ye and Shreeve method [98] for the estimation of density over a wide range of temperatures and pressures,

$$\rho = \frac{M}{NV(a + bT + cP)}, \tag{11.4}$$

where ρ is the density, M is molecular weight, N is the Avogadro constant, and a, b, and c are coefficients. This estimation method for density was subsequently utilised elsewhere [88, 95, 100]. The Tait equation [101] has also been used to fit density at different temperatures and pressures [94, 96, 97, 102]:

$$\rho = \frac{\rho(T, P = 0.1 \, \text{MPa})}{\left\{ 1 - C \ln \frac{(B + P)}{(B + 0.1)} \right\}}, \tag{11.5}$$

where $\rho(T, P = 0.1 \, \text{MPa})$ is obtained from Equation (11.2) or Equation (11.3), and the coefficient B is defined as $B = b_1 + (b_2/T)$. The coefficients b_1, b_2, and C are obtained by fitting the Tait equation to experimental data.

11.4   VISCOSITY

Viscosity is another important property for ionic liquids. As with density, the fluid design of liquid–liquid extractors, distillation columns, reactors, process piping, and other units found in various chemical and pharmaceutical industries requires knowledge of the viscosities of fluids. At room temperature, ionic liquids display a broad range of viscosities, from 10 to several 1000 cP (even
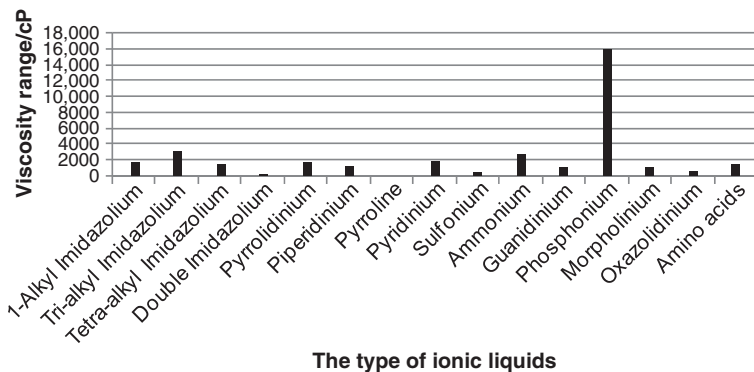
Figure 11.7 The viscosity range of different types of ionic liquids. The data are from Reference 4.

several 10,000 cP) and significantly higher (see the Figure 11.7). Thus, the viscosities are usually higher by one to three orders of magnitude compared with traditional organic solvents. This brings many negative influences for the chemical industry operating processes and could become a limiting factor for ionic liquid scale-up applications. In fact, ionic liquids can be used with mixing solvents with lower viscosities in the actual process, lowering the high viscosity of ionic liquids, and often the reactants will also have this effect. In other applications, the higher viscosities of ionic liquids may be favourable, for example, lubrication or supported membrane separation [10].

The viscosity of ionic liquids is different from the density, in that it shows a remarkable influence of both temperature and impurity: a small increase in temperature or the presence of a trace of impurities can result in dramatic decreases in viscosity. It is now believed that the main impurity sources in room-temperature ionic liquids are the water content and the organic solvent content. So after measuring the viscosity, it is important to immediately measure the water content of the ionic liquid using Karl–Fischer titration or coulometry. In addition, investigations from Queen's University Ionic Liquid Laboratories (QUILL) suggested that the presence of even low concentrations of chloride in the ionic liquids substantially increases the viscosity, and in all cases, the viscosity increased dramatically with the concentration of chloride ions [11].

It is well known that hydrogen bonding can cause proton chemical shifts to move to lower field in nuclear magnetic resonance (NMR) spectra. The increase in viscosity is related to an increase in the cohesive forces via hydrogen bonding between the chloride and the protons of the imidazolium ring. This is the reason for different viscosities of the same ionic liquid in Table 11.5.

Viscosity is mainly determined by a combination of van der Waals forces, hydrogen bonding, and Coulombic interactions. The effect of cation head groups on viscosity can be seen from Table 11.5:

TABLE 11.5 The Viscosities of Conventional Ionic Liquids at 298.15 K

Ionic Liquids	η/mPa·s	Reference	Ionic Liquids	η/mPa·s	Reference
[C$_2$mim][BF$_4$]	78	58	[C$_2$mim][NTf$_2$]	36.5	73
	37	8, 37, 103		45.9	111
	42	45		33	112
	38	104		34.2	113
	66	56		34.7	114
	54.4	105		37	57
[C$_3$mim][BF$_4$]	103	8, 37, 45	[C$_4$mim][NTf$_2$]	32.1 (293 K)	115
[C$_4$mim][BF$_4$]	219	20, 46, 57, 60		54.5	46
	180	8, 37, 45		69	20
	233	50, 56		80	56
	248	58		35.9	116
[C$_5$mim][BF$_4$]	308	85		50.5	73
[C$_6$mim][BF$_4$]	220	45		45.6	113
	310	50, 56		52 (293 K)	47, 83, 87, 117
	380	58		52	57
[C$_8$mim][BF$_4$]	440	50, 56	[C$_5$mim][NTf$_2$]	59	85
	492	58	[C$_6$mim][NTf$_2$]	80.1	73
	439	57		71	57
[C$_{10}$mim][BF$_4$]	930	56	[C$_8$mim][NTf$_2$]	80.7	118
[C$_3$mim][PF$_6$]	312	106		69.7	37
	450	107		90.37	119
	371	108		95	73

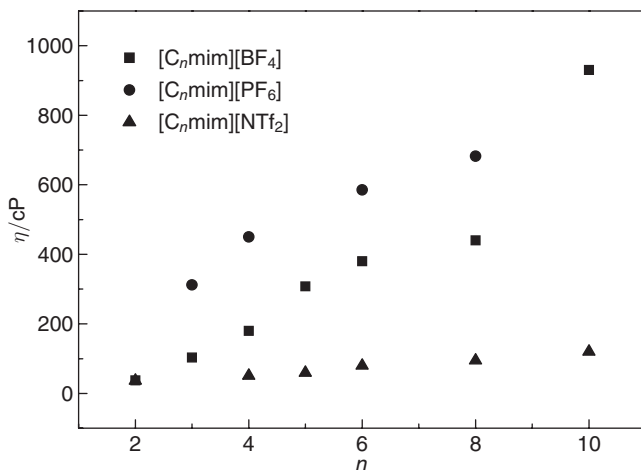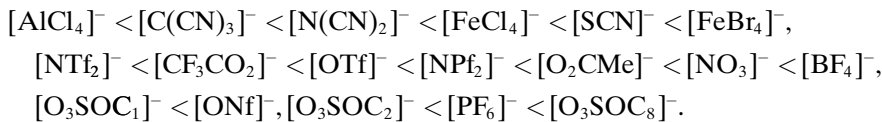| Compound		Ref.	Compound		Ref.
[C$_4$mim][PF$_6$]	450	20		87	57
	393	109		92.51	86
	397	60		90	37
[C$_6$mim][PF$_6$]	493	58	[C$_{10}$mim][NTf$_2$]	120.2	73
	560	109		88	37
[C$_8$mim][PF$_6$]	585	20, 57	[C$_4$mim][NTf$_2$]	83 (293 K)	87
	682	20, 57	[C$_2$F$_3$mim][NTf$_2$]	248 (293 K)	87
	710	109	[C$_4$mim][NPf$_2$]	111.6	37
	810	56	[C$_4$mim][O$_2$CMe]	139.7	73
[C$_4$mim]Cl	3950 (303 K)	110	[C$_4$mim][CF$_3$CO$_2$]	70	120
[C$_4$mim]Br	Solid	58		76.9	90
[C$_4$mim]I	Solid	58	[C$_4$mim][OTf]	90	56
[C$_4$mim][O$_3$SOC$_1$]	1110	20, 56, 60		83.2	73
	180	56	[C$_4$mim][ONf]	373	56
	188	73	[C$_4$mim][NO$_3$]	165.27	89
	213	72	[C$_4$mim][SCN]	51.7	121
[C$_4$mim][O$_3$SOC$_1$]	379.1	72	[C$_4$mim][N(CN)$_2$]	37	56, 121
[C$_4$mim][O$_3$SOC$_8$]	888.6	73		28.8	73
[C$_4$mim][AlCl$_4$]	26	56	[C$_4$mim][C(CN)$_3$]	31.802	88
[C$_4$mim][FeCl$_4$]	34	37		27.318	88
[C$_4$mim][FeBr$_4$]	62	37			

Figure 11.8 The viscosities of the ionic liquids vs. the chain length of cations.

1. It seems that the viscosities of the ionic liquids $[C_n mim]X$ ($X = [BF_4]$, $[PF_6]$, or $[NTf_2]$) increase progressively with increasing alkyl chain length of the cation (see Figure 11.8). This result is contrary to the effect on densities because van der Waals interaction increases with increasing alkyl chain length.

2. It can be seen clearly by comparing the results for $[^iC_4 mim][NTf_2]$ and $[C_4 mim][NTf_2]$ that branching the alkyl chain reduces the rotational freedom and hence makes the ionic liquids more viscous.

3. As with density, the introduction of other elements or functionalities on to the cation may either increase or reduce the van der Waals interaction, thus increasing or reducing the viscosity of the ionic liquids. For example, introducing groups containing fluorine increases the viscosity significantly, cf., $[C_2 mim][NTf_2]$ and $[C_2 F_3 mim][NTf_2]$ (see Table 11.5).

The effect of anion head groups on viscosity can also be seen from Table 11.5. For ionic liquids with the cation $[C_4 mim]^+$, the viscosities increase in the order

$$[AlCl_4]^- < [C(CN)_3]^- < [N(CN)_2]^- < [FeCl_4]^- < [SCN]^- < [FeBr_4]^-,$$
$$[NTf_2]^- < [CF_3 CO_2]^- < [OTf]^- < [NPf_2]^- < [O_2 CMe]^- < [NO_3]^- < [BF_4]^-,$$
$$[O_3 SOC_1]^- < [ONf]^-, [O_3 SOC_2]^- < [PF_6]^- < [O_3 SOC_8]^-.$$

For the ionic liquids containing the anion $[O_3 SOC_n]^-$, the viscosities increase progressively with increasing alkyl chain length in the order (the same effect as noted with alkyl chains on the cation)

$$[O_3SOC_1]^- < [O_3SOC_2]^- < [O_3SOC_8]^-.$$

The viscosities of ionic liquids containing fluorinated alkyl chains became higher due to strong van der Waals interaction, such as in the series

$$[OTf]^- < [ONf]^-, [NTf_2]^- < [NPf_2]^-.$$
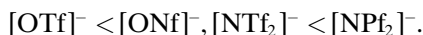
Although the ionic liquids with the $[NTf_2]^-$ anion, also containing a fluorinated alkyl chain, have strong van der Waals interaction, their viscosities are actually lower than other conventional ionic liquids. This is possibly because the reduced degree of the viscosity caused by the weak hydrogen bonds surpasses the increased degree of the viscosity caused by the van der Waals interactions. The results for the anions with similar structure, for example, $[AlCl_4]^-$ and $[FeCl_4]^-$, may be due to the difference in the mass of the central atom. This result was similar for densities.

The viscosities of ionic liquids may be reduced by methods other than structure modification. For example, the viscosities of ionic liquids can be decreased markedly with increasing temperature. Gardas and Coutinho developed a group contribution method for the viscosities of ionic liquids using an Orrick–Erbar approach, Equation (11.6) [99], and the viscosities of 29 ionic liquids were fitted:

$$\ln \frac{\eta}{\rho M} = A + \frac{B}{T}, \tag{11.6}$$

where η and ρ are the viscosity and density, respectively, M and T are the molecular weight and absolute temperature, respectively, and A and B are adjustable coefficients. However, the Orrick–Erbar method 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, a new correlation, Equation (11.7), based on the Vogel–Tammann–Fulcher (VTF) equation [122–124] was proposed to predict viscosities of ionic liquids at atmospheric pressure as a function of temperature [88, 95, 125–128],

$$\ln \eta = A_\eta + \frac{B_\eta}{T - T_{0\eta}}, \tag{11.7}$$

$$A_\eta = \sum_{i=1}^{k} n_i a_{i,\eta}, \tag{11.8}$$

$$B_\eta = \sum_{i=1}^{k} n_i b_{i,\eta}, \tag{11.9}$$

where T is the absolute temperature, and A_η, B_η, and $T_{0\eta}$ are adjustable coefficients. A_η and B_η can be obtained by a group contribution method according

to Equation (11.8) and Equation (11.9), respectively, where n_i is the number of groups of type i, k is the total number of different groups in the molecule, and $a_{i,\eta}$ and $b_{i,\eta}$ are parameters. $B_\eta/T_{0\eta}$ is known as Angell strength parameter, so $T_{0\eta}$ is similar for all the ionic liquids studied. The calculated value of the viscosity is in good agreement with the corresponding experimental volume for the ionic liquids studied [88, 95, 125–128]. The experimental viscosity values for [C_6mim][PF_6] and [C_8mim][PF_6] at high pressure were fitted to a Tait-form equation by Tomida et al. [125],

$$\ln(\eta_p + \eta_0) = E \ln[(D + P)/(D + 0.1)], \tag{11.10}$$

where η_p and η_0 are the viscosities at P and 0.1 MPa, respectively, and E and D are adjustable parameters. If the value calculated with the VTF equation is substituted for η_0 in Equation (11.10), the viscosity at arbitrary temperature and pressure can be interpolated [126].

As mentioned previously, Krossing and coworkers proposed a strong relationship between the molecular volumes and the physical properties of ionic liquids [40]. Since the viscosity of a fluid is inversely proportional to the mobility of the ions within it, the viscosity is related to V_m and E_a according to Equation (11.11) and Equation (11.12), respectively [40],

$$\eta = a e^{bV_m}, \tag{11.11}$$

$$\eta \propto e^{E_a/RT}, \tag{11.12}$$

where a is the empirical pre-exponential factor, b is an empirical constant, and V_m is the molecular volume. E_a is the minimum energy that a particle must possess to move. The viscosity can be obtained using a VTF equation. Such a hypothesis is reasonable since the volume of the ions in a fluid is clearly related to the minimum energy required for them to move [40].

11.5 SURFACE TENSION

Surface tension is an important property in the study of physics and chemistry at free surfaces, as it affects, *inter alia*, the transfer rates of vapour absorption at the vapour–liquid interface [10]. It also is a measurement of the cohesive energy present at an interface and is usually quantified as a force/length measurement. This property is responsible for many of the dynamic behaviours of liquids, and is important to researchers and engineers in chemical process and reactor engineering fields. The values of surface tension are dependent on the liquid structure and orientation.

Experimental data for the surface tension of ionic liquids are very scarce and currently mostly limited to imidazolium-based ionic liquids, alkylammonium-based protic ionic liquids, and a dozen amino ionic liquids [74, 77, 129–133]. The values of surface tension lie in the range of 1.55–65.0 mN m^{-1}. Up to now,

TABLE 11.6   The Values for Surface Tension of Ionic Liquids at 300.15 K

Entry	Cation, $[A]^+$	Anion, $[X]^-$	$\gamma/mN\ m^{-1}$	Reference
1	$MeNH_3$	HCO_2	43.1	132
2	$EtNH_3$	HCO_2	38.5	132
3	$PrNH_3$	HCO_2	33.3	132
4	$BuNH_3$	HCO_2	31.9	132
5	C_2mim	BF_4	54.4	136
6	C_2mim	CH_3BF_3	45.2	136
7	C_2mim	$C_2H_5BF_3$	42.5	136
8	C_2mim	$C_3H_7BF_3$	38.0	136
9	C_2mim	$C_4H_9BF_3$	34.2	136
10	C_2mim	$C_5H_{11}BF_3$	33.8	136
11	C_2mim	CH_2CHBF_3	44.3	136

the reported values of surface tension are all lower than for water (71.97 mN m^{-1} at 298 K), except for the values reported for $[C_4mim][Zn_3Cl_7]$ (78.3 mN m^{-1} at 318 K) [134]. It should be noted, however, that the value for $[C_4mim][ZnCl_3]$ is 57.49 mN m^{-1} at 313.15 K [133], and the anions of both these materials are incorrectly formulated [135]. However, the values of surface tension for ionic liquids are generally higher than for many organic solvents.

The trends in surface tension changes for different types of ionic liquids have similar principles. As can be seen in Table 11.6, for ionic liquids with similar anions, the surface tension decreases with an increase in alkyl chain length of the imidazolium cation, while for the ionic liquids having the same cation, the surface tension also decreases with an increase in alkyl chain length in inions. As seen in Table 11.5, for the common cation $[C_2mim]^+$, the surface tension shows the order

$$[BF_4]^- >> [CH_3BF_3]^- > [CH_2CHBF_3]^- > [C_2H_5BF_3]^-$$
$$> [C_3H_7BF_3]^- > [C_4H_9BF_3]^- \sim [C_5H_{11}BF_3]^-.$$
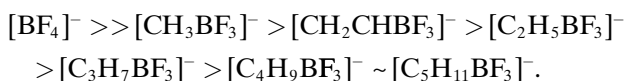
An exception is that the value for surface tension of $[C_4mim][Zn_3Cl_7]$ is higher than that of $[C_4mim][ZnCl_3]$ (but again note that the anions of both these materials are incorrectly formulated [135]). Structure changes to either the cation or the anion had a similar effect on the surface tension, indicating that both ions are present at the surface and influence the surface tension. From these trends in surface tension with ion size, it may be inferred that the energy required to break the ionic liquid–air interface is related to the ion–ion interactions: the larger the ions, the lower their interactions with each other.

Drummond and coworkers studied a series of 25 protic ionic liquids [129] to determine the effect of structural changes on the surface tension, including the effect of hydroxyl groups, increasing alkyl chain lengths, branching, and the differences between inorganic and organic anions. It was found that for the branched protic ionic liquids, the branching decreased the surface

tension, consistent with more hydrocarbon units per unit surface area. Thus, 2-methylpropylammonium methanoate and 2-methylbutylammonium methanoate have higher values of surface tension than those of butylammonium methanoate. The addition of a hydroxyl group has the same effect as the addition of an alkyl group, and will cause a significant increase in the surface tension, due to the combination of higher cohesive energy from the additional hydrogen bonding, and a reduction in the effective amount of hydrocarbon situated at the surface.

Hydroxyl groups at the end of the chain lead to higher surface tensions than those branched off the side of the chain. This was shown by the surface tension of ethanolammonium methanoate (65.0 mN m^{-1} at 298.15 K) and ethylammonium glycolate (49.3 mN m^{-1} at 298.15 K) being higher than those of 2-propanolammonium methanoate (46.2 mN m^{-1} at 298.15 K) and ethylammonium lactate (39.3 mN m^{-1} at 298.15 K), respectively. The reason is that the small anion causes little interruption to the surface packing of cations. The inorganic anions lead to relatively high surface tensions.

In general, the surface tension of many ionic liquids exhibits almost linear decreases while temperature increases. From Figure 11.9, we can see that the decreasing trend in surface tension is very clear for ionic liquids having $[C_2mim]^+$, $[C_3mim]^+$, or $[C_5mim]^+$, and the relationship is expressed by the Eötvös equation,

$$\gamma V_m^{2/3} = \kappa(T_c - T), \tag{11.13}$$

where V_m is the molar volume of the liquid, according to the Eötvös equation, T_c is critical temperature, and k is an empirical constant.
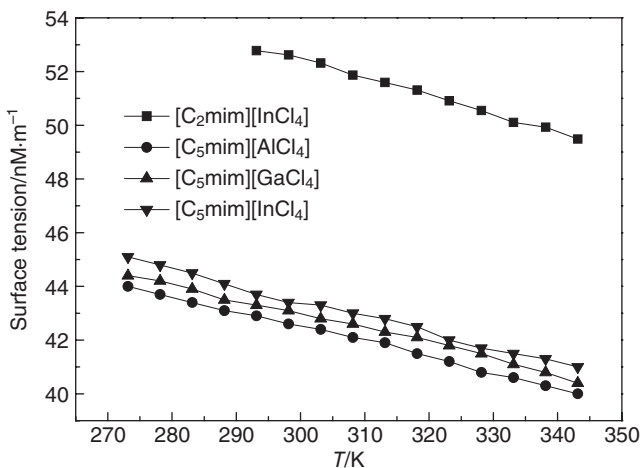

Figure 11.9   The values surface tension for several types of ionic liquids at different temperatures.

11.6   CONCLUSIONS

Ionic liquids have shown excellent performance in many areas, including catalysis, separations, organic synthesis, material preparation, and biomass conversion; this caused a rapid transition into an international scientific research hot spot. This resulted in a massive surge in the generation of physicochemical property data, which has provided a solid foundation for the screening and design of ionic liquids, equipment optimisation, and process simulation. In addition to the accumulation of data on ionic liquids, there has also been significant progress in modelling and predictive methodology, but there are still problems that cannot be ignored. Until now (1) a unified standard purity assessment method for analysing ionic liquids has not been established, which has created many inconsistencies in the measurement of physicochemical properties of ionic liquids; (2) standard determination methods of various physicochemical properties have not been established, resulting in small, and sometimes significant, differences in reported values for the same ionic liquid (although some recommendations do now exist) [118, 137]; (3) the current simulation work is based or developed on conventional models—theoretical models have not yet been established that are unique to ionic liquids, and there is no new theory breakthrough. Therefore, established accurate, standard analytical techniques and experimental methods, and a unified evaluation system, are problems to which we urgently need a solution in the research field of physicochemical properties of ionic liquids—only in this way will reliable data be accumulated to permit meaningful modelling. Then, by combining molecular dynamic simulations and quantitative calculations, comprehensive and systemic structure–property relationships will be revealed, new and simple prediction method will be established, and this will inevitably result in new breakthroughs in the fundamental understanding of ionic liquids.

ACKNOWLEDGEMENTS

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