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(H, Li)Cl and LiOH Hydration: Surface Tension, Solution Conductivity and Viscosity, and Exothermic Dynamics

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Abstract

We systematically examined the effect of (H, Li)Cl and LiOH solvation on the O:H–O bond network deformation, surface tension (contact angle), solution electrical conductivity, thermomix, and viscosity evolution aiming to clarifying the functionalities for ions, lone pairs, and protons acting in these solutions. Results confirmed that H^+ and electron lone pair ‘:’ introduction turns out the $(H_3O^+, OH^-) \cdot 4H_2O$ motifs and that the Li^+ and Cl^- form each a hydration volume through the screened electrostatic polarization. The $(H_3O^+, OH^-) \cdot 4H_2O$ turns an O:H–O bond into the $H \leftrightarrow H$ anti–HB that disrupts the HCl solution network and its surface tension and into the $O \rightleftharpoons O$ super–HB compressor that raises the LiOH solution surface tension and viscosity, as well as the solution temperature during solvation. The Li^+/Cl^- ion reserves/reduces its hydration volume because of the complete/incomplete screen shielding by the ordered hydrating H_2O dipoles and the $Cl^- \leftrightarrow Cl^-$ repulsion. The invariant/variant Li^+/Cl^- hydration volume dictates, respectively, the linear/nonlinear concentration dependence of the Jones–Dole viscosity. Except for the HCl/ H_2O surface tension and LiOH/ H_2O viscosity, the conductivity, surface tension, and viscosity of these solutions follow the Jones–Dole notion that underscores the faction of bond transition from the mode of water to hydration.

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Content entry

Graphic abstract

Proton H^+ , lone pair : , Li^+ and Cl^- injection mediates cooperatively the HB network, conductivity, surface tension, and viscosity of $(\text{H}, \text{Li})\text{Cl}$ and LiOH solutions through $\text{H} \leftrightarrow \text{H}$ fragilization, $\text{O} \leftrightarrow \text{:O}$ compression, ionic screened polarization, $\text{Cl}^- \leftrightarrow \text{Cl}^-$ repulsion, solvent $\text{H}-\text{O}$ bond elongation, and undercoordinated solute $\text{H}-\text{O}$ bond contraction.

1. Introduction

As a set of model system, HCl, LiCl, and LiOH solvation mediates their hydrogen bonding network and properties, which is ubiquitously important to aqueous chemistry and cell living. Considerable efforts have been made from the perspectives of classical thermodynamics, molecular dynamics, proton and lone pair transportation since the 1900's when Arrhenius (1), Brønsted–Lowry (2, 3), and Lewis (4) defined the acid and base dissolution in terms of electron pair donation and acceptance and Hofmeister (5) discovered the salt series order in regulating the solution surface tension and the solubility of proteins.

The performance of salt solutions was ever attributed to the dissolved ions that serve as a structural maker or a breaker (6), in addition to the effect of ionic specification (7), quantum dispersion (8), quantum fluctuation (9), skin induction (10), and solute–solvent interactions (11). For example, increasing the concentration of chloride, bromide and iodide solutes stiffens the H–O stretching vibration frequency associated with O:H nonbond weakening, so the Cl^- , Br^- , and I^- anions were attributed as water structure breakers. Solute that can stiffen the O:H phonon was defined as structure maker alternatively.

Debating is still underway on the manner and mobility of proton and lone pair transporting in the Lewis solutions (12-14). The prominent notions of Grotthuss (12) and Zundel (14) suggests that the proton/lone-pair stays alone and moves freely from one H_2O molecule to another or shuttles randomly between two positions off midway of the adjacent O atoms to form the $\text{H}^+\cdot 2\text{H}_2\text{O}$ complex. These notions were associated with invocation of the thermal hopping (15), structural fluctuating (16), and quantum tunneling (17). Zundel's scheme is identical to the transitional quantum tunneling of Bernal-Fowler-Pauling (18, 19). Eigen (13) proposed in 1964 an $\text{H}_3\text{O}^+:3\text{H}_2\text{O}$ (H_9O_4^+) complex and explained that the H_3O^+ core interacts with its three H_2O neighbors through O:H and keeps the lone pair of the H_3O^+ free; the neighboring three H_2O molecules faced their lone pairs simultaneously to the H^+ of the H_3O^+ . This set of notions assumed an OH^- in a basic solution to follow the same H_3O^+ motion dynamics in an acidic solution as it was assumed that an OH^- is an H_2O molecule with an H^+ proton missing. Therefore, the H_3O^+ differs from the OH^- is merely the reversable polarity and the proton and lone pair perform equally in transportation (20).

However, it remains a challenge to discriminate the functionalities of the protons, anions, cations, and electron lone pair ‘:’ on the HB network and properties of the aqueous solutions (21, 22). In complement to the molecular or solute spatial and temporal transportation, we examined the solute-solvent bonding dynamics and its consequence on the HB transition and solution conductivity, surface tension, and viscosity from the perspective of aqueous charge injection and O:H–O transition (22), with the aid of the differential phonon spectrometrics (DPS) (23), detection of solution conductivity, surface tension and solution viscosity.

2. Theory: solvation bonding dynamics

2.1. The solvent: conservation and restriction

Liquid water is in a crystal-like form with a well-defined lattice geometry, strong correlation, unique O:H–O bond interaction, and high fluctuation. For a specimen having N number oxygen atoms, there are $2N$ numbers of protons H^+ and lone pairs ‘:’, apart from the dangling H–O radicals and lone pairs at the open ends of the network. The $2N$ numbers and the O:H–O bond configuration will conserve irrespective of the structural geometry of the matrix unless H^+ or ‘:’ is added in. A tetrahedral $H_2O \cdot 4H_2O$ motif (four H_2O molecules surround the center H_2O with fixed orientations to form the O:H–O bonds, see Figure 1a inset) best describes the ordered structure of water because of its higher C_{3v} symmetry and the O:H–O bond orientation restriction. The H_2O molecule and its H^+ is subject to restriction in motion. If the H_2O at the center rotates around the C_{3v} symmetrical axis over 60° in the $5H_2O$ motif, $H \leftrightarrow H$ and $O : \rightleftharpoons O$ repulsion will present, which is energetically unfavorable. On the other hand, the high H–O bond energy of ~ 4.0 eV prevents the H^+ from being dissociated or from its translational tunneling between adjacent H_2O molecules (24).

As the basic structure and energy-exchange unit, the O:H–O bond integrates the intermolecular weaker O:H nonbond of ~ 0.1 eV energy and the intramolecular stronger H–O polar-covalent bond other than either of them alone (23). The key to the O:H–O bond is the Coulomb coupling between electron pairs on adjacent oxygen ions. The asymmetrical, short-range, and the O–O Coulomb coupling relaxes the segmented O:H–O bond cooperatively in an ever-unexpected manner under any perturbation (25). As illustrated in Figure 1b, an external stimulus dislocates the O atoms in the same direction along the O:H–O bond. The stronger H–O bond always relaxes less than the weaker O:H. The proton H^+ is set as the coordination origin. Molecular undercoordination (26), liquid heating (27), and salt hydrating (28) have the same effect on the H–O shortening and O:H lengthening but mechanical compression

(29) has an opposite effect on O:H–O relaxation.

Consequently, the O:H–O bond segmental length, d_x , energy, E , phonon frequency, $\Delta\omega_x$, and the Debye temperature, $\Delta\Theta_{Dx}$, relax cooperatively according to the $\Delta\Theta_{Dx} \propto \Delta\omega_x \propto (E/d^2)_x^{1/2}$ relations (27). The segmental Θ_{Dx} determines the shape and the energy E_x determines the integral of the segmental specific heat $\eta_x(\Theta_{Dx})$, and the superstition of the segmental $\eta_x(\Theta_{Dx})$ governs the phase structure and thermodynamics of water and ice such as ice floating (28).

Figure 1. (a) The O:H–O bond segmental length d_L – d_H correlation matches that of the compressed ice (P) (30), cooling water and ice (31, 32), and undercoordinated water molecules (33-40). (b) The manners of O:H–O bond relaxation under external perturbation. Inset a shows the 5H₂O motif for water and ice. (Reprinted with permission from (25))

2.2. Solvation bonding dynamics

The high molecular polarity endows water dipoles to impinge into and dissolve a soluble crystal such as (H, Li)Cl and LiCl into carriers of charge in forms of Cl[−], Li⁺, H⁺ and lone pair ‘:’, as formulated as follows:

LiCl	+ nH ₂ O	⇒	Cl ⁻ + Li ⁺ + nH ₂ O	polarization; hydrating H ₂ O shielding
HCl		⇒	Cl ⁻ + H ₃ O ⁺ ·4H ₂ O + (n-5)H ₂ O	H ₃ O ⁺ ·4H ₂ O motif;
			Cl ⁻ + H ₂ O(H ⁺ ↔H ⁺)OH + (n-1)H ₂ O	H↔H anti-HB fragilization
LiOH		⇒	Li ⁺ + OH ⁻ ·4H ₂ O + (n-4)H ₂ O	

			$\text{Li}^+ + \text{H}(\text{O}^{3-} \leftrightarrow \text{O}^{2-})\text{H}_2 + (\text{n}-1)\text{H}_2\text{O}$	$\text{OH}^- \cdot 4\text{H}_2\text{O}$ motif; $\text{O} \leftrightarrow \text{O}$ super-HB compression and polarization
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The solvation injects the H^+ , Li^+ , Cl^- and lone pairs ‘:’ into the solutions. Ions interact with their neighboring water molecules through electrostatic polarization and H_2O dipolar screen shielding in the respective solutions to form the supersolid hydration shells (28). The hydration shell size varies with the local electric field of the ionic solute and the solute-solute interactions. The H^+ and the ‘:’ do not stay alone to move or shuttle freely but they are attached to one H_2O to form the H_3O^+ and the OH^- , which breaks the 2N number conservation for pure water. The restriction of the neighboring H_2O molecular orientation endows the tetrahedrally coordinated H_3O^+ and OH^- to form the $(\text{H}_3\text{O}^+, \text{OH}^-) \cdot 4\text{H}_2\text{O}$ motifs, as Figure 2 a and b insets illustrated. The $(\text{H}_3\text{O}^+, \text{OH}^-) \cdot 4\text{H}_2\text{O}$ motifs and the ionic hydration volumes may undergo Brownian or drift motion under a fluctuating or a graded thermal or electric field by keeping the following ingredients. These ingredients discriminate the functionalities of H^+ , Li^+ , Cl^- and ‘:’ on the network bonding dynamics and solution properties (23):

- 1) **$\text{H} \leftrightarrow \text{H}$ anti-HB point breaker.** The $\text{H} \leftrightarrow \text{H}$ repulsion disrupts the bonding network and the surface tension of an acidic solution, having the similar effect of heating on the $\text{O}:\text{H}-\text{O}$ bond segmental length and energy relaxation. Liquid heating lengthens the $\text{O}:\text{H}$ but shortens the $\text{H}-\text{O}$ and the thermal fluctuation depresses the surface tension (27).
- 2) **$\text{O} \leftrightarrow \text{O}$ super-HB point compressor and polarizer.** The $\text{O} \leftrightarrow \text{O}$ super-HB has the similar effect of mechanical compression that shortens the neighboring $\text{O}:\text{H}$ and lengthens the $\text{H}-\text{O}$ bond and the polarization raises the surface tension (21).
- 3) **Undercoordinated solute $\text{H}-\text{O}$ bond contraction.** The less-coordinated OH^- (compared to H_2O) undergoes $\text{H}-\text{O}$ bond contraction and phonon stiffening (26). The solvent/solute $\text{H}-\text{O}$ bond elongation/contraction emits/absorbs energy to heat up the solution upon LiOH solvation (41).
- 4) **Ionic point polarizer.** The Li^+ and Cl^- serve each as a point polarizer in the involved solutions to align, cluster, polarize, and stretch the $\text{O}:\text{H}-\text{O}$ bond in a hydration-shell manner. The polarization has the similar effect of molecular undercoordination on the $\text{O}:\text{H}$ elongation and $\text{H}-\text{O}$ bond contraction and polarization to raise the surface tension (28). The electrification shortens and stiffens the $\text{H}-\text{O}$ bond, shortens the $\text{H}-\text{O}$ phonon time, and makes the solution viscoelastic, thermally more stable.

3. Results and Discussion

3.1. DPS confirmation

Figure 2 compares the full-frequency Raman spectra for the concentrated (H, Li)Cl and LiOH solutions. Except for the characteristic peak evolution of the O:H and the H-O centered (200, 3000) cm^{-1} no features can be resolved for possible solute-solvent bond formation unless the sharp peak at 3610 cm^{-1} and the broadening of the 3200 cm^{-1} to the lower frequencies for the LiOH basic solutions. The H-O peak is a superposition of the coordination-resolved bulk (3200), skin (3450), and the dangling H-O radicals (3610 cm^{-1}) components (26). Figure 2 d illustrates the O: $\rightleftharpoons$:O super-HB and H $\rightleftharpoons$ H anti-HB due to the excessive lone pair and proton.

The DPS in Figure 2(b, d, f) shows the segmental ω_x DPS for the concentrated (H, Li)Cl and LiOH solutions. HCl stiffens the H-O phonon by Cl^- polarization as the H^+ does not polarize the solvent molecules. The small hump below 3100 cm^{-1} features the effect of H $\rightleftharpoons$ H repulsion that elongates the neighboring H-O bond. The small valley at 3650 cm^{-1} arises from the skin preferential occupation of the Cl^- anions whose stronger electric field stiffens the dangling H-O phonon from 3610 to 3650 cm^{-1} and the large anions shield the signal from being detected in Raman spectroscopy. The Cl^- polarization transits the ω_L from 200 to 120 cm^{-1} and the ω_H from 3200 to 3480 cm^{-1} . Cl^- polarization has the same effect of heating on the O:H-O bond relaxation and the H $\rightleftharpoons$ H fragilization has the same effect of thermal fluctuation on the surface tension depression. The O:H-O bond segmental specific heat disparity entitles the O:H to undergo thermal expansion and the H-O to be subject to contraction (26).

Results in Figure 2d confirms the effect of O: $\rightleftharpoons$:O compression to lengthen the neighboring H-O bond and softens its phonon to 3100 cm^{-1} and below and the undercoordinated solute H-O bond contraction featured at 3610 cm^{-1} . The sharp peak at 3610 cm^{-1} is identical to the dangling H-O bond that undergoes 10% contraction from 0.01 to 0.009 nm (42). The O: $\rightleftharpoons$:O compressor ($< 3100 \text{ cm}^{-1}$; $> 220 \text{ cm}^{-1}$) has the similar effect of pressure ($< 3300 \text{ cm}^{-1}$; $> 200 \text{ cm}^{-1}$) on the phonon frequency shift of liquid water (21). The H-O bond of the undercoordinated aqueous solute follows the bond order-length-strength and nonbonding electron polarization (BOLS-NEP) notion (26) – bond-order deficiency shortens and stiffens bonds between undercoordinated atoms with an association of electron polarization.

Figure 2. Full-frequency and DPS Raman spectra for the concentrated (a, b) HCl/H₂O (43), (c, d) LiOH/H₂O(41), (e, f) and LiCl/H₂O solutions. Insets a and c illustrate the H₃O⁺·4H₂O and OH⁻·4H₂O motifs transiting an O:H-O bond into the respectively framed (c) H $\leftrightarrow$ H anti-HB point breaker and (b) O: $\leftrightarrow$:O super-HB point compressor and polarizer of the insets (44). Inset e shows the Li⁺ and Cl⁻ point polarizers.

The DPS ω_H for the LiOH solutions may clarify the origin for the phonon lifetime in the ultrafast processes (45, 46). The longer 200 ± 50 fs lifetime features the slower energy dissipation of the 3610

cm^{-1} peak and the other shorter 1–2 ps lifetime on characterizes the energy dissipation of the <3100 cm^{-1} peak. The $\text{O}:\leftrightarrow:\text{O}$ repulsion in the LiOH dissolution is about four times that of the $\text{H}\leftrightarrow\text{H}$ in HCl solutions, because the two pairs of lone pairs packed closely.

The phonon abundance transition (the DPS ω_{H} peak area) for LiCl solutions is greater than the HCl solution as the H^+ does not polarize its neighbor HBs (44). Compared with HCl solutions, the narrower ω_{H} peak and the higher abundance for LiCl solutions evidence that the polarization of the Cl^- and Li^+ is greater than the Cl^- alone. LiCl solvation has the similar effect of molecular undercoordination on the H–O bond contraction (28).

3.2. Fraction of bond transition: solute-solute interaction

An integral of the ω_{H} DPS peaks gives rise to the phonon abundance transition, $f_{\text{x}}(\text{C})$, from the ordinary water to the hydrating by solvation at a molecular concentration C, as shown in Figure 3. Because of the incapability of the proton $f_{\text{H}}(\text{C}) \equiv 0$, the $f_{\text{HCl}}(\text{C}) = f_{\text{Cl}}(\text{C})$ and one can obtain $f_{\text{Li}}(\text{C}) \equiv f_{\text{LiCl}}(\text{C}) - f_{\text{HCl}}(\text{C}) \propto \text{C}$. The $f_{\text{LiCl}}(\text{C})$ and $f_{\text{HCl}}(\text{C})$ are in the same form of $f_{\text{x}}(\text{C}) = a[1 - \exp(-\text{C}/\text{C}_0)]$ toward saturation, as shown in Figure 3a.

The division $f(\text{C})/\text{C}$ is proportional to the number of bonds (or H_2O molecules) within the hydration shell per solute, which reflects the solute-solvent and solute-solute interactions. The polarized hydrating H_2O molecules weaken the ionic electric field by screen shielding, which determines the hydration volume. The invariant hydration volume of Li^+ , shown in Figure 3a, suggests that its electric field of the small Li^+ (ionic radius = 0.78 Å) is fully-screened by its hydrating H_2O molecules and the Li^+ is not interfered by any other solutes. However, the pronounced $\text{Cl}^- \leftrightarrow \text{Cl}^-$ repulsion at higher concentrations, or smaller solute separations, weakens the local electronic field of the large Cl^- (radius = 1.81 Å) and hence reduced the hydration volume. The number inadequacy of the highly ordered H_2O dipoles in the supersolid or semi-rigid hydration shell could not fully screen the electric field of the Cl^- solute (23). Surprisingly, the variant hydration shell size of the Cl^- is always smaller than that of the fully screened Li^+ .

Figure 3b shows the linear $f_{\text{OH}}(\text{C}) \propto \text{C}$ for the OH^- transiting from the H–O bond into the lengthened H–O bonds (< 3100 cm^{-1}) of the solvent and the shortened H–O phonons (3610 cm^{-1}) of the solute. The effect of Li^+ ionic polarization was annihilated by the $\text{O}:\leftrightarrow:\text{O}$ compression and the

undercoordinated solute H–O contraction. The linear dependence of the $f_{\text{OH}}(C)$ for the <3100 and the 3610 cm^{-1} peaks calibrate the concentration-resolved capability of $\text{O}:\rightleftharpoons:\text{O}$ compression and the number of OH^- hydroxides in the solution. Table 1 summarizes the H^+ , Li^+ , Cl^- , and lone pair ‘:’ capabilities of transiting the $\text{O}:\text{H}-\text{O}$ bonds in terms of the fraction coefficients in Figure 3.

Figure 3. The fraction coefficients for $\text{O}:\text{H}-\text{O}$ bond transition from the mode of ordinary water to the (a) $(\text{H}, \text{Li})\text{Cl}$ and (b) LiOH hydration associated with solution temperature rise due to exothermic solvation (41). The variant hydration shell size (the slope of $f(C)$) of the Cl^- is always smaller than that of the fully screened Li^+ .

Figure 3b also shows the calorimetric results of the concentrated $\text{LiOH}/\text{H}_2\text{O}$ solutions (41). The solution temperature increases linearly with the $\Delta f(C)$. Energy emission by the solvent $\text{H}-\text{O}$ bond elongation under $\text{O}:\rightleftharpoons:\text{O}$ compression and energy absorption by the solute $\text{H}-\text{O}$ bond contraction due to OH^- undercoordination raises the solution temperature. The $\text{H}-\text{O}$ emits about 150% of the $\sim 0.10 \text{ eV}$ $\text{O}:\text{H}$ energy that limits the energy of molecular dynamics even evaporation.

Table 1 Functionalities of the H^+ , Li^+ , Cl^- , and lone pair ‘:’ on the $\text{O}:\text{H}-\text{O}$ bonds transition and Jones-Dole viscosity.

charged solute	fraction coefficient $f(C)$	solute capability
H^+	0	incapable of polarization but $\text{H} \leftrightarrow \text{H}$ formation
lone pair ‘:’	$0.985C$ ($<3100 \text{ cm}^{-1}$)	$\text{O}:\rightleftharpoons:\text{O}$ compression
HO^-	$0.322C$ (3610 cm^{-1})	proportional to number of lone pairs ‘:’
Li^+	$2.734C$ (3500 cm^{-1})	invariant hydration volume
Cl^-	$0.0690 \times [1 - \exp(-C/0.0507)]$	variant hydration volume due to $\text{Cl}^- - \text{Cl}^-$ repulsion
$\text{Cl}^- + \text{Li}^+$	$0.7676 \times [1 - \exp(-C/0.1807)]$	capability superposition of Li^+ and Cl^-
Jones-Dole viscosity (47)	$= AC^{1/2} + BC$ $\propto [1 - \exp(-C/C_0)]$	nonlinear: Cl^- polarization and $\text{Cl}^- - \text{Cl}^-$ repulsion linear: Li^+ polarization

$\Delta\eta(C)/\eta(0)$	(for salt solution)	
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3.4. Surface tension, viscosity, and LiOH exothermic solvation

Figure 4a and b compares the relative contact angle, $\Delta\theta(C)/\theta(0)$ ($\theta(0) = 76.5^\circ$), between glass substrate and the (H, Li)Cl and LiOH solutions to feature the variation of surface tension. The $H \leftrightarrow H$ fragilization disrupts the solvent network and surface tension, which has the same effect of thermal fluctuation on the surface tension (44). This observation agrees with molecular dynamics (MD) calculations on the H^+ induced network fragmentation (48). The $H \leftrightarrow H$ fragilization explains the corrosive, dilutive, and skin-stress destructive nature of the acidic solutions. However, LiCl and LiOH solvation raises the surface tension because of the ionic and $O:\leftrightarrow:O$ polarization, having the same effect to that of molecular undercoordination. Polarization and undercoordination shortens the H–O bond and lengthens the O:H and raise the supersolidity of the water molecules packed in the respective region (28). The surface tension of LiOH/H₂O is proportional to the fraction of the $f_{LiOH}(C)$ coefficient and the surface tension of LiCl/H₂O follows the Jones-Dole fashion:

$$\Delta\eta(C)/\eta(0) = AC^{1/2} + BC \propto f_{LiCl}(C) \propto a[1 - \exp(-C/C_0)]$$

Where A, B, a and C_0 are fitting parameters for the viscosity and the fraction coefficient derived from DPS. The consistence trends of viscosity and surface tension for LiCl solutions implies that the Cl^- hydration contributes nonlinearly and the Li^+ linearly to the viscosity and surface tension. Likewise, the $O:\leftrightarrow:O$ polarization dictates the surface tension of LiCl solutions.

Figure 4. The relative contact angle (surface tension) between glass substrate and droplets of concentrated (a) Li(Cl, OH) and (b) HCl solutions. The $\Delta\theta(C)/\theta(0)$ for Li(Cl, OH)/H₂O follows the Jones-Dole notion for viscosity that underscores the fraction of hydrogen bonds transition.

Figure 5 compares the electric conductivity and the relative viscosity for the concentrated (H, Li)Cl and LiOH solutions. Results revealed the following:

- 1) The conductivity follows the respective $f(C)$ trends except for the LiOH solution whose $f(C)$ depends linearly on the concentration but the $\sigma(C)$ follows the Jones-Dale expression for the viscosity. The viscosity of (H, Li)Cl solutions is proportional to the respective $f(C)$. The $H \leftrightarrow H$ and $O:\leftrightarrow:O$ fragmented hydration volumes shall ease charge transportation, which leads to the $\sigma_{HCl} > \sigma_{LiOH} > \sigma_{LiCl}$ order at higher concentrations. Ions and their hydration volume may serve as carriers for the current flow that is subject to scattering as an added mechanism of transporting. Further investigation under variation of the measuring electric field would derive the carrier mobility in solutions.
- 2) However, the η_{HCl} increases with solute concentration in contrasting to the surface tension. The $H \leftrightarrow H$ fragilization disrupts the surface tension and the $H \leftrightarrow H$ and the $X^- \leftrightarrow X^-$ repulsions govern the viscosity of acid solutions. The η_{HCl} increases slightly slower than the η_{LiCl} because of the $H \leftrightarrow H$ fragmentation.
- 3) The $O:\leftrightarrow:O$ strong repulsion derives the much greater viscosity with $d^2\eta/dC^2 > 0$ for LiOH solutions. This unexpected concentration trend of viscosity elevation is consistent to those of the divalent (Ma, Ca, Cs)(Cl, Br)₂ solutions (49, 50) and the NaClO₄ and LiClO₄ (51) solutions. The strong $O:\leftrightarrow:O$ and multiple solutes repulsion should be responsible for the viscosity of the basic, divalent and complex salt solutions.

Table 2 summarizes observations of the O:H–O segmental cooperative relaxation in length, vibration frequency, solution conductivity, surface tension, and viscosity upon (H, Li)Cl and LiOH solvation.

Figure 5 The relative viscosity for the concentrated (a) HCl, (b) LiCl and (c) LiOH solutions and the conductivity of these measuring solutions.

Table 2. Rules for H^+ , Li^+ and Cl^- acting in (H, Li)Cl and LiOH solutions.

	fraction of HB transition	surface stress	conductivity	viscosity	
solute	f(C)	$\Delta\gamma_s(C)$	$\Delta\sigma(C)$	$\Delta\eta(C)$	remark
H ⁺	0	< 0	> 0	< 0	H↔H fragilization, non-polarizability
lone pair	f'(C) ∝ C	>0		> 0	O:⇔:O compression and polarization
Li ⁺	f'(C) ∝ C				fully-screened polarization, invariant hydration volume
Cl ⁻	f'(C) > 0 f''(C) < 0				partially-screened polarization, Cl ⁻ ↔ Cl ⁻ repulsion, variant hydration volume
solute OH ⁻	f' ₃₆₁₀ (C) ∝ C				solute H–O contraction
LiOH/H ₂ O	f'<3000(C) ∝ C				Solute H–O elongation

HCl/H ₂ O	$f'(C) > 0$ $f''(C) < 0$	< 0			H $\leftrightarrow$ H disruption, Cl ⁻ polarization
LiCl/H ₂ O		> 0			Cl ⁻ and Li ⁺ screened polarization

4. Conclusion

A combination of the O:H–O bond cooperativity notion, DPS detection, measurements of contact angle, electric conductivity, calorimetric property and viscosity has clarified the rules for H⁺, Li⁺, Cl⁻ and lone pair':' acting in the (H, Li)Cl and LiOH solutions, which shall shed light on the understanding of solvation of other solutes:

- 1) Hydration of H⁺, lone pairs, Li⁺ and Cl⁻ mediates the HB network and properties of the solutions through H $\leftrightarrow$ H point fragilization, O: $\leftrightarrow$:O compression and polarization, Cl⁻ and Li⁺ polarization and hydrating H₂O dipolar screen shielding, Cl⁻ $\leftrightarrow$ Cl⁻ repulsion, and solvent H–O bond elongation and solute H–O bond contraction.
- 2) HCl solvation and liquid water heating share the same ω_H blueshift and the ω_L redshift associated with surface tension depression governed by different mechanisms. Cl⁻ polarization in acid solution and the O:H–O segmental specific heat disparity of liquid water dictate the same trend of O:H and H–O phonon frequency shift. The H $\leftrightarrow$ H fragilization in acid solution and liquid water thermal fluctuation depress the surface tension.
- 3) LiOH solvation shares partly the effect of mechanical compression on softening solvent ω_H from above 3100 cm⁻¹ to its below. The O: $\leftrightarrow$:O compression is much stronger than the 1.35 GPa for room-temperature water icing. The undercoordinated solute H–O bond contracts by 10% of it is in the bulk, which also the length of the dangling H–O radicals featured at 3610 cm⁻¹.
- 4) The Cl⁻ in acid and Li⁺ in basic solutions have their same functions in salt solutions but the the effect of O: $\leftrightarrow$:O compression and solute H–O contraction annihilate the effect of Li⁺. The Cl⁻ $\leftrightarrow$ Cl⁻ repulsion presents in acid and salt solutions of higher concertation, which weaken the Cl⁻ electric field and the hydration volume.

- 5) Polarization raises yet fragilization and thermal fluctuation disrupt the solution network and surface tension. The competition of energy emission by H–O bond elongation and energy absorption by H–O contraction dictates the exothermic or endothermic solvation. Molecular motion or evaporation dissipates energy capped at the O:H cohesive energy of ~ 0.1 eV/bond.

5. Experimental procedures

To examine the predictions, we performed the Raman spectroscopy and contact angle (surface tension) detection. Analytical grade (H, Li)Cl and LiOH dissolved into the deionized water for the confocal Raman spectroscopy at the ambient conditions (Renishaw inVia) in back-scattering configuration with a spectral resolution of 1 cm^{-1} . 150 μL solution was injected in a quartz cell and excited by a DPSS laser (emission wavelength 532 nm, output power 38 mW). Each spectrum sums four scans with an exposure time of 30 seconds. The solution concentration in M (Mol/kg) was converted to molar ratio by the relation: $M/(1000/18+M)$.

A Raman spectral peak shape is the probability function of phonon frequency distribution. The integral of the peak area is the phonon abundance that is proportional to the number of bonds contributing to signal detection. The peak width is the fluctuation order of the vibrating bonds. The frequency shift $\Delta\omega_x$, as a function of its length d_x and energy E_x , is the bond stiffness. The subscript $x = \text{L}$ denoting the O:H nonbond and $x = \text{H}$ the H–O bond characterized at vibration frequencies ($\sim 200\text{ cm}^{-1}$, $\sim 3200\text{ cm}^{-1}$) in for water.

The DPS was conducted by subtracting the referential peak collected from deionized water from the ones of the solutions upon all the spectral peak are being normalized. The DPS resolves the transition of the phonon abundance (peak area) and stiffness (frequency shift) by solvation. The integral of the DPS peak, $f_x(C)$, represents the fraction of bonds transiting from water to the hydration volume. The division, $f_x(C)/C$, is proportional to the number of bonds per solute in the first hydration subshell, which characterizes the ionic local electric field.

A drop sharp analysis system (Krüss GmbH, Germany) was used to measure the contact angles. Dropping the solution droplets onto the glass surface at ambient temperature and measure the angle ten times for average made at different position of the glass. Conductance measurements were carried out at room temperature using two platinum black electrodes. The electrode of constant 1 was used to

test conductivity in the 0.00~20mS/cm and electrode constant 10 test the range of 20~200mS/cm。 A temperature compensation constant of 2.12%for NaCl solution). Each solution was tested five times and took the average upon calibration with respect to the literature reference. Viscosity was performed used the detector at the room temperature (298K and 281K) under the 60 Hz rotating perturbation.

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