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ARTICLE

In situ investigation of halide co-ion effects on SDS adsorption at air/water interfaces

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Co-ions are believed to have a negligible effect on surfactant adsorption, but we show here that they can significantly affect the surfactant adsorption at the air/water interface. Sum frequency generation vibrational spectroscopy (SFG) was employed to examine the effects of three halides (Cl⁻, Br⁻ and I⁻) on the adsorption of the anionic surfactant, sodium dodecyl sulphate (SDS), at the air/water interface. The SFG spectral features of both the interfacial water molecules and the C-H vibrations of the adsorbed surfactant alkyl chains were analysed to characterize the surfactant adsorption. We demonstrate and compare the effects of the three halides, as well as explain the unusual effect of Br⁻, on the interfacial SDS and water molecules at the air/aqueous interface. It was observed that each of the three co-ions has a unique effect on the adsorption and conformation of the interfacial surfactant molecules at low halide concentrations of 10 mM - 50 mM, when the effect of halides on interfacial water structure is believed to be negligible. This discovery implies that not only do they influence surfactant adsorption indirectly via the interfacial water network but also that there is an interaction occurring between these co-ions and the negatively charged head-groups at the interface via hydration by the interfacial water molecules. Even though this interaction/competition is likely to occur only between the surfactant head-groups and the halides, the surfactant hydrophobic tail was also observed to be influenced by the co-ions. These observed behavioural differences between the co-ions cannot be explained by the variation of charge densities. Therefore, further studies are required to determine the mode of action of halides influencing the adsorption of surfactant which gives Br⁻ such a unique effect.

ARTICLE

1. INTRODUCTION

Surfactants are used in a wide range of industrial applications because of their ability to change the interfacial properties. In order to perform their functions, these surfactants must accumulate effectively at the desired interface with a suitable conformation. Surfactant adsorption can largely be described by thermodynamic treatments provided that the molecular parameters for (hydrophobic) chain-interface, chain-solvent and interface-solvent interactions are well defined and described. Therefore, knowledge of these interactions is essential to our understanding of the adsorption and conformation of surfactants at the air/liquid interface.¹

Studies into the effect of solvents on surfactant adsorption have shown that the adsorption is greatly influenced by the interaction of surfactant molecules with the counter-ions of the salts present in the solution. These counter-ions are believed to immobilize the Stern layer in different ways and thereby alter the surfactant adsorption, the critical micelle concentration (CMC), as well as the size and shape of the micelles.²⁻⁵ Conversely, it is thought that co-ions do not usually bind to similarly charged surfactant head-groups and, therefore, this interaction is unlikely to play a role in the surfactant adsorption.⁶

To further understand the mechanisms at play, this study is concerned with the effects of three halide co-ions (Cl⁻, Br⁻ and I⁻) on the adsorption of an anionic surfactant, sodium dodecyl sulphate (SDS), onto the air/water interface, *in situ* and real time using sum frequency generation vibrational spectroscopy (SFG). These three halide anions are all considered as anions with low charge density (chaotropes). Their interaction with water molecules is weak relative to the strength of water-water interaction.⁷ It has been shown that at high salt concentrations, the interfacial halide concentrations increase proportionally to the ionic radii, following the order: I⁻ (2.20 Å) > Br⁻ (1.95 Å) > Cl⁻ (1.80 Å). However, at low salt concentrations (less than 50 mM), no substantial change in the water SFG signals in the 3000-3800 cm⁻¹ range by the halide salts has been detected, indicating that they interact weakly with the interfacial water molecules.⁸ This leads to the rationale that at low concentrations, the halides do not affect the adsorption of surfactants. Here we aim to clarify this rationale experimentally.

Over the last two decades there have been a large number of studies on the hydration shells of halides⁹⁻¹¹. However, few studies have examined the effects of halides on the interfacial water structure and the adsorption of surfactants at the air-water interface. Recently, Allen et al. used conventional and phase sensitive SFG to observe the different effects of Br⁻ on the interfacial water and glycerol molecules at air/liquid interfaces and found that the halide effects were not linearly related to their ionic radii, charge densities or even hydration shell radii.¹² The current study was designed to investigate the effects the three halides, as well as the unique effect of Br⁻, on the interfacial structure of SDS and water molecules at the air/water interface. It was unexpectedly observed that each of the three co-ions had a unique effect on the adsorption and conformation of the interfacial surfactant molecules at low halide concentrations of 10 mM - 50 mM. This observation implies that not only do they influence surfactant adsorption indirectly via the interfacial water network but also that there

may be an interaction occurring between these co-ions and SDS head-groups facilitated by the interfacial water hydration at the interface. Even though this interaction/competition is likely to occur only between the surfactant head-groups and the halides, the surfactant hydrophobic tail was also seen to be influenced by the co-ions.

2. MATERIALS AND METHODS

2.1 Materials

Sodium chloride (ACS reagent grade, 99.0% purity), sodium bromide (bioXtra, >99% purity), and sodium iodide (ACS reagent grade, ≥ 99.5% purity) and sodium dodecyl sulphate (SDS, >99% purity) were purchased from Sigma Aldrich. To remove trace dodecanol as a product of SDS hydrolysis over time, SDS was purified by dissolution in ethanol, recrystallization and separation. The process was usually repeated between 3 and 5 times. The purity of the purified SDS then was tested by surface tension measurements which showed no minimum in the SDS surface tension curve (Figure S1). Freshly purified water (by an Ultrapure Milli-Q unit from Millipore, USA) with a resistivity of 18.2 MΩ.cm was used to make all the solutions used in the experiments.

In the SFG experiments, specific volume of the concentrated surfactant aqueous stock solution (5 mM) was injected into a reservoir of 20 mL to achieve the desired concentration (0.05 mM). A magnetic micro-stirrer was used for mixing for 10 s to ensure a homogeneous concentration distribution of the added surfactant molecules. The system was then left to equilibrate for at least one hour at room temperature before measurements were conducted. For surface pressure measurements, a Nima tensiometer (sensitivity of 0.1 mN/m) and a Pt Wilhelmy plate were used. The surface pressure was monitored and recorded every 1s by a computer. Contamination on the Wilhelmy Pt plate was removed by burning using a micro beam flame until the Pt turned bright, as per recommendation of the manufacturer. The clean Pt plate was fully wetted by the surfactant solutions used in this paper. The surface pressure was measured *in situ* and real time using the same experimental setup (sub-phase volume and surface area) of the SFG experiment to ensure experimental consistency. All experiments were carried out at room temperature of approximately 23°C.

2.2 SFG spectrometer

In the SFG experiments, the visible beam and the tunable IR beam were overlapped spatially and temporally on the solution interface. The visible beam was generated by frequency-doubling the fundamental output pulses (1064 nm, 10 Hz) of 20 ps pulse-width from an EKSPLA solid state Nd:YAG laser. The tunable IR beam was generated from an EKSPLA optical parametric generation/amplification and difference frequency system based on LBO and AgGaS₂ crystals. The tunable IR beam energy only fluctuated with a standard deviation of 3.0%, while that of the visible beam was 1.5%. In our SFG measurements, the incident angles of the visible was $\alpha_{vis} = 60^\circ$ and that of the IR was $\alpha_{IR} = 54^\circ$.

The quantities $\chi_{ssp}^{(2)}$ (s polarised SFG, s polarised visible and p polarised infrared polarisation combination) and $\chi_{ppp}^{(2)}$ (p polarised SFG, p polarised visible and p polarised infrared polarisation combination) reflect the observed SFG intensities in the laboratory frame. They are related to $\chi_{yyz}^{(2)}$ and $\chi_{zzz}^{(2)}$ as follows:

$$\chi_{ssp}^{(2)} = -L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)\sin\beta_2\chi_{yyz}^{(2)} \quad (1)$$

$$\chi_{ppp}^{(2)} = \begin{pmatrix} -L_{xx}(\omega)L_{xx}(\omega_1)L_{zz}(\omega_2)\cos\beta\cos\beta_1\sin\beta_2\chi_{zzz}^{(2)} \\ -L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2\chi_{zzx}^{(2)} \\ +L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2\chi_{zzx}^{(2)} \\ +L_{zz}(\omega)L_{zz}(\omega_1)L_{zz}(\omega_2)\sin\beta\sin\beta_1\sin\beta_2\chi_{zzz}^{(2)} \end{pmatrix} \quad (2)$$

where $L_{ii}(\omega)$ is a Fresnel coefficient corrected for local fields, and β , β_1 and β_2 are angles of the SFG signal, visible and IR beams with respect to the surface normal, respectively. For an C_{3v} symmetry point group on an isotropic surface, $\chi_{xxz}^{(2)} = \chi_{zzx}^{(2)}$. For this SFG experimental geometry, we have

$$\begin{aligned} L_{xx}(\omega)L_{zz}(\omega_1)L_{xx}(\omega_2)\cos\beta\sin\beta_1\cos\beta_2 &\approx \\ L_{zz}(\omega)L_{xx}(\omega_1)L_{xx}(\omega_2)\sin\beta\cos\beta_1\cos\beta_2 & \end{aligned} \quad (3)$$

At a methyl tilt angle of around 30° , the asymmetric mode component $\chi_{xxz}^{(2)}$ is negligible relatively to $\chi_{zzz}^{(2)}$. Therefore, the Fresnel coefficient ratio ssp/ppp in this tilt angle range is calculated to be 3.4. Further details on the calculations of these coefficients are available in the work of Wang and Zhuang.^{13, 14}

2.3 SFG water O-H stretch regime

For neat water, there are generally two SFG peaks observable in the $3000\text{-}3800\text{ cm}^{-1}$ region which was detected by fine-tuning at the middle (3400 cm^{-1}) in our measurements. There is one narrow peak centred at around 3700 cm^{-1} and one broad continuum spanning from 3000 cm^{-1} to 3600 cm^{-1} . While the narrow peak at 3700 cm^{-1} is commonly assigned to the free OH at the interface, the origin of the broad peak is still under debate: some believe that this continuum arises from the dynamic fluctuation of water molecules while others support the hypothesis that it is due to multiple hydrogen bond species coexisting among the surface water molecules.¹⁵⁻¹⁸ In our study, two major peaks at around 3180 cm^{-1} and 3450 cm^{-1} were observed in the water spectra in the $3000\text{-}3800\text{ cm}^{-1}$ range, featuring the "ice-like" and disordered characters, respectively.^{8, 19}

2.4 SFG C-H stretch regime

The conformational information about the surfactant hydrophobic alkyl chains can be obtained from the C-H vibrational stretches which are detectable by SFG in the $2800\text{-}3000\text{ cm}^{-1}$ spectral range. The SFG signal was fine-tuned at the middle of 2900 cm^{-1} . With negligible gauche defect, the alkyl tail tilt angle can be calculated from the orientation of the terminal methyl group of the chain. In the ssp polarisation combination, the peak at around 2878 cm^{-1} (methyl symmetric stretch) and 2940 cm^{-1} (methyl Fermi resonance) are used because they are sensitive to the orientation of the alkyl tail while the peak at 2970 cm^{-1} (methyl asymmetric stretch) is used in the ppp polarisation combination.

The correlation between the macroscopic hyperpolarisability components $\chi_{yyz}^{(2)}$ and $\chi_{zzz}^{(2)}$ of the methyl group possessing C_{3v} symmetry point group and its tilt angle, θ , can be established as follows:

$$\chi_{yyz}^{(2)} = \frac{1}{2}N\beta_{ccc} \left[(1+r)\langle\cos\theta\rangle - (1-r)\langle\cos^3\theta\rangle \right] \quad (4)$$

$$\chi_{zzz}^{(2)} = 2N\beta_{aca} \left(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle \right) \quad (5)$$

where N is the number density of interfacial molecules, β_{lmn} is a component in the microscopic molecular hyperpolarisability tensor. $r = \beta_{aac} / \beta_{ccc} = 2.3$ was experimentally measured by Zhang et al.²⁰ The ratio $\beta_{aca} / \beta_{aac} = 4.2$ was also determined experimentally by Watanabe et al.²¹

Because the tilt angle θ is not likely to take a single value but a narrow distribution instead, the average value $\langle\cos\theta\rangle$ of this distribution was used in place of $\cos\theta$ in the analysis. For all-trans alkyl chains, the axis of the terminal methyl group makes an angle of 37° to the surface normal.²¹

The disturbance of the hydrophobic alkyl chain can be observed via the methylene C-H stretches. Spectroscopically, the methylene group possesses C_{2v} symmetry characters, which determine the macroscopic hyperpolarisability tensor components as described by the following equations:

$$\begin{aligned} \chi_{yyz}^{(2)} &= N(\beta_{aac} + \beta_{bbc} + 2\beta_{ccc})\langle\cos\theta\rangle / 4 \\ &+ N(\beta_{aac} + \beta_{bbc} - 2\beta_{ccc})\langle\cos^3\theta\rangle / 4 \end{aligned} \quad (6)$$

$$\chi_{zzz}^{(2)} = N\beta_{aca} \left(\langle\cos\theta\rangle - \langle\cos^3\theta\rangle \right) \quad (7)$$

where $\beta_{aac} / \beta_{ccc} = 1.67$, $\beta_{bbc} / \beta_{ccc} = 0.33$ and $\beta_{aca} / \beta_{ccc} = 1.35$ as calculated from the dipole moment and the polarisability derivative of a single C-H bond.²² It is noted that the methylene C_2 axis generally lies perpendicularly to the symmetric axis of the tail and the tilt angle θ in the above-described equations is the angle between the surface normal and the symmetric axis of the C_{2v} point group. If the alkyl chains are in their all-trans conformation, the vibrational modes of the methylene groups should be invisible due to the inversion-symmetric property of the system. In the presence of gauche defects, the inversion-symmetry is broken and the terminal methylene group starts to show in the SFG spectra. The strongest observable vibrational mode of the terminal methylene group should be the symmetric mode at 2850 cm^{-1} . Therefore, a strong SFG intensity of this mode observed in ssp polarisation combination can be approximately interpreted as the significant existence of gauche defects and the surfactant alkyl chains do not orient completely vertically to the interfacial plane. The gauche defect also randomizes the orientation of the terminal methyl groups, leading to an overall SFG signal drop of all methyl C-H vibrational modes.

3. RESULTS AND DISCUSSIONS

3.1 Effects of halide co-ions of low concentrations on pre-adsorbed SDS molecules at the air-water interface

The adsorption of SDS at the air/water interface under the influence of halide ions Cl^- , Br^- and I^- was studied by adding small volumes of salt solutions to an equilibrated $50\text{ }\mu\text{M}$ surfactant solution with SDS molecules pre-adsorbed at the interface. In the absence of the added salts, the SFG signals of C-H stretches of adsorbed SDS were very weak. After adding the salts into the solution, two phenomena were observed for all three halide co-ions:

(1) the C-H signals from the hydrophobic chains underwent significant changes and (2) there was a change in the SFG signal of the interfacial water layer. Unexpectedly, the changes did not reflect the differences in the halide charge densities. It can be seen from the ppp spectra in the C-H regime in Figure 1a that the peak at 2970 cm^{-1} became increasingly dominant with increasing concentration of Br^- . The SFG intensity of this peak correlates with the asymmetric stretch of the terminal methyl group. The ppp SFG signal of the peak at 2970 cm^{-1} increased dramatically in the case when the salt concentration was increased from 10 mM to 40 mM (shown by the red and blue curve in Figure 1a, respectively), while the ssp signals did not change substantially (Figure 1b). According to Eqs. (4) and (5), an increase in the intensity ratio of $\chi_{ppp\text{ sym}}^{(2)} / \chi_{ssp\text{ sym}}^{(2)}$ implies a

larger tilt angle θ (Figure S2). However, it is worth remembering that in the case of methyl terminal group θ is the angle between the C_3 axis and the surface normal, and the C_3 axis is 37° away from the alkyl chain axis. Thus, the Br^- concentration of 40 mM causes the alkyl chain to adopt a more vertical orientation. If all the alkyl tails are assumed to adopt the all-trans conformation, their exact tilt angle can be derived. Unfortunately, the peak at 2850 cm^{-1} in the ssp spectrum (Figure 1b) indisputably shows the spectroscopic evidence of significant gauche defect. Even though it is difficult to propose an accurate alkyl chain tilt angle because of the gauche defect, it can be qualitatively concluded that the alkyl chains stand up upon adding Br^- into the SDS solution. The gauche defect indicates further that the alkyl chain-alkyl chain interaction among the surfactant molecules is not very well ordered.

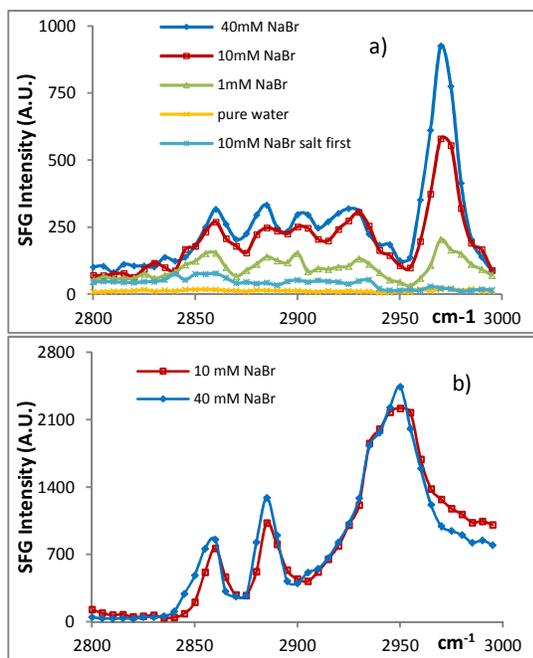


Figure 1. Effect of bromide co-ion of low concentrations added into a $50\text{ }\mu\text{M}$ SDS solution on SFG spectra, obtained in ppp polarisation combination (a) and ssp polarisation combination (b), of C-H stretches of SDS pre-adsorbed at the air-water interface. The ppp spectra of SDS at the surfaces of pure water and the solution of 10 mM NaBr added prior to the addition of SDS are extremely weak.

While the SFG signals in the C-H regime became discernable after adding 1 mM NaBr, these signals only became evident after adding 10 mM NaCl (spectrum not shown) and only were strong after adding 40 mM NaCl (Figure 2). The increase in SFG signal

intensity in the C-H vibrational range was more sensitive to adding Cl^- than to I^- (Figure 2), which agrees with their relative charge densities. However, the same trend was not observed with Br^- (Figure 1 vs. Figure 2). In principle, the appearance of these SFG signals does not necessarily imply an increase in the surface excess of the surfactant since an enhanced SDS adsorption does not give rise to any SFG signal if the interfacial surfactant molecules assemble in a random fashion. Furthermore, surface pressure measurements showed that at the same salt concentration (10 mM), NaCl enhanced the SDS adsorption to only slightly greater extent than NaBr (Figure 3a). Therefore, the increase in C-H signals with adding NaBr must be due to the ordered assembly of the SDS layer. This possibility will be discussed in Section 2.2.

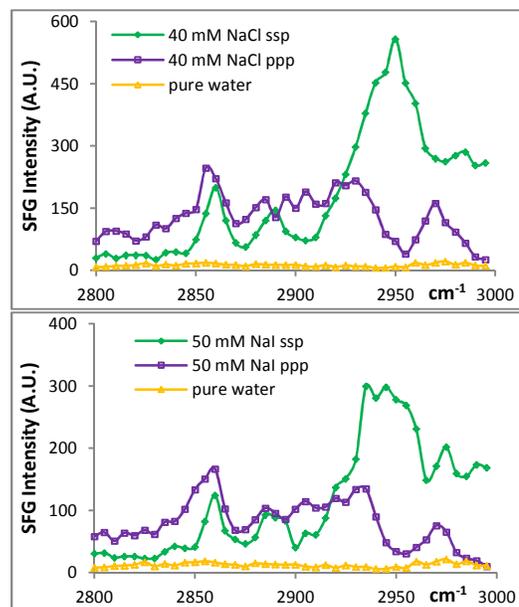


Figure 2. Effect of Cl^- and I^- co-ions added into a $50\text{ }\mu\text{M}$ SDS solution on SFG spectra of C-H stretches of SDS pre-adsorbed at the air-water interface.

There was a common spectral feature observed after the addition of all three halides: The SFG intensity of the methylene symmetric stretch at 2850 cm^{-1} was strong in comparison to the methyl symmetric stretch at 2878 cm^{-1} , which is an indication of a strong gauche defect among the surfactant molecules. However, Br^- distinguishes itself from the other two halide co-ions by a much stronger effect on the SFG signal of the surfactant alkyl chains, especially the methyl symmetric stretch (2878 cm^{-1}) and the asymmetric stretch (2970 cm^{-1}) observed in the ssp and ppp polarisation combinations, respectively (Figure 1). If the SFG intensity increases of these peaks were due to the gauche defects, the same phenomenon should be observed with all three halides, which was not the case. With this argument being ruled out, it is more likely that the surfactant alkyl chains adopt a more vertical orientation upon the addition of Br^- to the sub-phase.

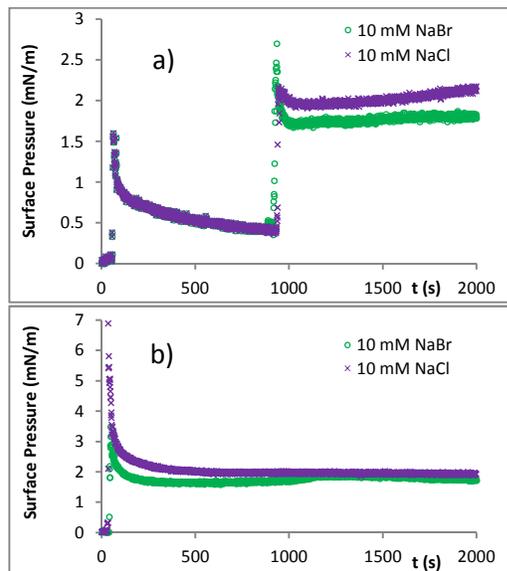


Figure 3. Effect of 10 mM NaCl and 10 mM NaBr on SDS adsorption ($50 \mu\text{M}$ bulk concentration) as detected by dynamic surface pressure measurements. The order of salt and SDS additions into water has different effects on surface pressure: a) adding salts at 900s after SDS (added at 0s) further increased the SDS surface pressure, b) salts added before adding SDS (at 0s) did not change the surface pressure of water but increased the dynamic surface pressure of SDS-salt solutions.

In the interfacial water SFG signal regime of $3000\text{--}3800 \text{ cm}^{-1}$, the SFG intensity went up slightly with the addition of 10 mM NaI and NaCl, and surprisingly decreased in the case of NaBr addition (Figure 4c). Furthermore, the “free dangling O-H” peak at 3700 cm^{-1} vanished upon the addition of Br^- (Figure 5a). Because SFG is a nonlinear optical spectroscopic technique, its signal intensity depends on both the surface coverage and the relative molecular orientation in the laboratory frame. Therefore, a decrease in the water signal in the case of NaBr addition does not necessarily indicate a surfactant adsorption decrease. Instead, the interfacial water molecules may just have lost their previous level of order as evidenced by the disappearance of the free O-H dangling mode at 3700 cm^{-1} . Alternatively, this SFG signal drop can be explained by the chaotropic property of bromide (at high bromide concentration). However, since Br^- was used at low concentrations, this alternative explanation is unlikely, given that the literature has reported that halides are only able to affect the interfacial water structure at high concentrations, i.e., about 4 M and 2 M for NaCl and NaBr, respectively.⁸ In addition, if it is indeed the chaotropic property of this halide family that breaks the order of the interfacial water layer, leading to the above mentioned SFG signal loss, then the increased water signal after the addition of Cl^- and I^- (Figure 4c) is difficult to explain.

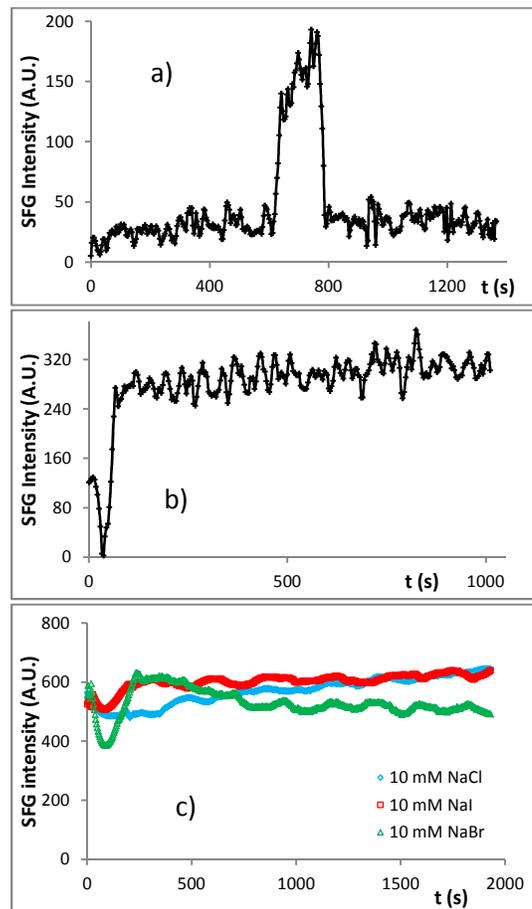


Figure 4. Time dependence of ppp SFG signals of the SDS methyl asymmetric stretch at 2970 cm^{-1} under influence of 50 mM NaI (a) and 11 mM NaBr (b) as added into $50 \mu\text{M}$ SDS solutions at time $t = 40 \text{ s}$, and ssp SFG water signals (c) at 3200 cm^{-1} of $50 \mu\text{M}$ SDS solution surface after adding the halides at $t = 100 \text{ s}$. The sharp peak in a) normally occurred with some delayed time after the addition of NaI and then disappeared, while the peak in b) occurred almost instantly after adding NaBr and then disappeared.

The SFG signals in both the C-H and O-H regimes support the idea that the addition of Br^- pushes the surfactant molecules further away from the bulk and these SDS molecules adsorbed to the surface with their hydrophobic tails inserted in the hydrophobic region of the existing SDS layer. However, the head-groups of these newly adsorbed molecules appeared to have insufficient energy to blend perfectly in the existing interfacial SDS molecules. These molecules, therefore, settled at a deeper interfacial depth, resulting in multiple distinct distributions of adsorbed SDS molecules. This surfactant headgroup distribution fashion has also been proposed by Ivanov et al. and Morgner et al. with and without the effects of counter-ions, respectively.^{23, 24} As a result of this non-planar headgroup distribution, the interfacial water molecules adopt a randomised orientation distribution. This interaction scenario may explain the decrease in the water signal in the $3000\text{--}3800 \text{ cm}^{-1}$ region and the strong vertical orientation of the adsorbed surfactant molecules.

A different interaction scheme was observed for Cl^- and I^- additions. The SFG water signals increased upon the additions of these salts and the SFG signals in the C-H regime were similar for both cases (Figure 2). Thus, despite having different ionic radii, Cl^- and I^- affected the surfactant adsorption in a

similar manner and Γ^- just needs to be more populated than Cl^- to achieve the same ability in both fashion and magnitude. The lower charge density of Γ^- makes the ion act slowly, which was observed in the time dependent SFG measurement (Figure 4a). The SFG signal of the methyl asymmetric mode rose dramatically at approximately 600s after adding 50 mM NaI (at 40s), and then interestingly vanished at around 800s. This observation was not likely to be caused by the fluctuation of the incidence laser beams since the propagated error of the SFG signal was only around 6.5%. It is worth noting that even though the equilibration of SDS solution is a rather fast process with duration typically less than 1 s, the effects caused by the halide ions to the pre-formed (pre-adsorbed) SDS layer may take much longer time. This delay was evidenced by the changing surface pressure and SFG signal intensity over 1000s period as evidenced by Figures 3a and 4c, respectively. Conversely, the adsorption and surface equilibration of SDS from dilute Br^- and Cl^- solutions happened very quickly (Figure 3b) as compared to the case of the absence of the pre-formed SDS layer. To explain the sudden rise and fall in Figure 3a, we hypothesize that the alkyl tails were inserted into the hydrophobic region of the existing surfactant layer. During the insertion, the alkyl tails may have temporarily obtained a more vertical orientation to the plane of interface. After the insertion was completed, the alkyl chains joined the common horizontal orientation of the existing network (Figure 4a). It is noted that this temporary insertion phenomenon was not observed with the addition of NaCl, possibly due to the stronger charge density of Cl^- , creating an energy barrier that prevented the “temporary insertion” from occurring.

The increase in the SFG water signals and the persistent spectral features in the C-H regime suggest that these three halide co-ions expel/push some surfactant molecules from the bulk to the interface, leading to an increase in the surface excess. The charge density of Cl^- seems to be strong enough to “push” the newly adsorbed surfactant molecules closer to the interface, allowing for the formation of a well-blended surfactant layer. It was experimentally observed that Γ^- , with its lower charge density, needs to be more populated to gain a strength comparable to Cl^- (Figure 2). This well blended scheme appears to enhance the surfactant adsorption with minimal surfactant conformation changes. It would also explain the slight increase of the SFG signal of the interfacial water.

3.2 Effects of halide co-ions on SDS adsorption onto the air-water interface from dilute halide salt-SDS solutions

Here the adsorption of SDS at the air/water interface in the presence of halide co-ions was first studied by adding SDS to the dilute Br^- solutions. Specifically, we injected 5 mM SDS stock solution into 10 mM Br^- solutions to obtain the final SDS concentration of 50 μM . Interestingly, adding SDS into the solution of co-ions lowered the SFG signals of interfacial water and SDS molecules. In particular, a slight decrease in the water O-H (Figure 5a) and a twenty-fold decrease for C-H symmetric stretch (Figure 1b vs 5d) were observed.

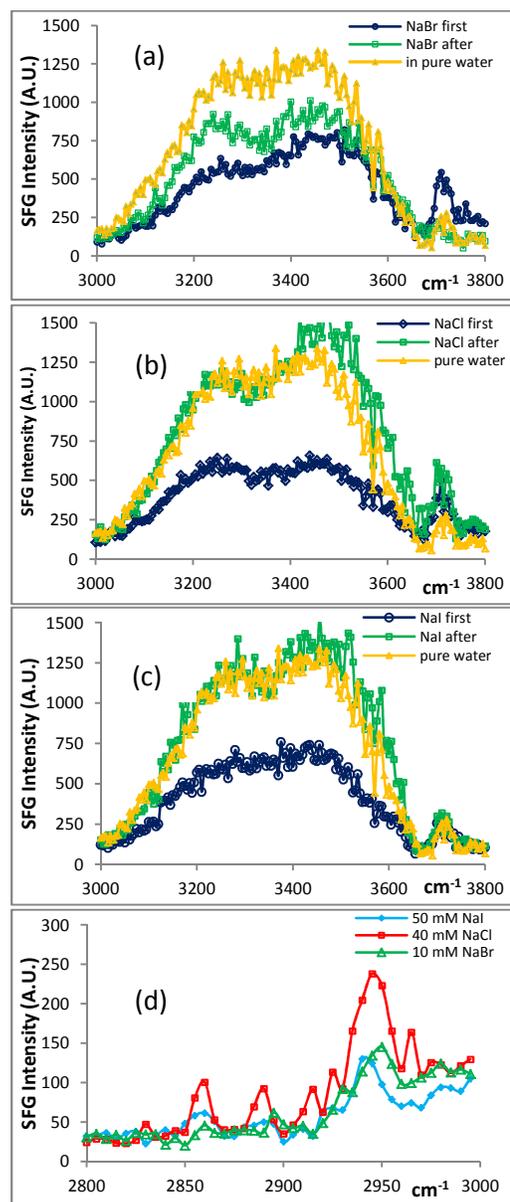


Figure 5. (a), (b), (c): SFG water signals of the (50 μM) SDS-salt systems of NaBr (10mM), NaCl (40 mM) and NaI (50 mM) with orders of addition: salts before SDS and salts after SDS. (d) ssp SFG C-H signals of the SDS-salt systems when salts were added into water prior to adding SDS.

Despite the dramatic differences in SFG signals both in O-H and C-H regimes, surface pressure measurement showed that the enhanced adsorption of SDS caused by the co-ions was only slightly reduced if the co-ions were added prior to, rather than after, the SDS addition (Figure 3a and 3b). Thus, the reason for reversing the order of bromide and SDS addition affecting SDS adsorption and interfacial surfactant molecular conformation is yet to be determined. SDS has a much higher surface activity than bromide due to the high transfer energy of its hydrophobic alkyl tail; an adsorption competition between SDS and bromide at the interface is unlikely to occur. Traditionally, ions are thought to be absent from the outer most water layer due to the image repelling force. However, more recent experimental and theoretical investigations have proposed a revised picture of the surface structure of salt

solutions.²⁵⁻²⁷ It is now widely believed that, there is a dipole induction in the highly polarisable anions at the water surface. This dipole would compensate for the image force and stabilise the anions at the outer most water layer. Most importantly, these polarisable anions present at the air/water interface would then be available for chemical reactions and interactions, as has been observed experimentally.²⁸⁻³⁸ It is, therefore, possible that interfacial halides indirectly influences the SDS adsorption by changing the hydration ability of interfacial water molecules in interacting with the surfactant headgroup and/or altering the interfacial water layer which then dictates the ordering of the surfactant adsorption layer. The effects of halide co-ions on the interfacial water layer are reflected in the spectral changes observed in the 3000-3800 cm^{-1} , especially the free dangling OH peak at 3700 cm^{-1} (Figure 5a). A similar SFG signal decreasing trend was observed with 40 mM Cl^- and 50 mM I^- (Figures 5a,b,c) when the salt/SDS addition ordering was reversed.

3.3 Adsorption of SDS onto the air-water interface at high halide concentrations

It was found that increasing the concentration of halide salts caused the interfacial SDS molecules to pack in a different fashion. At a Br^- concentration of 0.5 M, soluble SDS molecules were strongly expelled to the air/water interface. A strong gauche defect would still exist among the surfactant hydrophobic tails, as evidenced by the strong peak at 2850 cm^{-1} collected in ssp polarisation combination (Figure 6). Therefore, an accurate orientation data analysis of this alkyl chain based on the terminal methyl groups is impossible. However, the relative SFG intensities of the methylene symmetric stretch at 2850 cm^{-1} (ssp), the methyl symmetric stretch at 2878 cm^{-1} (ssp) and the methyl asymmetric stretch at 2970 cm^{-1} (ppp), and the stronger SFG signals in this C-H regime in the case of Br^- when compared to Cl^- at the same concentration (Figure 6) all indicate that these adsorbed surfactant molecules assemble in a fairly vertical orientation. At this high concentration of Br^- , the soluble surfactant molecules are given a 'good push' towards the surface where they adopt a more or less vertical orientation despite there are already bromide co-ions present at the interface.

An entirely different surfactant packing scheme was observed under the influenced of 0.5 M NaCl . Figure 6 shows that the interfacial surfactant molecules suffer a very strong gauche defect among their alkyl chains and are likely to have adopted a more disordered conformation and a horizontal orientation. This is evidenced by the four-fold weaker overall SFG signal in the C-H regime, the dominating methylene peak (symmetric 2850 cm^{-1} , ssp and asymmetric 2915 cm^{-1} , ppp), the weaker methyl symmetric stretch peak (2878 cm^{-1} , ssp) and the much weaker methyl asymmetric stretch peak (2970 cm^{-1} , ppp).

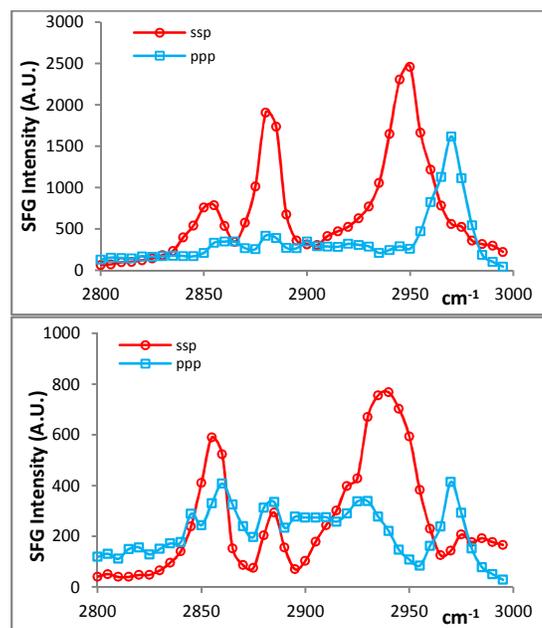


Figure 6. SFG C-H signals of SDS (50 μM) in concentrated salt solutions of 0.5 M NaBr (top) and 0.5 M NaCl (bottom).

4. Summary and Conclusions

Bromide co-ion was experimentally shown *in situ* and real time to have a different effect on the adsorption of SDS molecules at the air/water interface than chloride and iodide co-ions. Our SFG observations suggest that Br^- enhances SDS adsorption by causing the newly adsorbed surfactant molecules to adopt a vertical orientation at the air/water interface and that this occurs at both low and high salt concentrations. However, the adsorption enhancement ability of Cl^- and I^- does not seem to have such ability. Br^- could, therefore, result in significant changes in the surface properties of the adsorption layer such as interfacial viscoelasticity, foam formation and stability. In addition, the two halides Cl^- and I^- were shown to affect surfactant adsorption in a similar way despite differences in their ionic radii and charge densities. Further, the SFG data also demonstrate that the ordering of SDS and salt additions to the water also significantly affects the surfactant adsorption and that salt concentration was a critical factor in determining surfactant adsorption at low bulk surfactant concentrations. Although in this report we are unable to provide a quantitative explanation for this interesting peculiarity, this observation hopefully attracts some attention from researchers in the field of chemical modelling and computation. Finally, this study provides valuable information on the mechanisms by which halide co-ions affect surfactant adsorption at the air/water interface. Understanding the mechanism at play is essential to the refinement of chemical modelling and to adaptations for industry applications.

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Notes and references

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Table of Contents Entry

Halide co-ions are shown to strongly influence adsorption of anionic surfactant SDS unexpectedly.

