Thiocyanate Ions Form Antiparallel Populations at the Concentrated Electrolyte / Charged Surfactant Interface

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ABSTRACT

Anions, such as nitrate and thiocyanate, play significant roles in the separation of lanthanides and actinides. The molecular-scale details of how these anions behave at aqueous interfaces are not well understood. This is especially true at high ionic strengths, where classical mean field theories fail. Since most separation processes are conducted at high ionic strength conditions, a thorough experimental and theoretical understanding of these systems are necessary. Here, we describe the interfacial structure of thiocyanate anions at a soft charged interface up to 5 M bulk concentration with combined phase-sensitive vibrational sum frequency generation (PS-VSFG) spectroscopy and molecular dynamics (MD) simulations. At low concentrations thiocyanate ions are mostly oriented with their sulfur end pointing towards the charged surfactants. At high concentrations a new thiocyanate population emerges with their sulfur end pointing towards the bulk liquid. The emergence of the new population happens after an apparent saturation of the interface and a plateau in concentration dependent VSFG signal. The -CN stretch frequency is different for up and down oriented SCN\(^-\) ions, which indicates that they are in, on average, different coordination environments. MD simulations confirm the emergence of oppositely oriented SCN\(^-\) ions. Together, these results demonstrate the formation of a completely new interfacial SCN\(^-\) profile with significantly different orientational ordering above 1 M bulk concentration, providing the key molecular-level insights for the interfacial behavior of complex anions in highly concentrated solutions.
The organization of anions at charged aqueous interfaces has been a topic of long-standing interest due to its impacts on various industrial and environmental processes, such as chemical separations, ice nucleation, ion transport, and drug delivery.1-5 These processes are strongly affected by the intrinsic properties of the interface where the molecular structure and ion speciation may significantly differ from those in the bulk.1, 2, 6-8 As interface sensitive probes became more available, our understanding of these interfaces has developed remarkably in the last two decades.1, 6, 7 However, interfaces of concentrated electrolytes are still relatively understudied and poorly understood. For instance, it is typically accepted that the Debye length becomes very small (<1 nm), at high salt concentrations. Recent studies showed that this is only correct below ~1 M ionic strength, after which the Debye length increases anomalously with ionic strength. Since its first observation in ionic liquids,9 the effect has been observed in aqueous solutions10 and proven to be important at flat interfaces and in colloidal systems alike.11 The implications of this phenomenon for complex anion organization at aqueous interfaces are still unknown. Here, we demonstrate that thiocyanate, a complex anion with a permanent dipole moment, adopts a non-classical interfacial structure at high ionic strengths, which cannot be readily explained by established mean field theories.

The interfacial behavior of anions is very important in chemical separations of multivalent heavy ions. For instance, in liquid-liquid extraction (LLE), metal ions are transferred from an aqueous phase into an organic phase with the help of the amphiphilic extractant molecules.12 In many cases extractants are neutral or positively charged, requiring the transfer of anions with the target metal ions in order to form neutral or anionic complexes in the organic phase.13-15 Interestingly, in most cases these metal-anion complexes are not stable in the aqueous phase, raising the question where and how these complexes form.13, 16 This question becomes more
important when the character of the anion dramatically affects extraction trends.\textsuperscript{13, 14} For instance, quaternary amine extractants extract heavy lanthanides better in the presence of thiocyanate but prefer light lanthanides in the presence of nitrate.\textsuperscript{13, 14, 17} We have recently demonstrated that the significant differences between the interfacial behavior of nitrate and thiocyanate can explain the different extraction mechanisms observed with lanthanides.\textsuperscript{14} However, earlier studies were limited to ion concentrations less than 500 mM.

There are studies of the air/aqueous interface of high concentration thiocyanate solutions in the absence of any surfactants.\textsuperscript{18-20} These classical vibrational sum frequency generation (VSFG) studies, measuring the CN stretch mode at $\sim$2075 cm$^{-1}$, show that the average orientation of SCN$^-$ anions are 45° with respect to the surface normal.\textsuperscript{18, 20} Concentration dependent VSFG and molecular dynamics (MD) simulations suggested that SCN$^-$ anions may cluster.\textsuperscript{19, 20}

In this Letter, we combine classical VSFG and phase sensitive VSFG (PS-VSFG) experiments with MD simulations to investigate the interfacial interaction of thiocyanate anions with positively charged DPTAP (1,2-dipalmitoyl-3-trimethylammonium-propane chloride) monolayers (Figure 1) at the air/aqueous interface, up to 5 M bulk thiocyanate concentrations. We chose DPTAP to model the commonly used industrial extractant quaternary ammonium TOMA$^+$, because it forms a stable monolayer due to its long hydrophobic chain and has been commonly used to study the adsorption of anions.\textsuperscript{21, 22} The experiments are performed at a surface pressure of 20 ± 2 mN/m, where the molecular area is 43 Å$^2$. The VSFG signal, as a function of the bulk concentration, increases with [SCN$^-$] before it plateaus at around 100 mM, but then start changing significantly above 1 M. PS-VSFG experiments and MD simulations show that the changes are due to the emergence of a new thiocyanate population with antiparallel orientation and overall broadening of the orientational ordering of the thiocyanate anions.
The schematic representation of PS-VSFG setup and its description are given in Figure S1. The theoretical details of classical and phase-sensitive VSFG have been provided elsewhere.\textsuperscript{23-27} The classical VSFG measures the square of the second order non-linear susceptibility, $|\chi^{(2)}|^2$, given in equation 1. Where $\chi^{(2)}_{NR}$ is the non-resonant component, $A_\nu$ is the resonance amplitude, $\omega_\nu$ is the resonant frequency, and $\Gamma_\nu$ is the damping constant of $\nu^{th}$ vibrational mode which describes the linewidth of the transition. Thus, the real (Re $\chi^{(2)}$) and imaginary (Im $\chi^{(2)}$) components that characterize the dispersive and absorptive band shape of the spectrum cannot be resolved directly. This limitation is overcome by the use of PS-VSFG measurements where the interference between the signal from the sample and the local oscillator (LO) provides the phase of $\chi^{(2)}$, and thus the Im $\chi^{(2)}$ can be obtained.\textsuperscript{28} Hence, the vibrational resonances of the interfacial molecules free from the non-resonant background and the molecular level information of the interfacial ions, including their absolute “up” and “down” orientations are obtained.\textsuperscript{29,30}

\begin{equation}
I \propto |\chi^{(2)}|^2 \propto |\chi^{(2)}_{NR} + \sum_\nu \frac{A_\nu}{\omega_{IR} - \omega_\nu + i\Gamma_\nu}|^2 \tag{1}
\end{equation}

\begin{equation}
\text{Im} \chi^{(2)} = \sum_\nu \frac{A_\nu \Gamma_\nu}{(\omega_{IR} - \omega_\nu)^2 + \Gamma_\nu^2} \tag{2}
\end{equation}

\begin{equation}
\text{Re} \chi^{(2)} = \chi^{(2)}_{NR} + \sum_\nu \frac{A_\nu (\omega_{IR} - \omega_\nu)}{(\omega_{IR} - \omega_\nu)^2 + \Gamma_\nu^2} \tag{3}
\end{equation}

GROMACS\textsuperscript{31} software package was used to simulate DPTAP/aqueous interface at five different NaSCN concentrations (Figure 1b). The CHARMM force field\textsuperscript{31,32} was used for all atoms except for water molecules where SPC/E model was used.\textsuperscript{33} Additional simulation details are provided in the SI.
Figure 1. (a) Schematic representation of the positively charged air/aqueous interface with DPTAP monolayer. Visible 532 nm beam and tunable IR overlap at sample interface to generate VSFG signal. The delayed LO generated from the y-cut quartz travel collinearly with the VSFG signal to generate an interference pattern. (b) Snapshot of a simulation of interfacial region with SCN⁻ anions and DPTAP monolayer.

VSFG spectra of -CN stretch region collected from air/aqueous interface under PPP and SPS polarizations at a wide range of NaSCN concentrations, spanning from 0.1 μM to 5 M, are shown in Figure 2 (each letter in PPP and SPS correspond to the polarization of SFG, Visible, and IR beams respectively). The signal intensity under PPP polarization is higher and monotonically increases with increasing NaSCN concentration until 100 mM, but, interestingly, it decreases with increasing concentration above 1 M. The VSFG signal under SPS polarization is relatively small and saturates at lower concentrations (~ 1 mM). The saturation of the interface at very low bulk concentrations is not surprising, considering the strong surface affinity of SCN⁻ ions, such that
they can even interact with negatively charged surfaces.\textsuperscript{34, 35} As NaSCN concentration increases above 1 M, the SPS signal start increasing again until 2 M and stays constant up to 5 M. Under SSP polarization (Figure S6), the VSFG intensity is smaller than the signals under SPS and PPP polarizations and does not change with increasing concentration.

![Figure 2](image)

Figure 2. (a and c) The variation of CN-stretch VSFG intensity with NaSCN concentration under PPP and SPS polarizations respectively. The solid lines are the best fits to the experimental data using equation 1. (b and d) The variation of fit amplitudes as a function of NaSCN concentration.
The VSFG intensity is a function of the number density of the SCN\(^-\) ions and their orientational ordering.\(^{36}\) Therefore, it is not a direct measure of the ion adsorption. In a similar system with SeCN\(^-\) anions, we used X-ray fluorescence near total reflection (XFNTR) together with VSFG to overcome this ambiguity.\(^{37}\) XFNTR provided the total number density of interfacial ions directly, exploiting the element specific X-ray fluorescence from Se. We demonstrated that the interfacial number density of SeCN\(^-\) ions saturate at much lower bulk concentrations (~1 mM), but the PPP signal continues to increase as a result of reorganization of anions between Stern and diffuse layers. Interestingly, SPS signal saturated approximately at the same bulk concentration with the XFNTR signal, suggesting that it might be a better representative of the interfacial anion concentration. The PPP signal was more sensitive to up-down oriented SeCN\(^-\) ions and, therefore, as they become more parallel to the surface normal, the PPP intensity increases, although the total number density does not change.

The results presented in Figure 2 with SCN\(^-\) follow a similar trend with the earlier SeCN\(^-\) study.\(^{37}\) SPS signal saturates around 1 mM, while PPP signal continues to increase until 100 mM. Then, both signals do not change significantly until 1 M bulk concentration. Earlier studies were limited to this range. Here, we show that both SPS and PPP signals start to change above 1 M but in opposite trends. We hypothesize that the total number of ions starts to increase, leading to an increase in the SPS signal. However, the new ions adsorbing at the interface have, on average, an antiparallel orientation, leading to a decrease in the PPP signal. Next, we test this hypothesis with PS-VSFG experiments.

Figure 3a shows the total \(|\chi^{(2)}|^2\), Re \(\chi^{(2)}\), and Im \(\chi^{(2)}\) spectra of DPTAP/aqueous interface of 1.5 M NaSCN solution. Re \(\chi^{(2)}\) and Im \(\chi^{(2)}\) spectra exhibit dispersive and absorptive band shapes, respectively.\(^{25}\) We focus on the Im \(\chi^{(2)}\) spectra (Figure 3b) obtained for 0.5 to 2 M of
NaSCN to investigate the interfacial orientation of anions. A single positive band centered at 2074 cm\(^{-1}\) is observed for 0.1 and 0.5 M NaSCN concentration. At 1 M, a small negative band at 2063 cm\(^{-1}\) appears. The intensity of the negative band increases with concentration and appears to saturate at 2 M bulk NaSCN concentration. The Im \(\chi^{(2)}\) spectra at 0.1 M and 4 M NaSCN are given in Figure S7. The solid lines in Figure 3b are the fits to the experimental data using equation 2. The linewidth of the spectrum at \(\leq 0.5\) M is smaller compared to the linewidth at \(\geq 1\) M, indicating broader absorption at higher concentrations when both up and down orientations are present.

The single positive band at \(\leq 0.5\) M is due to sulfur-up orientation of SCN\(^{-}\) anions at the positively charged DPTAP interface. At higher concentrations, the appearance of the negative band indicates that a new population of SCN\(^{-}\) emerges with sulfur-down orientation. The positive and negative bands are separated by 11 cm\(^{-1}\) suggesting different -CN coordination environments.

Figure 3. (a) \(|\chi^{(2)}|^2\), Re \(\chi^{(2)}\), and Im \(\chi^{(2)}\) spectra of DPTAP/aqueous interface measured by PS-VSFG in presence of 1.5 M NaSCN. (b) Im \(\chi^{(2)}\) spectra for different NaSCN concentrations measured under PPP polarization with PS-VSFG. The solid lines are the best fit to the experimental data using equation 2.
MD simulations support these interpretations and provide additional information on the orientational organization of the thiocyanate anions. The angular distribution of SCN\(^-\) anions at the interfacial region under the DPTAP monolayer is shown in Figure S4. At lower SCN\(^-\) concentrations, the angular distributions show a preferential orientation of \(~20-40^\circ\) with respect to the surface normal. However, at higher concentrations, this skewed distribution becomes broader, showing significant quantities of thiocyanate molecules having orientations that are greater than 90\(^\circ\). The broadening of the orientational distribution agrees with the result obtained from the PS-VSFG measurements where the negative band in the Im \(\chi^{(2)}\) spectra grow beyond 1 M concentration.

Figure 4. Plot of the density weighted N-C unit vector from the surface normal at the interface as a function of bulk SCN\(^-\) concentration from the simulations. The surface normal is defined as the unit z vector pointing from the bulk towards the charged interface, such that positive values of
cos(θ) correspond to the sulfur atoms pointing up (towards the interface). Positive values in the distance from the GDS corresponds to positions on the vapor phase side of the GDS.

Figure 4 shows the time averaged density of SCN⁻ ions in the z-direction binned according to the position of the z coordinate of C atom, ⟨ρ(z)⟩, multiplied with the averaged cosine angle, ⟨cos(θ)⟩, between the N-C unit vector and the surface normal. The z-position is defined relative to the Gibbs dividing surface (GDS), where the SCN⁻ density is half its bulk value. This product has been utilized as an estimate of the experimental VSFG signal. With increasing concentration up to 4.90 M, the positive peak (sulfur-up, θ < 90°) grows, mainly driven by the increasing SCN⁻ concentration at the interface (Figure S2). However, at 5.71 M, ⟨ρ(z)⟩(cos(θ)) decreases significantly as the orientational ordering of SCN⁻ ions broadens (Figure S3). Further, at 4.90 M and 5.71 M concentrations, a negative peak (sulfur-down, θ > 90°) appears around 0.8 nm from the Gibbs dividing surface (GDS).

At the two highest concentrations in Figure 4, the thickness of the region where ⟨cos(θ)⟩ is nonzero increases with mostly sulfur-down ions closer to the bulk region. We suggest that these changes correspond to the ones we observe around 1.5 – 2 M bulk concentration in VSFG and PS-VSFG experiments. The bulk concentrations in simulations do not correspond to the experimental values directly because of the limited size of the simulation box. However, the trends can be followed more clearly. PS-VSFG detects two populations, with positive and negative bands, at two different wavenumbers, probably a result of the different solvation environments of the up- and down-oriented ions. The red shifted CN- vibration can be assigned to the ions observed near the bulk. Since those ions will have a near complete solvation with comparatively stronger coordination to the water molecules in the vicinity, they will show a decreased vibrational frequency. We have previously demonstrated that a sub-ensemble analysis of MD simulations can
identify the populations leading to a certain VSFG signal in experiments.\textsuperscript{12, 22} However, a similar analysis is beyond the limits of this Letter and will be explained in another study.

Collectively, the effect of broadening of the SCN\textsuperscript{-} orientational distribution, including sulfur-down orientations, corroborates our experimental observation of classical VSFG (Figure 2b). Further, Figure S4 shows that the number of SCN\textsuperscript{-} ions that show an orientation of 90° from the surface normal saturates at higher concentrations. As the $\langle \rho(z) \rangle \langle \cos(\theta) \rangle$ product decreases significantly, the interfacial population of SCN\textsuperscript{-} ions does not change significantly, supporting the interpretation that the SPS signal is more directly correlated with the number density of the ions (Figure 2d).

Figure 5 summarizes the results. At lower concentrations (<1 M), SCN\textsuperscript{-} ions have mainly one type of orientation, sulfur-up. At concentrations above 1 M, as the number of ions at the interface starts to increase, overall orientational ordering broadens, and a new population with opposite orientation emerges. This transition coincides with the ionic strength threshold at which Debye length start to increase in previous surface force apparatus measurements.\textsuperscript{10} At these high concentrations, ion-ion correlations are also expected to play a role in the unexpected increase in interfacial ion concentration.\textsuperscript{40, 41}
Figure 5. Cartoon representing the organization of anions below (a) and above (b) 1 M bulk NaSCN concentration. Sulfur-up ions dominate the low concentration structure, and a sulfur-down population emerges at high concentrations.

The second population of anions with opposite orientation has significant implications and require further investigations in an extensive study with metal ions. It is known that SCN\(^{-}\) coordinates with trivalent lanthanide and actinide ions through its nitrogen.\(^{42}\) The changes in the orientational ordering of interfacial SCN\(^{-}\) ions at high concentrations may affect the formation of neutral and anionic complexes of heavy ions during interfacial transport and chemical separations.

In summary, classical and phase-sensitive VSFG spectroscopy experiments, in combination with MD simulations, provided a detailed description of interfacial organization of SCN\(^{-}\) anions at a concentrated solution interface. The VSFG spectra obtained under different polarizations are deconvoluted to obtain the information on surface-bound SCN\(^{-}\) anions, \(\chi_R^{(2)}\). The \(\text{Im} \chi^{(2)}\) spectra provided direct evidence of up and down orientation of interfacial anions at higher concentrations. The experimental results are consistent with corresponding MD simulations that
demonstrate broader orientational distributions of interfacial anions at higher concentrations. These results pave the way for predictive understanding of ion adsorption and transfer at highly concentrated aqueous solution interfaces.

ASSOCIATED CONTENT

The following files are available free of charge.

A brief description of PS-VSFG experimental methods with scheme, VSFG spectra of CN stretch region under SSP polarization, fit parameters, Im $\chi^{(2)}$ spectra for 0.1 M and 4 M NaSCN concentrations, MD simulations methods, and parameter files for GROMACS simulations. PDF

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REFERENCES


