1 What Is an Ionic Liquid?

ANDREW P. ABBOTT and KARL RYDER
Chemistry Department, University of Leicester, Leicester, UK
PETER LICENCE and ALASDAIR W. TAYLOR
School of Chemistry, University of Nottingham, Nottingham, UK

1.1 INTRODUCTION

The history of ionic liquids is well documented, and it is widely recognised that the work of Walden produced the first recorded materials that were deliberately ionic and molten at ambient temperature [1]. The classification of ionic liquids as salts that are liquid below 100°C is arbitrary and non-satisfactory because it does not answer the philosophical question ‘When is an ionic liquid not an ionic liquid?’ This seemingly pointless pedantry is important, as almost all uses of ionic fluids involve the dissolution of molecular components. The issue is therefore how much solute can be added before the molecular character dominates the ionic character. It has been shown by numerous authors that the inclusion of a small amount of certain impurities can have a profound effect upon the physical and chemical properties of an ionic liquid [2–4].

Arbitrary descriptions are unsatisfactory as it is difficult to predict what materials will fall into this classification. It would be simple to view ionic liquids as an extension of molten salts or, alternatively, they could be viewed as a fundamentally different type of material. The most suitable method will probably be to describe them as extreme versions of molten salts. The main issue associated with the differentiation of high-temperature (mainly inorganic) and lower-temperature (predominantly organic) salts is accounting for the differences between the transport properties of the fluids. Clearly, the higher-temperature systems are relatively fluid because they generally have smaller ions and larger void volumes, allowing greater mobility of the ions and resulting in high ionic conductivities. What is less evident is why the properties of the higher-temperature systems vary with chemical compositions, whereas the lower-temperature systems share significant similarities.

Ionic Liquids Completely UnCOILed: Critical Expert Overviews, First Edition.
Edited by Natalia V. Plechkova and Kenneth R. Seddon.

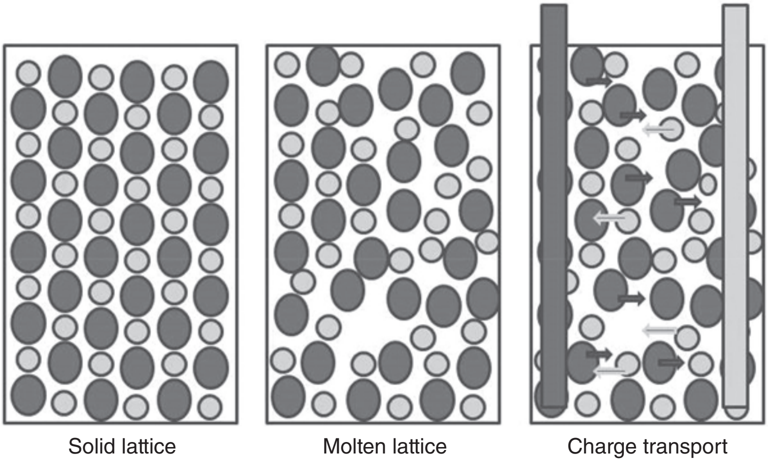

Figure 1.1 Schematic of the melting and charge transport processes in an ionic liquid.

In a seminal discussion by Bockris and Reddy [5], the issue of charge transfer in ionic liquids was discussed even before ionic liquids became a distinct research theme. The term ionic liquid is used extensively in their work: 'Pure liquid electrolytes therefore are liquids containing only ions, the ions being free or associated'. They identify the key issues of the difficulty of describing charge transfer in ionic liquids. When an electric field is applied, why do ions move with such extensive inter-ionic forces? An ionic liquid is a molten lattice, which means that empty space is poured into the fused salt. It seems logical therefore that it is this space that allows the ions in the *quasi*-lattice to move past each other. The process of melting and charge transport is shown schematically in Figure 1.1.

1.2 DILUTE AQUEOUS SOLUTIONS

To understand ionic liquids, it is informative to first review the mechanism by which charge is transported in dilute ionic solutions in molecular solvents, and how this changes with increasing salt concentration. It is also necessary to review the work on concentrated electrolyte solutions and see at which point the theories deviate from observed values, and why these deviations occur.

The conductivity of a strong 1:1 electrolyte in an aqueous solution at infinite dilution is well known [6]. The Nernst–Einstein relation shows that the limiting molar conductivity, Λ_m^0, of an electrolyte is related to the diffusion coefficient, D^0, of the ions by Equation 1.1:

$$\Lambda_m^0 = \left(\frac{z^2F^2}{RT}\right)\left(D_+^0 + D_-^0\right) \tag{1.1}$$

where z is the charge of the ion, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The Stokes–Einstein relation, Equation 1.2, is generally used to relate the diffusion coefficient to the radius of the species, R, and the viscosity of the medium, η:

$$D^0 = \frac{kT}{6\pi\eta R} \tag{1.2}$$

It is very important to note that both Equations 1.1 and 1.2 are derived for spherical species at infinite dilution in a structureless dielectric or in a medium where the size of the diffusing species is much larger than the solvent molecules. Combining Equations 1.1 and 1.2 yields Equation 1.3:

$$\Lambda_{\mathrm{m}}^{0} = \frac{z^2 Fe}{6\pi\eta}\left(\frac{1}{R_+} + \frac{1}{R_-}\right) \tag{1.3}$$

As the ionic concentration increases, the conductivity, σ, is given by Equation 1.4:

$$\sigma = \left(u_+ z_+ + u_- \mid z_- \mid\right) cF \tag{1.4}$$

where u_+ and u_- are the mobilities of the ions and c is the concentration of the charge carriers. The decrease in molar conductivity with increasing electrolyte concentration is due initially to ionic atmosphere effects, and then the formation of ion pairs. Once ion pairing occurs, none of the above equations are strictly valid because the concentration of charge carriers is not equal to the concentration of ions in solution. The effect of ion pairing increases as the electrolyte concentration increases, as the electrolyte becomes weaker, or as the polarity of the solvent decreases. Triple ions form as the concentration increases further, and a concomitant increase in molar conductivity is observed. The mobility of the triple ions is clearly different to that of the single ions, and Equation 1.4 has to be modified. This approach has been extensively applied to quaternary ammonium electrolytes in non-aqueous solvents, and numerous ion pairs and triple ion formation constants have been determined for many systems [7–9]. The Fuoss–Kraus equation, Equation 1.5, can be used to obtain the equilibrium constants for the ion pair dissociation, K_{p}, and triple ion dissociation, K_{T}:

$$\frac{\Lambda\sqrt{c}}{\Lambda_{\mathrm{m}}^{0}} = \sqrt{K_{\mathrm{p}}} + \frac{2c\sqrt{K_{\mathrm{p}}}}{3K_{\mathrm{T}}} \tag{1.5}$$

The difficulty with using this analysis was in determining Λ_{m}^{0} with non-aqueous electrolyte solutions. To solve this issue, Walden derived an empirical rule where for a given electrolyte [6],

$$\Lambda_{\mathrm{m}}^{0}\eta^{0} = \text{constant} \tag{1.6}$$

It is however only valid at infinite dilution for a given electrolyte. The rule is clearly a consequence of Equation 1.3.

At extremely high electrolyte concentrations, the molar conductivity decreases down to a limiting value, which is that of the pure salt. This decrease has previously been ascribed to viscosity effects [6].

1.3 IONIC LIQUIDS

Clearly, if the salt is liquid under the measurement conditions, then its behaviour can be determined across the complete concentration range with a molecular solvent. This trend is shown in Figure 1.2 for various electrolyte systems. It can clearly be seen that the polarity of the molecular solvent affects the mole fraction at which the maximum in molar conductivity occurs. It could be argued that the maximum in Figure 1.2 is due to the competition between the number of charge carriers and the mobility of the ionic species. The analysis of concentrated electrolyte solutions is extremely complex.

Stokes noted that charge mobility becomes the dominant factor at high electrolyte concentrations and termed the observation the '*viscosity effect*'.

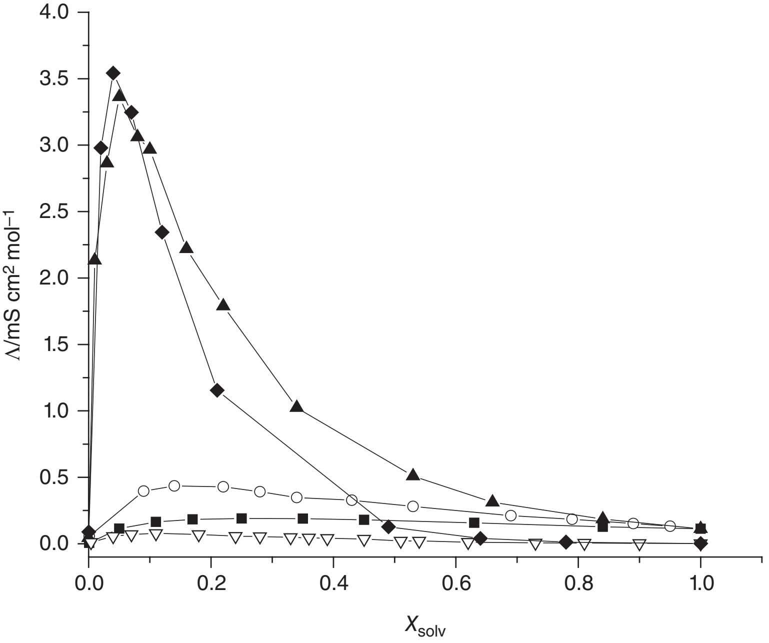

Figure 1.2 Molar conductivity of ionic liquid mixtures with various molecular solvents as a function of their mole fraction. The curves represent: ■ $[C_2mim][BF_4]$-propylene carbonate; ○ $[C_2mim][BF_4]$-*N*-methylformamide; ▲ $[C_2mim][BF_4]$-water; ∇ $[C_3mim]$Br-propylene carbonate; ◆ $[C_3mim]$Br-water. The data were taken from Ref. [4].

Stokes originally dealt with the molar conductivity of electrolytes in viscous solutions by empirically applying a fractional Walden rule, Equation 1.7:

$$(\Lambda_{\mathrm{m}}\eta)^{\alpha} = \text{constant (C)} \tag{1.7}$$

where α is a decoupling parameter that depends on the ionic size. Values of α have been found to vary between 0.61 and 0.74 [10]. This was first applied to molten salts [11, 12]. Numerous groups have found empirically that the molar conductivity of an ionic liquid is inversely proportional to the viscosity of the liquid and have erroneously invoked the 'Walden rule', Equation 1.6, as a method of describing what an ionic liquid is, without noting the two critical factors upon which it is based: namely, it is defined for one given ion, and the ions are at infinite dilution. Ionic liquids that do not obey the Walden rule have been classified as super-ionic or sub-ionic [13–15]. Figure 1.3 shows the so-called Walden plots for a variety of ionic liquid systems. This is a totally empirical relationship that is observed for a group of electrolytes that have similar ion sizes, and the validity of this can be seen from Equation 1.3. It can therefore be questioned why this works if the ions are not at infinite dilution.

Schreiner et al. recently published a critique of the use of the Walden rule with ionic liquids [17]. They suggested that use of the empirical approach from Stokes, Equation 1.7, explains the observed deviations from the so-called ideal Walden plot, since each salt will have a different value of C and α:

$$\log\left(\Lambda_{\mathrm{m}}^{0}\right) = \log(C) + \alpha \log\left(\eta^{-1}\right) \tag{1.8}$$

One approach to explain this observation has been to invoke a model of charge mobility occurring via hole transfer, which was developed by Fürth [18, 19] and applied to molten salts by Bockris [5]. The model did not fit experimental data for high-temperature systems due to the large number of suitably sized holes at high temperatures, which were able to take the small charge carriers. Ionic association decreased the number of charge carriers and hence the model broke down. The same basic model was applied to ionic liquids and found to fit extremely accurately [20, 21].

It was proposed that the reason that ionic liquids fit this model so accurately is due to the small number of suitably sized holes available at ambient temperatures that are able to accommodate the exceptionally large ions [21]. Under these conditions, the holes are effectively at infinite dilution, and this is the reason that Equation 1.3 becomes valid. It was shown that the viscosity of an ionic liquid could be accurately modelled using a gas-like model where mobility was hindered by the probability of finding a hole large enough for an ion to move into. The liquids that do not fit hole theory tend to be those whose ions are less spherical. Modifications to this theory have been made by Zhao et al., who took into account the asymmetric nature of the cation, and this significantly improved the prediction of the conductivity of long chain salts [22].

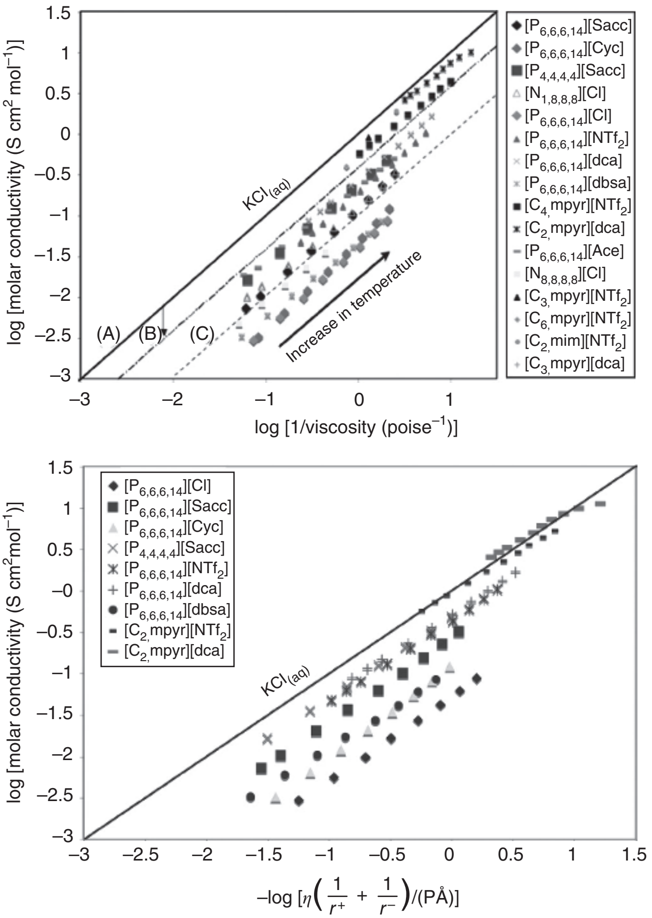

Figure 1.3 Walden plot (upper) and modified Walden plot (lower) for a variety of ionic liquids. For the upper curve, (A) is the ideal Walden plot line for KCl, (B) is the Walden plat taking account of ionic size, and (C) is the Walden plot if the conductivity was only 10% of the ideal value. Source: MacFarlane et al. 2009. Reproduced by permission of the PCCP Owner Societies.

Bockris and Reddy [5] proposed that the diffusion coefficient of species in an ionic liquid could be modelled by assuming that it is the hole itself that is diffusing. Modifying Equation 1.2 such that the term R is replaced by the radius of the void leads to theoretical diffusion coefficients that are closer to the measured values [23]. This simplification would however imply that all species in a given liquid would diffuse at the same rate in a given liquid, which is not born out in experiment. Bockris, moreover, combined the hole theory with the Stokes law to define a term that incorporated the mass of the diffusing species [5]. The difficulty of applying this theory is the requirement for a term that defines the energy required to remove a mole of material from the surface to infinity. This is naturally difficult to determine for an ionic liquid and hence this theory has never been applied.

An alternative approach has been to explain deviations from the Walden plot as arising from ion pairing, or systems that are not true ionic liquids [16]. This naturally ignores the invalidity of the Walden rule, and the correlation between Λ_m and η must be viewed as purely an empirical coincidence. The fact that molar conductivity is inversely proportional to viscosity is due to the fact that the ionic size is large and so changes in R^{-1} are relatively small. Application of Equation 1.3 to the data in Figure 1.3 (upper) brings more of the data onto the ideal slope, and this is shown in Figure 1.3 (lower), disproving that deviations from the Walden Rule are due to ion pairing. Not all data lie on the line, but those that deviate tend to correspond to large and non-spherical ions.

Watanabe and co-workers [24–26] measured the diffusion coefficient of ions in an ionic liquid as a function of the anion and cation and noted a discrepancy from the values calculated using Equation 1.2 when using the hard sphere radius of the ion. It was suggested that Equation 1.2 could be written as in Equation 1.9:

$$D = \frac{kT}{c\pi\eta R_s} \tag{1.9}$$

where c is a variable constant for each electrolyte and R_s is the hydrodynamic or Stokes' radius. Values of c were calculated between 4.1 and 4.4. However, c is only a function of whether the species diffuses in a lateral or rotational motion, and so this approach is not strictly valid [24]. The group however took the diffusion coefficient and calculated a theoretical molar conductivity, Λ_{NMR}, according to Equation 1.10:

$$\Lambda_{NMR} = \frac{N_A e^2 (D_+ + D_-)}{kT} \tag{1.10}$$

which was compared with the measured conductivity. The ratio of the molar conductivity calculated from the impedance measurement (Λ_{imp}) to that obtained from the ionic diffusivity (Λ_{NMR}) was determined, and the ratio $\Lambda_{imp}/\Lambda_{NMR}$ was found to be less than unity. This observation was ascribed to 'only part of the diffusive species in the ionic liquid contributes to the ionic conduction due to the presence of ionic association' [24]. The ratio $\Lambda_{imp}/\Lambda_{NMR}$ was defined by the term ionicity and was found to be in the range 0.5–0.8 for many ionic liquids. This is relatively high, however, and does not really correlate with the chemical differences in the liquids, that is, as the ions become larger and the charge is more delocalised, the ion pairing should decrease. While there is undoubtedly an effect of ionic interaction, it is proposed that this does not directly limit the molar conductivity.

This work, along with all other diffusion studies in ionic liquids, depends on the validity of the Stokes–Einstein equation and here lies the main discrepancy with the analysis of most diffusion coefficient data in ionic liquids. To be strictly accurate, the distance term, R, in Equation 1.3 should be replaced by the

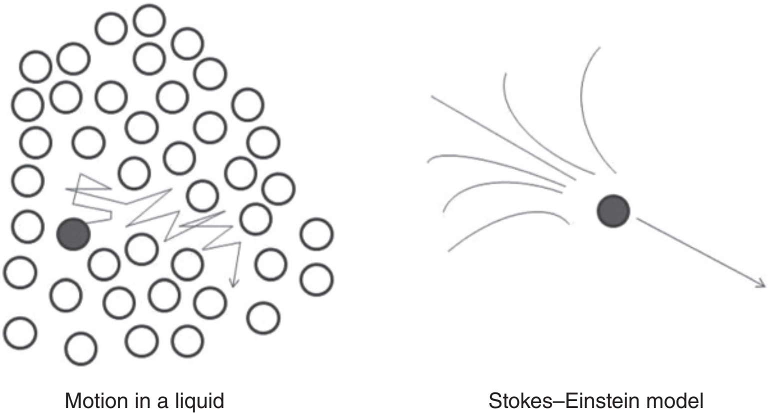

Figure 1.4 Comparison of the actual case of diffusion in an ionic liquid and the model from which the Stokes–Einstein equation is derived. Adapted from Ref. [29].

correlation length, ξ, which is only really equivalent to the radius of the diffusing species when the size of the diffusing particle is large compared with the solvent particles [27]. Equation 1.3 was initially derived to describe the random movement of microscopic particles in a liquid where the structureless dielectric assumption is valid [28]. The motion particles in a liquid and in the Stokes–Einstein model are shown schematically in Figure 1.4.

The observation that the Stokes–Einstein equation holds for ions in molecular solvents is a convenient coincidence that ignores the limitations of the model. The fact that the Stokes–Einstein equation fits the diffusion of molecules in a molecular solvent at all is remarkable, given the complexity of solvent–solute interactions. It has been noted that, in glass-forming mixtures, significant deviations from the Stokes–Einstein equation occur at temperatures below about 1.3 times the glass transition temperature, T_g [30]. This has been explained in terms of 'spatial dynamical heterogeneities', that is, there are tightly structured domains and regions with larger free volume where movement is possible.

Affouard et al. [31] used molecular dynamics simulations to model the mobility of species in simple mixtures of Lennard-Jones A–B particles. The breakdown of the Stokes–Einstein equation occurs at different temperatures depending on the particle decoupling. Simulations also show that faster moving particles show jump-like motion between vacancies. Ionic liquids are well known to be glass formers and have three-dimensional local structure [32]. Assuming that most liquids have a T_g lying between −40 and +20°C [33], that would make the temperature range where deviations from Equation 1.3 occur as anywhere from the melting point to between 303 and 380 K, which is the typical range over which diffusion coefficients are measured.

Classical diffusion can be described by Equation 1.3 when the radius of the sphere is small compared with the mean free path. With ionic liquids, the mean free path can be less than the radius of the ion, and hence the ion can be considered as moving via a series of discrete jumps where the correlation length is a measure of the size of the hole into which the ion can jump. Appreciating why deviations from the Stokes–Einstein equation occur shows why a model based on holes becomes appropriate. The approximate nature of the Stokes–Einstein equation is often overlooked and is discussed in detail by Bockris and Reddy [5, p. 379]. There are numerous aspects that need to be taken into account, including that it is derived for non-charged particles, it is the local viscosity rather than the bulk that is required, and the ordering effect of the ions exhibits an additional frictional force that needs to be explained.

The diffusion coefficients for 1-ferrocenylmethylimidazolium bis{(trifluoromethyl)sulfonyl}amide, $[FcC_1mim][NTf_2]$, in a variety of imidazolium-based ionic liquids were measured recently by Taylor [34, 35]. Using these diffusion coefficient data in Equation 1.3, the size parameter was found to vary from 3×10^{-10} m to 9×10^{-10} m, depending on the temperature and ionic liquid used as solvent, as shown in Figure 1.5. The distance parameter should be independent of temperature and should be the size of the probe molecule (~5×10^{-10} m in radius). The observation that there is a significant change with temperature demonstrates the breakdown of the assumption of a structureless dielectric. The disparity between the radius calculated using Equation 1.3 and the hard sphere radius arises because the correlation length is now comparable with the size of the vacancy into which the ion has to jump. It can therefore be concluded that

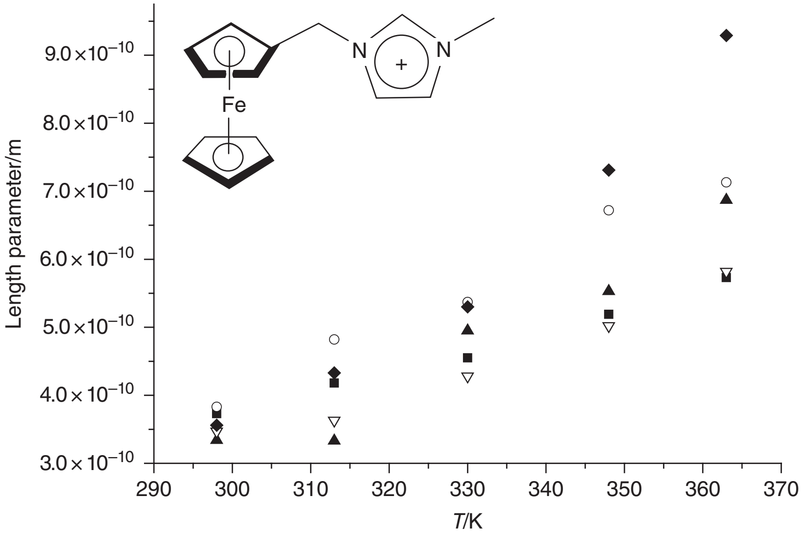

Figure 1.5 Plot of distance parameter, calculated from Equation 1.3 as a function of temperature, for 1-ferrocenylmethylimidazolium bis{(trifluoromethyl)sulfonyl}amide, $[FcC_1mim][NTf_2]$, in a variety of ionic liquids. The points represent solutions in: ■ $[C_2mim][NTf_2]$; ○ $[C_4mim][NTf_2]$; ▲ $[C_8mim][NTf_2]$; ∇ $[C_4mim][BF_4]$; ◆ $[C_8mim][BF_4]$. The data were taken from Ref. [34].

diffusion coefficient data, far from giving information about the extent of ionic association, actually reveal information about the structure of the ionic liquid.

Most important, and probably overlooked until now, is the fact that the adherence of so much data to Equation 1.3 signifies that the systems are limited by the mobility of charge rather than the number of charge carriers. This further supports the idea that ion pairing is unimportant in controlling conductivity in ionic liquids.

It is proposed that an ionic liquid is the mirror image of an ideal electrolyte solution but is governed by the same rules, that is, the charge-carrying species are independent of each other. Thus, for a large proportion of ionic liquids, we can assume that conductivity occurs by a hole-hopping mechanism [21]. If these holes are at infinite dilution, classical dilute electrolyte solution thermodynamics are obeyed and ionic association can be ignored. It must however be stressed that ionic interaction clearly occurs, but this does not appear to affect the number of charge carriers since the hole concentration is much lower than the number of free ions. The concept of ionic association is probably not helpful in an ionic liquid until a significant amount of a diluent is added to the system.

1.4 CONCLUSION

It is proposed that an ionic liquid is different to a molecular solution or a molten salt in the way that it transports charge. In ionic liquids, it appears to be the mobility of the voids rather than the number of charge carriers that governs charge transport. Classical diffusion is not obeyed due to the invalidity of the central assumption of the Stokes–Einstein equation, namely, the correlation length is insignificant compared to the size of the diffusing species. It is therefore appropriate to consider a species moving in an ionic liquid by a series of discrete jumps. It is this mechanism that will be unique to ionic liquids, and a definition based on this principle will allow for the incorporation of different amounts of molecular components of different polarity. While this may not appear to advance our understanding of what an ionic liquid is, it could be concluded that an ionic liquid becomes a solution or a molten salt under the conditions when the Stokes–Einstein equation becomes valid.

REFERENCES

1 Walden, P., Über die molekulargrösse und elektrische Leitfähigkeit einiger gesehmolzenen Salze, *Bull. Acad. Sci. St. Petersburg* **8**, 405–422 (1914).

2 Seddon, K.R., Stark, A. and Torres, M.-J., The influence of chloride, water and organic solvents on the physical properties of ionic liquids, *Pure Appl. Chem.* **72**, 2275–2287 (2000).

3 Zhang, J., Wu, W., Jiang, T., Gao, H., Liu, Z., He, J. and Han B., Conductivities and viscosities of the ionic liquid [bmim][PF_6] plus water plus ethanol and [bmim][PF_6] plus water plus acetone ternary mixtures, *J. Chem. Eng. Data* **48**, 1315–1317 (2003).

4 Jarosik, A., Krajewski, S.R., Lewandowski, A. and Radzimski, P., Conductivity of ionic liquids in mixtures, *J. Mol. Liq.* **123**, 43–50 (2006).

5 Bockris, J.O'M. and Reddy, A.K.N., *Modern Electrochemistry*, Vol.**1**, Plenum Press, New York (1970).

6 Robinson, R.A. and Stokes, R.H., *Electrolyte Solutions*, Butterworths, London (1959).

7 Fuoss, R.M., Properties of electrolytic solutions, *Chem. Rev.* **17**, 27–42 (1935).

8 (a)Fuoss, R.M. and Kraus, C.A., Ionic association. II. Several salts in dioxane-water mixtures, *J. Am. Chem. Soc.* **79**, 3304–3310 (1957). (b)Fuoss, R.M. and Kraus, C.A., Properties of electrolytic solutions. II. The evaluations of Λ_0 and of K for incompletely dissociated electrolytes, *J. Am. Chem. Soc.* **55**, 476–488 (1933).

9 Abbott, A.P. and Schiffrin, D.J., Conductivity of tetra-alkylammonium salts in polyaromatic solvents, *J. Chem. Soc. Faraday Trans.* **86**, 1453–1459 (1990).

10 Longinotti, M.P. and Corti, H.R., Fractional Walden rule for electrolytes in supercooled disaccharide aqueous solutions, *J. Phys. Chem. B* **113**, 5500–5507 (2009).

11 Biltz, W. and Klemm, W., Über das elektrische Leitvermögen und den Molekularzustand geschmolzener Salze, *Z. Anorg. Allg. Chem.* **152**, 267–294 (1926).

12 Pugsley, F.A. and Wetmore, F.E.W., Molten salts: Viscosity of silver nitrate, *Can. J. Chem.* **32** (9), 839–841 (1954).

13 Angell, C.A., Byrne, N. and Belieres, J.-P., Parallel developments in aprotic and protic ionic liquids: Physical chemistry and applications, *Acc. Chem. Res.* **40**, 1228–1236 (2007).

14 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).

15 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).

16 MacFarlane, D.R., Forsyth, M., Izgorodina, E.I., Abbott, A.P., Annat, G. and Fraser, K., On the concept of ionicity in ionic liquids, *Phys. Chem. Chem. Phys.* **11**, 4962–4967 (2009).

17 Schreiner, C., Zugmann, S., Hartl, R. and Gores, H.J., Fractional Walden rule for ionic liquids: Examples from recent measurements and a critique of the so-called ideal KCl line for the Walden plot, *J. Chem. Eng. Data* **55**, 1784–1788 (2010).

18 Fürth, R., On the theory of the liquid state. III. The hole theory of the viscous flow of liquids, *Math. Proc. Cambridge Philos. Soc.* **37**, 281–290 (1941).

19 Fürth, R., On the theory of the liquid state. II. The hole theory of the viscous flow of liquids, *Math. Proc. Cambridge Philos. Soc.* **37**, 281–290 (1941).

20 Abbott, A.P., Application of hole theory to the viscosity of ionic and molecular liquids, *ChemPhysChem.* **5**, 1242–1245 (2004).

21 Abbott, A.P., Model for the conductivity of ionic liquids based on an infinite dilution of holes, *ChemPhysChem.* **6**, 2502–2505 (2005).

22 Zhao, H., Liang, Z.-C. and Li, F., An improved model for the conductivity of room-temperature ionic liquids based on hole theory, *J. Mol. Liq.* **149**, 55–59 (2009).

23 Abbott, A.P., Harris, R.C., Ryder, K.S., D'Agostino, C., Gladden, L.F. and Mantle, M.D., Glycerol eutectics as sustainable solvent systems, *Green Chem.* **13**, 82–90 (2011).

24 Tokuda, H., Hayamizu, K., Ishii, K., Susan, M.A.B.H. and Watanabe, M., Physicochemical properties and structures of room temperature ionic liquids. 1. Variation of anionic species, *J. Phys. Chem. B* **108**, 16593–16600 (2004).

25 Tokuda, H., Hayamizu, K., Ishii, K., Susan, M.A.B.H. and Watanabe, M., Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation, *J. Phys. Chem. B* **109**, 6103–6110 (2005).

26 Tokuda, H., Ishii, K., Susan, M.A.B.H., Tsuzuki, S., Hayamizu, K. and Watanabe, M., Physicochemical properties and structures of room-temperature ionic liquids. 3. Variation of cationic structures, *J. Phys. Chem. B* **110**, 2833–2839 (2006).

27 Stillinger, F.H. and Hongdon, J.A., Translation-rotation paradox for diffusion in fragile glass-forming liquids, *Phys. Rev. E* **50**, 2064–2068 (1994).

28 Einstein, A. and Fürth, R., *Investigation on the Theory of Brownian Movement*, Dover, New York (1956).

29 Cussler, E.L., *Diffusion*, 3rd edition, Cambridge University Press, Cambridge (2009).

30 Kholodenko, A.L. and Douglas, J.F., Generalized Stokes–Einstein equation for spherical-particle suspensions, *Phys. Rev. E* **51**, 1081–1090 (1995).

31 Affouard, F., Descamps, M., Valdes, L.-C., Habasaki, J., Bordat, P. and Ngai, K.L., Breakdown of the Stokes–Einstein relation in Lennard-Jones glassforming mixtures with different interaction potential, *J. Chem. Phys.* **131**, 104510 (2009).

32 Del Popolo, M.G. and Voth, G.A., On the structure and dynamics of ionic liquids, *J. Phys. Chem. B* **108**, 1744–1752 (2004).

33 Zhou, Q., Lu, X., Zhang, S. and Guo, L., Physicochemical properties of ionic liquids, in *Ionic Liquids Further UnCOILed: Critical Expert Overviews*, eds. N.V. Plechkova and K.R. Seddon, John Wiley & Sons, Inc., Hoboken, NJ (2013).

34 Taylor, A.W., Electrochemistry *in vacuo*, PhD Thesis, University of Nottingham, 2010.

35 Taylor, A.W., Licence, P. and Abbott, A.P., Non-classical diffusion in ionic liquids, *Phys. Chem. Chem. Phys.* **13**, 10147–10154 (2011).