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ABSTRACT
Specific ion effects at interfaces are important for a variety of thermodynamic properties of electrolyte solutions, like surface tension and the phase behavior of surfactants. We report the relative surface affinity of Na\(^+\) and D3O\(^+\) at both the D2O-air and the sodium dodecyl sulfate (surfactant)-covered D2O surface by studying the alignment of interfacial D2O, using vibrational sum frequency generation spectroscopy. The surface propensity of ions is found to be a function of both the nature of the ion and the nature of the surface. Specifically, for the charged, surfactant-covered interface, Na\(^+\) has a higher affinity than D3O\(^+\). In contrast, D3O\(^+\) has a higher affinity than Na\(^+\) at the air-D2O interface. The relative surface affinity of cations thus depends on both details of the cation and the type of interface.

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INTRODUCTION
Ion specificity is important in various biochemical processes that frequently occur at the interface of water and lipid membranes of surfactants such as counterion dictated adsorption of surfactants at air-solution interfaces.1 It is proposed that at the water-air interface covered with charged organic monolayers, the coulomb interaction dictates the specific ion adsorption.2,3 On the contrary, properties such as ion polarizability,4 ion size,5 dispersion forces, and hydration energy6 have been proposed to be dictating the ion adsorption at the neat water-air interface. It is indeed possible that different factors dominate specific ion adsorption at different interfaces. However, though water is an integral part of aqueous interfaces, the role of water itself in determining the ion specificity in the presence and absence of charged organic monolayers is not well understood. Therefore, it is important to understand the ion-specific effects on interfacial water organization in the presence of different types of ions and surfactants.

Surfactants are typically amphiphilic, owing to their characteristic nonpolar alkyl chains and polar head groups. They can adsorb at both polar (aqueous) and non-polar interfaces. At and beyond their critical micelle concentration (CMC), surfactants form a closely packed monolayer at the interface of water with air. The polar head groups directly interact with the water molecules and reduce the surface tension of water.

Due to this adsorption ability, surfactants are widely used in various industrial and biological applications, often in combination with salts and acids. The combination of surfactants and ions is also ubiquitous in the environment. In seawater, for instance, surfactants further interact with other chemicals and affect various physiochemical properties such as surface adsorption of these chemicals.7 Amongst different surfactants, those with charged head groups are abundant and interact strongly with water and aqueous electrolyte solutions.8,9 Surface tension studies, radiochemical studies, and simulations indicate that the counterions compete for surface adsorption at the water surface covered with charged surfactants.2,3,10 In mixtures of monovalent cations, cations with smaller hydrated radius (i.e., higher charge density) tend to replace those with larger hydrated radius. Studies on charged lipid-covered aqueous interfaces have shown that the
counterion concentration next to the lipid monolayer is much higher than in the subphase, as predicted by the Gouy-Chapman model. The counterions screen the charge of the head groups and thereby influence the way interfacial water molecules align and interact with the surfactant/lipid head groups.

The resulting properties of such charged lipid/surfactant covered interfaces thus depend on the interplay of the surface charge, the presence of the counterions, and the water molecules. While this general understanding of charged interfaces exists, the details of how the structure of such charged surfaces depends on the type and concentration of counterions in solution are a priori unknown. To the best of our knowledge, the effect of protons on the alignment of water at such interfaces has not been reported, to date. This is surprising, considering the ubiquity of protons and their importance for countless physiochemical phenomena including protein (un-)folding and ion and charge transport through biological cell membranes.

To study the effect of protons on the alignment of water at a surfactant-covered aqueous surface, we have investigated a monolayer of sodium dodecyl sulfate (SDS, R–O–SO\(_3^-\)) on a D\(_2\)O subphase containing excess D\(_2\)O\(^+\). We have compared the results to those obtained from a subphase containing Na\(^+\) and to the results from the same subphases without the surfactant, i.e., at the D\(_2\)O-air interface. As shown in Fig. 1(a), SDS has a negatively charged head-group and Na\(^+\) as a counterion. It is a widely used component in, for example, shampoos, detergents, and toothpastes. As such, aqueous solutions of SDS containing various electrolytes are abundant in the environment. MD simulations have shown that for an SDS-covered water surface, SDS-head groups are hydrated and a significant population of Na\(^+\) is present within these hydration shells. These Na\(^+\) bridge different surfactant head groups and thereby stabilize the self-assembled monolayer (SAM). As mentioned above, here, we compare the interaction of D\(_2\)O\(^+\) and Na\(^+\) with SDS. We determine the surface affinity of both ions by measuring the extent of water alignment, i.e., the extent of non-centrosymmetric organization of water, by vibrational Sum Frequency Generation (SFG).

SFG has been widely used to study the behavior of water in contact with surfactant and lipid monolayers and the bare water-air interface of aqueous electrolyte solutions. In SFG spectroscopy, a broadband IR pulse, spatiotemporally overlapped with a narrowband 800 nm pulse, impinges the sample. When the IR light is resonant with a molecular vibration, the SFG response is enhanced, resulting in a strong sum frequency signal. Centrosymmetric media like bulk water have zero SFG response, owing to the selection rules of the method. At the interface, however, the centrosymmetry is broken, resulting in an SFG signal from the interfacial water. This preferential alignment of water molecules is higher in the presence of charges at the interface like a monolayer of ionic surfactants. As a first order approximation, a more highly charged surface results in more aligned water molecules, giving rise to a higher SFG signal. At such surfactant-covered water surfaces, counterions present in the subphase can screen the charge and reduce the SFG intensity. Thus by monitoring the

SFG intensity as a function of the concentration of excess charges, we can quantify the relative surface affinity of Na\(^+\) and D\(_2\)O\(^+\). Note that the correlation between the degree of water alignment and SFG signal intensity breaks down at low ionic strength.

We find that at the SDS covered aqueous interface, the relative interfacial affinity of Na\(^+\) is higher than that of D\(_2\)O\(^+\). At the bare water-air interface, the affinity order is the opposite. The relative surface affinity of counterions is thus interface dependent. Moreover, the order of the alkyl chain of the SDS-SAM is lower in the presence of D\(_2\)O\(^+\) than in the presence of Na\(^+\) indicating that the order of the SAM also depends on the type and concentration of the counterion present.
RESULTS AND DISCUSSIONS

Figure 1(b) shows the SFG intensity in SSP polarization (S— for SFG and VIS, P— for IR) as a function of infrared frequency, recorded from the surface of a 12 mM SDS solution in D₂O without any excess ion and with co-containing Na⁺ and D₃O⁺ at different concentration ratios with a total cation concentration of 0.1M. The pink curve shows the SFG intensity in the absence of any excess ions, and the red and the dark green in the presence of 0.1M D₃O⁺ and Na⁺, respectively. The other three curves are responses in the presence of co-existing Na⁺ and D₂O⁺, where the total cation concentration is fixed at 0.1M. Each spectrum has a broad response that extends from ~2100 cm⁻¹ to ~2700 cm⁻¹ and three narrower responses between ~2800 cm⁻¹ and ~3000 cm⁻¹. The broad feature is the vibrational response of the O-D groups located near the monolayer of SDS. As discussed in detail in Ref. 15, there are two sub-ensembles of OD groups at this interface which vibrate at ~2390 cm⁻¹ and ~2510 cm⁻¹. The OD groups that vibrate at ~2510 cm⁻¹ are hydrogen bonded to the head groups of SDS (R–O–SO₃⁻), and the ones that vibrate at ~2390 cm⁻¹ are not directly in contact with O–SO₃⁻ groups, yet aligned under the influence of their electric field. The relatively sharp peaks at ~2846 cm⁻¹, ~2870 cm⁻¹, and ~2910–2980 cm⁻¹ are different C–H vibrations of the alkyl chain of SDS.

The SFG intensity in the presence of both 0.1M D₃O⁺ and Na⁺ is significantly lower in the OD stretch region than in the absence of any excess ions in the solution. As predicted by the Gouy-Chapman model¹² and shown by simulations,¹⁴ the Na⁺ concentration near the charged monolayer head groups is extremely high even in the absence of any excess ions in the solution. Addition of excess Na⁺ enhances the counterrion concentration near the surface resulting in an increased charge screening and a concomitant reduction of the aligned water (D₂O) molecules, thus reducing the SFG intensity. The SFG intensity along the OD stretch region gradually increases with increasing D₃O⁺ to Na⁺ bulk concentration ratio. It indicates that the preferential alignment of D₂O molecules near the charged head groups increases with the replacement of Na⁺ by D₃O⁺. This, in turn, indicates that the concentration of cations at the SDS–D₂O interface decreases with increasing relative bulk concentration of D₃O⁺. D₃O⁺ apparently adsorbs slightly less than Na⁺ at the interface.

This observation can be explained by considering the ion radii of the cations and the implicit size restrictions imposed by the finite dimension of the electrical double layer (EDL) near the charged interface. Previous studies have already pointed out that smaller univalent cations are preferred within the EDL,²³¹⁰ a larger number of smaller ions can remain within a constrained volume causing a better charge neutralization, thereby lowering the Gibbs free energy. Following this argument, our results thus indicate that D₃O⁺ should have a larger ion radius than Na⁺. X-ray and neutron diffraction studies indeed support this notion. The inter-nuclear distance between the central oxygen atom of H₂O⁺ and the oxygen atom of its nearest neighbor is ~0.252 nm in HCl solution. For DCl, it is even larger: ~0.288 nm. For sodium, however, both simulations and diffraction methods consistently report that the nuclear distance between the sodium ion and the nucleus of oxygen of the nearest H₂O is ~0.235 nm.²⁴

Since these SFG responses arise from D₂O molecules strongly aligned due to the electrostatic field of the SDS head groups, they possibly involve both pure χ(2) and χ(3) driven responses.¹⁷,²²,²³,²⁵ In the present work, we focus on the relative changes in the intensities in the presence of D₃O⁺ and Na⁺. Therefore, we treat these intensities as an effective χ(2) response, and we make no distinction between relative contributions of χ(2) and χ(3). The Debye length decreases from 1 μm in the SDS covered pure D₂O surface to 1 nm in SDS covered D₂O containing 0.1M D₃O⁺ and/or Na⁺ (see the details in the supplementary material). Possibly the SFG response from the pure D₂O case is a combined pure χ(2) and χ(3) response, while the SFG response in the presence of 0.1M excess ions is dominated by the χ(3) contribution.

Not only the preferential organization of interfacial D₂O but also the organization of the monolayer seems to be different for D₂O⁺ and Na⁺. The CH stretch modes, simultaneously measured in the experiments, provide information about the alkyl chain conformation. In particular, the ratio of intensities of the CH₂ symmetric stretch (2846 cm⁻¹) and the CH₃ symmetric stretch (2870 cm⁻¹) modes of the SDS monolayer [see the inset in Fig. 1(b)]. In contrast, the presence of 0.1M D₃O⁺ causes a ~50% reduction in the CH₂ symmetric stretch intensity. Since the SDS concentration (12 mM) is far above the CMC, it is likely that the Debye length is large enough to cause the CH vibration responses, therefore, indicates that the presence of D₃O⁺ causes a disordering of the alkyl chain.

The Na⁺ concentration next to the SAM head groups is very high, due to the Coulomb interactions, even in the absence of any excess ions in the solution.¹² In the presence of 0.1M excess Na⁺ in the sub-phase, the order of SAM alkyl chains hardly differs from that of neat D₂O. On the contrary, in the presence of 0.1M D₃O⁺, the SAM is disordered compared to that of neat D₂O, indicating that the directional characters of hydrogen bonding between the head groups and the counterions, in addition to the Coulomb interaction, are apparently important in determining the order of the SAM. The two cations are geometrically very different: D₃O⁺ has a “tripod” structure,²⁶ as opposed to the spherical shape of Na⁺. As a result, the ability of those two cations to act as bridges between different head groups is undoubtedly different. Second, although the pKa of SDS in bulk-H₂O is ~1.5, the surface pKa is expected to be ~0, based on reports regarding similar systems.¹¹,²⁷ Therefore, at a bulk D₃O⁺ concentration of 0.1M, i.e., pH = 1, ~10% of the SDS molecules should be protonated. The protonation of SDS molecules reduces the repulsion amongst the head groups, which is also expected to affect alkyl chain arrangement. Nevertheless, the effects of the presence of 0.1M D₃O⁺ in the subphase on the preferential
alignment of D₂O molecules and the alkyl chains of the SAM at the interface are slightly different than in the presence of 0.1M Na⁺. The D₂O molecules are preferentially more aligned, but the alkyl chains are preferentially less aligned in the presence of 0.1M D₃O⁺ compared to that of 0.1M Na⁺. Both effects occur simultaneously.

Evidently, Na⁺ and D₃O⁺ perturb the noncentrosymmetric order of interfacial D₂O and the packing order of SDS-SAM to a different extent. Therefore, an interesting question is, whether all these effects are (non-)additive when more than one type of cation coexist in the solution. If the effects are additive with respect to their bulk concentrations then the intensity from a solution, containing a mixture of cations, should be equal to the square of the linear combinations of the χ(2) response from the solution containing only one or the other cation. If the effects are additive with respect to their surface concentrations, it requires precise knowledge of their surface concentration which is not known.

Since calculating mixtures of the spectra as a linear combination of the response of the pure solutions requires knowledge of the χ(2), we have quantitatively analyzed the data by fitting with an established procedure. According to this procedure, the SFG signal is proportional to the square of the second-order nonlinear susceptibility χ(2) of the sample and intensity of both incoming IR and Visible (VIS) light,

\[ I_{\text{SFG}} \propto |\chi^{(2)}|^2 I_{\text{VIS}} I_{\text{IR}}. \]

The second order nonlinear susceptibility χ(2) is a sum of a non-resonant contribution χNR(2) (consisting of an amplitude ANR and a phase φNR) and resonant contribution(s) χR(2). Each χR(2) is expressed in terms of a Lorentzian line shape with area An, central frequency ωn, and bandwidth Γn (half width at half maximum)

\[ |\chi^{(2)}|^2 = |\chi^{(2)}_{\text{NR}} + \chi^{(2)}_{\text{R}}|^2 = |A_{\text{NR}} e^{i\phi_{\text{NR}}} + \frac{A_n}{\omega_n - i \Gamma_n + i \Gamma_n}|^2. \]  

The spectra recorded for the SDS-covered pure aqueous Na⁺ and D₃O⁺ solutions are fitted with eight resonant peaks (See Table 1 in the supplementary material for assignment details). The bandwidths and peak positions of all the bands as well as the non-resonant area and phase from this fit are subsequently interpolated to describe the intermediate spectra.

Figure 1(c) shows that the three spectra for co-existing Na⁺ and D₃O⁺ can be described very well by the square of the linear combinations of the χ(2) response (see the supplementary material) from pure Na⁺ and pure D₃O⁺, implying that the effect is simply additive.

The observation that Na⁺ has higher surface affinity at the SDS-water interface is in contrast with the conclusion drawn for the electrolyte-air interface, for which, at very high concentrations (~1M), H₂O⁺ has been found to have higher interfacial affinity than Na⁺. Here, we have monitored the modulation of interfacial D₂O alignment at the air–D₂O interface as a function of the bulk D₃O⁺ and Na⁺ concentration ratio at IM constant ionic strength using vibrational SFG spectroscopy. Unlike the SDS case presented above, the alignment of interfacial D₂O at the air–water interface is enhanced by the presence of ions, and the enhancement of the SFG intensity is a measure of the surface affinity of an ion. By systematically changing the Na⁺ and D₃O⁺ ion concentration ratio, and quantitatively monitoring the change in the SFG intensity, we have studied not only the relative surface affinity of the two ions but also the gradual evolution of interfacial water alignment under the influence of the relative concentration ratio of these two ions.

Figure 2(a) shows the SFG responses in SSP polarization at the D₂O-air interface, for pure D₂O and in the co-presence of Na⁺ and D₃O⁺ at different concentration ratios at IM total ionic strength. As opposed to the SDS case, higher ionic concentration at the air–D₂O interface enhances the preferential D₂O alignment. To ensure an optimum signal to noise ratio, we have chosen here a IM ionic strength.

Each spectrum consists of two main features: a sharp peak centered at ~2700 cm⁻¹ and a relatively broad feature that extends between ~2000 cm⁻¹ and ~2600 cm⁻¹. The sharp
The SFG intensity hardly changes when adding IM Na\textsuperscript{+} to D\textsubscript{2}O, meaning that the alignment of interfacial D\textsubscript{2}O molecules in the presence of IM Na\textsuperscript{+} is almost identical to that of pure D\textsubscript{2}O: Na\textsuperscript{+} has no or very weak surface affinity towards the D\textsubscript{2}O-air interface, as, apparently, does Cl\textsuperscript{−}. In contrast, with increasing fraction of D\textsubscript{2}O\textsuperscript{−}, the intensity around ~2000–2600 cm\textsuperscript{−1} increases and that around 2700 cm\textsuperscript{−1} decreases. The D\textsubscript{3}O\textsuperscript{+} ions add charges to the D\textsubscript{2}O-air interface, increasing the alignment of interfacial water. Since D\textsubscript{3}O\textsuperscript{+} has a “tripod” structure and can make three strong hydrogen bonds with the neighboring D\textsubscript{2}O molecules, the preferential alignment of interfacial D\textsubscript{2}O molecules with their D atoms pointing towards bulk increases with increasing bulk D\textsubscript{2}O\textsuperscript{−} concentration, thus resulting in an enhanced SFG intensity around the ~2000–2600 cm\textsuperscript{−1} region. The reduction in intensity of the dangling OD peak can be a result of a real reduction in vibrational amplitude and/or a change in its angular distribution with respect to the surface normal. More studies to comment conclusively on these observations are ongoing. In any case, we find that, at the D\textsubscript{2}O-air interface, D\textsubscript{3}O\textsuperscript{+} indeed is more surface active than Na\textsuperscript{+} at 1M concentration, in agreement with previous reports.\textsuperscript{32,33}

Although, for pure D\textsubscript{2}O, \(\chi^{(2)}\) does not contribute to the SFG response, D\textsubscript{2}O containing ions certainly can.\textsuperscript{34–36} The increase in the SFG response in Fig. 2(a) is, therefore, possibly caused by simultaneous changes in pure \(\chi^{(2)}\) along with changes in \(\chi^{(3)}\) driven responses. In this study, we are interested only in relative changes in the total SFG intensity, and we therefore consider, as mentioned above, the combined effects as changes in an effective \(\chi^{(2)}\) response.

Figure 2(b) shows the experimental SFG spectra in the presence of IM Na\textsuperscript{+} and D\textsubscript{3}O\textsuperscript{+} along with the fitted spectra (details of the fits are given in the supplementary material). Panel (b) also shows the experimental SFG spectra in the co-presence of Na\textsuperscript{+} and D\textsubscript{3}O\textsuperscript{+} along with the corresponding squared \(\chi^{(2)}\) spectra constructed with linear combinations of the \(\chi^{(2)}\) response of IM D\textsubscript{2}O\textsuperscript{−} and Na\textsuperscript{+} solutions obtained by fitting. The linear combinations significantly differ from the experimental spectra specifically around 2350 cm\textsuperscript{−1}, meaning that the effects are not additive, unlike in the case of SDS. It qualitatively proves that apparently, the surface concentration of adsorbed D\textsubscript{3}O\textsuperscript{+} does not increase linearly with its bulk concentration.

CONCLUSION

In summary, we have reported the relative interfacial affinity of two ubiquitous cations, Na\textsuperscript{+} and D\textsubscript{3}O\textsuperscript{+} (equivalent to H\textsubscript{3}O\textsuperscript{+} in H\textsubscript{2}O\textsubscript{−}), and their effects on interfacial water organization at both the water-air and the surfactant-covered aqueous solution interface using SFG spectroscopy. Due to ionized head groups (\(\sim\)O–SO\textsubscript{3}−) of SDS, the interface is negatively charged. Both cations screen this surface charge, yet the screening ability depends slightly on the charge and radius of the cation. The surface propensity of Na\textsuperscript{+} is marginally higher than that of D\textsubscript{3}O\textsuperscript{+}. Moreover, the order of the alkyl chain of SDS also depends on the type of ions in the solution: D\textsubscript{3}O\textsuperscript{+} makes the alkyl chains more disordered than Na\textsuperscript{+}. Also these two effects are additive with respect to the co-existence of the two ions.

In contrast, at the nominally neutral air-aqueous solution interface, D\textsubscript{3}O\textsuperscript{+} has much higher surface propensity than Na\textsuperscript{+}. As such, the surface propensity of Na\textsuperscript{+} and D\textsubscript{3}O\textsuperscript{−} at the SDS-covered water surface is opposite to that at the air-water interface. However, the surface propensity and the ability to perturb the interfacial D\textsubscript{2}O alignment in the water-air interface is significantly non-additive with respect to co-existence of the two cations. Apparently, the surface adsorption of D\textsubscript{3}O\textsuperscript{+} is not linearly related with its bulk concentration at the air-D\textsubscript{2}O interface. The ion-specific effect is larger for the nominally neutral air-water interface than for the charged SDS-D\textsubscript{2}O interface, where screening of that charge is, to a first approximation, independent of details of the cation.

SUPPLEMENTARY MATERIAL

The supplementary material contains the details of the experimental setup, fitting parameters for the fits shown in Figs. 1 and 2, the equation used for linear combinations of the fitted spectra shown in Figs. 1(b) and 2(b), and the Debye length and surface charge density.

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