

## Ionic Liquids: How Well Do We Know Them?



This journal has been the major source for phase diagrams and thermodynamic data. Over the years it has provided valuable information about various new, existing, and old materials systems to academia and industry communities. However, significant scientific and technological advances involve basic and applied research in a variety of phase diagrams related to diffusion-controlled topics. One of these notable examples is the thermodynamic properties of new “room-temperature ionic liquids (RTIL).” The RTIL have been actively pursued for their potential replacement in traditional organic solvents and molten salts.

Ionic liquids (IL) are room-temperature salts composed entirely of ions and have a wide liquidus temperature range. They have several important properties such as: wide electrochemical window, extremely low volatility, nonflammability, corrosion resistance to plastics and carbon steels, high thermal stability, high ionic conductivities, and high solvating capability. Variations in cations and anions can produce a large number of ionic liquids. Properties of ionic liquids depend on the structure of ions. Typical ionic liquid cations include *N*-butylpyridinium, and 1-alkyl-3-methylimidazolium or 1,3-dialkylimidazolium. Common anions are  $[\text{Cl}]^-$ ,  $[\text{Br}]^-$ ,  $[\text{PF}_6]^-$ , and  $[\text{BF}_4]^-$ .

The development of low-temperature and environmentally benign technologies for metals processing is an industrial challenge for the 21st century. The driving forces for development of these technologies are to reduce energy consumption and to lower investment costs and the greenhouse gas emissions. Ionic liquids are considered to be the most promising candidates due to their low toxicity and lower environmental impact. The cost analysis made for the large-scale production of chloride ionic liquids ( $\text{C}_n\text{mim}[\text{Cl}]$ ) showed that these IL cost about \$2.16/kg. Toxicity tests on standard test organisms showed that these are within the acceptable limits. They are generally more toxic than acetone, acetonitrile, and methanol but less toxic than phenol, ammonia, and chlorine.

When considering ionic liquids as alternatives for organic solvents or molten salts, the properties that concerned researchers most are their physicochemical and thermodynamic properties. However, not all these properties are equally important to heat transfer or metal extraction applications. Obviously, the liquid temperature range, heat capacity, and thermal stability of ionic liquids deserve the priority for determining the operating temperature range and heat transfer efficiency. Only in recent years has significant literature on heat capacities of ionic liquids become available. Information on the measurement of thermodynamic properties such as heat capacity, enthalpy, entropy, and Gibbs energy as a function of temperature for ionic liquids were sporadically reported. Availability of these fundamental properties data are important for the application of ionic liquids in several electrochemical and energy-conversion systems.

Thermodynamic properties of ionic liquids are conveniently determined by thermogravimetric/differential thermal analysis (TG/DTA). A new method, “DTA mass-difference baseline” was used to measure the overall enthalpy change of ionic liquids from DTA curves. Based on the polynomial relationship fitted from the heat capacity data, the other thermodynamic properties such as enthalpy, entropy, and Gibbs energy data were obtained. The ( $\text{C}_4\text{mim}[\text{Cl}]$ ) data showed that standard enthalpy and entropy changes increase with increasing temperature, while the standard Gibbs energy change decreases with increasing temperature within the temperature range studied (25-250 °C). The standard enthalpy of melting and enthalpy of vaporization for ( $\text{C}_4\text{mim}[\text{Cl}]$ ) were determined to be 0.92 and 11.07 kJ/mol, respectively.

Ionic liquids are generally more viscous than traditional organic solvents or molten salts used in metal production industries, as shown in Table 1. This is a limiting factor because operational costs associated with pumping and mixing may become prohibitive. However, the addition of cosolvents to IL can lower the viscosity to an acceptable level. Another way to avoid this problem is to design and synthesize ionic liquids with low viscosity. The bistriflimide-based ionic liquids generally have lower viscosity than their equivalent fluorophosphates or fluoroborates. The melting point and viscosity of ionic liquids with dicyanamide anion  $\text{N}(\text{CN})^-$  were reported as low as  $-21$  °C and 21 mPas, respectively.

When ionic liquids are used as electrolytes in metal production technologies, their electrolytic conductivities are of critical importance. However, very little conductivity data are available for ionic liquids. Reported conductivity data for some ionic liquids are not in complete agreement among the researchers due to difference in sample purity. Table 1 summarizes the electrical conductivity of common ionic liquids, molten salts, and aqueous electrolytes used in industrial metal extraction processes. It can be seen that the electrical conductivity generally decreases with the increase in anion size of ionic liquids. With the addition of inorganic or organic solvents, electrolytic conductivity was improved significantly to levels that are comparable or even superior to organic solvents.

**Table 1** Typical physicochemical characteristics of ionic liquids, molten salts, and aqueous electrolytes

Ionic liquids	Density ( $\rho$ ), kg/m <sup>3</sup>	Viscosity ( $\eta$ ), cp	Electrical conductivity ( $k$ ), S/m	Operating temperature	
				$T_{\text{melt}}$ , °C	$T_{\text{onset}}$ , °C
<b>Molten salts</b>					
NaCl	1.55	1.02 (900 °C)	375 (850 °C)	801	...
Al <sub>2</sub> O <sub>3</sub> + Na <sub>3</sub> AlF <sub>6</sub> + AlF <sub>3</sub> + CaF <sub>2</sub>	~2.12	...	~130	950	...
<b>Ionic liquids</b>					
C <sub>4</sub> mim[Cl] + AlCl <sub>3</sub> (50% mol)	1.24	27	1.00	...	...
C <sub>4</sub> mim[Tf <sub>2</sub> N]	1.43	69	0.41	-104 ( $T_g$ )	439
C <sub>4</sub> mim[BF <sub>4</sub> ]	1.12	154	0.35	-81	403
C <sub>4</sub> mim[PF <sub>6</sub> ]	1.36	371	0.15	10	349
<b>Aqueous</b>					
CuSO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O/electrorefining	1.21	1.01	62.7	...	<80
CuSO <sub>4</sub> + H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O/electrowinning	1.11	0.70	27.4	...	<80

Another significant advantage of ionic liquids is their high thermal stability, which enables their use over a wide operating temperature range. Long-term thermal stability of several common ionic liquids has been reported. The (C<sub>4</sub>mim[Cl]) starts to degrade at 260 °C, whereas decomposition of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (C<sub>4</sub>mim[Tf<sub>2</sub>N]) begins at 450 °C. Thermal stabilities of di-alkylimidazolium-based salts were strongly dependent on salt structure. The relative anion stabilities were observed as Tf<sub>2</sub>N<sup>-</sup> > PF<sub>6</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup> >> Cl<sup>-</sup>. The melting and thermal decomposition temperatures of commonly used ionic liquids, organic solvents, and molten salts data are shown in Table 1. The most ionic liquids are liquidus over a wide temperature range (-104-350 °C) and begin to decompose around 350 °C.

Recently, considerable efforts were made in investigating the transport properties of chloroaluminate imidazolium ionic liquids since they are most promising electrolytes for replacing molten salts and organic solvents. Studies using cyclic voltammetry (CV) and chronoamperometry (CA) showed that the electrodeposition of aluminum in electrolyte of concentration (AlCl<sub>3</sub>:C<sub>4</sub>mim[Cl] = 1.5:1.0) at 30 °C is a diffusion-controlled process. The diffusion coefficient of the electroactive species Al<sub>2</sub>Cl<sub>7</sub><sup>-</sup> ions in these ionic liquids was determined to be  $0.63 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ . Effective techniques with satisfactory accuracy are yet to be developed for the determination of transport properties for ionic liquids.

In summary, relatively little research effort has been made toward the fundamental understanding of the phase equilibria and phase transformations of ionic liquid mixtures. The experimental investigations for determining these properties are usually time consuming and expensive. Also, certain characteristics of ionic liquids posed barriers for the determination of such properties. Low vapor pressure and high viscosity make them unsuitable for determination of such properties using spectroscopic techniques. Variation in ionic liquid purity is also another major factor in reported discrepancies in physicochemical and thermodynamic property data.

With the aforementioned opportunities and challenges, significant efforts are needed to generate thermodynamic and transport property data. It is also important to standardize the ionic liquid synthesis procedures and develop regulations for grades of ionic liquid purity. This will enhance our understanding and acceptance of these wonderful liquids for the development of next-generation industrial technologies.

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