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The behavior of water molecules at the surface of nonionic surfactant (monomyristolein) and effects of monovalent ions on the behavior are investigated using the heterodyne-detected vibrational sum frequency generation spectroscopy. It is found that water molecules at the surface are oriented with their hydrogen atoms pointing to the bulk, and that the degree of orientation depends on the anion strongly but weakly on the cation. With measured surface potentials in those saline solutions, it is concluded that the heterogeneous distribution of anions and cations in combination with the nonionic surfactant causes the water orientation. This heterogeneous distribution well explains the contrasting order of anions and cations with respect to the ion size in the Hofmeister series. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4919664]

Aggregation and dispersion are ubiquitous phenomena in colloidal systems. In the standard interpretation of the aggregation/dispersion of colloids by interactions between themselves, the solvent, i.e., water, has been assumed to be the homogeneous medium. This means that the heterogeneity of water orientation and dynamics in a hydration layer have only little effects. On the other hand, there exist some phenomena that are not interpreted through the ordinary interactions such as an electrostatic interaction and van der Waals interaction.[1] One of examples is the clouding phenomenon of micelles of nonionic surfactant or nonionic polymers.[2,3] With increasing temperature, the aggregation occurs in aqueous solutions inspite of the decreased translational entropy of the colloids. This has been explained by the dehydration of the colloids. The gain of translational entropy acquired by water molecules freed under the dehydration overcomes the entropy loss of colloids. For bilayer systems of neutral lipids, surfactants and polymers, effect of the hydration water on their interaction has long been discussed through a hydration force.[1,4,5] However, the relation between the heterogeneity and the colloidal interactions is still actively investigated.[5] Recent reports claimed that the effect of the heterogeneity of water orientation and dynamics is more significant than expected,[6–8] especially in the presence of ions.[9]

The heterogeneity of water orientation and dynamics at the surface of colloids should have a strong relation with the so-called Hofmeister effect.[10] Colloidal proteins are aggregated by addition of ions in water (salting-out) with systematic dependence on the species of added ions. Even when charges of ions are common, the behavior is entirely different in many cases. Not only for colloidal proteins, similar phenomena have been reported for many colloidal systems.[11–14] Although the mechanism of the Hofmeister effect is still a matter of dispute, it has been considered that the disturbance or structuring of the water network by ions results in the change in the interactions between colloids. In conformity with this idea, ions have been classified into "water structure maker" or "water structure breaker."[11–13] Effect of anions is known to be stronger than that of cations. The order of anions for "water structure maker" is $SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^- > SCN^- > ClO_4^-$.[11] When monatomic and monovalent ions are compared, a smaller ion is more effective for "structure making" since the electric charge is denser. On the other hand, the standard order of cations is $NH_4^+ > K^+ > Na^+ > Li^+ > Mg^{2+} > Ca^{2+} > Ba^{2+}$, where a smaller cation has weaker effect among monatomic and monovalent ions, i.e., the orders with respect to the ion size are contrasting between anions and cations. The contrasting trend is one of the mysteries of the Hofmeister series. It is noted that the order can vary depending on the system and that even a partial reversal of the order has often been reported.[11]

In contrast to the charged colloids, for which the electrostatic interaction dominates their aggregation/dispersion, the effect of the heterogeneity of water, in principle, becomes obvious in neutrally charged colloids.[2,3,9,14] Unfortunately, due to the lack of suitable experimental methods, the hydration states of the neutrally charged colloids and the effect of ions on them have long remained unexplored. In 2009, the molecular orientation of the interfacial water around surfactant monolayers had been reported in detail on the basis of heterodyne-detected vibrational sum frequency generation (HD-VSFG) spectroscopy, which enables us to obtain the phase of the second-order nonlinear susceptibility, $\chi^{(2)}$.[15] Since then, an increasing number of reports have been published on the interfacial properties of water molecules such as the molecular orientation and hydrogen-bonding network at the surfaces of ionic surfactants or zwitterionic lipids

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using this technique.[15–18] However, the molecular orientation of water molecules at the surface of nonionic surfactant monolayers and the effect of solvated ions have not been fully investigated.

In the present study, we investigate effects of monovalent salts on the interfacial properties of water molecules at Langmuir monolayer of a nonionic surfactant; monomyristolein, by the HD-VSFG spectroscopy. Based on the results of the HD-VSFG of the surfactant monolayer and electrostatic surface potentials (ζ potential) of its bilayer, it is concluded that the cooperativity of nonionic surfactant and solvated anions orients water molecules at the surface, while water molecules are only weakly oriented at the surface without ions. The orientation of water molecules exhibits the salt dependence in accordance with the Hofmeister effect.

A nonionic surfactant, monomyristolein (Fig. 1, molar mass; 300.50 g mol^{-1}), was purchased from NU-CHEK PREP, INC. (Elysian, MN, USA). Six monovalent salts, LiCl (>98%), LiBr (>98%), NaCl (>99.5%), NaBr (99.5%-100.3%), KCl (>99%), KBr (>99%) were from NACALAI TESQUE, INC. (Kyoto, Japan). Heavy water (D$_2$O, isotopic purity of >99.9%) was purchased from Cambridge Isotope Laboratories, Inc. (MA, USA). These were used without further purification. The ordinary water (mainly of H$_2$O) used is of MilliQ (18.2 MΩ cm).

For HD-VSFG measurements on Langmuir monolayers, monomyristolein was mixed with a 500 mM of each saline solution so as to be 1 mM (approximately 0.03 wt.% in pure water), which is much higher than critical micellar concentrations (CMC) of usual nonionic surfactant.[19] To determine whether the origin of VSFG signal of the OH vibration is from a water molecule or a head group of the surfactant, both the H$_2$O and D$_2$O were used as solvents. A Langmuir monolayer was formed by pouring 20 ml of each solution in a Teflon cell (surface area: 67 mm × 67 mm). The measurements of samples with D$_2$O were performed within 18 h after the sample preparation to avoid hydrogen-deuterium exchange between a head group of monomyristolein and D$_2$O.[20]

Our HD-VSFG spectroscopic system is described elsewhere.[21] The wavelength of the visible beam was 630 nm and the infrared beam covered the frequency range of the CH and OH stretching modes. All measurements were performed in the SSP (VSFG, visible, and infrared beams were set to S-, S-, and P-polarized) polarization combination. For the reference, a z-cut quartz was used. All measurements were performed at room temperature. Some details specific to this study including data manipulation procedure are given in the supplementary material.[20] The $\chi^{(2)}$ has a non-zero value only when the system has a broken inversion-symmetry, i.e., when some transition

dipole moment of chemical bonds in molecules at a surface is oriented. The sign and the amplitude of the imaginary part of $\chi^{(2)}$ reflect the direction and the strength of the orientation, respectively.[15–18]

For measurements of electrostatic surface potentials (ζ potentials), monomyristolein was mixed with 100 mM of each saline solution so as to be about 0.1 mM. At higher concentrations of salts, the proper voltage could not be impressed because of an electric current in solutions, whereas the effect of a salt became unclear at lower concentrations.

The surface potentials were measured with a microscope-type ζ potential meter (ZEECOM ZC-3000, Microtec Co., Ltd. (Chiba, Japan)) at a stationary phase. Voltage for electrophoresis was kept at 1.56 V cm^{-1} and 500 aggregative particles were measured. All measurements were done at room temperature.

Figure 2(a) shows the imaginary parts of $\chi^{(2)}$ obtained from monomyristolein monolayers on the saline solutions of H$_2$O. In the CH stretching region,[22] negative features are observed at 2855, 2880, 2920, 2936, and 3010 cm^{-1}, which are assigned to the symmetric CH$_2$ stretching, the symmetric CH$_3$ stretching, Fermi resonance of the symmetric CH$_2$, Fermi resonance of the symmetric CH$_3$, and the CH vinyl stretching mode of the surfactant, respectively. A positive band is observed at 2965 cm^{-1}, which is due to the anti-symmetric CH$_3$ stretching mode. Appearance of these non-zero Im[$\chi^{(2)}$] signals for all samples confirms that monomyristolein molecules form a Langmuir monolayer on the surface of the solutions.

Im[$\chi^{(2)}$] signals between 3050 and 3450 cm^{-1}, originated from the OH stretching vibration, are compared in detail in Fig. 2(b). Ignoring the ripples superimposed on spectra due to the instruments and spectrum manipulation method, the signal was found to be very small in the case that the solvent was pure water. It was slightly positive at around 3100 cm^{-1} and slightly negative at around 3400 cm^{-1}, being similar to the Im[$\chi^{(2)}$] spectrum from the air-pure water surface.[15,23] With any salt examined, the signals around 3050–3450 cm^{-1} become clearly negative. On the other hand, only weak Im[$\chi^{(2)}$] signals were observed in the 3050–3450 cm^{-1} region from the monolayers on the D$_2$O solutions regardless of the existence or the species of ions (see Fig. 3). Since the OD stretching vibrations are expected at around 2400–2800 cm^{-1} (Ref. 24) and the hydrogen-deuterium exchange is almost negligible in this case,[20] this observation clearly indicates that the negative Im[$\chi^{(2)}$] in the 3050–3450 cm^{-1} region from the samples with H$_2$O solutions was originated from the OH stretching vibration in H$_2$O molecules, and that the hydroxyl groups of the surfactant did not contribute to them. The negative Im[$\chi^{(2)}$] around 3050–3450 cm^{-1} in the SSP polarization combination indicates that water molecules at the surfactant monolayer orient with their hydrogen atoms pointing to the bulk[15] probably due to the Coulomb forces of the anions, while the water molecules are only weakly oriented without ions as indicated by the small signal amplitude. Water molecules that contribute to the signals include those in the hydration shell.

Now, we discuss the Im[$\chi^{(2)}$] amplitude of OH band of the samples with H$_2$O solutions in Fig. 2. For all cations, the signal looks more negative with chloride than with bromide. To
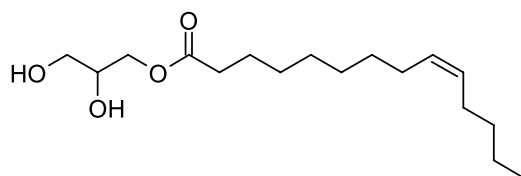
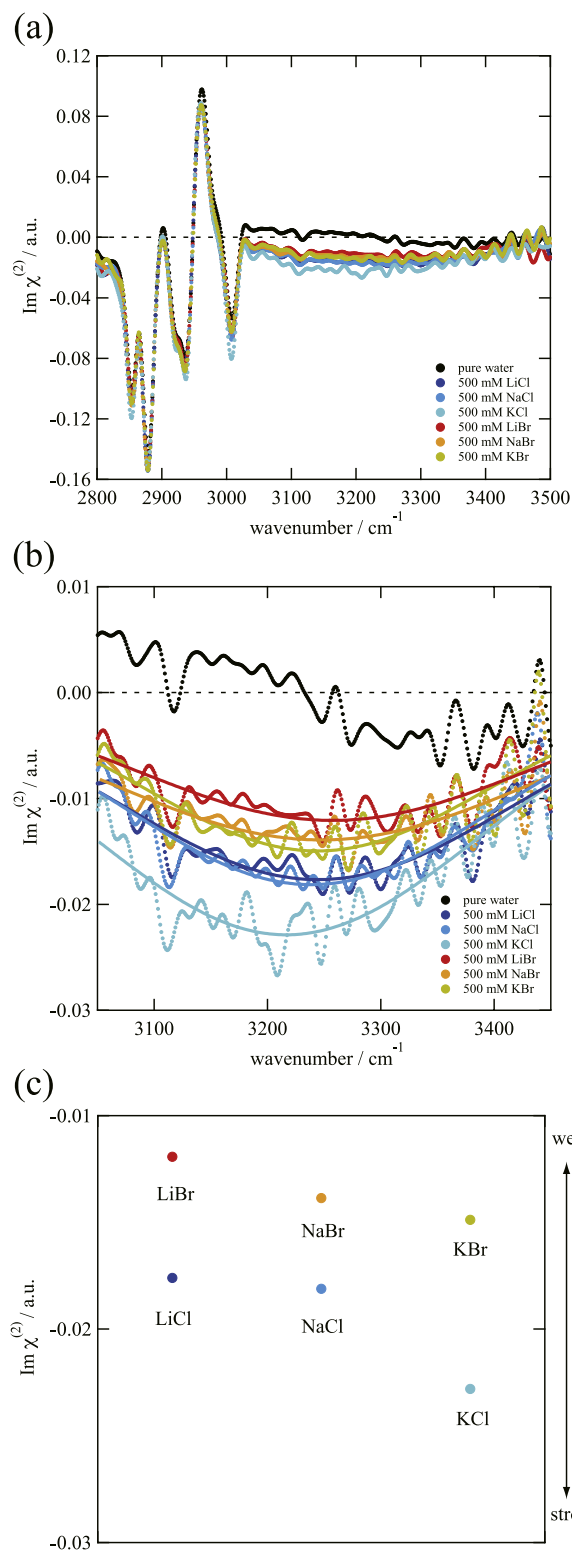FIG. 1. Chemical structure of monomyristolein.

(a)

(b)

(c)

FIG. 2. Imaginary part of the second-order nonlinear optical susceptibility, Im[$\chi^{(2)}$], obtained from the HD-VSFG of monomyristolein monolayer on saline solutions of H$_2$O. (a) Im[$\chi^{(2)}$] in a whole range of wavenumber for all samples. (b) Im[$\chi^{(2)}$] between 3050 and 3450 cm^{-1} and the fitted line with Gaussian (solid line). (c) Im[$\chi^{(2)}$] at 3230 cm^{-1} of the fitted line.
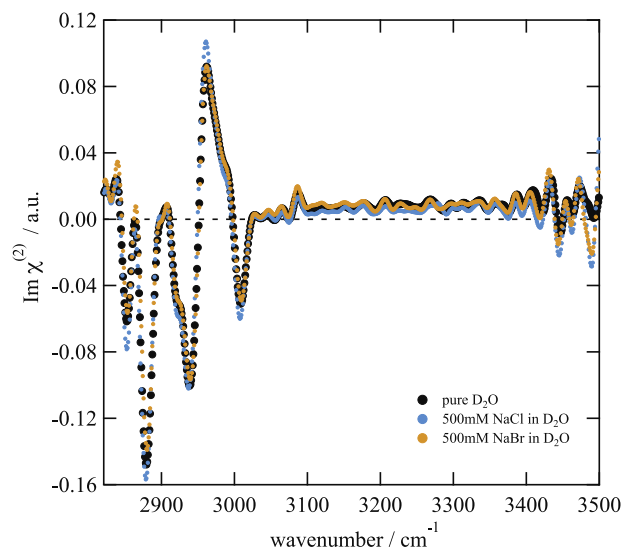

FIG. 3. Imaginary part of the second order nonlinear susceptibility, Im[$\chi^{(2)}$], of monomyristolein monolayer on pure D$_2$O, NaCl/D$_2$O solution, and NaBr/D$_2$O solution.

ions, are plotted in Fig. 2(c). It is clear that they have the anion dependence. With a chloride ion, the Im[$\chi^{(2)}$] is more negative than with a bromide ion. That is, a chloride ion more strongly orients water molecules with the H atoms pointing into the bulk than a bromide anion. In contrast to the anion dependence, the cation dependence is smaller. The order of the absolute amplitudes is K$^+$ > Na$^+$ > Li$^+$. To summarize the ion dependence, a smaller anion orients water molecules more strongly than a larger anion, while a smaller cation orients more weakly than a larger cation. These contrasting orders are the same as the standard Hofmeister series.

In previous studies, it has been shown that the HD-VSFG spectrum from an interface of the air-saline solution is different from that of the air-pure water interface.[25,26] The ion dependence was also reported. However, the reported difference is much smaller than that observed in the present study between surfaces of the surfactant-pure water and the surfactant-saline solutions, inspite of the salt concentrations four times larger than the present study. The Im[$\chi^{(2)}$] signals from the air-saline solution surfaces still remain positive around 3100 cm^{-1} and negative around 3400 cm^{-1}, implying only a weak orientation of water molecules, which is comparable to the case at the air-pure water interface. Namely, without salts, the VSFG spectrum in the OH stretching region from the surfaces of the air-pure water and that from the surfactant-pure water interfaces is similar to each other, indicating the similar weak orientations of water molecules at both surfaces. On the other hand, the strong orientation of water molecules by ions occurs only at the surfaces of surfactant monolayers, indicating the cooperativity between the surfactant monolayer and ions.

To elucidate the mechanisms of the orientation of water molecules at the monomyristolein surface by ions, distributions of ions around the surfaces were investigated through measurements of the electrostatic surface potentials of monomyristolein aggregates in the saline solutions. The surface potentials of monomyristolein aggregates in each saline solution are shown in Table I. The potentials are slightly negative around −5.5 mV for all solutions and

extract the vibrational resonance component, Im[$\chi^{(2)}$] spectra between 3050 and 3450 cm^{-1} are fitted with a Gaussian and the resulting Im[$\chi^{(2)}$] at 3230 cm^{-1}, where the Im[$\chi^{(2)}$] signal is almost 0 for the sample with pure water without

TABLE I. The electric surface potentials (ζ potentials) of monomyristolein in 100 mM of saline solutions. Values in the parentheses are the standard deviations.

ζ / mV	Li	Na	K
Cl	−5.4 (2.3)	−5.3 (2.2)	−5.2 (1.9)
Br	−6.4 (2.7)	−5.6 (2.0)	−5.9 (2.0)

exhibit little ion dependence. Since the measured surface potential is a potential including the electric double layer, the negative potentials indicate that anions favorably distribute closer to the monomyristolein surface than cations. Such a heterogeneous distribution is similar to the case of the air-water interface.[25,27,28]

The heterogeneous distribution of anions and cations supposedly induces the downward orientation of water at the surface of monomyristolein monolayers with their hydrogen atoms pointing to the bulk, as schematically shown in Fig. 4. Since anions come closer to the surface, water around the monolayer is sandwiched by surfactants and anions. Even if the surfactant hardly affects the orientation of water molecules, anions strongly interact with water molecules. Then, the interfacial water molecules are, on average, oriented with directing their hydrogens to anions, as observed by the HD-VSFG spectroscopy (Fig. 2).

Although the dependence on neither anion nor cation is recognized in the surface potentials, the ion-dependent orientation of water molecules is plausibly interpreted coherently with the heterogeneous distribution of anions/cations and the size of ions. It is natural to consider that chloride ions with a smaller size interact with water more strongly than bromide ions with a larger size. Then, chloride ions will orient water molecules more strongly than bromide ions, resulting in more negative Im[$\chi^{(2)}$]. The dependence on cation is also interpreted through the heterogeneous ion distribution. When cations come close to the surface, they cancel the downward-orientation of water molecules caused by anions. The cancellation will be more effective with a smaller cation, i.e., Li$^+$ in the present study. Thus, the contrasting orders against the ion size between anions and cations for the amplitude of Im[$\chi^{(2)}$] is reasonable.

The stronger effect assumed for anions than cations has been generally accepted as a general trend in the Hofmeister series of ions.[10–14] The interpretation automatically leads to the stronger dependence on anion of the degree of water orientation at the surface, because of the heterogeneous distribution of anion/cation. Besides, this interpretation of the contrasting orders against the ion size between anions and cations is compatible with the Hofmeister series. It is, thus, to be regarded as a microscopic mechanism of the Hofmeister effect for systems consisting of water, salt(s), and neutral surfaces. The cooperativity among nonionic surfactant, ions, and water causes the heterogeneous distribution of anions/cations, resulting in the marked effect of the ion size. Other factors will be necessary to be taken into account for systems with charged surfaces.[16] In this respect, the Hofmeister effect might be a name for not a single, definite effect but combinations of effects.

In summary, from the HD-VSFG spectra and the surface potentials of monomyristolein surfaces in saline solutions, it is concluded that the cooperativity of anion and nonionic surfactant induces the orientation of water molecules at the monolayer surface. Since anions distribute closer at the surface than cations, water between anions and surfactants is oriented with their hydrogen pointing to the bulk. Due to the size of anions, i.e., degree as "a water structure maker," a chloride ion has a larger effect on water orientation than a bromide ion. The low degree of orientation of water molecules with the Li$^+$ ion is also interpreted on the basis of the size of cations, which cancels more effectively the orientation caused by anions. Thus, the contrasting orders of the Hofmeister series with respect to the ion size between anions and cations are interpreted through the heterogeneous distribution of anions and cations. The ion-dependent orientation of water molecules likely has a relation to the salt dependence of the interactions between membranes dispersed in saline solutions. The study on the relation is under way.

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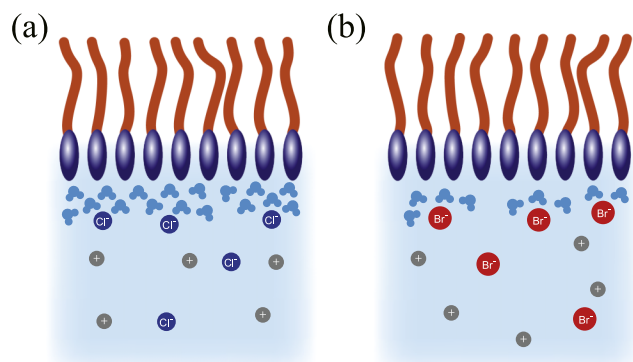
(a)   (b)

FIG. 4. Schematic image of ion distributions and orientation of the interfacial water molecules. Water molecules orient more strongly with chloride (a) than with bromide (b).

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