Vapour pressure isotope effect studies on ionic solutions and the structure of electrolyte solutions

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A comparison of vapour pressure isotope effect (VPIE) in single ionic solutions, i.e., hydrogen isotope effects in the dehydration of alkali metal ionic forms of resins (Li\(^+\), Na\(^+\), K\(^+\) and Cs\(^+\) forms) and corresponding aqueous alkali metal chloride solutions at various concentrations and temperatures has been made. Theory of VPIE for cationic solutions having 3 water sub-systems and anionic solutions having 2 water sub-systems has been developed. Single ion solutions (Li\(^+\) at 303K, Na\(^+\) at 318K, K\(^+\) at 333K and Cs\(^+\) at 353K) show all the features arising from the hydration shell models and predicted by the theory of VPIE in their \(a\) (separation factor) versus \(m\) (molality) plots. The absence of these features in the \(a\) versus \(m\) plots in low concentration region (\(\sim 2m\)) for the corresponding chloride solutions (namely, LiCl, NaCl, KCl and CsCl) is primarily due to the separate contributions from various water sub-systems to overall separation factor. At high concentrations and at all temperatures, in alkali metal chloride solutions the various water sub-systems get disturbed because of sharing of water molecules and \(a\) versus \(m\) plots in this region differ markedly from the corresponding single ion plots. The separation factors, \(a(M^+ + Cl^-)\) \((M^+ =\) alkali metal ion) for hypothetical MCI solutions (where cation cosphere-anion cosphere interactions are absent) have been computed using single cation and chloride ion separation factors at different concentrations and temperatures. At low temperature, at or below 303K, where water structure is strong and the hydration shell structure is comparatively weak, the cosphere-cosphere interaction is constructive \(\{a(M^+ + Cl^-)\text{ values }< a(MCI)\text{ values}\}\). At higher temperatures (for example, at 353 K), where hydration shell structure is stronger than water structure, the cosphere-cosphere interaction arising from sharing of water molecules is destructive \(\{a(M^+ + Cl^-)\text{ values }> a(MCI)\text{ values}\}\). This study shows that hydration shell models based on the water sub-systems are real and contribute proportionately to thermodynamic property of an electrolyte solution, like VPIE.

Though aqueous electrolyte solutions have been studied most extensively\(^1\)\(^-\)\(^3\), only scanty information is available about the properties of individual ions\(^2\)\(^-\)\(^3\). Direct information about individual ions (single ions) in water is available either from gas phase mass spectrometry\(^4\)\(^,\)\(^5\) or theoretical quantum mechanical calculations\(^6\). Both these approaches are limited to a few water molecules (\(\sim 10\) per ion. Thermodynamic properties of electrolyte solutions have been resolved into separate anion or cation properties only by using extra thermodynamic assumptions\(^7\).

Solvent isotope effects in aqueous electrolyte solutions have been discussed in detail by Friedman and Krishnan\(^7\). Free energies of transfer, \(\Delta G^\circ\), of electrolyte, MX\(_z\) (where, \(z = 1\) or \(2\)), that is,

\[
MX_z(H_2O) \rightarrow MX_z(D_2O)
\]

and the corresponding single ions have been analysed. The standard free energies of transfer of single ions from \(H_2O\) to \(D_2O\) are independent of concentration, because the standard and reference states are defined in terms of the salt. These analyses were based on the differences in the transfer thermodynamic functions of the ions of the same charge (for example, alkali metal cations) and yielded valuable information about the water in the cosphere of the ions.

Recently, single ion solutions have been studied using a novel approach\(^8\)\(^-\)\(^13\). In strong acid (Dowex 50W) or strong base (Dowex 1) ion exchange resins in monovalent ionic forms, the ionogenic groups are osmotically inactive and unhydrated. In the absence of strong electrostatic interactions between ionogenic groups (e.g., \(-SO_3^-\) and counter ion (e.g., alkali metal cations), the resin bead behaves like a container for counter ions and water (as ionogenic groups are unhydrated and ion-
hydratation of the ions, or, in other words, to what extent the results of VPIE in single ion solutions show the predicted effects of hydration (model) of ions and (ii) As the absence of effects of hydration on VPIE in aqueous electrolyte solutions are attributed to cosphere interactions, we expect that this comparison of VPIE of single ion and electrolyte solutions would lead to a better understanding of cosphere-cosphere interactions.

**Theoretical aspects of VPIE in ionic solutions**

In order to put these VPIE in their proper perspective, theory of VPIE in ionic solutions has been developed taking into consideration all the known features of ionic hydration.

VPIE for aqueous solution is defined as:

\[ \text{VPIE} = \frac{P_{\text{H}_2\text{O}}}{P_{\text{D}_2\text{O}}} = R \]

where the condensed phase, \( (\text{cond}) \), is either pure water \( (R=R^w) \) or electrolyte solution \( (R=R^m) \) or ionic solution \( (R=R^a \text{ or } R^c; R^a \text{ anionic solution, } R^c \text{ cationic solution}) \). The isotopic equilibrium involved in the VPIE studies of electrolyte solutions is related to the hypothetical reaction

\[ \text{H}_2\text{O (cond.)} + \text{D}_2\text{O (vapour)} = \text{H}_2\text{O (vapour)} + \text{D}_2\text{O (cond.)} \]

The equilibrium constant, \( K \), for this reaction, when the condensed phase is pure water is \( K = R^w \); when the condensed phase is an electrolyte solution, whose concentration is \( m \), the equilibrium constant is \( K^m = R^m \). VPIE studies in electrolyte solutions give directly this equilibrium constant\(^{15}\).

Following the method developed by earlier workers\(^{15,23} \), \( K \) can be written as

\[ \ln K = -\frac{1}{N} \left( \ln Q_{\text{H}_2\text{O}}/Q_{\text{D}_2\text{O}} \right)_{\text{vapour}} - \left[ \ln Q_{\text{H}_2\text{O}}/Q_{\text{D}_2\text{O}} \right]_{\text{cond}} \]

where \( N \) is the total number of water molecules and \( Q_{\text{H}_2\text{O}} \) and \( Q_{\text{D}_2\text{O}} \) are molar partition functions of isotopic molecules.

Bigeleisen and Mayer\(^{23,24} \) have formulated \( Q_{\text{H}_2\text{O}}/Q_{\text{D}_2\text{O}} \)'s [in Eq. (4)] in terms of reduced partition function ratios, where the translational, rotational and electronic parts cancel out. Thus, reduced partition function ratio denoted as \( s/s'f \) is simply the ratio of vibrational partition functions. For vapour phase,

\[ s/s'f = \prod_{i} \mu_i/\mu_i' e^{-\mu_i/2} e^{-\mu_i'/2} . (1-e^{-\mu_i})/(1-e^{-\mu_i'}) \]

where, \( \mu = h\nu/kT \) and \( s \) and \( s' \) are symmetry numbers and prime (') refers to the molecules with heavier isotope. For water molecules in the...
gas phase, $3n-6$ is 3 and for condensed phase where rotational and translational motions are hindered, that is, become librational modes, the product is over $3n$ frequencies,

$$s/sf = \prod_i^{3n} \mu_i / \mu_i e^{-\mu_i^2 / 2} (1 - e^{-\mu_i^2}) / (1 - e^{-\mu_i^2})$$

Thus, the isotopic separation factors can be directly correlated with vibrational and librational frequencies. Further, as the condensed phase changes, e.g., from water to LiCl solution ($m$) or to Li$^+$ in resin phase ($m$), the separation factor changes due to change in vibrational and librational frequencies of water molecules in these systems. These, in turn, reflect the varying interactions of water molecules in these systems, i.e., reflect the changes in force constants for vibrational modes of water molecules as they exist in vapour phase or pure liquid water or LiCl solution ($m$) or Li$^+$ in resin phase ($m$). Thus, these separation factors have a direct correlation with molecular interactions.

The difference between the vapour pressure ratios of pure solvent and solutions, that is, $R^o$ and $R^m$ (Eq. (2)) can be expressed as $\Delta \ln R$

$$\Delta \ln R = \ln R^o - \ln R^m \ldots (7)$$

where, $R^o$ and $R^m$ are defined by Eq. (2) for pure solvent and the solution. Thus, $\Delta \ln R$ can be formulated only in terms of partition function, $Q$, of condensed phase, because the vapour phase partition function ratios in Eq. (7) cancel out, that is,

$$\Delta \ln R = -\frac{1}{N} \ln \left[ \left( \frac{Q_{D}}{Q_{H}} \right)_{\text{solvent}}^N - \ln \left( \frac{Q_{D}}{Q_{H}} \right)_{\text{solute}}^N \right] \ldots (8)$$

For pure water partition functions have already been formulated. In electrolyte solutions, where both cations and anions are present, cosphere interactions do not permit a simple formulation of partition function. In single ionic solutions (cationic or anionic), where such interactions are absent, and adequate information about ion-water interactions are available, one can conceptually define partition functions in a straightforward manner. In the following, we have first formulated partition functions for cationic and anionic solutions separately. Then the partition functions of hypothetical electrolyte solution, where cation cosphere and anion cosphere interactions are absent, can be developed in terms of the partition functions for single ion solutions.

In the last two decades, because of development in the theoretical and experimental study of electrolyte solutions (in particular, MD simulation studies of Heinzinger et al.25,26 neutron diffraction study of Enderby, Nielsen27-29 and quantum mechanical studies of Fugiwara30 and many others31), a detailed picture of the ions as they exist in electrolyte solutions has emerged. A detailed description of hydration model, used in the present study, is available in literature1,21. In brief, the cation can have primary and secondary hydration shells, where depending upon the cation, water molecules are equally or less strongly bound than in water. In anions, except in fluoride ion solutions, hydration shell water molecules are equally or less strongly bound than in bulk water.

Cationic solutions have three water sub-systems: primary hydration shell, secondary hydration shell and bulk water, that is,

\[ \text{Water}_{\text{primary}} = \text{Water}_{\text{secondary}} = \text{Water}_{\text{bulk}} \]

where, superscript 'c' denotes cation, and $Q_1$, $Q_2$, and $Q_3$ are the molar partition functions of the three sub-systems (namely, primary hydration and secondary hydration shells, and bulk water, respectively). Further, assuming that the number of water molecules in the primary and secondary hydration shells are independent of H and D substitution, we can write the reduced partition function ratio of the condensed phase as:

$$Q_{bc}(H/D) = \left( \frac{Q_{D}}{Q_{H}} \right)_{\text{solvent}} \cdot \left( \frac{Q_{D}}{Q_{H}} \right)_{\text{solute}} \ldots (11)$$

where, superscript 'c' denotes cation, and $Q_1$, $Q_2$, and $Q_3$ are the molar partition functions of the three sub-systems (namely, primary hydration and secondary hydration shells, and bulk water, respectively). Further, assuming that the number of water molecules in the primary and secondary hydration shells are independent of H and D substitution, we can write the reduced partition function ratio of the condensed phase as:

$$Q_{bc}^c = \left( \frac{Q_{DH}}{Q_{DH}} \right)_{\text{solvent}} \cdot \left( \frac{Q_{DH}}{Q_{DH}} \right)_{\text{solute}} \ldots (12)$$

Relation (12) applies to those systems where the number of water molecules per cation is greater than the water molecules required to complete the primary and secondary hydration shells. In a situation, where the number of water molecules per...
cation are not sufficient to complete the primary and secondary hydration shells of the ion, but more than required to complete the primary hydration shell, there will be no water present as bulk water and $Q_3$ will not contribute to $Q_{\text{solute}}$ (H/D). For such systems, therefore,

$$Q_{\text{solute}}^{c} \frac{(H/D)}{a} = \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_1} \cdot \left( \frac{Q_{2H}}{Q_{2D}} \right)^{n_2} \ldots (13)$$

where $n_1 + n_2 = 1$. Consequently, in the $\Delta \ln R^c$ expression (Eq. (12)), $Q_3$ will have a value of 1, that is,

$$\Delta \ln R^c = -\frac{1}{N} \left[ \ln \left( \frac{Q_{1H}}{Q_{1D}} \right)^N - \ln \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_1} \right] \times \frac{Q_{2H}}{Q_{2D}}^{n_2} \ldots (14)$$

Finally, in a system where the number of water molecules per ion are insufficient even to complete the primary hydration shell, there will be no water present in bulk or secondary hydration shell and all the water will be present as primary hydration shell water. For such systems, isotopic partition function ratio is given by:

$$Q_{\text{solute}}^{c} \frac{(H/D)}{a} = \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_1} \ldots (15)$$

where $n_1 = 1$. Consequently, in the $\Delta \ln R^c$ expression (Eq. (12)), $Q_3$ and $Q_2$ will have a value of 1.

In the case of halide ions in solution, particularly chloride ions, only primary hydration shells and bulk water exist. Thus, the molar partition function for water in these systems becomes,

$$Q_{\text{solute}}^a \frac{(H/D)}{a} = \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_1} \cdot \left( \frac{Q_{3H}}{Q_{3D}} \right)^{n_3} \ldots (16)$$

where $Q_a$ is the molar partition function of water present as hydration shell of anion, $Q_3$ is the molar partition function of pure water, $n_a$ is the mole fraction of water present as hydration shells of anion and $n_3$ the mole fraction of water present as free water, with $n_a + n_3 = 1$. $\Delta \ln R^a$ for pure anionic solutions then becomes,

$$\Delta \ln R^a = -\frac{1}{N} \left[ \ln \left( \frac{Q_{1H}}{Q_{1D}} \right)^N - \ln \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_1} \right] \times \left( \frac{Q_{3H}}{Q_{3D}} \right)^{n_3} \ldots (17)$$

In a system where the number of water molecules per anion are insufficient even to complete the primary hydration shell, there will be no water present as bulk water. For such systems, the isotopic partition function is written as:

$$Q_{\text{solute}}^a \frac{(H/D)}{a} = \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_a}$$

where $n_a = 1$. Consequently, in the $\Delta \ln R^a$ expression (Eq. (17)), $Q_3$, will have a value of 1, that is,

$$\Delta \ln R^a = -\frac{1}{N} \left[ \ln \left( \frac{Q_{1H}}{Q_{1D}} \right)^N - \ln \left( \frac{Q_{1H}}{Q_{1D}} \right)^{n_a} \right] \ldots (19)$$

However, because of rapid exchange of water between the various sub-systems, experimentally only single averaged out value for VPIE can be obtained, to which separation factor the various water sub-systems contribute proportionately.

In electrolyte solutions, where both anion and cations are present, partition function for the condensed phase in terms of separate molar partition function can be formulated as:

$$Q_{\text{cond}}^{\text{elect}} = \left[ \left( \frac{Q_{\text{cond}}^a}{Q_{\text{cond}}} \right)^{n_a} \left( \frac{Q_{\text{cond}}^b}{Q_{\text{cond}}} \right)^{n_b} \right]^{1/2} \ldots (20)$$

This will be strictly, valid for dilute solutions where cation cosphere and anion cosphere interactions are absent. At higher concentrations where sufficient water is not available for the formation of hydration shells of anions and cations, the situation becomes very complicated because of cosphere interactions. Water molecules are shared by anion and cations in order to form their hydration shells. This in turn changes $Q_1$, $Q_2$ and $Q_3$; Eq. (20) will be no longer valid. But, it will still give the value of VPIE in the hypothetical case where cosphere interactions are absent. Thus, a comparison of VPIE observed in electrolyte solutions and computed from single ion values at the same concentration and temperature will provide an insight into the cosphere interaction.

**Results and Discussion**

The isotopic equilibrium (Eq. (3)) is related to the equilibrium involving $H_2O$ and HDO (Eq. (21)) (at low D content, where $D_2O$ does not exist):

$$H_2O_{(\text{cond})} + \text{HDO}_{(\text{vapour})} \rightleftharpoons H_2O_{(\text{vapour})} + \text{HDO}_{(\text{cond})} \ldots (21)$$

The equilibrium constants for Eqs (3) and (21) are related; $K = R = \alpha^2$, where, $\alpha$ is the equilibrium constant of Eq. (21).
The overall separation factors obtained from VPIE studies of electrolyte solutions or resin phase are the sum of the various contributions to reduced partition function ratios for various water sub-systems or corresponding separation factors. Using the same subscripts as above, and putting \( \varepsilon = \alpha - 1 \), we have

\[
e_{\text{obs}} = e_1 n_1 + e_2 n_2 + e_3 n_3 \tag{22}
\]

for cation, and

\[
e_{\text{obs}} = e_a n_a + e_3 n_3 \tag{23}
\]

for anions; where \( e_{\text{obs}} = \alpha_{\text{obs}} - 1 \), \( e_1 = \alpha_{\text{prim}} - 1 \), \( e_2 = \alpha_{\text{sec}} - 1 \), \( e_3 = \alpha_{\text{bulk}} - 1 \), \( \alpha_{\text{bulk}} = \alpha_w \); \( e_a = \alpha_a - 1 \) and \( n_i 's \) are the mole fraction of water in the various sub-systems\(^\text{12}\). Dehydration studies of ions in the resin phase\(^\text{8-13}\) (that is, single ion solutions) directly give the equilibrium constants for Eq. (21) or the separation factors.

VPIE data on electrolyte solutions have been reported\(^\text{15}\) as \( \Delta \ln R \). In order to make direct comparison with resin phase data, we have converted it to \( \alpha \), related to Eq. (21). Resin phase data have been obtained at 303K, 318K, 333K and 353K\(^\text{8,12,13}\). van Hook et al.\(^\text{15}\) have not reported data at all these temperatures, but have given temperature coefficients for various systems. Using these coefficients, data for various systems at required temperatures have been computed.

Resin phase data have been reported between 303K and 353K for alkali metal cations and chloride ions (for Na\(^+\), however, only at 353K)\(^\text{8-13}\) at various \( n_w \), where \( n_w \) is the number of moles of water per equivalent of resin or per mole of counter ion. Experimentally determined \( \alpha \) values \( (\alpha_{\text{obs}}) \) are reproducible and accurate to \( \pm 0.003 - \pm 0.004 \) \( (\text{refs 8-13}) \). Relevant experimental details are published elsewhere\(^\text{8-13}\). To compare these data with aqueous electrolyte solution data, \( n_w \) is converted to molality, \( m \), of the counter ion, using

\[
m = \frac{55.5}{n_w} \tag{24}
\]

VPIE of electrolyte solutions (LiCl, NaCl, KCl, CsCl) and single ion solution (Li\(^+\), Na\(^+\), K\(^+\), Cs\(^+\) and Cl\(^-\) ) data as \( \alpha \) versus \( m \) plots at 303 K and 353 K are given in Figs 1 to 4.

Amongst the VPIE data on electrolyte solutions\(^\text{15}\) only LiCl solutions have been studied in a wide range of concentration (2 to 15 \( m \) ). The other alkali metal halide solutions have been studied only between 2 to 6 \( m \), due to solubility restrictions, though the single ion data, which do not suffer from this restriction, are available up to \( 25m \) (refs 12, 13). Hence, a detailed discussion is possible only for LiCl solutions and Li\(^+\) (resin).

LiCl\( (aq) \) and Li\(^+\)-form of the resin

Figure 1 shows that \( \alpha \) for LiCl solutions at both temperatures (curves 2 and 5) remain constant and equal to \( \alpha_w \) (where \( \alpha_w \) is the separation factor for pure water at a particular temperature), up to 5 \( m \) and then decreases, up to the highest concentration studied, that is, 15 \( m \). \( \alpha \) values at 353K are much lower than those at 303K. In the case of (single) Li\(^+\)-solutions in resin matrix at 303K and 353K (curves 1 and 4), the behaviour is totally different. Even at the lower value of \( m \), \( \alpha > \alpha_w \), and continues to increase with \( m \), up to \( \sim 5m \), where it has the maximum value. Then it decreases sharply up to 11 \( m \) and then remains constant (upto 28 \( m \)). At 353K (curves 4, Fig. 1) these features are very much sharpened though the maximum value at \( \sim 5m \) and the limiting values at \( > 11m \) are comparable at the two temperatures. The enhanced sharpness of maximum at \( \sim 5m \) arises because of lower value of \( \alpha_w \) \( (m = 0) \) at 353K.

As discussed in earlier publications\(^\text{8-13}\), in single Li\(^+\) solutions (resin phase studies) beyond 11 \( m \) only primary hydration shell exists, between 11 \( m \) and 5 \( m \) both primary and secondary hydration shells are present and below 5 \( m \), bulk water is also present along with these hydration shells.

When only primary hydration shell of ions is present (at concentrations \( > 11m \)), where water molecules are most strongly bound to the cation but no hydrogen bonding among water molecules is possible, \( \alpha \) is expected to be very much lower than \( \alpha_w \). Hydrogen isotope effect studies on the dehydration of hydrated CuSO\(_4\)·5H\(_2\)O crystals\(^\text{32}\), where water molecules are present as primary hydration shell of copper ions, have shown that \( \alpha_w \) is in the region of \( \sim 1.02 \). This is further supported by the computation of vibrational frequencies from MD simulations of water in a 13.9 \( m \) LiCl solutions\(^\text{33}\), where only primary hydration shell would be present. The stretching frequencies were 3216 cm\(^{-1}\) and 3240 cm\(^{-1}\) compared to 3656 cm\(^{-1}\) and 3757 cm\(^{-1}\) in the gas phase, implying that the contribution of these frequencies to VPIE will be much lower in 13.9 \( m \) LiCl solution than in pure water and lead to lower values of VPIE in salt solutions. The variation of \( \alpha \) beyond 11 \( m \) are then governed by Eq. (15) and Eq. (22) \( ( \text{with } n_2 = 0, n_3 = 0) \), which predicts a constant low value of \( \alpha \). The contribution of secondary hydration shell water (in the concentration region 5 to 11 \( m \)) is expected to be greater than \( \alpha_w \), because secon-
Fig. 1—Variation of $\alpha$ with $m$ for Li$^+$ (resin) and LiCl(aq). 1. Li$^+$ (303K); 2. LiCl (303K); 3. (Li$^+$ + Cl$^-$) (resin) (303K); 4. Li$^+$ (353K); 5. LiCl (353K); 6. (Li$^+$ + Cl$^-$) (resin) (353K).

Primary hydration shell water molecules are hydrogen bonded to primary hydration shell water molecules more strongly (than in pure water), as primary hydration shell water molecules are polarized in the field of $M^+$ ion $^{21}$ ($M$ = alkali metal ion) (Eqs (13) and (22) (with $n_3 = 0$) are valid in this region). Newton and Friedman $^{34}$ have computed shifts in the stretching and librational ($v_L$) frequencies of water molecules in the primary hydration shell and secondary hydration shell water molecules which are hydrogen bonded to water molecules in the primary hydration shell by ab initio calculations. A decrease in the stretching frequencies of water molecules in the former category (i.e., of water molecules in the primary hydration shell of cation) and an increase in $v_L$ of water molecules in the latter category (that is, secondary water molecules hydrogen bonded to the primary hydration shell water molecules). This was interpreted as an enhancement of hydrogen bonding in the latter case with increase in the charge of the cation. Both of these observations are consistent with the above analysis. Bulk water also contributes to VPIE (in the concentration region 0 to 5 m) with $\alpha_{\text{prim}} < \alpha_c < \alpha_{\text{sec}}$ ($\alpha_{\text{prim}}$, separation factor due to primary hydration shell and $\alpha_{\text{sec}}$, that due to secondary hydration shell) (Eqs (11) and (22) are valid in this region). The variation of overall value of $\alpha$ with $m$ is due to the three water sub-systems contributing in different proportions. Thus, resin phase data provides a clear-cut evidence for the validity of the hydration model for cations. Theory of VPIE explains all the features of $\alpha$ versus $m$ curve for Li$^+$-forms of resin.

The absence of these features in the variation of VPIE with $m$ arising due to hydration shell structure around Li$^+$ in aqueous LiCl solutions is not surprising. In a recent neutron diffraction isotope substitution (NDIS) study $^{35}$ of LiCl solutions at ambient temperature, it was concluded that intermolecular and intramolecular structure of 1 m LiCl solution and pure water are indistinguishable. This means that VPIE of LiCl solutions of low concentration would be the same as in pure water. Beyond 2 to 3 m LiCl solutions, there will not be sufficient water present to complete the cospheres of Li$^+$ and Cl$^-$. For example, in 3 m LiCl solution, 39 moles of water would be required for complete hydration of Li$^+$ and 18 moles of water for the hydration of Cl$^-$, making cation-anion cosphere to overlap and affect the secondary hydration shell of Li$^+$. Beyond this concentration, cosphere interactions would affect the hydration shell structures of both primary and secondary hydration shells. In the above mentioned study $^{35}$ of LiCl solution, it was further shown that in 10 m LiCl (a), intermolecular water structure is very different from pure water. In
this system, all the water molecules should be part of primary hydration shell of Li$^+$, with no hydrogen bonding. The study has shown that water molecules are under the influence of chloride ions or instead of no hydrogen bonding in 10 m LiCl only 19% of total number of hydrogen bonding in pure water are present. This explains the higher value of \( \alpha \) in LiCl (aq.) at \( \geq 10 \) m at 303 K compared to \( \alpha \) values for Li$^+$ in resin phase. While discussing the solvent isotope effects, Friedman and Krishnan$^7$ have concluded that hydrogen bonding is of little significance in the stabilisation of cospheres. As discussed above, it is shown that it is valid only for primary hydration shell. The different mechanism of stabilisation of the secondary hydration shell part of the cosphere, thus, could not be isolated from a discussion of the thermodynamic functions of transfer. Thus, in the resin phase studies, where these cosphere interactions are absent, one can see the effect of secondary hydration of Li$^+$ on VPIE, but not in aqueous LiCl solutions, where these cosphere interactions are present.

The data on Li$^+$ form of the resin (curve 4, Fig. 1) and LiCl(aq) (curve 5, Fig. 1) at 353 K provide a more striking evidence of these cosphere interactions as well as the effect of hydration shell structure on VPIE. As \( \alpha_w \) (353 K) < \( \alpha_w \) (303 K), its contribution to overall \( \alpha \) is much lower at 353 K. Hence, \( \alpha \) increases more sharply between 0 and 5 m at 353 K. As \( \alpha_w \) does not contribute beyond 5 m, and \( \alpha_{sec} \) and \( \alpha_{prim} \) are independent of temperature, the variation of \( \alpha \) with \( m \) beyond 5 m at both temperatures are similar (see also Fig. 6). Thus, \( \alpha_{max} \) and \( \alpha_{lim} \) (limiting value of \( \alpha \) at higher concentration) are nearly the same at both temperatures (curves 1 and 4, Fig. 1, curves 2 and 4, Fig. 6). \( \alpha_{lim} \) represents a situation where water-water interactions are completely absent; a situation envisaged by van Hook$^{15}$ at very high concentrations and described as a completely distorted state of water. At 303 K, \( \alpha \) for LiCl(aq) at 15 m was far from \( \alpha_{lim} \) (curve 2, Fig. 1), whereas at 353 K, \( \alpha \) for LiCl(aq) in 15 m solutions (curves 5, Fig. 1) almost approaches the limiting value due to much lower value of \( \alpha_w \) at this temperature. Besides, as discussed above, the effect of chloride ion on the primary hydration shell of Li$^+$ make \( \alpha_{LiCl(aq)} > \alpha_{aq} \) (resin) in the concentration range 10 m to 15 m.

**NaCl, KCl and CsCl aqueous solutions and Na$^+$, K$^+$ and Cs$^+$ ionic forms of resins**

Plots of \( \alpha \) versus \( m \) for K$^+$ form of the resin, KCl(aq), Cs$^+$-form of the resin and CsCl(aq) at 303 K and 353 K are given in Figs 2 and 3. At 303 K the values of \( \alpha \) for both K$^+$ and Cs$^+$ forms of the resin (curve 1, Fig. 2 and curve 1, Fig. 3, respectively) are lower than \( \alpha_w \) and show steady decrease with increase in \( m \). Limiting value of \( \alpha \) (where \( \alpha \) is independent of \( m \)) is reached at much higher concentrations for K$^+$ (~18 m) (curve 1, Fig. 2) and barely seen for Cs$^+$ (~28 m) (curve 1, Fig. 3). At 353 K, K$^+$ (resin) (curve 4, Fig. 2) and Cs$^+$ (resin) (curve 4, Fig. 3) show a maximum, \( \alpha \) for KCl(aq) (curves 2 and 5, Fig. 2) and CsCl(aq) (curves 2 and 5, Fig. 3) decrease with increase in \( m \) at both 303 K and 353 K with no possibility of a maximum even at the higher temperature. Molecular dynamic simulation studies$^{25}$ show that about 7.8 to 8.0 water molecules are present in the cosphere of K$^+$ and Cs$^+$. At 353 K, the concentration at which maximum is seen in the case of K$^+$ (curve 4, Fig. 2) and Cs$^+$ (curve 4, Fig. 3), 8-9 water molecules are present in the cospheres of K$^+$ and Cs$^+$ and consistent with the values observed in MD simulation studies. \( \alpha_{lim} \) is reached at 20-22 m, corresponding to 2-3 water molecules in the primary hydration shell. From this it can be inferred that the cosphere of K$^+$ and Cs$^+$ at 353 K is composed of distorted H-bonded composite hydration shell containing primary and secondary hydration shell water molecules.

For Na$^+$ form of the resin data are available only at 353 K, \( \alpha \) versus \( m \) plots for NaCl(aq) and Na$^+$ (resin) are given in Fig. 4. A maximum is observed in the \( \alpha \) versus \( m \) plot at 353 K for Na$^+$ (resin) (curve 3, Fig. 4), indicating the existence of a well-defined secondary hydration shell around Na$^+$. The variation of \( \alpha \) vs \( m \) for NaCl(aq) (curve 4, Fig. 4) is similar to that observed in the case of LiCl(aq) (Fig. 1).

The \( \alpha \) versus \( m \) plots at 303 K and 353 K for LiCl(aq), NaCl(aq), KCl(aq) and CsCl(aq) remain more or less constant between 0 and 4 m for all the alkali metal chloride solutions, the data for which are available for all the alkali metal chloride solutions and between 4 and 6 m it decreases for LiCl(aq), NaCl(aq), and CsCl(aq). The data for KCl(aq) at 6 m are not available. The rate of decrease of \( \alpha \) with \( m \) for the different electrolytes (Fig. 5) follow the sequence: CsCl(aq) > NaCl(aq) > LiCl(aq), at 303 K. At 353 K, the slopes are more or less the same for LiCl(aq), NaCl(aq) and CsCl(aq). Hydration shell structure around the alkali metal cation decreases in the series: Li$^+$ > Na$^+$ > K$^+$ > Cs$^+$. Hence, the destructive effect of Cl$^-$ is maximum in the case of LiCl solutions and least in the case of CsCl solu-
Fig. 2—Variation of $\alpha$ with $m$ for $K^+$ (resin) and KCl (aq). 1. $K^+$ (303K); 2. KCl (303K); 3. ($K^+ + Cl^-$) (resin) (303K); 4. $K^+$ (353K); 5. KCl (353K); 6. ($K^+ + Cl^-$) (resin) (353K)

Fig. 3—Variation of $\alpha$ with $m$ for Cs$^+$ (resin) and CsCl (aq) and Cl$^-$ (resin). 1. Cs$^+$ (303K); 2. CsCl (303K); 3. (Cs$^+ + Cl^-$) (resin) (303K); 4. Cs$^+$ (353K); 5. CsCl (353K); 6. (Cs$^+ + Cl^-$) (resin) (353K); 7. Cl$^-$ (353K); 8. Cl$^-$ (353K)
Chloride form of the resin

It is generally recognised that in alkali chloride solutions, hydration of the cations is the most prominent feature in aqueous solutions. Therefore, we have selected CsCl solution to compare with the resin phase data, i.e., single Cl⁻ solutions, as Cs⁺ is known to be the least hydrated amongst the alkali cations.

\( \alpha \) versus \( m \) plots for Cl⁻ form of the resin at 303 K (curve 7) and 353 K (curve 8) are shown in Fig. 3, along with Cs⁺-form of the resin. The values of \( \alpha \) is always lower than \( \alpha_w \) at 303 K (curve 7) and it decreases continuously with increase in concentration and reaches a limiting value at \( -13 \) \( m \), where about 2-3 water molecules are associated with Cl⁻. However, at 353 K, \( \alpha \) increases with concentration showing a maximum at \( -5 \) \( m \) (\( \sim 11 \) water molecules). As discussed in detail elsewhere, in solutions of \( 13 \) \( m \) and above, because of the preferred symmetric orientation of water molecules around Cl⁻ (Cl⁻, -H, -H, O), linear H-bonding is not possible. With increase in the number of water molecules in the system, that is decreasing concentration, the water molecules around Cl⁻ will reorient themselves to form linear H-bonded cluster around Cl⁻. The polarising effect of Cl⁻ causes a slight increase in linear H-bond strength among the water molecules in this cluster compared to the bulk water structure at 353 K, resulting in the observed maximum at \( -5 \) \( m \) concentration in the \( \alpha \) versus \( m \) plot at 353 K (curve 8, Fig. 3). A discussion of solvent isotope effects in electrolyte solutions has led to a general conclusion that the stabilisation of the cosphere of the anion is due to increased hydrogen bonding. However, single ion studies of Cl⁻ (resin) (see above) at very high concentration has shown that the stabilisation of the cosphere occurs by electrostatic interaction. Cl⁻-water interactions are, thus, concentration dependent which determines the orientation of water molecules. In the concentration region where linear H-bonds are formed, temperature plays an important role because of its effect on water structure itself.

A comparison of Cl⁻ data (curves 7 and 8, Fig. 3) with different alkali halide solutions shows that it has some similarities with CsCl solutions or...
single Cs⁺ solutions (Fig. 3). At 303 K, α decreases with m up to 6m as in CsCl or Cs⁺, but the decrease is sharper for Cl⁻ compared to CsCl or Cs⁺. At higher temperature, both Cs⁺ and Cl⁻ show a maximum but the decrease in α beyond 8m is again much sharper for Cl⁻. These features underline the differences between cation and anion hydration. Strengthening of hydrogen bonded structure of water occurs in the secondary hydration shells of cations and in the primary hydration shell of the anion. At 303 K, Cl⁻, K⁺ and Cs⁺ emerge as structure breakers as generally understood.

Effect of temperature on the structure of the hydration shell around alkali metal ions

The above discussions show that VPIE studies provide valuable information about the stabilities of primary and secondary hydration shells. The appearance of maximum in α versus m plots is a clear evidence for the existence of a stable secondary hydration shell arising from very strong cation-water interactions in the primary hydration shell. In VPIE both water-water and cation-water interactions play important roles. Cation-water interactions are temperature independent, but the water-water interactions are strongly temperature dependent. Thus, VPIE seems to be temperature dependent. Hydration shells are formed at the expense of water structure. At lower temperatures where H-bonded water structure is very stable (high α), only strong cation-water interactions can lead to stable hydration shells. Thus, stronger the cation-water interaction, the lower would be the temperature where secondary hydration shell will be stable and maximum observed in α versus m plots. For example, for Li⁺ resin maximum is observed at 303 K (Fig. 1), for K⁺ at 333 K (Fig. 8) and for Cs⁺ at 353 K (Fig. 3).

ε₁ and ε₂ are independent of temperature and N₁ (ref. 36) and N₂ (refs 12, 13) vary very slightly with temperature (where N₁ and N₂ are the number of water molecules in primary and secondary hydration shells). ε’s and N’s for various alkali metal cations have been reported. ε₁ is strongly temperature dependent and its values in the temperature range 273 K to 373 K are available. Using these values, α versus m curves for Li⁺, Na⁺, K⁺ or Cs⁺ in resin phase at any temperature, can be computed, using the appropriate value of ε₁ at that temperature (and using Eq. (22)).

α versus m plots for different alkali metal ions are not available at the following temperatures: Li⁺ (293 K); Na⁺ (303 K, 313 K, 318 K); K⁺ (323 K). Accordingly, they have been computed as described above, and are given in Figs 6 to 9. From these plots, it can be seen that the temperatures at which the maximum in α versus m plots for various alkali metal ions appear at the following sequence: Li⁺ (303 K) < Na⁺ (318 K) < K⁺ (333 K) < Cs⁺ (353 K). The appearance of maximum in the α versus m plots at progressively higher temperatures as one goes from Li⁺ to Cs⁺, indicates the relative strengths of hydration shells around the alkali metal ions, which decrease with increase in ionic radii, that is, from Li⁺ to Cs⁺. As the cation size increases, the secondary hydration shells are stabilised at increasingly higher temperatures (greater the temperature, the weaker is the bulk water structure).

Computation of VPIE of aqueous electrolyte solutions from corresponding single ion data

It is clear from the above discussions that the features of the hydration model of ions and their consequences on the VPIE are faithfully reproduced in the VPIE of single ion solutions (resin phase studies). The absence of these features in VPIE of electrolyte solution has been qualitatively attributed to the cosphere interactions (for example, in LiCl solutions of more than 2m concentration). Theoretically VPIE in an hypothetical electrolyte solution, where cosphere interactions are absent, can be computed from VPIE of single ion solutions using Eq. (20). VPIE computed for such LiCl, NaCl, KCl and CsCl solutions at 303 K and 353 K have been plotted in Figs 1 to 4.

Upto 4m, there is a good agreement between [Li⁺ + Cl⁻] and LiCl(aq) values of VPIE (curves 2 and 3, Fig. 1) indicating that the cosphere interactions are absent up to this concentration. Further, the absence of maximum in VPIE for LiCl (aq) (m > 3) at 303 K is due to the contribution to overall α from water molecules in various water sub-systems. The values of VPIE computed for 2m solutions of (Na⁺ + Cl⁻), (K⁺ + Cl⁻) and (Cs⁺ + Cl⁻) (curves 2, Fig. 4, curve 3 in Figs 2 and 3, respectively) are also in good agreement with the corresponding MCl values at 303 K.

However, at higher concentrations, VPIE values for all MCl solutions (curves 2 in Figs 2, 3 and curve 1 in Fig. 4) are higher than (M⁺ + Cl⁻) values and the difference increases with increase in concentration up to 6m, the concentration upto which data for all MCl solutions are available. In LiCl solutions (Fig. 1), the difference between LiCl (curve 2, Fig. 1) and (Li⁺ + Cl⁻) (curve 3, Fig. 1) increases up to 10m and then seems to decrease. It implies that between 5m and 10m,
where secondary hydration shell of Li⁺ is being progressively depleted, the presence of chloride ions instead of destroying the hydration shell structure by cation-anion cosphere interactions, is actually stabilising the water structure. This can arise by sharing of water molecules between the hydration shells of lithium and chloride ions. In a recent NDIS study of 10 m LiCl solution, this sharing of water molecules between chloride and lithium ions has been directly observed. The same is true for NaCl, KCl and CsCl solutions at 303 K. The stabilisation of water structure in MCI solutions by chloride ions decrease in the order: LiCl > NaCl > KCl > CsCl.

Fig. 6 — Variation of \( \alpha \) with \( m \) for Li⁺ (resin)
1. 293K (computed); 2. 303K; 3. 333K; 4. 353K

Fig. 7 — Variation of \( \alpha \) with \( m \) for Na⁺ (resin)
1. 303K (computed); 2. 318K (computed); 3. 353K

Fig. 8 — Variation of \( \alpha \) with \( m \) for K⁺ (resin)
1. 303K; 2. 323K (computed); 3. 333K; 4. 353K

Fig. 9 — Variation of \( \alpha \) with \( m \) for Cs⁺ (resin)
1. 303K; 2. 333K; 3. 353K.
The data for \((M^+ + Cl^-)\) and MCI solutions at 353 K show opposite trends (compared to 303 K) at concentrations above 2\(m\). VPIE values for \((M^+ + Cl^-)\) are higher than MCI values at 353 K (Figs 1 to 4). At this temperature all the cations possess secondary hydration shell as indicated by the maximum in VPIE plots for single ions (curves 4, in Figs 1 to 3 and curve 3 in Fig. 4 for Na\(^+\) and curve 8, in Fig. 3 for Cl\(^-\)). As the sharpness of the maximum in these plots follow the sequence: \(Li^+ > Na^+ > K^+ > Cs^+\), the difference between \((M^+ + Cl^-)\) and MCI solutions (curve 5 and 6 in Figs 1 to 3, curves 4 and 5 in Fig. 4) also decreases in the same sequence. \((Li^+ + Cl^-)\) data at 353 K (curve 6, Fig. 1), do show a maximum at \(\sim 5m\) (which is absent in LiCl(aq) data, [curve 5, Fig. 1]), and at very high concentration \((>10m)\), as at 303 K, \((Li^+ + Cl^-)\) data are lower than LiCl(aq) data.

Because of the relatively greater stability of hydration shells at higher temperatures compared to bulk water, the anion cosphere-cation cosphere interactions are destructive in the concentration region where secondary hydration shell is being depleted. However, at higher concentrations cation cosphere-anion cosphere interactions are constructive even at higher temperatures.

Anion cosphere-cation cosphere interactions appear to be constructive when the water structure is stronger than the hydration shell structure (that is, at lower temperature) and destructive when hydration shell structure is stronger than the water structure (that is, at higher temperature), and at intermediate concentrations where secondary hydration shells can exist.

In conclusion, the present study has shown that, the threed water sub-system model for cation hydration and two water sub-system model for anion hydration are contributing proportionately to the properties of aqueous electrolyte solutions. Further, the study has established that all the alkali metal cations behave as structure makers at some temperature. The greater the hydration of the cation, the lower is the temperature at which it behaves as structure maker. Thus, the structure making properties of Li\(^+\) appear at 303 K and above, whereas Cs\(^+\) behave as structure maker beyond 353 K only. The presence of chloride anion in alkali halide solutions produces interesting effects in VPIE. The variation of \(\alpha\) in all MCI solutions at different temperatures are very different from single cation or single anion solutions. These differences in MCI and single ion solutions can be fully accounted for either in terms of the varying contributions of different water sub-systems to the overall effect or cosphere-cosphere interactions. At low temperatures, where the cation as well as halide ion are structure breakers, a stabilising effect of the cation cosphere-anion cosphere interaction on the water structure is seen: \(\alpha(M^+ + Cl^-) < \alpha(MCl)\). At higher temperatures, where cations and chloride ions are structure makers, cosphere interactions produce a destructive effect on the water structure, in the concentration region where secondary hydration shells exist: \(\alpha(M^+ + Cl^-) > \alpha(MCl)\). This obviously is due to the different ways in which cations and anions form their hydration shells.

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