

# Counterion Effect on Interfacial Water at Charged Interfaces and Its Relevance to the Hofmeister Series

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**S** Supporting Information

**ABSTRACT:** Specific counterion effects represented by Hofmeister series are important for a variety of phenomena such as protein precipitations, surface tensions of electrolytes solutions, phase transitions of surfactants, etc. We applied heterodyne-detected vibrational sum-frequency generation spectroscopy to study the counterion effect on the interfacial water at charged interfaces and discussed the observed effect with relevance to the Hofmeister series. Experiments were carried out for model systems of positively charged cetyltrimethylammonium monolayer/electrolyte solution interface and negatively charged dodecylsulfate monolayer/electrolyte interface. At the positively charged interface, the intensity of the OH band of the interfacial water decreases in the order of the Hofmeister series, suggesting that the adsorbability of halide anions onto the interface determines the Hofmeister order as previously proposed by Zhang and Cremer (*Curr. Opin. Chem. Biol.* **2006**, *10*, 658–663). At the negatively charged interfaces, on the other hand, the OH band intensity does not depend significantly on the counter-cation, whereas variation in the hydrogen-bond strength of the interfacial water is well correlated with the Hofmeister order of the cation effect. These results provide new insights into the molecular level mechanisms of anionic and cationic Hofmeister effects.

The Hofmeister series originally describes the order of the ability for ions to precipitate proteins out of solutions, named after Hofmeister. For example, the ions in the left side of the Hofmeister series in Figure 1 stabilize native structure of proteins and salt out proteins, while the ions in the right denature and solubilize proteins.<sup>1–4</sup> This order of the ion effect can be

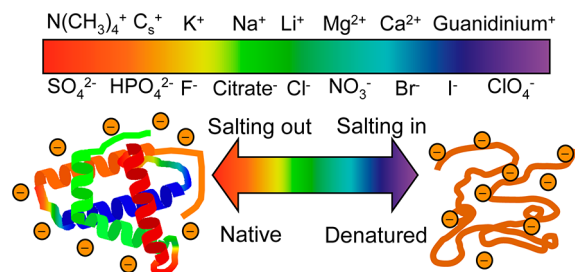


Figure 1. Conceptual sketch of the Hofmeister series.

found not only in protein precipitations but also in a variety of macroscopic phenomena such as surface tensions of electrolyte solutions,<sup>5</sup> phase transitions of simple surfactants,<sup>6,7</sup> etc. Because of this extensiveness, the Hofmeister counterion effects have been investigated in many research fields. Despite its importance and the vast amount of macroscopic observations, the microscopic mechanism of the Hofmeister series is still under debate.

Because the order in the Hofmeister series can be found even for the surface tension of salt solutions<sup>5</sup> where no macromolecule exists, it is believed that the Hofmeister series is related with ion–solvent interaction rather than ion–macromolecule interaction. Indeed, it had been claimed that structure-making ions (the ions that induce more hydrogen bonding) promote precipitation of macromolecule in solution, while structure-breaking ions (the ions that bring about less hydrogen bonding) solubilize it.<sup>8</sup> However, a careful analysis of the thermodynamic parameters (entropy, partial heat capacity) of variety of salt solutions revealed that structure making/breaking properties of ion in bulk solutions do not exactly match with the Hofmeister series,<sup>9</sup> and no straightforward correlation was found between the bulk water structure and the Hofmeister series.<sup>3</sup> Recently, it is considered that the Hofmeister series microscopically pertains to the interface between a macromolecule and ion solution.<sup>3</sup> Therefore, it is essential to study the interfacial water structure to elucidate the mechanism that gives rise to the Hofmeister series.

Water structure at aqueous interfaces can be studied by vibrational sum frequency generation (VSFG) spectroscopy. VSFG spectroscopy provides interface-selective vibrational spectrum based on a breaking of the inversion symmetry at interfaces, and it has been applied to study interfacial water structure at various aqueous interfaces.<sup>10,11</sup> Using negatively and positively charged interfaces, the effect of cationic and anionic counterions on the structure of interfacial water can be separately examined by VSFG spectroscopy. Previously, Cremer et al. studied the counteranion effect at various aqueous interfaces by using VSFG spectroscopy.<sup>12–14</sup> They found a good correlation between the anion Hofmeister series and the OH band intensities in the VSFG spectra of the neutral polymer,<sup>12</sup> positively charged monolayer,<sup>13</sup> and charged mineral interfaces.<sup>14</sup> Based on this, they concluded that, at least for anions, the Hofmeister counterion effect is originated from the direct interaction between a macromolecule and the anion.<sup>13</sup> Although this conclusion is quite convincing, two questions are left unsolved: (1) Is the direct interaction predominant also between

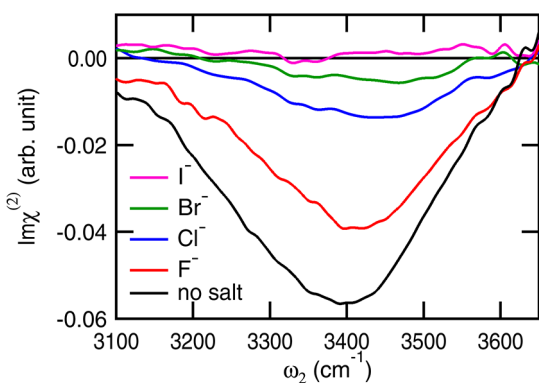
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the negatively charged interfaces and the counter cations? (2) Does hydrogen-bond structure of interfacial water play any role on the Hofmeister series?

To answer these questions, we investigated the counterion effect on the water structure at interfaces of monolayers of positively charged cetyltrimethylammonium bromide ( $\text{CTA}^+\text{Br}^-$ ) and negatively charged sodium dodecyl sulfate ( $\text{Na}^+\text{DS}^-$ ) surfactants, which are formed at the air/water interface. The critical micelle concentrations of these surfactants are known to follow the order of the Hofmeister series,<sup>6,7</sup> so that they provide relevant interfaces to study the origin of the Hofmeister counterion effect. We employed an advanced nonlinear spectroscopy, i.e., heterodyne-detected (HD-) VSG spectroscopy,<sup>15,16</sup> combined with isotopic dilution technique.<sup>17–20</sup> While conventional VSG spectroscopy only provides modulus square of the second-order nonlinear susceptibility ( $|\chi^{(2)}|^2$ ), HD-VSG provides the imaginary part of  $\chi^{(2)}$  ( $\text{Im}\chi^{(2)}$ ) which is an intrinsic interfacial vibrational spectrum. The  $\text{Im}\chi^{(2)}$  spectrum is free from the spectral deformation which is unavoidable in a  $|\chi^{(2)}|^2$  spectrum, and hence the structural information on the interfacial water can be evaluated straightforwardly from the  $\text{Im}\chi^{(2)}$  spectra. In addition, to investigate hydrogen-bond structure from the vibrational spectra, it is necessary to employ isotopically diluted water ( $\text{HOD-D}_2\text{O}$ ) to eliminate the vibrational coupling existing in  $\text{H}_2\text{O}$  (or  $\text{D}_2\text{O}$ ) molecules.<sup>17,18,21,22</sup> The combination of HD-VSG and isotopically diluted water enables us to compare not only the intensity of the OH stretch band in the interfacial spectra but also its peak position which is directly related to the hydrogen-bond strength of water at the interfaces.

In the first set of experiments, the anion Hofmeister series was investigated at positively charged  $\text{CTA}^+$  interfaces with excess amount (0.5 M) of sodium halides. The  $\text{Im}\chi^{(2)}$  spectra in Figure 2



**Figure 2.**  $\text{Im}\chi^{(2)}$  spectra of air/water interfaces of aqueous 0.1 mM CTAB solution in isotopically diluted water without excess salt (black) and containing 0.5 M NaF (red), NaCl (blue), NaBr (green), and NaI (magenta).

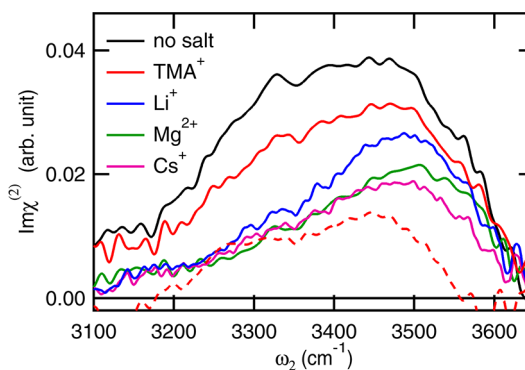
shows a negative OH stretching band of water near the positively charged  $\text{CTA}^+$ /isotopically diluted water interfaces.<sup>16</sup> The major species that gives the OH resonance is the HOD molecule at the given isotopic concentration. The negative sign of the OH band corresponds to the net “hydrogen-down” orientation of the interfacial water, i.e., the hydrogen of water points away from the positively charged interface.<sup>16</sup> The high salt concentration (0.5 M) employed in this experiment induces the Helmholtz electric double layer in which the counterions are located in the very vicinity of the interface region. In this case, the observed OH band is attributable to the water molecules confined in between charged monolayer and counterions. These water molecules are

expected to be oriented on average by the electric field and thus  $\chi^{(2)}$  active.

As clearly seen in Figure 2, the OH band intensity decreases with increasing the size of halide ( $\text{F}^- \rightarrow \text{I}^-$ ). With  $\text{F}^-$  ion, the intensity decreases only moderately with respect to the intensity without salt. In contrast, the OH band intensity is virtually zero for  $\text{I}^-$ , indicating that oriented water molecules scarcely exist in between  $\text{CTA}^+$  and  $\text{I}^-$ . These ion effects can be explained by the adsorption of larger halides onto the positively charged surfactant. The  $\text{F}^-$  ion is known to have a strong hydration shell,<sup>23</sup> and therefore it gets difficult to approach closely to the surface. This results in a relatively thick Helmholtz layer and thus a larger OH band intensity. For the larger halides, the Helmholtz layer becomes thinner due to the contact adsorption, giving the smaller  $\chi^{(2)}$ . X-ray studies have reported that  $\text{Br}^-$  counterions are directly bound to the  $\text{CTA}^+$  headgroup,<sup>24</sup> in preference to  $\text{Cl}^-$  ions.<sup>25</sup>  $\text{I}^-$  has the strongest interaction with  $\text{CTA}^+$ , and among these salts, only  $\text{I}^-$  induces precipitation in 0.1 mM  $\text{CTA}^+$  at 1 M. These  $\text{Im}\chi^{(2)}$  spectra show that the direct interaction, in other words, contact ion pair formation, is the major cause for the Hofmeister counterion effect of the halides, in agreement with a previous conventional VSG study by Cremer et al.<sup>13</sup>

The peak position of the OH stretch band at the  $\text{CTA}^+$  interface without excess salt and at the  $\text{CTA}^+/\text{F}^-$  interface is  $\sim 3400 \text{ cm}^{-1}$  (Figure 2). This indicates that the hydrogen-bond strength of the interfacial water at these interfaces is comparable to that in the bulk neat water. In contrast, the peak frequencies of the OH stretch band at the  $\text{CTA}^+/\text{Cl}^-$  and  $\text{CTA}^+/\text{Br}^-$  interfaces are higher by  $\sim 50 \text{ cm}^{-1}$ , indicating that the hydrogen bond is weakened at the  $\text{CTA}^+/\text{Cl}^-$  and  $\text{CTA}^+/\text{Br}^-$  interfaces. The peak frequency for the  $\text{CTA}^+/\text{I}^-$  interface cannot be determined due to the virtually zero OH band intensity.

The second set of experiments was conducted at the interfaces of the negatively charged dodecylsulfate ( $\text{DS}^-$ ) surfactant with various chloride salts of cations. The obtained  $\text{Im}\chi^{(2)}$  spectra are shown in Figure 3, which show positive OH stretch bands due to



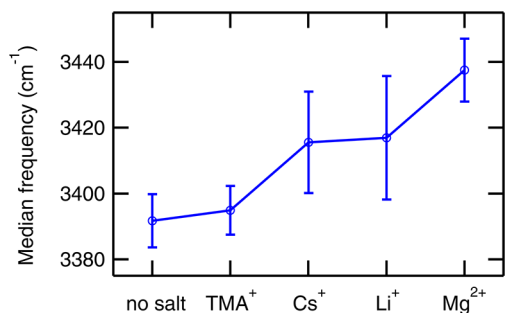
**Figure 3.**  $\text{Im}\chi^{(2)}$  spectra of air/water interfaces of aqueous 0.5 mM SDS solution in isotopically diluted water without salt (black) and containing 0.5 M of chloride salt of  $\text{TMA}^+$  (red),  $\text{Li}^+$  (blue),  $\text{Mg}^{2+}$  (green), and  $\text{Cs}^+$  (magenta).  $\text{TMA}^+$  at higher concentration (4 mol/kg) (red dashed line) is also shown for comparison.

the net “hydrogen-up” orientation of interfacial water, i.e., the hydrogen of water points to the negatively charged interface.<sup>16</sup> In contrast to the  $\text{Im}\chi^{(2)}$  spectra of  $\text{CTA}^+$  interfaces with anions, the OH band was clearly observed with all the salts examined, and the OH band intensity depends on the cation only weakly. More importantly, there is no clear correlation between the intensity of the OH stretch band and Hofmeister series. This result indicates

that contact adsorption is not predominant in the case of  $\text{DS}^-/\text{cation}$  interfaces, and hence the cation Hofmeister series does not directly reflect the propensity of contact adsorption at these interfaces.

A close view of the  $\text{Im}\chi^{(2)}$  spectra reveals that the peak frequencies of the OH band at the  $\text{DS}^-/\text{Li}^+$ ,  $\text{DS}^-/\text{Cs}^+$ , and  $\text{DS}^-/\text{Mg}^{2+}$  interfaces are blue-shifted up to  $3500\text{ cm}^{-1}$ . This frequency is significantly higher than the IR absorption maxima of the bulk water ( $3410\text{ cm}^{-1}$ )<sup>26</sup> or the peak in the SDS without salt spectrum (black curve in Figure 3). This indicates that the hydrogen-bond structure of the interfacial water in the Helmholtz layer is less hydrogen bonded than in the bulk water. Contrary to the case of metal cations, the  $\text{Im}\chi^{(2)}$  spectrum of  $\text{DS}^-/\text{tetramethylammonium}^+$  ( $\text{TMA}^+$ ) interface (solid red curve in Figure 3) differs only slightly from that of SDS without excess salt. The  $\text{DS}^-/\text{TMA}^+$  interface does not show any noticeable spectral shift even at a higher  $\text{TMA}^+$  concentration (4 M) where the OH band intensity is even weaker than that at any other  $\text{DS}^-/\text{metal cation}$  interfaces (dashed red curve in Figure 3). This implies that the interfacial water structure depends on the counterion, but it does not directly depend on the thickness of the electric double layer.

For more quantitative discussion, the median frequencies of the OH stretch band were evaluated for each  $\text{DS}^-/\text{cation}$  interface (see Supporting Information (SI)). The median OH stretch frequency, which reflects the hydrogen-bond strength of the interfacial water, shows a good correlation with the cation Hofmeister series (Figure 4). Together with the fact that contact



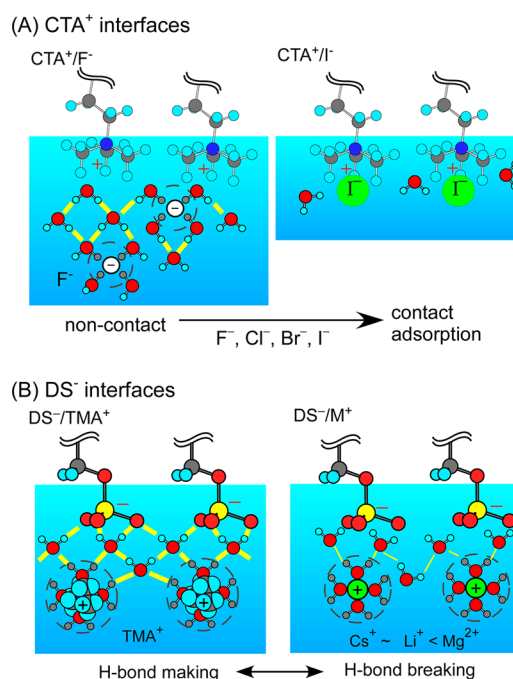
**Figure 4.** Median frequencies of the OH bands in the  $\text{Im}\chi^{(2)}$  spectra of the  $\text{DS}^-/\text{cation}$  interfaces vs Hofmeister series. The median frequency is defined in SI and calculated from the signal between  $3100$  and  $3640\text{ cm}^{-1}$ . The values shown by circles are the average of four independent sets of experiments, and the error bars represent the standard deviation.

adsorption is absent at these interfaces, this correlation strongly indicates that the Hofmeister counterion effect of cations arises from the difference in the interfacial water structure. This mechanism obviously differs from the mechanism for the anion Hofmeister series. Recently, Cremer et al. also studied cation Hofmeister series at negatively charged mineral interfaces using conventional VSGF.<sup>27,28</sup> They observed drastic change in the intensity of the OH band by introducing cations, but those intensities were not well correlated with the Hofmeister series, contrary to the anion Hofmeister series at positively charged interfaces. The direct observation of the frequency shift of the OH band by HD-VSGF indicates the change in the hydrogen bonding of interfacial water induced by the Hofmeister cations.

The order of the hydrogen-bond strength observed at the  $\text{DS}^-/\text{cation}$  interfaces is different from that observed for bulk ion solutions. Thus, it is necessary to investigate interfacial water structure rather than the bulk water structure to understand

macromolecule-counterion interaction. In fact, the FTIR spectrum of the bulk concentrated  $\text{MgSO}_4$  solution in isotopically diluted water shows a “red-shift” (Figure S1), suggesting that the water molecules inside the hydration shell of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  ions are strongly hydrogen bonded compared to the bulk water. In contrast, the  $\text{Im}\chi^{(2)}$  spectrum of the  $\text{DS}^-/\text{Mg}^{2+}$  interface clearly shows a “blue-shift” (Figure 3), implying that the hydrogen bonding of the interfacial water in the Helmholtz layer is significantly weaker than that in the bulk water. The different spectral shift between the bulk and interface can be attributed to the different regions probed by the bulk and interface spectroscopies. FTIR is sensitive to the water in the first solvation shell which is the most abundant in the concentrated salt solution. On the other hand, VSGF is highly likely less sensitive to the water in the first solvation shells of the counter cations because it is expected that the solvation shells are spherical on ensemble average and hence that  $\chi^{(2)}$  is less active due to the quasi-inversion symmetry. Thus, the observed  $\chi^{(2)}$  signal is likely attributable predominantly to the interfacial water molecules that is located in between the headgroup and the counterion but not directly hydrating the cation.

Figure 5 sketches the water structures of the positively and negatively charged interfaces which are indicated by the present



**Figure 5.** Schematic models of the (a)  $\text{CTA}^+$  and (b)  $\text{DS}^-$  interfaces. Yellow line represents the hydrogen bond. Gray hydrogen inside the dashed circles is less  $\chi^{(2)}$  active.

study. For the anion Hofmeister series, the effect of halide is well characterized by the contact adsorption of the halide onto the interface (Figure 5a). The strongly hydrated  $\text{F}^-$  ions allow the interface to hold a number of water molecules in the interfacial region, while weakly hydrated  $\text{I}^-$  tends to remove water molecules from the interfacial region by the contact adsorption. For the cation Hofmeister series (Figure 5b), the cations do not form contact ion pairs with the sulfate headgroup, and a substantial number of interfacial water molecules remain in the Helmholtz layer for all the cations examined. However, the hydrogen-bond strength of interfacial water at the negatively

charged interfaces significantly varies with the cations in accordance with the Hofmeister series. As indicated by the shift of the OH stretching frequency, TMA<sup>+</sup> does not substantially disturb hydrogen-bonding structure of interfacial water, but Cs<sup>+</sup>, Li<sup>+</sup> and Mg<sup>2+</sup> disturb it, in the order of the Hofmeister series. The observation of the frequency shift at the DS<sup>-</sup>/cation interfaces raises another interesting issue about the water–ion interaction. Because the first solvation shell may be expected to be practically  $\chi^{(2)}$  inactive, the observed frequency shift is assignable to the water molecules out of the first solvation shell of the cations. This means that the effect of the cation on the water structure reaches beyond the first solvation shell. Although this discussion is rather speculative, the ion effect beyond the first solvation shell has been suggested also in time-resolved infrared and THz spectroscopic study of MgSO<sub>4</sub> solution.<sup>29</sup>

Finally, we mention the influence of the interface (headgroup of the surfactants) on the results. In the present study, trimethylammonium and sulfate headgroups are employed as positively and negatively charged headgroups, respectively. The large halide forms an ion pair with the positively charged interface, but the cation does not at the negatively charged interface. Generally, the sulfate is considered to be strongly hydrated<sup>30</sup> and therefore tends to avoid ion pair formation. A part of the reason why cations do not adsorb on the negatively charged interface may be attributable to this property of the sulfate. Another choice of anionic headgroup may allow the contact ion-pair formation with some cations.

In summary, the present experiments have examined the counterion effect on the interfacial water at the positively and negatively charged surfactant interfaces to consider the origin of the Hofmeister series. Using HD-VSFG spectroscopy, we directly monitored the intensity and frequency of the OH stretch band of interfacial water at the charged interfaces in the presence of various salts. The results showed that the order of the halide anion effects at the positively charged interface can be explained by the propensity of the ion to adsorption. On the other hand, it was indicated that the order of the cation effects at the negatively charged interfaces arises from the difference in the hydrogen-bond strength of interfacial water which is cooperatively influenced by the interface and counter cations. The present work shows that the mechanisms of the Hofmeister effect for anion and cation can be different and that weak indirect interaction through hydrogen bonding play a prominent role when strong direct interaction is absent. The presence of two distinct mechanisms, direct and indirect interactions, can also explain why cations often show smaller salt effects compared to anions. Although further experiments are needed to rationalize the Hofmeister series on protein, the present experiments suggest that the hydrogen-bond strength of water at the interfaces is important in addition to the adsorption propensity of the ions and that different mechanisms compositely play roles on the anionic and cationic Hofmeister series.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Experimental details, bulk FTIR spectra and Im  $\chi^{(2)}$  spectra in the CH region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

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