What's an Ionic Liquid?

by Keith E. Johnson

> *"When I use a word," Humpty Dumpty said, in rather a scornful tone,*
> *"it means just what I choose it to mean – neither more nor less."*
> *"The question is," said Alice, "whether you can make words mean so many different things."*
> Lewis Carroll, *Through the Looking Glass*

Introduction to the Phrase "Ionic Liquids"

"The Structure and Properties of Ionic Melts" was the title of a Faraday Society Discussion held in Liverpool in 1961; it dealt exclusively with molten inorganic salts.[1] "Ionic Liquids" was the title of Chapter 6 of the textbook *Modern Electrochemistry* by Bockris and Reddy, published in 1970: it discussed liquids ranging from alkali silicates and halides to tetraalkylammonium salts.[2] The modern era of ionic liquids stems from the work on alkylpyridinium and dialkylimidazolium salts in Colorado in the late 1970s.[3] The term ionic liquids was introduced[4] to cover systems below 100°C, one reason being to avoid the words "molten salts" in phrases such as "ambient temperature molten salts," another to create an impression of freshness and a third, perhaps, for patent purposes. The first "Conference on Ionic Liquids" took place in Salzburg in 2005, Molten Salts 7 in Toulouse in 2005 had one of ten sessions devoted to Ionic Liquids; but the International Symposia on Molten Salts of ECS from 1976 to the present have not shown discrimination on the basis of temperature, beyond scheduling of groups of papers. EUCHEM 2006 dealt with Molten Salts and Ionic Liquids with the content of each session usually mixed.

Modern Ionic Liquids

The properties of a modern ionic liquid are summarized in Table I. Particularly significant are (*i.*) the low vapor pressures in most instances which contrast the environmental problems of volatile organic solvents and (*ii.*) moderate specific conductivities, usually in the same range as those of aqueous electrolytes. It is found that many such systems are excellent solvents or catalysts for organic reactions[3] and some simple processes such as electrodeposition.[5] Unfortunately, one finds reports of new "ionic liquids" without data on conductivities, which would establish that they are dissociated to some extent at least into ions.

Table I. Modern ionic liquids.

A salt	Cation and or anion quite large
Freezing point	Preferably below 100°C
Liquidus range	Often > 200°C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually < 10 mScm^{-1}, "Good"
Molar conductivity	< 10 Scm^2 mol^{-1}
Electrochemical window	> 2V, even 4.5 V, except for Brønsted acidic systems
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

Liquids Comparisons

How do these ionic liquids compare with other liquids, especially those which conduct electricity? Table II presents some illustrative data. One property that we emphasized recently is the molarity of the liquid[6] (a straightforward quantity except for mixed systems such as a basic chloroaluminate containing both Cl$^-$ and AlCl$_4^-$ in significant amounts). The molarity is important regarding kinetic measurements, including conductivities.

Table II indicates a range of molarities of many liquids from 1 to 60, with water at 55, liquid alkali halides up to 35 (LiCl) and most organic salts less than 10. Specific conductivities span a far greater range from the metal sodium through molten inorganic salts in the Scm^{-1} region to organic salts (the modern ionic liquids) and aqueous solutions in the mScm^{-1} region and finally to the near non-conducting but ionizing acetic acid and water at μScm^{-1}. Combining these data into molar conductances is illuminating. We see comparable values for simple inorganic salts alone and in aqueous solutions* but much smaller values for the low temperature semi-organic and organic systems. Thus these modern ionic liquids must consist of IONS AND ION PAIRS, (undissociated molecules), while liquid alkali halides are purely IONIC and aqueous electrolytes behave as a mixture of hydrated ions and the molecular solvent water. Figure 1 attempts to picture these differences.

Acid-Base Properties and Water Interactions

While simple salts such as KCl can be thought of as the product of an electron transfer between elements, organic salts can be traced to a proton transfer between an acid and base. Cations such as emim$^+$ and n-bupy$^+$ result from the alkylation of the bases

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* Extrapolation of aqueous solution molar or equivalent conductances to infinite dilution, at which ion pairing is eliminated, gives many values in the 100 to 150 Scm^2 mol^{-1} range,[11] the exceptions involving H$^+$ and OH$^-$ for which the Grotthus mechanism operates.[2]

Table II. Properties of various liquids.

Compound *Ionic Liquids*	**Temp. °C**	**Molarity Mol L^{-1}**	**Spec Cond Scm^{-1}**	**Molar Cond Scm^2 mol^{-1}**	**Visc. cP**	**Ref.**
NaCl	900	25.3	3.88	154	1.05	2
LiCl	780	35	7.59	217		2
$NaNO_3$	450	21.4	0.72	34	6.9	2
Na_2SiO_3	1750	≈18	4.8	≈270		2
$AlCl_3$ (63%) – NaCl	175	5.8	0.24	41	3.85	7
LiCl-KCl	450	29.7	1.57	53	2.44	7
$[(CH_3)_3S][HBr_2]$	25	7.3	0.034	4.7	20.5	8
emimCl(60%)-$AlCl_3$	25	5.3	0.0065	1.2	47	8
emim Al_2Cl_7	25	3.4	0.015	4.4	14	8
bmim CF_3CO_2	20	5.1	0.0032	0.6	73	8
bupy BF_4	25	5.5	0.0019	0.3	103	8
emim$[(CF_3SO_2)_2N]$	25	3.7	0.0057	1.5	31	8
Others						
H_2O	25	55.3^a	4 x 10^{-8}	7 x 10^{-7}	0.895	2
0.1 M aq. KCl	25	0.1^b	0.013	129	0.9	2
Na	100	40.4	1.04 x 10^5	2.6 x 10^6	1.058	2
H_2SO_4	25	0.049^b	0.0104	212	24.55	9
CH_3COOH	25	17.5^a	8 x 10^{-9}	4.6 x 10^{-7}	1.056	10
HF	0	50.1^a	1 x 10^{-6}	2 x 10^{-5}	0.256	9

a = total molarity • b = ionic molarity • emim = 1-ethyl-3-methyl-1*H*-imidazolium • bmim = 1-butyl-3-methyl-1*H*-imidazolium • bupy = 1-butylpyridinium

Hmim$^+$ and py$^+$. Anions such as NO_3^-, $AlCl_4^-$ and PF_6^- derive from Lewis acid – base reactions:

$$O^{2-} + N_2O_5^- \rightarrow 2NO_3^-$$
$$Cl^- + AlCl_3^- \rightarrow AlCl_4^-$$
$$F^- + PF_5^- \rightarrow PF_6^-$$

It is also possible for Lewis neutral ions to add further Lewis acids to form acidic ions, *e.g.*, $Al_2Cl_7^-$, $Sb_2F_{11}^-$, HBr_2^-.

As a result we can obtain Lewis basic, neutral or acidic ionic liquids, exemplified by the well-researched haloaluminates. In addition we can make protic acidic liquids which are simultaneously of any Lewis aspect.[12] How is proton chemistry in ionic liquids related to proton chemistry in water?

First, acidic protons in ionic liquids often occur as anions, *e.g.*, HCl_2^-, HBr_2^-, $H_2Br_3^-$, rather than cations. Second, protons bonded to bases such as pyridine and l-methylimidazole are not labile.[13] Do these bases behave in line with their pk$_b$'s in water? No. Bases in ionic liquids appear to act in accordance with their gas phase proton affinities (l-methylimidazole > pyridine > ammonia).[14] The complicating factor of course is solvation in water. One can, however, obtain Hammett acidity data for some systems which make fair chemical sense.[15]

What happens when water is added to an ionic liquid or not completely removed at some stage in its preparation?

1. Some anions such as $AlCl_4^-$ and HCl_2^- are irreversibly decomposed.
2. Water may bind strongly to one of the ions.
3. Water may dissolve the liquid until it forms a saturated salt solution; unlike the case of dissolving a solid salt, the other phase will be liquid and it may or may not contain water.
4. At high temperatures, species such as $Li(H_2O)\rho^+Cl^-$ may decompose to LiOH and HCl[7].

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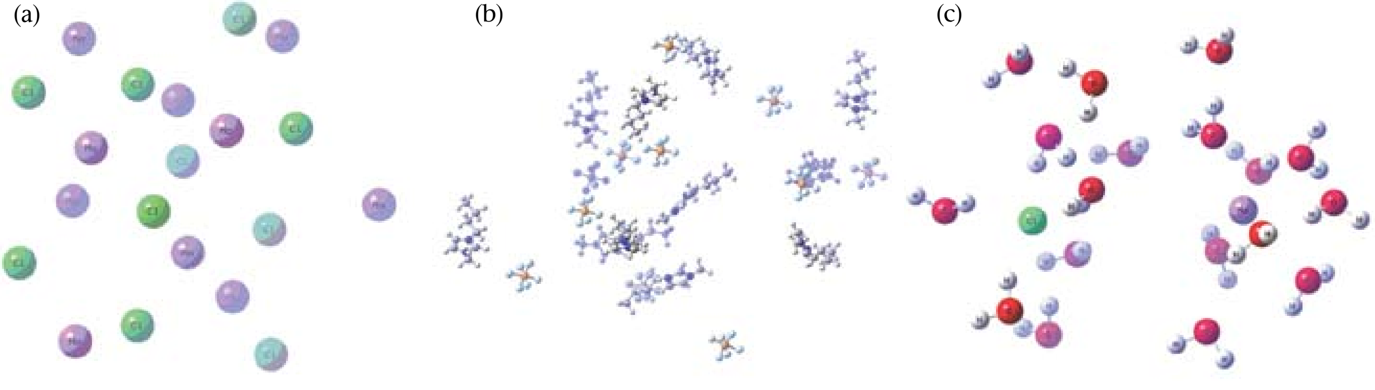

Fig. 1. *Representation of (a) liquid NaCl, (b) molten bmim PF_6, and (c) aqueous NaCl.* Courtesy of A. East and Q. Li

Table III. Electrode processes of ionic liquid solvents.

Process	Examples
1. Cation Reduction	$K^+ + e^- \rightarrow K$ $bmim^+ + e^- \rightarrow bmim \rightarrow bmim_2 \rightarrow$
2. Anion Reduction	$NO_3^- + 2e^- \rightarrow NO_2^- + O^{2-}$ $O^{2-} + NO_3^- \rightarrow NO_2^- + O_2^{2-}$ $CO_3^{2-} + 4e^- \rightarrow C + 3O^{2-}$ $Al_2Cl_7^- + 3e^- \rightarrow Al + AlCl_4^- + 3Cl^-$
3. Anion Oxidation	$SO_4^{2-} - 2e^- \rightarrow SO_3 + ½ O_2$ $CO_3^{2-} - 2e^- \rightarrow CO_2 + ½ O_2$ $BF_4^- - e^- \rightarrow BF_3 + ½ F_2$ $F_2 + bmim^+ \rightarrow C_nF_{n+2}$
4. Proton Reactions	$NO_{3-} + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$ $HCl_2^- + e^- \rightarrow ½ H_2 + 2Cl$

Electrochemistry of Ionic Liquids— The General Situation

Once we have established from conductivity measurements that a liquid is ionic (not ionic/molecular), its temperature and complexity should not pose special problems for using it as a solvent for electrochemistry. Table III lists the types of electrode processes one encounters.[16] With inorganic cations, the solubility of a metal in its salt may arise while the reduction of organic cations is complex and irreversible. Following chemical reactions such as attack of an electrode reaction product on the opposite ion in the system can also occur (F_2 *vs.* $bmim^{+}$[17], O^{2-} *vs.* NO_3^-).

Detecting Your Ionic Liquid

The following (Scheme 1) is a sequence of steps prompted by finding two 19th century pieces of work: (a) Gardner's observation[18] of maximum-boiling point compositions for mixtures of several bases with acetic acid (he incorrectly called these specific mixtures compounds not azeotropes); and (b) Zawidzki's vapor pressure studies[19] of pyridine mixed with formic, acetic and propionic acids (good data even if some fine details are questionable).

Scheme 1. Detecting an ionic liquid.

(a) For an acid-base system HA + B:

Clue #1	Vapor pressures of some mixtures show large negative deviation from Raoult's law: compound forms
Clue #2	${}^{/}$H NMR spectra show downfield shift of HA's proton with B addition: BHA is ionized to BH^+A^-
Clue #3	Some mixtures show σ values in the $mScm^{-1}$ range, far greater than for the components: BH^+A^- dissociates

The overall chemistry

$$B + HA \leftrightarrow BH^+A^- \leftrightarrow BH^+ + A^-$$

is then governed by the ionization and dissociation constants

$$K_i = \frac{[BH^+A^-]}{[B][AH]}$$

and

$$K_d = \frac{[BH^+][A^-]}{[BH^+A^-]}$$

with the ionic liquid containing the ions BH^+ and A^- and the ion-pair BH^+A^-.[20-22] In practice, one may also have to include the self-ionization of HA and the formation of hydrogenates $H_nA_{n+1}^-$.

(b) For the salt MX or BRA where R = alkyl:

Clue #1	Very low vapor pressures: stable compound in liquid
Clue #2	NMR data less dramatic: may suggest BR^+A^-
Clue #3	σ values at least in the $mScm^{-1}$ range: MX or BR^+A^- dissociation

For the acid-base systems the vapor may consist of the ionic compound or the original components,[23] whereas the breakdown of BR^+A^- (*e.g.,* emimCl) into B and RA is probably irreversible.[24,25] The behavior of the vapor should correlate with the gas phase proton affinities.

Conclusion

An ionic liquid is characterized by a specific conductivity in the $mScm^{-1}$ range as a minimum, together with a molar conductivity probably exceeding 0.1 Scm^2 mol^{-1}. In addition, the liquid should only contain ions with lesser numbers of ion pairs or parent molecules. Ionic liquids tend to have low dielectric constants, which means they are not ionizing solvents. One can assign an ionicity to an ionic liquid in terms of its conductivity and, presumably one might attempt to describe any liquid in this manner but ignoring the chemical properties of excess solvent molecules could lead to significant errors.

Thus in answer to the opening question, "What is an ionic liquid?" I prefer the answer, "Just a liquid salt consisting of ions and ion pairs." ■

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