Application of Hole Theory to Define Ionic Liquids by their Transport Properties[†]

Andrew P. Abbott,* Robert C. Harris, and Karl S. Ryder

Chemistry Department, University of Leicester, Leicester, LE1 7RH, United Kingdom

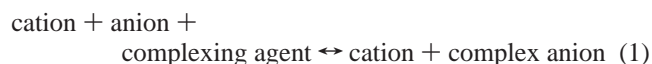*Received: November 1, 2006; In Final Form: January 15, 2007*

Eutectic mixtures of quaternary ammonium salts with Lewis or Brønsted acids have been described as ionic liquid, but doubt exists over the compositional range for which this description is valid. In the current work, the conductivity, viscosity, density, and surface tension of a number of glycolic mixtures with choline chloride are measured over the mole fraction range 0 to 0.33. The data are fitted to hole theory, and it is proposed that the composition at which the measured conductivity matches the theoretical value is the point at which hole mobility becomes the dominant mechanism for charge mobility. For the mixtures of ethylene glycol and butanediol, this occurs at a ChCl mole fraction of approximately 0.2.
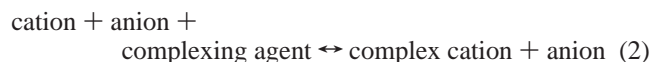
Introduction

Ionic liquids are without doubt in their hiatus at the beginning of the 21st century, and yet there is significant confusion about what an ionic liquid actually is. The recognized definition as an ionic material that is liquid below 100 °C leaves significant question as to what constitutes an ionic material. Some authors like to limit the definition to cations and so-called discrete anions, e.g., BF_4 and NO_3^-, although this is unsatisfactory, as it excludes the original research in the area on chloroaluminate systems. These are less easy to categorize as ionic, as they depend upon complex equilibria and consist of a variety of anionic species. The concentrations of the ionic species are strongly affected by the composition of the different components.

Others have classified ionic liquids into first and second generation ionic liquids,[1] where first generation liquids are those based on eutectics and second generation have discrete anions.[2] We have sought to further divide the first generation liquids into a variety of types depending on the nature of the Lewis or Brønsted acid that complexes the halide anion to form an ionic complex.[3] While there is some dispute whether eutectics with Brønsted acids constitute ionic liquids at all, there are others who seek to widen the description of ionic liquids to include materials such as salt hydrates.[4]

What is clear is that all ionic liquids form due to delocalisation of charge and this can be described by an equilibrium
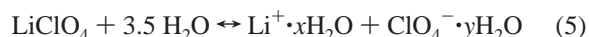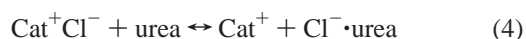
$$\text{cation} + \text{anion} + \text{complexing agent} \leftrightarrow \text{cation} + \text{complex anion} \quad (1)$$

or potentially

$$\text{cation} + \text{anion} + \text{complexing agent} \leftrightarrow \text{complex cation} + \text{anion} \quad (2)$$

with the vast majority focusing on the former case.

The confusion arises from the magnitude of the equilibrium constant. For discrete anions such as BF_4^- and even $((CF_3SO_2)_2N)^-$, the equilibrium lies clearly to the right of eq 1. For eutectic based liquids, the equilibrium constant depends upon the strength of the Lewis or Brønsted acid such that a variety of complex anions are possible. Hence, all of the following could be described as ionic liquids

$$Cat^+Cl^- + AlCl_3 \leftrightarrow Cat^+ + AlCl_4^- \quad (3)$$

$$Cat^+Cl^- + \text{urea} \leftrightarrow Cat^+ + Cl^-\cdot\text{urea} \quad (4)$$

$$LiClO_4 + 3.5\,H_2O \leftrightarrow Li^+\cdot xH_2O + ClO_4^-\cdot yH_2O \quad (5)$$

but there must be a point where the Lewis or Brønsted acid is in considerable excess and the system becomes a solution of salt in the acid. A similar scenario also exists with the incorporation of diluents or impurities. Many ionic liquids with discrete anions are hydrophilic, and the absorption of water is found to sometimes have a significant effect upon the viscosity and conductivity of the liquids.[5–7] What is required is a simple method of distinguishing the properties of ionic liquids from those of a concentrated solution.

In the current work, we will present physical data on mixtures formed between quaternary ammonium halides and a variety of glycol hydrogen bond donors as a function of salt concentration. These will provide evidence for the change in properties from those of an ionic liquid to those of a solution.

Experimental

Choline chloride (ChCl) (Aldrich 99%) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Ethylene glycol (EG), 1,4-butanediol (butylene glycol, BG), and glycerol (all Aldrich >99%) were used as received. The eutectic mixtures were formed by stirring the two components at 100 °C until a homogeneous colorless liquid was formed. The liquids were cooled at a rate of 1 °C min^{-1}, and the freezing point was taken as the temperature at which the first solid began to form. The viscosity was determined using a Brookfield DV-E viscometer fitted with a thermostated jacket. The conductivity and its temperature dependence were determined using a Jenway 4071 conductivity meter with temperature and conductivity probes. A Kruss K11 tensiometer equipped with a thermostatted jacket, was used for the surface tension experiments. The equilibrium geometry and volumes of the ions and hydrogen

bond donors were calculated using a Hartree−Fock method utilizing an STO-3G model provided by commercially available software.[8]

Results

Angell[9] has shown that for ionic liquids with discrete anions the molar conductivity is inversely proportional to the viscosity of the liquid and this correlation is virtually independent of the cation and anion. This has been used as a method of defining the properties of an ionic liquid. We have recently used hole theory to show that Angell's observation is due to a different mechanism of charge transfer in ionic liquids from that encountered in ionic solutions or high-temperature molten salts.[10,11] Hole theory was initially developed by Fürth[12] as an alternate view of the liquid state and later expanded by Bockris et al. for use with molten salts.[13] The model was found to have serious limitations in molten salts because ionic association significantly affects ionic activity. A discussion of the various models for pure fused salts is given by Stillinger.[14] However, in ionic liquids the large ion size and low temperatures mean that hole sizes are comparatively small. The probability of ions being able to move is several orders of magnitude smaller than in molten salts and so the role of ionic association can be ignored for charge transfer. Under these conditions Hole theory is an excellent model for the mobility of charged species.

We have shown that under these conditions the viscosity of a fluid, η, can be modeled by assuming it behaves like an ideal gas,[10] but its motion was restricted by the availability of sites of the ions/molecules to move into. Hence, it was shown that

$$\eta = \frac{mc/2.12\sigma}{P(r > R)} \quad (6)$$

where m is the molecular mass (for ionic fluids this was taken as the geometric mean), $\bar{c}$ is the average speed of the molecule ($=(8kT/\pi m)^{1/2}$), σ is the collision diameter of the molecule ($4\pi R^2$), and k is the Boltzmann constant. The probability of finding a hole of radius, r, greater than the radius of the solvent molecule, R, in a given liquid, ($P(r > R)$) is given by integration of eq 7[10]:

$$P \cdot dr = 0.601a^{7/2}r^2e^{-ar} \, dr \quad (7)$$

where $a = 4\pi\gamma/kT$ and γ is the surface tension. The good correlation obtained between the calculated and measured viscosities showed that it is valid to think of the viscosity of ionic fluids as being limited by the availability of holes. It therefore follows that charge transfer should occur in the same manner, hence ion motion depends on the migration of holes in the opposite direction. Since the fraction of suitably sized holes in ambient temperature ionic liquids is very low the holes can be assumed to be at infinite dilution and can be described by combining the Stokes−Einstein and Nernst-Einstein equations (eq 8)[11]: where z is the charge on the ion and e is the electronic

$$\lambda_+ = z^2F \, e/6\pi\eta R_+ \quad (8)$$

charge. An expression can therefore be obtained for the molar conductivity of both ions: This explains Angell's observation

$$\Lambda = z^2F \, e/6\pi\eta(R_+ + R_-) \quad (9)$$

that all ionic liquids display a correlation between the molar conductivity and the fluidity.[9] Although the size of the ion is also a variable in eq 9, in practice all of the ionic species that
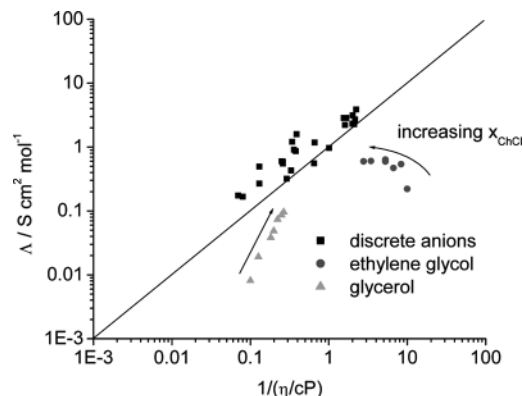

Figure 1. Plot of molar conductivity vs fluidity for a range of ionic liquids with discrete anions and mixtures of ChCl with glycerol and ethylene glycol at 20 °C.

form ionic liquids have relatively similar dimensions ($R \approx 3 - 4$ Å). Hole theory therefore potentially provides a method by which the dilution of ionic liquids can be quantified because eq 9 will no longer be valid when hole mobility does not limit conductivity.

Figure 1 shows a plot of molar conductivity versus fluidity ($1/\eta$) for the data presented in a recent review by Gali'nski et al. for ionic liquids with discrete anions.[15] The scatter in Figure 1 is thought to be primarily due to the difference in size between the ions. It has previously been shown that eutectic mixtures of quaternary ammonium salts with hydrogen bond donors form liquids at ambient temperatures and the conductivity of these liquids obey eq 9.[16] We have assumed that these liquids can therefore be classified as ionic liquids and Figure 1 shows some that these data fit the classification of Angell.[9]

The ability to vary the composition of Lewis or Brønsted acid adds an additional dimension to the tuneability of the eutectic-based ionic liquids. To test the hypothesis that an ionic liquid can become a solution is relatively difficult, as most complexing agents are solid at ambient temperature and hence a true test should be conducted at the melting point of the complexing agent. This adds the additional complexity that the interaction between the anion and the complexing agent will be significantly affected by the temperature. Lecocq et al.[17] used ^{13}C and ^{35}Cl NMR spectroscopy to show that at 110 °C 1BMMICl:1ZnCl$_2$ varies its structure with time from [BMMI]$^+$-[ZnCl$_3$]$^-$ to [BMMI...Cl...ZnCl$_2$]. What is important, however, is the behavior of ionic liquids at ambient temperature. The only exceptions that we have found are with diols and triols which are liquid at ambient temperature and form relatively shallow eutectics when mixed with quaternary ammonium salts. These liquids have been shown to be very useful for electropolishing stainless steel as they are benign and simple to synthesize and recycle.[18,19]

Table 1 shows the conductivity, viscosity, density, and surface tension of three glycolic mixtures with ChCl: ethylene glycol, 1,4-butanediol, and glycerol. An interesting phenomenon occurs in the different liquids. For EG and BG, the viscosity increases as salt is added to the mixture as would be expected for most salt solutions. For glycerol, however, the viscosity decreases when ChCl is added. This is because the diols form linear aggregates of hydrogen-bonded molecules, whereas glycerol with its three OH moieties is a three dimensionally hydrogen-bonded liquid imparting greater order, higher density, and higher surface tension than the other glycols. The addition of salt to glycerol breaks up this structure by complexing the OH moieties to the anion of the salt. This causes a significant decrease in

TABLE 1: Physical Properties of Various ChCl: Glycol Mixtures as a Function of Composition at 20.0 °C

| ChCl: Ethylene Glycol							
% ChCl	5	10	15	20	25	30	33
density/gcm^{-3}	1.114	1.115	1.115	1.117	1.118	1.118	1.12
viscosity/cP	10	12	15	19	19	29	36
conductivity/mS cm^{-1}	3.74	7.52	8.14	8.53	8.74	7.92	7.61
surface tension/mN m^{-1}	48.1	47.3	45.3	47	45.4	47.2	49
ChCl: Glycerol							
density/gcm^{-3}	1.242	1.234	1.219	1.21	1.203	1.192	1.181
viscosity/cP	998	790	548	503	450	401	376
conductivity/μS cm^{-1}	106.4	243	470	580	850	964	1047
surface tension/mN m^{-1}	63.7	60.2	60.8	57.4	50.8	48.5	55.8
ChCl: 1,4Butanediol							
density/gcm^{-3}	1.021	1.026	1.036	1.046	1.052		
viscosity/cP	78	84	78	88	140		
conductivity/μS cm^{-1}	593	923	1271	1606	1654		
surface Tension/mN m^{-1}	46.4	46.8	46.9	47.4	47.6		

the surface tension opening up the free volume of the liquid, causing a decrease in the density and allowing greater movement of the ionic species.

Figure 2 shows the molar conductivity of choline chloride in a number of glycolic liquids. The molar conductivity was calculated by

$$\Lambda = \kappa M/\rho \qquad (10)$$

where κ is the conductivity, ρ is the density, and M is the molar mass which is take as being the molar mass of the two components multiplied by their mole fraction in the mixture. The ionic radii were calculated using commercially available software assuming that each chloride ion is coordinated by one glycol molecule.[8] The only other viable assumption is that two glycol molecules coordinate the chloride ion. The difference in radii between the two complexes is approximately 0.6 Å, and this causes a change in the calculated molar conductivity of approximately 10%. FAB-MS shows the presence of the chloride coordinated to both one and two glycol molecules, and presumably the composition of the two species will depend upon the composition of the two components in the mixture.

At low concentrations, most of the ions exist as ion pairs, and the molar conductivity is relatively low. As the concentration of salt increases, the molar conductivity increases as the concentration of triple ion increases according to This is well-

$$3ChCl \leftrightarrow Ch_2Cl^+ + ChCl_2^-$$
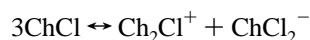
known to occur in nonaqueous solutions.[20,21] As the salt concentration increases, the amount of free solvent decreases, and at some point there must be no free solvent molecules as
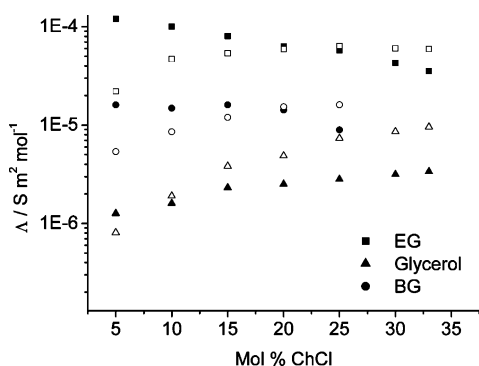

Figure 2. Plot of molar conductivity vs ChCl content for a variety of mixtures with different glycols at 20 °C. Open symbols are the measured values and filled symbols are the values calculated using eq 9.

they are all coordinated to the ions. At this point the movement of free "solvent" is prohibited, and it is only ionic species that can move. Under these conditions the mobility of the complex species is severely hindered due to their size and the decreased free volume of the liquid. For EG a maximum is observed in molar conductivity at approximately 25 mol % ChCl. According to eq 9, the limiting molar conductivity will be inversely proportional to the viscosity, and it would be expected that the molar conductivity would decrease as hole mobility replaced ion mobility as the dominant factor in charge transport. It is at this composition where hole mobility overtakes ion mobility as the dominant mechanism for charge-transfer that we propose an ionic liquid is formed.

Figure 1 shows the molar conductivity of the glycolic mixtures as a function of fluidity. It is clear that the molar conductivity values of the dilute solutions differ significantly from the Walden rule which is to be expected as the conductivity is dependent upon the number of charge carriers and the main mobile species which govern the fluidity of the liquid are the glycol molecules. Hence, the conductivity is greater than that predicted by eq 9. As the concentration of salt increases, the number of free solvent molecules decreases, and the conductivity approaches that of the other liquids where mobility is limited by hole mobility. Hence, the definition by Angell that all ionic liquids obey the same conductivity versus fluidity correlation is a good approximation to determining whether a material is an ionic liquid. A more rigid definition is possibly that an ionic liquid is a fluid where eq 9 is valid the justification being that in an ionic liquid the transport of charge is limited by hole mobility.

To determine the composition at which the eutectics in Figure 2 change from being ionic liquids to solutions of salt in glycols, the molar conductivity was calculated using eq 9 and plotted against the measured conductivity, and it can be seen that significant deviations are seen up to a composition of 20% EG and BG. Thereupon relatively good correlation was observed. BG could not be studied above 25 mol % because the temperature at which a homogeneous solution formed was above 20 °C. The other isomers of BG (1,2-, 1,3- and 2,3-) were also tested and showed similar trends to those observed for 1,4-BG, but these all reached supersaturation above 20 mol % at 20 °C and hence approached the properties of ionic liquids but could not exhibit the decrease in molar conductivity with concentration.

For glycerol the correlation between the values calculated from eq 9 and the measured values is closer a lower concentrations. This could be seen as an exception that shows the validity

of the assumption, insofar as the very high viscosity of the pure fluid and the low free volume, as indicated by the high surface tension, mean that charge transport is still limited by hole transport, only in this exceptional case the mobility of the "solvent" molecules (i.e., glycerol) is not due to them all being complexed to the Cl^- but rather in this case they are hindered from moving by other solvent molecules.

If the mobility of charge is limited by the availability of suitably sized holes, then one diagnostic test for determining where most ionic liquids take on the properties of solutions would be that the molar conductivity passes through a maximum where ion mobility and hole mobility are at equilibrium.

Conclusions

It has been shown that mixtures of quaternary ammonium salts with glycols form homogeneous fluids with the properties of ionic liquids when the mole fraction of the salt exceeds 0.2. At higher salt concentrations, the dominant mode of charge transport is via the mobility of holes, and the mixture has the viscosity and conductivity characteristic of an ionic liquid, and below this concentration the properties can be described by the theories related to concentrated ionic solutions.

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