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2019

Sun, C. Q., Huang, Y., & Zhang, X. (2019). Hydration of Hofmeister ions. *Advances in Colloid and Interface Science*, 268, 1–24. doi:10.1016/j.cis.2019.03.003

<https://hdl.handle.net/10356/144732>

<https://doi.org/10.1016/j.cis.2019.03.003>

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Hydration of Hofmeister Ions

(135 refs, 23 figs, 19 k words)

Chang Q Sun,¹ Yongli Huang², Xi Zhang³

Highlight

- *Ionic hydration stiffens the H–O and meanwhile softens the O:H phonon cooperatively.*
- *Hydrating H₂O dipoles full-screen a cation to keep its constant hydration volume.*
- *Inter-solute repulsion limits an anionic hydration volume in a $f(C) \propto 1 - \exp(-C/C_0)$ way.*
- *Ionic negativity, polarity, radius, shape, and valence discriminate the performance of an ion.*
- *Inter-solute repulsion, and ionic polarization stem the properties of a solution.*

Abstract

Water dissolves salt into ions and then hydrate the ions in an aqueous solution. Hydration of ions deforms the hydrogen bonding network and triggers the solution with what the pure water never shows such as conductivity, molecular diffusivity, thermal stability, surface stress, solubility, and viscosity, having enormous impact to many branches in biochemistry, chemistry, physics, and energy and environmental industry sectors. However, regulations for the solute-solute-solvent interactions are still open for exploration. From the perspective of the screened ionic polarization and O:H–O bond relaxation, this work features the recent progress and a perspective in understanding the hydration dynamics of Hofmeister ions in the typical YI, NaX, ZX₂, and NaT salt solutions (Y = Li, Na, K, Rb, Cs; X = F, Cl, Br, I; Z = Mg, Ca, Ba, Sr; T = ClO₄, NO₃, HSO₄, SCN). Phonon spectrometric analysis turned out the $f(C)$ fraction of bond transition from the mode of deionized water to the hydrating. The linear $f(C) \propto C$ form features the invariant hydration volume of small cations that are fully-screened by their hydration H₂O dipoles. The nonlinear $f(C) \propto 1 - \exp(-C/C_0)$ form describes that the number insufficiency of the ordered hydrating H₂O dipoles partially screens the anions. Molecular anions show stronger yet shorter electric field of dipoles. The screened ionic polarization, inter-solute interaction, and O:H–O bond transition unify the solution conductivity, surface stress, viscosity, and critical energies for phase transition.

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1. Wonders of Hofmeister Salt Solutions

1.1. Concurrent Status and known facts

Injection of ions by salt solvation distorts the hydrogen bond (O:H–O or HB with ‘:’ being the electron lone pair) network and triggers the solution with unexpected properties compared with the deionized water that serves as the solvent. Solvation dynamics has been amusing the community with debating mechanisms despite overwhelming contributions made since 1888 when Frank Hofmeister [1] discovered the ionic series order on protein solubility and the solution surface stress. Salt solvation is ubiquitously important to innumerable reactions occurring to living and nonliving systems, which has profound impact to many biological, chemical, and environmental issues [2-4] such as DNA engineering [5], disease curing and health caring [2, 6]. Salt solvation changes the solution viscoelasticity [7, 8], thermal and mechanical stability [9], critical energies in terms of temperatures and pressures for phase transition [10, 11], and even reduces the friction when the salt solutions are used as lubricants [12-14]. Ionic hydration forms a stiffener and cylindrical volume coupling a cation and a pair of point defects in the adjacent graphite-oxide layers. The stiffer ‘(-) ~ (+) ~ (-)’ vertical hydration volume enlarges the graphene-oxide layer separation from 0.33 up to 1.5 nm, which could be promising for sea water purification [15, 16].

The anionic abilities in precipitating certain egg proteins follow the Hofmeister series order and solute concentration dependent [17-22]. The phonon was explained by means of water structure order maker that shortens the O:H distance and water breaker that does it otherwise [23-25], ionic specification and affinity matching [8, 26], quantum dispersion [8, 27], skin induction [28], and length range of interaction [29], and many more. Hydrogen bond quantum dispersion was believed important in ligand-water interaction [30] and cellobiose-water interactions [31].

Ions could be categorized as having the ‘salting in’ and ‘salting out’ effect on solubility of a protein [32]. The ‘salting in’ refers to the stronger ionic solubility of proteins that are surrounded by ions, which lowers the electrostatic energy of the protein to raise the proteins’ solubility, and vice versa. It is expected that the ionic size, electronegativity, and polarity determine the ions acting on the surrounding water molecules leading to salting in or salting out proteins in aqueous solutions.

Compared with the monovalent ions of the same centration C , the Z^{2+} and $2X^{-}$ in a divalent salt solution “hardens” drinking water and they are harmful to living creatures [33, 34]. From the

perspective of classical thermodynamics, namely, the density, isothermal compressibility, and surface tension, a coarse-grained electrolyte solution model was proposed, being capable of reproducing some trends on how salts influence the diffusivity and viscosity of the solutions [35, 36].

Salt solvation differs the local physical–chemical properties of the hydration volume from those of unsalted water. Spectroscopic techniques by means of electron, phonon, and photon excitation sources have been employed to investigate the solvation dynamics. For instances, neutron scattering probes the phonon density-of states [37, 38]. Near edge X-ray absorption fine structure (NEXAFS or XAS) resolves the effect of H–O bond relaxation and charge polarization on the O–K pre-edge peak shift [39]. Micro liquid-jet photoelectron spectroscopy (PES) records the molecular site resolved binding energy and energy dissipation lifetime of the hydrated electrons [40]. The sum frequency generation (SFG) spectroscopy probes information regarding dipolar orientation and the skin dielectrics, at the monolayer air/solution interface [41]. The ultrafast two–dimensional infrared (2DIR) absorption spectroscopy records the lifetime for molecular motion dynamics as a function of solution viscosity [42]. The presently used differential phonon spectrometrics (DPS) collects quantitative information on the abundance-stiffness-fluctuation transition of O:H–O bonds from ordinary water to the hydrating [43, 44].

A neutron diffraction investigation of nickel chloride hydration as a function of solute concentration, pressure, and temperature revealed that heating can reduce the Ni^{2+} and Cl^- hydration volume [45]. Monte Carlo simulation and neutron diffraction [34] showed that the electrostatic field from the divalent cations in (Mg, Ca) Cl_2 solutions strengthens their interactions with solvent water molecules to form a more rigid and stable supersolid, first hydration shell [44, 46], compared with the monovalent ionic solutions.

Molecular dynamics (MD) computations and light-scattering investigation suggested that the negatively charged carboxylic acid side-chain groups preferring pairing with smaller to the bigger cations [47, 48]. This phenomenon was attributed to the different proteins’ surface sensitivity to the Na^+ or K^+ cations, because the Na^+ ‘poisons’ the proteins more readily than the K^+ , which might be a clue why the cytosol is rich in K^+ but poor in Na^+ [49]. Similarly, the positively charged side-chain groups of the basic amino acids pair are more efficiently interacting with smaller cations, than larger anions, resulting in an reverse Hofmeister ordering at these sites [50, 51]. Interactions with these charged groups can be comparable to - or even overwhelm - those with the backbone, which would then cause the Hofmeister reversal for the peptide or protein.

The ionic solute–water dipolar interaction affects water’s reorientation dynamics and the H–O (ω_H) and D–O (ω_D) stretching vibrational frequencies in the H₂O + D₂O mixture solvent. For instance, Smith et al [52] probed the phonon spectra of the H₂O+D₂O mixture with and without the solvation of 1 mol K(F, Cl, Br, I) and uncovered that larger anions with lower electronegativity could stiffen the ω_H more than the contrast. The F[−] has negligible effect on the ω_H phonon frequency shift.

From 2DIR spectroscopy and MD simulations, Park and coworkers [53] found that 5% NaBr addition stiffens the D–O stretching vibration frequency from 2509 to 2539 cm^{−1} in the HOD + H₂O solutions and the phonon frequency shifts with the number ratio of $N_{H_2O}/N_{NaBr} = 8, 16, \text{ and } 32$. Higher solute concentration induces more significant ω_{D-O} peak shift with weaken screened by the hydrating H₂O dipoles or other anions. The ω_{D-O} blueshift raises its lifetime. NaBr hydration not only causes the ω_{D-O} blueshift but also slows the molecular dynamics – or in another term, the rate of phonon energy dissipation varies inversely with the phonon frequency – high frequency phonons have longer lifetime. An increase of NaBr concentration also raises the solution viscosity, which is accompanied by lowering the translational motion dynamics of water molecules or the order of the molecular fluctuation dynamics. Salt such as (Na, CLi)I [54, 55], Na(Br, ClO₄)[53], and Mg(ClO₄)₂ [56-58] solvation also shifts positively the ω_H of the hydroxyl group (OH[−] or OD[−]).

DFT optimizations [59] suggested that within the closest hydration shell of an I[−] anion, the I–H distance is about 40% longer and the H–O is some ~1% shorter than the O:H and H–O respectively in bulk water. However, the O:H in the hydration shell is 29% longer and the H–O is 0.9% shorter. The X[−] capability of inducing X[−]·H–O and O:H–O relaxations obeys the I[−] > Br[−] > Cl[−] Hofmeister series order.

The elastic second harmonic scattering from > 0.05 M (Cs, Li, K, Na, Rb)(Cl, NH₄) and (Ca, Mg, Sr)Cl₂ solutions showed the ionic specificity in both the local electronic anisotropy and in the H₂O molecule nanoscopic orientation ordering [60]. Cations with higher valences and smaller sizes affect more than anions the charge distribution around ions and the structural orientation of water molecules in the extended hydration shells. As it has been confirmed that ions in salt [11, 19, 61, 62], basic [11], and acidic [63, 64] solutions serves each as a charge center to align, cluster, stretch and polarize its neighboring H₂O molecules to form a supersolid hydration shell. Within the hydration volume, the H–O bond turns to be stiffer and the O:H nonbond softer.

Extensive attention has also been paid to the ionic effect in complex salts [65-68]. A combination of MD simulations and ultrafast IR measurements [65] suggested that the rotational mobility of the SCN⁻ in KSCN solutions is relatively higher. 2DIR investigation [57] revealed that the ω band shifts positively as the NaClO₄ molar concentration is increased from 5 to 10%. An interplay of the liquid jet NEXAFS, MD simulations, and *ab initio* electronic structure calculations, Yin and coworkers [69] elucidated that MgCl₂ salt ions affect the electronic properties of water molecules in the close vicinity – short-range.

Salt solvation lowers the critical temperature for homogeneous ice nucleation, T_N , substantially. Reducing the H₂O/LiCl molecular number ratio from 100 to 7, the aqueous solution performs the same in lowering the T_N of the solution from 248 to 190 K [55]. The O:H nonbond energy, E_L , is related to the T_N and the H–O bond energy, E , to the melting temperature T_m [70], according to Einstein's relation of $\Theta_{Dx} \propto \omega_x \propto (E/d^2)_x$ with subscript $x = L$ and H for the O:H and H–O interactions. Θ_{Dx} is the Debye temperature.

Salt solvation raises the solution viscosity. The viscosity is an important macroscopic parameter that is often used to classify water-soluble salts into structure order making or structure breaking. In an aqueous solution, the solute molecules can be taken as Brownian particles to move with a drift diffusivity $D(\eta, R, T)$ of Stokes-Einstein relation [71]. The solution viscosity η changes with the solute concentration C , in terms of the Jones–Dale notion [72, 73],

$$\Delta\eta(C)/\eta(0) = AC^{1/2} + BC.$$

The prefactor A is related to the inter-solute ionic interactions and keeps a constant for the alkali halide solutions. The B describes the solute-solvent molecular interactions. The $\eta(0)$ is the reference of water. However, it has been [46] clarified the cationic polarization governs the linear term whilst the interanion repopulation and anionic polarization dictates the nonlinear term of the Jones–Dale description. For the basic and acid solutions, divalent and complex molecular salt solutions, the viscosity does not follow the notion of Jones–Dale, showing the $\partial^2\eta/\partial C^2 > 0$, originating from the dominance of polarization and solute-solute repulsion.

The diffusivity and viscosity are correlated to the H–O phonon relaxation time $\tau(\omega)$ obtained from the 2DFR spectroscopy,

$$\frac{I(\omega, t)}{I(\omega, 0)} = \exp[-t / \tau(\omega)]$$

One can gain the $\tau(\omega)$ recording and simulating the decay profile in the 2DIR experiments. The $\tau(\omega)$ varies not only with the exciting frequency but also the solute concentration, solute type, temperature, and molecular coordination environment [42]. Cooling or increasing solute concentration could prolong the $\tau(\omega)$. The H-O dangling bond, vibration is featured at (3700 cm^{-1} , 850 fs) in the SFG (at 3610 cm^{-1} of Raman spectrum) diffuses slower than those in the skin (3450 cm^{-1} , 500 fs) and in the bulk (3200 cm^{-1} , 250 fs). Alternatively, the lifetime can be related to the rate of vibration energy dissipation – higher vibration energy requires a longer time for dissipation [44].

Using a polarization selective IR pump-probe spectroscopy, Wei, Zhou and Bian [74] examined the cation effects on the D–O phonon relaxation dynamics of water molecules in (Li, Na)ClO₄ aqueous solutions. They found that D–O peak splits into two components and the viscosity increases dramatically, with $\partial^2\eta/\partial C^2 > 0$. The Li⁺ has a much weaker effect than the Na⁺ on the population peak at 2630 cm^{-1} , and thus its effect on the D–O bond relaxation dynamics is hardly resolvable.

One can modulate the solution viscosity by changing solution temperature or solute concentration. The phonon lifetime increases linearly with the viscosity of SCN[−] and CO₂ solutions and the drop of solution temperature [75, 76]. The phonon lifetime dependence on the solution viscosity verifies that the H–O bond stiffening slows down the molecular dynamics in the supersolid hydration volume, or the energy dissipation rate is proportional to the phonon frequency.

In contrast, an ultrafast pump-probe spectroscopy examination of the ionic effect on the phonon relaxation time of water molecules in Mg(ClO₄)₂, NaClO₄, and Na₂SO₄ solutions suggested that an addition of ions does not affect the rotational dynamics of the free water molecules outside the first hydration shells or enhance or breakdown the HB network in liquid water [77]. However, supported by neutron diffraction [78] and viscosity measurements [79], Tielrooij et al [80] showed that a certain kind of salts do have an effect on the dynamics of water molecules of longer distance away from the ionic solute of multiple shells. A terahertz and femtosecond IR spectroscopic investigation revealed that the Mg, Li, Na, and Cs cations and S, Cl, I anions can interact strongly with H₂O molecules well beyond the first hydration shell of water molecules.

An IR examination [81] of the $\Delta\omega_{D-O}$ in the CsCl, (K, Cs)F, and (Na, K)I, solutions of 0.04D₂O+0.96H₂O solvent correlated the $\Delta\omega_{D-O}$ to the solute capability of structure making ($B > 0$) and breaking ($B < 0$) in Jones – Dale notion. They attributed the $\Delta\omega_{D-O}$ redshift at 2500 cm⁻¹ for (Na, K)I and CsCl to the structure breaking but the $\Delta\omega_{D-O}$ blueshift for (K, Cs)F to structure order making. Slight $\Delta\omega_D$ redshift does happen only at higher solute concentrations, arising from the partially-screened anion-anion interaction that weakens the local electric field of the anion and reduces its hydration volume.

The high elasticity, solubility, and viscosity of the supersolid skin of the deionized water and the ionic hydration shells have been attributed to the electrostatic polarization by molecular undercoordination or by the ionic hydration [2, 44]. The supersolid phase has slower molecular motion, shorter H–O bond, longer lifetime, longer O:H; lower T_N , and higher T_m . The skin supersolid stems the hydrophobicity of water, slipperiness of ice, and Mpemba effect – warm water cools faster because of the lower mass density and high thermal diffusivity [82, 83].

1.2. Debating Mechanisms

Numerous hypothetic theories have been developed on the solute-solvent interactions and solvation dynamics. Kim Collins [8, 26], a biologist at Maryland, proposed the “ion-water affinity matching”, assuming that cations and anions of comparable hydration free energies tend to pair in water. Salt solvation effect not only depends on the ions, but also shows its cooperativity with other ions as a collection. Ion pairing influences the capability of aqueous solutions on activity coefficients, dissolving proteins, and surface stress. It is currently believed that Hofmeister effect results from the versatile abilities of ions to replace water molecules at the surfaces. The different surface potential and stress could be used to explain how ions affect protein’s stability through indirect interactions [79].

One can hardly explain the specific ion properties of electrolyte solutions if based solely on electrostatics without considering quantum mechanical effect or specific ion dispersion with other ions and water molecules [27]. Collins’s rule could be extended the dispersion interactions to the ionic interactions in calculations, which could explain some puzzles of electrolyte solutions [8]: the solvation energy differences among ions of the same size, the small repulsion of I⁻ at the air/water interface, and the ionic affinity of large ions for each other in water embodied in Collins’s rules.

Conversely, Liu et al [28] identified the Hofmeister effect is strong in the Ca^{2+} and Na^{+} exchange on a charged surface over a broad range of ionic strengths. They disputed that their findings result from a strong force of ion-surface induction than the classical induction, dispersion, hydration, or ionic size. The strength of this induction force was about 104 times that of the classical induction force, which could be comparable to the Coulomb interaction force. The presence of the observed strong non-classical induction force suggested that energies of electrons in the deeper bands of ions and atoms at the interface might be important but underestimated, and it is just the underestimated energies determine the Hofmeister effects. Yes, indeed, the ions and H-O bond at a surface perform different from they do in the bulk because of bond contraction, quantum entrapment and polarization effect [44].

Hofmeister [1] interpreted his observations from the framework of electrolytic dissociation and tried to connect the observed ions ordering with their strength of hydration, denoted as the water-absorbing effects of salts. Hofmeister's effort was eventually framed into the theory of ionic structure-making and structure-breaking during the 1930-1950s [23-25].

However, it is hard to tell a simple story about the effect of ionic hydration on solution properties using any single concept under a given condition. Zangi et al. [84] showed in 2006, ions of high charge quantity (q) could induce salting-out by promoting the hydrophobic interactions to aggregate the proteins. Conversely, the low- q ions could have either a salting-out or a salting-in effect, depending on the ionic concentrations. Without considering the nature of the protein surface itself or solvent-solute-protein interactions, it could be impossible to rationalize the ordering of ions, or exceptions to the Hofmeister behavior [85].

1.3. Challenge and objectives

Currently, the majority approaches is focused on the solute motion dynamics, hydration length scale, water structure making or breaking, salting in or out and molecular relaxation lifetime by taking an H_2O molecule as the basic structure element. However, solute capabilities, solute-solute and solute-solvent interactions and their effect on the HB network transition and charge polarization is a high challenge. Correlating the H-O bond and O:H nonbond interactions, transition of HB length and phonon abundance-stiffness, H-O bond energy dissipation, molecular motion dynamics, solute diffusivity, solution viscosity, surface stress, and critical energies (pressures and temperatures) for phase transitions is necessary. Most importantly, discriminating the effects of Hofmeister ions on the

hydrogen bonding network distortion and solute properties is the foremost tasks of the community [86].

In fact, the nature of the chemical bond bridges the structure and properties of a molecule and a crystal [87] and the formation, dissociation and relaxation of the chemical bond and nonbond and their associated energetics, localization, entrapment, and polarization of electrons in various energy levels govern the performance of a substance [88]. Bond length and energy relaxation dictate the phonon frequency shift and the electron polarization and solute-solute interaction dictate the solution conductivity, hydrophobicity, surface stress, viscosity, and solubility of the solution [89, 90]. The joint effect of bond relaxation and charge polarization dictates the performance of water, ice and aqueous solutions [87, 88].

It is the opinion of the practitioners that one shall transit from the solvation molecular dynamics to hydration bonding dynamics. Intermolecular O:H, $H \leftrightarrow H$, and $O \rightleftharpoons O$ interactions, and the screened ionic polarization in association of the O:H–O cooperative relaxation would be essential. One should treat solvent water as a highly-ordered crystal rather than the randomly ordered structure or protons being freely motion. Consideration of the anomalous performance of water solvent from the perspective of ion electrification is necessary. Focusing on the O:H–O segmental relaxation and the associated polarization in the first hydration subshell would be suffice [3, 4, 20].

Progress in the NaX[19], YI [61], complex NaT [59], and divalent ZX_2 [91] hydration dynamics has confirmed consistently our proposals of solvation charge injection. Salt hydration creates Hofmeister ions that form each a point or a dipolar charge center to align, cluster, stretch, and polarize water molecules to form supersolid hydration volume. H–O contraction and O:H elongation take place with an association of strong polarization in the supersolid hydration volume [82, 92] associated with ω_H blueshift and ω_L redshift. The supersolidity due to electric polarization by charge injection and molecular undercoordination is elastic, and thermo-mechanically stable. Water clusters, skins of water and ice, droplets and nanobubbles perform similarly to the ionic hydration volume. Encouragingly, this way of approach has enabled discrimination of the solute functionalities on the hydrogen bonding network relaxation and property change of salt solutions [46].

With the aid of DPS and XAS spectrometrics, we will be focused on the length, manner, strength of ionic field interacting with the hydrating O:H–O bonds in the hydration volume, and the effect on the

network deformation by bond relaxation and transition from the mode of water to hydrating. A systematic examination of the hydration dynamics of Hofmeister ions in the typical YI, NaX, ZX₂, and NaT salt solutions (Y = Li, Na, K, Rb, Cs; X = F, Cl, Br, I; Z = Mg, Ca, Ba, Sr; T = ClO₄, NO₃, HSO₄, SCN) has led to discrimination of the functionalities and the ions. Progress evidence the essentiality of the framework of solvation charge injection, O:H–O bond cooperativity, and the power of the DPS and XAS spectrometrics. Developed strategies and knowledge about factors dictating the properties of the solutions such as conductivity, surface stress, supersolidity, viscosity and the capability of phase boundary dispersion would provide important impact to related fields such as solute-protein interface, colloid-matrix interfaces, water distillation and pollution control, and energy and environment science.

2. Experimental and Theoretical Strategies

2.1. O:H–O Bond Segmental Length-stiffness Relaxation

As the primary unit of structure and energy storage, the O:H–O bond couples the intermolecular weaker O:H nonbond (often taken as hydrogen bond with ~0.1-0.2 eV interaction energy) and the H–O polar-covalent bond of ~4.0-5.0 eV binding energy by the Coulomb repulsion between electron pairs on adjacent oxygen anions [2]. Under external perturbation such as mechanical compression, cooling or heating, molecular undercoordination, and electromagnetic radiation, the asymmetrical, short-range, and coupled oscillator pair relaxes its segmental length and energy cooperatively as illustrated in Figure 1 insets. The relaxation of the O:H–O segmental length and the bond angle changes the system energy, but fluctuation contributes little on an average to the energy variation.

Calculations results Figure 1 performed using the COMPASS 1998 force field of Sun H [93] confirmed that an external stimulus dislocates both O ions in the same direction but by different amounts. The O:H–O segments relax always in a ‘master-slave’ manner. The arrows denote the master segments and their shifting directions under the given degrees of freedom. The slopes and the curvatures of the relaxation curves within the same panel follow the $(\Delta d_L/\Delta q)/(\Delta d_H/\Delta q) < 0$ and the $(\Delta^2 d_L/\Delta q^2)/(\Delta^2 d_H/\Delta q^2) < 0$ coupling manners with q being the variable of perturbation, which means that one curve increases and the other decreases in the opposite curvatures. The stronger H–O bond always relaxes less than the weaker O:H nonbond with respect to the H⁺ being taken as the coordination origin. The relaxation of the $\angle$ O:H–O angle θ only contributes to the crystal geometry and mass density. The O:H–O bond bending has its own independent vibration mode and interferes little to the H–O or the O:H stretching vibrations [2]. The HB cooperative relaxation is the key to the

water and ice when subjecting to molecular undercoordination, mechanical compression, thermal excitation [2, 18], and acid, base, and salt solvation [94, 95].

Figure 1. O:H–O bond segmental length cooperative relaxation stimulated by (a) compression, cooling of (b) Liquid and (c) quasisolid (QS) phase (unit in °C), and the (d) $(\text{H}_2\text{O})_N$ clusters of varied molecular coordination numbers. Arrows show the master pieces and their relaxation directions. The H–O bond always relaxes less than the O:H and both of them relax contrastingly in their curvatures and slopes, irrespective of the applied stimulus or the structural order because of the O–O Coulomb repulsive coupling (reprinted with permission from [2]).

2.2. Ionic Injection: Polarization and O:H–O Transition

At solvation, an n number of H_2O dipoles dissolves the salt crystal into a pair (or cluster) of counterions. An n_{HY} number of H_2O dipoles hydrates a cation and n_{HX} dipoles hydrates one anion in their first-vicinal hydration shells. The rest n_r number of molecules is free or in the high-order hydration shells of the binary and the ternary salt solutions:

The molecular concentration of a salt solution is $C = 1/(1 + n)$. The inverse of C , $1/C = 1 + n_{HY} + n + n_r$. The n_{HY} and n_{HX} are dipoles located in the first vicinal subshells of the respective cation and anion.

Hydration of ions produces no regular covalent or ionic bond, or without charge sharing, between solute ions and solvent water molecules but distorts the O:H–O network by polarization and screen shielding. Ions serve each as a point, or a dipolar, charge source of electric field radiating away from the positive charge sources and into the negative sources. The ionic field aligns, clusters, polarizes and stretches neighboring water molecules which in turn screen the electric field of the centering ions to form the supersolid [92] or semirigid [96, 97] hydration volume. The hydration volume varies with ionic charge quantity, polarity, shape, and the structure order of the solvent. If fully screened by the solvent molecules, the solute keeps a constant hydration volume, otherwise, varies with solute concentration, as its electric field will be weakened by the presence of other ions of the same kind. Therefore, the screened ionic polarization and the solute-solute interaction govern the performance of a solution. Figure 2 inset illustrates the separated ion pair and its screened polarization by the hydrating H₂O dipoles.

The ionic hydration shell size and the ionic polarizability determine the solution properties. Polarization determines surface stress, polarization and solute repulsion determines solution viscosity. The hydration shell size varies with the ionic electronegativity, charge quantity, polarity, radius, shape, and the structure order of the solvent. The shell size may vary with the solute concentration and type, but detecting means has yet been unavailable.

A Raman vibration mode features the Fourier transformation of all bonds vibrating in the same frequency, irrespective of their locations, orientations, or even structural geometry and order. The peak shape features the distribution probability, and the peak corresponds to the maximum probability. The peak area is the phonon abundance that is proportional to the number of bonds being detected and the spectral peak width (FWHM) to the fluctuation order of the vibrating bonds [2, 18].

Figure 2. Full-scan Raman spectra for the (a) solute-type dependent, 0.06 molar ratio NaX/H₂O solutions and the (b) NaI/H₂O solutions as a function of solute concentration collected under the ambient conditions. Inset a illustrates the ionic hydration and screened polarization of the separated ion pairs. The DPS of (c) ω_L (O:H stretching vibration mode) and (d) the ω_H (H-O mode) for the concentrated NaI/H₂O solutions with inset c showing the $f_{\text{NaI}}(C)$ coefficient, for the HB transition from water to the first hydrating subshell of the pairing I⁻ and Na⁺ ions. The ω_H DPS for the concentrated (e) NaCl/H₂O and (f) NaBr/H₂O solutions (reprinted with copyright permission from [19])

The O:H–O bond segmental length relaxation turns out the stiffness variation featured by the stretching vibration frequency shift, $\Delta\omega_x$, in the first order approximation, as a function of its length d_x and energy E_x [2]. Inclusion of high-order nonlinear interactions only offsets the peak position slightly without adding any new features of vibrations [2, 7],

$$\Delta\omega_x \propto \sqrt{E_x/\mu_x} / d_x \propto \sqrt{(k_x + k_c)/\mu_x}$$

The subscript $x = L$ represents the O:H nonbond of $\sim 200 \text{ cm}^{-1}$ vibration frequency and $x = H$ denotes the H–O bond of $\sim 3200 \text{ cm}^{-1}$ phonon frequency vibrating in the bulk water, see the full-frequency Raman spectrum for pure water in Figure 2. The k_x and k_c are the force constants or curvature of the respective segmental interaction potentials and O–O Coulomb coupling potentials at equilibrium. The $\Delta\omega_x$ also varies with the reduced mass μ_x of the specific x oscillator. However, from the full-scan Raman spectral profile, one could hardly be able to resolve quantitatively the fraction of bonds transition by solvation.

However, a difference between the spectra (DPS) collected from liquid water with and without salt solvation can resolve the transition of the phonon stiffness (frequency shift), abundance (peak area) and fluctuation (peak width) from the vibration mode of pure water (the valley) to the hydration volume (the peak) upon all spectral peaks being area normalized [98, 99], as demonstrated in Figure 2. The DPS removes phonons in the intermediate frequencies to purify O:H–O relaxation information of the hydrating H₂O dipoles within the first hydration subshells. The fraction coefficient of bond transition, $f_x(C)$, or the integral of the DPS peak, represents the relative number of bonds, or phonons, transiting from the deionized water to the first hydrating subshell as a function of solute concentration C .

The $f_x(C)$ is proportional to the total number of bonds of $C \times A$ number solute and its division $f_x(C)/C$ is proportional to the number of HBs per solute in the first hydration subshell, which characterizes the ionic hydration volume and its local electric field. $A = 6.022 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant.

3. Ionic Polarization and O:H–O Bond Transition

3.1. Na(F, Cl, Br, I) Solvation

Examination of Na(F, Cl, Br, I) solvation aims to discriminate the functionalities of X^- anions one from another on the O:H–O phonon frequency shift and bond transition as the Na^+ is assumed to perform identically in these NaX solutions.

Figure 2 compared the X^- solute capability of transiting the O:H–O bonds in terms of number fraction (abundance), stiffness (frequency shift), and structure order (FWHM) from the mode of ordinary water to the hydrating mode. The X^- capability of bond transition follows the $I^- > Br^- > Cl^-$ Hofmeister series order. The solute capability of polarization increases as one switches the X from Cl to Br and I. The X^- of larger radius and less electronegative effects more significantly on the O:H–O bonds transition. The X^- and Na^+ have the same effect of ionic polarization that shortens the H–O bond and stiffens its ω_H phonon. The O:H nonbond always relaxes in the opposite direction to the H–O bond under perturbation. The $\Delta\omega_x$ recovers slightly at higher concentration, which suggests weakening of the electric field in the hydration shells. However, Raman spectroscopy can hardly discriminate the effect of Y^+ from the effect of X^- on contributing to phonon relaxation.

The comparison of the Raman spectra for the 0.06 molar ratio NaX/H₂O solutions and for the concentration dependent NaI/H₂O solutions and the spectrum of deionized H₂O shows that salt hydration indeed stiffens the ω_H from 3200 to 3450 cm⁻¹ and softens the ω_L from 200 to ~75 cm⁻¹ cooperatively. The ω_H hydration mode overlaps the skin H–O modes of water and ice featured at 3450 cm⁻¹, which means that H–O bond in water skin and in the ionic hydration shell has the identical length and energy though the ionic polarization and molecular undercoordination are different degrees of freedom [44]. No vibration feature is resolved for any possible solute-solvent bond formation.

Figure 3. The fraction coefficients for the concentrated (a) NaX/H₂O, (b) HX/H₂O ($f_{\text{H}}(C) \cong 0$ [43]), (c) Na⁺ derived from $f_{\text{Na}}(C) = f_{\text{NaX}}(C) - f_{\text{HX}}(C)$, and (d) the contact angles between the NaX/H₂O solutions and glass substrate. The quasi-linear $f_{\text{Na}}(C)$ varies slightly with the X⁻ type. The contact angle approximate the effect of polarization as there lack means for liquid-solid interface energy determination (reprinted with copyright permission from [19, 43]).

The Raman spectra for the NaF hydration was not included due to its invariant spectral shape and peak shift within the limited solubility of 0.022. The $\Delta\omega_{\text{H}}$ blueshift for the NaX/H₂O solutions recovers slightly at higher concentrations by anion-anion repulsion that weakens the ionic electric field. The second valley at 3620 cm⁻¹ arises from the X⁻ preferential skin occupancy. Theses X⁻ anions stiffen the H–O dangling bond by some 10 cm⁻¹ and shields its vibration signal from being detected in the Raman spectroscopy.

Figure 3 compares the fraction coefficients for bond transition and the contact angles between solution and glass substrate for the concentration dependent NaX/H₂O solutions, and the $f_{\text{Na}}(C) = f_{\text{NaX}}(C) - f_{\text{HX}}(C)$ [43]. The quasi linear $f_{\text{Na}}(C)$ for the Na(Cl, Br) solutions is an indication of slight Na⁺ - X⁻

attraction which raises the electric field in the Na^+ hydration volume. The $f_X(C) = a[1-\exp(-C/C_0)]$ nonlinearity results from the involvement of the $X^- \leftrightarrow X^-$ repulsion that weakens the X^- capability of polarization. The strength ionic of polarization depends on the solute concentration. The solute type dependent halogenic ionic capability of HB transition and polarization varies with the same $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^- \sim 0$ (saturates at 0.022) Hofmeister series order [100].

These observations evidence that the intermolecular O:H nonbond and the H–O intramolecular bond relax cooperatively, and one shall consider the strong correlation when dealing water and solutions. For concise presentation, we will be focused on the ω_H DPS features unless it is presented. Quantitative information on the fraction of bond transition is critical to make the progress in understanding hydration bonding dynamics. Interested readers may visit original references for the Raman full scans and the ω_L DPS.

The spectral analysis revealed the solute type and concentration dependent capabilities of the halogenic solutes:

- 1) Raman spectra revealed no extra vibration features for the solute-solvent or solute-solute bond formation. Cations and anions stay alone as isolated charge centers polarizing O:H-O bond to form the hydration volume of finite sizes.
- 2) Ionic hydration has the same, or even stronger, effect of skin molecular undercoordination on the HB relaxation and polarization, lengthen the O:H nonbond, and meanwhile, shortening the H–O bond associated with phonon frequency shift (ω_L , ω_H) from (200, 3200) to (75, 3500) cm^{-1} , by weakening the O–O Coulomb repulsion [44].
- 3) The ionic capability of H–O bonds transition and electron polarization, from the vibration mode of pure water to its hydrating varies with the solute concentration and type. Inter-anion repulsion presents at higher solute concentration. The quasi-linear $f_{\text{Na}}(C)$ form suggests its invariant hydration volume because of the full shielding by the hydrating H_2O dipoles.
- 4) An ion of larger radius and lower electronegativity has a stronger effect of polarization. The effect of NaF could be hardly resolved using phonon spectroscopy, which may evidence that the Na^+ and F^- stay closely to form the contact ionic pair having only 0.022 ($n_{\text{H}_2\text{O}}/n_{\text{NaF}} \approx 45/1$) saturation solubility.
- 5) The X^- polarizability follows the $X(R, \eta) = \text{I}(2.2, 2.5) > \text{Br}(1.96, 2.8) > \text{Cl}(1.8, 3.0) > \text{F}(1.33, 4.0) \approx 0$ Hofmeister series order with R and η being the ionic radius and electronegativity. The

discrepancy between the $f_X(C)$ and $f_Y(C)$ indicates the number inadequacy of the highly-ordered hydrating H_2O dipoles to partially screen the X^- and the $X^- \leftrightarrow X^-$ repulsion turns to be significant at higher solute concentrations.

3.2. (Na, K, Rb, Cs)I Solvation

One can also discriminate the Y^+ capabilities of bond transition and polarization one from another by spectrometrically examining the Y type and concentration resolved YI solutions as the I^- is assumed to perform identically in these specimens. The difference among the full-frequency Raman spectra of aqueous (Na, K, Rb, Cs)I solutions of the same molar concentration are hardly resolvable.

Regardless of the cation type, the ω_H and the ω_L cooperative frequency shift is consistent with that for the Na(Cl, Br, I) solutions, which further confirms the O:H–O cooperativity though the cation-induced phonon frequency shift is less significant than that induced by anions. For the ω_H mode, the skin phonon component with frequencies centered at $\sim 3450\text{ cm}^{-1}$ is more pronounced. Following the order of $Y(R, \eta)$: $Li^+(0.78\text{\AA}, 1.0)$, $Na^+(0.98, 0.9)$, $K^+(1.33, /0.8)$, $Rb^+(1.49, 0.8)$, $Cs^+(1.65, 0.8)$ [101], the ionic size and electronegativity of the alkali cations determine their capabilities of polarization.

Using the same DPS iteration for the ω_H peaks results in the fraction coefficient for the concentrated YI/H_2O solutions, which feature the Y^+ cation capability of transiting the O:H–O bonds. Figure 4 shows that (a) the YI solutes have compatible $f_{YX}(C)$ for O:H–O bond stiffness transition but (b) well-dispersed capabilities of polarizing electrons. The slight $f_Y(C)$ deviation from its linear form at shorter solute distance may suggest the presence of $Y^+ \leftrightarrow Y^+$ repulsion (c) for the larger Cs^+ and K^+ cations. Alkali cations follow the $Na^+ > K^+ > Rb^+ > Cs^+$ Hofmeister polarizability order. The stronger cation polarizability originates from the high surface charge density of the tiny cations. The distinctive alkali ionic polarizability may be responsible for the activation or inactivation of their reaction channels [102] and hypertension medication and prevention involving cations. For instance, NaCl solvation enhances hypertension more than KCl solvation.

Figure 4. Concentration dependent ω_H DPS for (a) KI/H₂O, (b) RbI/H₂O, (c) CsI/H₂O, and (d) their contact angles between glass substrate. The fraction coefficients for (a) YI/H₂O and (b) Y⁺ cations derived from $f_Y(C) = f_{YI}(C) - f_{HI}(C)$ (refer to Figure 3b) and (c) the contact angles for the concentrated YI/H₂O solutions. The cations show a compatible capability of bond transition but well-dispersed Na⁺ > K⁺ > Rb⁺ > Cs⁺ Hofmeister polarization order. The tiny $f_Y(C)$ (Y = K, Cs) deviation from linear dependence indicates involvement of cation-cation repulsion at higher concentrations (reprinted with copyright permission from [61, 103])

3.3. Divalent (Mg, Ca, Sr)(Cl, Br)₂ Solvation

The ZX_2/H_2O solution bonding network is an interlock of the ordered, tetrahedrally-coordinated H_2O and the ZX_2 lattices. The ZX_2 dissolves into a Z^{2+} and $2X^-$ ions and each of them serves as a center source of electric field interacting with hydrating H_2O molecules and other solutes. Figure 5a inset illustrates the $2H_2O$ structural unit cell of four identical $O:H-O$ bonds for the solvent water. Figure 5b inset shows the proposed $2ZX_2$ unit cell for the solute. Solutes do not form any ionic or covalent bonds to the solvent molecules but each of them clusters, polarizes, and stretches the neighboring $O:H-O$ bonds. Ions are screened by their hydrating H_2O molecules to form the supersolid hydration volumes (inset of Figure 5c) – the hydration volumes are highly polarized, gel-like, thermally more stable associated with $H-O$ contraction and $O:H$ elongation [46].

The cations and anions form a tetrahedral unit, mimicking the $2H_2O$ cell with four identical $Z^{2+} \sim X^- \sim Z^{2+}$ interaction units through electrostatic force. The smaller Z^{2+} occupies the center and the vertices of the tetrahedron. Four larger X^- anions sitting at the midpoint between adjacent Z^{2+} cations. In the solute bonding network, the $Z^{2+} \leftrightarrow Z^{2+}$ and $X^- \leftrightarrow X^-$ repulsions coexist with the $Z^{2+} \sim X^-$ attraction but the interaction strengths will be subject to the solute concentration and the extent of the screen shielding by the hydrating H_2O dipoles. Compared with the YX solutions of the same concentration, there exist $2X^-$ and one Z^{2+} . The folded number of X^- and the high valence of Z^{2+} should stem the difference between the ZX_2/H_2O and the YX/H_2O solutions.

The ionic size, charge sign, charge quantity, electronegativity, ionic separation, and the screen shielding by hydrating H_2O determine the strength of the solute ionic electric field. Ionic electrification shortens and stiffens the $H-O$ bond associated always $O:H$ nonbond elongation and softening [46](see inset d). The $O:H-O$ segmental length, vibration frequency, and the phonon abundance transition in the DPS fingerprint directly the locally screened electronic field and the hydration volume size.

Once again, salt solvation shifts the $O:H$ and the $H-O$ phonon cooperatively without adding any vibrating features of new bond, as shown in Figure 5. The ZX_2 hydration stiffens the $H-O$ phonon and softens the $O:H$ phonon simultaneously without being able to discriminate the charge sign difference between the $2X^-$ and the Z^{2+} ions.

Figure 5. Raman spectra of the divalent (Ca, Mg, Sr)(Br, Cl)₂/H₂O solutions. Inset a shows the 2H₂O unit cell consisting of four O:H–O bonds. The small pairing dots stand for the nonbonding electron lone pairs “:” of oxygen. Inset b shows the 2ZX₂ geometry analogous the 2H₂O by taking off the “:”. Inset c illustrates the Z²⁺ and X⁻ hydration on and the screened polarization effects. Inset d shows polarization stretched O:H–O bond. Inset e denotes the stretching vibration frequencies of the O:H and the H–O bond (reprinted from permission of [91])

Figure 6. The H-O phonon DPS for the concentrated $\text{ZX}_2/\text{H}_2\text{O}$ solutions. Ions hydration transits the H-O bonds from the mode of deionized water centered at 3200 cm^{-1} to the hydration states at $\sim 3450 \text{ cm}^{-1}$. The valley at 3620 cm^{-1} features the skin preferential occupancy of anions that strengthen the H-O dangling bond and shield the signals of detection (reprinted from permission of [91])

The DPS for the concentrated $\text{ZX}_2/\text{H}_2\text{O}$ solutions shows the H-O phonon stiffness transition from 3200 cm^{-1} (the DPS valley) to $\sim 3450 \text{ cm}^{-1}$ (the DPS peak). The O:H nonbond responds to ionic polarization oppositely and shifts its phonon from $\sim 200 \text{ cm}^{-1}$ to $\sim 110 \text{ cm}^{-1}$ for the ZCl_2 and to ~ 100

cm^{-1} for the ZBr_2 solutions, instead of shifting to 75 cm^{-1} by YX monovalent salt solutions, which shows the weaker polarizability of the denser ZX_2 solutes than the YX. The second valley at 3620 cm^{-1} results from the stiffening of the dangling H–O bond featured at 3610 cm^{-1} by the stronger field of the X^- ions that occupy preferentially at the solution surface. However, the spectral signal of the dangling bond is annihilated by the anions during Raman detection. These features verify the effect of divalent salt on polarizing O:H–O bonds. In contrast, the monovalent YX solutes transit the H–O and phonons from (3200, 200) to (~ 3500 , 75) cm^{-1} . The local electric fields around the ions in the ZX_2 solutions is weaker because of the superposition of the repulsion between the like ions of shorter separations.

With the given that the $f_{\text{H}}(C) \cong 0$ [43] as the H^+ does not polarizes its surroundings but forms the $\text{H} \leftrightarrow \text{H}$ anti-HB, one has $f_{\text{X}}(C) \cong f_{\text{HX}}(C)$. The X^- anion performs the same as it does in the YX solutions to polarize neighboring HBs to form the supersolid hydration volume. Therefore, $f_{\text{Z}}(C) \cong f_{\text{ZX}_2}(C) - f_{\text{HX}}(2C)$. The $f_{\text{HX}}(2C) = f_{\text{X}_2}(C)$ stands for the folded number of X^- anions in the ZX_2 solutions. The $f_{\text{Z}}(C)$ and $f_{\text{X}_2}(C)$ can thus be separated from the $f_{\text{ZX}_2}(C)$ obtained by integrating the ω_{H} DPS peak.

Figure 7 compares the $f_{\text{ZX}_2}(C)$, $f_{\text{Z}}(C)$, and $f_{\text{X}_2}(C)$ for the concentrated ZX_2 solutions. The six $f_{\text{ZX}_2}(C)$ profiles grow in the exponential form toward saturation, as shown in Figure 7a, are categorized in three groups according to the solute valences. Results show the solute capabilities of O:H–O bond polarization follows: $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Br}^- > \text{Cl}^-$ Hofmeister series order. The $f_{\text{ZX}_2}(C)$ increases with the ion size and with the drop of electronegativity [ion($R/\text{\AA}$, η)[101]: $\text{Mg}^{2+}(0.78, 1.30)$, $\text{Ca}^{2+}(1.0, 1.06)$, $\text{Sr}^{2+}(1.27, 1.00)$; $\text{Cl}^-(1.81, 3.00)$, $\text{Br}^-(1.96, 2.80)$].

One can obtain the $f_{\text{X}_2}(C) = f_{\text{X}}(2C)$ from Figure 7a by converting the C into $C/2$ in the lateral axis. One can find from the $f_{\text{X}_2}(C)$ slope that the $\text{X}^- \leftrightarrow \text{X}^-$ repulsion keeps throughout the change of concentration because of the large X^- radius [46]. Number inadequacy of H_2O molecules in the highly-ordered hydration volume only partially screens the X^- ionic electric field, being consistent with the YX solutions.

Figure 7. The fraction coefficient of (a) $f_{ZX2}(C)$, $f_{HX}(C)$ [63], and (b) $f_Z(C)$. The slopes and curvatures of the $f(C)$ profiles feature the ionic hydration volume and its local electric field (reprinted from permission of [91])

As shown in Figure 7b, the $f_Z(C)$ shows a linear form at $C \leq 0.05$, and then follows the same $f_X(C) \propto 1 - \exp(-C/C_0)$ trend toward saturation. The subscript a and b denote the Z^{2+} in the respective $Z(Cl, Br)_2$ solutions. The critical molecular ratio $C = 0.05 = 1/20$ means that 20 H_2O molecules are shared by one set of $Z^{2+} + 2X^-$ solutes. At such a critical ratio or lower concentration, the hydrating H_2O

dipoles fully screen the Z^{2+} , and the $Z^{2+} \leftrightarrow Z^{2+}$ repulsion or the $Z^{2+}-X^-$ attraction is negligible. The $Z^{2+}-X^-$ attraction is annihilated by the $Z^{2+} \leftrightarrow Z^{2+}$ repulsion that becomes dominance.

Conversely, at higher concentration, the $Z^{2+} \leftrightarrow Z^{2+}$ repulsion presents because of their shorter distance and high valences. The absence of $Y^+ \leftrightarrow Y^+$ repulsion from the monovalent salt solutions suggests that the electric field of the Z^{2+} has a longer distance nature. The charge quantity difference between Z^{2+} and Y^+ and the folded number of $2X^-$ discriminate the performance of the divalent salt solutions from the monovalent salt of the same concentration.

3.4. Complex Na(SCN, NO₃, ClO₄, HSO₄) Solvation

To examine the complex NaT solute capability of HB transition, one needs to repeat the DPS and the contact angle iterations. Figure 8 compares the full-frequency Raman spectra for the NaT/H₂O solutions of different 0.016 molar concentration (T = SCN, NO₃, ClO₄, HSO₄). Except for the intra-anion bonding features, no solute-solvent bond vibration is resolved. The solvation shifts the H-O and O:H vibration frequencies in the similar manner of YI and NaX solutions.

Figure 8. (a) Full-scan and (b) enlarged region for the intra-anion bonding Raman spectra for the NaT/H₂O complex salt solutions (T = SCN, HSO₄, NO₃, ClO₄) (reprinted with copyright permission from [59])

Figure 9 shows the DPS processing derivatives on the segmented O:H-O bond relaxation. Ionic hydration transits a fraction of O:H-O bonds from the mode of deionized water into the hydrating, which shift the H-O and O:h phonons from (3200, 180) to (~3500, 75) cm⁻¹. The DPS also resolves

the anion preferential skin occupation [19, 59], which agrees with SFG measurements that shows the anisotropic ClO_4^- dipolar at the air/solution interface with twice polarizability tensor of the bulk water [104].

The phonon frequency shifts relax in the 0.010 ~ 0.082 concentration regime: NaClO_4 (3600→3550 cm^{-1}), NaNO_3 (retains 3520 cm^{-1}), NaHSO_4 (3500→3520 cm^{-1}), NaSCN (3500→3480 cm^{-1}). These observations suggest the stronger local electric field to relax the HBs, and on the other hand, the slower decrease of the electric because presence of stronger anion-anion repulsion at high concentrations. The larger anionic volume and surface charge density stem their high sensitivity to the solute concentration compared with the alkali halides.

Figure 9. Concentration dependence of the ω_H DPS for (a) NaT complex solutions. Solute polarization stiffens the H–O phonon and raises the structure order (FWHM). The shift from 3200 to 3500 cm^{-1} and above suggests the stronger local electric fields of anions. The molecular T^- anions show insignificant skin preferential occupation (reprinted with copyright permission from [59])

The DPS peak is the phonon abundance gain of the hydration volume from the bulk loss at lower frequencies. Being similar to alkali halides, complex ionic hydration shifts the (ω_H , ω_L) from (3200, 180) to (3500, 75) cm^{-1} .

Figure 10 compares the solute capability of bond transition and polarization of the concentrated NaT/H₂O solutions. Observations suggest the following:

- 1) The transition coefficient $f_T(C) \propto 1 - \exp(-C/C_0)$ not only varies with solute type but also increases with solute concentration toward saturation with bigger decay constants. The complex dipolar anions decay their electric fields in length faster than the monoatomic X^- ions because of their dipolar nature in the anisotropic charge distribution surrounding the complex anions, as illustrated in Figure 8 insets.
- 2) The saturation constant $C_0 \sim 5.6 - 37.2$ (Figure 10a) for the Na-based complex salt in contrasting to those of X^- in NaX (Figure 3a, $C_0 = 0.11-0.25$) and of Y^+ in YI (Figure 4f, $C_0 = 0.06-0.12$) solutions. The larger C_0 of the $f_T(C)$ for the Na-based complex salt solutions approaches a linear dependence. A slower decay means the gradual increase of the anion-anion repulsion with the reduction of the inter-anion separation. The greater saturation constant means a weaker anion $\leftrightarrow$ anion repulsion and the shorter ionic electric field.
- 3) However, the greater H–O frequency shift up to 3500 cm^{-1} evidences the stronger polarizability. Molecular anions in the salt solutions have short-range yet stronger local electric fields, being identities of the typical dipolar anisotropy.
- 4) Complex salt salvation raises the surface stress and the polarizability of the Na-associated T^- ions are slightly weaker than those of NaX and YI because of the greater anion sizes and the dipolar shorter interaction lengths of the complex salt anions.
- 5) The concentration resolved ω_H shift is very sensitive to the type of the dipolar ions. However, the $f_T(C)$ performs contrastingly. The dual features mean that the anionic hydration volume varies slowly but the local electric field changes rapidly because of the larger anionic dipolar volume. On the other hand, the T^- molecular dipoles do not show skin occupation preference.

Therefore, considering the solute capability of O:H–O bond transition from the mode of deionized water to its hydrating in terms of the O:H–O bond stiffness, number fraction, structure order, electron polarization and their concentration and type dependence would be efficient. Consideration of the intermolecular nonbond interaction and intramolecular H–O bond cooperativity is necessary. Charge

injection by monatomic ions or molecular dipoles mediate the solution network and polarize electrons in different ways, which dictates the solution properties such as the surface stress, solution temperature, critical energies for phase transition through the intra- and intermolecular cooperative bond relaxation as pursued presently.

Figure 10. The fraction coefficient $f(C)$ for the (a) NaT and (b) T⁻ obtained by $f_{NaT} - f_{Na(in NaBr)}$ estimation and (c) the contact angle for the concentrated NaT/H₂O solutions on glass substrate. The longer C_0 for $f_T(C)$ suggests that the solute-solute interactions is rather weak. The NO₃⁻ and HSO₄⁻ anions is less than the Na⁺ capable of forming the hydration volume (reprinted with copyright permission from [59]).

3.5. Solute Capabilities

One has to consider two factors determining the hydration vome size and the HB stiffness in the volume: the $\Delta\omega_x(C)$ shift represent the bond stiffness and the $f(C)$ for the abundance. The following further explains the $f_X(C)$ and $f_Y(C)$. It has been intensively justified that $f_H(C) \cong 0$ [43]. One can thus derive $f_{HX}(C) - f_H(C) = f_X(C)$, which means that only the X⁻ polarizes its O:H–O bonds and transforms the H–

O phonon upon HX acid is solvated. As the X^- anion in the (H, Y)X solutions is assumed to perform the same. The $f_X(C)$ and $f_Y(C)$ vary with the ionic radius and electronegativity of the same kind of ions. The best fitting of the integrals, see Figure 11, confirms, $f_H(C) \cong 0$, $f_{Y,X}(C) = a[1-\exp(-C/C_0)]$ towards saturation, which would suffice to resolve the ionic capabilities of bond transition. Results in Figure 11 suggest the following:

- 1) The high $f_{YX}(C)$ value at each concentration is a superposition of the Y^+ and the X^- polarizability, and thus $f_X(C) \cong f_{HX}(C)$, and $f_Y(C) \cong f_{YX}(C) - f_{HX}(C)$.
- 2) The quasi-linear $f_Y(C)$ increases and then surpasses the $f_X(C)$ at a certain point of concentration. The constant $f_Y(C)$ slope means that the number of bonds per solute conserves in the hydration volume. The H_2O dipoles in its hydration shells fully-screen the electric field of a small Y^+ cation. Thus, a cation does not interact with any kind of solutes in the Y^+ involved solutions.
- 3) The exponential $f_X(C) \propto 1-\exp(-C/C_0)$ form toward saturation indicates that the inadequate number of H_2O molecules in the hydration volume only partly screens the large X^- because of the geometric limitation to H_2O molecules packed in the hydration volume, which proves the highly ordered solvent molecular structures. The anion solute can thus interact with their alike – only anion-anion repulsion exists in the X^- - involved solutions with a weaker and longer electric field. Therefore, the $f_X(C)$ increases gradually approaching to saturation, the hydration volume turns to be smaller, which limits the X^- solute capability of bond transition.
- 4) Ions ($Z^{2+} + 2X^-$) in divalent salt solutions perform differently from YX monovalent because of the Z^{2+} charge quantity and the folded number of the $2X^-$. The $2X^-$ shows stronger repulsion because of its high density. The Z^{2+} also shows slight repulsion at high concentrations.
- 5) In contrast, the hydration volume of the complex molecular anions retain their sizes. The local electric field of the molecular anions is stronger, but the length of interaction is shorter, showing the nature of dipolar electric field – shorter yet anisotropic.

Table 1 summarizes the discriminative ionic capabilities on the performance of their respective solutions.

Table 1. Ionic discriminative functionalities on the HB transition and solution properties variation.

solution		fraction coefficient	formulation	functionality
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HX [63, 64]	$H \leftrightarrow H$ pointer breaker and Y^+ polarizer	$f_H(3500)$	0	H_3O^+ formation and $H \leftrightarrow H$ repulsion
		$f_{OH}(<3100)$	$>\approx 0$	$H \leftrightarrow H$ repulsion elongated solvent H–O bond (mechanical compression [11, 105])
		$f_{HX} = f_X(3500)$	$a[1-\exp(-C/C_0)]$ shorter C_0 for X	X^- hydration volume reduction and constant ω_H shift due to solute field shielding
YX [19, 61, 62]	ionic polarizers	$f_{YX} - f_{HX} = f_Y(3500)$	stable ω_H	constant Y^+ hydration volume Resolvable surface stress
NaT [59]		$f_Y \propto C$ (~ 3500)	longer C_0 ω_H reverse shift	Z^- molecular dipolar anions; shorter yet stronger electric field
(Mg, Ca, Sr)(Cl, Br) ₂ [91]		$f_Y = C$ (< 0.05 and then exponential)	3450; 100 cm ⁻¹)	$Sr^{2+} > Ca^{2+} > Mg^{2+}$; $Br^- > Cl^-$

Figure 11. Comparison of the ionic $f_{YX}(C)$ for (a) NaI/H₂O, (b) NaBr/H₂O, and (c) KCl/H₂O solutions and their respective decomposition. The concentration dependent (d) contact angles for HX acidic, YOH basic, and YX salt solutions (reprinted with permission from [19, 63, 106]).

4. Supersolid Hydration Shells

4.1. O:H–O Segmental Length, Energy and Stiffness

Salt solvation results in $\Delta d_H < 0$, $\Delta d_L > 0$, $\Delta \omega_H > \Delta E_H > 0$, and $\Delta \omega_L < \Delta E_L < 0$ for a fraction of O:H–O bonds by ionic polarization with respect to the ordinary bulk water. The ω_x peak shifts give rise immediate information of the segmental length and energy when calibrated against the known bulk and skin features at different temperatures [2]. One can estimate the segmental length and energy with a certain tolerance for the HBs in hydration shells of the aqueous solutions [63].

Table 2 O:H–O bond identities in the neat water and in the YX salt solutions. ^{a,b}

	H ₂ O (277 K)	H ₂ O (skin)	Ionic hydration volume
ω_L (cm ⁻¹)*	200	75	65-90
ω_H (0.022)	3150	3450	≥ 3500
ω_H (0.059)	-	-	≥ 3500
d_L (Å)	1.70	2.0757	≥ 2.0
d_H (Å)	1.00	0.8893	≤ 0.89
E_L (meV)	95	59	≤ 59
E_H (eV)	3.98	4.97	≥ 4.43
O–O (Å)	2.695[2]	2.965	≥ 2.965

^a change with respect to the ordinary bulk water.

^b all examined cases show the electrification effect on the O:H–O elongation with slight difference of the extent.

* Subject to polarization and fluctuation. Polarization raises the ω_L slightly upward and fluctuation widens the peak.

Table 2 lists the basic information about H–O and O:H bond lengths, energies, vibration frequencies in the bulk water and in the supersolid skin and ionic hydration volume. The relaxation trend of segmental length, phonon frequency, cohesive energy, and polarization would suffice to accounting for the functional activities of the solutions, including the solubility, surface stress, viscosity, and the critical temperatures for phase transition.

4.2. Thermal XAS and DPS: H–O Bond Stability

Figure 12 compares the thermal NEXAFS spectra for bulk water and 5M LiCl solutions. Thermal heating shifts the pre-edge peak for the liquid water negatively faster than that for the LiCl solutions, which is suggested as the O:H undergoes thermal elongation at different rates for the deionized water and LiCl solutions [107]. At 25 °C, the cation effect on the pre-edge shift from the value of 534.67 eV to deeper in alkali chlorides is remarkable: Li^+ (0.27 eV), Na^+ (0.09 eV), and K^+ (0.00 eV). The energy shift of Li^+ in the 5 M LiCl solution (0.30 eV) is close to that happened to the 3 M LiCl/H₂O solution. On the other hand, in the NaCl solution, the anion effect is small: Cl^- (0.09 eV), Br^- (0.04 eV), and I^- (0.02 eV). The energy trend of the pre-edge shifts is the same as the DPS ω_{H} shifting positively for the solutions and the skin of water [108].

Density functional theory calculations revealed that within the first hydration shell of an I^- anion, the I:H distance is about 40% longer and the H–O is some ~1% shorter than the O:H and H–O respectively in bulk water. However, in the subsequent hydration shell the H–O is 0.9% shorter while the O:H is 29% longer [59]. The (Li, Na, K):O distances are (1.99, 2.37, 2.69) Å derived from molecular dynamics calculations [107] and (1.9, 2.34, 2.65) Å from neutron diffraction [78, 107, 109] compared to 1.70 Å for O:H in 4 °C water. The X⁻ - O distance in the (Cl⁻, Br⁻, I⁻)-H–O configuration are (3.26, 3.30, 3.58 compared to the O–O distance of 2.70 in 4 °C water) Å. The phonon frequencies (ω_{H} , ω_{L}) shift from (3200, 200) to (3450, 75-120) cm⁻¹.

The contributions from the Li:O polarization or the O:H binding energy are negligibly small. At polarization, the H–O bond becomes shorter and stiffer, the stiffer H–O bond is thermally more stable than those in the bulk of deionized water, as it does in the water skin [108].

Figure 13 compares the XAS pre-edge thermal shift for the bulk water and the supersolid hydrating water in the Li^+ hydration shell and the Raman H–O phonon thermal shift for the concentrated

KCl/H₂O solutions encapsulated in a silica capillary tube [110]. The XAS peak of the hydration oxygen shifts negatively slower than it is in the bulk water. The Raman peak 1 at 3200 cm⁻¹ corresponds to the ω_H for ordinary bulk water and peak 2 at 3450 cm⁻¹ to the skin ω_H mode. At the ambient temperature, ionic polarization shifts the 3200 cm⁻¹ up to overlapping the 3450 cm⁻¹. Heating and polarization enhance each other to shorten and stiffen the H–O bond at different rates, depending on the solute concentration. In the liquid phase below 373 K, the ω_H shifts with temperature and more with the solute concentration. The ω_H shifts further as the temperature increases, but the increasing rate reverts with solute concentration. At 373 K and above, the liquid partially becomes vapor up to the saturation pressure of 100 MPa. The thermal reversion of the ω_H shift between 373 and 473 K shows that the hydrating H–O bonds are thermally more stable than that of the deionized water in liquid and vapor phases. The polarization distorted H–O bonds are hardly further deformed.

Figure 12. Temperature resolved XAS for bulk water and 5M LiCl solutions. Broken lines are references collected at 25 °C. Insets show the structures of pure water and the hydrating molecules and the pre-edge negative shift due to H–O thermal contraction dominance (reprinted with permission from [107])

Figure 13. Thermal stability of the supersolid (a) Li⁺ hydrating volume probed using NEXAFS [107] and (b) the H–O components of concentrated KCl/H₂O solutions probed using Raman spectroscopy [108]. The $E_{\text{edge}}(T)$ for the O in the supersolid hydration volume shifts negatively less than that in the bulk water. The thermal reversion at 373–473 K further proves the thermal stability of the supersolid hydrating H–O bonds (reprinted with permission from [107, 110])

4.3. Solution XAS: Polarization Dominance

Figure 14 compares the XAS for the concentrated LiCl/H₂O, 3M YCl/H₂O and NaX/H₂O solutions. Salt solvation shifts the pre-edge peak to the positive direction in contrasting to the effect of heating that shifts the peak in the negative direction. It appeared conflicting that heating and ionic polarization share the same effect of H–O bond contraction. Bond contraction dictates the energy shift of all the core level and valence band [99], as the O:H binding energy contributes insignificantly to the energy level shift.

To clarify the inconsistency of pre-edge peak shift induced by heating and ionic polarization, one must consider the competition between H–O bond contraction and electrostatic polarization on the energy level shift [99]. Firstly, electrons transiting from O 1s (K) level to the upper edge (the occupied 4a₁ orbital) of the valence band absorbs energy equals to the XAS pre-edge peak energy, E_{edge} . Secondly, separation between the energy shifts of the valence band and the O 1s level from

their respective energy level of an isolated O atom determines the XAS pre-edge shift, $\Delta E_{\text{edge}} = \Delta E_{1s} - \Delta E_{\text{vb}}$. Thirdly, the involved energy levels undergo positive shift because of the addition of the local crystal potential to the intra-atomic potential, which is proportional to the binding energy of bond in the first coordination neighbors, according to the tight-binding approximation [111]. A contraction of the neighboring bonds shifts the energy levels further – deepens the energy levels further - quantum entrapment occurs [99]. The amount of energy shift varies from level to level because of the screening of the potential by electrons in the outer orbitals. Therefore, the energy of the valence band composed of electrons in the outermost orbital shifts more than an inner energy level. One has thus, $\Delta E_{\text{vb}} > \Delta E_{1s}$, and $\Delta E_{\text{edge}} = \Delta E_{1s} - \Delta E_{\text{vb}} < 0$, negative shift due to bond contraction.

On the other hand, electrostatic polarization changes the situation contrastingly. Charge polarization screens and splits the local potential and then shifts a proportion of electrons up in energy bands causing their negative shift, then, $-\Delta E_{\text{vb}} > -\Delta E_{1s}$, and thus $\Delta E_{\text{edge}} = \Delta E_{1s} - \Delta E_{\text{vb}} > 0$, positive shift takes place due to the polarization. In fact, bond contraction by molecular undercoordination or salt solvation is associated with polarization. Therefore, H–O bond thermal contraction without polarization results in the pre-edge energy negative shift. For the salt solution, ionic polarization becomes dominance, which overweight the effect of H–O bond contraction on the binding energy shift. The polarization shifts the energy levels up and thus, $\Delta E_{\text{edge}} = \Delta E_{1s} - \Delta E_{\text{vb}} > 0$. Therefore, the XAS pre-edge shift is very sensitive to the local energetic environment, being capable of discriminating the effect of entrapment by bond contraction and charge polarization. If the entrapment and polarization is compatible, no shift will occur to the XAS pre-edge energy peak.

Figure 14. O NEXAFS spectra of 3M (a) YCl (Y = Li, Na, K), (b) NaX (X = Cl, Br, I), and (c) the concentrated LiCl solutions collected at 25 °C. Insets show magnification of the pre-edge positive shift due to polarization dominance (Reprinted with permission from [39, 107])

4.4. XAS Capability: Entrapment and Polarization

The consistency between Raman and XAS observations confirmed the thermal stability of the supersolid hydration volume and clarifies the origins of the pre-edge energy shift due to competition between thermal H–O bond contraction and charge polarization. Observations verified the following:

- 1) The XAS pre-edge shift features the energy difference between the O 1s core level shift ΔE_{1s} and its valence band shift ΔE_{vb} from their energy levels of an isolated O atom: $\Delta E_{edge} = \Delta E_{1s} - \Delta E_{vb} < 0$ [92] when the H–O contraction, $\Delta E_H > 0$, is dominant [99]. In contrasting, $\Delta E_{edge} = \Delta E_{1s} - \Delta E_{vb} > 0$ when polarization becomes dominant, as polarization shifts all energy levels upwardly. Competition between H–O bond contraction and polarization dictates the pre-edge energy shift that is in a contrasting manner of the XPS O 1s level shift.
- 2) The H–O bond undergoes energy gain in liquid water heating [62], skin molecular undercoordination [92], and polarization [44]. The shortened H–O bonds are thermally and mechanically more stable because the stiffened bonds are less sensitive to perturbation. It is harder to further deform an already deformed H–O bond by stimulations such as heating in the present case: $(d|E_H|/dT)_{supersolid}/(d|E_H|/dT)_{regular} < 1$ and $(d\omega_H/dT)_{supersolid}/(d\omega_H/dT)_{regular} < 1$.
- 3) The QS phase upper boundary is at 4 °C for regular water and it seems at 25 °C for the supersolid states according to the slopes of the XAS profile in Figure 13. The supersolidity disperses outwardly the QS phase. Outside the QS phase, O:H–O bond follows the regular thermodynamics: $dd_L/dT > 0$, $dd_H/dT < 0$.
- 4) The local electric field of a small cation is stronger than that of a larger anion because of the $X^- \leftrightarrow X^-$ repulsion due to the insufficient number of the hydrating dipoles with the ordered molecular structure of the supersolid hydration shells [46].

5. Solution Property Modification

5.1 Diffusivity, Viscosity, and HB Polarizability

In aqueous solutions, solute and molecules drift randomly under thermal fluctuation by collision, which varies with the viscosity of the solution. Stokes-Einstein diffusivity $D(\eta, R, T)$ [71], Jones–Dale viscosity $\eta(C)$ [72], and the fraction coefficient $f(C)$ for O:H–O bonds transition from the mode of water to hydrating are correlated as follows.

$$\left\{ \begin{array}{ll} \frac{D(\eta, R, T)}{D_0} &= \frac{k_B T}{6\pi\eta R} \quad (\text{Stokes} - \text{Einstein}) \\ \frac{\Delta\eta(C)}{\eta(0)} &= A\sqrt{C} + BC \quad (\text{Jones} - \text{Dale}) \\ f(C) &= a[1 - \exp(-C/C_0)] \quad (\text{Fraction} - \text{HB} - \text{transition}) \end{array} \right. .$$

The diffusivity depends on the viscosity η , temperature T , and drifting particle size R . H–O phonon relaxation time increases with the viscosity and the molecular diffusivity according to convention. One can adjust the prefactors A and B of the viscosity to match the $f(C)$ for bond transition in salt solutions to clarify their origins.

Salts solute overdosing endows both the relative viscosity and the $f_{YX}(C)$ with a negative curvature towards saturation because of the contribution of anion-anion repulsion. It is true that the viscosity and surface stress of the monovalent salt solutions arise from ionic polarization represented by $f_{YX}(C)$. The $f_Y(C) \propto C$ and the $f_X(C) \propto 1 - \exp(-C/C_0)$ contribute to the linear and nonlinear part of the Jones-Dale notion. The $f_X(C) \propto 1 - \exp(-C/C_0)$ is a superposition of the anion-solvent and anion-anion interactions.

SFG measurements [75, 76] confirmed that the SCN^- and CO_2 solution viscosity increases with solute concentration or the cooling rate of solution. Thus, one can reconcile quantitatively the number of bond transition, surface stress, solution viscosity, hydration-shell supersolidity, H–O phonon frequency, H–O phonon lifetime, molecular drift diffusivity, and phase boundary dispersivity, consistently by ionic polarization to shorten and stiffens the H–O bond and lengthen and soften the O:H nonbond.

Figure 15 shows correlation between the Jones–Dale viscosity and the fraction coefficient $f_{YX}(C)$ for the concentrated (a) $\text{Na}(\text{I}, \text{Cl})/\text{H}_2\text{O}$ [19], (b) $\text{LiBr}/\text{H}_2\text{O}$ [46], (c) $\text{LiCl}/\text{H}_2\text{O}$ [112], and (d) $\text{HCl}/\text{H}_2\text{O}$ acidic [112] solutions. Inset b shows that the $\text{LiBr}/\text{H}_2\text{O}$ surface stress follows the same $f_{\text{LiBr}}(C)$ exponential trend of the relative viscosity with different coefficients because of the molecular undercoordination effect that enhances the ionic polarization.

However, the viscosity of (H, Li)Cl solutions shows the same increasing trend of $f_{XY}(C)$ for O:H–O polarization [112] or Jones-Dale expression though HCl solvation depresses the surface stress of an acidic solution, indicating different origins. The $H \leftrightarrow H$ fragilization disrupts the surface stress but the Cl^- polarization and the $H \leftrightarrow H$ and $Cl^- \leftrightarrow Cl^-$ repulsions raise the viscosity of an acidic solution.

Figure 15. Correlation between the Jones–Dale relative viscosity and the fraction coefficient $f_{YX}(C)$ for the concentrated (a) Na(I, Cl)/H₂O [19], (b) LiBr/H₂O [46], (c) LiCl/H₂O [112], and (d) HCl/H₂O [112] solutions. Inset b shows that the LiBr/H₂O surface stress follows the same $f_{LiBr}(C)$ exponential trend of the relative viscosity with different coefficients.

In contrast, as shown in Figure 16, the viscosities of the LiOH basic solutions, the complex (Na, Li)ClO₄ and the divalent ZX_2 ($Z = Mg, Ca, Sr, X = Cl, Br$) solutions do not follow the negatively curvature saturation for the $f_{YX}(C)$ [59] or the Jones-Dale description. The $O \leftrightarrow O$ strong repulsion derives the much greater viscosity with $d^2\eta/dC^2 > 0$ for LiOH basic solutions [112]. This unexpected concentration trend of viscosity elevation is consistent to those of the divalent (Ma, Ca, Cs)(Cl, Br)₂ solutions [91, 113] and the (Li, Na)ClO₄ [74] solutions.

Figure 16. Viscosity of the concentrated (a) LiOH/H₂O [112], (b) complex (Li, Na)ClO₄/H₂O[74], and (c, d) divalent (Mg, Ca, Sr)(Cl, Br)₂/H₂O [91, 113] solutions disobey the $f_{YX}(C)$ or Jones-Dale description because of the ionic polarization and solute-solute repulsion.

The divalent (Mg, Ca, Sr)(Cl, Br)₂ salts dissolve into the Z^{2+} and $2X^-$ ions at the same concentration of the monovalent YX salt. The folded $2X^-$ anionic density and the stronger divalent Y^{2+} electric field drive the high viscosity. The viscosity $[\ln(\eta/\eta_0)]^{-1} - 1/C$ profiles for the (Mg, Ca, Sr) (Cl, Br)₂ solutions could be simulated using two C_0 values of 0.08 and 0.05 at 0.01 molar concentration. The viscosity of (Li, Na)ClO₄ solutions follows closely the trend of the CaCl₂ solutions. The folded $2X^-$ concentration and the large amount Y^{2+} charge lead to the $X^- \leftrightarrow X^-$ and $Y^{2+} \leftrightarrow Y^{2+}$ repulsions that are absent from the monovalent salt solutions. These shorter and stronger interactions could be the origin of the viscosities disobeying Jones–Dale notion or the $f_{ZX_2}(C)$.

Therefore, the mechanisms of solution viscosity and surface stress are different. Ionic polarization and $H \leftrightarrow H$ fragilization govern the surface stress yet the ionic polarization and anion-anion repulsion dictate the solution viscosity.

5.2 Solution Electrical Conductivity

Figure 17 compares the electric conductivity for the concentrated (H, Li)Cl and LiOH solutions [112]. The conductivity follows the respective $f(C)$ trends. The solution conductivity is in the $\sigma_{\text{HCl}} > \sigma_{\text{LiOH}} > \sigma_{\text{LiCl}}$ order at higher concentrations. However, the $\sigma(C)$ of the LiOH solution does not follow its $f(C) \propto C$ fashion [43] or the Jones-Dale description. Ions and their hydration volume may serve as carriers for the current flow that is subject to scattering as an added mechanism of transporting. $\text{H} \leftrightarrow \text{H}$ and $\text{O} \leftrightarrow \text{O}$ fragmentation of the hydration volumes shall ease the transportation. Further investigation under variation of the measuring electric field would derive the carrier mobility in solutions.

Figure 17. Electric conductivity of the concentrated (H, Li)Cl and LiOH aqueous solutions follow the $f(C)$ coefficient or the viscosity of Jones-Dale (reprinted with permission from [112])

Figure 18 compares the conductivity $\sigma_{\text{YX}_2}(C)$ and surface stress (contact angle $\theta_{\text{YX}_2}(C)$) for the divalent ZX_2 solutions. The $\sigma_{\text{YX}_2}(C)$ and $\theta_{\text{YX}_2}(C)$ share the similar manner of $f_{\text{YX}_2}(C)$ exponential saturation toward high solute concentration. These identities follow the same: $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Br}^- > \text{Cl}^-$ Hofmeister series order. These concentration trend consistency evidences their common origin of solute polarization. The $\sigma_{\text{YX}_2}(C)$ drops at higher solute concentration as the thicker solutions may be subject to lower carrier mobility because of the strong localization in the supersolid hydration volume.

Figure 18. Solute concentration and solute type resolved (a) solution conductivity and (b) contact angles for the ZX_2 solutions follow the same trend of exponential decay of the fraction coefficient toward saturation and the $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Br}^- > \text{Cl}^-$ Hofmeister capability order. The conductivity disruption at higher concentrations suggests that thicker supersolid solution depresses the carrier mobility (reprinted from permission of [91])

5.3 QS Boundary Dispersion

One of the important phenomena of salt solvation is that solvation melts snow by lowering the freezing temperature T_N of the snow. The ΔT_N drops with the increase of NaCl or CaCl_2 concentration in their solutions. The effect of CaCl_2 solvation into the $\text{Ca}^{2+} + 2\text{Cl}^-$ three-body solutes is more pronounced than the NaCl transition into the $\text{Na}^+ + \text{Cl}^-$ two-body on depressing the T_N that follows the $1 - \exp(C/C_0)$ manner [44].

Why does the ionic hydration depress the T_N of the solution?

Figure 19 defines the T_N and T_m by a superposition of the O:H–O segmental specific heat curves [65]. The characteristics of a specific heat curve is its thermal integral over the full temperature range and its Debye temperature Θ_{Dx} [2]. The $\Theta_{Dx} \propto \omega_x \propto (E/d^2)_x^{1/2}$ determines the saturation rate and the integral corresponds to the segmental cohesive energy E_x . According to Einstein relation, $\Theta_{Dx} \propto \omega_x$, the $(\Theta_{Dx}, \omega_x) = (198 \text{ K}, 200 \text{ cm}^{-1})_{x=L}$ and $(\sim 3000 \text{ K}, 3200 \text{ cm}^{-1})_{x=H}$. The superposition of the two specific heats derives two intersections that correspond to the temperatures of extreme densities. For the deionized water, they are valued at $(4^\circ \text{C}, 1.0 \text{ g cm}^{-3})$ and $(-15^\circ \text{C}, 0.92 \text{ g cm}^{-3})$, which matches closely the critical temperatures for melting T_m and homogeneous ice nucleation, T_N [2]. Water

undergoes liquid-ice phase transition and turns its density from the highest to the lowest by passing through the quasisolid (QS or quasiliquid) phase. The QS boundaries remain no constant but change with external stimulations such as compression [114], molecular undercoordination [115-117], salting [11, 118], electric polarization [18], etc.

Figure 19. Definition of the QS boundary by O:H–O segmental specific heats superposition that resolves the phase diagram under ambient pressure of the Liquid, Quasisolid (QS), I_{h+c} and XI phases. The intersections correspond to the density extreme at 277 K and 258 K as the QS boundaries, which are close the melting (T_m) and homogeneous ice nucleation (T_N) temperature. Ionic polarization by salt solvation disperses the QS boundaries outwardly (broken lines) by (reprinted with permission from [65])

The specific heat superposition specifies five phases having different specific heat η_H/η_L ratios: Ice XI ($\eta_H \approx \eta_L \approx 0$), solid I_{h+c} ($\eta_H/\eta_L > 1$), quasisolid (QS, $\eta_H/\eta_L < 1$), liquid ($\eta_H/\eta_L > 1$), and Vapor ($\eta_H > 0$, $\eta_L \approx 0$), determining the O:H–O bond thermal relaxation dynamics. The segment of a lower η_x value undergoes the regular thermal expansion, but the other part relaxes oppositely when the specimen is heated. The O:H always relaxes more than the H–O does. In the liquid and solid phases, $\eta_H/\eta_L > 1$, O:H contracts more than H–O expands at cooling, volume expands. In the QS phase, H–O contracts less than O:H expansion at cooling so ice floating takes place [65]. Little O:H–O frequency change of ice XI [119, 120] has been resolved below 100 K as both specific heat curves approach zero – the O:H and the H–O respond not to thermal excitation [65].

The phase boundaries change with the Θ_{Dx} that is proportional to the ω_x of the characteristic phonon. Therefore, supercooling or T_N depression and superheating or T_m elevation happen under a perturbation. From the dimensionality wise, a certain kind of energy determines the critical temperature for phase transition. As demonstrated, the T_m is proportional to the H–O energy and the T_N to the O:H energy through the relationship, $\Theta_{Dx} \propto \omega_x \propto (E/d^2)_x^{1/2}$ [70]. One may tune the T_m and T_N by adjusting the O:H–O segmental length and energy through perturbation.

As salt solvation shifts the vibration frequencies and the Debye temperatures (ω_H, ω_L ; Θ_{DL}, Θ_{DH}) from (3200 cm⁻¹, 200 cm⁻¹; 192 K, ~3000 K) to (3500 cm⁻¹, 75 cm⁻¹; 80 K, ~3400K). On the other hand, salt solvation relaxes the H–O bond and O:H nonbond length (d_H, d_L) from (1.0 Å, 1.70) to some (0.95, 1.95) Å and change the bond energy (E_H, E_L) from (4.0, 0.1) to (>4.0, <0.1)) eV. These happenings depress the T_N and raises the T_m , and thus the salted snow defreeze from Solid to the gel-like QS at some -20 °C or lower.

Precisely, salt anti-icing is the process of T_N , rather than T_m , depression. Salt solvation raises the T_m instead. However, mechanical compression does contrastingly to disperse the QS raise boundary inwardly to raise the T_N but lower the T_m , the well-known phenomenon of Regelation – ice melts by compression and freezes again when the pressure is relieved [70]. The anti-icing also happens to the molecular undercoordination at the water skin or water at the hydrophobic interface [117].

5.4 Hydrating H₂O Numbers

According to the present understanding, ions in electrolyte solutions polarize their surrounding H₂O molecules to form each a supersolid hydration volume. The hydration volume may have multiple shells and leave some molecules free from being polarized. H₂O molecules in a solution can thus be categorized into groups of hydrating and free in a dilute solution. The hydrating ones within the hydration volume freeze at a lower temperature than those free [18]. This principle allows Wang and co-workers [121] to discriminate, for the first time, the number of free molecules (n_f) from the hydrating ones (n_h) in an aqueous solution consisting of $n = n_h + n_f$ number of H₂O molecules as follows:

Mass concentration of aqueous solute: $W_m/(W_m + n \times 18)$

Mass concentration of hydrated solute: $(W_m + n_h \times 18)/(W_m + n \times 18)$

The aqueous solution is expressed as $M \cdot nH_2O$ with M and n being the respective number of solutes and solvent molecules. W_m is the molar mass of the solute. One can tune the n_h by matching the universal $T_H - C$ curve for a referential specimen of known n_H value. One can determine the n_H from measurement in the phase precipitation of the free from the hydrating water by cooling. The free water freezes first and then leave the rest hydrating molecules to crystalize at even lower temperatures. One can separate the remaining solution from the ice of free water before the second freezing occurs and then to elucidate the n_H value. By doing so, $n_H = 10$ was derived for the $CaCl_2$ ($Ca^{2+} + 2Cl^-$) solutes, which means that one $CaCl_2$ molecule has ten H_2O molecules hydrating the $CaCl_2$ at saturation. With the known $n_h = 10$ reference, one can then calibrate $n_h = 5$ from the $T_H - C$ curves for a $NaCl$ ($Na^+ + Cl^-$) solute instance [121]. Table 3 and Figure 20 show the hydrating H_2O molecular numbers per solute derived using phase precipitation approach.

Figure 20. The (a) mass concentration $W_m/(W_m + n \times 18)$ and (b) the calibrate $(W_m + n_h \times 18)/(W_m + n \times 18)$ T_H for various electrolyte solutions [122-134]. For the mixed solutions, the composition is specified with the weight percentage of the minor solute (reprinted with permission from [121]).

Figure 20 shows the T_H variation of the aqueous solutions and the hydrated solute concentration of a collection of electrolyte solutions with a derivative of the n_H values. The T_H were obtained by measuring emulsified samples of $1 \sim 10 \mu m$ in diameter.

The T_H depression by ionic hydration is within the expectation of QS boundary dispersion by polarization. According to the present O:H–O cooperativity notion, dissolved ions polarize water molecules to form each a hydration volume of supersolidity associated with T_m elevation and T_H depression [44] because of the QS boundaries dispersion by electrostatic polarization. The T_H variation reflects the local electric field that determines the O:H–O segmental energy and vibration frequencies.

Table 3 Hydrating H₂O molecular numbers per electrolyte solute (reprinted with permission from [121], Supplementary Information)

Solute	Hydration number, n_h
LiCl	6
CaCl ₂	10
Ca(NO ₃) ₂	7
MgCl ₂	12
ZnCl ₂	7
MgCl ₂ +ZnCl ₂ (1:1)	16.4
MnCl ₂	9
Mn(NO ₃) ₂	11.7
CrCl ₃	17
Cr(NO ₃) ₃	13.8
AlCl ₃	19
FeCl ₃	15
Fe(NO ₃) ₃	15.8
Glycerol	1.5
Dimethyl sulfoxide	3.0
Ethylene glycol	1.0
1,2,4-butanetriol	1.9
PEG300	6.8
H ₂ SO ₄	6.9
HNO ₃	4.1
H ₂ O ₂	2.0

5.5 Effective Hydrating Number of H₂O Dipoles

The division of the $f_Y(C)$ and $f_X(C)$ by the solute concentration C corresponds to the number of H–O bonds per ion (n_h/ion) in the first hydration subshell, which characterizes the ionic hydration volume and its local electric field. The derived n_h/ion may under-estimate the real value as the DPS distills only H–O bonds subjecting to strongest electric field. Those H–O bonds initially deformed by skin molecular undercoordination can hardly be further deformed by the polarization [44]. However, the derived n_h/ion values show us their concentration trends and contrast across their relative hydration volume sizes.

One can derive the hydrating number of H–O Bonds $n_H(C)$ per ion by a division of the DPS profiles, $f(C)/C$, for X^- in HX acid solutions (Figure 3b), Na^+ in NaX (Figure 3) [19], (K^+ , Rb^+ , Cs^+ in YI (Figure 4e)[103], and the $n_H(C)$ per complex solute in the divalent ZX_2 (Figure 7a) [91], and NaT solutions (Figure 10a) [59]. Figure 21 and Figure 22 show the corresponding results.

If fully screened by the hydrating dipoles, the ion will keep its hydration volume constant, otherwise, the shell size varies depending on the inter-solute interactions. Adjacent counterionic attraction enhances the local electric field to enlarges the hydration shell, otherwise, like ionic repulsion does it contrastingly. Therefore, the screened ionic polarization and the solute-solute interaction govern the performance of a concentrated solution through ionic hydration shell size modulation. The quasilinear $f_Y(C) = f_{YX}(C) - f_X(C) \cong bC$ for the concentrated $\text{YCl}/\text{H}_2\text{O}$ and $\text{YI}/\text{H}_2\text{O}$ solutions indicates that the Y^+ has a constant hydration volume whose size varies insignificantly with solute concentration and slightly with its counterions, as shown in Figure 21a. However, the X^- capability of H–O bonds transition follows the $f_X(C) = a[1 - \exp(-C/C_0)]$ manner toward saturation, arising from the dominance of anion-anion repulsion at higher concentrations. The $n_H(C) = f_X(C)/C$ per anion drops with the separation between adjacent anions. The insufficiency number of the ordered H₂O dipoles in the hydration volume only partly screens the anionic potential.

Figure 21. The effective number $n_h(C)$ of (a) the first vicinal HBs per cation and (b) the concentration dependence of the $n_h(C)$ for X^- in $\text{HX}/\text{H}_2\text{O}$ [43] solutions. (reprinted with permission from [135])

For the ternary ZX_2 and complex binary NaT counterions in the divalent salt solutions [91], we need one more condition to discriminate the hydration volume of Z^{2+} from that of the $2X^-$. The $2X^-$ may not perform the same in the divalent solution and the Z^{2+} will be different from the Y^+ because of the solute density and charge quantity difference. However, we can estimate the $n_h(C)$ per set of $Z^{2+} + 2X^-$ for reference. Results in Figure 22 show the $\text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Br}^- > \text{Cl}^-$ Hofmeister hydration volume size order. For the complex NaT salt solutions [59], the $n_h(C)$ drops slightly with solute separation and the $\text{Na}(\text{ClO}_4, \text{SCN})$ have larger hydration volume than the $\text{Na}(\text{NO}_3, \text{SO}_4)$ solutes. The dipolar T^- with short yet stronger electric field and the high Z^{2+} charge quantity and $2X^-$ density differentiate the $n_h(C)$ trend for the binary NaT and the ZX_2 ternary counterions

Figure 22. Concentration resolved $n_h(C)$ per solute for (a) NaT binary solute and (b) NaX_2 ternary counterions (reprinted with permission from [135]).

6. Perspectives

A combination of the framework of O:H–O bond cooperativity and ionic hydration, the ZPS and XAS spectroscopies, and the conductivity, surface stress and viscosity detection, has enabled discrimination of the functionalities of typical Hofmeister ions. Examination of the YX alkali halides, the ZX₂ divalent salts, and the Na-based complex salt solvation bonding dynamics has led to the following knowledge (Y = Li, Na, K, Rb, Cs; X = F, Cl, Br, I; Z = Mg, Ca, Ba, Sr; T = ClO₄, NO₃, HSO₄, SCN):

- 1) Water dissolves salt into the smaller Y⁺ and Z²⁺ cations and larger X⁻ and molecular T⁻ anions of different charge, polarity, and size and shapes. Each of the ions serves as a point, or a dipolar polarizer that aligns, clusters, polarizes, and stretches the surrounding O:H–O bonds to form the supersolid hydration volume. X⁻ anions show preference of skin occupation while the Y⁺, Z²⁺, and the dipolar T⁻ do it insignificantly. The T⁻ molecular solute shows the shorter and stronger field of a dipole.
- 2) Salt solvation relaxes the hydrogen bonding network through the ionic screened polarization, solute-solute interaction, without direct bond forming between the solute ions and solvent molecules. Ionic hydration shortens and stiffens the hydrating H–O bond but O:H nonbond relaxes contrastingly, which triggers the solution with properties that deionized water never shows.
- 3) The Y⁺ has an almost invariant hydration volume because it is full screened by its hydrating H₂O molecules but the Y⁺ shows stronger polarization to raises the surface stress in the order of Na⁺ > K⁺ > Rb⁺ > Cs⁺. The hydration volume of a Z²⁺ cation varies slight at higher concentration because its high valence and longer range of interaction. The Z²⁺ shows the Sr²⁺ > Ca²⁺ > Mg²⁺ order of polarization. The Y²⁺ ~ 2X⁻ is less capable of transiting O:H–O bond stiffness than the monovalent salt solutions as the superposition of the Y²⁺ ~ 2X⁻ ionic fields.
- 4) The X⁻ capability of bond transformation follows the order of I⁻ > Br⁻ > Cl⁻ > F⁻ ~ 0, and the hydration volume decrease gradually with anion separation. The number inadequacy of the ordered hydrating H₂O molecules screens partly the electric due to the presence of inter-anion repulsion. The dipolar T⁻ anion has a shorter and stronger field and its hydration volume reduces insignificantly with solute concentration. Higher solute concentration does not affect the shell size but weakens the electric field in the hydration shells.

- 5) The solution conductivity varies with solute concentration in the $f_{YX}(C) \propto 1 - \exp(-C/C_0)$ form. The hydration volume serves as the carrier for current flow that is subject to scatter. A thicker solution limits the conductivity by depressing the carrier mobility.
- 6) The ionic polarization dictates the surface stress unless the network is disrupted by $H \leftrightarrow H$ fragilization for the case of acid solutions. The linear $f_Y(C)$ coefficient of polarization contributes to the linear part of the surface stress and solution viscosity. The exponential $f_X(C) \propto 1 - \exp(-C/C_0)$ form, fingerprinting anion-anion repulsion, contributes to the $C^{1/2}$ term of Jones-Dale viscosity for the YX solutions.
- 7) The viscosity of the YOH basic solutions, divalent ZX_2 and complex YT salt solutions disobey the Jones-Dale convention because of the dominance of inter-solute repulsion and ionic polarization.
- 8) Having the same supersolidity of undercoordinated water molecules, variation of bond stiffness of the hydrating H_2O disperses the QS phase boundary to raise the T_m and depresses the T_N through the Einstein relation: $\Theta_{DX} \propto \omega_x$. Divalent salt has a stronger effect than the monovalent salt on depressing the QS boundary dispersion and on elevating the solution viscosity because of its higher $2X^-$ ionic number and Z^{2+} charge-quantity.
- 9) The DPS can distill the fraction-stiffness-fluctuation transition of the $O:H-O$ bonds from the vibration mode of deionized water to the hydration and identify the preference of ions skin occupation. The NEXAFS can resolve the effect of thermal $H-O$ bond contraction and the effect of ionic polarization on the pre-edge peak shift. Combination of the DPS and XAS with other time-resolved electron/phonon/phonon spectrometrics would be promising for comprehension of the hydration dynamics.
- 10) Amplifying solvation research from the perspective of solvation molecular dynamics to ionic hydration induced $O:H-O$ transition and the screened polarization would be essential to substantiate our knowledge.

Extending the experimental and theoretical strategies and the understandings of the Hofmeister ionic hydration to fields of colloid and interface science, solute-protein interface, and molecular crystals would be more fascinating and rewarding.

Conflicts of Interest

There is no conflicting interest to declare.

Acknowledgement

Financial support from the National Natural Science Foundation of China (Nos. 11872052; 21875024) are all gratefully acknowledged.

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