

1 Ionic Liquids in the Temperature Range 150–1500 K: Patterns and Problems

C. AUSTEN ANGELL

Department of Chemistry and Biochemistry, Arizona State University,
Tempe, Arizona

Abstract

In this chapter we trace some of the developments in ionic liquids physical chemistry from the crimson metal–molten salts of Humphrey Davy’s original melt electrolysis discoveries of elements, to the newest ambient-to-200 °C fuel cell electrolytes. We discuss the origin of a common pattern of behaviour for ionic liquids as they are cooled down, often reaching the glassy state—a pattern that extends from the liquid orthosilicates of the earth’s mantle to the subambient temperature ionic liquids of the present era. However, where glasses are rare among orthosilicates and are generally limited to the complex anion “polymerised” silicate liquids (Bockris’s “island anions”), they are the general result of cooling the ambient ionic liquids of current interest, even though the anions are always simple. How to maintain high fluidity along with low vapour pressure is the challenge. The highest ambient temperature fluidities are obtained with ionic liquids of the proton transfer variety, and they rival aqueous solutions in conductivity—a consequence of optimising Coulomb cohesion and charge carrier concentration in the absence of solvent. These protic ionic liquids (PILs) show much promise as fuel cell electrolytes and also as biopreservatives. We illustrate the great range of electrolyte character that can be obtained with PILs, using an energy level diagram for proton transfers, and then compare the fuel cell performances of electrolytes of organic cations with that of their inorganic cation cousins.

1.1 INTRODUCTION

It is now a little over 200 years since Sir Humphrey Davy, in England, first saw the deep crimson colour of sodium metal dissolved in molten sodium chloride [1]. He was in the process of using electrochemically driven decomposition to produce, for the first time, a free alkali metal element and was observing the consequence of some dissolution of the liberated metal in the liquid salt. This followed Volta's invention of the voltaic "pile" that provided the driving force for the decomposition, by only a few years (which this author finds remarkable).

We select three particular themes to highlight as we follow developments in understanding of ionic liquids from Davy's time to the present era. The themes are (1) ionic liquids that are coloured as a result of particular light-absorbing structural features, (2) ionic liquids providing interconversion of chemical and electrical forms of energy, and (3) ionic liquids transforming to glassy solids in consequence of failure to crystallise. Presently, the low temperature versions of Davy's liquids are being found useful in fuel cells that permit the reverse of Davy's process—namely, the release of electrical energy by conversion of elements (hydrogen and oxygen) to the chemically combined state (water). The narrative will be brief and sweeping and will be strongly and transparently stamped by the author's personal experience over a fifty year period of research in ionic liquids. It is by no means intended to be an account of the field of ionic liquids as a whole.

When the writer was a graduate student in chemical metallurgy at Melbourne University in the 1950s, the understanding of silicate liquids of metallurgical relevance was in a primitive state. Although molten calcium magnesium silicates had long been used in the production of iron by a chemical reduction process (using carbon as the source of electrons to liberate the metal from its combined state), the literature of the time mostly referred to the high temperature liquids in terms of *molecules* of the chemical compounds from which they were formed. Thus the furnace slag contained MgO molecules, CaO molecules, and SiO₂ molecules. In a radical departure from the thinking of the time, John Bockris at Imperial College had recently [2, 3] launched the idea that these highly fluid materials actually consisted of free cations of the alkaline earth elements moving in a sea of silicate anions of varying complexity. The writer's M.Sc. supervisor, thermodynamicist Mervyn Willis [4, 5], liked the idea and encouraged him to accept a fellowship in Bockris's new laboratory in the United States at the University of Pennsylvania. At that time, a subfield of Bockris's "ionic liquids"—one that was designated "molten salts" (because they were more simply constituted than the molten silicates)—was under intense investigation. This was because of the molten-salt-cooled nuclear reactor project that was then under development at Oak Ridge National Laboratory. The reactor was very successfully using molten alkali fluorides and fluoroberyllates as the medium for heat transfer between reactor and turbine. (After highly successful demonstrations, this project was moth-balled in the 1960s as doubts about the future of nuclear energy arose, but it may well be resurrected in the present climate of crisis consequent on the threat posed by carbon energy based global warming.)

Harry Bloom, from the University of Hobart in Tasmania, Australia, was a visiting scientist in Bockris's laboratory. As a student at Melbourne University, Bloom had studied complex anions in molten salts [6] under displaced German physical chemist Erich Heymann, who had come from the early German school of molten salt chemists. The problem of identifying complex anions (like $[\text{CdCl}_4]^{2-}$ that, in aqueous solutions, moved toward the anode in an electric field) in a medium containing no solvent was one of the many intellectual basketballs constantly in the air in Bockris's lab. My assignment was to study diffusion of the individual ions in the complex-containing ($\text{CdCl}_2 + \text{KCl}$) system [7].

In contrast to the field of metallurgical silicate liquids, molten salt studies had been relatively advanced since the early part of the 20th century. The German school had studied a great many lower-melting systems. They had already shown that the Walden rule, Eq. (1.1) [8], that reliably related the equivalent conductivity Λ of aqueous solutions to their viscosities, η ,

$$\Lambda\eta = \text{constant} \quad (1.1)$$

broke down seriously for molten silver halides and needed to be replaced by the "fractional" Walden rule:

$$\Lambda\eta^\gamma = \text{constant} \quad (1.2)$$

where γ is a constant $0 < \gamma < 1$.

The fractional Walden rule, which implied that the Arrhenius activation energy for conductivity was lower than that for viscosity, found a natural interpretation in terms of one of the ionic species ions being smaller than the other, hence capable of squeezing through smaller gaps in the condensed phase structure. This decoupling of the ionic motions reached an extreme in the case of silver salts of large polarisable anions. These were later to become important components of the "superionic" family of ionic glasses, and thus the stage was already set for the understanding of these materials, which would get much research attention in the second half of the century as electrolytes for solid state batteries. Success in this respect required a breakdown of Eq. (1.1) by some 12 orders of magnitude [9]!

Interestingly enough, the original Walden rule finds a new lease on life in current studies of ionic liquids of the ambient temperature variety, where the Walden plot, in the form $\log(\Lambda)$ versus $\log(\eta^{-1})$ is being used as a classification diagram to distinguish "normal" ionic liquids from "poor" ionic liquids, on the one hand, and "superionic" liquids on the other hand [10, 11]. An example will be seen at the end of this chapter. The search for "superprotonic" electrolytes for fuel cell applications is in full swing at this time. Superprotonics are the holy grail of the fuel cell discipline and will briefly be considered later.

The study of complex anions was very pertinent to the Oak Ridge National Laboratory nuclear reactor program, which had also benefited from the talents of prewar displaced German physical chemists. At Oak Ridge, people were studying the "weak field" analogues of the "basic" MgO-SiO_2 metallurgical slags, represented by solutions of alkali fluorides and the Lewis acid BeF_2 (all ion charges halved relative to the MgO-SiO_2 melts). Complexation of the fluoride ions [12], to yield tetrahedral

$[\text{BeF}_4]^{2-}$ and $[\text{Be}_2\text{F}_7]^{3-}$ anions, reduced the Coulomb energy of the liquid, lowering liquidus temperatures and also lowering viscosity [13] to give fluids with the excellent heat transfer characteristics needed for a successful nuclear reactor program.

The high degree of analogy to silicate systems presented by the $\text{LiF}-\text{BeF}_2$ system was not of great interest to Oak Ridge scientists, but became the centre of attention in the East German laboratory of Vogel. Vogel et al. [14] not only determined the phase diagram but showed that, in solutions rich in BeF_2 , the glass-forming solutions underwent a liquid–liquid phase separation [15] during cooling, similar to that which had been identified in silica-rich $\text{Li}_2\text{O}-\text{SiO}_2$ glasses.

A further analogy was waiting to be made, using molten chlorides closer in nature to those with which the field is currently so involved. With ZnCl_2 as the network glass former and pyridinium chloride as the network breaker (or “modifier”), Eastal and Angell [16] demonstrated that the glass-forming properties of the binary chloride system were highly analogous to those of the $\text{Na}_2\text{O}-\text{SiO}_2$ system.

While complex anions that could be enlarged into glass-forming networks were clearly of interest, complex cations were not to be neglected. The rare earth analogues of Humphrey Davy’s crimson alkali metal–alkali halide solutions were then under study at Imperial College in the group of John Bockris’s former student, John W. Tomlinson. The writer had the privilege of working under Tomlinson as the Imperial College Stanley Armstrong fellow and studied the deep scarlet solution formed by the solution of metallic cadmium in CdCl_2 [17]. Rather than forming the liquid equivalent of blue-purple alkali chloride crystal f-centres (lattice vacancies containing an excess electron), which was Gruen and co-workers’ [18] interpretation of Humphrey Davy’s crimson alkali halide solutions, the excess cadmium in CdCl_2 appeared to form metal dimers, $[\text{Cd}_2]^{2+}$.

1.2 VISCOSITY AND GLASS-FORMER PHENOMENOLOGY IN “SIMPLE” IONIC LIQUIDS

While it is now common knowledge that ambient temperature ionic liquids of current interest frequently supercool and vitrify, there was a time when most inorganic ionic liquid researchers would consider the formation of ionic glasses, in the absence of covalently bound networks, to be impossible.

The first evidence to the contrary was provided by Russian researchers engaged in the study of binary phase diagrams [19], who reported that in some simple salt systems there were liquid compositions that failed to crystallise during normal cooling. A useful survey of (alkaline earth + alkali metal nitrate) solutions by the German group of Thilo [20] showed this was systematically related to the relative sizes of monovalent and divalent cations and was connected to the existence in favourable systems, of very low eutectic temperatures.

The observations by Thilo et al. [20] were preceded by Dietzel and Poegel [21], who carried out a detailed study of crystallisation rates and glass formation in the now classic $(\text{Ca}(\text{NO}_3)_2 + \text{KNO}_3)$ system. They found that the composition 38% $\text{Ca}(\text{NO}_3)_2$ was particularly resistant to crystallisation, although it was well on the $\text{Ca}(\text{NO}_3)_2$ -rich side of the eutectic composition. The 40:60 mole % composition in

this system (now affectionately known as CKN) has since become one of the most thoroughly investigated of all ionic liquid systems and has been the test case for sophisticated new experimental techniques. For instance, the neutron spin-echo technique [22], by means of which the intermediate scattering function needed for testing the Götze mode-coupling theory of glass-forming liquids [23] was first determined, employed CKN as the test liquid.

The finding that glasses can be formed in systems as simply constituted as CKN (two cations each with the argon electronic structure, and a small triangular anion) provided the motivation for most of this writer's researches in the physical chemistry of liquids [24].

The especially simple behaviour of the CKN system is illustrated [25, 26] by the way that a spread of precise conductivity data covering several orders of magnitude, obtained when composition and temperature are both varied, can be collapsed onto a single straight line when the data are treated using the relation now known outside the ionic liquid field as the Vogel–Fulcher–Tammann (VFT) [27–29] equation (after the independent (1921–1926) works of early authors who used it to describe the temperature dependence of viscosity for many single-component [29], as well as complex, silicate mixture compositions [28]). For the most typical glass-former transport property, the viscosity, this is expressed by:

$$\eta = \eta_0 \exp(B/[T-T_0]) \quad (1.3)$$

where η_0 , B , and T_0 are constants, and T_0 varies linearly with composition. (In the present author's opinion, Eq. (1.3) should be called the Tammann–Fulcher equation to recognise the weight of Tammann's contribution. After all, Vogel never studied a supercooled liquid, and the equation used by him to describe some liquid viscosities was not of the form of Eq. (1.2), but instead a much less suggestive mathematical equivalent. The idiosyncratic [30] designation, VFT equation, that the writer introduced in 1972 [31]—and which is now widespread in use—was a protest against the chronological convention, and an attempt to credit the superior understanding demonstrated in Tammann's writings of the equation's implications. T_0 , of course, represents the temperature at which the viscosity would diverge on extended supercooling. It distinguishes the equation from the Arrhenius law obtained when $T_0 \rightarrow 0$ K, and implies the existence of some sort of transition that terminates the liquid state. The nature of this transition, and even its existence, has been the focus of unresolved argument among glass theorists for many decades.

The simple relation of the parameter T_0 to the experimental glass transition temperature T_g is shown in Figure 1.2. When the linear increase of T_0 is combined with Eq. (1.3), a simple relation for the conductivity at any temperature and composition is obtained [25]. This permits the data of Figure 1.1a to be collapsed to the single straight line shown in Figure 1.1b.

If B in Eq. (1.3) is replaced by the product DT_0 , or T_0/F , as in Eq. (1.4a) and (1.4b),

$$\eta = \eta_0 \exp(DT_0/[T-T_0]) \quad (1.4a)$$

$$= \eta_0 \exp(T_0/F[T-T_0]) \quad (1.4b)$$

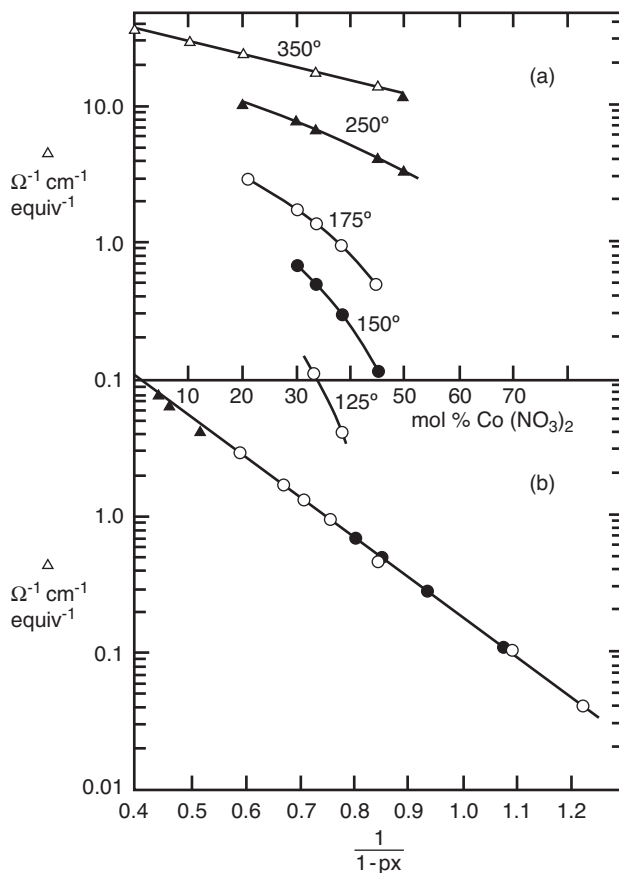


FIGURE 1.1 Simple behaviour of the physical properties of solutions in the binary system ($\text{KNO}_3 + \text{Ca}(\text{NO}_3)_2$), which is glass forming in the range 33–45% $\text{Ca}(\text{NO}_3)_2$. (a) Isotherms of conductivity versus mole % $\text{Ca}(\text{NO}_3)_2$. (b) Collapse of the data for part (a) to a single line using an equation derived from Eq. (1.3) on the assumption that T_0 is linear in composition (as demonstrated in Fig. 1.2) (From Angell [25, 26] with permission.)

then the values of the parameters D and F quantify the deviation from Arrhenius behaviour that the data exhibit. This deviation has become known as the fragility of the liquid [32] and can be represented numerically by the parameter F , although a number of other metrics are more commonly used [33]. The calcium–potassium nitrate system exhibits one of the largest values of F that has been observed (though the increase of the Arrhenius slope with decreasing temperature appears to saturate above T_g [34]). Since the dramatic breakdown of the familiar Arrhenius law is one of the most striking features of glass-forming liquids, CKN has attracted a lot of attention from investigators of the physics of glass-forming liquids. When F is large, the value of T_0 lies close to the experimental glass transition temperature, as can be seen in

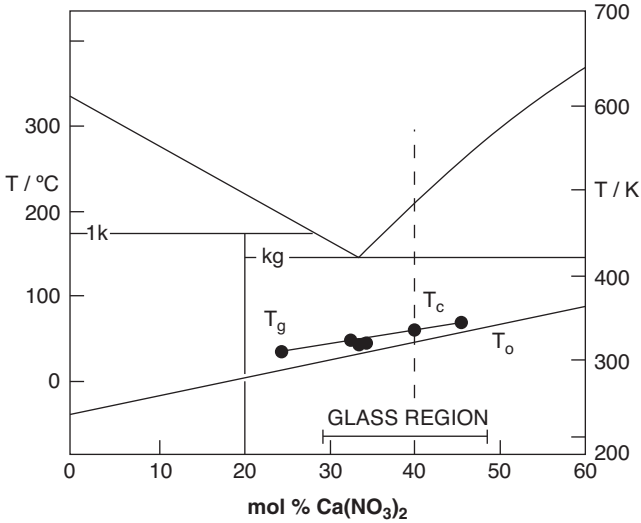


FIGURE 1.2 Phase diagram for the glass-forming binary system ($\text{KNO}_3 + \text{Ca}(\text{NO}_3)_2$), showing the relationship of the parameters T_0 of Eq. (1.3) to experimental glass temperatures, T_g , and composition. (From Angell [25] with permission.)

Figure 1.2, which shows the relation of each of T_g and T_0 to the phase diagram for this system [25].

1.3 STRONG AND FRAGILE IONIC LIQUIDS

By using the experimentally determined glass transition temperature T_g as a parameter to scale the temperature in an Arrhenius plot, the data from many different types of liquids can be placed on the same diagram. This allows demonstration of the pattern of behaviour that is characteristic of glass-forming liquids [35, 36]. For ionic liquids, a selection of data for cases where only simple ions are present is shown in Figure 1.3 [37], and they are seen to all exhibit rather extreme deviations from Arrhenius behaviour. The lowest temperature cases are data in the low viscosity range for low melting liquids of the 1-butyl-3-methylimidazolium cations neutralised by different anions. Glass-forming derivatives [9] of the silver halides studied by the early German workers are contained in Figure 1.3a and are seen to exhibit the lowest viscosities that have been measured among this group. The manner in which the viscosities of this family of glass formers group together when plotted in T_g -reduced form is shown in Figure 1.3b.

Note how the data for the 1-butyl-3-methylimidazolium salt melts [10] fit smoothly into the overall ionic liquid pattern [35]. It is a matter of interest that the currently much-researched ambient temperature ionic liquids provide a great many examples of this otherwise rather uncommon phenomenon—the single-component glass former.

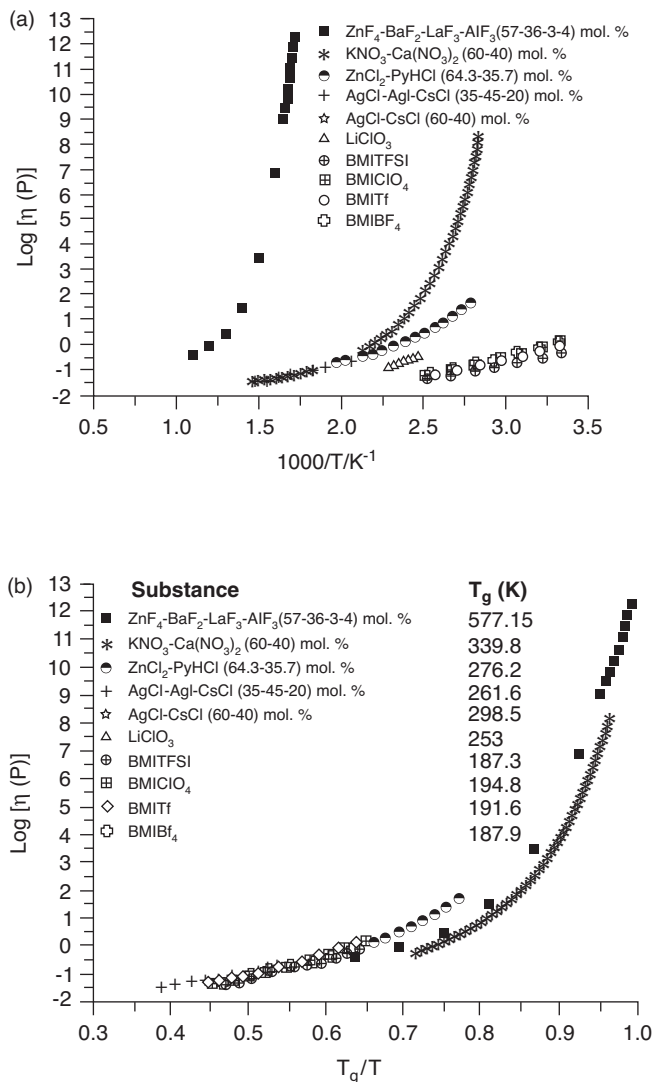


FIGURE 1.3 (a) Arrhenius plots of the viscosities of ionic liquids ranging from molten fluorides to silver halide–alkali halide mixtures, down to $[C_4mim][BF_4]$. Glass temperatures, at which the viscosities reach values of about 10^{12} Pa·s are given in the legend. (b) The same data, plotted in T_g -reduced Arrhenius form, in order to reveal the strong deviations from the Arrhenius law, known as high fragility, of these liquids [37].

The reason that glass formation among ambient temperature liquids is common is the same as the reason that their melting points are low despite the strong Coulombic forces acting between the ions. When melting points are low relative to intermolecular forces, failure to crystallise during cooling is a common consequence. It is due to the

high viscosity at the melting point. Empirically, it is found that when viscosity at the melting point rises above about 0.1 Pa·s (water at ambient, 0.001 Pa·s), the probability of nucleation of the stable phase during normal cooling becomes low [38]. Thus the low melting point is the phenomenon to be understood. It is a consequence of the difficulty that compounds with irregularly shaped charged particles encounter in packing their particles efficiently into three-dimensionally ordered lattices, while maintaining a symmetrical charge distribution. Then the entropy of the liquid state tends to dominate the thermodynamics, stabilising the liquid, and consequently pushing down the melting points. This common glass-forming tendency exhibited by low-melting ionic liquids has been discussed in more detail elsewhere [11] and will not be further dealt with here.

Low melting points relative to forces between particles is a characteristic of the “network” liquids that make up the “glass formers” of classical glass science. In these cases, however, the extended network structure prevents the temperature from having its usual strong effect on the volume of the liquid, and the deviation from Arrhenius behavior in their transport properties is then much smaller. We see this when these liquids, and their partly disrupted binary solutions, are included in Figure 1.3b. Then we get the complete “strong and fragile liquids” pattern [32, 35, 36] for ionic liquids seen in Figure 1.4.

The presence of the single-component glass-forming chloride [39, 40], ZnCl_2 in the centre of the diagram, is to be noted. ZnCl_2 is a dense tetrahedral network [41, 42] with Zn-Cl-Zn angles averaging only 110° [43], to be compared with SiO_2 , Si-O-Si angles averaging 140° with a wide distribution [44]. The intermediate range order

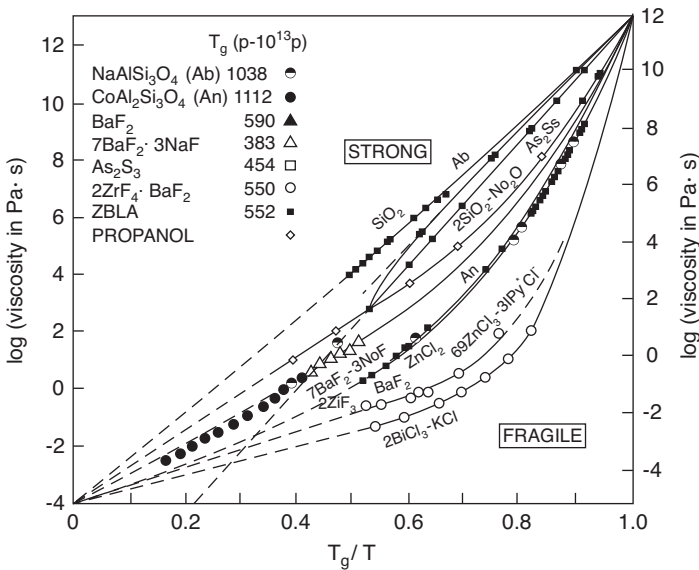


FIGURE 1.4 T_g -scaled Arrhenius plot of ionic liquids with simple halide anions. (From Angell [35] with permission.)

measured by the sharpness of the second and third neighbour peaks in the radial distribution function [43] is much smaller in the case of ZnCl_2 . This leads to much more fragile behaviour.

The fragility is further increased when the weak network is disrupted by “chemical scissoring” of the Zn–Cl bonds, using a second salt with basic chloride ions. To study this effect, it proved necessary to use a lower melting second component than any of the inorganic chlorides. A suitable choice [45] proved to be the organic salt pyridinium chloride, which had earlier been used by Dieter Gruen in studies of ligand field spectroscopy of nickel and cobalt ions [18]. Data for solutions of the pyridinium chloride– ZnCl_2 system [16] are included in Figure 1.4 and are seen to approach the fragile limit of this data collection.

1.4 ROLE OF COMPLEX ANIONS IN DEVELOPMENT OF AMBIENT TEMPERATURE IONIC LIQUIDS

Halides of organic cations have proved very useful for the study of complex anions and their effects on molten salt properties. The dramatically different effects of complexation on the liquid viscosity are well illustrated by the 1976 study of Hodge [46, 47], who used the lower melting 2-methylpyridinium chloride as the source of the Lewis base chloride.

Data seen in Figure 1.5 show that the cohesive energy of an ionic liquid is lowered most strongly when chloride ions are complexed by iron(III) chloride to produce the large singly charged $[\text{FeCl}_4]^-$ anion. This observation led to the prediction that, among ionic liquids of a given cation, the tetrachloroferrate(III) salt should be the most fluid and also the most conductive, even more so than the well-studied ionic liquids containing $[\text{AlCl}_4]^-$ anions [48, 49]. The veracity of this expectation is

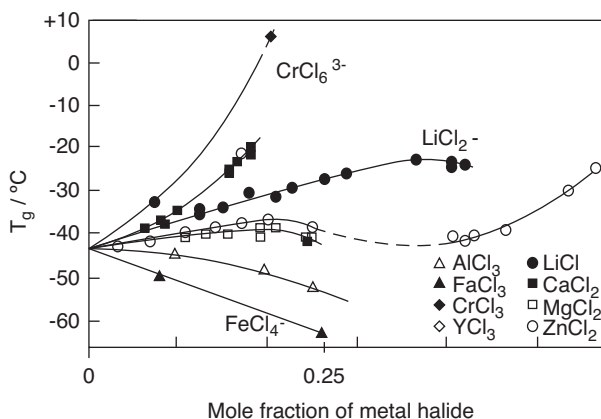


FIGURE 1.5 Variation of T_g of the simple chloride glass former, 2-methylpyridinium chloride, on chloride complexation with various Lewis acids. (Adapted from Angell et al. [46].)

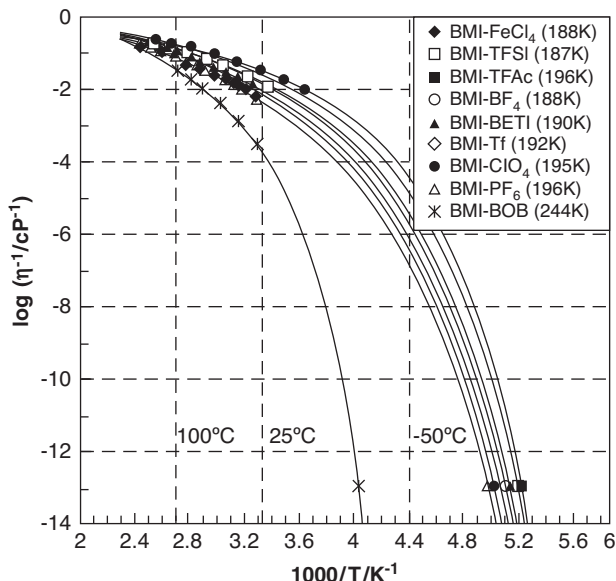


FIGURE 1.6 Fluidity data for a number of salts of the 1-butyl-3-methylimidazolium cation, showing that the tetrachloroferrate(III) is more fluid than any of the fluorinated anion salts, in accord with its lowest T_g seen here ($\log \eta^{-1} = 10^{-13}$). (From Xu et al. [10] with permission.)

demonstrated in Figure 1.6 for 1-butyl-3-methylimidazolium salts. For the 25°C conductivity, the tetrachloroferrate(III) is half an order of magnitude above any others in the group. The increase of ionic mobility by complexation seen here is no different in principle from the use of BeF_2 additions to alkali fluoride melts utilised in the molten salt reactor technology discussed in the introduction. There, the addition of 1 mole of BeF_2 replaced two high charge intensity fluoride anions with a doubly charged anion of much larger dimensions, for a net decrease in cohesion.

The fluorinated anion ($[\text{BF}_4]^-$ and $[\text{PF}_6]^-$) salts that are frequently cited in the literature of the ambient temperature ionic liquids [50–52] are to be understood in the same terms. Unfortunately, like these two fluorinated anions, the tetrachloroferrate anion is slowly hydrolysed by water, and applications of ambient temperature ionic liquids usually require the presence of water-stable anions. The fluorinated species, however, are unpolarisable, and so minimise the effect of the van der Waals contributions to the liquid cohesion. This characteristic of fluorinated anions was first noted in a 1983 study of binary solutions of lithium halides with organic salt halides by Cooper, where the replacement of iodide anions by the equivalent amount of $[\text{BF}_4]^-$ anions was predicted to lead to an increase of ambient temperature conductivity, and then shown to do so (in a note added in proof) by some two orders of magnitude [53]. Cooper's further extensive syntheses and measurements on viscosity and conductivity of a family of tetraalkylammonium tetrafluoroborate salts, unfortunately, remained unpublished (for over two decades) until 2003 [10].

In the meantime, Cooper and O'Sullivan [54] reported, in 1992, the first systematic study of ambient temperature water-stable ionic liquids, using triflate and related anions combined with dialkylimidazolium-type cations. This announcement, presented at one of the Electrochemical Society's International Molten Salt Conferences, and eventually published in the Proceedings [54] was immediately followed by a communication by Wilkes and Zaworotko [55], who had been working on similar salts, and the field of high fluidity, water-stable, ionic liquids was launched.

The only significant improvements in fluidity of water-stable, noncorrosive, ionic liquids since that time have come from MacFarlane's group (dicyanamides [56–58]) and the study of protic (as opposed to aprotic) cation salts [59], with which we will concern ourselves after discussing a further important aspect of the organic cation halides.

1.5 SPECTROSCOPIC ASPECTS OF ORGANIC CATION HALIDES

An aspect of organic cation halide salts which has escaped emphasis so far but which is important in understanding the high fluidities of the tetrachloroferrates(III), and so is deserving of further exploitation, is the high Lewis basicity of the halide anions. This is due to the relatively weak effective positive charge intensity of the larger organic cations, which leaves the electron density natural to the chloride anion almost unperturbed—and hence available for donation to stronger Lewis acidic cations. This effect is manifested in the sharp and intense electronic spectra of transition metal cations observed when their halides are dissolved in organic cation halides.

Figure 1.7, from the work of Gruen and McBeth [45], compares the spectra of Ni^{2+} dissolved in molten pyridinium chloride (Fig. 1.7a) with that found in the LiCl-KCl eutectic and LiCl itself (Fig. 1.7b). The sharp spectral lines are consistent with an almost undistorted tetrahedral structure that gives rise to the brilliant blue colour of the solution. Nickel(II) can also serve as a probe for structural changes in binary solutions, for instance, in the binary system (2-methylpyridinium chloride + ZnCl_2), sharp and highly temperature-dependent changes can be seen in the vicinity of stoichiometric complexes characteristic of the solvent system. These are reminiscent of the unique and informative spectra of such species as the previously unknown NiCl_3^- anion, which was detected by Brynstad and Smith [60] in a narrow composition region of the ($\text{CsCl} + \text{AlCl}_3$) system, in which the chloride anion activity changes precipitously across the $[\text{AlCl}_4]^-$ stoichiometry [61]. In systems with organic cations, because of the high chloride ion basicity in the first component, comparable chloride ion activity changes can occur in the crossover stoichiometry of less dominant anion species than $[\text{AlCl}_4]^-$. The consequent possibility of unusual complex anion stoichiometries and symmetries remains to be exploited.

An even clearer use of ionic liquids in transition metal coordination chemistry was that of Abkemeier and Angell, who needed a room temperature molten chloride for the first application of the newly invented diamond anvil high pressure cell in the study of pressure effects on coordination numbers. They used ethanolaminium

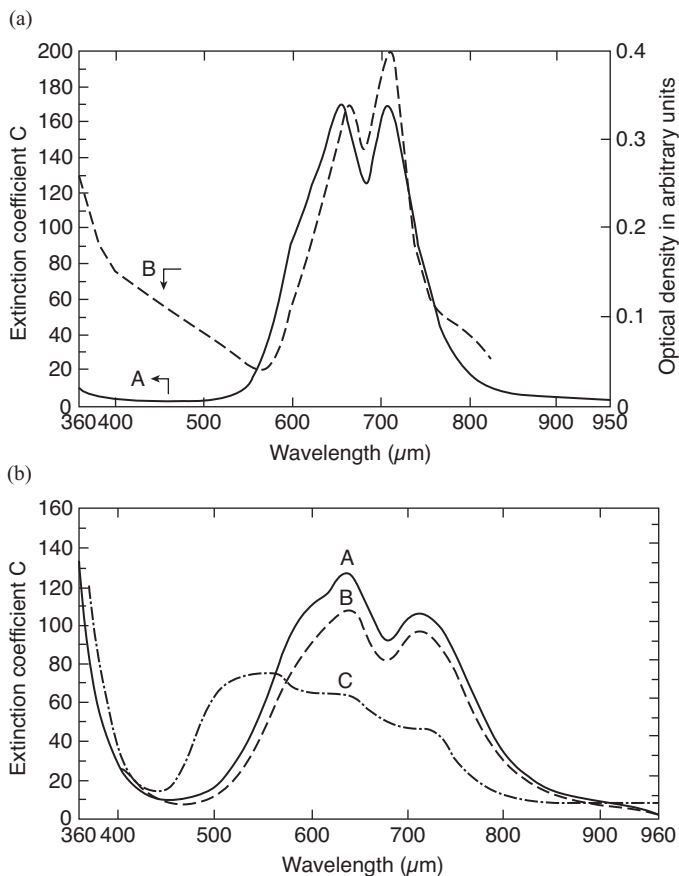


FIGURE 1.7 (a) The electronic (visible) spectrum of Ni²⁺ dissolved at a concentration of 1×10^{-4} M in pyridinium chloride. (b) The equivalent spectrum in LiCl–KCl solutions at two different LiCl contents. The tetrahedral character is almost lost in the LiCl-rich solution, in which the second nearest neighbor to the nickel(II) is most probably Li⁺. (From Gruen and McBeth [45] with permission.)

chloride as the ambient temperature noncrystallising component of a mixture with ethylammonium chloride to study nickel(II) spectra during pressure increases up to 1 GPa [62], and observed the conversion from $[\text{NiCl}_4]^{2-}$ at ambient pressure to $[\text{NiCl}_6]^{4-}$ at higher pressures, the equilibrium constant change yielding a ΔV within 10% of the volume of 2 moles of chloride ion.

Advantage has recently been taken of this sharpness and intensity of complex species electronic spectra to study the time dependence of specific structural changes in ionic liquids, and thereby to permit comparison of chemical order relaxation times with the relaxation times that determine the glass transition in the same solution [63]. In solutions containing large components of both an aprotic ionic liquid chloride and a source of –OH ligands, such as sorbitol, or different sugars, cations like Co^{2+}

distribute themselves between octahedral $\{\text{Co}(\text{OH})_6\}$ sites and tetrahedral $\{\text{CoCl}_4\}$ sites, and the distribution is temperature dependent. A sudden change in temperature can cause a shift in the populations of the two types of sites, and this is registered very sensitively by the change in intensity of the $[\text{CoCl}_4]^{2-}$ peaks (by contrast, the octahedral absorption bands are very weak [63], because the d-d transitions are strongly forbidden in octahedral symmetry). The change in the tetrahedral band intensities, as a function of time, monitors the change in chemical order of the cobalt(II) species, and it is a question of interest whether or not this chemical order relaxation is slaved to the overall structural relaxation of the glass-forming system. Previous studies of related spectroscopically monitored chemical orders have suggested that it is, but none have been as sensitively detected as that manifested in an organic cation-based ionic liquid system.

Some data for the latter case are shown in Figure 1.8, both for up-jumps and down-jumps to the same final temperature. When similar studies are made for the volume of a glass former, the approach to equilibrium is found to be strongly asymmetrical, with the approach from a lower temperature being much slower than the approach from a higher temperature. (This is known as the “nonlinearity” of relaxation, one of the three “non”s of glass former phenomenology.) Figure 1.8 shows that in the case of chemical order relaxation, the equilibration kinetics can be linear. The observations, of course, are being made on a very minor component of the solution, but so are many

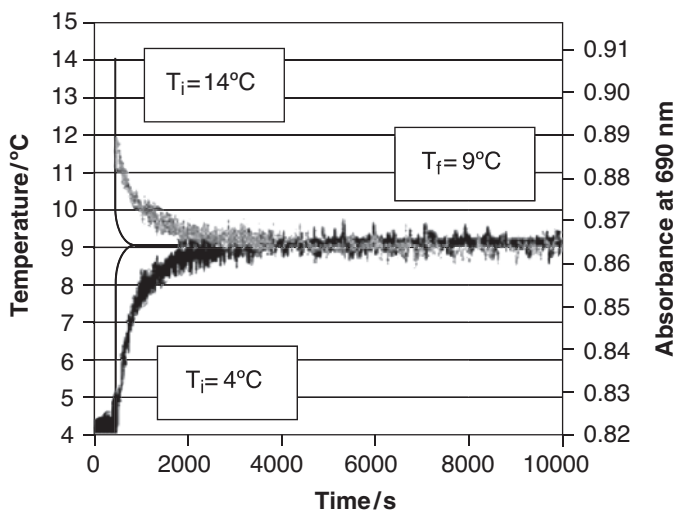


FIGURE 1.8 Time dependence of the intensity of the cobalt(II) tetrahedral absorption in the system described in text, following 4°C temperature up-jumps and down-jumps to the same final temperature. (The much faster equilibration of the temperature is shown by the less noisy curves near the left axis of the figure.) In contrast to the effect of the same jumps on the density of a liquid near its glass temperature, the relaxations are exponential and also symmetrical, consistent with the longer time scale required for the coordination change at 9°C relative to the enthalpy relaxation time monitored by calorimetry. (From Martinez and Angell [63] with permission.)

probe studies of glass former kinetics [64, 65]. The relation between chemical order relaxation and physical order relaxation (monitored by volume or enthalpy changes) is one of the important questions in glass science that has not yet been properly investigated.

1.6 OTHER SPECTROSCOPIES

There are many spectroscopic tools that are applicable to the study of ionic liquids. One of particular value for the case of protic ionic liquids is proton NMR spectroscopy. The reason is that the ^1H NMR spectrum is sensitive to how completely the proton is transferred from the donor species (protic acid) to the basic species. Indeed, the proton chemical shift on the N-H proton can be used in the same way as an indicator ion is used, to probe the change in proton activity as the 1:1 stoichiometry is approached and then passed.

An example of such a titration curve was given long ago by Angell and Shuppert [66], who studied the effect on the proton transferred to pyridine by HCl (giving pyridinium chloride) when the acid strength of HCl was increased by complexing with a Lewis acid, AlCl_3 . This is an analogue of the formation of superacids by adding a strong Lewis acid (like SbF_5) to a strong protic acid (like HSO_3F). Indeed, these authors showed that with excess AlCl_3 , the ^1H chemical shift approached the free gaseous pyridinium cation value.

The ^1H chemical shift is currently being used as a way of characterising the effective acidity of protic ionic liquids [67], and thereby using them to control the stability of folded proteins in aquated versions of these media that are being harnessed for protein folding studies [68] and for biopreservation (see last section).

1.7 PHYSICAL PROPERTIES OF PROTIC IONIC LIQUIDS

In contrast to the systems described earlier, the protic ionic liquids, of which ammonium chloride is the elementary inorganic example, are formed very simply by proton transfer from an inorganic acid to an organic base. The base is usually a primary, secondary, or tertiary amine, or a nitrogen atom in a heterocyclic ring (which may or may not be resonance stabilised) [69]. The properties of the ionic liquid formed in this manner depend quite strongly on the relative strengths of the acids and bases between which the proton is transferred [70].

In order to simplify the prediction of protic ionic liquid properties, Angell and co-workers [37, 70] have generalised the Gurney proton energy level diagram [71] not just to deal with proton transfers between acid and base species in an aqueous environment, but rather to describe the energy changes when a proton moves between any proton donor and proton acceptor pair, in the absence of any solvent at all. So far, the spacings in the diagram have been based on the known aqueous $\text{p}K_{\text{a}}$ values, and hence are only semiquantitative, but these will in time be replaced by energy data obtained from electrochemical studies and other direct measures such as vapour pressure changes [70].

An example of the energy level diagram [37] is provided in Figure 1.9. Acid protic electrolytes result when the proton falls from an occupied level on a superacid to a vacant level on a weak base, for example, from triflic acid to fluoroaniline, or to water, while neutral electrolytes arise when the proton transfers from a moderate acid like nitric or trifluoroethanoic acid to ethylamine or cyclopentylamine. Provided the proton falls across a gap of 0.7 eV or more, the electrolyte is a “good” ionic liquid, meaning the proton resides on the base for at least 99% of the time.

Protic ionic liquids, in which the proton energy change is not greater than 1 eV, seem to have low glass temperatures and also high fluidities and ionic conductances.

	Occupied	Vacant	pK_a	E/eV
Acid Electrolytes	HSbF ₆	SbF ₆ ⁻		
	HBOB	BOB ⁻		
	HTFSI	TFSI ⁻		
	HTf	Tf ⁻	-14	0.83
	HSO ₃ F	SO ₃ F ⁻		
	HClO ₄	ClO ₄ ⁻	-10	0.59
	H ₂ SO ₄	HSO ₄ ⁻	-9	0.53
	HPO ₂ F ₂	PO ₂ F ₂ ⁻		
	HNO ₃	NO ₃ ⁻	-1.30	0.08
	CH ₃ SO ₃ H	CH ₃ SO ₃ ⁻	-0.60	0.04
2-fluoropyridine H ⁺	2-fluoropyridine	-0.43	0.03	
CF ₃ COOH	CF ₃ COO ⁻	-0.25	0.01	
Neutral Electrolytes	H ₂ O ⁺	H ₂ O	0	0
	H ₃ PO ₄	H ₃ PO ₄ ⁻	2.12	-0.13
	1,2,4-1H-triazole H ⁺	1,2,4-1H-triazole	3.00	-0.18
	HF	F ⁻	3.20	-0.19
	HCOOH	HCOO ⁻	3.75	-0.22
	CH ₃ COOH	CH ₃ COO ⁻	4.75	-0.28
	ImH ⁺	Im	6.99	-0.41
	hydrazine H ⁺	hydrazine	7.96	-0.47
	NH ₄ ⁺	NH ₃	9.23	-0.55
	EtNH ₃ ⁺	EtNH ₃	10.63	-0.63
Bu ₂ NH ₂ ⁺	Bu ₂ NH	11.25	-0.67	
Basic Electrolytes	H ₂ O	OH ⁻	14	-0.83
	NH ₃	NH ₂ ⁻		
	OH ⁻	O ²⁻ (Na ⁺)	28	-1.66

FIGURE 1.9 The proton energy level diagram for predicting the ionicities of ionic liquids resulting from the falling of a proton from an occupied level (on an acid molecule) to a vacant level (on a basic molecule or on a divalent anion; in the latter case the counteraction(s) must remain to balance the new anion charge). (From Belieres and Angell [81] with permission.)

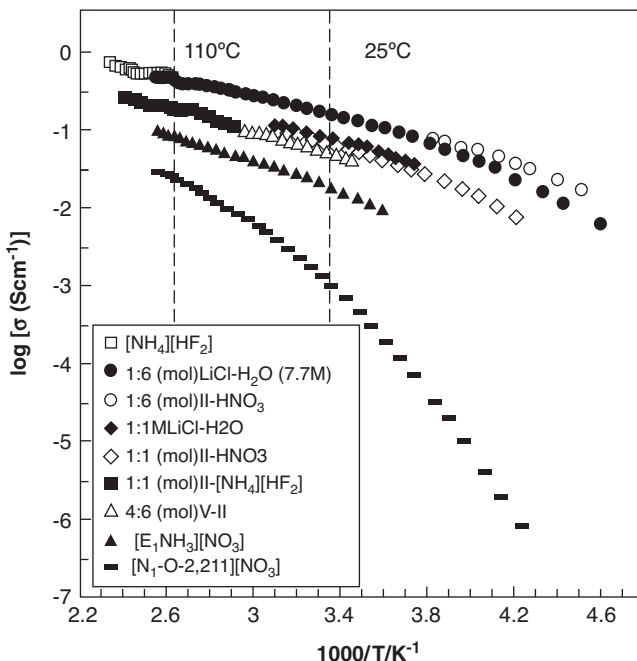


FIGURE 1.10 Conductivities of various protic ionic liquids (and one aprotic case) compared with those of aqueous LiCl solutions to show how the aqueous solutions are not unique with respect to high ionic conductivity. (From Xu and Angell [59] with permission.)

A typical case is ethylammonium nitrate, known since 1914 [72]. The ionic conductances of some protic ionic liquids [59, 73] are shown in Figure 1.10, along with those of aqueous LiCl to show that, for some salts like dimethylammonium nitrate [59] and hydrazinium methanoate [74], the conductivities at ambient temperature can be as high as those found in aqueous solutions [59, 73].

1.8 PROTIC IONIC LIQUIDS AS FUEL CELL ELECTROLYTES

It is astonishing that protic ionic liquids had been known for nearly a century before it was realised [75, 76] that they could serve as the proton carriers in fuel cell electrolytes. In fact, they can serve very well in this role and can provide electrolytes of a type that are simply not available in systems in which water is a major contributor to the acid–base equilibrium.

When the protic salt serving as the fuel cell electrolyte is formed by a transfer in which the protons decrease their energy by about an electron volt, it seems that the fuel cell is able to realise its theoretical voltage, at least for low current densities. The observation implies that, under these conditions, the energy barrier for oxygen reduction to water vanishes, though the reason for this simple behaviour is not yet clear. Figure 1.11 shows the relation between the proton gap and the open circuit cell

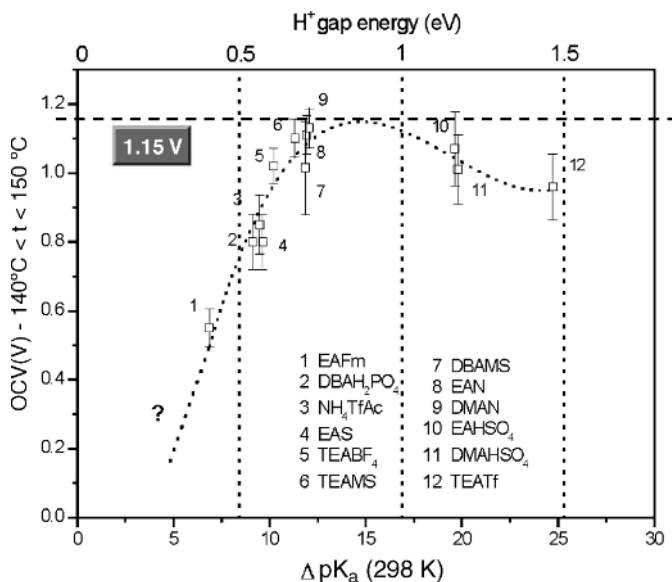


FIGURE 1.11 Open circuit voltages of $\text{H}_2(\text{g})\text{--O}_2(\text{g})$ fuel cells in relation to the proton gap characteristic of fuel cell electrolyte. (From Belieres et al. [82] with permission.)

voltage [77]. When the gap is too small, the proton transfer is incomplete, the conductivity is low (though the fluidity may be exceptionally high), and the fuel cell voltage output is also small.

1.9 INORGANIC FUEL CELL ELECTROLYTES

It is even more astonishing that, until 2006 [77], it had not been realised that mixtures of ammonium salts can be used as protic electrolytes for fuel cells running above 80°C (hydrazinium salts could be used to much lower temperatures [73]). Applied as fuel cell electrolytes, the ammonium salts give more stable performance than electrolytes containing organic cations. The IR-corrected polarisation curves for some inorganic electrolyte fuel cells are shown in Figure 1.12, using the logarithmic (“Tafel plot”) form. The plateau current at the theoretical voltage can now be extended out beyond $50\text{ mA}\cdot\text{cm}^{-2}$ in inorganic systems to be described in future articles. The occurrence of such high cell voltage–current combinations shows that it is now possible to increase the efficiency of chemical-to-electrical energy conversion considerably above the levels that are currently being obtained in, for instance, the phosphoric acid fuel cell.

An advantage of the phosphoric acid electrolyte, at the moment, is that the conductivity of the molecular liquid is higher, due to the presence of a considerable “dry” proton mobility. This superprotonic component, illustrated in Figure 1.13, is unfortunately not present in the protic ionic liquids, which mostly lie on or below the “ideal” Walden line [10]. It may be necessary to compromise on power output for the

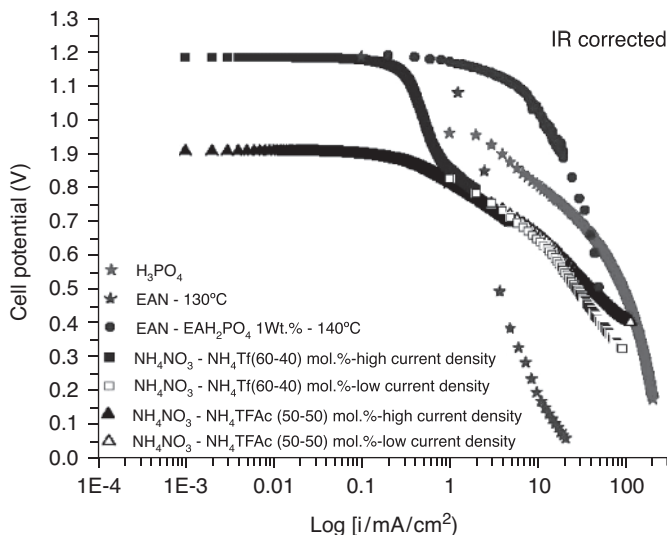


FIGURE 1.12 IR-corrected polarisation curves for hydrogen/oxygen fuel cells utilising inorganic and organic cation ionic liquid electrolytes. (From Belieres et al. [82] with permission.)

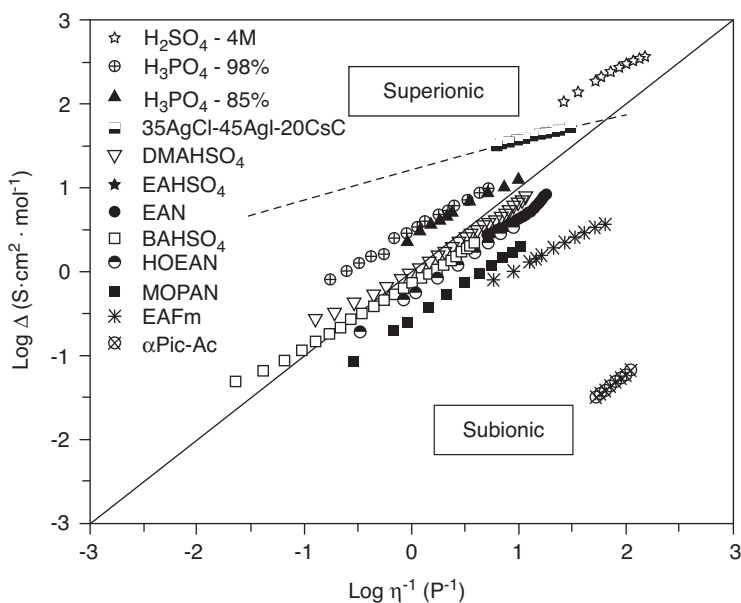


FIGURE 1.13 Walden plot showing the behaviour of equivalent conductivity expected from precise correlation with liquid viscosity solid line, with examples of subionic behaviour in some protic salt cases, and superprotonic behaviour in some (acid + water) systems, and a molten silver caesium halide mixture. (From Belieres et al. [83] with permission.)

sake of energy efficiency, if some breakthrough in conduction mechanisms is not forthcoming.

What are the prospects for development of really fast proton conducting materials, preferably solids? It is known, for instance, that nature has developed nanochannel proteins [78] that promote proton mobilities exceeding, by factors of 20, the normal mobility of protons in dilute acid solutions. Thus it is certainly not impossible that nanochannel structured polymers, or ionic liquid crystals with similar characteristics, could be discovered. The required number density of such channels seems improbable of achievement, however.

1.10 BIOPRESERVATION

An exciting new role for ionic liquids may lie in the storage and manipulation of sensitive biomolecules. Fujita et al. [79] have recently reported that the protein cytochrome *c* is remarkably stabilised in solution in a nontoxic dihydrogenphosphate ionic liquid, and we have found that lysozyme in 200 mg·cm⁻³ concentration is still folded after three years in ambient solutions that have large ethylammonium nitrate concentrations [80]. Certainly the ability of proteins to recover their native states after repeated unfoldings is enhanced by solution in protic ionic liquids of optimised proton activity [68]. Many developments in this general area are to be expected in the future (for instance, see the recent “Crucible” column by Phillip Ball; <http://www.rsc.org/chemistryworld/Issues/2009/April/ColumnThecrucible.asp>).

1.11 CONCLUSION

While the 200 years since Humphrey Davy began electrochemistry have seen wonderful advances in many areas, the progress in the specific area of fuel cells since the field began 150 years ago has been less impressive. It is to be hoped that the long-awaited breakthroughs needed to help this source of electrical energy realise its theoretical promise will become one of the new achievements of this very young branch of the very old “ionic liquids” discipline.

ACKNOWLEDGEMENTS

Most of the work described here has been supported by the NSF, under grants from the Solid State Chemistry division, for which the writer is very grateful. Recent studies on fuel cells have been carried out under the auspices of the DOD Army Research Office, grant no. W911NF-04-1-0060.

REFERENCES

1. Davy, H., *Researches, Chemical and Philosophical*, Biggs and Cottle, Bristol, 1800.
2. Bockris, J. O., Tomlinson, J. W., and White, J. L., The structure of the liquid silicates—partial molar volumes and expansivities, *Trans. Faraday Soc.* **52**, 299–310 (1956).

3. Tomlinson, J. W., Heynes, M. S. R., and Bockris, J. O., The structure of liquid silicates. 2. Molar volumes and expansivities, *Trans. Faraday Soc.* **54**, 1822–1833 (1958).
4. Willis, G. M., Physical-chemistry of lead extraction, *J. Metals* **31**, 28 (1979).
5. Davey, T. R. A., and Willis, G. M., Review of developments in extractive metallurgy of lead, zinc, and tin in 1978, *J. Metals* **31**, 17 (1979).
6. Bloom, H., and Heymann, E., *Proc. R. Soc.* **A188**, 392, (1947).
7. Angell, C. A., and Bockris, J. O., A technique for the measurement of diffusion coefficients in molten salts, *J. Sci. Instrum.* **35**, 458–461 (1958).
8. Walden, P., *Z. Phy. Chem.* **55**, 207, 246 (1906).
9. Angell, C. A., Fast ion motion in glassy and amorphous materials, *Solid State Ionics* **9–10** (Dec), 3–16 (1983).
10. Xu, W., Cooper, E. I., and Angell, C. A., Ionic liquids: ion mobilities, glass temperatures, and fragilities, *J. Phys. Chem. B* **107**, 6170–6178 (2003).
11. Angell, C. A., Xu, W., Yoshizawa, M., Hayashi, A., Belieres, J.-P., Lucas, P., and Videa, M., Physical chemistry of ionic liquids, inorganic and organic, protic and aprotic, in *Electrochemical Aspects of Ionic Liquids*, H. Ohno (Ed.), Wiley, Hoboken, NJ, 2005.
12. Hitch, B. F., and Baes, C. F., An electromotive force study of molten lithium fluoride–beryllium fluoride solutions, *Inorg. Chem.* **8**, 201 (1969).
13. Robbins, G. D., and Braunstein, J., Electrical conductivity and mobility in molten LiF–BeF₂ mixtures and a comparison with molten silicates, *Phys. Abstr. Papers Am. Chem. Soc.* [**Sept**] 86 (1970).
14. Vogel, W., Reiss, H., and Seifert, J., On the structure and properties of beryllium fluoride glasses containing CoF₂, *Glass Technol.* **24**, 133–138 (1983).
15. Vogel, W., Phase separation in glass, *J. Non-Crystalline Solids* **25**, 170–214 (1977).
16. Eastale, A. J., and Angell, C. A., Phase equilibria, electrical conductance, and density in glass-forming system zinc chloride + pyridinium chloride—a detailed low-temperature analog of silicon dioxide + Sodium oxide system, *J. Phys. Chem.* **74**, 3987 (1970).
17. Angell, C. A., and Tomlinson, J. W., Diffusion and electrical conductance measurements in solutions of cadmium dissolved in molten cadmium chloride, *Discuss Faraday Soc.* **32** (1962).
18. Gruen, D. M., Spectrophotometry of fused salts, *Q. Rev.* **19**, 349, (1965).
19. Protsenko, I., *Zh. Obshch. Khim.* **20**, 1365 (1950).
20. Thilo, E., Wieker, C., and Wieker, W., *Silic. Tech.* **15**, 109 (1964).
21. Dietzel, A. and Poegel, H. J., in *Proceedings III International Congress on Glass*, A. Garzanti (Ed.), Nello Stabilimento Grafico Di Roma Della, Rome, Venezia, 1953, 1954, p. 219.
22. Mezei, F., Knaak, W., Farago, B., Neutron spin-echo study of dynamic correlations near the liquid-glass transition, *Phys. Rev. Lett.* **58**, 571–574 (1987).
23. Bengtzelius, U., Gotze, W., and Sjolander, A., Dynamics of supercooled liquids and the glass-transition, *J. Phys. C Solid State Phys.* **17**, 5915–5934 (1984).
24. Angell, C. A., Success of free volume model for transport in fused salts, *J. Phys. Chem.* **68**, 218 (1964).
25. Angell, C. A., Free volume model for transport in fused salts—electrical conductance in glass-forming nitrate melts, *J. Phys. Chem.* **68**, 1917 (1964).

26. Angell, C. A., Viscous flow and electrical conductance, *J. Chem. Phys.* **46**, 4673–4679 (1967).
27. Vogel, H., *J. Phys. Z.* **22**, 645 (1921).
28. Fulcher, G. S., *J. Am. Ceram. Soc.* **8**, 339 (1925).
29. Tammann, G., and Hesse, W. Z., *Z. Anorg. Allgem. Chem.* **156**, 245 (1926).
30. Scherer, G. W., Editorial comments on a paper by Fulcher, *J. Am. Ceram. Soc.* **75**, 1060–1062 (1992).
31. Angell, C. A., and Bressel, R. D., Fluidity and conductance in aqueous-electrolyte solutions—approach from glassy state and high-concentration limit. 1. $\text{Ca}(\text{NO}_3)_2$ solutions, *J. Phys. Chem.* **76** (22), 3244 (1972).
32. Angell, C. A., Relaxation in liquids, polymers and plastic crystals—strong fragile patterns and problems, *J. Non-Cryst. Solids* **131**, 13–31 (1991).
33. Richert, R., and Angell, C. A., Dynamics of glass-forming liquids. V. On the link between molecular dynamics and configurational entropy, *J. Chem. Phys.* **108**, 9016–9026 (1998).
34. Weiler, R., Bose, R., and Macedo, P. B., *J. Chem. Phys.* **53**, 1258 (1970).
35. Angell, C. A., Spectroscopy, simulation, and the medium range order problem in glass, *J. Non-Cryst. Solids* **73**, 1 (1985).
36. Angell, C. A., Formation of glasses from liquids and biopolymers, *Science* **267**, 1924–1935 (1995).
37. Belieres, J.-P., and Angell, C. A., Ionic liquids: preparation and characterization of new protic ionic liquids, and the proton transfer energy level diagram, *J. Phys. Chem. B* **111**, 4926–4937 (2007).
38. Uhlmann, D. R., Kinetics of crystallization, *J. Non-Cryst. Solids* **7**, 337 (1972).
39. Goldstein, M., and Nakonecz, M., Volume relaxation in zinc chloride glass, *Phys. Chem. Glasses* **6**, 126 (1965).
40. Eastal, A. J., and Angell, C. A., Viscosity of molten ZnCl_2 and supercritical behavior in its binary-solutions, *J. Chem. Phys.* **56**, 4231 (1972).
41. Angell, C. A., and Wong, J., Structure and glass transition thermodynamics of liquid zinc chloride from far-infrared, Raman, and probe ion electronic and vibrational spectra, *J. Chem. Phys.* **53**, 2053 (1970).
42. Wilson, M., and Madden, P. A., Voids, layers, and the first sharp diffraction peak in ZnCl_2 , *Phys. Rev. Lett.* **80**, 532–535 (1998).
43. Wilson, M., and Madden, P. A., Short-range and intermediate-range order in MCl_2 melts—the importance of anionic polarization, *J. Phys. Condensed Matter* **5**, 6833–6844 (1993).
44. Dupree, E., and Pettifer, R. F., Determination of the Si—O—Si bond angle distribution in vitreous silica by magic angle spinning NMR, *Nature* **308**, 523–525 (1984).
45. Gruen, D. M., and McBeth, R. L., Tetrahedral NiCl_4^{2-} ion in crystals and in fused salts—spectrophotometric study of chloro complexes of nickel(II) in fused salts, *J. Phys. Chem.* **63**, 393–395 (1959).
46. Angell, C. A., and Hodge, I. M., and Cheeseman, P. A., Molten salts, in *International Conference on Molten Salts*, J. P. Pemsler (Ed.), The Electrochemical Society, 1976, p. 138.
47. Sun, X. G., Xu, W., Zhang, S. S., and Angell, C. A., Polyanionic electrolytes with high alkali ion conductivity, *J. Phys. Condensed Matter* **13**, 8235–8243 (2001).

48. Boon, J. A., Carlin, R. T., Elias, A. M., and Wilkes, J. S., Dialkylimidazolium–sodium chloroaluminate ternary salt system—Phase-diagram and crystal-structure, *J. Chem. Crystallogr.* **25**, 57–62 (1995).
49. Carlin, R. T., and Wilkes, J. S., Complexation of Cp_2MgCl_2 in a chloroaluminate molten-salt—Relevance to homogeneous Ziegler–Natta catalysis, *J. Mol. Catal.* **63**, 125–129 (1990).
50. Rogers, R. D., and Seddon, K. R., Ionic liquids—solvents of the future? *Science* **302**, 792–793 (2003).
51. Wasserschied, P., and Keim, W., *Angew. Chem. Int. Ed.* **39**, 3773–3789 (2000).
52. Rogers, R. D. and Seddon, K. R. (Eds.), *Ionic Liquids: Industrial Applications to Green Chemistry*, ACS Symposium Series Vol. 818, American Chemical Society, 2002.
53. Angell, C. A., Origin and control of low-melting behavior in salts, polysalts, salt solvates, and glassformers in *Molten Salts: From Fundamentals to Application: NATO-ASI*, M. Gaune-Escarde (Ed.), Kluwer Academic Publishers, Kas, Turkey, 2002, pp. 305–322.
54. Cooper, E. I., and O’Sullivan, E. J. M., New, stable, ambient-temperature molten salts, in *Proceedings of the 8th International Symposium on Molten Salts*, Electrochemical Society, 1992, pp. 386–396.
55. Wilkes, J. S., and Zaworotko, M. J., Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, *J. Chem. Soc. Chem. Commun.* 965–967 (1992).
56. MacFarlane, D. R., Golding, J., Forsyth, S., Forsyth, M., and Deacon, G. B., Low viscosity ionic liquids based on organic salts of the dicyanamide anion, *Chem. Commun.* 1430–1431 (2001).
57. MacFarlane, D. R., Forsyth, S. A., Golding, J., and Deacon, G. B., Ionic liquids based on imidazolium, ammonium and pyrrolidinium salts of the dicyanamide anion, *Green Chem.* **4**, 444–448 (2002).
58. Forsyth, S. A., Batten, S. R., Dai, Q., and MacFarlane, D. R., Ionic liquids based on imidazolium and pyrrolidinium salts of the tricyanomethanide anion, *Aust. J. Chem.* **57**, 121–124 (2004).
59. Xu, W., and Angell, C. A., Solvent-free electrolytes with aqueous solution - like conductivities, *Science* **302** (5644), 422–425 (2003).
60. Brynestad, J., and Smith, G. P., Evidence for a 3-coordinate complex of nickel(II), *J. Am. Chem. Soc.* **92**, 3198 (1970).
61. Smith, G. P., Dworkin, A. S., Pagni, R. M., and Zingg, S. P., Bronsted superacidity of HCl in a liquid chloroaluminate— AlCl_3 -1-ethyl-3-methyl- ^1H -imidazolium chloride, *J. Am. Chem. Soc.* **111**, 525–530 (1989).
62. Angell, C. A., and Abkemeier, M. L., Diamond cell study of pressure-induced coordination change for Ni(II) in liquid chloride solvents, *Inorg. Chem.* **12**, 1462–1464 (1973).
63. Martinez, L.-M., and Angell, C. A., *Physica* **314**, 548–559 (2002).
64. Cicerone, M. T., and Ediger, M. D., Relaxation of spatially heterogeneous dynamic domains in supercooled ortho-terphenyl, *J. Chem. Phys.* **103**, 5684 (1995).
65. Blackburn, F. R., Wang, C. Y., and Ediger, M. D., Translational and rotational motion of probes in supercooled 1,3,5-tris(naphthyl)benzene, *J. Phys. Chem.* **100**, 18249 (1996).
66. Angell, C. A., and Shuppert, J. W., NMR studies of the Lewis acid–base reactions between pyridinium chloride and the acids, ZnCl_2 and AlCl_3 , *J. Phys. Chem.* **84**, 538–542 (1980).

67. Belieres, J.-P., Byrne, N., Cherry, B. R., Holland, G. P., Yarger, J. L., and Angell, C. A., On the use of proton NMR to classify the strength of acids and superacids, *J. Am. Chem. Soc.*, submitted for publication.
68. Byrne, N., and Angell, C. A., Protein unfolding, and the “tuning in” of reversible intermediate states, in protic ionic liquid media, *J. Mol. Biol.* **378**, 707–714 (2008).
69. Yoshizawa, M., Ogihara, W., and Ohno, H., Design of new ionic liquids by neutralization of imidazole derivatives with imide-type acids, *Electrochem. Solid State Lett.* **4**, E25–E27 (2001).
70. Yoshizawa, M., Xu, W., and Angell, C. A., Ionic liquids by proton transfer: vapor pressure, conductivity, and the relevance of ΔpK_a from aqueous solutions, *J. Am. Chem. Soc.* **125**, 15411–15419 (2003).
71. Gurney, R. W., *Ionic Processes in Solution*, Dover Publications, New York, 1962.
72. Walden, P., *Bull. Acad. Imper. Sci. (St. Petersburg)*, 405–422 (1914).
73. Sutter, E. J., *Hydrogen Bonding and Proton Transfer Interactions in Hydrazine-Based Binary Liquids and Related Systems*, Ph.D. thesis, Purdue University, 1970.
74. Sutter, E. J., and Angell, C. A., Glass transitions in molecular liquids. I. Influence of proton transfer processes in hydrazine-based solutions, *J. Phys. Chem.* **75**, 1826–1831 (1971).
75. Susan, M. A. B. H., Noda, A., Mitsushima, S., and Watanabe, M., Bronsted acid–base ionic liquids and their use as new materials for anhydrous proton conductors, *Chem. Commun.*, 938–939 (2003).
76. Angell, C.A., Xu, W., Belieres, J.-P., and Yoshizawa, M., International Patent WO 2004114445 (2004).
77. Belieres, J.-P., Gervasio, D., and Angell, C. A., Binary inorganic salt mixtures as high conductivity electrolytes for $>100^\circ\text{C}$ fuel cells, *Chem. Commun. (Cambridge)*, 4799–4801 (2006).
78. Wu, Y., and Voth, G. A., A computer simulation study of the hydrated proton in a synthetic proton channel, *Biophys J.* **85**, 864–875 (2003).
79. Fujita, K., MacFarlane, D. R., and Forsyth, M., *Chem. Commun.* **4034**, (2005).
80. Byrne, N., Belieres, J.-P., and Angell, C. A., Reversible folding–unfolding, aggregation protection, multi-year stabilization in high concentration protein solutions, *Chem. Commun.*, 2714–2716 (2007).
81. Belieres, J.-P., and Angell, C. A., Protic ionic liquids: preparation, characterization, and proton free energy level representation, *J. Phys. Chem. B*, **111**, 4926–4937 (2007).
82. Belieres, J.-P., Gervasio, D., and Angell, C. A., Binary inorganic salt mixtures as high conductivity electrolytes for $>100^\circ\text{C}$ fuel cells, *Chem. Commun.* 4799–4801 (2006).
83. Belieres, J.-P., Xu, W., Markusson, H., Gervasio, D., and Angell, C. A., Protic ionic liquids: a new class of fuel cell electrolytes addressing oxygen over-voltage and water electro-osmosis problems, to be published.