



# Properties of ionic liquid solvents for catalysis

John S. Wilkes\*

Department of Chemistry, United States Air Force Academy, 2355 Fairchild Drive, Suite 2N225, USAF Academy, Colorado, CO 80840-6230, USA

Received 31 July 2003; accepted 17 November 2003

## Abstract

Ionic liquids are good solvents for catalytic reactions. The rational selection of the appropriate ionic liquid solvent for a particular reaction requires general knowledge of the properties of ionic liquids, and the details of some properties of the specific ionic liquid solvents being considered. The solvent properties of ionic liquids that are relevant to catalysis are discussed, and sources of the values of those properties for ionic liquids are identified. A roadmap for the literature values of density, viscosity, melting and glass transition temperatures, thermal stability, empirical solvent parameters, absorption, toxicity, surface tension, heat capacity, and thermal conductivity is provided.

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**Keywords:** Density; Viscosity; Melting and glass transition temperatures; Thermal stability; Empirical solvent parameters; Absorption; Toxicity; Surface tension; Heat capacity; Thermal conductivity

## 1. Introduction

The increased interest in ionic liquids by chemists and technologists clearly is due to the utility of ionic liquids as solvents for reaction chemistry, including catalytic reactions. The desire for “green” solvents for industrial processes is partially responsible for this, but also many chemists now realize that ionic liquids offer some unique properties as solvents. Furthermore, ionic liquid solvents have the prospect for custom design of the solvent to meet specific requirements for a particular reaction type. Some barriers to the use of ionic liquids are the bewildering variety of ionic liquids reported in the literature, and the lack of a handbook of these new solvents.

There are perhaps about five common types of cations, and a similar number of anions that comprise most ionic liquids. Salts built on the 1,3-dialkylimidazolium cation (imidazolium) and various polyatomic anions (e.g.,  $\text{AlCl}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $(\text{CF}_3\text{SO}_2)\text{N}^- = \text{Tf}_2\text{N}^-$ ) are the most commonly used ionic liquids reported since an early paper on these types of materials in 1982 [1]. There is no generally accepted shorthand notation for ionic liquids. I will use the fairly common notation best understood by example: 1-butyl-3-methylimidazolium

bis(trifluoromethylsulfonyl)amide as  $\text{bmim}[\text{Tf}_2\text{N}]$ . Structural variations of those types of cations and anions permute to thousands of ionic liquids that can be readily prepared by simple procedures described in the literature. If one considers the prospect of binary and ternary mixtures, which are common in high temperature inorganic molten salts, there are trillions of permutations. Fortunately, a relatively small number of ionic liquids are commonly employed as reaction solvents. Even so, the few dozen of the common salts span a wide range of physical and solvent properties. Ideally we would like to have available the ionic liquid equivalent of the classic solvent handbook by Riddick et al. [2]. In this paper, I will identify the solvent properties particularly important to catalytic reaction chemistry, then point to sources for values of those properties. The reader will not find an exhaustive compilation of properties, but rather a roadmap to be used to find those properties in the literature. Only single salts (not binary or higher mixtures) are considered here, in order to reduce the complexity of the discussion.

The usefulness and scope of ionic liquids as solvents and in organic reactions and catalysis has been reviewed sufficiently recently [3,4]. It is especially instructive to read the table of 51 different reactions in ionic liquid solvents compiled by Olivier-Bourbigou and Magna [4]. The large majority of reactions employed ionic liquids with the 1,3-dialkylimidazolium cation. Reichardt, in his book on solvents for organic reactions, states the generally accepted rule for selecting a solvent for a reaction, “... maximum

\* Tel.: +1-719-333-6005; fax: +1-719-333-2947.

E-mail address: [john.wilkes@usafa.af.mil](mailto:john.wilkes@usafa.af.mil) (J.S. Wilkes).

Table 1  
Solvent properties

Thermal properties	General physical properties	Spectroscopic properties	Chemical properties	Toxicity and safety	Electrical properties	Colligative properties
Heat of vaporization [7]	Surface tension [13]	Refractive index [11,17]	Empirical solvent parameters [20]	DOT and UN hazard class [22]	Ionic conductivity	Freezing point constant
Heat of formation [8]	Density [11,14]	Critical temperature, critical pressure [18]	Acidity and basicity [21]	Toxicity [23,24]	Electrochemical window	Boiling point constant
Heat capacity [9]	Viscosity [11]	Optical activity [19]		Flash point [25]	Dielectric constant [11,26]	
Thermal conductivity [10]	Vapor pressure [15]	Absorption (UV-Vis-IR window, UV-cutoff, IR window compatibility)		Disposal	Dipole moment [11]	
Thermal stability	Surface tension and wetting [16]					
Melting point [11]						
Glass transition temperature						
Boiling point [11,12]						

working range between melting and boiling point, good solubility of reactants and products (or sometimes insolubility of the products), compatibility with the analytical methods employed, and usually high degree of purity” [5]. Other solvent properties are important as well, but it is clear that ionic liquids often meet the basic criteria for an appropriate solvent.

## 2. Properties of solvents for catalysis

Solvents may be classified in several ways. One finds solvents organized by chemical constitution, by acid–base behavior, by solute–solvent interactions, or by properties. This paper is organized by properties. Several well known compilations of solvent properties provide the complete list of solvent properties in Table 1 [2,5,6]. See the references within the table for details about those properties.

Not all of those properties are equally important to catalytic reactions, and some are not relevant at all. Solvent properties are organized according to importance to catalysis in ionic liquids in Table 2. Exactly which category to place a property in is a matter of judgment. The “must know” column is the values of properties needed to do even preliminary studies of reactions in an ionic liquid. The “know eventually” column is properties that must be determined if the reaction is to be scaled-up or commercialized. The properties in the “irrelevant” column either are not important for reaction chemistry, or are not applicable to ionic liquids. For example, the lack of volatility of ionic liquids may be the single most attractive property of ionic liquids for use as reaction solvents. Because the volatility is low or zero, the vapor pressure, boiling point, critical pressure, heat of vaporization and flash point have no meaning in most ionic liquids. There are exceptions to this statement, since the au-

thor is well aware that very acidic chloroaluminate ionic liquids do have a measurable vapor pressure of  $\text{Al}_2\text{Cl}_6$  [27].

Most of the remainder of this paper is discussion of the important ionic liquid solvent properties relevant to catalytic reactions, and reaction chemistry in general. Most importantly, the sources of the values of those properties will be cited, and the scope of the values described for each source. The properties discussed below are very likely to be sensitive to the purity of the ionic liquid sample being measured. For example, the viscosity is substantially affected by contamination by chloride or water [28]. Properties in the “irrelevant” column of Table 2 will not be discussed in detail.

### 2.1. Density

The density is the most often measured and reported physical property of ionic liquids, probably because nearly every application requires knowledge of the density. In general, ionic liquids are denser than water. Table 3 contains references to compilations of density values and the scope of the measurements in terms of anions and cations in the ionic liquids measured.

Many of the density values reported are at a single temperature, usually at 20 or 25 °C. Reports of temperature parameters (always linear) are most valuable.

### 2.2. Viscosity

The viscosity of ionic liquids usually is reported as the dynamic viscosity, also called the viscosity coefficient. It affects diffusion of solutes and practical issues, such as stirring and pumping. Ionic liquids are inherently much more viscous than molecular solvents, and vary over a range of <10 to >1000 cP at room temperature. Sources of viscosity values are in Table 4. Viscosity temperature dependence in ionic liquids is more complicated than in most molecular solvents, because most do not follow ordinary Arrhenius behavior. Most temperature studies fit the viscosity values to the VTF equation, which adds an additional adjustable parameter (glass transition temperature) to the exponential

Table 2  
Solvent properties of ionic liquids for catalysis

Must know	Know eventually	Irrelevant
Density	Surface tension and wetting	Vapor pressure
Viscosity	Heat capacity	Ionic conductivity
Melting point	Thermal conductivity	Electrochemical window
Glass transition temperature	DOT and UN hazard class	Dielectric constant
Thermal stability		Dipole moment
Empirical solvent parameters		Heat of vaporization
Absorption		Heat of formation
Toxicity		Boiling point
Disposal		Critical temperature
		Critical pressure
		Refractive index
		Optical activity
		Freezing point constant
		Boiling point constant
		Flash point

Table 3  
Density

Authors	Reference	Scope
Trulove and Mantz	[29]	39 imidazolium 22 non-imidazolium single temperatures
Rooney and Seddon	[30]	32 imidazolium single temperatures
Seddon et al.	[31]	24 imidazolium temperature parameters primary reference
Dzyuba and Bartsch	[32]	19 imidazoliums Three with temperature parameters
Rogers and co-workers	[48]	14 imidazolium single temperatures

“Imidazolium” refers to ionic liquids with 1,3-dialkylimidazolium cations, sometimes with other substituents on the ring.

Table 4  
Viscosity

Authors	Reference	Scope
Trulove and Mantz	[29]	39 imidazolium 22 non-imidazolium single temperatures
Rooney and Seddon	[33]	30 imidazolium single temperatures
Seddon et al.	[31]	24 imidazolium temperature parameters primary reference
Dzyuba and Bartsch	[32]	15 imidazolium figures only, values not tabulated
Rogers and co-workers	[48]	29 imidazolium single temperature
MacFarlane et al.	[34]	Four imidazolium and pyrrolidinium dicyanamides low viscosity
Ue et al.	[35]	imidazolium[F-HF] very low viscosity

term. The bottom two entries in Table 4 are notable because they report ionic liquids with relatively low viscosity.

### 2.3. Melting point and glass transition temperature

The melting points of ionic liquid solvents define the lower end of the liquidus range. The low vapor pressure and very wide liquidus range are probably the two properties that make the ionic liquids so attractive as solvents, compared to molecular solvents. Many or most ionic liquids are prone to supercooling, which makes melting points difficult to measure. For example, this author once prepared a new ionic liquid and worked with it for 2 months before noticing that it had crystallized in an NMR tube. The supercooling of ionic liquids causes freezing points to be notoriously unreliable and irreproducible. Many ionic liquids form glasses, for which glass transition temperatures are usually reported instead of melting points. The glass transitions tend to be very low ( $< -50^{\circ}\text{C}$ ) and viscosity very high at such cold temperatures, so the solvents are not really useful for most reaction chemistry at sub-zero temperatures (except for situations where glassy media are desirable). Table 5 directs the reader to several compilations of the melting and glass transition temperatures of ionic liquids.

### 2.4. Thermal stability

Thermal decomposition defines the upper limit of the liquidus range. Most ionic liquids used as solvents are so stable that the upper temperature limit is not an issue for reaction chemistry. Thermal stability usually is reported as the

Table 5  
Melting points and glass transitions

Authors	Reference	Scope
Holbrey and Rogers	[36]	21 imidazolium melting points
Rooney and Seddon	[37]	Nine imidazolium melting points
MacFarlane et al.	[34]	Seven dialkylpyrrolidinium & tetraalkylammonium dicyanamides
Grätzel and co-workers	[38]	25 imidazolium melting points Nine more identified as Tg's
Dzyuba and Bartsch	[32]	15 imidazolium melting points 19 Tg's
Rogers and co-workers	[48]	Imidazoliums 20 melting points, 11 glass transitions

thermal gravimetric analysis (TGA) onset temperature. The TGA onset temperature has the advantage of being well defined reproducible, and easy to measure. It is clear from a TGA thermogram that some decomposition occurs at temperatures less than the onset temperature. Isothermal gravimetric analysis experiments provide more realistic assessment of thermal stability, but such experiments cannot be reduced to a single number that reflects the stability. It is safe to say that ionic liquids with higher TGA onset temperatures are more stable than liquids with lower onsets, when measured under the same conditions. If an application requires long-term stability at relatively high temperature, then more extensive isothermal experiments should be done. For example, the TGA onset for emim[BF<sub>4</sub>] is 445 °C, while an isothermal experiment shows that the same ionic liquid decomposes at 0.0130 wt.%/min at 250 °C. Some of the very few compilations of thermal stability values are listed in Table 6.

### 2.5. Empirical solvent parameters

For molecular solvents there is a considerable body of knowledge on how solutes and cosolvents behave in solvents. It is important to know this in order to predict and understand solubility and the effects of solvents on reactions. Numbers are compiled that allow chemists to choose appropriate solvents for their application. For convenience I will call these indicators “empirical solvent parameters”. Examples are cohesive pressure ( $c$ ), internal pressure ( $\pi$ ), Hildebrand solubility parameter ( $\delta$ ), miscibility numbers ( $M$ -number), kauri-butanol number (KB-number), dipole moment of solvent molecules ( $\mu$ ), and dielectric constant ( $\epsilon$ ). The most used and misused term to describe solvent–solute behavior is “polarity”. The commonly held

Table 6  
Thermal stability

Authors	Reference	Scope
Rogers and co-workers	[48]	22 imidazolium
Rogers and co-workers	[39]	Six imidazolium cations having urea, thiourea or sulfide moieties on a side chain; PF <sub>6</sub> <sup>-</sup>
Van Valkenburg et al.	[49]	Three imidazolium TGA onset and isothermal

molecular view of polarity clearly is not appropriate to ionic liquid solvents. Until recently there was no systematic examination of the complicated nature of solute–ionic liquid interactions. Armstrong and co-workers [40] have taken into account multiple simultaneous interactions by observing the retention of numerous probe molecules in gas chromatography columns that have ionic liquid stationary phases. The experiments with 36 probe molecules produced five interaction parameter coefficients for each of 17 different ionic liquids. Each interaction parameter coefficient is an indicator of the importance of a particular type of solvent–solute interaction.

They reveal the polarizability of the ionic liquid, the interaction with pi- and non-bonding electrons in solutes, the hydrogen bond acidity and basicity, and the dispersion force interactions. The chemist will have an excellent basis for choosing a solvent for a particular application based on the knowledge of this array of interactions. The 17 ionic liquids studied to date are nine imidazolium salts (mostly 1-butyl-3-methylimidazolium and the usual anions), seven trialkylammoniums (some with unusual anions), and *N,N*-butylmethylpyrrolium Tf<sub>2</sub>N. One hopes that this method will be applied to a wider variety of ionic liquids in the near future.

## 2.6. Absorption

Absorption is a short term for the ability for the ionic liquid solvent to be a clear spectroscopic solvent. Since most ionic liquids are clear and colorless, the visible spectrum part of this issue is easily determined by eye. The parameter most often used for molecular solvents is UV-cutoff, which is available in several handbooks. Unfortunately there are no tables of spectroscopic properties of ionic liquid solvents. Despite the dearth of conveniently compiled spectroscopic specifications, ionic liquids are well suited to most spectroscopies. Examples are UV-Vis-NIR [41–43], IR [44] and NMR [45]. Users of ionic liquid solvents will have to search the primary literature for the suitability for a particular ionic liquid for the analysis they intend to use in their reaction.

## 2.7. Toxicity

Until very recently little data have been published on the safety of ionic liquids. Researchers who work with small amounts and who use normal protective equipment and precautions have not reported any adverse effects. The author has more than 25 years of experience in handling ionic liquids and supervising technicians and students who prepare and use them. I have seen no indication that any ionic liquids are extraordinarily toxic. The worst incident with ionic liquids in my lab was a student who spilled about 50 g of crude emim[Cl] (an uncrystallized liquid) onto and into his shoe. He waited an hour before removing the shoe and washing his feet. The skin on his foot became soft, swollen and red. He was treated in the medical clinic by washing with water

and antiseptic soap, and was told to not wear shoes until the symptoms subsided. After several days the skin returned to normal appearance, and the student never experienced any other symptoms related to this incident. The leather shoe, however, could not be saved.

Chemical toxicity is measured in two principal ways. The threshold limit value (TLV used in the US) and the similar maximale arbeitsplatzkonzentrationen (MAK und biologische arbeitsstofftoleranzwerte used in Germany) are the maximum concentrations (ppm) allowed in air for chronic inhalation exposure. The low vapor pressure of ionic liquids makes these measures irrelevant. The LD<sub>50</sub> values (dose for 50% mortality, usually in grams of chemical per kilogram of body mass) are appropriate for situations where an ionic liquid is ingested through the mouth or skin. It is likely that some companies that have scaled-up the preparation of ionic liquids have done toxicity tests, but have not published them.

Recently an academic group in Germany reported the results of the toxicological tests of a series of ionic liquids with imidazolium cations and PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and tosylate anions tested in two mammalian cell lines and a bacterial culture [46]. The imidazolium cations used have one *N*-methyl, and the other *N'*-alkyl substituent varied from C3 to C10. They found that the toxicity of the various ionic liquids spanned a range of about 1000× (from least to most toxic). Most interestingly, the most toxic of the ionic liquids has about the same toxicity as the least toxic of four common organic solvents (methanol, acetone, acetonitrile, MTBE) that they tested with the same protocol. Most of the ionic liquids were less toxic than the organic solvents by several orders of magnitude. This is very good news for advocates of ionic liquid solvents. The same group also propose a scheme based on structure activity relationships that may extend a small number of toxicity studies to a wide range of ionic liquid compositions [47].

## 2.8. Disposal

Disposal is included as a “must know” solvent property, because many or most, industrial, government and perhaps academic laboratory researchers must state a plan for waste disposal before experiments are started. I know of no published guidelines for safe disposal of any ionic liquids. This author disposes of ionic liquids segregated as halide waste, which is removed periodically by a contractor who specializes in hazardous waste disposal. If reactions with ionic liquid solvents are scaled-up, then disposal becomes a more important issue. The cost of large amounts of ionic liquids will require the development of efficient recycling of the solvent.

## 2.9. Surface tension and wetting

The properties in the “know eventually” category are seldom needed in the small-scale discovery phase of research and development, but will be necessary for the chemical en-



engineering of larger scale reactions. Surface tension can reveal some fundamental features of a liquid, but few studies of this property have been reported. The single compilation of surface tension values includes eight variously substituted imidazolium liquids with several of the common anions [48]. The surface tension of the ionic liquids is between that of organic solvents and water.

### 2.10. Heat capacity

Heat balance is seldom a consideration in laboratory scale reactions, but is important when engineering a large-scale reaction. Heat capacity of the solvent is needed for thermal management of large reactors. The heat capacity of several imidazolium ionic liquids have been measured, and found to be higher than water. The values were determined by modulated differential thermal calorimetry are emim[BF<sub>4</sub>], 1.281 J/g/°C; bmim[BF<sub>4</sub>], 1.659 J/g/°C, 1,2-dmpim[Tf<sub>2</sub>N], 1.196 J/g/°C [49].

### 2.11. Thermal conductivity

Thermal conductivity is another property most important for the chemical engineering of a process with a large amount of ionic liquid. This is a seldom measured property, but the thermal conductivity of a few ionic liquids has been measured by the transient hot wire method. The values are emim[BF<sub>4</sub>], 0.200 W/m/K; bmim[BF<sub>4</sub>], 0.186 W/m/K; dmpim[Tf<sub>2</sub>N], 0.131 W/m/K [49]. The reference materials used in these measurements were water and toluene. The thermal conductivities of the three ionic liquids are much closer to toluene than water.

### 2.12. Hazard class

The regulations for the transportation of hazardous materials require labeling of containers that identify they type of hazard the chemicals present. Some ionic liquids are reactive and corrosive (the chloroaluminates), but most are more safe than organic solvents. Ionic liquids do not appear in the handbooks of DOT or UN hazard classifications, because they are relatively new and have not been transported in large quantities.

Ionic liquids are often said to be nonflammable. The lack of vapor pressure implies no flash point, however, anionic liquid will burn if a flammable substance is dissolved in it. For example, 50 wt.% hexane dissolved in an imidazolium Tf<sub>2</sub>N ionic liquid ignites readily with a match, and burns with a yellow flame. After the mixture has finished burning, the residue is the apparently unchanged (but hot) clear colorless ionic liquid [50].

## 3. Prediction of properties

Even at this early stage of development of ionic liquids the task of measuring and compiling all properties of all

ionic liquids is a daunting challenge. Fortunately it may be possible to predict some of the important properties of ionic liquids; either from first principles or by structure–property correlations. Katritzky and co-workers have developed the strategy and software for predicting properties of many materials based on quantitative structure–property relationships (QSPR). Recently that group has applied their methodology to the prediction of melting points of ionic liquids [51]. Most of the compounds in the datasets used in the study have higher melting points than those of ionic liquids, but the method did appear to correlate structures of many imidazolium salts with melting temperatures. Maginn and co-workers have used a similar QSPR approach to predict melting points, but with a more focused set of quaternary ammonium salts [52]. The validation of this approach to the complete matrix of properties needed to characterize an ionic liquid solvent will be a substantial task, but not as great as preparing and measuring every property of every possible ionic liquid. The goal of predicting the structure of an ionic liquid that has a set of properties specified by the chemist for a particular use may very well be attained in the foreseeable future.

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