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Effect of Halide Anions on Structure of 1-butanol Monolayer/water Interface Probed by Sum-frequency Vibrational Spectroscopy

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Abstract: In this report, we use a sum-frequency generation vibrational spectroscopy to measure SFG spectra from 1-Butanol monolayers on pure water and halide saline solution interfaces. These spectra indicate that halide anions have different effects on the structure of 1-Butanol monolayer/water interfaces. The obtained SFG spectra suggest that the I^- anions mostly disturb the interfacial structure due to their largest surface propensity among those investigated.

Keywords: Interfacial structure, Sum-frequency vibrational spectroscopy, 1-Butanol, halide salt.

1. Introduction

Halide ions in seawater have been recognized as reactants in ozone depletion processes [1]. However, a detailed effect of halogen ion on the water surface structure has not been suggested due to the lack of tools to probe liquid surfaces specifically. As ultrafast laser technology has been developed recently, the sum-frequency generation vibrational spectroscopy (SFGVS) gives not only static information on surfaces but also dynamic properties of surface molecules [2].

Sum-frequency generation (SFG) is a second-order nonlinear optical process that has an intrinsic sensitivity to the struture at surfaces and interfaces. In the SFVS we can control the polarization of both two incident waves as well as the output (sum-frequency) wave. By choosing an appropriate polarization combination for each SFG measurement we can also get the information of molecular orientation at the surface or interface.

Molecules like fatty acids, lipids, and long-chain alcohols, which have both hydrophobic and hydrophilic parts, can form a Langmuir monolayer on water surface [3]. The structure of Langmuir monolayers resembles biological membranes and becomes a good research model for 2-dimensional systems. Normally, the hydrogen bondings between the interfacial water molecules and the hydrophilic head groups help form the Langmuir monolayer. In general, the presence of dissolved ions

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in water subphase affects the molecular orientation and the structure of the interfacial layers, but until recently the mechanism of this process has not yes become clear.

In order to gain an insight into the impact of halide anions on the interfacial layers, in this report we use the SFGVS technique to investigate the structure of the 1-Butanol monolayer/water interface with various halide anions of Cl^-, I^-, and F^- dissolved in the water subphase.

2. Experimental method

2.1. Optical setup

The SFG spectroscopy system that we use to measure SFG spectra, is EKSPLA - SF41 system. Experimental setup diagram SFG is described as Figure 1. In this system, we used a mode-locked Nd:YAG pico-second laser (PL2251A) as a pump source with wavelength of 1064.2 nm, energy of 50 mJ/pulse, pulse width of 30 ps, and repetition rate of 50 Hz. This fundamental beam is directed into a second-harmonic unit (H500). The second harmonic at 532.1 nm and fundamental beam at 1064.2 nm from H500 were used to pump an OPG/OPA/DFG system (EKSPLA – PG501) and obtained tunable waves covering a mid-infrared range from 2.3-10 µm. This IR beam and VIS-532.1 nm were guided to the samples with angles at $\varphi_{VIS} = 60^0$ and $\varphi_{IR} = 55^0$, respectively. Once the two incident waves satisfied the phase-matching condition, sum-frequency (SF) beam is generated in the reflection direction with an angle of $59{,}7^0 \pm 0{,}35^0$. The SF light was selected by a monochromator (MS3504) and then detected by photomultiplier tubes. So we obtained data of the SFG spectra. All of the spectra were taken in SSP polarization combination.

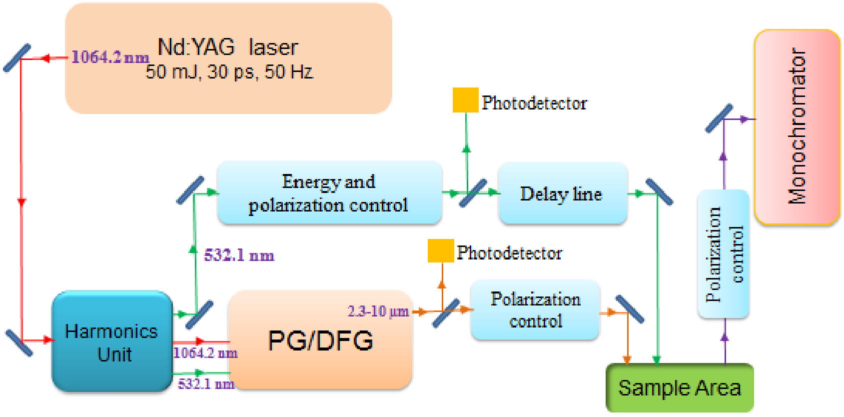


Figure 1. SFG spectrometer optical layout.

2.2. Sample preparing

1-Butanol (BuOH) (>99.5%, Merck), The saline solutions were prepared from sodium chloride (> 99% purity), sodium iodide (> 99% purity) and sodium fluoride (> 99% purity) dissolved in deionized water (pH ~ 5.7). The 1-Butanol monolayer was formed in 5 minutes after spreading the 1-Butanol solution on the surface of the saline solutions. In this study, the butanol solution concentration is maintained at 0.1 M.

3. Results and discussion

We have taken SFG spectra from 1-Butanol monolayer on saline solutions such as NaI, NaCl, and NaF with various saline concentrations. In each SF spectrum of Fig. 2, Fig.3, Fig.4, and Fig. 5 are dominated by the two prominent peaks at 2880 cm^{-1} and 2940 cm^{-1} corresponding to a symmetric stretching mode of the methyl group (CH_{3SS}) and CH_3 Fermi resonance (CH_{3Fr}). The two weakly observed peaks at ~2855 cm^{-1} and 2905 cm^{-1} corresponding to a symmetric stretching mode of the methylene group (CH_{2SS}) and CH_2 Fermi resonance (CH_{2Fr}) indicate that butanol molecules organize in all-trans conformations as predicted by other research [4].

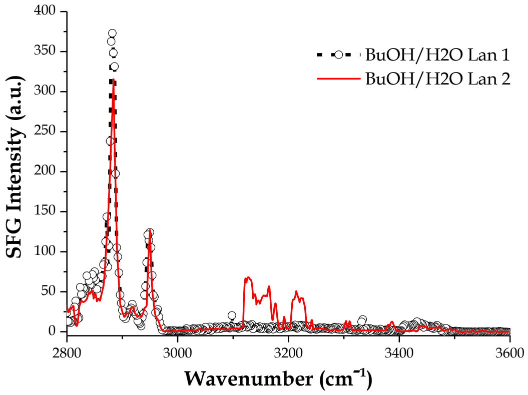
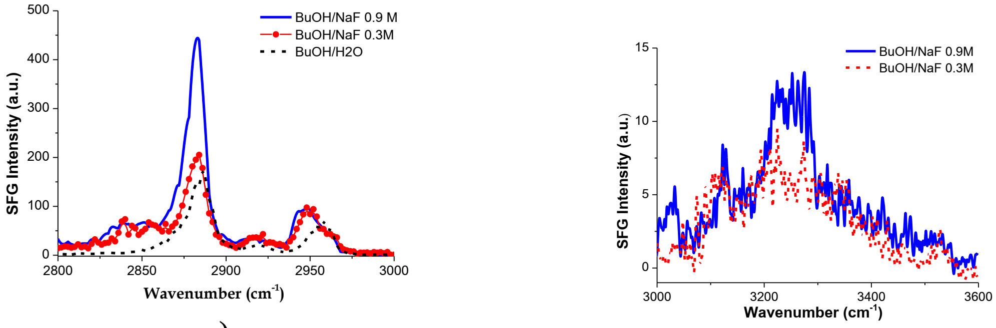


Figure 2. SSP SFG spectra of 1-Butanol/purewater interfaces.

In Figure 2, the OH stretching band broaden 3000 cm^{-1} to 3600 cm^{-1} is not stable because the 1-Butanol molecules of layers at the interface are dissolved in the water bulk. However, this band is stable as Fig. 3b, Fig. 4b, and 5b. Such that the presence of halide salts in the beneath solutions can reduce the solubility of 1-Butanol, known as the salting out effect.

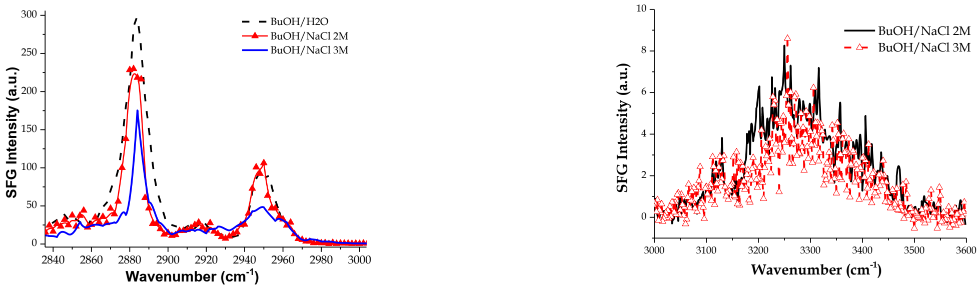


a) b)

Figure 3. SSP SFG spectra of 1-Butanol/NaF solutions.

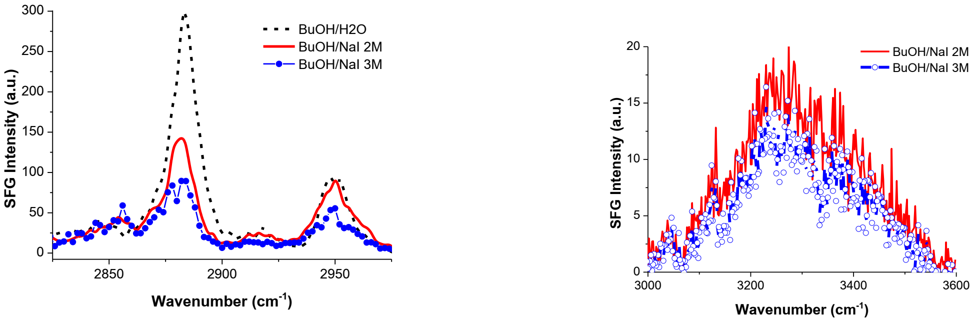
Figure 3 shows SFG spectra from the interface of the monolayer 1-Butanol/NaF solution with salinity ranging from 0.0 to 0.9 M, which is close to the saturation of NaF. In Fig. 3a, the peak intensity of CH_{3SS} mode from the 1-Butanol monolayer/NaF solution is significantly enhanced in compare to that from monolayer 1- Butanol/pure-water. The enhancement of this mode indicates an increasing interfacial order in the system with the presence of NaF in the subphase solution [4]. Other research, both in experiment and simulation [5, 6], show that the presence of F^{-} anions in the air/water interface enhances the hydrogen bonding network of the interfacial water layers. In another report of our group, we have also found this effect of NaF on the enhancement in the OH vibrational band from an Arachidic acid (AA) monolayer/water system. However, in the case of the AA monolayer/water system, we have observed an insignificant enhancement in the CH band. This result shows that the 1-BuOH monolayer is more sensitive to the ordering structure of the subphase interfacial water, and can be a better indicator of that ordering, due to a shorter hydrocarbon chain length of the BuOH in relative to the AA.

We observe a contrary effect of NaI and NaCl on the interfacial structure of the 1-BuOH monolayer/water system. In general, the presence of I^{-} and Cl^{-} ions in solutions decreases SFG signals both in the CH and OH bands, as seen in Fig. 4, and Fig. 5. The lowering of CH_{3ss} and CH_{3Fr} peaks indicates a disorder in the interfacial structure of the systems. Meanwhile, the emergence of a CH_{2ss} peak at 2850 cm^{-1}, shown in figure Fig. 5a, indicates a collapsing of the 1-BuOH monolayer when the NaI concentration reaches to 3M. Results of phase-sensitive SFG spectroscopy research [7], and molecular dynamic simulation [5], showed a high surface propensity of I^{-} and Cl^{-} ions on air/water interfaces. Due to the high surface propensity, I^{-} and Cl^{-} anions tend to disturb the interfacial network structure of the 1-BuOH monolayer/water system. This argument is in good agreement with SF spectra we have observed as the salt concentration increases, as indicated in Fig. 4 and Fig. 5.



a) b)

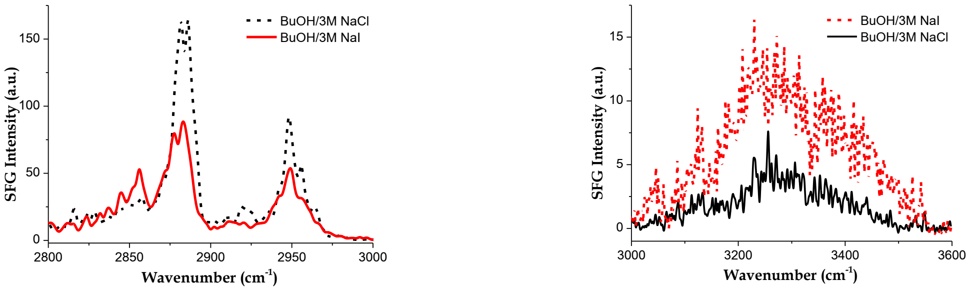
Figure 4. SSP SFG spectra of 1-Butanol/NaCl solutions.



a) b)

Figure 5. SSP SFG spectra of 1-Butanol/NaI solutions.

The decrease of SF intensity in the OH vibrational band represents a disturbance in the hydrogen-bonding network of the interfacial water layers. Both I^- and Cl^- ions lower the SF signals from this band, as seen in Fig. 4b, and Fig. 5b. However, when comparing between these two anions at the same concentration, as shown in Fig. 6, we observe different effects on the CH and the OH bands. In Fig. 6a, the SF signal intensities of CH3ss and CH3Fr peaks from the 1-BuOH monolayer/NaCl solution are larger than those from the 1-BuOH monolayer/NaI solution, whereas in Fig. 6b, the SF intensity of OH band from the monolayer/NaCl solution is significantly lower than that from the monolayer/NaI solution. Thus, the I^- ions have a stronger effect on the monolayer structure, whereas the Cl^- ions mainly disturb the interfacial water layers beneath. This result is a supportive empirical evidence which shows that the surface propensity of I^- anions is larger than that of Cl^- anions, as found in previous studies on air/water systems [5, 7].



a) b)

Figure 6. SSP SFG spectra of 1-Butanol/NaI and NaClsolutions.

To qualitatively determine the order of the 1-BuOH monolayer structure, we evaluate the SF intensity ratio between the CH_{3ss} and the CH_{2ss} modes. The larger this ratio, the more order the monolayer is [4]. Those ratios for 2M and 3M concentrations of NaCl and NaI are given in table 1.

Table 1. Calculated I_{CH_3} / I_{CH_2} ratios for the 1-BuOH/NaCl and NaI solutions

Salt Concentrations	I_{CH_3} / I_{CH_2} **In NaCl**	I_{CH_3} / I_{CH_2} **In NaI**
2 M	6.0	2.9
3 M	5.3	1.7

In table 1, the ratio I_{CH_3} / I_{CH_2} at the salt concentration of 2M of NaI is about half of that of NaCl. At the salt concentration of 3M, this ratio of NaI is only about one-third of NaCl, at which the monolayer is nearly collapsed under the disturbance of I^- ions. This evaluation is quite compatible with calculation results of an MD simulation study by Pavel Jungwirth et. al [5].

4. Conclusions

We have investigated the 1-Butanol monolayer/water interfacial system with various halide anions concentration in the water subphase using sum-frequency vibrational spectroscopy. We have observed a “structure-making” effect of F^{-} anions on the interfacial layers of the system, *i.e.* the SF signals from the interface are enhanced in the presence of F^{-} anions. On the other hand, Cl^{-} and I^{-} anions disturb network structures at the interface. Due to the larger surface propensity, iodide (I^{-}) has a more disruptive effect on the monolayer, whereas chloride (Cl^{-}) has more disturbance on the hydrogen bonding network of the interfacial water beneath.

References

[1] Roland von Glasow, Sun, sea and ozone destruction, Nature, 453, (2008) 1195-1196,

[2] Y. R. Shen, Surface properties probed by second-harmonic and sum-frequency generation, Nature, 337 (1989) 519-525

[3] D. Myers, Surfaces, Interfaces, and Colloids: Principles and Applications, Wiley-VCH Publishers, New York, 1999.

[4] Lisa L. Van Loon, Rena N. Minor, and Heather C. Allen, Structure of Butanol and Hexanol at Aqueous, Ammonium Bisulfate, and Sulfuric Acid Solution Surfaces Investigated by Vibrational Sum Frequency Generation Spectroscopy, J. Phys. Chem. A, (2007), 111, p 7338-7346.

[5] Pavel Jungwirth, and Douglas J. Tobias, Ions at the Air/Water Interface, J. Phys. Chem. B, 2002, 106, p 6361-6373.

[6] Elizabeth A. Raymond and Geraldine L. Richmond, Probing the Molecular Structure and Bonding of the Surface of Aqueous Salt Solutions, J. Phys. Chem. B, 108 (2004) 5051-5059.

[7] Chuanshan Tian, Steven J. Byrnes,Hui-Ling Han, and Y. Ron Shen, Surface Propensities of Atmospherically Relevant Ions in SaltSolutions Revealed by Phase-Sensitive Sum Frequency VibrationalSpectroscopy, Journal Physical Chemistry Letters 2 (2011) 1946.