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Ion-Specific Water-Macromolecule Interactions at Air/Aqueous Interface: An Insight into Hofmeister Effect

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ABSTRACT: The specificity of ions in inducing order/disorder in macromolecules is introduced as Hofmeister series; however, the detailed underlying mechanism is still not comprehensible yet. We utilized surface-specific sum frequency generation (SFG) vibrational spectroscopy to explore the Hofmeister effect at air/polyvinylpyrrolidone (PVP)-water interface. The spectral signature observed from the ssp polarization scheme reveals ion-specific ordering of water molecules following the Hofmeister series attributed to the ion-macromolecule interactions. Along with this, the presence of ions does not reflect any significant influence on the structure of the PVP macromolecule. However, the ppp-SFG spectra in the CH-stretch region reveal the impact of ions on the orientation angle of vinyl chain CH₂-groups which follows the Hofmeister series: SO₄²⁻ > Cl⁻ > NO₃⁻ > Br⁻ > ClO₄⁻ > SCN⁻. The minimal orientation angle of CH₂-groups indicates significant disordering in PVP vinyl chains in the presence of chaotropic anions ClO₄⁻ and SCN⁻. The observation is attributed to the ion-specific water-macromolecule interactions at the air/aqueous interface. It is compelling to observe the signature of spectral blue shifts in the OH-stretch region in ppp configuration in the presence of chaotropic anions. The origin of spectral blue shifts has been ascribed to the existence of weaker interactions between the interfacial water molecules and the backbone CH-, CH₂-moieties of the PVP macromolecules. The ion-specific modulation in water-macromolecule interactions is endorsed by the relative propensity of anion's adsorption towards the air/aqueous interface. The experimental findings highlight the existence and cooperative participation of ion-specific water-macromolecule interactions in the mechanism of the Hofmeister effect, along with the illustrious ion-water and ion-macromolecule interactions.

INTRODUCTION

In 1888, Franz Hofmeister proposed a series of anions ranked according to their potency to salt out (precipitate) proteins from their aqueous solutions, known as the Hofmeister or lyotropic series as follows:¹



Apart from its significance in protein solubility, the series is known to govern various fundamental processes such as controlling surface tension of electrolyte solutions, enzymatic activity, stability of colloids and micro-emulsions, phase separation, water evaporation, and depletion of the ozone layer.²⁻⁵ Despite its diverse applicability, a complete understanding of the conceptual framework behind the Hofmeister effect has eluded researchers to date. Two hypotheses have been put forward to explain the underlying mechanism. The first explains the Hofmeister effect in terms of ion-water interactions, i.e., the ability of ions to make or break hydrogen (H) bonds in water. The ions on the left of the series are called kosmotropes (structure makers) which are known to become highly hydrated and salt out proteins from their aqueous solution, thus bringing order to the protein structure. In contrast, the right-aligned ions are called chaotropes (structure breakers) which are weakly hydrated and salt-in protein molecules in their aqueous solution, thus

disorder the protein structure.^{3,5-6} Although this approach successfully explains the surface tension of the vapor-electrolyte interface,² the range over which an ion's impact on water structure persists is still under debate.⁷⁻¹¹ The second hypothesis involves the role of dispersion forces between ions and the macromolecule towards the Hofmeister effect. This is realized from the current understanding of the relative propensity of ions to be adsorbed at the hydrophobic macromolecule surface.^{8,12-20} However, the existing mechanism based on ion-water and ion-macromolecule interactions lacks water-macromolecule interactions, which play an imperative role in determining the structural stability and functionality of the macromolecules.²¹⁻²² In a recent theoretical study, Willow et al. considered the significant contribution of ion-specific water-macromolecule interactions in explaining the salt-in effect.¹¹ In addition, Lakshamanan et al.²³ and Song et al.²⁴ performed dilational rheology of bovine serum albumin (BSA) and translational diffusivity of water molecules near the lipid surfaces, respectively. Their experimental results indirectly suggest that the presence of ions significantly modulates the strength of the bonding environment of water molecules near the macromolecule surfaces. However, spectroscopic evidence of ion-specific water macromolecule interactions and a detailed molecular-level insight into the underlying mechanism is still lacking. Therefore, it is essential to probe the ion-specific water structure near the macromolecule

and the associated conformational changes in the macromolecule at the air/aqueous interface.

Sum frequency generation (SFG) vibrational spectroscopy is a robust tool that has been extensively utilized to study the structure of water and macromolecules at the interfacial region.^{4,12-14,25-32} Previously, Cremer and co-workers have performed SFG spectroscopy in the ssp-polarization scheme to investigate the Hofmeister effect at various aqueous interfaces carrying charged monolayer, neutral polymer, and charged mineral interfaces.^{3,13-14} Their observations established that the Hofmeister effect can be explained in terms of ion-macromolecule interactions. Despite observing a convincing correlation between OH-intensity and the anion Hofmeister series, the following concerns remain unprobed: (a) Do ions affect the strength of water-macromolecule interactions? If yes, then (b) what is the underlying mechanism? (c) Do these ion-specific water-macromolecule interactions contribute to the structural order/disorder of the macromolecule at the air/aqueous interface?

To answer these questions, we have investigated the Hofmeister effect at the air/aqueous interface carrying a neutral polymer polyvinylpyrrolidone (PVP) using ssp and ppp-polarization schemes of SFG vibrational spectroscopy (figure 1a and 1b). It is well accepted that the SFG spectroscopic investigations in different polarization schemes, i.e., ssp and ppp are necessary to probe the vibrational signatures of surface moieties involved in various intermolecular interactions present at the air/aqueous interface.²⁶⁻²⁸ For example, Tyrode et al.²⁶ investigated the hydration state of non-ionic surfactants at the air/aqueous interface and reported a new OH-feature at $\sim 3580\text{ cm}^{-1}$. The observed feature was absent in ssp-SFG spectra but significantly appeared in ppp-OH spectral configuration. The feature was then attributed to the asymmetric vibrations of water molecules involved in non-hydrogen bond type weak interactions at the air/aqueous interface. Wei et al.²⁷ performed SFG investigations of pristine air/water interface in different polarization schemes to report the OH-feature at $\sim 3550\text{ cm}^{-1}$, which appears distinctively in the ppp-scheme compared to the ssp-SFG spectra. Later, Gan et al.²⁸ attributed this OH-feature to singly H-bonded water at the air/water interface. The past findings motivated us to utilize SFG spectroscopy in different polarization schemes to perform a thorough molecular-level investigation of the Hofmeister effect at the air/aqueous interface.

The ssp-SFG spectra at the air/PVP aqueous interface showed that the ion-specific variation in OH-region intensity follows the Hofmeister series, whereas the CH-peak intensities remained nearly superimposed. In contrast, ppp-SFG spectra highlighted significant variation in CH-peak intensities in the presence of Hofmeister ions. Here, we have performed a detailed analysis to quantify the CH_2 -group orientation angle to probe the impact of ions on the polymer chain ordering at the air/aqueous interface, which follows the Hofmeister series. In comparison to kosmotropes, the chaotropes bring significant disorder to the polymer structure, which intriguingly is correlated with the ion-specific variation in the water structure at the air/PVP aqueous interface. We demonstrate that compared to kosmotropes, the chaotropes induce weaker intermolecular interactions between the interfacial water molecules and the hydrophobic surface moieties ($-\text{CH}$, $-\text{CH}_2$ of polymer backbone),

which in turn disrupts the PVP structure at the air/aqueous interface.

EXPERIMENTAL SECTION

Materials

Polyvinylpyrrolidone (PVP) of Molecular weight $M_w = 40000$ and all the six inorganic sodium salts (sodium sulphate, sodium chloride, sodium bromide, sodium nitrate, sodium perchlorate and sodium thiocyanate) were purchased from Sigma Aldrich and used without any further purification. In order to avoid the interference of OH-region intensity with the CH-region peaks, we have also carried out some SFG experiments in high purity heavy water (D_2O) with 99.9 atom % D was purchased from Sigma Aldrich. The aqueous solutions of 0.05 wt % PVP were prepared by dissolving calculated amount of the polymer in de-ionized water or D_2O . The concentration of the PVP used in the present study forms a saturated macromolecule monolayer at the air/aqueous interface. This was verified by using various higher PVP polymer concentrations in the solution where no further changes in the SFG spectral profile is observed. The ion-specific effects were carried out at a concentration of 1M for all the sodium salts in the polymer aqueous solution.

Sum Frequency Generation Vibrational Spectroscopy

SFG is a three-wave mixing process where two input beams, visible and infrared (IR), overlap spatially and temporally at the interface to produce the SFG beam.^{4,12-14, 25-32} The schematic layout is given in figure 1b. In the present study, we used an SFG spectrometer (EKSPLA, Lithuania, SFG061), consisting of a picosecond Nd:YAG laser system (PL2231-50).⁴ It is a mode-locked, diode-pumped solid-state laser that provides a 30 ps infrared (IR) beam at 1064 nm with an output energy of 40 mJ at a repetition rate of 50 Hz. The fundamental beam (1064 nm) is then used in the second harmonic generation (SHG) unit (SFGH500-2H) to generate a visible beam at 532 nm. Potassium dideuterium phosphate (K^*DP) nonlinear crystals are employed in the SHG unit to double the frequency of the incident fundamental beam of 1064 nm. The infrared beam (1064 nm) and the second harmonic (532 nm) beam are then fed to the optical parametric generation (OPG), optical parametric amplification (OPA), and difference frequency generation (DFG) unit (PG501-DFG2) to produce the tunable IR output from 2300 nm to 16000 nm. Two BBO-crystals are used in the OPG/OPA units, whereas AgGaS_2 (2300 nm -12000 nm) and GaSe (8000 nm -16000 nm) crystals are used in the DFG unit. The fixed frequency visible 532 nm (diameter $\sim 200\text{ }\mu\text{m}$ with 500 μJ energy/pulse) and tunable IR beams (diameter $\sim 150\text{ }\mu\text{m}$ with 235 μJ energy/pulse at 3000 nm) are incident on the sample surface at angles $\sim 63^\circ$ and $\sim 56^\circ$ with respect to the surface normal to produce the SFG signal. The resultant sum frequency signal is reflected at an angle of $\sim 61^\circ$ and then guided through steering optics toward the detection unit. The detection unit consists of a monochromator (MS2001) with a wavelength resolution of 0.06 nm and a photomultiplier tube (PMT), (Hamamatsu R7899). All the units are automated, and their functioning is controlled by LabVIEW software. The spatial and temporal overlapping of visible and IR beams at the sample surface and the strength of SFG signal have been optimized at the peak position of 3704 cm^{-1} at which the signal of free OH is maximum

in the OH stretching region of water molecules at the air/water interface.

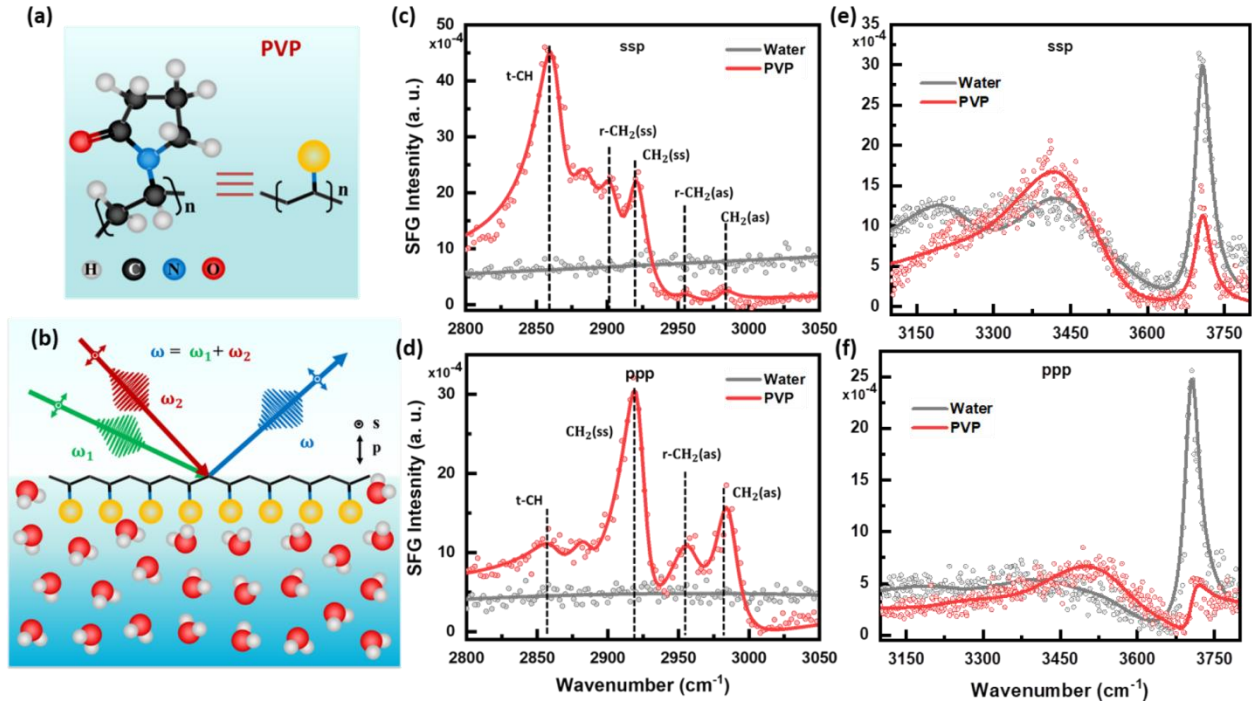


Figure 1. (a) Molecular structure of PVP polymer. (b) Schematic illustration of air/PVP-water interface probed by SFG spectroscopy with the scope to perform polarization-dependent studies such as in ssp and ppp, polarization configuration. Here, the three letters indicate the states of polarization of the fields in the sequence of SFG, visible and infrared beams, respectively. The letters s and p stand for the beam polarization perpendicular and parallel to the plane of incidence. SFG spectra at the air/PVP-water interface in the CH-stretch region (panel c in ssp and d in ppp) and OH-stretch region (panel e in ssp and f in ppp). The scattered points in the plots (panel c-f) represent experimental data, while the solid line is the Lorentzian fit to the spectra. The details of fitting parameters are given in tables S2-S3 of the supporting information.

The SFG signal is proportional to the modulus square of the effective second-order nonlinear susceptibility, $\chi^{(2),\text{eff}}$ which carries the vibrational signature of the molecules present at the interfacial region.^{4,13-14, 26-28, 32}

$$I \propto |\chi^{(2),\text{eff}}|^2 I_1 I_2 \quad (2)$$

Here, I_1 and I_2 are the intensities of visible and IR beams, respectively. The second-order susceptibility $\chi^{(2),\text{eff}}$ consists of a non-resonant term and a resonant Lorentzian term,^{4,13-14, 26-28, 32} expressed as:

$$\chi^{(2),\text{eff}} = \chi_{\text{NR}}^{(2)} + \sum_{\nu} \frac{A_{\nu}}{(\omega_{\nu} - \omega_2 - i\Gamma_{\nu})} \quad (3)$$

Here, $\chi_{\text{NR}}^{(2)}$ is the non-resonant component of the susceptibility, and the second term is the resonant part represented by a Lorentzian function. Resonance occurs when ω_2 (IR frequency) matches with the vibrational characteristic frequency (ω_{ν}) of the molecules present at the interface. Here, A_{ν} and Γ_{ν} are the amplitude and the half-width at half maxima (HWHM) of the Lorentzian line shape, respectively. All the SFG spectra are collected in different polarization schemes (ssp and ppp) in the CH- and OH-stretching region from 2800 to 3800 cm^{-1} at a step size of 2 cm^{-1} and acquisition per step of 200 and are fitted with

Lorentzian line shape using equations (2-3). The detailed theory of $\chi^{(2),\text{eff}}$ with L-factor calculations and spectral fitting parameters are given in Sections S2 and S3. The aqueous samples for SFG measurements are prepared in deionized water (Merck Millipore direct-Q3, 18 M Ω .cm) and heavy water (D_2O). We used a Teflon sample cell (diameter $\sim 5\text{cm}$) to carry the aqueous samples for SFG measurements. The sample cell is cleaned before the experiment using a piranha solution (3:1 v/v of concentrated sulphuric acid to 30% hydrogen peroxide solution) and then rinsed thoroughly with deionized water. The same procedure is followed for cleaning of all the glassware used during the experiments. All the experiments are conducted at the temperature of $21.5 \pm 0.5^\circ\text{C}$.

RESULTS AND DISCUSSION

The SFG spectra in the CH-stretch region for air/PVP-water interface in ssp- and ppp-polarization configurations are presented in figure 1(c) and (d), respectively. The spectral features positioned at 2863 cm^{-1} , 2903 cm^{-1} , 2924 cm^{-1} , 2956 cm^{-1} , and 2984 cm^{-1} correspond to the characteristic signature of tertiary C-H, symmetric stretching modes of ring- CH_2 , and vinyl chain CH_2 groups, and asymmetric stretching modes of ring- CH_2 , and vinyl chain CH_2 groups of PVP polymer respectively.³³ It is evident that the SFG peaks for symmetric CH-stretch modes are more intense in ssp-spectra (figure 1c), whereas the asymmetric

CH-stretch modes contribute significantly in the ppp-spectra (figure 1d). The observation agrees with the symmetry and polarization selection rules of the SFG vibrational spectroscopy.³⁴ The absence of SFG signatures in the CH-stretch region for the air/water interface (grey curve) marks the pristine nature of the water used for the SFG experiments (Figures 1c and 1d).

The signatures of interfacial water structure in pristine conditions at the air/water interface and in the presence of PVP at the air/PVP-water interface are recorded in ssp and ppp-SFG schemes. The spectral signatures are illustrated in figures 1e and 1f, respectively. The ssp-SFG spectrum at the pristine air/water interface consists of a broad region from 3100-3600 cm^{-1} attributed to the bonded water OH-oscillators. The sharp peak positioned at $\sim 3704 \text{ cm}^{-1}$ corresponds to the free-OH-oscillator protruding out of the interface. The assignment of peaks in the bonded OH-stretch region is less straightforward and continues to be ambiguous.^{4,25-27, 35-40} However, more often, the lower frequency peak located at $\sim 3240 \text{ cm}^{-1}$ is assigned to the strongly hydrogen (H)-bonded water, while the higher frequency peak $\sim 3440 \text{ cm}^{-1}$ corresponds to weakly H-bonded water. The relative intensity of both peaks provides qualitative insights into the H-bonding strength of water molecules in the interfacial region.^{4,36-39} Similar to the ssp-SFG spectrum, the ppp-spectrum at the pristine air/water interface (figure 1f) consists of a free OH feature at $\sim 3704 \text{ cm}^{-1}$. In contrast to the ssp-spectrum, the water structure in ppp configuration has no significant SFG intensity in the bonded OH-stretch region except a weak feature at $\sim 3540 \text{ cm}^{-1}$ characteristic of weakly H-bonded water species.²⁶⁻²⁸ Interestingly, the water spectral profile in the presence of PVP polymer at the air/PVP-water interface displays minor enhancement in intensity at $\sim 3440 \text{ cm}^{-1}$ and $\sim 3540 \text{ cm}^{-1}$ in ssp and ppp-SFG spectra (figure 1e and 1f), respectively. This can be attributed to the increase in weakly H-bonded water species owing to the presence of PVP polymer at the air/aqueous interface. The feature at $\sim 3540 \text{ cm}^{-1}$ in ppp-SFG spectrum at the air/PVP-water interface might be due to the involvement of water OH-oscillators in weak H-bonding interactions with the carbonyl groups of the pyrrolidone ring of PVP.⁴¹ In addition, the observed substantial decrease in the free OH intensity (Figures 1e and 1f) strongly indicates the disruption in the free OH oscillator population owing to the surface coverage by the PVP moieties at the interface.

To extract the molecular-level insight into anion-induced changes in the interfacial arrangement of polymer and water molecules, we have carried out the SFG experiments at the air/PVP-water interface for a range of salt solutions. Figure 2a represents the OH-stretch region of SFG spectra in ssp configuration at the air/PVP-water interface in various sodium salts at 1M concentration. The spectral features show that the SFG intensity in the OH-stretch region reflects the characteristic signature of anions present in the solution. We have observed significant ion-specific variation in the overall SFG intensity. For the case of the kosmotropic ion SO_4^{2-} , the changes in SFG intensity are minimal and comparable to that of the air/PVP-water interface. In contrast, a significantly enhanced SFG intensity is observed for the presence of weakly hydrated and most chaotropic ClO_4^- , and SCN^- ions at the air/aqueous interface. The variation in SFG intensity in the overall OH-stretch region can be ascribed to the induced ordering of water molecules in a surface field originated due to the presence of ions at the air/PVP-

water interface.¹²⁻¹⁴ In figure 2b, we have shown the variation in the amplitude of 3440 cm^{-1} peak taken from the SFG spectra (figure 2a) in the presence of various sodium

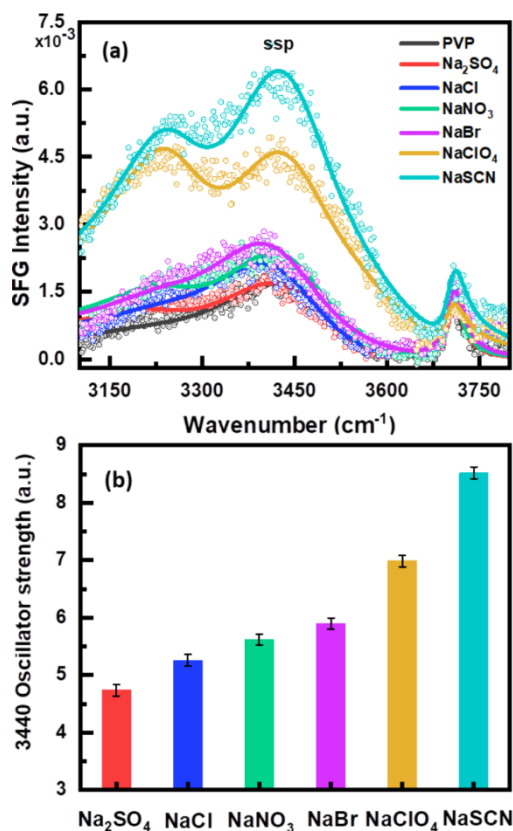


Figure 2. (a) ssp-SFG spectra at the air/PVP-water interface with 1M sodium salts in the aqueous subphase, showing anion-specific variation in the OH-region intensity. (b) Anion-specific variation in 3440 cm^{-1} OH-oscillator's strength shows a monotonic increase following the Hofmeister series. The data points are Lorentzian fit amplitudes to the 3440 cm^{-1} peak of SFG spectra as provided in panel (a). See table S4 of the supporting information for fitting parameters.

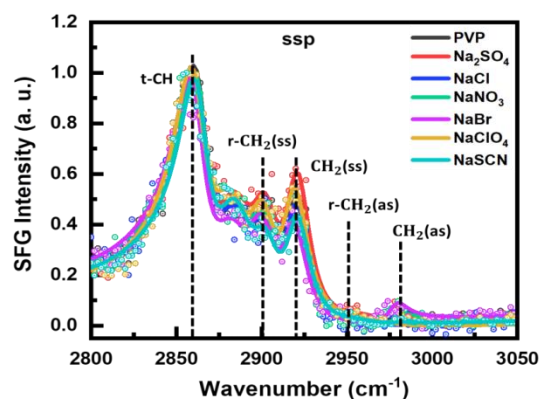


Figure 3. ssp-SFG spectra in CH-stretch region at air/PVP- D₂O interface in the presence of 1M sodium salts (Na₂SO₄, NaCl, NaNO₃, NaBr, NaClO₄, and NaSCN). All the spectra are normalized with respect to the intensity of the t-CH peak (2862 cm^{-1})

¹). The points show experimental data, and the solid lines are the Lorentzian fit curves. Fitting parameters are given in table S6 of the supporting information.

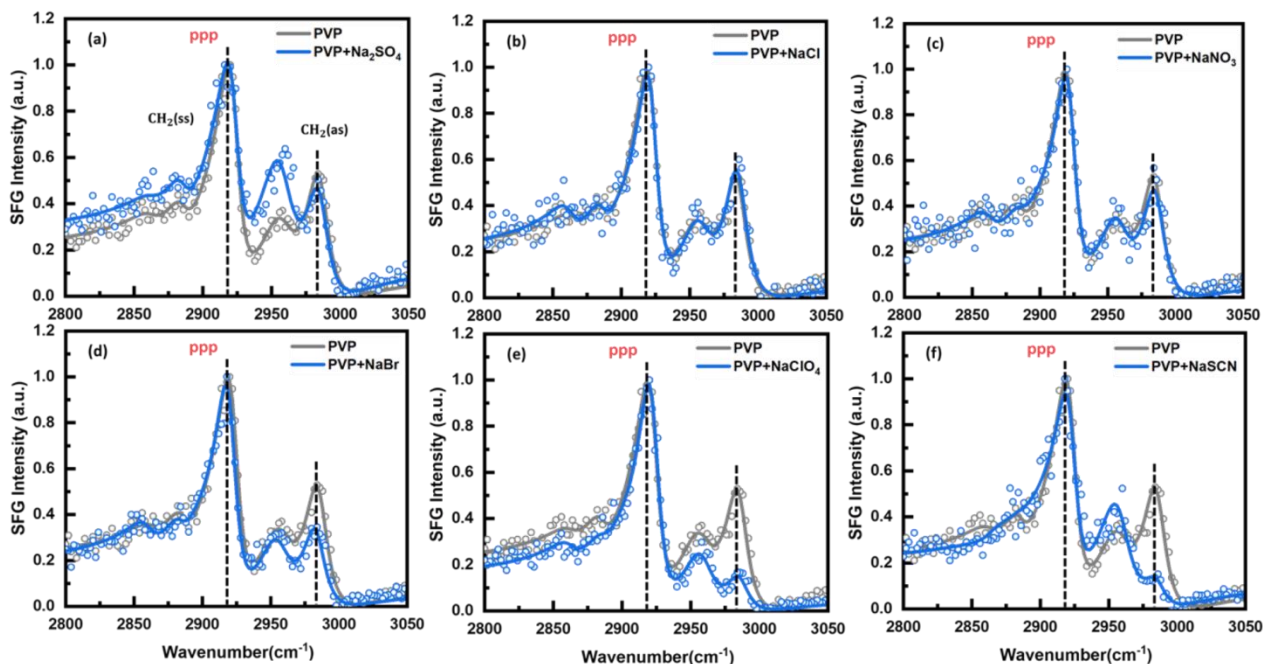
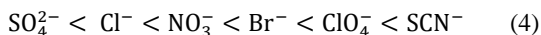


Figure 4. ppp-SFG spectra in the CH-stretch region at the air/PVP-D₂O interface in the presence of various Sodium salts at 1M concentration. All the SFG spectra are normalized with respect to the intensity of the CH₂ (ss) peak (2924 cm⁻¹). The points show experimental data, and the solid lines are the Lorentzian fit curves. Fitting parameters are given in table S7 of the supporting information.

salts. The observed monotonic increase demonstrates that the ion's influence on water structure at the air/PVP-water interface follows a Hofmeister trend.¹³



The observed trend in the ion-specific variation in OH-stretch region SFG intensity can be explained in terms of the relative propensity of each anion's adsorption towards the hydrophobic air/PVP-water interface, which is known to follow the Hofmeister series.^{11-13,16,18} The hydrophobic moieties (-CH, -CH₂) of the polymer backbone provide binding sites for the larger chaotropic and weakly hydrated anions to adsorb at the air/aqueous interface.¹⁶

Further, in the quest to find any impact of the anion-induced ordering of water structure on the structural arrangement of the polymer chains, we have carried out ssp-SFG experiments in the CH-stretch region (2800-3050) cm⁻¹ at the air/PVP-water interface (Figure S1). We have observed a dramatic variation in CH-peak intensities, especially from 2900-3050 cm⁻¹ in the presence of most chaotropic ClO₄⁻, and SCN⁻ ions at the air/PVP-water interface. The relative variation in the CH-peak intensities indicates the degree of ordering/disordering in the polymer chains as a function of ions present in the aqueous solutions. However, on close inspection of the combined SFG spectral signatures in CH-(Figure S1) and OH-stretch (Figure 2a) regions at the air/PVP-water interface, it appears that the significant SFG intensity in OH-stretch region for ClO₄⁻, and SCN⁻ might have interfered constructively with the CH-

signature to mislead the overall appearance of the SFG spectral profile from 2900-3050 cm⁻¹ (figure S1).

For further analysis, it is therefore necessary to isolate the SFG signature originating from the OH-stretch region to obtain a deconvoluted spectral profile in the CH-stretch region that is free from these interference effects. To achieve this, we performed the SFG experiments at the air/PVP-D₂O interface in the presence of 1M sodium salts (figure 3). From the SFG spectral signatures, it is quite clear that the previously observed ion-induced variations in SFG peak intensities in the CH-stretch region (2900-3050 cm⁻¹) at the air/PVP-water interface (Figure S1) are absent at the air/PVP-D₂O interface. The following observation with the D₂O solution confirms that the variation in CH-peak intensities in the water solution cannot be equated directly with the conformational changes in the polymer structure. In addition, we have observed that the CH-peak intensities are nearly superimposed within the experimental errors (figure 3), indicating no impact of sodium salts on the polymer (PVP) chain conformations at the aqueous interface.

On examining the air/PVP aqueous interface in ssp-SFG scheme, we conclude that the ions have negligible impact on the conformational changes in the polymer chains at the air/aqueous interface. However, an ion-induced ordering of the water structure has been observed, which is attributed to the ion-macromolecule interactions at the air/aqueous interface.¹³ Along with this, the ssp-SFG spectral profiles in figure 2 did not showcase any peak shift in the OH-oscillator frequency in the presence of ions at the air/aqueous interface. This indicates that the

investigation of the Hofmeister effect at the air/PVP-water interface solely using the ssp-mode of SFG spectroscopy is insufficient to address the concerns raised by Willow et al.¹¹, Lakshamanan et al.²³ and Song et al.²⁴ regarding the impact of ions on the strength of water-macromolecule interactions and their contribution in the Hofmeister effect at the air/aqueous interface.

Therefore, in order to perform a detailed investigation on the intermolecular interactions participating in the Hofmeister effect, we continued SFG investigations at the air/PVP aqueous interface in ppp-polarization configuration. Figure 4 presents the CH-stretch region of SFG spectra at the air/PVP-D₂O interface in ppp-polarization scheme. It is evident from the spectral features that the presence of ions brings significant changes to the relative SFG peak intensities at 2924 cm⁻¹(CH₂ (ss)), and 2984 cm⁻¹(CH₂ (as)), characteristic of symmetric and asymmetric CH-vibrational modes of vinyl chain methylene groups of PVP polymer. For better clarity, we have normalized all the SFG spectra with respect to the intensity of CH₂ (ss) mode peak position located at 2924cm⁻¹. The relative intensity variations for the peak positions 2924 cm⁻¹(CH₂ (ss)), and 2984 cm⁻¹(CH₂ (as)) are minimum with the presence of sulphate, chloride, and nitrate ions, whereas prominent effects are observed with perchlorate and thiocyanate anions. This indicates that the presence of ClO₄⁻, and SCN⁻ ions have significantly perturbed the interfacial conformation of polymer vinyl chains.

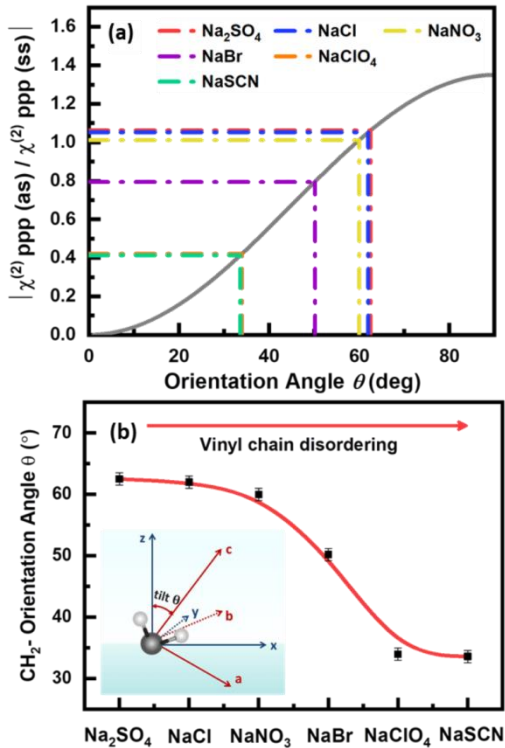


Figure 5. (a) Theoretical curve of $|\chi_{\text{ppp}}^{(2),\text{eff}}(\text{as}) / \chi_{\text{ppp}}^{(2),\text{eff}}(\text{ss})|$ as a function of orientation angle θ for CH₂-groups. The horizontal dashed lines are the experimental values of $|\chi_{\text{ppp}}^{(2),\text{eff}}(\text{as}) / \chi_{\text{ppp}}^{(2),\text{eff}}(\text{ss})|$ and the respective projection on x-axis gives the tilt angle values. The observed trend in the tilt angle values as a function of anions is shown in panel b, which follows the Hofmeister series (table S8). Lower CH₂-tilt angle

values indicate the onset of disorder in the vinyl chain of PVP in presence of weakly hydrated anions (ClO₄⁻, and SCN⁻).

To estimate the ion-induced conformational changes in the polymer structure, we have implemented a detailed theoretical analysis to calculate the orientation angle of CH₂-groups at the air/PVP-D₂O interface. It is a well-established fact that the lower orientation angle of CH₂-groups at the air/aqueous interface indicates significant disorder in the polymer chains.⁴²⁻⁴³ The orientation angle is estimated by the amplitude ratio of asymmetric and symmetric peaks of the vinyl chain methylene group in the ppp-SFG spectra (figure 4) as depicted by the left-hand side term of equation 5. Figure 5a presents the theoretical orientation curve as described by the right-hand term of equation 5. The details of the mathematical formulation (eq. 5) are given in section S2 of the supporting information.

$$\left| \frac{\chi_{\text{ppp}}^{(2),\text{eff}}(\text{as})}{\chi_{\text{ppp}}^{(2),\text{eff}}(\text{ss})} \right| = \left| \frac{5.89(\langle \cos\theta \rangle - \langle \cos^3\theta \rangle)}{\langle \cos\theta \rangle} \right| \quad (5)$$

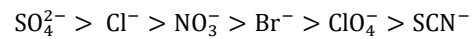
The ensemble average $\langle \rangle$ has been estimated with the delta ($\sigma = 0$) distribution function:^{4,32,35}

$$f(\theta) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(\theta-\theta_0)^2}{2\sigma^2}} \quad (6)$$

$$\langle \cos\theta \rangle = \int_0^\pi f(\theta) \sin\theta \cos\theta d\theta \quad (7)$$

$$\langle \cos^3\theta \rangle = \int_0^\pi f(\theta) \sin\theta \cos^3\theta d\theta \quad (8)$$

The horizontal lines shown in figure 5a are the experimental values of $|\chi_{\text{ppp}}^{(2),\text{eff}}(\text{as}) / \chi_{\text{ppp}}^{(2),\text{eff}}(\text{ss})|$ which are computed from the Lorentzian fitted amplitudes of the SFG spectra (figure 4). The fitting parameters are provided in table S7. The intersection points of the horizontal lines with the theoretical orientation curve give the information of the influence of ions on the orientation angles of CH₂ groups of the PVP polymer. The obtained tilt angle values of vinyl chain methylene groups are plotted in figure 5b as a function of various Hofmeister ions (table S8). The ion-specific orientation angles of CH₂ groups follow a monotonic trend according to the rank of anions in the Hofmeister series (equation 1).



The maximum value of orientation angle 62.5° is obtained in the presence of SO₄²⁻, while the minimum value of 33.6° is obtained for SCN⁻. The lower tilt angle values of CH₂-groups (figure 5b) as observed with ClO₄⁻ and SCN⁻ imply that the presence of the most chaotropic ions brings disorder to the PVP vinyl chain at the interface.⁴²⁻⁴³ The present finding of ion-specific structural changes in the polymer chains at the air/aqueous interface as probed by ppp-SFG spectra remained unearthed in ssp-polarization scheme.

Further, to investigate the possible correlation between the observed ion-induced changes in the polymer chain conformation and the interfacial water structure, we have probed the OH-stretch region at the air/PVP-water interface in ppp-polarization configuration. The SFG spectral features as shown in figure 6

reveal the significant impact of ions on the water structure at the air/PVP-water interface. The presence of SO_4^{2-} ions bring an overall enhancement in the OH-region SFG intensity. In contrast, in the presence of Cl^- , Br^- , NO_3^- , ClO_4^- and SCN^- ions, an increase in SFG intensity is observed in the OH-stretch region from 3450 to 3800 cm^{-1} at the air/PVP-water interface. The ion-induced variation in the SFG intensity from 3450 to 3800 cm^{-1} follows a Hofmeister series of anions to adsorb at the hydrophobic interface.^{2,11-15}

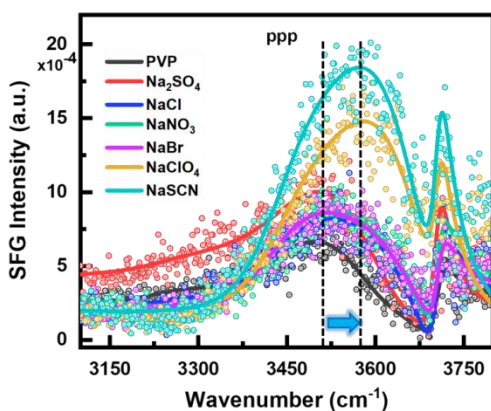


Figure 6. ppp-SFG spectra in OH-stretch region at air/PVP-water interface in the presence of 1 M Na_2SO_4 , NaCl , NaNO_3 , NaBr , NaClO_4 , and NaSCN . The points show experimental data, and the solid lines are the Lorentzian fit curves. Fitting parameters are given in table S9 of the supporting information.

Fascinatingly, we have observed a blue shift of around $\sim 40 \text{ cm}^{-1}$ for the OH-oscillator of frequency 3540 cm^{-1} . The blue shift is clearly visible in the case of ClO_4^- and SCN^- at the air/PVP-water interface. The change in the vibrational frequency of the OH-oscillator is a signature of modification in the bonding strength of the interfacial water molecules in the presence of chaotropic anions. For the pristine air/PVP-water interface, the water feature positioned at $\sim 3540 \text{ cm}^{-1}$ is attributed to the H-bonding interactions between water and C=O groups of the polymer.⁴¹ In the presence of ClO_4^- and SCN^- , we have attributed the OH-band at 3580 cm^{-1} to the non-hydrogen bonded water molecules involved in weak interactions with the hydrophobic moieties at the air/PVP-water interface.²⁶ Since the 3580 cm^{-1} band appears in the presence of chaotropic anions, it could have been interpreted as the OH-feature of weakly bonded water molecules surrounding the anions in spite of water molecules in weak interactions with the macromolecule. In order to justify the peak assignment, we have showcased the ppp-SFG spectra at the air/water interface carrying chaotropic anions in figure S2. The ppp-water structure for ClO_4^- is very similar to the water structure of pristine air/water interface. However, we did observe an enhancement at $\sim 3540 \text{ cm}^{-1}$ in the presence of SCN^- . This OH-feature corresponds to the water molecules involved in weak interactions with the thiocyanate anions at the interface. Evidently, the absence of OH-band $\sim 3580 \text{ cm}^{-1}$ at the air/salt-water interface justifies our interpretation of ion-specific weaker water-macromolecule interactions at the air/PVP-water interface. The weakly hydrated chaotropic anions (ClO_4^- and SCN^-) are more prone to being adsorbed at the hydrophobic -CH, and - CH_2 moieties of the PVP backbone.¹⁶ Therefore, we have attributed the ion-specific blue shifted OH-band centered

at $\sim 3580 \text{ cm}^{-1}$ to the non-hydrogen bonded water molecules involved in weak interactions with the backbone -CH, and - CH_2 moieties of PVP at the air/PVP-water interface.

Interestingly, the anion-induced variations in the water-macromolecule interactions (figure 6) are directly correlated with the changes in the macromolecule structure (figure 4-5) at the air/PVP aqueous interface. This enables us to comprehend the molecular level mechanism of the Hofmeister effect as follows: the weakly hydrated chaotropic anions (ClO_4^- , and SCN^-) which tend to adsorb towards the hydrophobic surface (-CH, - CH_2 of polymer backbone), offer binding sites to the surrounding water molecules to undergo weak interactions with the hydrophobic moieties of the macromolecule, and in turn disorder/destabilize the macromolecule structure at the interface. The current results provide experimental evidence to the recent Born-Oppenheimer molecular dynamic simulation study by Willow et al,¹¹ which emphasizes incorporating the water-macromolecule interactions in any explanation of the salting-in effect. Along with this, the present experimental work offers a comprehensive mechanism to understand the ion-induced variation in the strength of water-macromolecule interactions indirectly indicated by experiments of Lakshamanan et al.²³ and Song et al.²⁴

CONCLUSIONS

In summary, we have used SFG vibrational spectroscopy in ssp and ppp-polarization schemes to investigate the molecular-level mechanism of the Hofmeister effect at the air/PVP aqueous interface. The detailed quantitative analysis of the orientation angle of CH_2 -group of vinyl chains at the air/aqueous interface demonstrates the impact of ions on the ordering/disordering in the macromolecule structure that obeys the Hofmeister series. Large orientation angles of the CH_2 -group in the presence of kosmotrope (SO_4^{2-}) and small angle values with chaotropes (ClO_4^- and SCN^-) indicate the ability of kosmotropic/chaotropic anions to bring order/disorder to the polymer structure, respectively. We have monitored the intensity and frequency of the OH-stretching modes, which is the characteristic of water structure at air/aqueous interface in the presence of various salts. The blue shift in OH-band provides experimental evidence of the ion-induced variation in the strength of water-macromolecule interactions at the air/aqueous interface, which plays an important role in governing the Hofmeister effect. It has been demonstrated that the weakly hydrated anions (ClO_4^- and SCN^-) drive weak interactions between water and the hydrophobic surface moieties to offer vital contributions in disordering the macromolecule structure. The current work presents the mechanism of ion-induced modulation in water-macromolecule interactions and their participation in the Hofmeister effect alongside the known ion-water and ion-macromolecule interactions. We believe that the present experimental findings could be helpful in building a better understanding of the ion-specific and/or Hofmeister phenomenon, which profoundly prevailed in diverse physical systems.

ASSOCIATED CONTENT

Supporting Information includes ssp-SFG spectra in the CH-stretch region at the air/PVP-water interface in the presence of ions; ppp-SFG spectra in the OH-stretch region at the air/water interface in the presence of chaotropic ions; a detailed quantitative

description for the calculation of orientation angle of CH₂-groups at the air/PVP-D₂O interface, tables of Lorentzian fitting parameters of SFG spectra in ssp and ppp-polarization schemes, table for orientation angle values of CH₂-groups at the air/PVP-D₂O interface in the presence of ions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

VIS, Visible; IR, infrared; HWHM, Half width at half maxima; SFG, Sum frequency generation; PVP, polyvinylpyrrolidone.

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