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Review: Current studies on some physical properties of ionic liquids

Hua Zhao^a

^a Department of Food Science, Rutgers University, New Brunswick, NJ 08901, USA

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Review

CURRENT STUDIES ON SOME PHYSICAL PROPERTIES OF IONIC LIQUIDS

HUA ZHAO*

*Department of Food Science, Rutgers University,
New Brunswick, NJ 08901, USA*

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As a novel substituting solvent for organic solvents, low-temperature ionic liquids have attracted much attention as good media in organic synthesis and other chemical processes. Better understanding of physical properties of ionic liquids are very helpful in exploring reaction mechanisms and controlling reaction outputs. This review summarises current studies on several physical properties (melting point, vapor pressure and stability, polarity, miscibility, density, viscosity) that are important for organic reactions.

Keywords: Ionic liquids; Solvents; Organic synthesis; Clean technology

INTRODUCTION

An ionic liquid (IL) is a liquid containing only ions, but it is different from the classic definition of a molten salt [1]. A molten salt is usually defined as a highly-melting, highly viscous and highly corrosive liquid, while an ionic liquid is a liquid at low temperature ($< 100^{\circ}\text{C}$) and has lower viscosity. As the introduction of cleaner technologies is becoming a major concern in both industries and academia, using alternatives to the most damaging solvents has become a high priority. Organic solvents are high on the list of damaging chemicals for two simple reasons: (1) they are used in huge amounts, and (2) they are usually volatile liquids that are difficult to contain. Ionic liquids are considered as a substitute of those volatile organic solvents, not only because of its low vapor pressure and thus being environmental friendly, more importantly it may show the ability of catalysis as solvent or auxiliary. Moreover, ionic liquids also have many other attractive features, including chemical and thermal stability, non-flammability, high ionic conductivity, and a wide electrochemical potential window.

Ionic liquids usually consist of nitrogen-containing organic cations and inorganic anions. In fact, ionic liquids can now be produced with room temperature and below (as low as -96°C) melting point, which is an important reason why ionic liquids have been explored in many applications [1]. Their chemical and physical properties

* Email: huazhao98@yahoo.com

can be finely tuned for a range of applications by varying the cations or anions [2]. Alkylpyridinium (RPy⁺) chloroaluminate based ambient temperature ionic liquids have been known since 1950s [3]. However, it was the discovery of ethylimidazolium (EMIM⁺) based chloroaluminate ionic liquids in 1982 [4] that afforded the impetus for a dramatic increase in activity in this area.

Earlier reviews of current and potential applications of ionic liquid as solvents for catalytic synthesis, are available [1,5,6]. Ionic liquids have many favorable properties, such as good solvents for a wide range of inorganic, organic and polymeric materials, adjustable polarity, and catalytic effects, etc. Therefore, they have been investigated as reaction media in many organic and organometallic syntheses, including Diels–Alder reactions [7,8], Heck reactions [5,9,10], Friedel–Crafts reactions [5,11,12], alkylation [5,13,14], hydrogenation [15–17], hydroformylation [5,15] dimerization of butadiene [18,19], benzoin condensation [20], acylative cleavage of cyclic and acyclic ethers [21], and polymerization of methyl methacrylate [22]. They have also been used as solvents for extraction [23,24], multiphase bioprocess operations [25], and electrolytes in electrochemistry [26,27]. More recently, ionic liquids have been employed in the studies of enzymatic systems, such as lipase catalysed kinetic resolution of 1-phenylethanol in ionic liquids [28], enzymatic catalysis of formation of *Z*-aspartame in ionic liquids [29], catalyzing alcoholysis, ammoniolysis and perhydrolysis reactions by lipase in ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate [30], etc.

COMPOSITIONS OF IONIC LIQUIDS

The most commonly used cations in room temperature ionic liquids are alkylammonium, alkylphosphonium, *N,N'*-dialkylimidazolium (abbreviated as [RR'IM], for example, 1-ethyl-3-methylimidazolium as [EMIM]), and *N*-alkylpyridinium (abbreviated as [RPy]) cations (Fig. 1). And the most commonly used alkyl chains are methyl, ethyl, butyl, hexyl, octyl, and decyl, etc.

Numbers of anions have been investigated as listed in Table I. Various combinations of cations and anions provide finely designed ionic liquids for different applications.

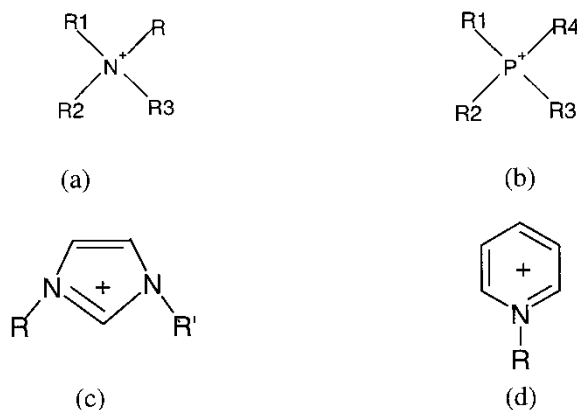


FIGURE 1 Important types of cations in ionic liquids: (a) Tetraalkyl-ammonium (b) Tetraalkyl-phosphonium, (c) *N,N'*-dialkyl-imidazolium and (d) *N*-alkyl-pyridinium cations.

TABLE I A list of some anions in ionic liquids and their references

<i>Anions</i>	<i>References</i>	<i>Anions</i>	<i>References</i>
BF ₄	[4]	(CF ₃ SO ₂) ₂ N	[33]
PF ₆	[31]	CF ₃ CO ₂	[33]
SbF ₆	[15]	B(Et ₃ Hex)	[34]
CH ₃ CO ₂	[4]	OTs ^a	[35]
HSO ₄	[32]	AuCl ₄	[36]
NO ₃	[4]	AlCl ₄	[37]
NO ₂	[4]	Carborane anions	[38]
CF ₃ SO ₃	[33]	(as 1-R-CB ₁₁ H ₆ Cl ₆)	

^aTs = H₃CC₆H₄SO₂ (tosyl).

MELTING POINT

Low-melting-point is an important reason that ionic liquids have become popular as a medium in organic reactions and other chemical processes. Molten salts usually have very high freezing points (for example, NaCl has m.p. = 803°C), while ionic liquids usually have melting points below 100°C and many of them are just liquids at room temperature. This characteristic of low-melting-point can be explained as replacing the simple inorganic cations by unsymmetrical organic cations [1]. From our discussion of the melting point data below, it can be seen that both cations and anions in the ionic liquids contribute to the low-melting-point feature.

The phase diagram of 1-(C_nH_{2n+1})-3-methylimidazolium tetrafluoroborate is shown as a function of carbon number in the alkyl chain in Fig. 2 [39]. The salts only crystallize on cooling when $n = 1$ and $n > 9$. The ionic liquids ($n = 2-9$) have a strong tendency of supercool, resulting in more viscous fluids, and eventually glasses. When $n > 12$, the liquid crystalline mesomorphism can be observed. When $n \leq 5$, the melting/glass points decrease as the chain length increases. It was explained [38] that alkylation pattern of the imidazolium cation affects the melting point and the packing inefficiency of the cation is the intrinsic reason of the low melting point. As $n > 5$ in Fig. 2, the glass/melting points increase when the carbon chain grows larger. The reason is that when the chain is so big, the alkyl chain itself becomes the main structure of the cation, not the imidazolium part. And it is known that alkanes have higher melting points for longer chain molecules. The same pattern can be found in the melting point data listed in Tables II and III.

The inorganic anion also accounts for the low melting point of an ionic liquid as well, and in some cases it even makes the most significant contribution for lowering the melting point. It has been argued that increasing size of the anion with the same charge can contribute to the decreasing of the melting point [6]. And it was also concluded that the C-alkylation of the anion could lead to low melting point by the introduction of a packing inefficiency [38]. Table IV compares the impact of anions on the melting points of some important ionic liquids.

In conclusion, low symmetry and packing efficiency may lead to low melting point of an ionic liquid. However, other factors may have impact on the melting point as well, such as weak intermolecular interaction (such as less hydrogen bonding) [33,43], and an average distribution of charge in the cation [44], etc.

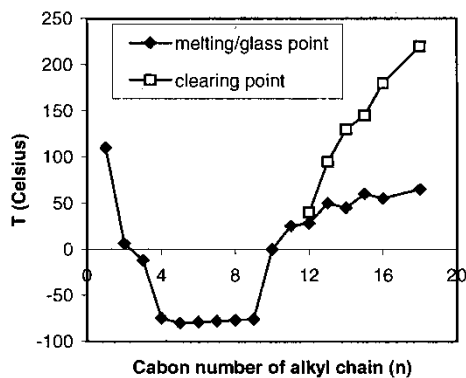


FIGURE 2 Melting, glass and clearing transitions of 1-(C_nH_{2n+1})-3-methylimidazolium tetrafluoroborate [39].

TABLE II Comparing melting points of imidazolium based ionic liquids

Salts	R	R'	Anion	m.p. (°C)	References
1	CH ₃	CH ₃	Cl	124.5–128	[40]
2	CH ₃	C ₂ H ₅	Cl	82–87	[40]
3	CH ₃	<i>n</i> -C ₃ H ₈	Cl	58–66	[40]
4	CH ₃	<i>n</i> -C ₄ H ₉	Cl	65–69	[40]
5	CH ₃	C ₂ H ₅	AuCl ₄	58	[36]
6	CH ₃	<i>n</i> -C ₃ H ₈	AuCl ₄	50	[36]

VAPOR PRESSURE AND CHEMICAL/THERMAL STABILITY

Clean technology requires the design of safe and environmentally benign chemical processes and thus reduces the waste from an industrial process to its minimum. Ionic liquids do not emit measurable vapor pressure, which makes them a part of the green chemistry. This attractive feature is one of the most important reasons that ionic liquids are emerging as novel alternatives for volatile organic compounds (VOCs) traditionally employed as industrial solvents. Also, due to this reason, in a distillation process, the azeotrope formation between the solvent and products does not occur.

The chloroaluminates based ambient temperature ionic liquids are water-sensitive and produce a lot of HCl while exposed to air [2]. Therefore, this type of ambient ionic liquid has to be rigorously protected from moisture and other oxide impurities. The chloroaluminates based ionic liquids have thus been limited to a narrow selection of organic substrates, such as Friedel–Crafts substrates [45]. On the other hand, the tetrafluoroborates, hexafluorophosphates and other newly developed ionic liquids are air and water stable. This development gives the ionic liquid more potential applications in a very wide range of chemical processes.

Ionic liquids are also thermally stable. This stability is limited by the strength of their heteroatom-carbon and heteroatom-hydrogen bonds respectively [6]. While 150°C is considered as maximum working temperature for most quaternary ammonium chloride salts, [EMIM][BF₄] (1-ethyl-3-methylimidazolium tetrafluoroborate) is stable up to 300°C [46] and [EMIM][(CF₃SO₂)₂N] (m.p. –3°C) is stable to more than 400°C [33].

TABLE III Melting points of alkoxyethyl type imidazolium based ionic Liquids [41]

<i>With anion: BF₄</i>				<i>With anion: PF₆</i>			
<i>Salt</i>	<i>R</i>	<i>R'</i>	<i>m.p. (°C)</i>	<i>Salt</i>	<i>R</i>	<i>R'</i>	<i>m.p. (°C)</i>
7	CH ₃	C ₃ H ₇ OCH ₂	Liquid	35	CH ₃	C ₃ H ₇ OCH ₂	Liquid
8	CH ₃	C ₄ H ₉ OCH ₂	Liquid	36	CH ₃	C ₄ H ₉ OCH ₂	Liquid
9	CH ₃	C ₅ H ₁₁ OCH ₂	Liquid	37	CH ₃	C ₅ H ₁₁ OCH ₂	Liquid
10	CH ₃	C ₆ H ₁₃ OCH ₂	Liquid	38	CH ₃	C ₆ H ₁₃ OCH ₂	Liquid
11	CH ₃	C ₇ H ₁₅ OCH ₂	Liquid	39	CH ₃	C ₇ H ₁₅ OCH ₂	37–38
12	CH ₃	C ₈ H ₁₇ OCH ₂	Liquid	40	CH ₃	C ₈ H ₁₇ OCH ₂	Liquid
13	CH ₃	C ₉ H ₁₉ OCH ₂	Liquid	41	CH ₃	C ₉ H ₁₉ OCH ₂	47–49
14	CH ₃	C ₁₀ H ₂₁ OCH ₂	56–57	42	CH ₃	C ₁₀ H ₂₁ OCH ₂	46–47
15	CH ₃	C ₁₁ H ₂₃ OCH ₂	61–62	43	CH ₃	C ₁₁ H ₂₃ OCH ₂	52–53
16	CH ₃	C ₁₂ H ₂₅ OCH ₂	62–64	44	CH ₃	C ₁₂ H ₂₅ OCH ₂	61–63
17	C ₆ H ₁₃	C ₃ H ₇ OCH ₂	Liquid	45	C ₆ H ₁₃	C ₃ H ₇ OCH ₂	Liquid
18	C ₆ H ₁₃	C ₄ H ₉ OCH ₂	Liquid	46	C ₆ H ₁₃	C ₄ H ₉ OCH ₂	Liquid
19	C ₆ H ₁₃	C ₅ H ₁₁ OCH ₂	Liquid	47	C ₆ H ₁₃	C ₅ H ₁₁ OCH ₂	Liquid
20	C ₆ H ₁₃	C ₆ H ₁₃ OCH ₂	Liquid	48	C ₆ H ₁₃	C ₆ H ₁₃ OCH ₂	Liquid
21	C ₆ H ₁₃	C ₇ H ₁₅ OCH ₂	Liquid	49	C ₆ H ₁₃	C ₇ H ₁₅ OCH ₂	Liquid
22	C ₆ H ₁₃	C ₈ H ₁₇ OCH ₂	Liquid	50	C ₆ H ₁₃	C ₈ H ₁₇ OCH ₂	Liquid
23	C ₆ H ₁₃	C ₉ H ₁₉ OCH ₂	Liquid	51	C ₆ H ₁₃	C ₉ H ₁₉ OCH ₂	Liquid
24	C ₆ H ₁₃	C ₁₀ H ₂₁ OCH ₂	37–39	52	C ₆ H ₁₃	C ₁₀ H ₂₁ OCH ₂	Liquid
25	C ₆ H ₁₃	C ₁₁ H ₂₃ OCH ₂	Liquid	53	C ₆ H ₁₃	C ₁₁ H ₂₃ OCH ₂	29–31
26	C ₄ H ₉ OCH ₂	C ₃ H ₇ OCH ₂	Liquid	54	C ₄ H ₉ OCH ₂	C ₃ H ₇ OCH ₂	47–49
27	C ₄ H ₉ OCH ₂	C ₄ H ₉ OCH ₂	Liquid	55	C ₄ H ₉ OCH ₂	C ₄ H ₉ OCH ₂	56–58
28	C ₄ H ₉ OCH ₂	C ₅ H ₁₁ OCH ₂	Liquid	56	C ₄ H ₉ OCH ₂	C ₅ H ₁₁ OCH ₂	36–40
29	C ₄ H ₉ OCH ₂	C ₆ H ₁₃ OCH ₂	Liquid	57	C ₄ H ₉ OCH ₂	C ₆ H ₁₃ OCH ₂	49–51
30	C ₄ H ₉ OCH ₂	C ₇ H ₁₅ OCH ₂	Liquid	58	C ₄ H ₉ OCH ₂	C ₇ H ₁₅ OCH ₂	56–58
31	C ₄ H ₉ OCH ₂	C ₈ H ₁₇ OCH ₂	Liquid	59	C ₄ H ₉ OCH ₂	C ₈ H ₁₇ OCH ₂	Liquid
32	C ₄ H ₉ OCH ₂	C ₉ H ₁₉ OCH ₂	Liquid	60	C ₄ H ₉ OCH ₂	C ₉ H ₁₉ OCH ₂	49–51
33	C ₄ H ₉ OCH ₂	C ₁₀ H ₂₁ OCH ₂	15–17	61	C ₄ H ₉ OCH ₂	C ₁₀ H ₂₁ OCH ₂	53–55
34	C ₄ H ₉ OCH ₂	C ₁₁ H ₂₃ OCH ₂	21–23	62	C ₄ H ₉ OCH ₂	C ₁₁ H ₂₃ OCH ₂	59–62

Table V illustrates the temperature (T_d) of 10% weight loss of ionic liquids during heating scan from room temperature by using thermogravimetry, which evidently indicates the ionic liquids are thermal stable.

POLARITY

Since solvent polarity and polarizability are the critical indexes of solvent strength, they may have significant influence on the chemical reactions. Although different characteristic parameters (for example, dielectric constant, dipole moments, refractive index, and polarizabilities, etc.) reflect the solvent strength from different aspects, solvent polarity can not be simply described by any one of those terms because the individual interactions between a solvent and a solute are not accounted for. Therefore, the studies of empirical scales of solvent polarity are adapted. As a common approach, fluorescent probes are applied to determine the solvent strength of organic solvents and have been recently used for some ionic liquids. For instance, three different fluorescent probes (e.g. pyrenecarboxaldehyde, pyrene and bromonaphthalene) were studied to establish the solvent properties of ionic liquid [EMIM][TFSI] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) [33]. And it was concluded that solvent strength of

TABLE IV Impact of anions on the melting points of ionic liquids

Salt	Compounds	m.p. (°C)	Reference	Salt	Compounds	m.p. (°C)	Reference
63	[EMIM][CoCl ₄]	100–102	[42]	75	[EMIM][CB ₁₁ H ₁₂]	122	[38]
64	[EMIM][NiCl ₄]	92–93	[42]	76	[EMIM][CB ₁₁ H ₆ Cl ₆]	114	[38]
65	[EMIM]Cl	87	[40]	77	[EMIM][CB ₁₁ H ₆ Br ₆]	139	[38]
66	[EMIM][SO ₄] (monohydrate)	70	[4]	78	[EMIM][1-CH ₃ -CB ₁₁ H ₁₁]	59	[38]
67	[EMIM][PF ₆]	58–60	[31]	79	[EMIM][1-C ₂ H ₅ -CB ₁₁ H ₁₁]	64	[38]
68	[EMIM][AuCl ₄]	58	[36]	80	[EMIM][1-C ₃ H ₇ -CB ₁₁ H ₁₁]	45	[38]
69	[EMIM][NO ₂]	55	[4]	81	[EMIM][1-C ₄ H ₉ -CB ₁₁ H ₁₁]	49	[38]
70	[EMIM][NO ₃]	38	[4]	82	[OMIM][CB ₁₁ H ₁₂]	70	[38]
71	[EMIM][AlCl ₄]	7	[37]	83	[OMIM][CB ₁₁ H ₆ Cl ₆]	67	[38]
72	[EMIM][BF ₄]	6	[39]	84	[EDMIM][CB ₁₁ H ₁₂]	156	[38]
73	[EMIM][CF ₃ SO ₃]	–9	[33]	85	[EDMIM][CB ₁₁ H ₆ Cl ₆]	137	[38]
74	[EMIM][CF ₃ CO ₂]	–14	[33]	86	[BDMIM][CB ₁₁ H ₁₂]	129	[38]
				87	[BDMIM][CB ₁₁ H ₆ Cl ₆]	101	[38]

Note: EMIM = 1-ethyl-3-methylimidazolium; OMIM = 1-octyl-3-methylimidazolium; EDMIM = 1-ethyl-2, 3-dimethylimidazolium; and BDMIM = 1-butyl-2, 3-dimethylimidazolium.

TABLE V Thermal properties of some ionic liquids

Salt	T_d (K)	Reference
[EMIM][BF ₄]	664	[47]
[EMIM][TFSI]	690	[47]
[EMIM][CF ₃ COO]	475	[33]
[BuPy][BF ₄]	615	[47]
[BuPy][TFSI]	677	[47]

Note: TFSI = bis(trifluoromethylsulfonyl)imide; BuPy = 1-butylpyridinium.

[EMIM][TFSI] is less than that of 1-hexanol using pyrenecarboxaldehyde, while similar to ethanol's using pyrene.

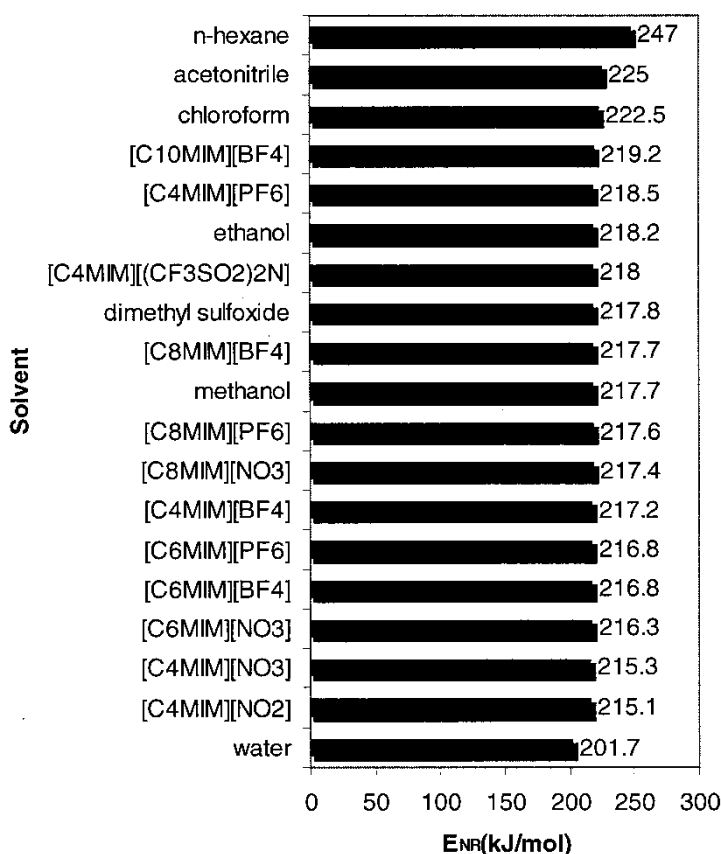
The solvent strength and polarity of four imidazolium and pyridinium based ionic liquids have been measured by two fluorescent probes AP and DAP [48]. In this study, the microscopic polarities are expressed in terms of the absorption energy of the betaine dye, $E_T(30)$, and can be calculated from the fluorescent lifetime $\lambda_{\text{fluor}}^{\text{max}}$ based on the correlation relationship. The larger value of $E_T(30)$ means stronger solvent strength and polarity. Table VI lists the fluorescent properties of DAP in ionic liquids or organic solvents at room temperature and the estimated $E_T(30)$ values [48]. The four studied ionic liquids in Table VI have close or stronger polarity than acetonitrile but less polar than methanol.

More systematical polarity studies of 1-C_nH_{2n+1}-3-methylimidazolium type ionic liquids have been reported by the Seddon research group [49]. In their research, the wavelength of maximum absorption (λ_{max}) was measured and the molar transition energies (E_{NR}) were calculated for solvatochromic dye Nile Red dissolved in the ionic liquids (Fig. 3). In this case, the smaller value of E_{NR} indicates stronger polarity a solvent has.

From Fig. 3, the polarity of [C₄MIM]⁺ type salts declines with the increasing size of anions NO₂, NO₃, BF₄, and PF₆. This is due to the spreading of negative charge on the anion, and thus less charge is available for interactions with solute Nile Red [49]. However, [C₄MIM][(CF₃SO₂)₂N] is an exception due to the negative charge partially delocalized within the anion [50].

TABLE VI Fluorescence properties of DAP in ionic liquids or organic solvents [48]

Solvent	$\lambda_{\text{fluo}}^{\text{max}}$	$E_T(30)$ (kJ/mol)
Hexane	437	129.7
[BuPy][BF ₄]	495	187.9
Acetonitrile	490	189.5
[C ₈ MIM][PF ₆]	503	196.0
[BMIM][PF ₆]	512	205.1
Ethanol	523	217.1
[BMIM][NO ₃]	525	218.2
Methanol	534	230.1
Water	562	264.0


 FIGURE 3 E_{NR} values for [C_nMIM][X] ionic liquids and organic solvents [49].

While the 1-alkyl chain was varied for both BF₄⁻ and PF₆⁻ type ionic liquids, the polarity increases with the increasing of *n* from 4 to 6, and thereafter it falls with further longer alkyl chain. This observation has correlation with the phenomena of maximum melting point which occurs at *n* = 6 for these salts, as described in the melting point section above.

As a tentative conclusion, the polarity of 1-alkyl-3-methylimidazolium ionic liquids is determined by anion for those consisting of short 1-alkyl chains and by the cation for those consisting of long 1-alkyl chains [49]. It was also observed that the longer alkyl groups on both cations and anions lead to great lipophilicity of the ionic liquids [51]. However, since more types of ionic liquids are actually involved in current organic reactions than summarized here, more consistent and comprehensive studies have to be done on the solvent strength and polarity.

MISCIBILITY

Ionic liquids are considered good solvents for a wide range of inorganic, organic and polymeric compounds [1]. The solubility of ionic liquids in water and organic solvents can be finely tuned by changing the structure of cation and anion. The influence of cation structure on the miscibility may be explained by two factors: (a) the similarity of the polarity between ionic liquid and the other fluid; (b) free space between molecules caused by large side chains. For example, 1-alkyl-3-methylimidazolium tetrafluoroborate ($[\text{RMIM}][\text{BF}_4]$) salts are miscible with water at 25°C when the alkyl group length is less than 6 carbons, while form a second phase with water at or above 6 [52]. Since a longer alkyl chain means less polarity and more hydrophobicity, the solubility of ($[\text{RMIM}][\text{BF}_4]$) is thus reduced in polar solvent water. The behavior is actually beneficial to the extraction operation due to this adjustable solubility of ionic liquids in the extraction phase. A successful example is the use of $[\text{BMIM}][\text{PF}_6]$ ($[\text{BMIM}]^+ = 1\text{-butyl-3-methylimidazolium}$), which forms triphasic mixture with alkanes and water [52]. $[\text{BMIM}][\text{PF}_6]$ was applied for the liquid–liquid extraction of erythromycin-A and for the *Rhodococcus* R321 catalyzed biotransformation of 1,3-dicyanobenzene (1,3-DCB) in a liquid–liquid two phase system [25].

Another instance of the cation influence on the miscibility is the investigation of the solubility of 1-octene in four different tri-*n*-alkylmethylammonium tosylate salts at 80°C [6]. With the increase of carbon number, the solubility of 1-octene accordingly increases. This may be because of the low polarity of 1-octene and larger free space between molecules for longer chain ionic liquids. Newly developed 3-alkoxy-methyl-1-alkyl based ionic liquids do not mix with water because of their antielectrostatic properties, but are miscible with acetone, chloroform, THF, ethyl acetate and DMF [41].

On the other hand, the anion in an ionic liquid usually shows a more impressive influence on the miscibility property. Generally, ionic liquids consisting of anion $[\text{CH}_3\text{COO}]^-$, $[\text{CF}_3\text{COO}]^-$, $[\text{NO}_3]^-$, Cl^- , Br^- , I^- , $[\text{Al}_2\text{Cl}_7]^-$, and $[\text{AlCl}_4]^-$ etc. are water soluble, while those containing anion $[\text{PF}_6]^-$, $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$, $[\text{BR}_1\text{R}_2\text{R}_3\text{R}_4]^-$ form biphasic mixture water. And the solubility of $[\text{BF}_4]^-$, $[\text{CF}_3\text{SO}_2]^-$ type mostly depends on the properties of the cation [53]. According to Bonhote's research [33], ionic liquids may be completely miscible with organic solvents if the dielectric constants of ionic liquids are larger than a certain limit. And this limit depends on the combination of each cation–anion pair (Table VII) [33]. In this case, the anion has much stronger influence on the miscibility than the changing of alkyl chain length in the cation.

TABLE VII Miscibility of some ionic liquids in water–organic solvents [33]

	<i>H</i> ₂ <i>O</i>	<i>CH</i> ₂ <i>Cl</i> ₂	<i>THF</i>	<i>Ethyl acetate</i>	<i>Toluene</i>	<i>1,4-Dioxane</i>
ϵ	80.10	8.93	7.58	6.02	2.38	2.01
[EMIM][CF ₃ SO ₃]	m	m	m	m	im	im
[EMIM][CF ₃ CO ₂]	m	m	m	pm	im	im
[EMIM][<i>n</i> -C ₃ F ₇ CO ₂]		m	m	pm	im	im
[BMIM][CF ₃ CO ₂]	m	m	m	m	im	im
[BMIM][<i>n</i> -C ₃ F ₇ CO ₂]	m	m	m	m	im	im

Note: m: miscible; pm: partial miscible; im: immiscible; ϵ is the dielectric constant.

DENSITY

The density of an ionic liquid depends on the length and type of substituents in the cation, and also on the kind of the anion. Figure 4 clearly illustrates that with the lengthening of alkyl chain, the density of 3-C_{*n*}H_{2*n*+1}OCH₃-1-methylimidazolium tetrafluoroborate salts declines linearly [41]. As a general conclusion, the density of comparable ionic liquids decreases when the bulkiness of the cation grows. This can explain the poor crystal packing that is formed between the bulky cation and the weakly complexing symmetrical anion [31].

Varying the structure of the anion also changes the density of ionic liquids. Figure 5 shows the density of 1-ethyl-3-methylimidazolium carborane type ionic liquids varies with the bulky size [38]. Replacing hydrogen atom by heavier elements such as F, Cl, Br, also increases the density of ionic liquids. This can also be verified by the data in Table VIII, where chain bulkiness and number of fluorine atoms affect the liquid density significantly.

The density of ionic liquids is also temperature dependent. Figure 6 shows the temperature dependence of density of [EMIM][BF₄] [47]. As temperature changes from 293 to 313 K, the density decreases linearly as the temperature increases.

VISCOSITY

Generally, it is considered that the viscosity of ionic liquids is determined by van der Waals forces and hydrogen bonding. Alkyl chain lengthening or fluorination in the cation increases the viscosity of the ionic liquids because of the stronger van der Waals interactions (Fig. 7 [33]). Methylation at C-2 position makes the density more viscous due to the hydrogen bonding suppression.

The viscosity of 1-*n*-butyl-3-methylimidazolium ([BMIM]) type ionic liquids with different fluorine containing anions is listed in Table IX [33]. The significant increase of viscosity from CF₃SO₃⁻ to *n*-C₄F₉SO₃⁻, and from CF₃COO⁻ to *n*-C₃F₇COO⁻, indicates stronger van der Waals interactions than the hydrogen bonding suppression in the case of *n*-C₄F₉SO₃⁻ and *n*-C₃F₇COO⁻. However, from CF₃SO₃⁻ to (CF₃SO₂)₂N⁻, the hydrogen bonding suppression is slightly overcompensates the increase caused by van der Waals attraction.

Viscosity–temperature data of several ionic liquids have been well fitted by Vogel–Tamman–Fulcher (VTF) equation [47] and the equation parameters are listed in Table X.

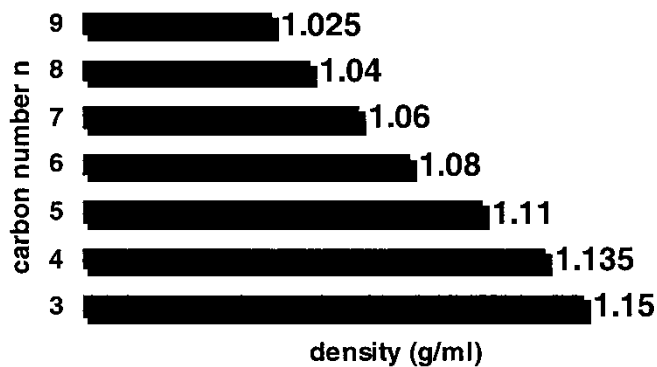


FIGURE 4 Density of 3-C_nH_{2n+1}OCH₃-1-methylimidazolium tetrafluoroborate [41].

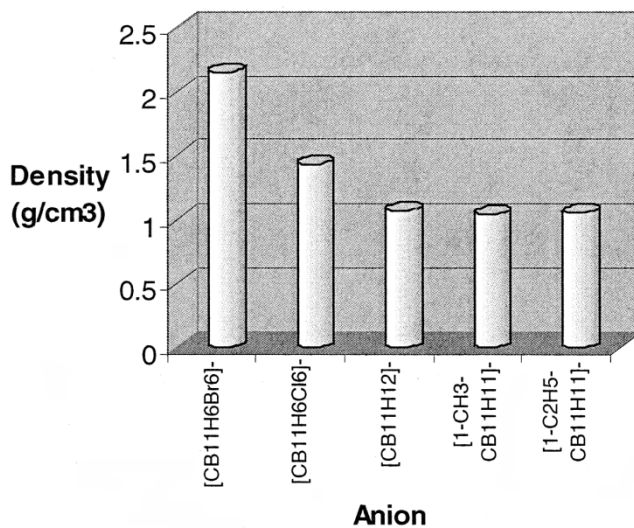
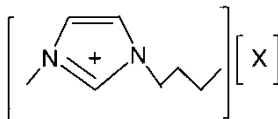


FIGURE 5 Influence of anion on the density of ionic liquid [EMIM][X] [38].

TABLE VIII Influence of fluorine atoms on the density of ionic liquids (22°C)



Anion [X] ⁻	Density (g/cm ³)	Reference
CF ₃ CO ₂ ⁻	1.209	[54]
CF ₃ SO ₃ ⁻	1.290	[55]
<i>n</i> -C ₃ F ₇ CO ₂ ⁻	1.333	[33]
(CF ₃ SO ₂) ₂ N ⁻	1.429	[56]
C ₄ F ₉ SO ₃ ⁻	1.473	[33]

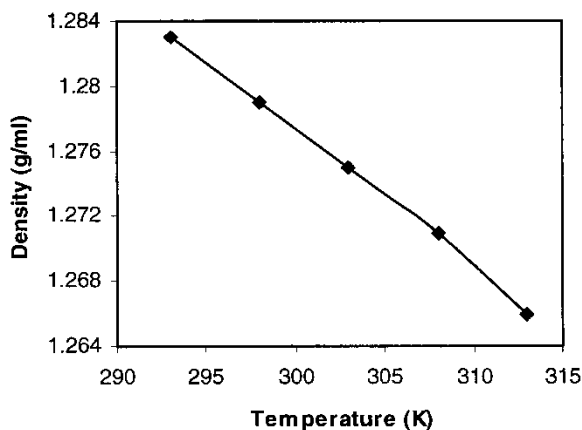


FIGURE 6 Density of [EMIM][BF₄] varies with temperature [47].

Viscosity

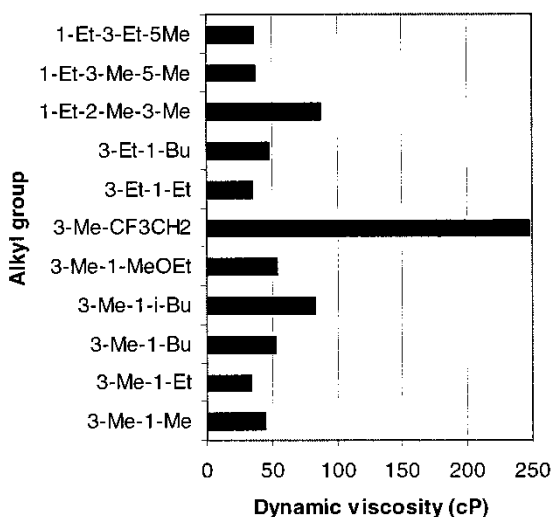
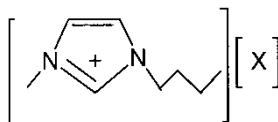


FIGURE 7 Dynamic viscosity at 20°C of imidazolium based (CF₃SO₂)₂N salts which are liquids or supercooled liquids at that temperature [33].

A recent study [53] indicates that the chloride impurities in the ionic liquids increase the viscosity, while the presence of water or other cosolvents decreases the viscosity. Fortunately, the influence of the addition of cosolvents can be fitted to mathematical equations, and therefore can be accounted in the design calculation precisely [53].

CONCLUSION

In summary, as a substitute for traditional volatile organic solvents in clean technologies, ionic liquids have potential applications in organic reactions, chemical pro-

TABLE IX Dynamic viscosity η of various [BMIM]⁺ ionic liquids (20°C) [33]

Anion [X] ⁻	η (cP)
CF ₃ SO ₃ ⁻	90
C ₄ F ₉ SO ₃ ⁻	373
CF ₃ CO ₂ ⁻	73
<i>n</i> -C ₃ F ₇ CO ₂ ⁻	182
(CF ₃ SO ₂) ₂ N ⁻	52

TABLE X VTF equation parameters for viscosity data [47] $\eta = \eta_0 \exp[B/(T - T_0)]$

	η_0 ($\times 0.1$ mPa s)	B ($\times 100$ K)	T_0 ($\times 100$ K)
[EMIM][BF ₄]	2.0	7.5	1.5
[EMIM][TFSI]	1.5	8.4	1.4
[BPy][BF ₄]	2.3	7.2	1.8
[BPy][TFSI]	1.2	8.5	1.6

Note: TFSI = bis(trifluoromethylsulfonyl)imide; BuPy = 1-butylpyridinium.

cesses, and even in enzymatic reactions. Element analysis [39], ¹H NMR chemical shifts study [39], X-ray crystallography [31], and X-ray absorption fine structure (XAFS) [57], are some general techniques for studying the structure of ionic liquids. With the further study of microstructure of ionic liquids, better understanding of the physical properties of ionic liquids should be available soon. And more systematic studies are much needed in order to have a complete ionic liquid database. This is an urgent task since ionic liquids have shown great opportunities in many organic reactions [58].

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