Chemical Potential Driven Reorganization of Anions between Stern and Diffuse Layers at the Air/Water Interface

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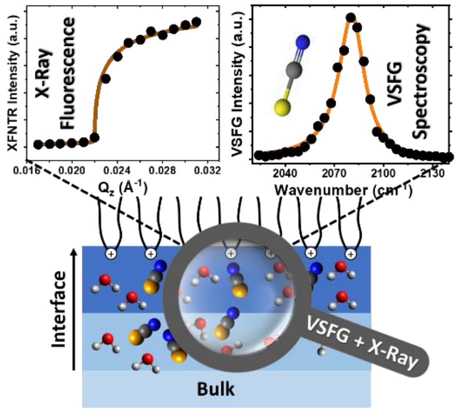
TOC Graphic



ABSTRACT

Ion adsorption and transfer at charged interfaces play key roles in various industrial and environmental processes. Molecular scale details of ion-ion, ion-water, and ion-surface interactions and their dependence on the character of the ion (ion-specific effects) are still debated. Complex ions, such as SCN^- and $SeCN^-$, are particularly interesting due to their unexpected adsorption trends which are ascribed to their permanent dipole moment and non-spherical shape. Here, we combine vibrational sum frequency generation (VSFG) spectroscopy and surface sensitive synchrotron X-ray studies to provide a detailed description of $SeCN^-$ adsorption at a charged surfactant monolayer at the air/aqueous interface. Using multiple polarization combinations in VSFG to probe the -CN stretch, we show that the average orientation of $SeCN^-$ anions with respect to the surface normal changes from 45° to 22° with the increasing KSeCN concentration. X-ray fluorescence experiments of Se K-edge and VSFG studies of -OH stretch show that $SeCN^-$ interfacial coverage (Stern layer + diffuse layer) saturates at very low bulk concentrations, but their orientational organization, distribution between Stern and diffuse layers, and effects on the hydrogen bonding network of the interfacial water continue to change with increasing bulk KSeCN concentration. X-ray reflectivity (XR) studies provide further evidence for increasing $SeCN^-$ population in Stern layer correlated with the orientational reorganization. These results show that the increasing chemical potential may lead to further reorganization of the adsorbed ions, even though the total interfacial ion population does not change. The reorganization of the interfacial ions and the water may be very important in chemical separations of heavy metals, where metal-anion complexes drive the selective ion transfer at aqueous interfaces.

INTRODUCTION

Aqueous interfaces and how ions behave near them control many important processes, such as protein folding,[1] ice nucleation,[2, 3] mineralization,[4, 5] drug delivery,[6] and chemical separations.[7-13] The common point of all these processes is that the molecular scale interface significantly differs from the bulk in terms of the ion concentration, the ion speciation, and the water structure. For instance, water is layered and orientationally ordered at interfaces,[14, 15] the dielectric constant is significantly lower (~ 5) than the bulk value (~ 80),[16, 17] and the ionic species that are not present in the bulk can be stable at the interface.[18] All these differences make it difficult to predict how ions behave at interfaces based on the bulk solution properties. The difficulty increases when the ion cannot be treated as a zero-dimensional unit charge interacting with an ideal surface. Its finite size, hydration enthalpy, polarizability, and bonding properties, which are usually considered in the context of ion-specific effects, as well as the nature of the surface functional groups may lead to complex adsorption trends.[19-21]

Ion-specific effects are usually considered in an empirical framework, where ions are listed in ascending or descending order with respect to a certain effect, such as their ability to salt out proteins as described in the Hofmeister series.[19, 20] It is not uncommon to see the certain ions switch positions on these empirical lists depending on the other factors in the system. In complex systems, where multiple enthalpic and entropic factors create an intricate free energy landscape, ion-specific effects may lead to qualitative differences in the ion adsorption and transfer mechanisms. For example, both nitrate (NO_3^-) and thiocyanate (SCN^-) are classified as chaotropic anions in the Hofmeister series but they organize interfacial structure differently.[22] Adsorption of NO_3^- does not change the interfacial water structure significantly with increasing concentration while SCN^- causes significant changes, resulting in the reorganization of the interfacial water. These nanoscale differences become very important in complex processes, such as chemical separations. For instance, in liquid-liquid extraction (LLE) of the rare earth metals, the extraction trends for heavy or light lanthanides are completely reversed in the presence of nitrate or thiocyanate.

Thiocyanate is one of the most studied pseudohalides due to its unique interfacial properties, and its applications in separation science and electrochemistry. It is a highly surface-active species with significant dipole moment ($\mu_{R-SCN} = 2.99\ D$),[23] which most likely navigates the ion to favorable orientation at interfaces. Recent experimental and theoretical studies have demonstrated the existence of enhanced concentration of SCN^- anions at the air/water interface even at very low bulk concentrations.[24, 25] Viswanath et al. and Bian et al. showed that the average tilt angle of SCN^- anions is 45° with respect to the surface normal at the free air/water interface.[24, 26-28] Saykally et al. have studied the thermodynamics of SCN^- adsorption, and its charge-transfer-to-solvent spectrum at air/water interface and analyzed the solvation environments.[29, 30] Selenocyanate ($SeCN^-$) has similar properties to that of SCN^- and have been used as a vibrational tag to investigate the solvent environments.[31] The strongest CN stretch frequency mode occurs at ~2070 cm^{-1} for SCN^- and ~2080 cm^{-1} for $SeCN^-$.[22, 32] This small change is due to the slight variation in hydrogen bond strength leading to different transition dipole moments.[33, 34] The dipole moment of $SeCN^-$ is reported slightly higher than that of SCN^- ($\mu_{R-SeCN} = 3.48\ D$).[23] Most of these studies are focused on investigation of the local structures and dynamics of anions at aqueous interfaces, but there are several unanswered questions which yet to be addressed such as interfacial hydration and organization of ions in LLE.

It is important to understand the impact of ion-specific effects in complex chemical processes, such as LLE of heavy and precious metals. In LLE metal ions are selectively transferred from an aqueous matrix into an organic phase with the help of amphiphilic molecules (also called extractants).[35] Since LLE is free energy driven at ambient conditions, it is relatively less energy intensive compared to other separation methods, such as distillation. The background anions in the aqueous phase have a significant impact on the extraction efficiency and selectivity. For example, heavy and light lanthanides are extracted better from SCN^- and NO_3^- solutions, respectively, when quaternary amine methyltrioctyl ammonium (TOMA) is the extractant.[36] Multiple factors, such as aqueous speciation of ions, interfacial interactions, nature of the diluent, and extractant-ion complexes formed in the organic phase are generally responsible for the selective transfer of the metal ions from an aqueous to an organic phase.[37, 38]

In separation science, it is well known that the interfacial region can affect the mass transfer and partitioning.[39, 40] However, it is poorly characterized due to the experimental inaccessibility of the interface in a real extraction system. Therefore, model interfacial systems consisting of air/liquid or liquid/liquid interfaces are used to understand the interfacial interactions between extractants and ions. In general, model systems having a Langmuir monolayer have been very effective to study the interfacial water structure,[41, 42] interaction of cations with monolayer,[43, 44] phase transfer of metal ions,[11] and water hydrogen bond rearrangement dynamics.[9, 45] With the advent of surface specific techniques such as vibrational sum-frequency generation (VSFG) spectroscopy, second harmonic generation (SHG) spectroscopy, and synchrotron X-ray scattering measurements, it has become possible to differentiate the interfacial phenomena from the bulk and study the structure and the dynamics of interfaces at the molecular level.[46-51]

VSFG and X-ray scattering are sensitive to different aspects of the interface. Therefore, their combination provides a significantly better understanding that cannot be obtained from one of them alone.[9, 22, 52, 53] For instance, VSFG signal intensity from the –CN stretch is a combination of the number density and the orientational ordering of the $SeCN^-$ ions. X-ray fluorescence near total reflection (XFNTR) provides the interfacial number density directly. Combining these two techniques allow decoupling the contributions from the orientational ordering and the number density in VSFG experiments.

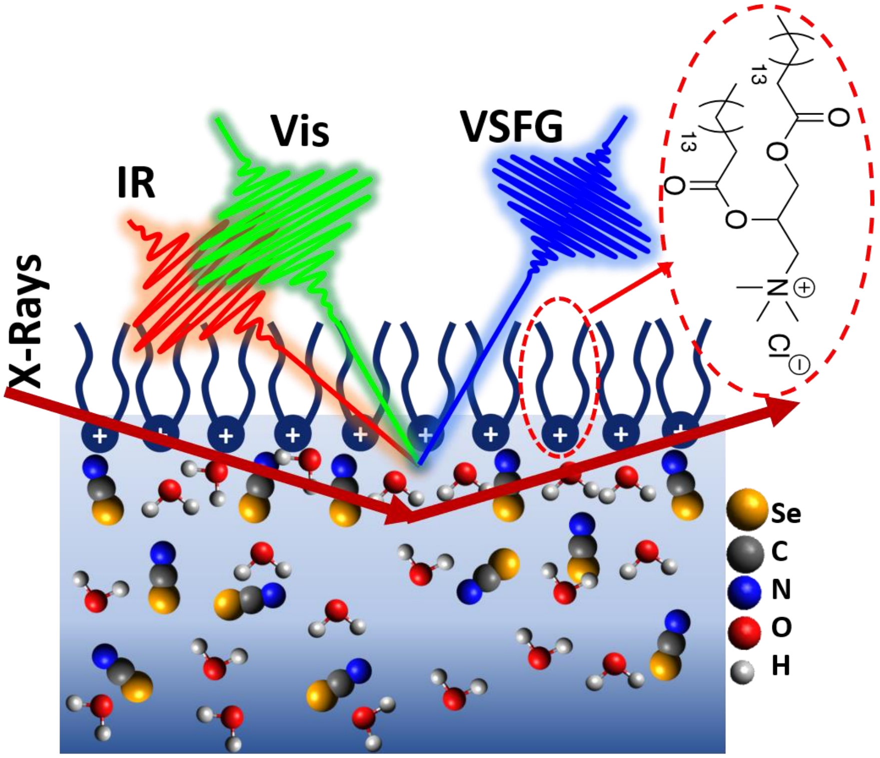


Figure 1. A schematic describing the VSFG and synchrotron X-ray experiments at the air/aqueous interface. The inset shows the structure of the DPTAP$^+$ surfactant.

We use a monolayer of DPTAP$^+$ to model the commonly used industrial extractant quaternary ammonium TOMA$^+$. DPTAP$^+$ forms a stable monolayer at air/aqueous interface due to its longer hydrophobic carbon chain. It has been extensively studied to investigate the adsorption of ions at charged interfaces.[22, 53-57] The schematic representation of air/aqueous interface with DPTAP$^+$ monolayer, in the presence of SeCN$^-$ anions in the subphase, is shown in Figure 1. Tunable IR and fixed visible beams are overlapped spatially and temporally to generate VSFG signal from the interface. Because bulk molecules have an inversion symmetry, the VSFG signal originates purely from the interfacial region.[58] The incoming X-ray beam is used to generate XFNTR and XR signals from the interface.

XFNTR is used to quantify the amount of $SeCN^-$ anions adsorbed to a charged $DPTAP^+$ monolayer at air/aqueous interface. The incoming beam of X-rays does not penetrate into the bulk phase at small incidence angles due to total external reflection and only excites the interfacial ions.[4, 59, 60] This is a highly surface sensitive technique which can quantify the elemental composition at the interface depending on the element's X-ray absorption energy. In XFNTR, the incident beam is directed to the interface slightly below and above the critical angle and the collected fluorescence signal is plotted as a function of the incidence angle. Below the critical angle, only the interfacial ions contribute to the fluorescence signal.[61, 62] Above the critical angle, both interfacial and bulk ions contribute to the signal.

Here, we combine VSFG, XFNTR and XR measurements to investigate the $SeCN^-$ adsorption at $DPTAP^+$ monolayer at the air/water interface. $SeCN^-$ is used because Se K-edge (12.66 keV), is more convenient than S K-edge (2.47 keV) for the XFNTR experiments. A comparison of XFNTR data to the VSFG signal from the –CN stretch under the same conditions showed that the $SeCN^-$ ions reorganize at the interface even after their interfacial number density is saturated as a function of the bulk concentration. VSFG studies of the -OH stretch of the water molecules and XR experiments support this interpretation and further elucidates that the reorganization is mainly due to the increasing $SeCN^-$ population in Stern layer in the expense of their decreasing population in diffuse layer.

EXPERIMENTAL METHODS

2a. Sample Preparation. Chloride salt of DPTAP was purchased from Avanti Polar Lipids and stored at −20 °C. Potassium selenocyanate (KSeCN, ≥98%) and HPLC grade chloroform

($CHCl_3$, ≥99.9%) were purchased from Sigma Aldrich. All glassware and sample cell used for the experiment were cleaned by soaking in a solution of Nochromix (GODAX Laboratories, Inc.) in concentrated sulfuric acid bath for 24 hours and rinsed with ultrapure water (18.2 MΩ.cm).

For the preparation of Langmuir monolayer, 0.25 mM DPTAP solution was made in chloroform and stored at −20 °C temperature. A circular polytetrafluoroethylene (PTFE) dish with 6 cm diameter was used as a sample cell for VSFG experiment. 0.25 mM DPTAP solution was added dropwise using 1 µL syringe (Hamilton, USA) in a sample cell containing 25 mL of subphase solution. A NIMA pressure sensor, with a chromatography paper as a Wilhelmy plate, was used to measure the surface pressure. All experiments were performed at a surface pressure of 10 mN/m at room temperature.

2b. VSFG Experiment. The VSFG measurements are acquired using an EKSPLA system, which has been described previously.[9, 22, 63] Briefly, the setup consists of a picosecond laser system, a harmonic unit, an optical parametric generator with difference frequency generation, a spectrometer and a photomultiplier tube detector connected to a monochromator. An amplified Nd:YAG laser system produces 29 ps pulses having 28 mJ energy centered at 1064 nm with a repetition rate of 50 Hz. The harmonic unit splits the 1064 nm laser, and a portion is passed through a second harmonic crystal to generate two beams of 532 nm. One of the 532 nm beams and the 1064 nm beam are used to generate a narrowband IR pulse tunable from 1000-4000 cm^{-1} via optical parametric generator and difference frequency generation. Other 532 nm laser beam which passes through an adjustable delay stage is overlapped spatially and temporarily with the IR beam to generate the sum frequency (SF) signal. The polarization of 532 nm is adjusted with a λ/2 waveplate, and the IR polarization is adjusted by using computer-controlled motorized mirrors.

The SFG signal polarization is selected using a Glan polarizer. The SFG signal is then directed to a monochromator and collected with a photomultiplier tube.

The VSFG spectrometer employs reflection geometry where the incident angles of the visible and IR beams are 60° and 55°, respectively, to the surface normal. The visible light is attenuated to an average energy of 600 μJ and the IR energy is maintained at 100 μJ for all measurements. A motorized piezoelectric rotation stage is used to rotate the sample to avoid beam damage. Each spectrum is collected with a 4 cm^{-1} increment over the range of 2800-3800 cm^{-1} and averaged over 300 laser shots per point. The spectra are collected under various polarization combinations and are normalized against the SFG spectrum of a z-cut quartz.

Theory of VSFG Spectroscopy. Vibrational sum-frequency generation (VSFG) is a second order non-linear spectroscopic process which is widely used for the investigation of interfacial molecular structure and dynamics. In VSFG, two input visible and IR laser beams at frequencies ω_{vis} and ω_{IR} overlap spatially and temporally on a sample surface to generate a sum frequency ($\omega_{SF\,=} = \omega_{vis} + \omega_{IR}$) signal. Due to quantum mechanical selection rule of VSFG spectroscopy, the process is forbidden in the centrosymmetric media and thus eliminates the contributions from bulk phase.[51, 64, 65] The intensity of the VSFG signal (I_{SF}) is proportional to the product of the intensities of the incident beams and the square of the effective second order non-linear susceptibility ($\chi_{eff}^{(2)}$) of the material interface. This can be expressed as;[66-69]

$$I_{SF} = \frac{8\pi^3 \omega_{SF}^2 \sec^2\beta}{c^3 n_1(\omega_{SF}) n_1(\omega_{vis}) n_1(\omega_{IR})} \left|\chi_{eff}^{(2)}\right|^2 I(\omega_{vis})\, I(\omega_{IR}) \qquad (1)$$

where, β is the reflection angle of the sum frequency field and n_1 is the refractive index of corresponding medium. There are 27 components of $\chi^{(2)}$ but in the case of azimuthally isotropic interface, there are only four independent non-vanishing components; $\chi_{xxz} = \chi_{yyz}$; $\chi_{zxx} =$

χ_{zyy}; $\chi_{xzx} = \chi_{yzy}$; $and\ \chi_{zzz}$, where z is defined to be the direction normal to the surface. These four components can be deduced by measuring VSFG at different polarizations: SSP, SPS, PSS and PPP, (SF, visible, and IR fields, respectively). The $\chi_{eff}^{(2)}$ consists of non-resonant ($\chi_{NR}^{(2)}$) and resonant ($\chi_{R}^{(2)}$) terms. The VSFG intensity is enhanced when the frequency of incidence IR beam is on resonance with a vibrational mode of an interfacial molecule.

$$\left|\chi_{eff}^{(2)}\right|^2 \propto \left|\chi_{NR}^{(2)} + \sum_q \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q}\right|^2 \tag{2}$$

Where, A_q is resonance amplitude, ω_q is resonant frequency, and Γ_q is damping constant of qth vibrational mode which describes the linewidth of the transition. The $\chi_{eff}^{(2)}$ term can also be expressed in the following form.

$$\chi_{eff}^{(2)} = N_s d(\langle cos\theta\rangle - c\langle cos^3\theta\rangle) = N_s d r(\theta) \tag{3}$$

where, N_s is effective surface number density, $r(\theta)$ is orientational distribution, θ is the molecular orientation angle to the surface normal, d is the susceptibility strength factor proportional to the hyperpolarizability value, and c is called the general orientational parameter.

2c. Synchrotron X-ray Experiments. XFNTR and XR are used for the investigation of interfacial population and organization of ions at air/aqueous interface. XR and XFNTR measurements were carried out using a Langmuir trough integrated with a synchrotron X-ray beamline at sector 15-ID-C, NSF's ChemMatCARS of the Advanced Photon Source at Argonne National Laboratory. X-ray energy was 17.3 keV and all experiments were conducted at room temperature. The Langmuir trough was enclosed in a gas-tight chamber and was purged with helium to reduce the beam damage and the background scattering. XR signal was recorded by a Pilatus 100 K area detector and XNFTR signal was recorded by a Votex-60 EX multicathode energy dispersive X-ray detector placed 10 mm above from the sample surface.

The XR data were measured as a function of the wave vector transfer, $\overrightarrow{Q_z} = (4\pi/\lambda)sin\alpha$ by varying the incidence angle (α). For 17.3 keV energy, the wavelength (λ) of the X-ray beam is 0.72 Å. The DPTAP monolayer is modeled by two-slabs for 2.5 μM and 25 mM samples, with one slab corresponding to the hydrophobic tail group and other for the hydrophilic head group plus the adsorbed ions. The intermediate concentration, 2.5 mM, sample required a three-box model. The thickness, electron density, and the roughness of the layers are determined by fitting the experimental data using a Parratt algorithm.[59, 62, 70] The X-ray energy of 17.3 keV used for the XNFTR measurement was above the K absorption edge of Se (12.66 keV).

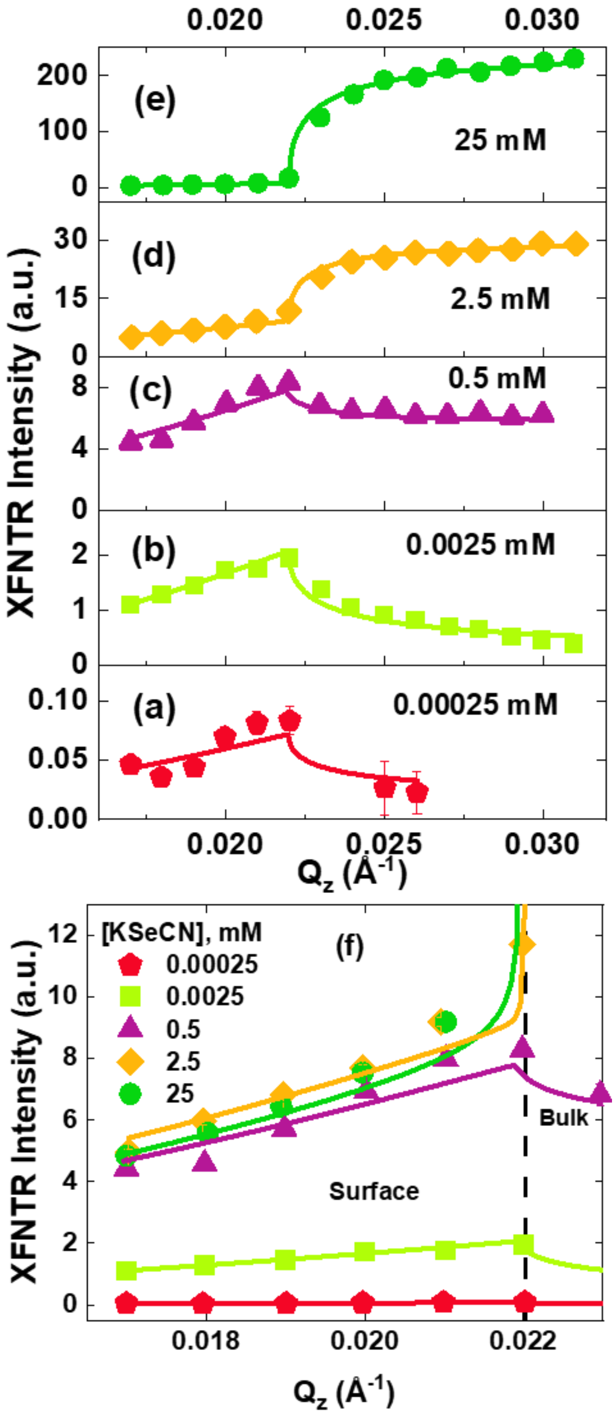


Figure 2. (a-e) XFNTR measurements at different SeCN$^-$ concentrations. The solid lines are the best fits to the experimental data. (f) Zoomed in version of the data and fit below the critical angle (Q_c ~ 0.022 Å^{-1}) for all data sets in a-e, displaying the change in XFNTR intensity due to SeCN$^-$ adsorption at the interfacial region.

RESULTS AND DISCUSSION

Figure 2 (a-e) show the variation of XFNTR intensity as a function of the vertical momentum transfer (Q_z) for $SeCN^-$ adsorption at DPTAP monolayer at various bulk KSeCN concentrations. A similar measurement from a 25 mM KSeCN solution without a monolayer was used for calibration (Figure S1). The solid lines are the best fits to the experimental data. The fits use a model that considers the geometry of the experimental setup, and the X-ray absorption and emission energies.[4, 71] In the presence of the monolayer, the intensity of XFNTR signal increases linearly with the increasing Q_z below the critical angle (Q_c = 0.022 $Å^{-1}$), indicating the anion adsorption at the interface. At low bulk concentrations, the signal intensity decreases above Q_c, due to the decreasing transmission and very small bulk concentration. Whereas, for higher bulk concentrations, the bulk signal dominates above Q_c. The data below the critical angle is shown in Figure 2(f) separately to better display the changes in fluorescence intensity caused by the interfacial ion adsorption. The total number of $SeCN^-$ anions adsorbed at the interface is saturated at 0.5 mM bulk concentration, which can be understood from the raw data without fitting (Figure 2f). The fit results show that the molecular area per $SeCN^-$ saturates at ~53 $Å^2$, which is slightly more than the area per $DPTAP^+$ molecule for high concentration samples (~43 $Å^2$, obtained from GID measurements, Figure S2),[22] suggesting that the charge neutrality is nearly satisfied between the positively charged headgroups and the adsorbed $SeCN^-$ ions. XFNTR does not distinguish between Stern and diffuse layers and provides the total number of interfacial $SeCN^-$ ions. Below, we discuss how the orientational ordering of $SeCN^-$ ions continues to change even after this overall saturation.

The vibrational signatures of CN stretch region (2000-2200 cm^{-1}) of $SeCN^-$ ions under PPP, SSP, and SPS polarization combinations are directly probed using VSFG spectroscopy. Figure 3 (a-c) shows the variation of VSFG intensity as a function of IR frequency at various KSeCN concentrations under different polarization combinations. A single-peak Lorentz function (equation 2) is used to fit the experimental data under PPP and SPS polarizations and the fit parameters are tabulated in Table S1. The signal intensity under PPP polarization is higher and monotonically increases with increasing KSeCN bulk concentration. On the other hand, VSFG signal under SSP and SPS polarizations are found to be less sensitive to the bulk concentration. Under SSP polarization, the VSFG intensity is almost indistinguishable from the background and does not increase with increasing concentration. The same measurement under SPS polarization results slightly higher intensity compared to SSP case and appears to increase slightly for the lowest three KSeCN concentrations before plateauing at around 0.025 mM.

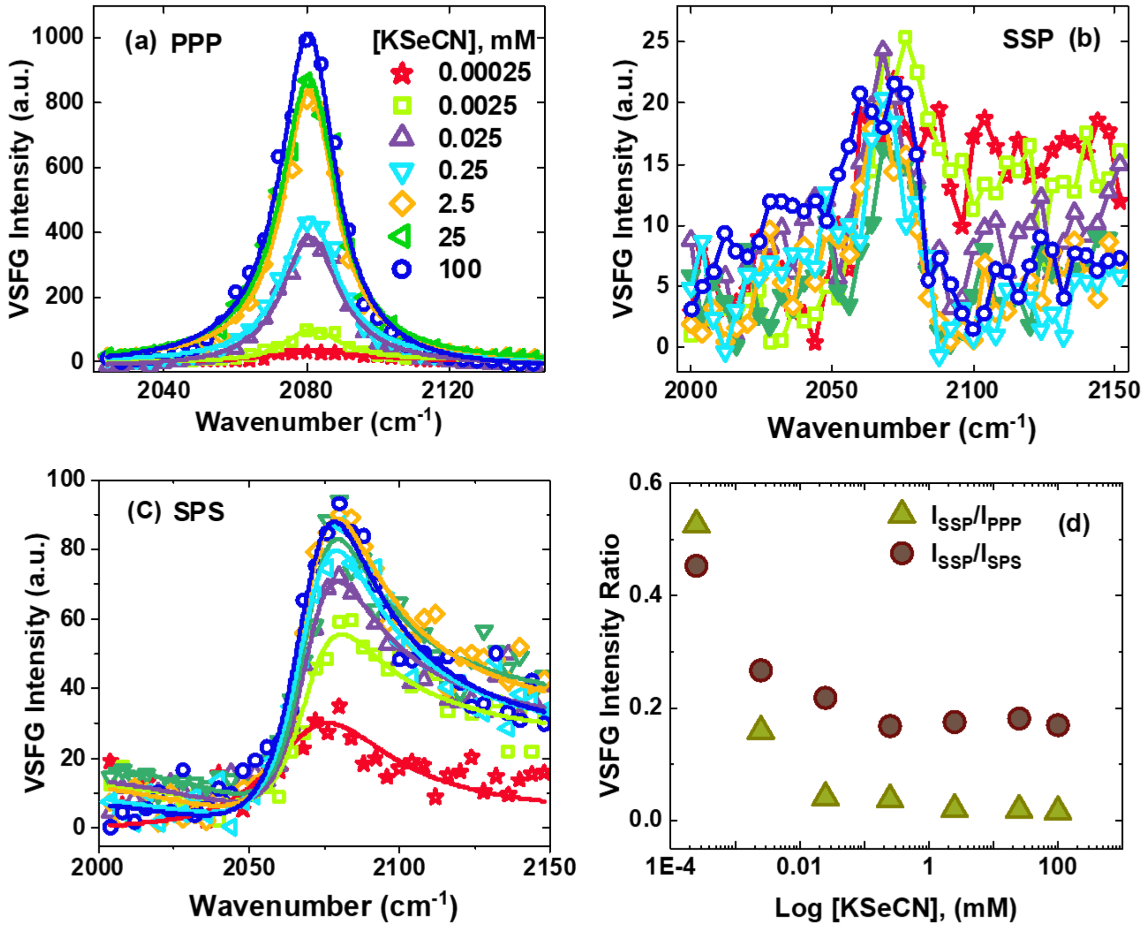


Figure 3. The variation of VSFG intensity for CN stretch region of $SeCN^-$ ions under (a) PPP, (b) SSP, and (c) SPS polarization combinations. The solid lines in (a) and (c) are the fits to the experimental data and in (b) are the lines following the data points as visual guides. Panel (d) is the variation of the ratio of the VSFG intensity obtained under different polarizations with KSeCN bulk concentration.

Relatively stronger VSFG signal under PPP polarization indicates a constructive interference between the $\chi^{(2)}$ components and $SeCN^-$ enrichment at the interface. The PPP polarization configuration probes the combination of zzz, xxz, zzx, and zxx components of $\chi^{(2)}$ while SSP and SPS selectively probes only xxz and xzx components, respectively. The intensity of VSFG signal is the product of effective number density (Ns) and the average orientation (r(θ)) of $SeCN^-$ anions at interface as given by equation 3. The SSP polarization probes the vibrational modes having a component of dipole moment perpendicular to the interface and the SPS detects those parallel to the interface.[72] The lower intensity obtained under SSP and SPS polarization suggests that the $SeCN^-$ anions have intermediate orientation. By taking the ratio of the SSP to PPP and SSP to SPS signal, it is possible to determine the actual orientation of $SeCN^-$ anions.[24, 66] The corresponding SSP to PPP signal ratio varies from 0.6 to 0.02, and the SSP to SPS signal ratio varies from 0.5 to 0.2 as the KSeCN concentration increases (Figure 3d). This suggests that the average orientation of anions with respect to surface normal ranges from 45° to 22° with the increasing KSeCN concentration.[24] At lower concentrations, anions are loosely packed and orient at greater angle with respect to surface normal but with the increasing concentration, they orient more parallel to the surface normal.

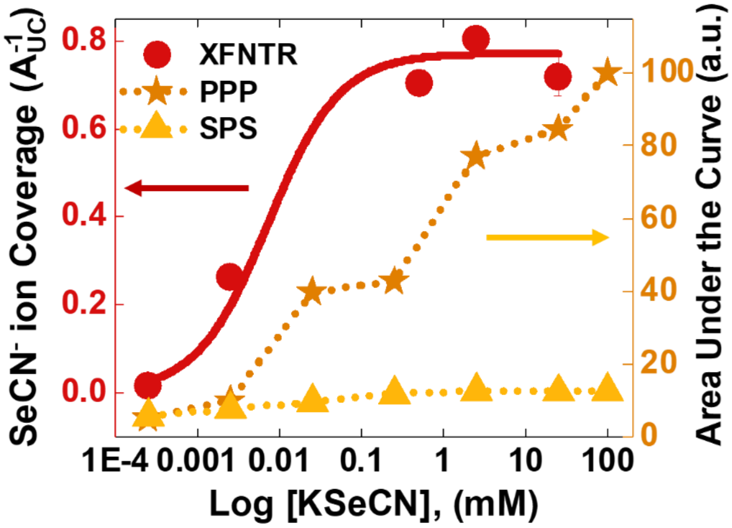


Figure 4. The variation of area under the CN stretch VSFG spectra (PPP and SPS polarizations) and the surface coverage of SeCN$^-$ ions as a function of KSeCN salt concentration obtained from XFNTR measurement. The red solid line in is the Langmuir fit to the corresponding XFNTR data set. The dotted lines are following the data points for clarity.

The results obtained from the analysis of XFNTR, and CN stretch of VSFG measurements are plotted together in Figure 4. Red circles are the average surface coverage of SeCN$^-$ anions obtained from XFNTR fit. Stars and triangles are the area under the curve of CN stretch region obtained from VSFG measurements under PPP and SPS polarizations, respectively, as a function of bulk KSeCN concentrations. The area under the curve is a function of the anion population and orientation (equation 3). A Langmuir adsorption isotherm is used to fit the SeCN$^-$ ion coverage obtained from XFNTR to display the variation. The full coverage (1 A_{UC}^{-1}, where A_{UC} is the unit cell area of a DPTAP molecule) is defined as the coverage when there is one SeCN$^-$ anion per DPTAP molecule at the interface. The surface coverage plot shows that the adsorption of SeCN$^-$ ions increases with increasing bulk concentration and appears to saturate at 0.5 mM. Conversely, the area under the curve of CN stretch region under PPP polarization does not appear to saturate. These two results together suggest that the orientational re-organization of $SeCN^-$ ions continue after their total number in Stern and diffuse layers saturate. The increase in the VSFG signal under PPP combination is not exactly monotonic but appears to have some steps, i.e. the intensity stays almost constant within certain bulk concentration ranges before jumping to a higher value. A similar behavior was observed with SCN^- in our previous studies.[22]

We used XR to investigate the details of the interfacial re-organization after apparent saturation of the $SeCN^-$ coverage (Figure 5). XR is sensitive to the electron density gradient at the interface.[4] Therefore, $SeCN^-$ ions adsorbing in Stern layer can be detected from their effects on the total electron density around the head group region of the DPTAP. However, $SeCN^-$ ions in diffuse layer that do not form a well-defined layer have much smaller effect on XR.[59] Since XFNTR is sensitive to all $SeCN^-$ ions in both Stern and diffuse layers, and XR is mostly sensitive to the $SeCN^-$ ions in Stern layer; their comparison will elucidate the relative distribution of $SeCN^-$ ions between these layers.

Figure 5a shows the X-ray reflectivity intensity (R) from DPTAP monolayer on 2.5 μM, 2.5 mM, and 25 mM KSeCN concentrations normalized to the Fresnel reflectivity (R_F) from an ideally flat interface. The solid lines are the best fits to the experimental data, using a box model. This model represents the interface as uniform electron density layers with error function interfaces (to account for the roughness) between them. Then, the calculated reflectivity is compared to the data and the fit parameters, including the length, electron density, and roughness are optimized using a least-squares fitting method (Table S2).[73] Electron density profiles (EDPs) are plotted by using these fit parameters (Figure 5b).

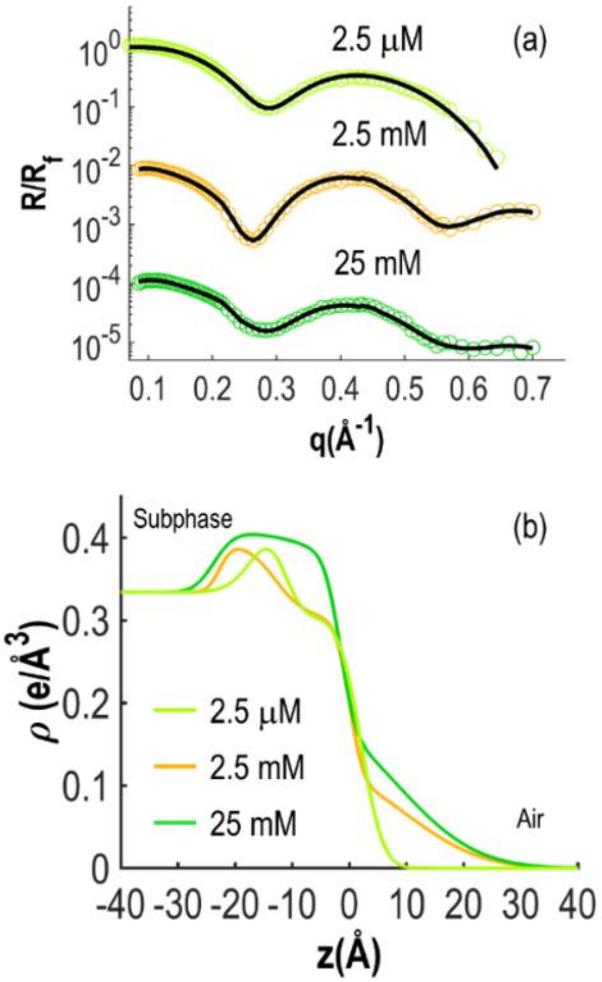


Figure 5. (a) XR data (symbols) and fit (lines) at three different bulk KSeCN concentrations. (b) EDPs derived from the fits to the XR data in (a).

The EDP of DPTAP on 2.5 μM KSeCN solution (Figure 5b) is very similar to that of on pure water which indicates negligible SeCN$^-$ adsorption in Stern layer. However, XFNTR shows 0.02 A_{UC}^{-1} coverage for SeCN$^-$, which corresponds to 1 SeCN$^-$ per 50 DPTAP$^+$. Similarly, VSFG shows small but detectable signal from SeCN$^-$ at all polarization combinations. As discussed above, the SSP/PPP and SPS/PPP intensity ratios suggest that the average angle from the surface normal is around 45° at this concentration (Figure 3d), which is very similar to the orientation observed with SCN$^-$ at the free air/water interface.[24] Therefore, it is reasonable to say that at 2.5

μM bulk concentration, all the $SeCN^-$ ions adsorb in diffuse layer and they do not directly interact with the DPTAP monolayer.

At 2.5 mM bulk concentration, the electron density at the headgroup region increases, suggesting some $SeCN^-$ adsorption in Stern layer. Also, the overall roughness of the interface increases. The increase in roughness is not specific to $SeCN^-$. A similar trend was observed even with simpler anions, such as Cl^-, Br^-, and I^-.[53] According to the XFTNR, the total coverage of $SeCN^-$ is saturated at this concentration (Figure 2 and 4).

At 25mM bulk concentration, the electron density of the headgroup region significantly increases. Considering that the total $SeCN^-$ coverage determined by XFNTR has already saturated, it is reasonable to suggest that at this concentration, the ions that were already adsorbed in diffuse layer move to Stern layer, but the total coverage does not change. This behavior is very similar to the two-step adsorption observed with $PtCl_6^{2-}$ anions in previous studies.[59, 74]

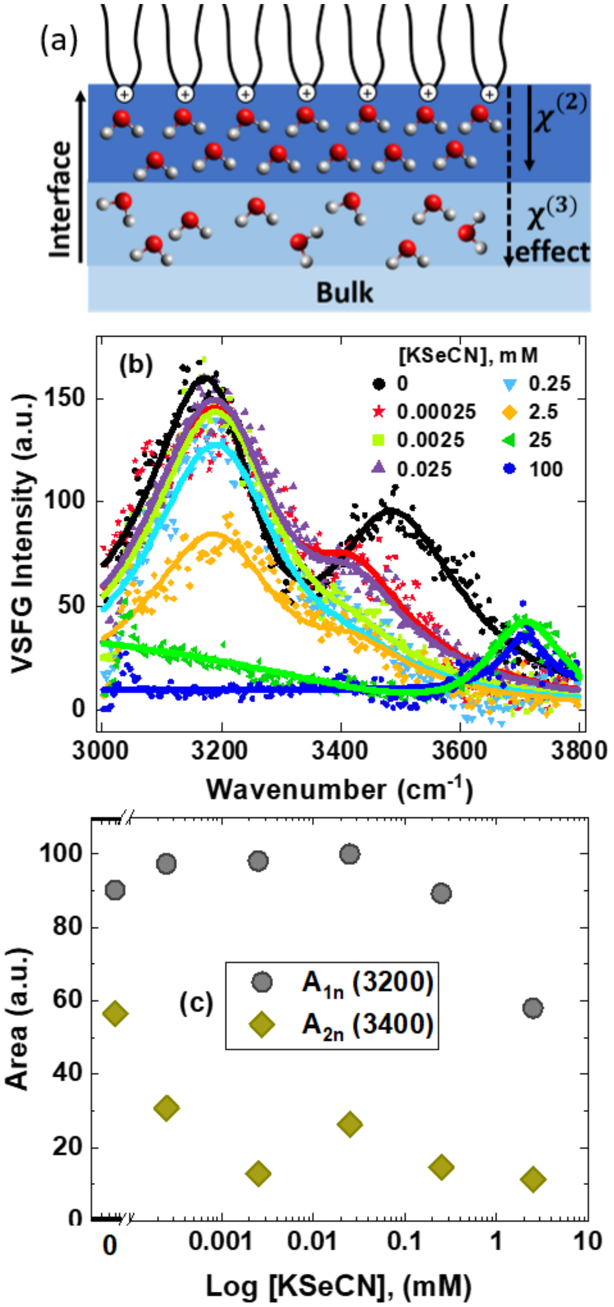


Figure 6. (a) Positively charged DPTAP$^+$ interface in absence of salt. (b) VSFG signal from the OH-stretching region of water at various KSeCN concentrations under the DPTAP monolayer. The solid lines are the fit to the experimental data using two Lorentzian peaks (centered at ~3180 cm^{-1} and ~3440 cm^{-1}) as described in the text. (c) The variation of the area under each Lorentzian peak as a function of the bulk KSeCN concentration.

The anion adsorption and its interfacial organization is further investigated by probing the OH stretch region of water under SSP polarization (Figure 6). The two peaks near 3200 cm^{-1} and 3400 cm^{-1} are characteristics of hydrogen bonded water molecules near the interface. Though the origins of these bands are still under debate, the bands at lower and higher wavenumber are assumed to originate from high degree and low degree of hydrogen bond ordering of the water molecules, respectively.[75, 76] The OH stretch region is fitted globally with two-peak Lorentz function using equation 2. The peak positions and widths were forced to be same for all concentrations, varying only the amplitude of the resonances. The fit parameters obtained are tabulated in Table S3. The area under the curve for each Lorentz peak is calculated and plotted as a function of KSeCN concentration (Figure 6c). The area under A_{1n} (3200 cm^{-1}) band, which originates due to the high degree of H-bonding, remains mostly unchanged until the bulk KSeCN concentration reaches to 0.025 mM and then drops at higher concentration. The band completely disappears for 25 mM and 100 mM salt concentrations. Conversely, the area under A_{2n} (3400 cm^{-1}) band which originates due to low degree of H-bonding sharply drops even for the lowest KSeCN concentration. With the increasing concentration, the 3400 cm^{-1} band either disappears or has very low intensity and only 3200^{-1} cm^{-1} band is visible. A qualitatively similar behavior was observed with SCN^{-} ions in our previous studies.[22] However, in that case, the 3400 cm^{-1} band disappeared at 0.025 mM bulk concentration, while it is still visible at 2.5 mM bulk concentration in this case. The overall line shape of 3200 cm^{-1} peak was also different with SCN^{-}.

The charged interface induces strong H-bonding networks in water molecules which relax away in a few nanometers (~2 nm), depending on the solution conditions,.[77] It is well known that the charged interface has second-order $\chi^{(2)}$ and third-order $\chi^{(3)}$ contribution to the VSFG signal.[78] The $\chi^{(2)}$ contribution is from the interfacial molecules (primarily from Stern layer) which are asymmetrically oriented and hence induce an electric dipole allowed VSFG signal. The static electric field of the charged interface also aligns the bulk water molecules (in diffuse layer), which is called $\chi^{(3)}$ effect, where $\chi^{(3)}$ is the third order nonlinear susceptibility of water. So, the $\chi_{eff}^{(2)}$ has contributions from $\chi^{(2)}$and $\chi^{(3)}$ effect which can be expressed as, $\chi_{eff}^{(2)} = \chi^{(2)} + \chi^{(3)} \phi (0)$, where, ϕ (0) is the surface potential which decays as a function of distance from the interface.[77, 79-83] In the absence of salt (0 mM KSeCN), the VSFG intensity of OH stretch region of water from the air/aqueous interface is strongly enhanced due to both $\chi^{(2)}$ and $\chi^{(3)}$ effects. This is schematically represented in Figure 6a. Addition of the salt decreases $\chi^{(2)}$ by breaking the interfacial H-bonding networks and eventually displacing water from the interface at higher salt concentrations. $\chi^{(3)}$effect decreases after the addition of salt due to screening of static electric field of the charged interface.

At lower KSeCN concentration, $\chi^{(2)}$ remains unaffected, but the $\chi^{(3)}$ effect decreases due to screening of the static electric field of the charged interface experienced by the water molecules in diffuse layer. As a result, the weakly H-bonded water networks in diffused layer starts to break and the intensity of the 3400 cm^{-1} band decreases. [84] This band is also shifted towards lower wavenumber region (red shift) which is the indication of increased interaction of water molecules with the surrounding ions, here SeCN^{-}.[85] The 3200 cm^{-1} band remains almost unchanged until the KSeCN bulk concentration is 0.25 mM, suggesting that the interfacial H-bonding network (or $\chi^{(2)}$) is barely affected up to this concentration. The negligible Stern layer adsorption determined by XR at lower KSeCN concentration supports this interpretation (Figure 5b). We hypothesize that weakly hydrogen bonded water molecules are affected from the presence of small number of SeCN^{-} ions but the strongly hydrogen bonded water molecules are not. Similar behavior was observed by Jena and Hore et al. at a charged silica interface under varying salt concentrations.[79,

[86] It is known that simple anions, such as Cl^-,[53] or the anions that do not disturb the weak H-bonding network significantly, such as NO_3^-,[22] lead to a more uniform decrease in VSFG signal mostly through the $\chi^{(3)}$ effect, without affecting the overall bimodal shape of the signal.

The 3200 cm^{-1} band decreases significantly (Figure 6c) as the concentration is increased from 0.25 mM to 2.5 mM KSeCN, which suggests that the ions start to move from diffuse to Stern layer. Consequently, the $\chi^{(2)}$ decreases due to breaking down of the strongly ordered interfacial H-bonding networks of water. The results obtained from the VSFG measurements of CN stretch region under PPP polarization also show a significant increase of its intensity (Figure 3a and 4) at this concentration window, referring to the possible transfer of ions and their reorganization. On the other hand, the slightly higher electron density profile at 2.5 mM KSeCN concentration compared to its value at lowest concentration (Figure 5b) suggests that the most of the $SeCN^-$ ions are still in diffuse layer.

At higher salt concentrations (≥25 mM), the H-bonding environment of water near the interface is heavily affected by the adsorption of $SeCN^-$ anions and the OH stretch bands at 3200 cm^{-1} and 3400 cm^{-1} disappear. At this concentration, both $\chi^{(2)}$ and $\chi^{(3)}$ effects are significantly decreased due to the displacement of ordered interfacial water network by the $SeCN^-$ anions. This agrees with the XR data which shows that the electron density of the headgroup region significantly increases at 25 mM bulk concentration, indicating enhanced Stern layer adsorption. Also, a new band around 3700 cm^{-1} appears. This band is commonly observed in the case of neat air/water interface and corresponds to the non-hydrogen bonded free OH that points towards the air. At air/water interface, more than 20% of water molecules have free non-hydrogen bonded OH which collectively give a sharp peak at 3700 cm^{-1}. This peak is expected to disappear in the presence of DPTAP monolayer, as observed at lower salt concentrations (≤2.5 mM).

Reappearance of 3700 cm^{-1} peak at higher concentrations can be due to a few reasons. One possibility is that the monolayer structure is disturbed, and some parts of the surface is open, allowing free OH bonds to stick out of the surface. However, this possibility is ruled out by investigating the CH stretch region (Figure S3). The absence of any significant gauche defect from CH_2 groups (2855 cm^{-1} band) for all concentrations indicates that the monolayer is well-packed and stable even at higher salt concentrations. Similarly, GID results show no difference between 2.5 mM and 25 mM samples (Figure S2). This is also supported by the monotonically increasing CN stretch intensity under PPP polarization (Figure 3a and 4), which could have decreased if the monolayer was largely disturbed and the overall surface charge density of DPTAP molecules decreased. There is slight decrease in CH peak intensity (CH_3 stretching at 2875 cm^{-1} and its Fermi resonance peak at 2937 cm^{-1}) at higher concentration which is the evidence of subtle disorder in the monolayer packing, but this is unlikely to be enough to cause any open regions in the monolayer. In the presence of a stable and well-packed monolayer, it is unlikely that the re-appearing 3700 cm^{-1} peak is solely a result of dangling OH.

A second possibility is that the 3700 cm^{-1} is originating from the water molecules coordinating to $SeCN^-$ ions. It is found that the shape and phase of dangling OH and the OH mode of water complexed with anions are similar.[84] This suggests that the origin of 3700 cm^{-1} peak at higher concentration could be the result of $SeCN^-$:H_2O complexation at Stern layer. Because, both XR (Figure 5b) and VSFG (Figure S3) do not show a significant difference in the tail region between 2.5 mM and 25 mM samples. The broadening of this peak compared to pure air/water interface indicates the presence of asymmetric bonding environments. Further investigations with molecular dynamics simulations can elucidate the origins of this peak as it was done in the case of 3600 cm^{-1} peak appearing in the presence of $PtCl_6^{2-}$ and $PdCl_4^{2-}$ anions.[9, 63] Nevertheless, VSFG studies of the OH stretch clearly show that the interfacial water reorganization continues above 0.1 mM bulk concentration.

Figure 7 summarizes the interpretation obtained by comparing all experimental data presented above. The change in interfacial water structure due to the adsorption of $SeCN^-$ ions as a function of KSeCN bulk concentration is demonstrated schematically by considering the three concentrations where the notable changes are observed. At very low concentration, 0.00025 mM, $SeCN^-$ ions are present only in diffuse layer without affecting Stern layer water structure. The total coverage is saturated around 0.5 mM bulk concentration according to XFNTR result, and at 2.5 mM, $SeCN^-$ ions start to move to Stern layer. At 25 mM, ions are significantly adsorbed at Stern layer which continue to reorganize until 100 mM bulk concentration. These results highlight the importance of investigating the anion adsorption and the corresponding interfacial water structure for the better understanding of chemical, physical, and biological processes.

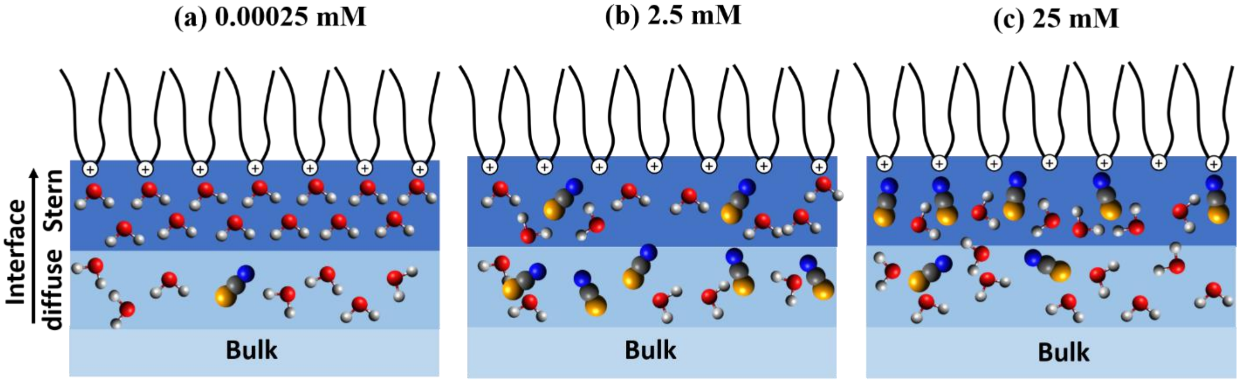


Figure 5. Schematic summarizing the results obtained from XFNTR, VSFG, and XR studies regarding the interfacial $SeCN^-$ and water organization as a function of bulk KSeCN concentration. (a) 0.00025 mM, ions are only in diffuse layer, (b) 2.5 mM, ions start to move to Stern layer but still majority of the ions are in diffuse layer, and (c) 25 mM KSeCN, ions are now mostly in Stern layer.

CONCLUSIONS

Complex anions, such as SCN^- and NO_3^-, play important roles in chemical separations and other environmental and industrial processes, yet very little is known about their interfacial effects. We have studied $SeCN^-$ adsorption at a positively charged DPTAP monolayer with multiple surface sensitive probes and identified important differences in the way they adsorb, compared to the simple anions, such as Cl^- or Br^-. At very low bulk concentrations (< 2.5 μM), $SeCN^-$ anions adsorb in diffuse layer only, without a direct interaction with the DPTAP. This is in contrast with the typical picture of ion adsorption at a charged interface, where the ions adsorb in Stern layer first. At intermediate bulk concentrations (~2.5 mM), $SeCN^-$ anion surface coverage reaches a maximum and the anions adsorb in both diffuse and Stern layers. They mostly disturb the weakly-hydrogen-bonded water molecules (3400 cm^{-1} region) but do not affect strongly-hydrogen-bonded water molecules (3200 cm^{-1} region). At the higher bulk concentrations (>25 mM), the total $SeCN^-$ surface coverage does not increase, but the majority of the anions move to Stern layer, their orientation become more parallel to the surface normal, typical water peaks (3200 and 3400 cm^{-1}) disappear, and a new water population appears creating a VSFG signal at 3700 cm^{-1}. These detailed observations were possible thanks to the complementary use of XFNTR, XR, and VSFG techniques which provided a unique sensitivity to the ions in diffuse and Stern layers as well as their orientational ordering. It is usually difficult to disentangle the effects of the number density and the orientational ordering on the VSFG signal intensity. Obtaining number density from XFNTR independently allowed a better interpretation of -CN stretch results. Utilizing XR to determine the ion adsorption in Stern layer helped in interpretation of the concentration dependent changes in CN and OH region VSFG experiments. These results clearly show that a simple quantitative list of strongly or weakly adsorbing ions (usually considered in the context of

Hofmeister series) is not enough to describe the ion-specific effects of complex anions. Their interfacial adsorption behavior and effects on the hydrogen bonding network change significantly as a function of the surface coverage, which in turn, expected to affect the resulting interfacial processes in the presence of these complex anions.

ASSOCIATED CONTENT

Supporting Information. Fit parameters of CN and OH stretch region of VSFG spectra, and XR measurements; XFNTR plot at 25 mM KSeCN bulk concentration in absence of DPTAP monolayer; GID results, and CH stretch region of DPTAP monolayer under SSP polarization in presence of different KSeCN concentration. (PDF)

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