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Interactions between Halide Anions and Interfacial Water Molecules in Relation to the Jones-Ray Effect

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Abstract

The Jones-Ray effect is shown to be governed by a different mechanism to enhanced anion adsorption. Halide ions at sub-molar concentrations are not exposed to the vapour phase; instead their first-solvating shell intimately interacts with the outmost water layer. Our novel proposal opens challenges to predicting related interfacial phenomena consistently.

Water is a remarkable molecule with unique physical and chemical properties arising from the extended hydrogen bonding network and not surprisingly there is continued investigation into fundamental aspects of water molecules at the air/aqueous interface. Despite these on-going efforts, however, there remain unanswered questions in a number of areas, including acidity[1-6], structure[7-9] and charge property of the outmost water layer at the air/aqueous interface[4, 10-11]. The presence of host ions in water increases the complexity of the system by altering the hydrogen bonding network both dynamically and structurally. That complexity, and the debates that arise, can be illustrated through surface tension, where a recent study has proposed that salt ions may be depleted from the air/aqueous interface by the image charge repulsion[12]. Indeed, there is much debate on this topic, which was initiated by Jones and Ray in 1934 when they utilised a newly invented differential tension-meter with an unsurpassed relative sensitivity of 0.001 percent to quantify the distribution of ions at the air/aqueous interface.[13-15] They reported a minimum in the surface tension at a low concentration of the order of 1 mM for 13 strong salts. This original observation is now known as the "Jones-Ray effect" and has remained neither unproven nor refuted since its first observation.

Recent theoretical[16-17] and experimental[18] studies utilising second harmonic generation spectroscopy (SHG) for anionic salts at dilute concentrations have generally supported the presence of the Jones-Ray effect through the adsorption enhancement of salts at the air/aqueous interface. Elevations in surface tension at increasing salt concentrations high have also been attributed to the image force resulting from increases the interfacial free energy excess due to the ion repulsion from the interface. The image force acts on the solute ions as well as the water molecules. Being doubly charged as compared to water's hydrogen atoms, the oxygen atoms experience a stronger image force and, therefore, lie further from the air/aqueous interface. Possessing extremely high polarity, water molecules close to the interface should have their net electric dipole moments pointing towards the bulk. However, the strong hydrogen bonding network may orient the interfacial water layer in such a way that the repulsive effect of the image force is lessened. In some instances, the image force even becomes attractive, and possibly facilitates the surface adsorption enhancement of polarisable anions.[12]

Surface ion enrichment is not a universally accepted phenomenon. For example, enhanced anion surface concentration of polarisable halides has been reported both theoretically and experimentally at high salt concentrations (1.0-2.0 M), [8, 19-20] whilst Richmond et al.'s SFG (sum frequency generation vibrational spectroscopy) data interpretation suggested that ions not be present in the outmost water layer.[7] Similar inconsistencies in observations have been reported for aqueous iodide systems. For example, Saykally et al.[21] reported an iodide surface enhancement of only around 40-60% of the bulk iodide concentration of 4 M, whilst Bonn et al.[22] reported a surface enhancement of 250% for an iodide bulk concentration of 3 M. There have been a number of other recent studies[23-26] involving either SFG or SHG measurements and focussing on relatively high concentration halide salt solutions. However, not much has been reported on the interfacial water structure at dilute salt concentrations in the Jones-Ray range below 10 mM. For this reason, the focus of this study was on undertaking SFG measurements in dilute salt concentrations in the 0-10 mM range to gain insight into the behaviour of interfacial water molecules under these conditions.

The experimental setup and SFG methodology used in this study have been published previously.[27-28] All sodium halide salts (NaF, NaCl and NaBr) were purchased from Sigma-Aldrich (ACS grade, purity >99%) and pre-treated by baking and filtering as reported by Allen's group.[29] Sodium iodide was not investigated due to its tendency to be oxidised to iodine and undergoing sublimation. The absence of organic impurities of these salts was confirmed by the absence of SFG signals in the C-H regime of 2800-3000 cm^{-1} (data not shown). The SFG signals in the ssp polarisation combination (s-polarised SFG signal, s- polarised visible incident beam and p-polarised tunable IR incident beam) in the O-H regime from 3000-3800 cm^{-1} were recorded for the sodium halide solutions as shown in

Figure 1. Spectral fitting in the O-H regime was not undertaken due to the complex nature of the hydrogen bonding scheme of the water network that has resulted in contrasting approaches. For example, Liu et al.[8] used five peaks at 3230, 3446, 3533, 3700 and 3751 cm^{-1} to fit their SFG signal; with the first three peaks having positive amplitude, whilst the last two having negative amplitudes. Conversely, Tahara and coworkers[30] utilised only three major bands at 3100 cm^{-1}, 3450 cm^{-1} and 3700 cm^{-1} in their heterodyne SFG study on neat water. Their data provided direct experimental information about the phase relationship among the SFG bands. In particular, the broad band at around 3200- 3600 cm^{-1} was found to be opposite in phase to the peak at 3100 cm^{-1} and 3700 cm^{-1}. Furthermore, the vibrational mode assignments of the three component bands at 3450 cm^{-1}, 3250 cm^{-1} and 3620 cm^{-1} of the broad band at 3200-3600 cm^{-1} have still been being debated, which not yet allows for a reliable data fitting.[30-31]

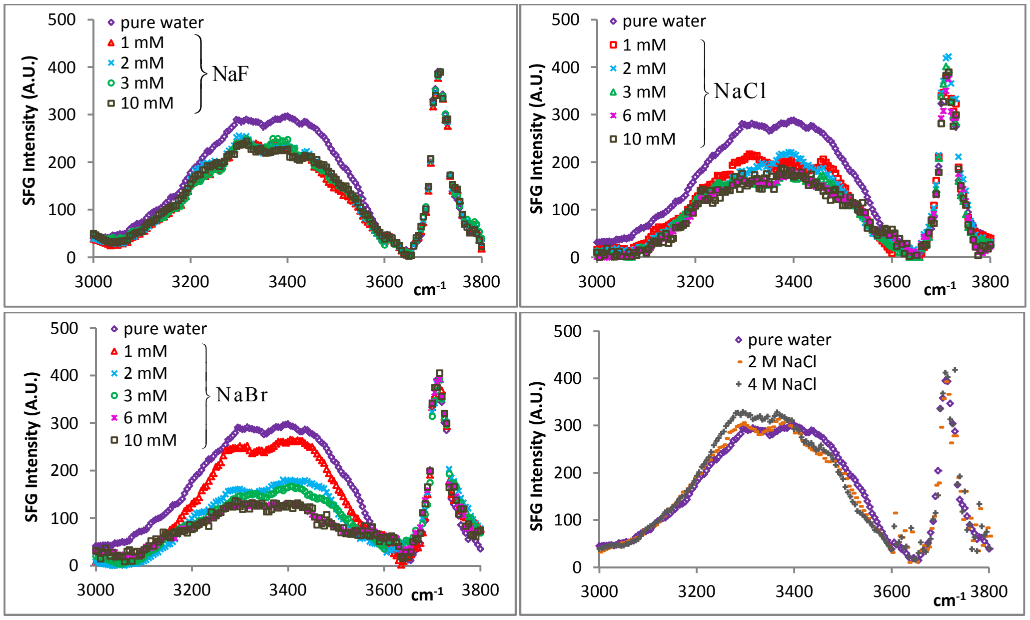

Figure 1. SFG spectra of dilute solutions of NaF, NaCl and NaBr. Data are also shown in the bottom-right figure for concentrated NaCl solutions as a reference (reproducing data reported in Refs 7 and 8). Intensities of free O-H peak at 3700 cm^{-1} remain unchanged.

In Figure 1 it can be seen that for both dilute and concentrated ion solutions the SFG signal intensity at wavenumber 3700 cm^{-1} is essentially the same for the different ion species and differences in concentration. The signal at 3700 cm^{-1} corresponds to that of free O-H bonds, which have been estimated to account for at least 20% of the all the O-H bonds available at the air/aqueous interface.[32] It is acknowledged that explicit quantification of the number of water molecules and ions at the air/aqueous interface is difficult since the measured SFG intensity might also be a function of orientation and hyperpolarisabilities in the macroscopic frame.[25] Assuming that the orientation of the free O-H bonds is not substantially affected by the introduction of salts,[23] then any presence of halide anions at the aqueous/air interface would lead to a lesser number of free O-H bonds and reduction in the SFG peak intensity at 3700 cm^{-1}. The observation that the intensity of the peak remains constant would suggest that no halide ions are present at the aqueous/air interface. Hence, any SFG spectral differences within the measured wavenumber range are most likely the consequence of the behaviour of the water molecules that are not in the outmost layer.[23]

It has been reported previously that the overall SFG intensity of the 3000-3650 cm^{-1} continuum decreases with fluoride but increases with the other halides.[7] However, it can be seen in Figure 1 that in the wavenumber range 3000-3650 cm^{-1} the SFG signal intensity has decreased significantly for dilute halide salt concentrations; whilst for high halide salt concentrations, the SFG signals actually slightly increased as also observed previously.[7-8] Richmond and colleagues attributed the reduction of SFG signal intensity to the enhancement of the hydrogen bonding network in the interface region by the fluoride ions.[7] However, this explanation does not apply to highly polarisable Br- ions since they are widely considered to be a "structure breaker" and unable to strengthen the water hydrogen bond network. The charge transfer between the halide anions and the first-hydrating shell generally leads to an enhanced Raman polarisability of the first solvating water O-H bonds[33-34] and for concentrated solutions of Cl-, Br- and I- ions an increase in SFG signal intensity is expected.[7-8]

To explain the decrease in SFG O-H signal strength of the 3000-3600 cm^{-1} band observed in this study, the argument based on the macroscopic centro-symmetry underlying the physics of SFG is employed. We attribute the SFG signal reduction to the geometric arrangement among the outermost water molecules to the anion first-solvating shell. Recently the orientation of both the free O-H bonds and the hydrogen-bonded O-H has been investigated by Gan et al.[35] Utilising the SFG technique they found that the free O-H bond pointed towards the vapour interface at an angle of 35° from the interface normal. They also independently calculated that the hydrogen-bonded O-H pointed towards the water phase with an orientation angle of 140 degrees. It has also been reported that some of the interfacial water molecules can have two hydrogen-bonded conformation[36] which leads to an overall dipole moment that points in the similar upward direction with these of the single hydrogen bonded OH (Figure 2). Such an overall molecular orientation scheme suggests that the direction of the dipole vector is approximately parallel to the interface, which agrees well with previous molecular dynamics simulation studies;[24, 37] and is also consistent with Shen et al.[38] where it was suggested that the outmost layer of water molecules was well-ordered rather than isotropic. Another anisotropic structure is, therefore, required for a medium to have an overall symmetry. Recent experimental and theoretical studies using Raman spectroscopy and Monte Carlo simulation also demonstrated that the halide ions created a highly anisotropic structure by affecting only the water molecules in their first-solvating shell and leaving the water molecules outside this shell almost intact.[33, 39] Given these descriptions of the halide first solvating shell, if the halide ions resided further from the air/aqueous interface than the first-solvating shell, the structure of the outmost water molecules would not be influenced by the halide ions. Consequently, changes in halide concentration would have no effect on SFG spectral features, which was not in line with either our SFG data or the reported data from various SFG groups.[7-8] Conversely, if the halide ions were exposed to the vapour phase, the population of the free O-H bonds would be reduced, leading to a drop in the SFG peak at 3700 cm^{-1}. These two hypothetical cases are evidently contradictory to the reported SFG observations at all halide salt concentrations and, therefore, are rejected.

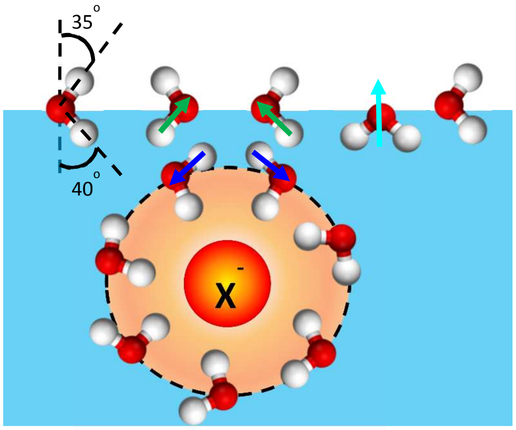

Figure 2. Schematic of halide ions with their first-solvating shell interacting with the outmost layer water molecules, leading to the weakened average water dipole moment at the interface and the reduced the water SFG signals in the 3000-3600 cm^{-1} broadband[43].

To explain both the unperturbed free O-H peak at 3700 cm^{-1} and the O-H broadband drop at low salt concentrations, we propose that the halide ions locate at an interfacial depth at which their first-solvating shell resides right below the outmost water layer as illustrated in Figure 2. In this arrangement, the outmost water layer at the interface should be located at the same distance away from the halide ions as their second-solvating shell. The proposed configuration can be verified by estimating the distance of the second-solvating shell of the halide ions by their first-solvating spheres and the intermolecular hydrogen bond length. The distances of the second-solvating shell for F^-, Cl^- and Br^- are approximately 4.5, 5.0 and 5.2 Å, respectively.[40] Molecular dynamic simulations[41] indicate that around 5 Å the mean force at the air/aqueous interface was found to diminish, resulting in the disappearance of the image repulsive force that keeps the halide ions away from the interface. Halide anions precisely at their second-hydration shell away from the air/aqueous interface should, therefore, experience no image force. Furthermore, it has also been suggested that dipole-dipole moment interaction between these two anisotropic environments influences the overall SFG susceptibility significantly at certain halide concentrations.[42] At halide salt concentrations greater than the Jones-Ray range, an increase in the SFG signal at 3450 cm^{-1} was observed because of either the real surface propensity enhancement of the halide ions or the reduced intermolecular coupling and Fermi resonance of the dominating anisotropic halide first-solvating shell. However, such discussion is beyond the scope of this communication. Briefly, our symmetry arguments, for the first time, are able to explain the Jones-Ray effect (and the other ion-specific effects) of F^- that has been experimentally reported by various techniques.[7-8, 23, 33] Being a small hard ion which is almost non-polarisable, F^- has been believed to be strongly expelled from the interface further into the water phase by the image force, leaving an ion-depleted surface layer approximately 3.5 Å thick as predicted by molecular dynamics simulation.[19] However, the Jones-Ray effect was observed with LiF salt,[13] indicating that the anions are not necessarily required to present at the surface to exhibit the Jones-Ray effect. Possessing low surface propensity, F^- cannot populate to the extent that the first-solvating shell dominates the SFG signal. Consequently, there is no SFG O-H signal enhancement observed with F^- at all concentrations.[7-8, 23] Furthermore, the anisotropic environment of the halide first-solvating shell reduces the net of the water dipole moments and, hence, the net of free energy of the water molecules, leading to a decrease in surface tension as observed by Jones and Ray. At higher salt concentration, the anions located at larger interfacial depth are further depleted by the stronger image force, resulting in an overall higher surface tension.

The SFG results reported in this study (Figure 1) indicate that there is a "critical" halide salt concentration at which the SFG O-H broad band stops decreasing. These "critical concentrations", at 1 mM (NaF) < 3 mM (NaCl) < 6 mM (NaBr), were observed to be within the Jones-Ray concentration range and inversely proportional to the charge density of the halide ions. The charge density reflects the image force strength within the Jones-Ray concentration range, and the halide ions stop approaching the aqueous/air interface when the image force is equal to that of the attractive force resulting from the anisotropic surface water layer

Conclusions

This study reports on SFG measurements on the interfacial water structure of dilute sodium halide solutions to shed some light on the controversial Jones-Ray effect. The SFG data suggest that the halide ions approach the surface and expose their first-solvating shell to the outmost water molecules. This interaction scheme decreases the Gibbs free energy of the outmost water layer and thereby reduces the surface tension as observed by Jones and Ray. Furthermore, this interpretation also explains the overall SFG signal drop in the O-H regime when dilute sodium halides are introduced. By distinguishing the Jones-Ray effect from the surface propensity enhancement of anions, our findings have provided additional information towards the accurate interpretation of this mysterious effect and open many challenges to predicting many related interfacial phenomena consistently.

Notes and references

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43 The arrows for the bond and molecular (net) dipoles are opposite to those used in the physics literature.