The Interplay of Electrostatic Interactions and Hydrophobic Hydration at the Surface of Tetra-n-alkylammonium Bromide Solutions

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Abstract

We use intensity and heterodyne-detected vibrational sum-frequency generation (VSFG and HD-VSFG) to study the structure of water at the surface of aqueous tetra-n-alkylammonium bromide (TAABr) solutions. We compare the water structure for four different n-alkyl chains (n = 1, 2, 3, 4). For solutions of tetra-n-alkylammonium bromides with short n-alkyl chains (n = 1, 2), we observe the structure of the surface water to be similar to the structure observed for simple inorganic salt solutions. For these solutions, the presence of Br^- at the interface is observed to lead to a small decrease in the average strength of the hydrogen bonds. For solutions of tetra-n-alkylammonium bromides with long n-alkyl chains (n = 3, 4), we observe a strong ordering of the water molecules at the solution surface. The water molecules show a net orientation of their O-H group towards the bulk, which can be explained from the high surface propensity of positively charged tetra-n-alkylammonium ions with long alkyl chains (n = 3, 4). With increasing concentration of TAABr this ordering decreases and at very high concentrations (> 2 M) the orientation of the water molecules reverses. This latter finding

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can be explained from the formation of aggregated clusters of TAA^+ cations and Br^- anions near the solution surface.

Introduction

Hydrophobic interactions play an essential role in several biological phenomena, such as protein folding and the formation of biological membranes.[1] This interaction is governed by the thermodynamics of the hydration of hydrophobic molecular groups. These thermodynamics show a remarkable dependence on the size of the hydrophobic solute. In particular, for small solutes with a typical size <1 nm, the entropy of hydration is negative, which indicates that small solutes are well accommodated in water, leading to an enhancement of the water structure and hydrogen-bonding network. In contrast, large solutes disrupt the water structure, leading to the formation of a vapour-like interface. An elegant theoretical description of this length-scale dependence was developed by Lum, Chandler and Weeks.[2,3]

Tetra-n-alkylammonium halides (TAAX, X = Br^-, Cl^- and etc.) are widely used as model systems to study hydrophobic phenomena, because the tetra-alkyl-ammonimum (TAA) ion is well soluble in water and its hydrophobicity can be tuned by varying the length of the alkyl chain. TAA^+ ions display both electrostatic and hydrophobic interactions. A number of studies have been performed on TAA salt solutions to investigate hydrophobic hydration and in particular the cross-over behavior of small and large hydrophobic solutes. Early thermodynamic and transport studies have pointed indirectly to an increased ordering of water around large TAA^+ cations such as tetrapropylammonium (TPA) and tetrabutylammonium (TBA).[4,5] In contrast to that, a later neutron diffraction study of TAABr solutions found that the hydrogen-bond structure of water around TAA^+ cations does not differ from that of bulk water, meaning that the structural enhancement of water commonly associated with hydrophobic hydration was not observed.[6,7] Recent small-angle x-ray scattering experiments did find the water structure around the hydrophobic TAA^+ ions to be enhanced compared to

bulk water. This enhancement was observed to be more pronounced for TPABr and TBABr solutions than for tetramethylammonium bromide (TMABr) and tetraethylammonium bromide (TEABr) solutions.[8]

With most spectroscopic techniques such as infrared or Raman, it is challenging to measure the effect of hydrophobic moieties on the structure of water, because the contribution of the hydration shells to the signal is usually much smaller than the bulk water signal. Here we use the surface-specific technique of vibrational sum-frequency generation (VSFG) spectroscopy to study the effects of TAA^+ and Br^- ions on the hydrogen-bond structure of water. In the dipole approximation, VSFG only yields a signal for systems that lack inversion symmetry. As a result, VSFG spectroscopy of aqueous solutions of TAABr yields a signal that specifically represents the structure of the water molecules at the solution surface.

Experimental

In the present work we use both intensity VSFG and heterodyne-detected VSFG (HD-VSFG). The latter technique allows the determination of the water orientation at the interfaces.[9–11] Details of our experimental setups have been given elsewhere.[12,13] Briefly: part of the output of commercial Ti:sapphire amplifier system (∼3.5 mJ, 35 fs, 800 nm) is used to pump a home-built optical amplifier (OPA) to generate a broad-band mid-IR pulse centered at ∼3 μm (∼10 μJ, bandwidth ∼300 cm^{-1}). The remaining part of the 800 nm pulse is spectrally narrowed, and focused together with the broad-band IR pulse to generate light at the sum frequency at the sample surface. The generated SFG light is detected with an Electron-Multiplied Charge Coupled Device (EMCCD, Andor Technologies). In the HD-VSFG setup, a broad-band IR pulse and a narrowband 800 nm pulse are focused first on a metal surface (gold) to generate a local oscillator SFG (LO-SFG) beam. Next the LO-SFG and the remaining IR and VIS beams are refocused onto the sample, producing a VSFG signal that interferes with the LO-SFG. All spectra in this paper were recorded with ssp

polarization combination (s-SFG, s-VIS, p-IR). The spectra are normalized to a reference SFG spectrum measured from z-cut quartz.

In the preparation of the samples we used water from a Millipore Nanopure system (18.2 MΩ cm). TMABr (≥98 %), TEABr (≥99 %), TPABr (≥98 %), TBABr (≥99 %), and TPACl (≥98 %) were purchased from Sigma Aldrich and used without further purification.

Results and Discussion

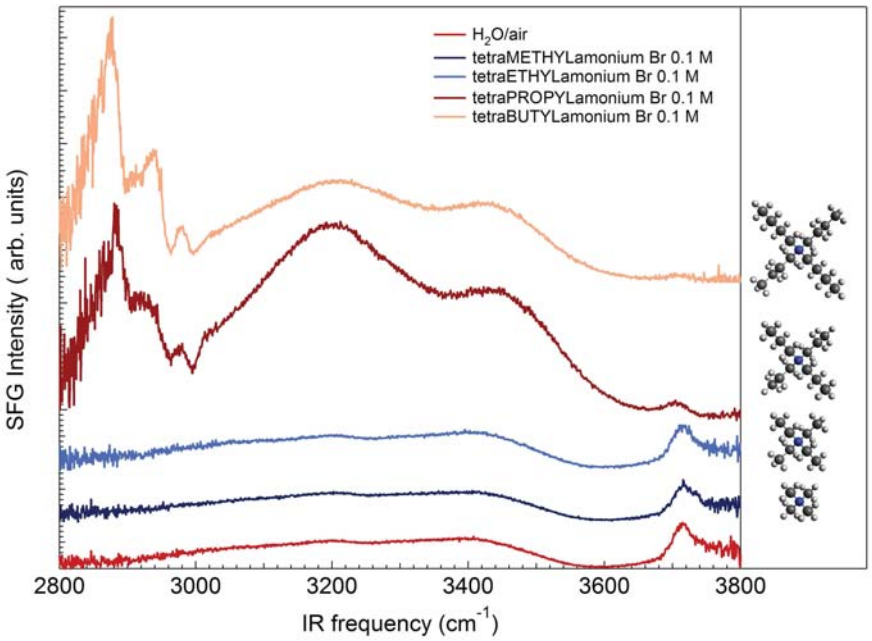

Figure 1: Intensity VSFG spectra of pure water and 0.1 M tetra-n-alkylammonium bromide salt solutions.

Figure 1 shows intensity SFG spectra of neat water and different 0.1 M concentration tetra-n-alkylammonium bromide (TAABr) solutions. The neat water/air spectrum consists of a broad spectral feature in the 3000 - 3600 cm^{-1} region and a sharp feature at 3700 cm^{-1}. The broad feature represents the response of hydrogen-bonded O-H groups. This band is inhomogeneously broadened, representing a large variety of hydrogen-bond structures and

hydrogen-bond strengths. Because of the strong intra- and intermolecular coupling of the O-H stretch vibrations, there is not a one-to-one correspondence between the strength of the donated hydrogen bond and the O-H stretch frequency. Nevertheless, strong hydrogen bonds correlate with low O-H stretch vibrational frequency and weak hydrogen bonds with high O-H stretch frequencies. The broad response contains a subtle substructure with two maxima at $\sim$3200 cm^{-1} and $\sim$3400 cm^{-1}. This substructure has been explained from the coupling of the symmetric OH stretch vibration and the overtone of the bending mode,[14] giving rise to a weak Evans window at the frequency of the bending overtone of $\sim$3300 cm^{-1}. A change in hydrogen-bond strength will lead to a shift of the broad feature and thus to a change in the relative intensities of the maxima at 3200 and 3400 cm^{-1}. The narrow peak at $\sim$3700 cm^{-1} is assigned to non-hydrogen-bonded OH groups and originates from water molecules for which one of the OH groups is sticking out of the surface.

The VSFG spectra of 0.1 M concentration tetra-methyl-ammonium bromide (TMABr) and tetra-ethyl-ammonium bromide (TEABr) solutions are practically indistinguishable from the pure water spectrum. In contrast, the VSFG spectra of tetra-propyl-ammonium bromide (TPABr) and tetra-butyl-ammonium bromide (TBABr) are quite different. The VSFG spectra of TPABr and TBABr solutions show a clear response in the spectral region of the CH stretch vibrations (2800 - 3100 cm^{-1}) that is not observed for the TMABr and TEABr solutions and also show a much higher intensity than the VSFG spectrum of bulk water in the O-H vibrational region. These observations indicate that TAA^+ ions with long alkyl chains (n = 3, 4) have a much higher surface propensity than TAA^+ ions with short alkyl chains (n = 1, 2).

In Figure 2 we present VSFG spectra of solutions of TEABr and TPABr at different concentrations. For TEABr (Figure 2a) the VSFG intensity shows a gradual increase with concentration, and there is no significant change in the shape of the spectrum, except for a small blue-shift at the highest measured concentration of 8 M. For TPABr the VSFG intensity strongly increases with concentration. At a bulk concentration of $\sim$0.001 M of TPABr, the

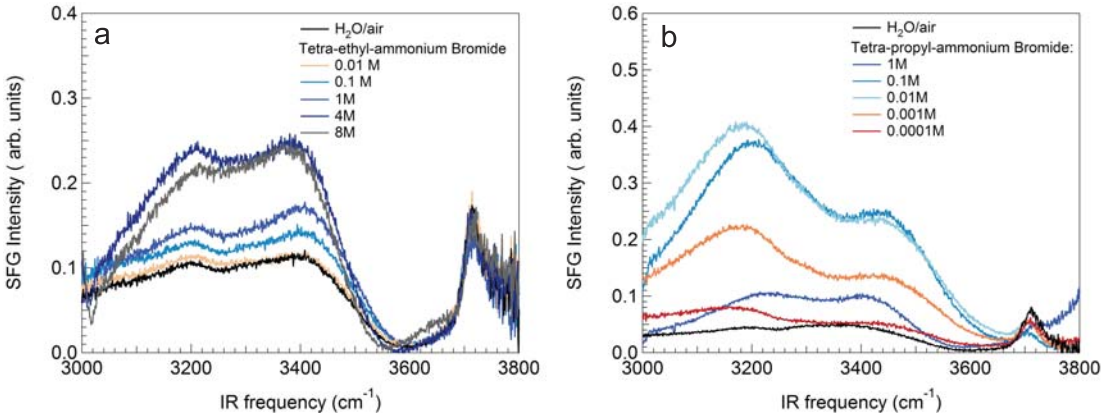

Figure 2: Intensity VSFG spectra of (a) TEABr and (b) TPABr salts at different concentrations.

VSFG intensity is already substantially higher than that of pure water. The VSFG intensity reaches a maximum value at a low bulk concentration of ∼0.01 M: a further increase of the concentration leads to a decrease of the VSFG signal. Besides the clear intensity changes, the addition of TPABr is observed to lead to a red-shift of the broad hydrogen bonded water band. Up to concentrations of 1 M, the low-frequency peak (∼3200 cm^{-1}) is much stronger than the high-frequency peak (∼3400 cm^{-1}), which is quite different from the VSFG signal of the surface of pure water, for which the two peaks are of approximately equal intensity.

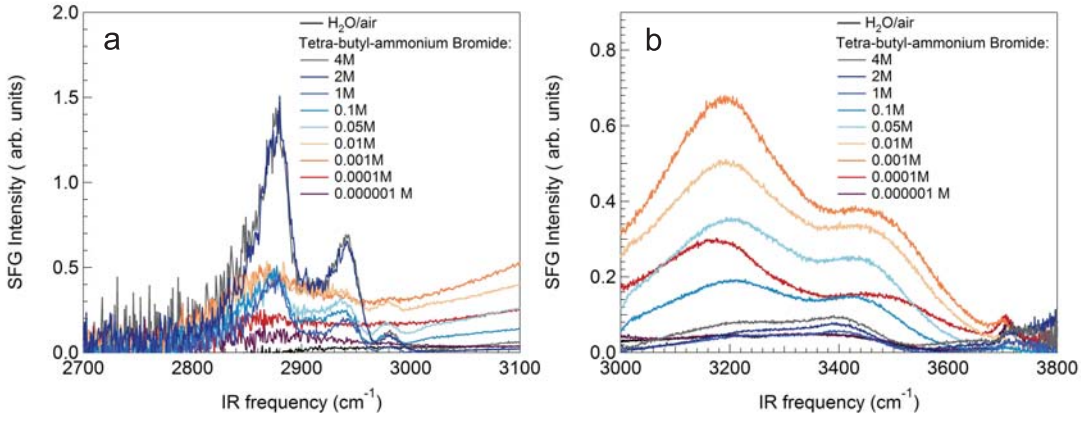

Figure 3: Intensity VSFG spectra of solutions at different concentrations of TBABr in H_2O. (a) Frequency region of the C-H stretch vibrations, and (b) frequency region of the O-H stretch vibrations.

In Figure 3 we present VSFG spectra of solutions of TBABr at different concentrations.

In Figure 3a we probe the C-H stretch vibrational region and here we observe a gradual increase of the bands at 2865 cm^{-1}, 2940 cm^{-1} and 2980 cm^{-1}. We assign these bands to the symmetric C-H stretch vibration, the Fermi resonance and the asymmetric C-H stretch vibration of the CH_3 groups of the butyl chains, respectively. In Figure 3b we probe the O-H stretch vibrational region of the interfacial water molecules. The VSFG spectra of TBABr solutions show a very similar shape and concentration dependence as the VSFG spectra of TPABr solutions in the same frequency region (Figure 2b). For TBABr the VSFG signal reaches a maximum intensity at an even lower concentration ($\sim$0.001 M for TBABr and $\sim$0.01 M for TPABr), which indicates that TBABr has an even higher surface propensity than TPABr. For concentrations >0.001 M the VSFG signal of TBABr solutions starts to decrease and at $\sim$1 M the VSFG spectrum in the O-H region looks quite similar to that of pure water. Finally, at higher concentrations (>1 M) the spectrum shows a slight increase again and the high-frequency peak of the O-H stretch spectrum becomes larger than the low-frequency peak.

The concentration range of the VSFG spectra of TPABr and TBABr solutions in the O-H stretch vibrational region can thus be divided into three regions: a low concentration range (0 - 0.01 M), in which the VSFG signal strongly increases and red shifts, indicating that the water molecules at the surface become much more oriented and more strongly hydrogen bonded; a medium concentration range (0.01 - 1 M), where the VSFG signal decreases and becomes less red-shifted, which means that the water molecules become less oriented and less strongly hydrogen bonded; and a high concentration range (1 - 4 M), where the VSFG signal again slightly increases and the spectral response gets blue-shifted, indicating that the probed water molecules are more weakly hydrogen bonded.

The red-shift of the VSFG spectrum of the O-H stretch vibrations is a quite interesting observation. Infrared absorption spectra of TBABr solutions that probe the response of the bulk water molecules do not show such a red-shift of the response of the O-H stretch vibrations (see Figure SI1). In fact, the infrared absorption shows a blue-shift of the O-H

stretch absorption band that gets more pronounced with increasing concentration. The blue shift can be explained from the fact that the hydrogen bonds between water molecules and bromide ions are weaker than water-water hydrogen bonds. As a result, the O-H stretch vibrations of water molecules hydrating the Br^- ions appear at higher frequencies (blue-shifted).[15] The Raman spectra of TMACl, TEACl and TPACl also show an enhancement of the high frequency water peak, which is explained from the formation of hydrogen bonds to Cl^- ions that are weaker than the hydrogen bonds between water molecules.[16] Clearly, the red shift of the O-H stretch VSFG response of low-concentration solutions of TPABr and TBABr solutions is quite anomalous and likely a highly surface-specific phenomenon.

To investigate the effect of TAABr salts on the orientation and hydrogen bonding of surface water molecules in more detail, we performed HD-VSFG experiments. In Figure 4 we present the imaginary part of $\chi^{(2)}$ (Im $\chi^{(2)}$) for the surfaces of pure water and tetra-n-alkylammonium bromide (n = 1, 2, 3, 4) solutions at different concentrations. The Im $\chi^{(2)}$ spectrum of pure water (Figure 4 a and b, red line) exhibits a positive sharp peak at ~3700 cm^{-1}, a negative region (~3200 - 3650 cm^{-1}) and a slightly positive region (~3100 - 3200 cm^{-1}). The sign of the Im $\chi^{(2)}$ is related to the orientation of the vibrational transition dipole moment with respect to the surface plane. A negative value of Im $\chi^{(2)}$ is associated with water molecules that are on average oriented with their dipoles pointing towards the bulk, while a positive Im $\chi^{(2)}$ is associated with water molecules pointing away from the bulk. Hydrogen-bonded OH groups at the water surface on average point down to the bulk, causing the negative band at frequencies ~3200 - 3650 cm^{-1}. The sharp positive feature at ~3700 cm^{-1} is assigned to non-hydrogen bonded OH groups pointing into air. The positive feature at frequencies ~3100 - 3200 cm^{-1} has been explained in different ways.[17,18]

The Im $\chi^{(2)}$ spectra of TMABr and TEABr differ only slightly from the Im $\chi^{(2)}$ spectrum of the pure water surface, in agreement with the intensity VSFG data (Figure 4 a and b). In contrast, the Im $\chi^{(2)}$ spectra of TPABr and TBABr are strongly concentration dependant. At low concentrations of TPABr or TBABr (~0.001 M), the Im $\chi^{(2)}$ spectra are negative

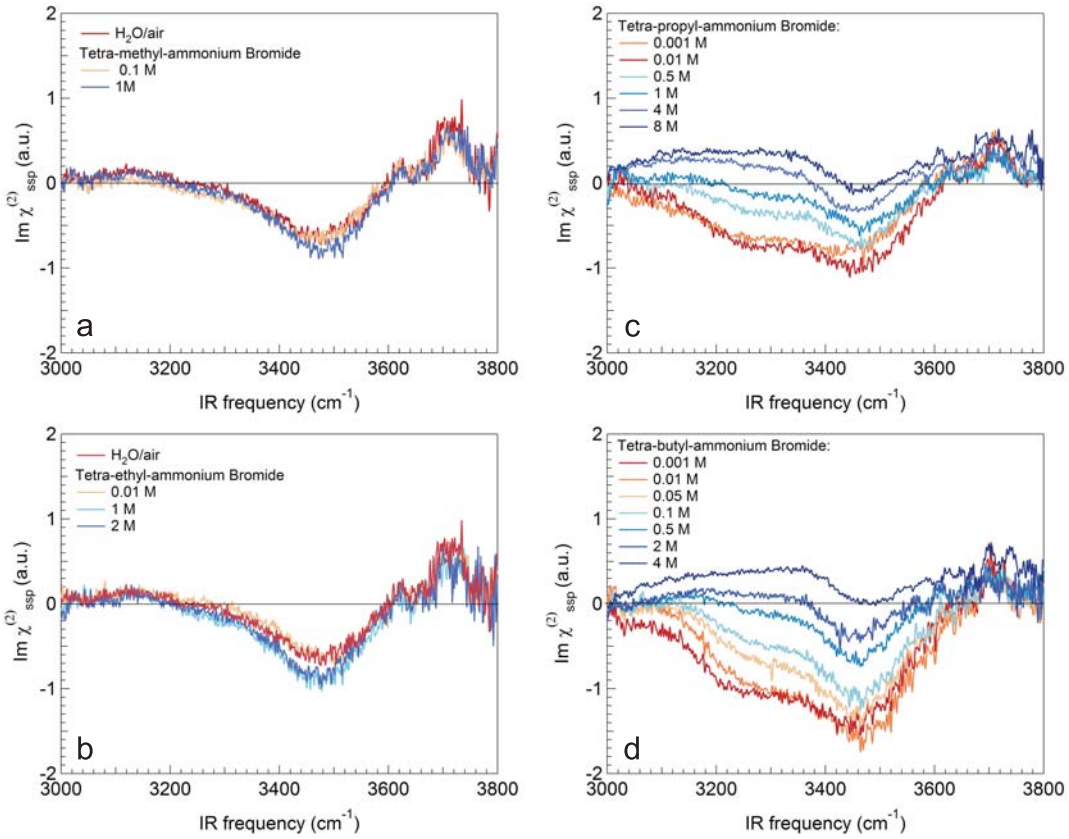

Figure 4: Imaginary $\chi^{(2)}$ spectra of (a) TMABr, (b) TEABr, (c) TPABr, and (d) TBABr at different concentrations (see legend).

throughout the hydrogen-bonded region, indicating that the water OH groups show a net orientation towards the bulk. Interestingly, the amplitude of this negative band decreases with increasing concentration. At high concentrations of TPABr (∼1 M) and TBABr (∼0.5 - 1 M) solutions the Im $\chi^{(2)}$ spectra become similar to the Im $\chi^{(2)}$ spectrum of the pure water surface. At extremely high concentrations of TPABr (∼8 M) and TBABr (∼4 M) the Im $\chi^{(2)}$ spectra acquire an overall positive sign, indicating that the O-H groups of the water molecules show a net orientation away from the water bulk. For solutions of tetra-propyl-ammonium chloride (TPACl) we observe a very similar concentration dependence of the Im $\chi^{(2)}$ spectrum of the water band (see Figure SI2).

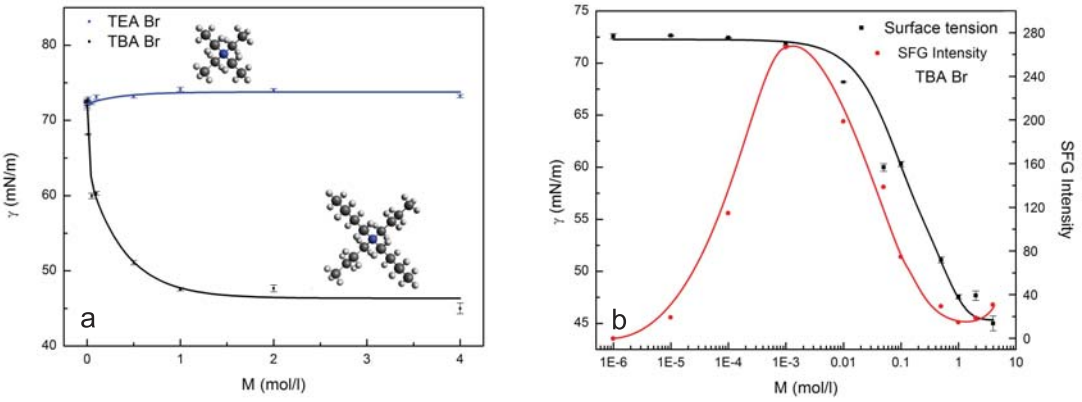

Figure 5: (a) Surface tension as a function of concentration for TEABr and TBABr solutions; (b) Surface tension and VSFG intensity at 3200 cm^{-1} as a function of concentration for TBABr solutions. The lines are guides to the eye.

The intensity and heterodyne-detected VSFG spectra of short-chain (n = 1, 2) TAABr salts are completely different from those of long-chain (n = 3, 4) TAABr salts. The VSFG spectra of solutions of short chain TAA^+ cations are quite similar to the VSFG spectrum of the surface of pure water, indicating a low surface propensity of these ions. Apparently, short chain TAA^+ cations are well solvated in bulk liquid water, which implies that the electrostatic interactions of the TAA^+ cations dominate over the hydrophobic interactions. In contrast, long chain TAA^+ cations are expelled from the bulk liquid leading to a high surface concentration. For long chain TAA^+ cations hydrophobic interactions between water

and the n-alkyl chains are hence more relevant than electrostatic interactions. This result agrees with surface tension measurements.[19] In Figure 5a we present the surface tension of solutions of TEABr and TBABr as a function of concentration. It is observed that the surface tension of TEABr remains constant (∼72 mN/m) over the whole studied concentration range of 0 - 4 M, whereas the surface tension of TBABr solutions strongly decreases with increasing concentration, reaching a low value of ∼45 mN/m for concentrations >1 M. In Figure 5b we compare the concentration dependence of the surface tension of TBABr with that of the intensity of the VSFG signal at 3200 cm^{-1}. It is seen that at low concentrations the VSFG intensity strongly increases with concentration, while the surface tension is negligibly affected. At concentrations >0.001 M both the VSFG intensity and the surface tension decrease, indicating a similar origin, i.e. the presence of a high density of TBA^+ and Br^- ions in the interfacial region. Figure 5b thus clearly shows that the surface tension is not representing the propensity of particular ions in the top molecular layers of the solution, but rather the interfacial salt concentration probed over a much larger depth.

For solutions of short-chain TAA^+ ions, the increase of the concentration leads to a small blue-shift of the hydrogen-bonded water band. This blue-shift indicates the presence of relatively weak hydrogen bonds and can be explained from the increased contribution of water O-H groups forming hydrogen bonds to Br^- ions. This result agrees with the work by Allen and coworkers in which it was shown that the addition of halide salts to water leads to a blue-shift of the intensity VSFG spectrum.[20,21] For TPABr and TBABr solutions the VSFG spectrum shows a strong red-shift at low concentrations, which obviously cannot be caused by hydrogen bonding to Br^- ions. In previous studies we found that the hydrogen bonds between water molecules become stronger at the interface of water and hydrophobic liquids like hexane, heptane and polydimethylsiloxane.[12] A similar result was found in advanced spontaneous Raman scattering studies of solutions of alcohols. In these studies it was shown that the hydrogen-bond structure of water hydrating the alkyl chains of the alcohols is enhanced in comparison to the hydrogen-bond structure of bulk liquid water.[22] Hence, the

observed red-shift of the intensity and VSFG spectrum of solutions of TPABr and TBABr can be explained from the hydration of the hydrophobic alkyl chains of these ions near the solution surface. In addition to the red-shift, we observe an increase in intensity of the VSFG spectrum of TPABr and TBABr solutions in comparison to bulk liquid water. This intensity increase can be explained from the electric field that is created by the large concentration of hydrophobic cations at the surface and the Br^- ions that on average are located deeper down in the liquid. Br^- ions tend to have a somewhat higher concentration at the surface than in the bulk.[23–25] However, in comparison to TPA^+ and TBA^+ ions the surface propensity of Br^- is weak. The separation of the positive TPA^+ and TBA^+ ions and the negative Br^- ions leads to an electric field pointing away from the surface, thereby orienting the water O-H groups towards the bulk phase, thus explaining the large negative value of Im $\chi^{(2)}$ of the water O-H band for low-concentration solutions of TPABr and TBABr. For the VSFG signal of the C-H vibrations the electric field effect is far less pronounced. In Figure 3a it is seen that the VSFG intensity of the C-H vibrations increases only gradually with increasing concentration. This strong difference in concentration dependence of the C-H and the water O-H signal can be explained from the fact that the water molecules possess a dipole moment, and thus strongly orient in the electric field created by TPA^+ and TBA^+ ions at the surface and Br^- ions deeper down in the liquid. The TPA^+ and TBA^+ ions do not possess a dipole moment as the alkyl chains are symmetrically (tetrahedrally) arranged around the N atom. For TPACl solutions we observe a similar concentration dependence of the Im $\chi^{(2)}$ spectrum of the water band, showing that Cl^- ions behave very similar to Br^- ions.

When the concentration of TPABr and TBABr is increased, the amplitude of the negative band decreases. This decrease can be explained from the decrease in distance between the centers of positive and negative charge in the interfacial region. As a result, there are less water molecules confined in between the TAA^+ and Br^- ions, and the VSFG signal decreases. At very high TPABr and TBABr concentrations, the TAA^+ cations and Br^- ions will form aggregated clusters at the solution surface, with a somewhat higher concentration of Br^-

ions deeper down in the solution. In Figure 6 we present a schematic picture of the interfacial configuration of the cations and anions at low and high concentrations of TPABr and TBABr. In the high-concentration regime there will be very few water molecules enclosed by the TAA^+ and Br^- ions, and the VSFG spectrum will become dominated by water molecules forming hydrogen bonds to the Br^- ions of the aggregated cation-anion layer at the surface. For these water molecules the O-H will have a net orientation away from the bulk, explaining the positive sign of the Im $\chi^{(2)}$ spectra in the high concentration regime. In addition, the hydrogen bonds to the Br^- ions are somewhat weaker than the hydrogen bonds between water molecules, thus explaining the blue-shift of the intensity and heterodyne detected VSFG spectra of highly concentrated solutions of TPABr and TBABr.

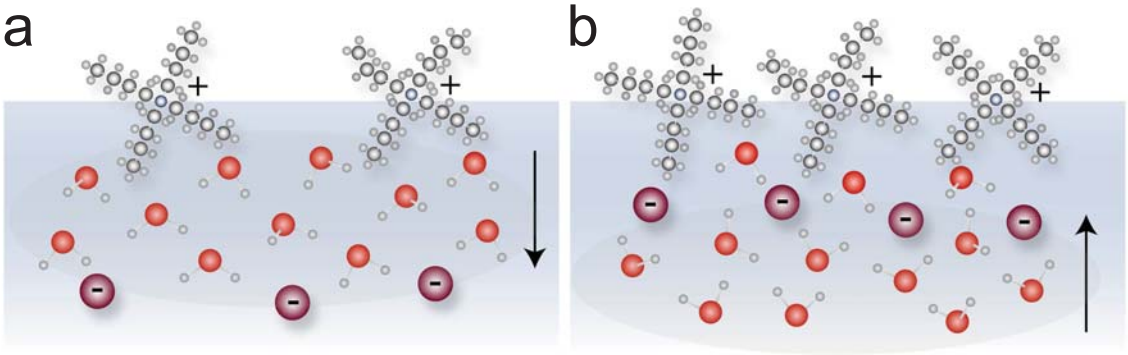

Figure 6: Schematic picture of the interfacial configuration of cations and anions at (a) low and (b) high concentrations of TPABr and TBABr.

Conclusions

We studied the surface properties of solutions of tetra-n-alkylammonium bromide salts using intensity and heterodyne detected vibrational sum-frequency generation (VSFG) spectroscopy. We observe that short-chain tetra-n-alkylammonium bromides (n = 1, 2) behave like simple inorganic salts. The TAA^+ ions show little surface propensity. As a result, the

VSFG spectra of short-chain tetra-n-alkylammonium bromides (n = 1, 2) are similar to the VSFG spectrum of pure liquid water. A slight blue shift of the spectrum is observed that can be explained from the contribution of water molecules forming hydrogen bonds to the Br^- ions. For long-chain tetra-n-alkylammonium bromides (n = 3, 4) we observe a very different VSFG spectrum, due to the high surface propensity of the tetra-propyl-ammonium and tetra-butyl-ammonium cations. At low bulk concentrations, the VSFG spectra are dominated by hydrophobic hydration effects, leading to a red-shift of the response of hydrogen-bonded water molecules. In addition the amplitude of the VSFG spectrum is strongly enhanced due to the orienting electric field that is created by the separation of the center of positive charge associated with the positive tetra-n-alkylammonium (TAA^+) ions at the surface and the center of negative charge associated with the Br^- ions deeper down in the solution. At high concentrations, the TAA^+ and Br^- ions form aggregated clusters at the solution surface and the VSFG spectrum is dominated by water molecules forming hydrogen bonds to the Br^- ions of these clusters.

Acknowledgement

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Supporting Information Available

In the supporting information we show linear IR spectra of TEABr and TBABr at different concentrations and Imaginary $\chi^{(2)}$ spectra of TPACl at different concentrations.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

References

(1) Ball, P. Water as an Active Constituent in Cell Biology. *Chem. Rev.* **2008**, *108*, 74–108.

(2) Lum, K.; Chandler, D.; Weeks, J. D. Hydrophobicity at Small and Large Length Scales. *J. Phys. Chem. B* **1999**, *103*, 4570.

(3) Chandler, D. Interfaces and the Driving Force of Hydrophobic Assembly. *Nature* **2005**, *437*, 640–647.

(4) Frank, H. S.; Evans, J. W. Free Volume and Entropy in Condensed Systems. 3. Entropy in Binary Liquid Mixtures; Partial Molar Entropy in Dilute Solutions; Structure and Thermodynamics of Aqueos Electrolytes. *J. Chem. Phys.* **1945**, *13*, 507–532.

(5) Wen, W.-Y. Structural Aspects of Aqueous Tetraalkylammonium Salt Solutions. *J. Sol. Chem.* **1973**, *2*, 253–276.

(6) Soper, A.; Finney, J. Hydration of Methanol in Aqueos-Solution. *Phys. Rev. Lett.* **1993**, *71*, 4346–4349.

(7) Dixit, S.; Crain, S.; Poon, W.; Finney, J.; Soper, A. K. Molecular Segregation Observed in a Concentrated Alcohol-Water Solution. *Nature* **2002**, *416*, 829–832.

(8) Huang, N.; Schlesinger, D.; D.Nordlund,; Huang, C.; Tyliszczak, T.; Weiss, T. M.; Acremann, Y.; Pettersson, L. G. M.; Nilsson, A. Microscopic Probing of the Size Dependence in Hydrophobic Solvation. *J. Chem. Phys.* **2012**, *136*, 074507–7.

(9) Nihonyanagi, S.; Mondal, J. A.; Yamaguchi, S.; Tahara, T. Structure and Dynamics of Interfacial Water Studied by Heterodyne-Detected Vibrational Sum-Frequency Generation. *Annu. Rev. Phys. Chem.* **2013**, *64*, 579–603.

(10) Ji, N.; Ostroverkhov, V.; Tian, C. S.; Shen, Y. R. Characterization of Vibrational Resonances of Water-Vapor Interfaces by Phase-Sensitive Sum-Frequency Spectroscopy. *Phys. Rev. Lett.* **2008**, *100*, 096102.

(11) Shen, Y. R. Phase-Sensitive Sum-Frequency Spectroscopy. *Annu. Rev. Phys. Chem.* **2013**, *64*, 129–50.

(12) Strazdaite, S.; Versluis, J.; Backus, E. H.; Bakker, H. J. Enhanced Ordering of Water at Hydrophobic Surfaces. *J. Chem. Phys.* **2014**, *140*, 054711.

(13) Strazdaite, S.; Versluis, J.; Bakker, H. J. Water Orientation at Hydrophobic Interfaces. *J. Chem. Phys.* **2015**, *143*, 084708.

(14) Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; Muller, M.; Bakker, H. J.; Bonn, M. Vibrational Response of Hydrogen-Bonded Interfacial Water is Dominated by Intramolecular Coupling. *Physical Review Letters* **2008**, *100*, 173901.

(15) Bergstrom, P.-A.; Lindgren, J.; Kristiansson, O. An IR Study of the Hydration of Ci0,- , NO3-, I-, Br, Cr, and SO:- Anlons in Aqueous Solution. *J. Phys. Chem.* **1991**, *95*, 8575–8580.

(16) Hidaka, F.; Kanno, H. Raman OD Stretching Spectral Differences between Aqueous and Alcoholic Tetraalkylammonium Chloride Solutions. *Chem. Phys. Lett.* **2003**, *379, 3-4*, 216–222.

(17) Pieniazek, P. A.; Tainter, C. J.; Skinner, J. L. Interpretation of the Water Surface Vibrational Sum-Frequency Spectrum. *J. Chem. Phys.* **2011**, *135*, 044701.

(18) Ishiyama, T.; Morita, A. Vibrational Spectroscopic Response of Intermolecular Orientational Correlation at the Water Surface. *J. Phys. Chem. C* **2009**, *113*, 16299–16302.

(19) Tamaki, K. Surface Activity of Tetra-n-Alkylammonium Halides in Aqueous Solutions. *Bull. Chem. Soc. Jpn.* **1974**, *47(11)*, 2764–2767.

(20) Liu, D.; Ma, G.; Levering, L.; Allen, H. C. Vibrational Spectroscopy of Aqueos Sodium Halide Solutions and Air-Liquid Interfaces: Observation of Increased Interfacila Depth. *J. Phys. Chem. B* **2004**, *108(7)*, 2252–2260.

(21) Verreault, D.; Allen, H. C. Bridging the Gap between Microscopic and Macroscopic Views of Air/Aqueous Salt Interfaces. *Chem. Phys. Lett.* **2013**, *586*, 1–9.

(22) Davis, J. G.; Gierszal, K. P.; Wang, P.; Ben-Amotz, D. Water Structural Transformation at Molecular Hydrophobic Interfaces. *Nature* **2012**, *491*, 582–585.

(23) Jungwirth, P.; Tobias, D. J. Specific Ion Effects at the Air/Water Interface. *Chem. Rev.* **2006**, *106*, 1259–1281.

(24) Ishiyama, T.; Morita, A. Molecular Dynamics Study of Gas-Liquid Aqueous Sodium Halide Interfaces. I. Flexible and Polarizable Molecular Modeling and Interfacial Properties. *J. Phys. Chem. C* **2007**, *111*, 721–737.

(25) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Counterion Effect on Interfacial Water at Charged Interfaces and Its Relevance to the Hofmeister Series. *J. Am. Chem. Soc.* **2014**, *136(17)*, 6155–6158.

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