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Ion – water interaction: Effects and consequences

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ABSTRACT

The continuum electrostatic model proposed by Debye and Huckel and successive studies was based on the assumption that interactions centering ions are strictly electrostatic in nature involving long range forces. The idea underwent a change with the advent of solution neutron and X-ray diffraction technique. Such investigations showed that ions do not significantly affect water molecules beyond 5Å, thus paving way for short range forces of chemical nature. More recently, several theoretical models have been proposed to supplement experimental findings.

KEYWORDS: Ions, hydration (water), Hofmeister series, chaotropes, kosmotropes

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1. INTRODUCTION

An understanding of the forces that govern ion – water interactions is of fundamental importance in aqueous, biological and environmental chemistry. It is widely believed that addition of salts to water introduces structural changes in the H-bonded network well beyond the adjacent shell of solvent molecules. Research on the influence of ions on long–range structure of hydrogen-bonded network of water[1,2] has enhanced our knowledge of how ion – water interactions give rise to bulk properties. In order to systemize the way ions affect the H-bonds in the aqueous bulk, the concept of structure making and structure breaking ions has been introduced.[3,4]The difference in their ability to enhance or disrupt the water H-bond network generally follow the renowned Hofmeister series,[5,6] originally framed to arrange the order of ions that precipitate out proteins in solution.A more elaborate description of the structural and dynamic interaction between solutes and water will help in better understanding of the main driving forces responsible for formation of electric double layer at interfaces, selective ion adsorption and separation, diffusion through solutions and membranes, protein denaturation or transport through ion channels in biological systems.

The first notable cornerstone in this field was the continuum electrostatic model of Debye and Huckel[7] that used macroscopic dielectric constant and was based on the assumption that interactions involving ions are electrostatic in nature. Addition of water to electrolytes led to their dissociation into component ions. This propelled the idea of presence of long-range electric fields in electrolyte solutions. Ions are considered as point charges, in this model, and the dipolar water molecule rearranges itselfin the long range electric field. This clearly implies of a difference between the structures of water around the ions to that of bulk water. The limitation of the model was in its neglect of finite ion size effects and prediction of all ions to be strongly hydrated. Later studies show the existence of weakly hydrated ions, such as ammonium, potassium, chloride and positively charged amino acid side chains that adsorb to non-polar surfaces and interface.[6,8-11]Sophisticated microscopic calculations have suggested that the polarisability of weakly hydrated ions and dispersion forces[12-14] may possibly be responsible for such surface interactions. The role of the polarisability of water molecule in driving the poorly hydrated chloride ion to neutral air/water interface[12,13,15] has also been indicated by such studies.It becomes difficult to draw a conclusion from such calculations, since “polarisability appears to be important primarily for its role in facilitating a larger average dipole moment on the water model”[15] and the Cl^- - H_2O interaction is mediated by an approximately linear H-bond rather than ion-dipole attraction.[16-18]

This article reviews the results of experimental and theoretical investigation on how ions interact with water molecules upon solvation. The work also briefs on the properties of water that poses a striking difference to other solvents and leads to its unique nature.

2. WATER STRUCTURE

The extensive hydrogen bonded network is generally accepted as the reason behind the remarkable structure of water. The average number of H-bonds per H_2O molecule present in the liquid is a useful measure of this extent.This may also provide an answer to the question of how the water structure is affected by the ions. The regular tetrahedral ice structure involving four hydrogen bonds around a molecule of water is disrupted in the molten state is known. The average co-ordination number of a cold liquid water molecule is supposed to be greater than four, suggestive of so-called interstitial molecules that are not typically H-bonded. There arises a need to define an “intact” hydrogen bond being distinct from “hydrogen bonded interstitial water”. This has been discussed in recent times by Xenideset al[19] and Kumar et al[20] among others, and has been addressed considering geometrical and energy aspects.Xenides et al[19] specified the O-O distance between adjacent water molecules in the range 2.5 Å – 3.5 Å, the hydrogen bonded O···H distance between 1.5 Å – 2.5 Å, and the O-H···Oangle,θ, to be $\geq 100°$. Kumar et al[20] have been, however, more restrictive, with O···H distance ≤ 2.41 Å and $\theta \geq 130°$. The interaction energy between the H-bonded water molecules has been suggested to be more negative than - 12.9 kJ mol^{-1}.Such conditions may be applicable to computer simulations referenced by Kumar et al but not to studies by experimental diffraction.

Ab initio quantum calculations and molecular dynamic computations[19] have shown the number of H-bonds per H_2O molecule to be 2.8 at 298 – 300 K, or in the range 3.2 – 3.4 from molecular dynamic computations employing SPC/E water,[20] taking into account the above criteria.According to Walrafen,[21] the difference of hydrogen bond energy dispersion between “strong” and “weak” H-bonds was obtained from the Raman intensities of the O – D stretching vibration in dilute HOD in H_2O. At a given wave number v_j, the energy obtained from the intensity I_j is defined as $E_j = -R[\delta \ln I_j / \delta(1/T)]_P$. Energy difference of 21.3 ± 2.1 kJ (mol hydrogen bonds)$^{-1}$ has been found between “strong”, short and linear H-bonds at v_j = 2440 cm-1 (typical of 1 da ice at 4 K) and “weak”, long and bent H-bondsat v_j 2650 – 2675 cm-1 (characteristic of supercritical HDO in H_2O at 0.9 g cm^{-1} and 673K).

3.DISTANCE OVER WHICH IONS INFLUENCE WATER

Different resonance techniques, *viz.* fluorescence resonance energy transfer, have shown that simple ions in water generate long-range (~ 30 Å or even more) electric fields.[22] It is based on the assumption that long-range electric fields are generated by such ions which are strong enough to orient water dipoles over large distances. However, recent spectroscopic and theoretical investigations have raised a question on such long-range effect of ions on the bulk water network. Neutron and X-ray diffraction,[23,24] Raman[25] and THz[26] spectroscopic studies and molecular dynamics (MD) simulations[25-31] (that have primarily concentrated on alkali halides) have led to the observation that only water molecules in the first hydration shell are perturbed by the weakly coordinated ions. The bulk water remains essentially unaffected. Infra-red studies[32,33] of large gas-phase water clusters, on the contrary, indicate that high-valent ions affect the hydrogen bonded network even beyond the first shell of salvation.

3.1 Effect of simple monovalent cations

From neutron and X-ray diffraction of Group-I ions Li^+, Na^+, K^+ and of water,[34]it is evident that with the decrease in surface charge density of the ions from Li^+ to Na^+ to K^+, the nearest water oxygen density peak is lowered and shifted away, indicative of weaker binding.The Na^+ – oxygen distance is shorter than O – O distance of pure water, denoting strong hydration of sodium ion. On the other hand, K^+ – oxygen distance is longer than O – O distance of pure water pointing to weak hydration for potassium ion. Surface charge density between that of Na^+ and K^+ is exactly where the Jones – Dole viscosity *B* co-efficient (a measure of water affinity) changes sign, suggestive of the strength of H_2O – H_2O interaction. Thus, a chaotrope (like K^+)is weakly hydrated, the nearest neighboring water molecule is distant and not oriented. The H_2O molecule immediately adjacent to a chaotropeis tumbling more rapidly (like that of an unbound water molecule) than that in the bulk, has been shown by NMR studies.[35]Lithium ion is supposedly surrounded by 0.6 tightly held H_2O molecules, sodium ion by 0.25 strongly bound H_2O molecules while potassium ion has none, suggested by gel sieving chromatography on Sephadex G-10.[36] Thus solution neutron and X-ray diffraction together with gel sieving chromatography indicate that the primary influence of ions on water is short range and only tightly bound water molecules are oriented. This technique also showed that H^+ ion (at 0.1 M) has 1.9 tightly held water and exists as dehydrate, and OH^- ion exist as trihydrate with 2.8 strongly bound water molecules.

Neutron and X-ray scattering study on 2 and 5 mol dm^{-3} aqueous solution of RbBr[37]point to poorer hydrogen bonding in the salt solution compared to neat water, indicative of the “structure breaking” nature of the salt. The number of H_2O molecules in the hydration shell of Rb^+ ion is 6 – 8[38] while that of Br^- ion is unavailable.[4] X-ray diffraction study of LiCl and NaCl solution by Bouazizi et al[39,40] show that the effect of the salt on O – O distance of water are evident from concentrations of 1.5 m solutions. Results of MD simulations[40] also showed that the hydration number around the cationdecrease with increase in salt concentrations, that is attributed to the probable substitution of some H_2O molecules in the first hydration shell by chlorine. Novikov et al[41] have thrown light on the diffusion mobility of water molecules following quasi-inelastic neutron scattering measurements carried out on 2.14 M LiCl and CsCl solutions. The results showed that diffusion ability is hampered around Li^+ ion while it is enhanced in the vicinity of Cs^+ ions in comparison to water in the bulk. However, no information could be gathered about the hydration shell beyond the four tetrahedrally co-ordinated H_2O molecules around Li^+ ion and eight H_2O molecules co-ordinated to Cs^+ ion.

Soper et al[23,42,43] undertook neutron diffraction investigations with isotope substitution (NDIS) together with computer simulation to interpret the diffraction data. It was found that the H_2O molecules in the first hydration shell of K^+ were oriented in a more disordered manner than those hydrating a Na^+ ion. Cl- ions instead formed H-bonded bridges with H_2O molecules and were readily accommodated into the H-bond network of water.[23]The O – O distance varied from 4.4 Å in pure water to 4.0 Å, primarily for the most concentrated (2.66 m) KI solution. The deviation of O – O – O angle distribution of neighboring H_2O molecules from that in pure water, was prominently seen in the 2.66 m concentrated solution of KF. The observations led to the possibility of a second hydration shell, with ions (except fluoride ion) perturbing the water molecules from the general tetrahedral orientation adopted in aqueous bulk water. Such distortion of H_2O structure was also supported by subsequent studies[42] and similar observations were reported with 1.38 and 3.27 m KCl solution. The O – O distance further shifted to ~ 3.4 Å in 3.27 m NaCl solution. A first hydration shell of 3.7 ± 0.3 water molecules around hydroxide ion was observed in NDIS study of 4.6 M NaOH solution.[44]However, these results do not significantly enhance the knowledge on the concept of structure making or breaking properties of anions.

Computer simulations have provided an important tool in the study of ion hydration. Elaborate and comparative discussion of merits of the computational methods employed is beyond the scope of this review. Results of semiempirical methods vary depending on the choice of different levels of theory and basis sets. An average hydration number n of 4.1 for Li^+ with Li^+ - O distance of 1.94 Å were reported by Tongraar et al.[45] They also depicted $n = 6.0$ and Li^+ - O 2.06 Å using only molecular dynamics with CF2 potential for water. Loeffler and Rode[46]later attested tetrahedral coordination of Li^+ ion by water and found polarisedH_2O molecules having longer O – H bonds. Studies of hydration of Na^+ and K^+ ions revealed $n = 5.6 \pm 0.3$ and 8.3 ± 0.3 for sodium and potassium ions respectively.[47] Na^+ - O distance of 2.33 Åand K^+ - O of 2.81 Å were found above.White et al[48]found average $n = 5.2 \pm 0.6$ and Na^+ - O distance of 2.33 Å at lower concentration (1.05 m) and higher temperature of 31°C. Computations on hydration of Cs^+ ion observed $n = 8.9 \pm 0.6$ and Cs^+ - O distance 3.22 Å.[49]

The results of large scale X-ray scattering (LAXS) at room temperature of sodium, potassium and caesium iodide in aqueous solution show that the Na^+, K^+ and Cs^+ions are all weakly hydrated with only a single hydration shell. The Na-O, K-O and Cs-O bond distances obtained are 2.43, 2.80 and 3.07 Å respectively, which support six, seven and eight-co ordinations respectively. The radial distribution functions obtained from the experiments also reveal an I-O bond distance of 3.5 Å in the hydrated iodide ion, and an intermolecular O····O distance of 2.9 Å in the aqueous bulk. The smaller Li^+ion is comparatively strongly hydrated,as is evident from double difference infrared spectroscopy (DDIR). The affected spectra of $LiClO_4$ and $NaClO_4$ point to a second sphere of hydration for Li^+ but not for Na^+. It has been concluded that the effect of heavier alkali metal ions on the structure of bulk water was too weak to make them spectroscopic ally distinguishable.[50]

$LiI(H_2O)_n$ and $CsI(H_2O)_n$ have been used as representatives to investigate microsolvation of ion-pairs employing integrated tempering sampling, molecular dynamics (MD) combined with quantum mechanical (QM) calculations.[51] The interaction of Li^+-I^- and Cs^+-I^- ion pairs with water molecules have been found to be different. Hydrogen bond, in this study, is considered, if O····O distance is less than 3.5 Å and O-H-O angle is greater than 120°. The average H-bond length and angle is 2.868 Å and 163.7° respectively in $(H_2O)_{20}$ cluster. It is evident from the results that addition of Li^+-I^- and Cs^+-I^- changes the average hydrogen bond lengths and angles. Li^+ and I^- ions shortens the average water-water H-bond distance (2.778 Å) and enlarges the <O-H-O (169.05°), in comparison to pure water cluster. On the contrary, Cs^+ and I^- ionsdo not have a significant effect on the O-H-O angle (164.8°) while causing slightly shortening of hydrogen bond (2.784 Å). Thus, it shows that LiI has a stronger capability of increasing the individual H_2O-H_2O interactions, with $LiI(H_2O)_n$ (n>5) clusters building up on a $Li^+(H_2O)_4$ motif. CsI only slightly perturbs the water cluster structure, and $CsI(H_2O)_n$favoursclathrate like network when n = 18 or 20.

Chen and Ruckenstein[52] employed molecular dynamics simulation using the nanoscale molecular dynamics program to calculate the hydration number of ions. They examined the electrolyte solutions of NaCl and KCl and evaluated the hydration numbers of individual ion both by the above procedure and the radial distribution function.The hydration number of Na^+ was found to be 5.4 ± 0.1 for both methods and is almost insensitive to electrolyte concentration.The hydration numbers for individual Cl^- ranged from 7.1 – 7.3. For KCl solution, hydration number of K^+ decreases from 6.8 to 6.3 as electrolyte concentration increasesfrom 0.1 mol/L to 1.0 mol/L. However, the hydration number of Cl^- remains approximately constant at 7.3 with increase in electrolyte concentration. They deciphered that introduction of an individual ion into the bulk water resulted in rupture of some H-bonds between the water molecules leading to the reorientation of H_2O molecules around the ions. The hydrogen bonding numbers of water of the first shell of hydration of individual K^+ ion is greater than that of Cl^- ion. This is because of the orientation of H_2O around the ions. The water molecules adjacent to K^+ behave as donors, in contrast those around Cl^- act as acceptors. Similar behavior has been observed in case of NaCl solutions. Thus, they have concluded that the hydrongen bonding numbers of H_2O of the first hydration shell of individual ions are sensitive to the nature of the ions but are insensitive to electrolyte concentration.

3.2Ions of high charge density

It has been established that the chaotrope Cl^- is weakly hydrated with virtually no tightly bound H_2O molecule from gel sieving chromatography,[36] in contrast to F^- that has five strongly bound waters. Four of such tightly bound water molecules are present in the first layer of hydration[53] and one in the second hydration shell of F^-, as indicated by gas phase vibrational predissociation spectroscopic study.

Study of hydration of ions using MD simulation[54] with SPC/E point charge model of H_2O revealed coordination number *n* of 6, 7, 8 and 8 for F^-, Cl^-, Br^-, and I^- respectively. Du et al[55] followed a similar line of investigation with concentration ranging from 0.22 M – 3.97 M. Variation on the effect of hydration of Cl^- ion with change in the corresponding cation (LiCl and RbCl) was observed. For chloride ion, *n* decreased from ~7.4 to ~5.3 with increase in concentration of RbCl. The coordination number of iodide in CsI pursued a similar trend from ~7.6 to ~5.7 in the said concentration limits. The average number of H_2O molecules occupying the first shell of a water molecule rises from 4.51 at zero salt concentration to ~6.2 in 3.97 M LiCl solution, but drops to ~3.8 in concentrated RbCl and CsI solutions.

Kemp and Gordon[56] studied the solvation of F^- and Cl^- ions by water applying effective fragment potentials (EFPs) for H_2O molecules and ab initio quantum mechanics for the anions. The EFP, HF and MP2 calculations predicted that 15 and 18 water molecules are required for "complete solvation" of F^- and Cl^- ions respectively. An ion being fully surrounded by H_2O molecules has been termed as completely solvated. Total and differential binding energies were investigated for all three levels of theory and results depicted correct qualitative trend.

Wang et al[57] followed a similar line of computation and analyzed the stabilization energies and ionic H-bonded structures of $X^-(H_2O)_n$clusters (X = F, Cl; n = 1 – 4) by employing semi-empirical methods. The outcome was compared with ab initio and DFT calculations. The ionic hydrogen bond strength of the clusters tended to be weaker with increase in the number of H_2O molecules. The ionic H-bond in fluoride cluster was found to be stronger than in chloride cluster of similar geometry. In addition, a second hydration shell was predicted for $Cl^-(H_2O)_4$cluster.

4. DEFINING AN ABBREVIATED HOFMEISTER SERIES

The alkali metal ions (along with hydrogen ion) and the halide ions comprise an abbreviated Hofmeister series and each may be classified into strongly hydrated species characterized by small size, high surface charge density; and weakly hydrated ones with large size and low surface charge density; relative to the strength of H_2O - H_2O interaction. kosmotropes H^+, Li^+, Na^+ // K^+, Rb^+, Cs^+ chaotropes (strongly hydrated) F^- // Cl^- , Br^- ,I^- (weakly hydrated)

where //denotes the strength of H_2O - H_2O interaction, the point at which the sign of the Jones-Dole viscosity coefficient *B* undergoes change.[58] NH_4^+ ion shows hydration characteristics similar to that of K^+.[58,59]

5. EVIDENCE – EFFECT OF IONS ON WATER STRUCTURE

The relation of the influence of ions on water structure to the viscosity coefficient *B* and the terms “structure making” and “structure breaking” emerging from this relation are ascribed to Gurney,[3] though Cox and Wolfenden[60] were the first to mention the structure of water in this connection. The coefficient *B* of the dynamic viscosity, η, of an electrolyte solution is derived from the Jones-Dole expression.[61] Some aqueous electrolytes increase the viscosity relative to pure water was observed much before Gurney.[3]

The strength of hydration was considered on the basis of the rate of exchange of water molecules between the hydration sphere of ions and bulk water.[62]Chloride ion is known to be weakly hydrated for coordinated H_2O molecules exchange on a timescale of less than 10^{-11} s, in addition, it has a negative Jones-Dole viscosity *B* coefficient. However, solution neutron diffraction studies by isotopic substitution technique depicted approximately well defined geometry of six watermolecules coordinated to the ion. Each H_2O molecule is linked to the Cl^- ion by an apparently linear H-bond, reflecting a primarily chemical interaction (a dipolar interaction would have an angle of ~52°, i.e. half of < H-O-H of 104.5° in water).[16] This is supported by ab initio calculations of halide – water binary or cluster compounds.[63]

The covalent character of hydrogen bond increases with increase in charge density and proton affinity of anions. Though electrostatic interactions is predominantly responsible for the classical H-bond, there is significant covalent character in strong hydrongen bonding and a dominant dispersive interaction in weak hydrogen bonding.[64,65]Avibrationally mediated redistribution of charge takes place within the anion - H_2O complex. The anion in a binary complex shows an increasing tendency to “pry apart” the H_2O molecule in the sequence $I^- < Br^- < Cl^- < O^- < OH^-$.Such results consolidate the notion of chemical nature ion – water interactions.

Dielectric relaxation spectroscopy was used to study the ion association in aqueous solution by Buchner et al.[66-71]The results pertained to the reorientation times of the H_2O molecules. The decrease in cooperative reorientation time ofbulk water with increase in salt concentration was indicative of the weakening of the H-bonded network of water. Studies of LiCl and Li_2SO_4 solutions[70]showed the predominance of the structure breaking effects of the anions over the structure breaking effect of the cation.

Water molecules are strongly bound to small ions of high charge density (kosmotropes) and are apparently immobilized. On the other hand, large monovalent ions of low charge density (chaotropes) "free up" adjacent H_2O molecules giving more mobility than in bulk water. F^-ion is strongly hydratedand K^+ ion is relatively weakly hydrated, though both ions are of comparable size. This may be explained on the basis of the tendency of the electronegative oxygen atom of H_2O to accept the negative charge transfer from fluoride ion. In contrast, positive charge transfer from potassium ion to H_2O is not as facile. In addition, cations interact with oxygen atom of H_2O but anions bind with the hydrogen atom of water, thus facilitating intra-shell H-bonding of H_2O molecules. This is also instrumental in stronger hydration of anions.[72]

Li et al[73] studied the H-bonded structure of water in aqueous solutions of sodium halides at different temperatures through Raman spectroscopy. The O–H stretching vibration was resolved to five Gaussians at 3051, 3233, 3393, 3511 and 3628 cm^{-1}. The two higher wavenumbers were assigned to H_2O molecules having less than three hydrogen bonds, while the three lower values corresponding to water molecules with ice-like four intact H-bonds, keeping in view the temperature dependence for pure water between 0 – 100°C. It was also observed that F^- ion does not have an appreciable effect on the Raman spectrum (at 20°C), but Cl^-, Br^- and I^- ions do so in an increasing manner towards further disruption of ice-like H-bonding.

FTIR spectroscopy was used by Nickolov and Miller[74]to investigate the influence of KF, CsF, NaI, KI and CsCl on the structure of water. They analyzed the O – D stretching vibration in 8% (mass) HOD in H_2O and projected breaking of H_2O structure from narrowing of bands and shifting of peaks to higher wavenumbers. Structure making effect was inferred from opposite trends. Appreciable salt concentration was however necessary for observation of such effects, with water to salt ratio optimally < 20. The two fluoride salts were possible structure makers while the remaining were structure breakers among the five salts under consideration, with effects of cation and anion compensating each other to some extent.

The assumption of the relation of the O – H stretching frequencies to the extent of H-bonding was challenged in paperpublished subsequently.[25] It proposed the difference in the spectra of electrolyte solutions to that of water to be primarily arising from electric fields of ions rather than reorientation of H-bonds beyond the first shell of hydration, following studies on 1M potassium halide solutions with 14 mol% HOD in D_2O. Monte Carlo computer simulations on a halide ion with 107 rigid H_2O molecules further attested these results. It has been suggested that the statistics of H-bond strengths are modified only weakly beyond the first salvation shell.

The dynamics of particles in aqueous solution of electrolytes have also been examined by applying molecular dynamics computer simulations.[75]Geiger reported the ratio of H_2O in the first shell of hydration, $D_{w\text{first shell}}/ D_{w\text{bulk}}$, to be greater than unity (upto 1.6 and 1.2 for ions of +0.67 and +1 charge units respectively).This ratio was found to be 1.4 for anions. The effect diminished in the second hydration shell. Other groups[76-78] employed different models to study reorientation times of water molecules, the results varied with the method used.

Different thermodynamic properties of aqueous solution of electrolytes have been utilized for the deduction of the influence of constituent ions on water structure. Corey[79] noted a correlation with the corresponding partial molar volume of H_2O in the study of adiabatic compressibility of salt solutions. He came to the conclusion that in presence of ions the liquid structure of H_2O turned more compact and coordinated.The study of the effect of ions on structure of water from the entropies of hydration applying other methods[80,81] have been reviewed earlier.[82]

6. DOMINENT FORCES ON IONS IN WATER

There is a tendency for oppositely charged ions having equal water affinity to come together in solution to form contact ion pairs. On the other hand, oppositely charged ions having varying water affinities tend to stay apart. The release of heat may be attributed to the formation of strong bonds and uptake of heat to the disruption of such strong bonds. It has been assumed that the strongest interactions in the system tend to govern the overall behavior of the system. The interactions in aqueous salt solutions of kosmotropes (small ions of high surface charge density that are strongly hydrated) and chaotropes (large ions of low surface charge density that are feebly hydrated) depict the following sequence of decreasing strength: kosmotrope – kosmotrope>kosmotrope – H_2O > H_2O – H_2O >chaotrope – H_2O >chaotrope – chaotrope.[58,83] For the standard heat of solution of a alkali halide to be negative; i.e. exothermic, it is a necessary but not a sufficient conditionfor one ion to be a chaotrope and the other to be a kosmotrope. Such salts on dissolution may undergo extensive dissociation, with the kosmotrope component having strong interactions with H_2O in solution than it has with the chaotrope in the crystalline salt, thus tending to evolve heat. The component ions of alkali halides constituted of two kosmotropes, in contrast, tend to stay together in aqueous solution, thus absorbing heat to break the strong kosmotrope – kosmotropebond. On dissolution of chaotrope – chaotrope alkali halides, the ion pairs stay together under the influence of strong H_2O–H_2O interactions, leading to heat intake for disruption of the relatively strong H_2O – H_2O linkage. It may be suggested from the preceding observation that oppositely charged ions having equal water affinity tend to remain as contact ion pairs in solution and those with differing water affinity tend to remain at a distance.[58,59,83]

This "Law of Matching Water Affinities" has important consequences in biology and chemistry.Thus the relative ease of hydration and dehydration of Na^+ and K^+ ions plays a major role in their passage across membranes. The role of contact ion pairing of anions with sodium and potassium ions has also been considered in biological discrimination between them.[84]The cause of influence of anions on the pH of buffers used in biochemical studies is suggested as being indirectly related to their hydration properties and may be somewhat responsible for enzymatic effects.[85,86]These results have raised questions on the effect of kosmotropic and chaotropic ions on ionic H_2O structure having a major role in biological processes. Other factors, direct hydration and dehydration, ion pairing, hydrophobic interactions, may possibly play a significant role.

7. CONCLUSION

The present work tries to gather the information available from the studies carried out in the past few decades in the field of ion – water interaction. It is not claimed that all relevant research has been included in its considerations. In conclusion, it may be said that the dominant forces exerted by ions on water are necessarily short range ones of chemical nature. The long range electric fields generated by simple ions in aqueous solution are relatively weak considering the strength of H_2O - H_2O interactions. The H_2O molecules incorporated in the first shell of hydration around ions are not engaged in H-bonding, with reference to the extent, geometry and dynamics that is prevalent in pure water.[4]Ultrafast spectroscopy[87] has cast some doubt regarding the effect of ions on the reorientation dynamics.The effects of ions on macroscopic water structure derived from dynamic studies (like viscosity, NMR relaxation) and thermodynamic studies (like entropy of hydration) are relevant to infinite dilution. Therefore, the H_2O outside the hydration shells are taken into account. Thus the structure breaking role of some large univalent ions depicted from such observations cannot be ignored.Future studies will further help in understanding the role of ions in structure making and structure breaking of water and also its subsequent consequences in chemical and biological fields.

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8. REFERENCES

1. Tobias DJ, Hemminger JC. Chemistry. Getting specific about specific ion effects.Science.2008; 319: 1197 – 1198.

2. Chen Y, Okur HI, Gomopoulos N et al. Electrolytes induce long-range orientational order and free energy changes in the H-bond network of bulk water. Sci. Adv. 2016; 2: e1501891.
3. Gurney RW. Ionic Processes in Solution. McGraw – Hill: New York; 1953.
4. Ohtaki H,Radnai T. Structure and dynamics of hydrated ions. Chem. Rev. 1993; 93: 1157 – 1204.
5. Hofmeister F. On the understanding of the effect of salts.Second report.On regularities in the precipitating effect of salts and their relationship to their physiological behavior.Naunyn-Schmiedebergs Arch. Exp. Pathol.Pharmakol.1888; 24: 247 – 260.
6. Collins KD, Washabaugh MW. The Hoffmeister effect and the behavior of water at interfaces.1985; 18: 323 – 422.
7. Debye P, Huckel E. On the theory of electrolytes. I. Freezing point depression and related phenomena. Phys. Z. 1923; 24: 185 – 206.
8. Washabaugh MW, Collins KD. The systematic characterization by aqueous column chromatography of solutes which affect protein stability.J. Biol. Chem. 1986; 261: 12477 – 12485.
9. Collins KD. Sticky ions in biological systems. Proc. Natl. Acad. Sci. USA. 1995; 92: 5553 – 5557.
10. Gopalakrishnan S, Liu D, Allen HC et al. Vibrational spectroscopic studies of aqueous interfaces: salts, acids, bases, and nanodrops. Chem. Rev. 2006; 106: 1155 – 1175.
11. Petersen PB, Saykally. On the nature of ions at the liquid water surface. Annu. Rev. Phys. Chem. 2006; 57: 333 – 364.
12. Vrbka L, Mucha M, MinofarB et al. Propensity of soft ions for the air/water interface. Curr.Opin.Colloid.2004; 9: 67 – 73.
13. Jungwirth P, Tobias DJ. Specific ion effects at the air/water interface. Chem. Rev. 2006; 106: 1259 – 1281.
14. Bostrom M, Tavares FW, Ninham BW et al. Effect of salt identity on the phase diagram for a globular protein in aqueous electrolyte solution. J. Phys. Chem. B. 2006; 110: 24757 – 24760.
15. Stuart SJ, Berne BJ.Effects of polarisability on the hydration of the chloride ion.J. Phys. Chem. 1996; 100: 11934 – 11943.
16. Powell DH, Barnes AC, Enderby JE et al. The hydration structure around chloride ions in aqueous solution. Faraday Discuss. 1988; 137 – 146.
17. Robertson WH, Johnson MA. Molecular aspects of halide ion hydration: the cluster approach. Annu.Rev. Phys. Chem. 2003; 54: 173 – 213.

18. Roscioli JR, Diken EG, Johnson MA et al. Prying apart a water molecule with anionic hydrogen bonding: a comparative spectroscopic study of the X – H_2O (X = OH, O, F, Cl and Br) binary complexes in the 600 – 3800 cm (-1) region. J. Phys. Chem. A. 2006; 110: 4943 – 4952.
19. Xenides D, Randolf B, Rode BM. Hydrogen bonding in liquid water: An ab initio QM/MM MD simulation study. J. Mol. Liq. 2006; 123: 61 – 67.
20. Kumar R, Schmidt JR, Skinner JL. Hydrogen bonding definitions and dynamics in liquid water. J. Chem. Phys. 2007; 126: 204107.
21. Walrafen GE. Effects of equilibrium H-bond distance and angle changes on Raman intensities from water.J. Chem. Phys. 2004; 120: 4868 – 4876.
22. Stryer L, Haughland RP. Energy transfer: a spectroscopic ruler. Proc. Natl. Acad. Sci. USA. 1967; 58: 719 – 726.
23. Mancinelli R, Botti A, BruniF et al. Hydration of Sodium, Potassium, and Chloride Ions in Solution and the Concept of Structure Maker/Breaker. J. Phys. Chem. B. 2007; 111: 13570 – 13577.
24. Burke CAE, Adya AK, Neilson GWA.A structural study of the aqua-anions NO_3^-, $BrO_3^-$and ClO_3^- by difference methods of X-ray diffraction. J. Phys.: Condens. Matter.1991; 3: 837 – 850.
25. Smith JD, Saykally RJ, Geissler PL. The effects of Dissolved Halide Anions on Hydrogen Bonding in Liquid Water.J. Am. Chem. Soc. 2007; 129: 13847 – 13856.
26. Funkner S, Niehues G, Schmidt DA et al. Watching the Low Frequency Motions in Aqueous Salt Solutions: The Terahertz Vibrational Signatures of Hydrated Ions. J. Am. Chem. Soc. 2012; 134: 1030 – 1035.
27. Lin YS, Auer BM, Skinner JL. Water structure, dynamics, and vibrational spectroscopy in sodium bromide solutions.J. Chem. Phys. 2009; 131: 144511.
28. Vchirawongkwin V, Kritayakornupong C, Tongraar A et al. Symmetry Breaking and Hydration Structure of Carbonate and Nitrate in Aqueous solutions: A Study by Ab Initio Quantum Mechanical Charge Field Molecular Dynamics. J. Phys. Chem. B. 2011; 115: 12527 – 12536.
29. Verde AV, Lipowsky R. Cooperative Slowdown of Water Rotation near Densely Charged Ions is Intense but Short-Ranged. J. Phys. Chem. B. 2013; 117: 10556 – 10566.
30. Stirnemann G, Wernersson E, Jungwirth P et al. Mechanisms of Acceleration and Retardation of Water Dynamics by Ions. J. Am. Chem. Soc. 2013; 135: 11824 – 11831.

31. Nigro B, Re S, Laage D et al. On the Ultrafast Infrared Spectroscopy of Anion Hydration Shell Hydrogen Bond Dynamics.J. Phys. Chem. A. 2006; 110: 11237 – 11243.
32. O’Brien JT, Williams ER. Effect of Ions on Hydrogen-Bonding Water Networks in Large Aqueous Nanodrops.J. Am. Chem. Soc. 2012; 134: 10228 – 10236.
33. Di Tucci MJ, Heiles S, Williams ER. Role of Water in Stabilizing FerricyanideTrianion and Ion-Induced Effects to the Hydrogen-Bonding Water Network at Long Distance.J. Am. Chem. Soc. 2015; 137: 1650 – 1657.
34. Skipper NT, Neilson GW. X-ray and neutron-diffraction studies on concentrated aqueous solutions of sodium nitrate and silver nitrate. J. Phys. Condens. Matter.1989; 1: 4141 – 4151.
35. Endom L, Hertz HG, Thul B et al. A microdynamic model of electrolyte solutions as derived from nuclear relaxation and self-diffusion data. Dtsch. Bunsenges.Phys. Chem. 1967; 71: 1008 – 1031.
36. Kinukhin MY, Collins KD. Dynamic hydration numbers for biologically important ions. Biophys. Chem. 2002; 99: 155 – 168.
37. Harkani I, Jovari P, Meszaros G et al. Neutron and X-ray diffraction studies of aqueous rubidium bromide solutions. J. Mol. Liq. 2007; 131-132: 60 – 64.
38. Vinogradov EV, Smirnov PR, Trostin VN. Russ. Chem. Bull. 2003; 52: 1253 – 1271.
39. Bouazizi S, Nasr S. Local order in aqueous lithium chloride solutions as studied by X-ray scattering and molecular dynamics simulations. J. Mol. Struct. 2007; 837: 206 –213.
40. Bouazizi S, Nasr S, Jaidane N et al. Local order in aqueous NaCL solutions and pure water: X-ray scattering and Molecular Dynamics simulations study. J. Phys. Chem. B. 2006; 110: 23515 – 23523.
41. Novikov AG, Rodnikova MN, Savostin VV et al. The study of hydration effects in aqueous solutions of LiCl and CsCl by inelastic neutron scattering. J. Mol. Liq. 1999; 82: 83 – 104.
42. Mancinelli R, Botti A, BruniF et al. Perturbation of water structure due to monovalent ions in solution. Phys. Chem. Chem. Phys. 2007; 9: 2959 – 2967.
43. Soper AK, Weckström K. Ion solvation and water structure in potassium halide aqueous solutions. Biophys.Chem. 2006; 124: 180 – 191.
44. Botti A, Bruni F, Imberti S et al. Solvation of hydroxyl ions in water. J. Chem. Phys. 2003; 119: 5001 –5004.
45. Tongraar A, Liedl KR, Rode BM. The hydration shell structure of Li^+ investigated by Born-Oppenheimer ab initio QM/MM dynamics. Chem. Phys. Lett. 1998; 286: 56 –64.
46. Loeffler HH, Rode BM. The hydration structure of the lithium ion.J. Chem. Phys. 2002; 117: 110 – 117.

47. Tongraar A, Liedl KR, Rode BM. Born-Oppenheimer ab Initio QM/MM Dynamics Simulations of Na^+ and K^+ in Water: From Structure Making to Structure Breaking Effects. J. Phys. Chem. A. 1998; 102: 10340 – 10347.
48. White JA, Schwegler E, Galli G et al. The solvation of Na^+ in water: First-principles simulations. J. Chem. Phys. 2000; 111: 4668 – 4673.
49. Schwenk CF, Hofer TS, Rode BM. "Structure Breaking" Effect of Hydrated Cs^+. J. Phys. Chem. A. 2004; 108: 1509 – 1514.
50. Mähler H, Persson I. A Study of the Hydration of the Alkali Metal Ions in Aqueous Solution.Inorg.Chem. 2012; 51: 425 – 438.
51. Liu CW, Wang F, Yang L et al. Stable Salt-Water Cluster Structures Reflect the Delicate Competition between Ion-Water and Water-Water Interactions. J. Phys. Chem. B. 2014; 118: 743 – 751.
52. Chen H, Ruckenstein E. Hydrated Ions: From Individual Ions to Ion Pairs to Ion Clusters. J. Phys. Chem. B. 2015; 119: 12671 – 12676.
53. Robertson WH, Diken EG, Price EA et al. Spectroscopic determination of the OH-solvation shell in the $OH\text{-}(H_2O)_n$ clusters. Science.2003; 299: 1367 – 1372.
54. Rasaiah JC, Lynden-Bell RM. Computer simulation studies of the structure and dynamics of ions and non-polar solutes in water. Philos. Trans. R. Soc. London, A. 2001; 359; 1545 – 1574.
55. Du H, Rasaiah JC, Miller JD. Structural and dynamic properties of concentrated alkali halide solutions: a molecular dynamics simulation study. J. Phys. Chem. B. 2007; 111: 209 – 217.
56. Kemp DD, Gordon MS. Theoretical Study of the Solvation of Fluorine and Chlorine Anions by Water. J. Phys. Chem. A. 2005; 109: 7688 – 7699.
57. Wang Q, Suzuki K, Nagashima U et al. Semiempirical investigations on the stabilization energies and ionic hydrogen-bonded structures of $F^-(H_2O)_n$ and $Cl^-(H_2O)_n$ (n=1-4) clusters. Journal of Theoretical and Applied Physics.2013; 7: 7.
58. Collins KD. Charge density-dependent strength of hydration and biological structure. Biophys. J. 1997; 72: 65 – 76.
59. Hewish NA, Neilson GW. Ammoinium ion coordination in concentrated aqueous ammonium-chloride. Chem. Phys. Lett. 1981; 84: 425 – 427.
60. Cox WM, Wolfenden JH. The viscosity of strong electrolytes measured by a differential method.Proc. R. Soc. London, A. 1934; 145: 475 – 488.
61. Jones G, Dole M. The viscosity of aqueous solutions of strong electrolytes with special reference to barium chloride.J. Am. Chem. Soc. 1929; 51: 2950 – 2964.

62. Samoilov OY. A new approach to the study of hydration of ions in aqueous solutions.Discuss. Faraday Soc. 1957; 24: 141 – 146.
63. Thompson WH, Hynes JT. Frequency shifts in the hydrogen-bonded OH stretch in halide-water clusters. The importance of charge transfer.J. Am. Chem. Soc. 2000; 122: 6278 – 6286.
64. Parthasarathi R, Subramanian V, Sathyamurthy N. Hydrogen bonding without borders: an atoms-in-molecules perspective. J. Phys. Chem. A. 2006; 100: 3349 – 3351.
65. Gilli G, Gilli P. Towards an unified hydrogen-bond theory. J. Mol. Struct. 2000; 552: 1 – 15.
66. Buchner R, Hefter G, Barthel J. Dielectric relaxation of aqueous NaF and KF solutions. J. Chem. Soc. Faraday Trans. 1994; 90: 2475 – 2479.
67. Buchner R, Hölzl C, Stauberl J et al. Dielectric spectroscopy of ion-pairing and hydration in aqueous tetra-*n*-alkylammonium halide solutions. Phys. Chem. Chem. Phys. 2002; 4: 2169 – 2179.
68. Chen T, Hefter G, Buchner R. Dielectric spectroscopy of aqueous solutions of KCl and CsCl. J. Phys. Chem. A. 2003; 107: 4025 – 4031.
69. Tromans A, May PM, Buchner R. Ion Pairing and Solvent Relaxation Processes in Aqueous Solutions of Sodium Malonate and Sodium Succinate. J. Phys. Chem. B. 2004; 108: 13789 – 13795.
70. Wachter W, Fernandez S, Buchner R et al. Ion Association and Hydration in Aqueous Solutions of LiCl and $Li_2SO_4$by Dielectric Spectroscopy J. Phys. Chem. B. 2007; 111: 9010 – 9017.
71. Wachter W, Kunz W, Buchner R et al. Is There an Anionic Hofmeister Effect on Water Dynamics? Dielectric Spectroscopy of Aqueous Solutions of NaBr, NaI, $NaNO_3$, $NaClO_4$, and NaSCN.J. Phys. Chem. A. 2005; 109: 8675 – 8683.
72. Combariza JE, Kestner NR. Jortner J. Energy-structure relationships for microscopic solvation of anions in water clusters.J. Chem. Phys. 1994; 100: 2851 – 2864.
73. Li R, Jiang Z, Chen F et al. Hydrogen bonded structure of water and aqueous solutions of sodium halides: a Raman spectroscopic study. J. Mol. Struct. 2004; 707: 83 – 88.
74. Nickolov ZS, Miller JD. Water structure in aqueous solutions of alkali halide salts: FTIR spectroscopy of the OD stretching band. J. Colloid Interface Sci. 2005; 287: 572 – 580.
75. Geiger A. Molecular dynamics simulation study of the negative hydration effect in aqueous electrolyte solutions. Ber. Bunsenges. Phys. Chem. 1981; 85: 52.
76. Heinzinger K. Computer simulations of aqueous electrolyte solutions. Physica B+C. 1985; 131: 196 –216.

77. Balbuena PB, Johnston KP, Rossky PJ et al. Aqueous Ion Transport Properties and Water Reorientation Dynamics from Ambient to Supercritical Conditions. J. Phys. Chem. B. 1998; 102: 3806 – 3814.
78. Chowdhuri S, Chandra A. Molecular dynamics simulations of aqueous NaCl and KCl solutions: Effects of ion concentration on the single-particle, pair, and collective dynamical properties of ions and water molecules.J. Chem. Phys. 2001; 115: 3732 – 3741.
79. Corey VB. Adiabatic compressibilities of some aqueous ionic solutions and their variation with indicated liquid structure of the water. Phys. Rev. 1943; 64: 350 – 357.
80. Marcus Y. The hydration entropies of ionsand their effects on the structure of water.J.Chem. Soc. Faraday Trans. 1.1986; 82: 233 – 242.
81. Friedman HL, Krishnan CV. In Water.A Comprehensive Treatise. Franks F. Ed. Plenum Press: New York; 1973; Vol. 3, p 1.
82. Marcus Y, Loewenschuss A. Standard entropies of hydration of ions. Annu.Rev. C (R. Soc. Chem. London). 1985; 1984: 81 – 135.
83. Collins KD. Ions from Hofmeister series and osmolytes: effects on proteins in solution and in the crystallization process. Methods.2004; 34: 300 – 310.
84. Jagoda-Cwiklik B, Vacha R, Lund M et al. Ion Pairing as a Possible Clue for Discriminating between Sodium and Potassium in Biological and Other Complex Environments. J. Phys. Chem. B. 2007; 111: 14077 – 14079.
85. Pinna MC, Salis A, Monduzzi M et al. Hofmeister Series: The Hydrolytic Activity of *Aspergillus niger* Lipase Depends on Specific Anion Effects. J. Phys. Chem. B. 2005; 109: 5406 – 5408.
86. Boström M, Loretti B, Fratini E et al. Why pH Titration in Protein Solutions Follow a Hofmeister Series. J. Phys. Chem. B. 2006; 110: 7563 – 7566.
87. Omta AW, Kropman MF, Woutersen S et al. Negligible Effect of Ions on the Hydrogen-bond Structure in Liquid Water. Science.2003; 301: 347 – 349.