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Relationship between Ionic Radius and Pressure Dependence of Ionic Conductivity in Water

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Abstract

Experimental measurements of ionic conductivity in water are analysed in order to obtain insight into the pressure dependence of limiting ionic conductivity of individual ions (λ^0) for ions of differing sizes. Conductivities of individual ions, λ^0 do not exhibit the same trend as a function of pressure for all ions. Our analysis suggests that the effect of pressure on ionic conductivity depends on the temperature. At low temperatures, the effect of pressure on relatively small ions such as Li^+ exhibit an increase in conductivity with pressure. Intermediate sized ions exhibit an increase in conductivity with increase in pressure initially and then at still higher pressures, a decrease in ionic conductivity is observed. Although there are data at low temperatures for ions of large radius, the effect of increased pressure is expected to lower conductivity with increase in pressure over the whole range. At higher temperatures, the dependence of conductivity on pressure changes and these changes are discussed. Divalent ions such as SO_4^{2-} exhibit different trends as a function of pressure at different temperatures. Both the divalent ions (Ca^{2+} and SO_4^{2-}) for which experimental data exists, exhibit an increase with pressure at lower temperatures. At slightly higher temperatures, a maximum in conductivity is seen as a function of pressure over the same range of pressure.

1. Introduction

Among the transport properties, the most accurately and relatively easily measured are the ionic conductivities. These have been extensively investigated in different polar solvents where different salts readily dissolve. The changes in conductivity with temperature, pressure, size of the ion, concentration, etc. have been measured. Therefore a large amount

of data exists in the literature for different salts in a wide variety of solvents.

The importance of understanding the conductivity data in different polar solvents can not be overemphasized. From a fundamental viewpoint it would lead to a capability to predict and control as well as manipulate the conductivity. Further, a knowledge of the underlying mechanism determining ionic motion can lead to increased understanding which could lead to an ability to design new materials with better conductivity. The technological spin-offs of all this development could be quite remarkable. Battery materials with higher conductivity and lower dissipation are a possibility. Light materials for battery could reduce the weight of the battery. Batteries under appropriate pressurized condition can probably perform better. Some of these ideas could also be of importance in fuel cell technology. The increased understanding can also lead to important advances in biochemistry and ion conduction across biomembranes and may help unravel the reasons for selectivity observed for potassium over sodium.

In spite of availability of a large amount of data, our understanding of the ionic conductivity in water or other solvents still remains rudimentary. The reason for this is the bewilderingly rich variety that the variation in conductivity exhibit as a function of the different conditions such as temperature, pressure, concentration, ion size, etc. It has been very difficult, if not impossible, even to explain the variation of conductivity with just a single variable such as ion size or pressure.

Influence of different variables on ionic conductivity have been investigated in the literature both experimentally and theoretically. Among the different variables that have been studied, the most widely studied is the influence of size dependence on ionic conductivity. These are discussed in most textbooks [1–5]. Solvents with hydrogen bonds such as water, methanol, ethanol, etc. as well as a number of non-hydrogen bonded solvents such as acetonitrile and pyridine are seen to exhibit a maximum in ionic conductivity as a function of the ion radius. This maximum has been seen in all polar solvents. Positively charged ions (e.g., alkali ions) as well as negatively charged ions (e.g., halide ions) show a maximum in conductivity suggesting that such a maximum exists irrespective of the sign of the charge on the ion or nature of the solvent. Thus, this maximum in conductivity is a universal behaviour of ions in polar solvents.

This maximum is responsible for the breakdown in Walden's rule which states that the product of limiting ionic conductivity of a solution Λ^0 with solvent viscosity η_0 is a constant, $\Lambda^0\eta_0 = c$. It is generally seen that this product goes through a maximum when plotted as a function of reciprocal of the ion radius. The maximum in Walden product arises from a similar maximum in conductivity. This breakdown is probably related to any

breakdown in Stokes law.

Water being an important and well known solvent and due to its importance in many chemical as well as biological processes, the conductivity maximum has been most widely studied in water as compared to other solvents [6]. The availability of measured conductivity data is extremely valuable, especially to verify the predictions of theories or calculations. Further, existence of accurate potentials to model water and interactions between water and the ion, has led to the detailed molecular dynamics simulations whose results are of great importance in relating the macroscopic behaviour with the microscopic properties and understanding the cause of the many of the macroscopic behaviour.

Early work of Born [7] was responsible for increased interest in study of conductivity maximum of ions in solution as a function of ionic radius. A number of groups have investigated the maximum in ionic conductivity in polar solvents [8–12]. These are aimed at providing a theoretical framework to understand the underlying cause for the observed size dependent maximum in ionic conductivity. The complexity of these electrolytic solutions has meant that there are completely different theoretical approaches to understand the maximum in conductivity.

One such theory is the solvent-berg model which put forward the suggestion that smaller ions are strongly interacting with the nearest neighbour shell of solvent molecules [13]. This was considered to be particularly true of cations since these are generally smaller in size than the corresponding anions and have a higher charge density. The ion essentially carries this shell of solvent molecules long enough that this leads to a larger effective diameter which lowers its conductivity to a value smaller than the conductivity of larger ions which have no strongly attached shells of solvent.

Another set of theoretical attempts to reproduce the observed conductivity variation with ion radius is based on continuum models. Here dielectric friction arising from polarization interaction between the ion field and the solvent is accounted for. Also accounted for is the hydrodynamic friction arising from the viscosity of the solvent η due to the van der Waals interaction which is relatively short ranged. Born, Fuoss, Boyd, Zwanzig and Hubbard and Onsager [7, 13–17] attempted to explain the observed maximum in terms of the slow relaxation of the dielectric medium (solvent), induced by the electric field of the ion as the ion diffuses. This gives rise to the dielectric friction, ζ_{DF} which is given by the expression (see Zwanzig [17, 18])

$$\zeta_{DF} = 3q_i^2(\epsilon_0 - \epsilon_\infty)\tau_D/(cr_i^3(2\epsilon_0 + 1)\epsilon_0) \quad (1)$$

where τ_D is the dielectric relaxation time of the solvent associated with the dynamical

properties in continuum treatments. Here ϵ_0 and ϵ_∞ are the static and high frequency dielectric constants of the solvent. r_i and q_i are the radius and charge of the ion. The friction due to shear viscosity of the solvent, the hydrodynamic friction (which may arise from the short-range interactions) is given by the Stokes law :

$$\zeta_{SR} = 4\pi \eta r_i \quad (2)$$

for slip boundary condition. Thus, the total friction on the ion, ζ is

$$\zeta = \zeta_{SR} + \zeta_{DF} \quad (3)$$

ζ_{SR} is higher, the larger the size of the ion. But ζ_{DF} has a $1/r_i^3$ dependence and is higher for ions with smaller radius. The result is that at some intermediate size of the ion, r_i , the total friction ζ is lowest when both the terms ζ_{SR} and ζ_{DF} are not too large. This explains the existence of a conductivity maximum. Hubbard and Onsager [16] have improved the treatment which leads to better agreement with the experimental mobilities.

Although the maximum in ionic conductivity can be reproduced by the continuum treatment for ions carrying a given type of charge – positive or negative – the theory does not permit distinction between them as ζ_{DF} depends on q_i^2 . Thus, the theory can not account for the two different curves in the plot of conductivity– $1/r_i$ obtained experimentally for positive and negative ions and two different maxima [19]. Clearly there is a need for more refined theories which treat the charge distribution of the solvent explicitly.

Wolynes proposed a microscopic theory to overcome some of the limitations of the continuum theories. He separated the contribution into those from the hard repulsive interaction ζ_{HH} and soft attractive interactions ζ_{SS} . The correlations between the soft and hard interactions are neglected. ζ_{HH} is identified with the hydrodynamic friction. Both solvent-berg and continuum treatments are limiting cases of this molecular theory. In this sense, this may be considered to be more general than other theories.

More recently, Bagchi and coworkers [20–22] have extended the molecular theory to permit self-motion of the ion. This provides a clearer picture of the various physical factors responsible for the friction on the moving ion. These are based on mode coupling theory and separate the overall friction into a microscopic ζ_{micro} and a hydrodynamic part ζ_{hyd} :

$$\frac{1}{\zeta} = \frac{1}{\zeta_{micro}} + \frac{1}{\zeta_{hyd}} \quad (4)$$

The ζ_{micro} has contributions from several terms. Direct binary collisions as well as the isotropic fluctuations in density lead to friction that are represented respectively by ζ_{binary}

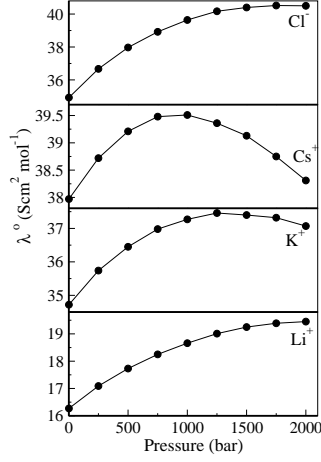


Figure 1: Variation of conductivity, λ^0 with pressure for monovalent ions at -5°C . The data have been taken from Takisawa et al. [26].

and $\zeta_{density}$. Coupling with polarization fluctuations is responsible for the dielectric friction ζ_{DF} . Thus,

$$\zeta_{micro} = \zeta_{binary} + \zeta_{density} + \zeta_{DF} \quad (5)$$

ζ_{hyd} is the hydrodynamic friction. This can be usually determined from transverse current-current correlation function. Although all these terms determine the overall friction on the ion, often some of these terms are less important than others. Thus, for some ions, Bagchi and coworkers suggest that some of these terms are small and can be neglected. More recent studies by Bagchi and coworkers have shown the importance of ultrafast solvation. It leads to a significant reduction in the contribution to friction experienced by the ion [23–25].

Fleming and coworkers [27], Barbara and coworkers [28] and Bagchi and coworkers [29] have shown the relationship between the solvation energy time correlation function and the dielectric friction. They have shown that both ion solvation dynamics and dielectric friction are influenced by the dynamics of the ion and the solvent. In other words, the dynamics that influences the ion solvation dynamics is also responsible for the dielectric friction. Bagchi and coworkers show that inclusion of the ultrafast mode in the dielectric relaxation is necessary to obtain closer agreement with the experimentally measured limiting ion conductivity Λ_0 .

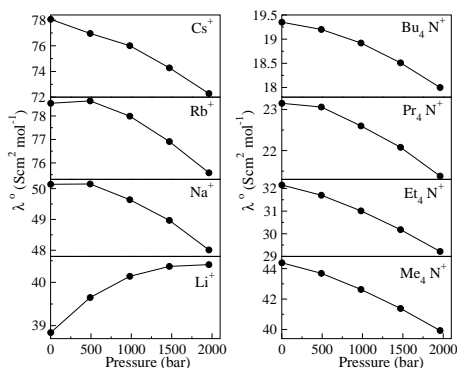


Figure 2: Variation of conductivity, λ^0 with pressure at 25°C for monovalent cations. Data taken from Ueno et al. [35].

There have been computer simulation studies on diffusion of ions in water and other solvents in the past two decades [30–33]. Computer simulations of Rasaiah and coworkers and Lynden Bell and coworkers [32, 33] on ion motion in water have clarified some aspects of this intriguing problem. Ion–water intermolecular potential was derived by fitting them to solvation energies of ions in embedded water clusters. They have carried out simulations to study the dependence of mobility on ion radius and charge. Their finding that both positively and negatively charged ions exhibit a maximum in diffusivity confirms the well known experimental results on alkali and halide ions which exhibit a maximum for intermediate sized ions. Simulations suggest that the solvent coordination around the ions depend crucially on the charge on the ion. However, they find no relation between the solvent coordination and mobility; this supports the view that solvent-berg model does not provide the required explanation to account for the maximum in conductivity. The precise size of the ion at which the maximum in mobility is seen also depends on the charge. Their calculations suggest that the dielectric friction model is more appropriate for larger ions while for small ions the solvent-berg model may be more appropriate. They obtained good agreement with experimental results.

Chandra and coworkers [30] have studied the effect of ion concentration on the hydrogen bond dynamics. They find that water molecules participating in five hydrogen bonds are more mobile as compared to four or fewer hydrogen bonds [31, 34]. They have also studied the effect of pressure on aqueous solutions. Studies have also been carried out on non-aqueous solutions.

Experimental studies date back to over several decades. But more recently, experimental studies of ionic mobility in water, alcohols, acetonitrile and formamide by Kay and Evans as well as Ueno and coworkers have shown the existence of a maximum in the Walden's product [35–40]. Investigations in D₂O show that the ratio of $\Lambda_0\eta_0$ in D₂O to that in H₂O also exhibits a maximum when plotted against r_{ion}^{-1} . Here Λ_0 is the limiting ion conductivity of the solution and η_0 is the viscosity of the solvent. Ionic mobility of cations has also been studied in a series of monohydroxy alcohol [35, 38]. It is generally observed that the mobility is lower in these alcohols than found in water. Further, the mobility is still lower in higher alcohols. Studies of ionic mobility also exist in solvents such as acetonitrile and formamide [35, 38, 39]. Both these solvents exhibit ultrafast solvation dynamics. For acetonitrile, an inertial component with a relaxation time of 70 fs and for formamide around 100 fs has been reported [41].

Recently, we proposed that the ionic conductivity maximum in polar solvents has its origin in the Levitation Effect [42, 43]. The latter is an effect that was observed for guests in zeolites and other porous solids. On increase in the size of the guest, the self diffusivity decreased initially when the size of the guest was significantly smaller than the size of the void and neck within the zeolites or other porous solids. However, the size of the guest was comparable to the size of the neck then, a maximum in self diffusivity was seen. This maximum has been shown to arise from the mutual cancellation of forces exerted on the guest by the zeolite leading to lower net force on the guest when its size is comparable to the size of the neck. The guest then is less confined relative to when it is smaller. A similar effect leading to a maximum in self diffusivity exists in solutions dominated by van der Waals interaction as well as in solutions with significant long-range interaction [44–47]. Thus, it appears that while the previous theoretical frameworks proposed based on continuum theories as well as microscopic theories provide a reason for the size dependent maximum in conductivity, they do not even attempt to explain the variation of conductivity with other variables such as pressure. Here we have collected all the conductivity data as a function of pressure and analyse them so as to obtain a clear idea of how the conductivities of ions in water are altered as a function of pressure. Such an understanding is necessary before one can put forward theories to explain the pressure dependence of conductivity for ions of different sizes.

2. Analysis of Experimental Measurements

Extensive amount of data is available in the literature for ionic conductivity in water of different salts. There are also several groups who have studied the dependence of ionic

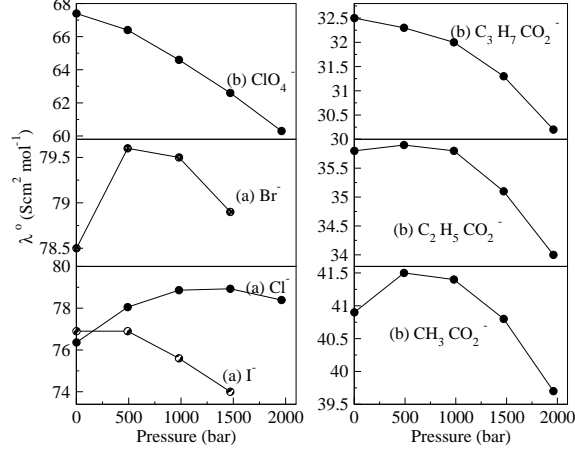


Figure 3: Variation of conductivity, λ^0 with pressure at 25°C for monovalent anions. Data taken from Nakahara and Osugi [48] and Shimizu and Tsuchihashi [49].

conductivity as a function of pressure [26, 35, 49–53]. Usually, the conductivity of the solution, Λ , is measured at several concentrations. These are analysed by means of Fuoss-Onsager equation [35, 51, 54]

$$\Lambda = \Lambda^0 - S\sqrt{c} + Ec \log c + Jc$$

of conductance of unassociated electrolytes. Here c is molar concentration, S and E are constants which are a function of Λ^0 and the solvent properties viscosity and dielectric constant. J is a function of ion size taken as an adjustable parameter. From this, Λ^0 , the limiting conductivity or conductivity at infinite dilution of the solution is obtained:

$$\lambda^0 = T_+^0 \Lambda^0.$$

Here, T_+^0 is the transference number at infinite dilution and λ^0 is the limiting ion conductivity at infinite dilution of the specific ion. Experimental details are not given here but those interested can find it from the cited references.

An analysis of λ^0 of the specific ion is investigated here since this is a simple quantity. In contrast, Λ^0 is the conductivity of the solution and its value depends on the conductivities of the cation as well as the anion. Although many studies in the literature report Λ^0 few studies report T_+^0 or λ^0 . The available data for analysis is therefore not extensive.

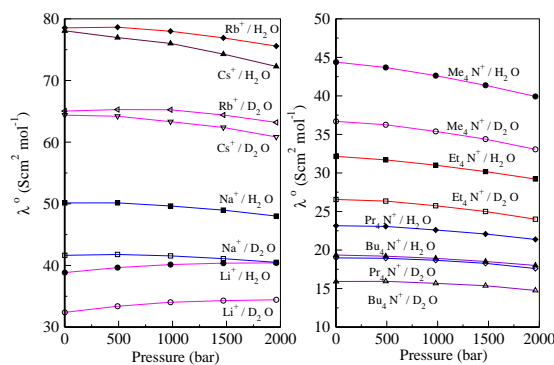


Figure 4: Variation of conductivity, λ^0 with pressure in light and heavy water for cations of differing sizes. Filled symbols are for light water and open symbols are for heavy water. Data taken from Ueno et al. [35].

$\Lambda^0 - p$ plots for monovalent ions of different sizes at -5°C : Figure 1 shows a plot of the variation of λ^0 as a function of the pressure, p , for Li^+ , K^+ , Cs^+ and Cl^- over a pressure range of 1-2000 bars. The measurements have been made at -5°C . We note that for Li^+ , the conductivity increases with pressure. For intermediate-sized ions at low temperatures, K^+ and Cs^+ , the conductivity increases initially and then subsequently decreases with pressure. Thus, a conductivity maximum is seen for these ions. We could not find any data for larger ions such as tetraalkyl ammonium ions. For Cl^- the behaviour is similar to what is seen for Li^+ . These data have been taken from Takisawa et al. [26].

A plot of λ^0 against pressure is shown for ions of different sizes of ions from the work of Ueno et al. [35] (see Figure 2). These measurements have been carried out at room temperature, 298K. Note that the trends seen in the earlier Figure are valid here also : small ions such as Li^+ exhibit an increase in conductivity with pressure. Intermediate sized ions exhibit a maximum in ionic conductivity at some intermediate pressure but larger ions (such as X_4N^+ , where $\text{X} = \text{Me}, \text{Et}, \text{Pr}, \text{Bu}$) show only a decrease in conductivity with pressure.

The data of Nakahara and Osugi and Shimizu and Tsuchihashi [48, 49] are shown in Figure 3. This shows a plot of λ^0 versus pressure, p , for monovalent anions at 25°C . For the larger anions such as I^- , ClO_4^- and $\text{C}_3\text{H}_7\text{CO}_2^-$ conductivity decreases with increase in pressure. But for anions of intermediate size (Br^- , Cl^- , CH_3CO_2^- and $\text{C}_2\text{H}_5\text{CO}_2^-$) a maximum in conductivity with increase in pressure is seen. This behaviour is what we observe in case of monovalent cations. It therefore appears that the maximum in conductivity

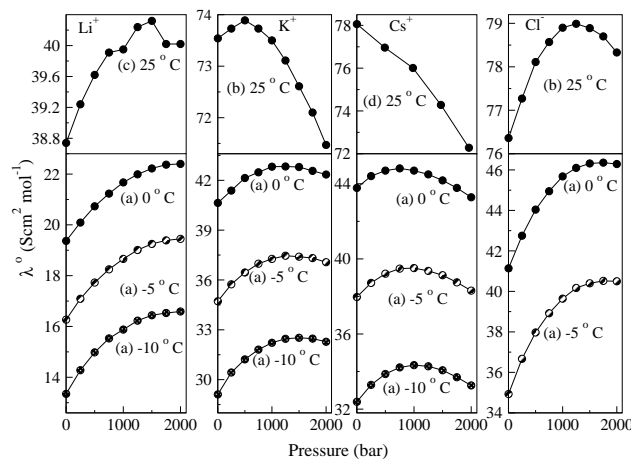


Figure 5: Variation of conductivity, λ^0 with pressure for monovalent ions over a range of temperature. The data have been taken from (a) Takisawa et al. [26] and (b) Nakahara et al. [55] and (c) Nakahara et al. [56] and (d) Ueno et al. [35].

depends on the size of the ion in a way that is independent of the nature of charge carried by the ion.

Figure 4 shows a plot of λ^0 versus pressure, p , for monovalent cations of different sizes in light and heavy water. From this figure, we can observe that conductivities in heavy water show a similar trend as we observe in case of light water; only a uniform lowering of conductivity is seen in heavy water as compared to light water. A reduction in conductivity in heavy water is attributed to stronger hydrogen bonding in heavy water as compared to light water. A sluggish solvent structure can lead to reduced mobility of the ion and not just the solvent.

Temperature dependance of $\Lambda^0 - p$ plots : In Figure 5 we show a plot of the variation of λ^0 with pressure over a range of temperatures. At higher temperatures, some changes are seen in the $\lambda^0 - p$ curves. Firstly, for ions such as Li^+ or Cl^- , the increasing conductivity with pressure changes to an increasing and decreasing trend with pressure exhibiting a maximum at some intermediate pressure. For the intermediate sized ions such as K^+ and Cs^+ the trend is seen to remain the same; however, the pressure at which the conductivity is maximum shifts to a lower pressure. For example, in the case K^+ the maximum conductivity is seen at a pressure of 1500 bars at $-10^\circ C$. By $25^\circ C$ the pressure at which the conductivity is maximum shifts to 500 bars. For Cs^+ the pressure at which the conductivity

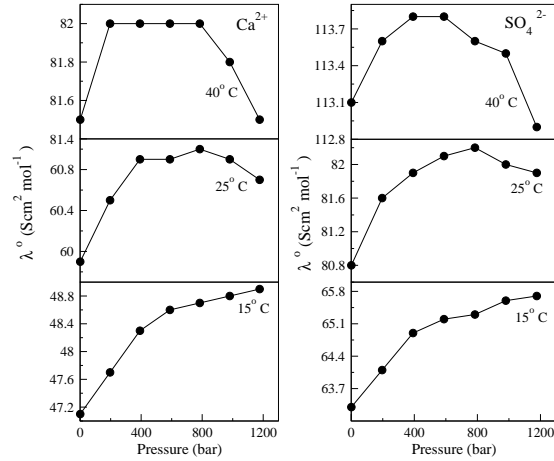


Figure 6: Variation of conductivity, λ^0 with pressure for divalent ions over a range of temperature. The data have been taken from Nakahara et al. [48].

ity is maximum shifts from 1000 bars at -10°C to 200 bars at 25°C . These data have been taken from the references mentioned in the figure caption.

Figure 6 shows a plot of λ^0 versus pressure, p , for divalent ions at different temperatures. This figure shows that divalent ions like Ca^{2+} and SO_4^{2-} also exhibit an increasing trend in conductivity as a function of pressure at lower temperature and shows maximum in conductivity with pressure at higher temperatures. These trends are similar to the trend seen in the case of monovalent ions.

3. Conclusions

We summarize the different behaviours and the conditions under which these trends are seen. Irrespective of whether they are cations or anions, or monovalent or divalent ions, the following trends are seen at a given relatively low temperature :

(a) small ions exhibit an increase in conductivity with pressure. (b) intermediate sized ions exhibit a conductivity maximum as a function of pressure. (c) conductivity decreases monotonically with pressure for large ions.

Similar trends are seen in heavy water, D_2O as well.

With increase in temperature, the following changes are seen for ions of different sizes:

(a) small ions : the increase in λ^0 is seen to change to a conductivity maximum at sufficiently high temperatures. (b) intermediate sized ions : there is shift of the maximum to

lower pressures. (c) larger sized ions : no change; only a decreasing trend is seen.

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