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A KINEMATIC APPROACH TO IONIC TRANSPORT IN AQUEOUS ELECTROLYTE SOLUTIONS AND STRUCTURAL THEORY OF HYDRATION OF ALKALI METAL IONS

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ABSTRACT

While considering the self-diffusion processes in aqueous electrolyte solutions, transport of ions, not only by jumps of single ions, but also by jumps of their solvation shells, are to be taken into account. Samoilov estimated the relative number of the two kinds of ionic jumps from experimental data on diffusion assuming an approximately uniform value for the α factor. In the present paper entirely different theory of the α factor based on the structural hydration model of one of the authors (S.V.T.) for alkali metal ions is given and its ion-wise values are calculated at different temperatures. The theory not only dispenses with the approximate fixation of α but also throws light on the structure of water, formation of clusters and their population variation with temperature.

INTRODUCTION

Kinetic properties associated with transport phenomena, such as diffusion, viscosity, thermal and electrical conductivities, are common to gaseous plasmas and electrolyte solutions since, as in gaseous plasmas, ions are also present in electrolytic solutions as the end result of dissociation even in the concentrated state. The great success of the Debye–Hückel theory for dilute aqueous electrolytes has shown beyond doubt that the perfect gas laws of kinetic theory also apply here as regards the distribution of energy amongst the ions in solutions. In the present paper, an attempt has been made to apply these laws to aqueous electrolyte solutions to account for the diffusion processes that occur in these solutions. Because of the immense importance

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of Na^+ and K^+ in biological systems, attention has been focussed mainly on alkali metal ions.

DIFFUSION IN AQUEOUS ELECTROLYTE SOLUTIONS

The properties of aqueous electrolyte solutions depend on interactions between ions and solvent molecules and therefore any theory of liquid solutions must be considered in relation to the structure of the solvent concerned. Water is probably the only molecular liquid that has been extensively studied. It is now well known that liquids lack long-range order and therefore the structure of water can only be understood quantitatively in terms of short-range order. The structures of ice and water are conditioned by the formation of hydrogen bonds between the molecules finally resulting in what are known as clusters or cells. The radial distribution curves[1] taken together indicate that the structure of water mostly remains hexagonal even at higher temperatures, implying the existence of short-range order, and the state of hydrogen bonding in water is somewhat loose as compared to that in ice. However, there are different opinions about the size of clusters and their percentage in relation to the total molecules, so that it is possible in principle to pass continuously from a cluster to a continuum[2]. When an electrolyte is added to water ion hydration is the end result. The hydration number of these ions is also a matter of choice and several hydration numbers are suggested for alkali metal ions[3].

The work of Bockris and Saluja[4] must also be mentioned in relation to hydration numbers. These authors point out the difference between the solvation or hydration number (SN) and the coordination number (CN). The latter represents the total number of water molecules in contact with an ion, whereas the former gives the number of water molecules which remain associated with an ion during its movement through solution. Usually the SN is less than the CN, but for very small ions the two are nearly equal and for very large ions SN tends to zero.

Though a general mechanism of translational diffusion of ions in the aqueous systems macroscopically could be one in which diffusion proceeds continuously by co-operative interaction with their neighbours, for which there is some support from computer simulation studies, still a microscopically valid picture is that diffusion does involve ionic jumps. The transport of ions in electrolyte solutions not only takes place by the activated jumps of single ions but also by the co-operative jumps of ions with their hydration or solvation cells. Considering both types of jumps Samoilov[5] has treated the problem of ionic self-diffusion in his monograph, however, without going into the solvation or hydration number involved, i.e., without specifying the number of water molecules in the hydration shell of an ion. Using relevant available experimental data on diffusion he calculated ΔE, the change in activation energy of jumps due to close hydration of ions. Amongst them for alkali metal ions, the values obtained were $+ 0.73$, $+ 0.25$, $- 0.25$ and $- 0.33$ kcal g $mole^{-1}$ for Li^+, Na^+, K^+ and Cs^+, respectively. These were then used to calculate the relative proportions of the average number of activated jumps of two kinds; the jumps of ions alone, n_1, and of ions with their hydration shells, n_2, from the relation

$$n_2/n_1 = \alpha e^{\Delta E/RT} \qquad (1)$$

where α was put equal to 0.0655. From these calculations he concluded that for 100 activated jumps of single Li^+, Na^+, K^+ and Cs^+ ions, on average about 23, 10, 4 and 4 jumps occur together with their hydration shells, respectively.

The value of α involved in the calculations of ΔE and n_2/n_1 both, as per definition[5] is a positive fraction for ions and depends on the ratio of the pre-exponentional factors A_2 and A_1 in the expressions for frequency of activated jumps of ions with and without their solvation shells, respectively, i.e., α equals A_2/A_1. Generally speaking each ion must have a specific α value which should also be temperature-dependent. However, according to Samoilov[5] an approximately uniform value of 0.0655 can be assumed, since α is determined by the pre-exponential factors A_1 and A_2 and the difference in activation energies does not directly affect α. The assumptions do not appear to be valid even prima facie, since by the very nature of the problem it is expected that, not only the formation of ion hydration shells in aqueous electrolytes solutions, but also the formation of clusters in pure water, should depend on the temperature. In addition the former will also depend on the nature of the ion. The α factor should not only vary from ion to ion but also from temperature to temperature. It is proposed herein to give an entirely different structural theory of "α" for alkali metal ions and to see how far α values reconcile the experimental data on diffusion of ions in aqueous electrolyte solutions and on self-diffusion in water. The theory can be extended to other ions also if their hydration models are specifically known.

STRUCTURE-BASED HYDRATION MODEL

After careful survey of several existing static and dynamic hydration models, one of the authors (S. V. Talekar) recently proposed a structural hydration model for alkali metal ions[6]. Of special interest to this model are two properties of water, the short-range order and the concept of bent hydrogen bonds. The former defines the equilibrium sites for exchange of water molecules and contributes to self-diffusion, and the latter allows formation of ionic hydration shells with six water molecules placed equivalently around an alkali ion; giving six as their hydration number.

The structure of the model[6] can be described in terms of a three-dimensional orthogonal cartesian coordinate system in which two water molecules are placed on each of the axes equidistant from the origin where the ion is located. The distance $M^+ \cdots OH_2$ varies from ion to ion. In this arrangement it is seen that lone-pairs of oxygen of H_2O in one plane point in the direction of hydrogens of the H_2O molecules in the other planes. A system of twelve non-linear hydrogen bonds are formed amongst the six-membered water molecules. This arrangement forms the ionic hydration shell.

The strength of the non-linear hydrogen bonding in this arrangement, V_{hb}, was calculated using a hydrogen bond potential function given by Lippincott and Schroeder[7], together with the modification of Moulton and Kromhout[8] for non-liner bonding. These calculations reveal that the non-linear hydrogen bonding is more pronounced in the hydration shells of Li^+ and Na^+, but is rather weak in the case of larger ions K^+, Rb^+ and Cs^+.

For the present study, we have recalculated V_{hb} values taking into account the modification in the lone-pair angle due to non-linear hydrogen bonding in the ionic hydration shells. The strength of non-linear hydrogen bonding in the structure is also calculated replacing the ion by cavity which is found to be of nearly the size of a water molecule, i.e., for a similar empty cell of six water molecules formed without affecting the lone-pair angle. The equation used was

$$V_{hb} = D\{1 - \exp[-n(r-r_0)^2/2r]\} - \bar{D}\cos^2\beta\exp[-\bar{n}(d-r-\bar{r}_0)^2/2(d-r)] + B\,e^{-\mu d} - A/d^m \quad (2)$$

after refs. 7 and 8, where d is the distance between two oxygen atoms forming bonds with hydrogen and r is the standard length of the stronger H–O bond (0.956 Å). The numerical values of constants D, $\bar{D}$, n, $\bar{n}$, r_0, $\bar{r}_0$, μ, A and B were the same as given in ref. 7. As for the parameter m, which determines the power law of electrostatic potential for bonds involving equivalent oxygen atoms, a suitable value between 3 and 6 may be chosen[7]. In the present calculations $m = 6$ was used to correspond with hexacoordination of the structural model. Values of angle β related to modification of the lone-pair angle and of distance d as evaluated from the structural model, together with the calculated V_{hb} values, are given in Table 1 for the hydration shells of alkali metal ions and for the empty cell of water molecules. Difference, ΔV_{hb}, as given in the last column of this table, represents the change in activation energy of jumps involving ionic hydration shells in the respective cases.

The ΔV_{hb} value is positive for Li^+ and Na^+ while negative for K^+, Rb^+ and Cs^+, thus leading to what may be called positive and negative hydration, respectively. A plot of ΔV_{hb} against ionic radii (average of Pauling and Goldschmidt radii) is given in Fig. 1, wherein also the ΔE values of Samoilov[5] are shown for comparison. Inspite of some variation of actual values for the corresponding ions in the two curves, they

TABLE 1

HYDRATION MODEL PARAMETERS

Ionic shell or water cell	*$O_1 \cdots O_2$ (d)Å*	*β°*	*$-V_{hb}$ kcal mole^{-1}*	*$\Delta V_{hb} = [V_{hb}^{H_2O} - V_{hb}^{i}]$ kcal mole^{-1}*
Li^+	3.054	2.90	1.8777	+1.6750
Na^+	3.450	0.90	0.3829	+0.1802
H_2O	3.660	0.00	0.2027	0.0000
K^+	3.874	−0.82	0.1231	−0.0796
Rb^+	4.016	−1.32	0.0939	−0.1088
Cs^+	4.326	−2.28	0.0572	−0.1455

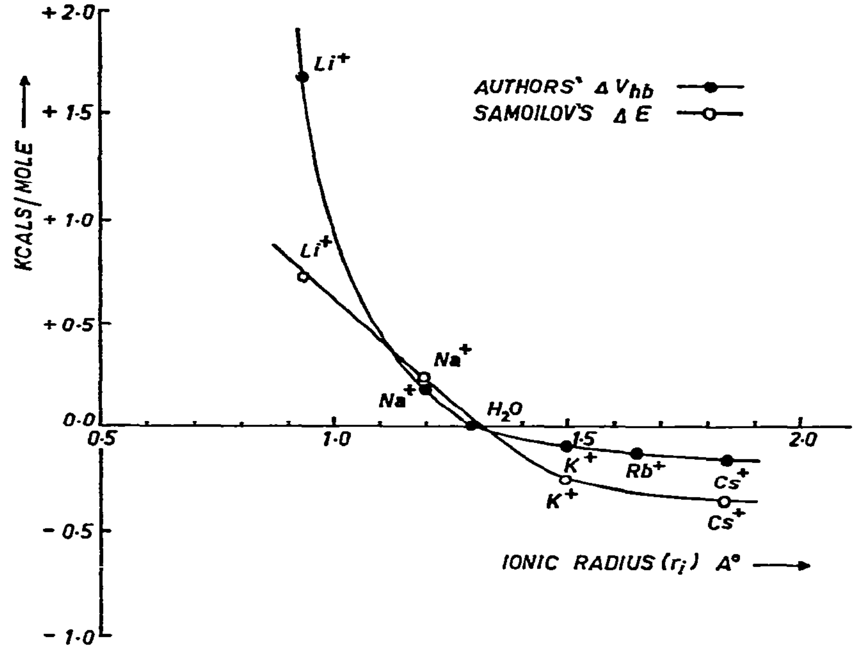

Fig. 1. Change in the activation energy as a function of ion size.

are similar in dividing the ions into two groups, Li^+ and Na^+ above, and K^+, Rb^+ and Cs^+ below, the $\Delta V_{hb} = 0$ line. Samoilov's curve crosses this line at 1.32 Å and ours at 1.295 Å, giving close agreement. As regards the actual values of ΔV_{hb}, they no doubt differ from Samoilov's ΔE values for alkali ions, but nonetheless are of the same order. The reasonable agreement between them is most striking in view of the fact that Samoilov's values are based on phenomenological considerations of thermochemical data whereas ours are based simply on the structural model of ionic hydration shells.

THEORETICAL CALCULATIONS OF α

Equation (2) giving V_{hb} in the structure-based hydration model is independent of temperature, since the structural parameters do not involve temperature. However, this can hardly be regarded as proof of temperature-independence because temperature was nowhere introduced in the analysis. The expression for V_{hb} is nevertheless a logical deduction and what is required is to associate temperature with V_{hb} energies so calculated. In processes like self-diffusion of water or diffusion of ions in electrolyte solutions, it is possible to associate temperature with these energies by considering the energy-wise distribution function of the diffusing particles.

Experience has shown, as mentioned before, that the thermal motion of constituent particles of aqueous electrolyte solutions can be treated with great success by the kinetic laws for a perfect gas. Since the Maxwell–Boltzman energy-wise distribution function is independent of the mass of the particles it will be valid for both the constituents of an aqueous electrolyte solution, namely the ions and the water molecules. The energy-wise distribution function $f(\varphi)$ at a temperature T (Absolute) representing the fractional number of particles having an energy φ is given by the well-known expression

$$f(\varphi) = \frac{2}{\sqrt{\pi}}(1/RT)^{3/2}\sqrt{\varphi}\exp(-\varphi/RT) \tag{3}$$

where φ is the energy per g mole of the particles and R is the universal gas constant. The range of energy φ is, as usual, from zero to infinity and all particles are covered by the range.

The different values of V_{hb} pertaining to the structure-based hydration model (vide supra) correspond to the formation of a cell or a cluster of six water molecules with an ion or cavity at the centre. Water molecules, therefore, must have a definite energy to form such clusters or cells. In aqueous electrolyte solution these will be continuously formed and destroyed, initially at different rates, but eventually dynamic equilibrium will ensue and then the time average number of these of a given energy will remain constant at a given temperature.

Since six water molecules form a single cell around an alkali ion or cavity, according to the structure-based hydration model[6], the probable number of cells will be one sixth of the number of water molecules which possess the required V_{hb} energy. Further, the end result will be the same, an ion hydration shell, whether a cell grows around an ion or it is formed first and then captures an ion. The latter appears more probable since clusters are known to be formed in pure water, i.e., in the absence of any ions. It may therefore be considered that ionic hydration shells are formed by capture of ions when the water cells encounter them in solution. However, each and every water cell that is formed may not be in a position to capture an ion and therefore a particular cell may or may not capture it. On the basis of the probability of random processes of two equally weighted alternatives one can surmise that if the number of cells is fairly large then half of them are expected to capture ions. Further, the capture will also be governed by the availability of ions for the purpose. Taking ionic concentration as a measure of availability and using expression (3), the actual number of ionic hydration shells in an electrolyte solution can be written as

$$n_s = \tfrac{1}{2}\frac{C \cdot n_w}{6}\left[\frac{2}{\sqrt{\pi}}(1/RT)^{3/2}\sqrt{V_{hb}}\exp(-V_{hb}/RT)\right] \tag{4}$$

where n_w is the total number of water molecules in the aqueous electrolyte solution and C is the ionic concentration in it. Since this total number of ions, n_i, will be equal to $C\,n_w$, the number of hydrated ions among them is then given by

$$n_s = 1/12\, n_i\, f(V_{hb}) \tag{5}$$

and that of naked ions by

$$n_n = n_i\,[1 - 1/12\, f(V_{hb})] \tag{6}$$

where $f(V_{hb})$ represents the expression $[(2/\sqrt{\pi})(1/RT)^{3/2}\sqrt{V_{hb}}\exp(-V_{hb}/RT)]$ in eqn. (4).

Assuming that pre-exponential factors, A_1 and A_2, in the expression of respective activated jump frequency, depend on the number of jumping entities and noting that every time a filled-in cell jumps it carries an ion within and that the distribution function is equally valid for both constituents of the aqueous electrolyte solution, the ions and the water molecules, one can directly correlate the α factor with the distribution function. Consequently, it can be written as

$$\alpha_i = n_s/n_n = f(V_{hb})/12 - f(V_{hb}) \tag{7}$$

By similar considerations applied to water if V_{hb} were to represent the energy corresponding to water molecules forming cells around cavities (i.e., empty cells) in water, the ratio of the number of such empty cells, n_c, to that of the remaining water molecules, and therefore α_w will be given by

$$\alpha_w = n_c/(n_w - 6n_c) = f(V_{hb})/6[1 - f(V_{hb})] \tag{8}$$

The α_i values calculated for alkali ions and α_w for water molecules at different temperatures are given in Table 2. From these one notes that as temperature rises, the values diminish monotonically except for Li^+, in which case they increase; but in no case is the α value greater than 0.1 for ions. In the diffusion process, while fixing an approximate uniform value of $\alpha = 0.0655$, the same for all ions and at all temperatures, Samoilov[5] had surmised that α cannot be greater than 0.1. The stipulation is amply justified by the theory of α given herein. The structural theory not only successfully accounts for the α factor pertaining to alkali ions, but also throws light on the formation of cells or clusters in water at different temperatures. The α (H_2O) values show that the number of cells or clusters decreases as temperature rises. For every 100 free water molecules there are about 88 cells at 10 °C and the number falls to about 31 at 80 °C. At 0 °C there are more clusters or cells than the number of free water molecules. It is rather uncertain to specify from the various existing theories of structures of water, the exact percentage of clusters of water molecules in water and its variation

TABLE 2

α-VALUES FOR DIFFERENT IONS AND WATER AT DIFFERENT TEMPERATURES

Temp.	α					
°C	Li^+	Na^+	K^+	Rb^+	Cs^+	H_2O
0	0.0102	0.0775	0.0705	0.0646	0.0534	1.1740
10	0.0109	0.0751	0.0671	0.0614	0.0507	0.8789
20	0.0116	0.0728	0.0640	0.0584	0.0482	0.7005
30	0.0124	0.0706	0.0611	0.0557	0.0458	0.5811
40	0.0130	0.0685	0.0584	0.0533	0.0437	0.4950
50	0.0136	0.0665	0.0560	0.0509	0.0417	0.4303
60	0.0142	0.0646	0.0536	0.0488	0.0399	0.3803
70	0.0147	0.0627	0.0515	0.0468	0.0382	0.3400
80	0.0154	0.0609	0.0495	0.0449	0.0366	0.3069

TABLE 3

n_2/n_1 RATIOS FOR IONS AND WATER

	Temp. (°C)	n_2/n_1 *Li^+*	*Na^+*	*K^+*	*Rb^+*	*Cs^+*	*H_2O*
Present authors	20	0.206	0.099	0.056	0.049	0.038	0.701
Samoilov	21.5	0.228	0.096	0.043		0.037	

with temperature. The theory of the α factor outlined herein gives directly a fair estimate in this respect.

ACTIVATED JUMPS OF IONS

The structural theory of the α factor can now be checked by calculating the proportion of activated jumps of ions with and without their hydration shells at some temperature (say 20°C). In eqn. (1) replacing ΔE by ΔV_{hb} of Table 1 and using values at 20°C from Table 2, the fraction n_2/n_1 is calculated for hydration shells of alkali metal ions and for water cells or clusters. These values are given in Table 3, in which is also given the n_2/n_1 ratio at 21.5°C as obtained for alkali ions by Samoilov[5] using his ΔE values and fixed $\alpha = 0.0655$. In the case of self-diffusion in water, Samoilov considered that here also the diffusion takes place by both kinds of jumps, i.e., the jumps of single water molecules and the jumps of cells of water molecules or clusters, but the two activation energies are the same, with the net result that though $(A_1 + A_2)$ is finite the ratio A_2/A_1 is unspecified. Consequently, since no α value was fixed for self-diffusion of H_2O, the ratio n_2/n_1 cannot be calculated from eqn. (1) in his case.

The two sets of n_2/n_1 values presented in Table 3 are in good agreement. One notes here that Samoilov's approximate fixation of α for ions and his evaluation of n_2/n_1 are both based on the experimental ionic diffusion data of Wang et al.[9]. On the other hand, the present theory of the α factor, as also the evaluation of n_2/n_1, do not use any of the diffusion data and are entirely based on the structural model[6] of one of the authors. It is therefore quite remarkable that there should be a striking agreement between two sets of n_2/n_1 values based on entirely different grounds.

CONCLUDING REMARKS

The problem of ionic hydration in electrolyte solutions can be divided into two regions: one that of close hydration and the other of distant hydration. The former is characterized by interaction of ions with the water molecules which are in the immediate neighbourhood of the ions and the latter by their interaction with more distant water molecules. The translation of ions and water molecules occurs through the equilibrium position in aqueous electrolyte solutions and depends on the height of potential barriers that separate these neighbouring equilibrium sites. The predominant role of close-range order in the properties of aqueous electrolyte solution is thus inherently implied. Consequently, the kinetic properties of solutions are mainly dependent on close hydration. The structural theory of the α factor given in the present paper deals mainly with close hydration and not only gives a basis to Samoilov's assumptions but also throws light on the structure of water, formation of clusters and their population variation with temperature.

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