

## Specific Ion Effects on Interfacial Water Structure near Macromolecules

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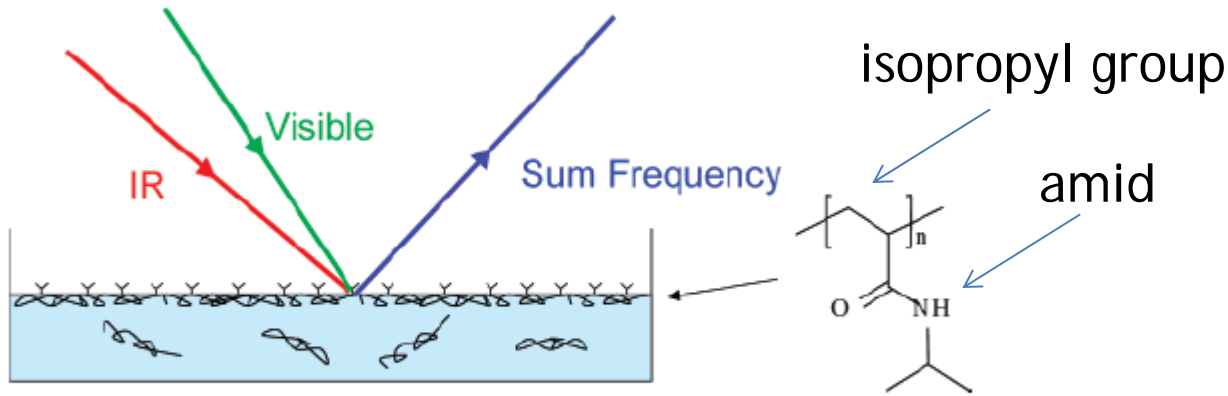
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**Abstract:** We investigated specific ion effects on interfacial water structure next to macromolecules with vibrational sum frequency spectroscopy (VSFS). Poly-(*N*-isopropylacrylamide) was adsorbed at the air/water interface for this purpose. It was found that the presence of salt in the subphase could induce the reorganization of water adjacent to the macromolecule and that the changes depended greatly on the specific identity and concentration of the salt employed. Ranked by their propensity to orient interfacial water molecules, sodium salts could be placed in the following order: NaSCN > NaClO<sub>4</sub> > NaI > NaNO<sub>3</sub> ≈ NaBr > NaCl > pure water ≈ NaF ≈ Na<sub>2</sub>SO<sub>4</sub>. This ordering is a Hofmeister series. On the other hand, varying the identity of the cation exhibited virtually no effect. We also showed that the oscillator strength in the OH stretch region was linearly related to changes in the surface potential caused by anion adsorption. This fact allowed binding isotherms to be abstracted from the VSFS data. Such results offer direct evidence that interfacial water structure can be predominantly the consequence of macromolecule–ion interactions.

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SEOK, SANGJUN

# Experimental Schematic



**Figure 1.** Schematic diagram of the experimental setup for using VSFS to monitor PNIPAM at the air/water interface. The structure of PNIPAM is also shown.

1. How is interfacial water structure affected by the presence of Hofmeister series?
2. How do these interactions contribute to the overall Hofmeister effect?

Hofmeister series

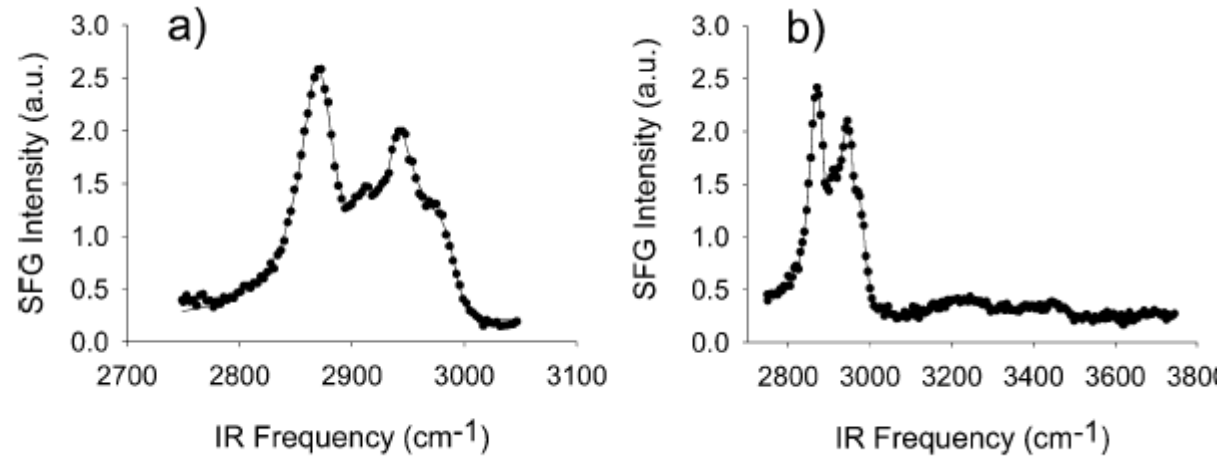


water structure  
break!! (kosmotropes)

water structure make!!  
(chaotropes)

# Results

## VSFG Spectral Features



**Figure 2.** VSFS spectrum of PNIPAM at (a) the D<sub>2</sub>O/air interface and (b) the H<sub>2</sub>O/air interface.

2874 cm<sup>-1</sup> CH<sub>3</sub> symmetric stretch

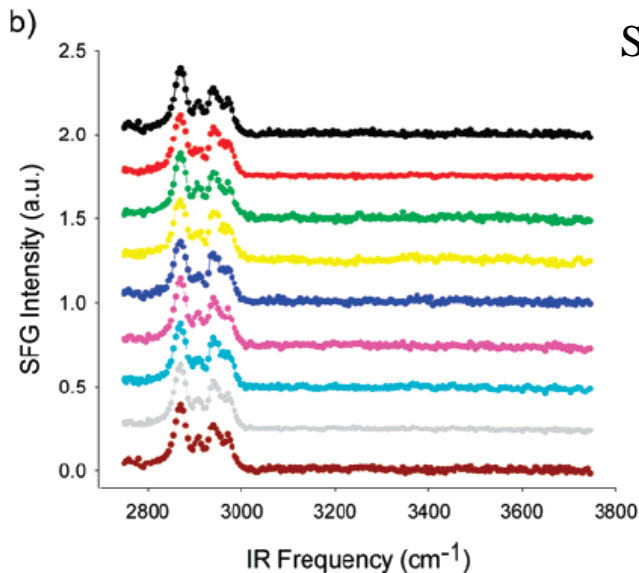
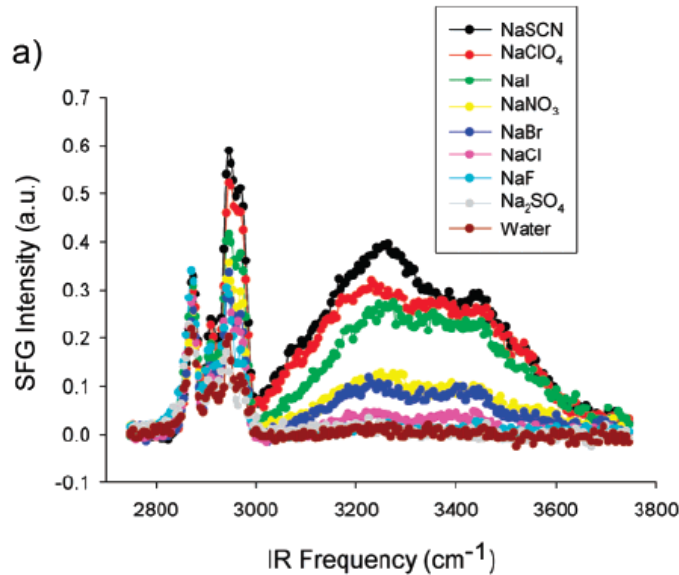
2913 cm<sup>-1</sup> methine?? Stretch

2839 cm<sup>-1</sup> fermi resonance

2880 cm<sup>-1</sup> CH<sub>3</sub> ays. stretch

# Results

## Effect of Anion Identity



**Figure 3.** (a) VSFS spectra show specific anion effects on PNIPAM adsorbed at the air/water interface. Each subphase contained 1 M of a given salt as indicated in the legend except for NaF and Na<sub>2</sub>SO<sub>4</sub>, which are measured with saturated solutions (~0.8 M for both salts). (b) The same experiments repeated with D<sub>2</sub>O. The spectra are offset for clarity.

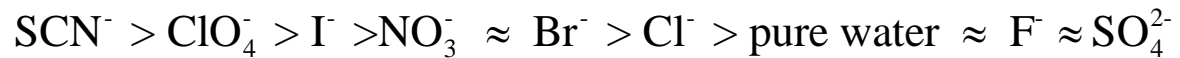
1 M salts :

NaSCN, CaClO<sub>4</sub>, NaI, NaNO<sub>3</sub>, and NaBr

~0.8M salts:

NaF and Na<sub>2</sub>SO<sub>4</sub>

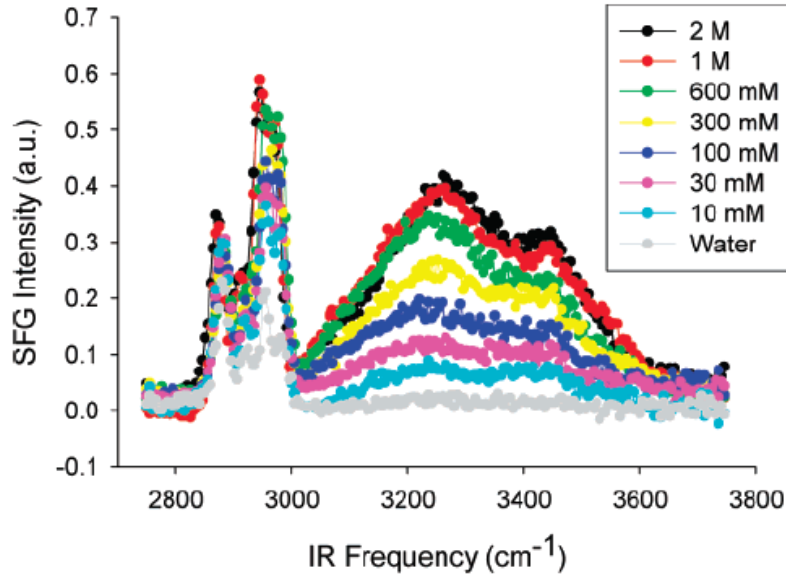
The OH stretch peak intensities were clearly anion specific and followed HS:



CH<sub>x</sub> stretch region was unaffected by salt concentration!!

# Results

## Effect of Chaotropic Anion Concentration



**Figure 4.** VSFS spectra of the air/PNIPAM/aqueous interface as a function of sodium thiocyanate concentration in the subphase.

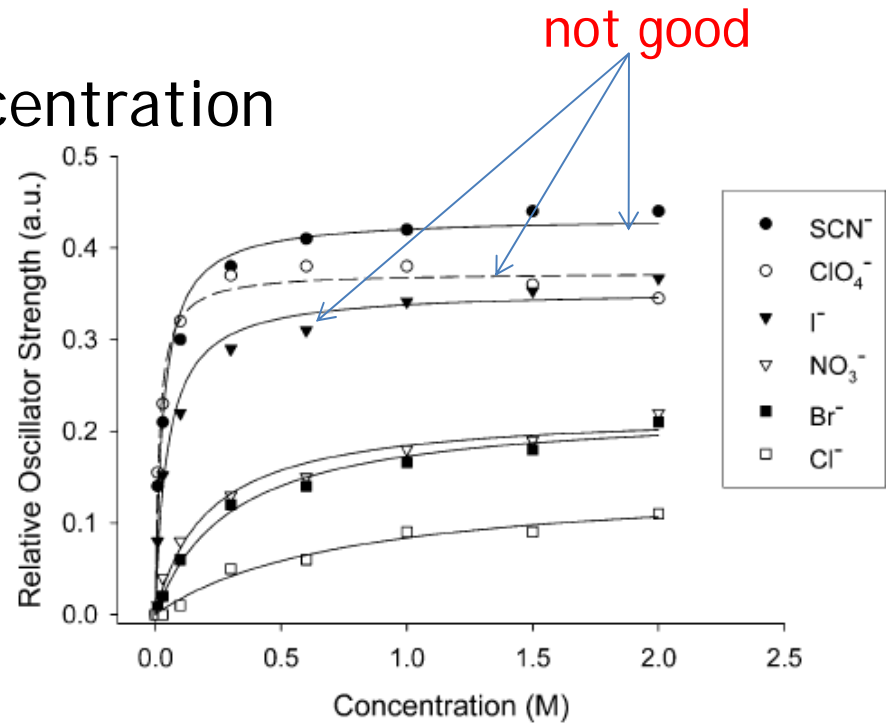
$$OS = \frac{B_{\max} C / K_{D,app}}{1 + C / K_{D,app}}$$

OS : oscillator strength

$C$  : chaotropic anion concentration

$B_{\max}$  : OS maximum value at infinite concentration

$K_{D,app}$  : apparent equilibrium dissociation constant



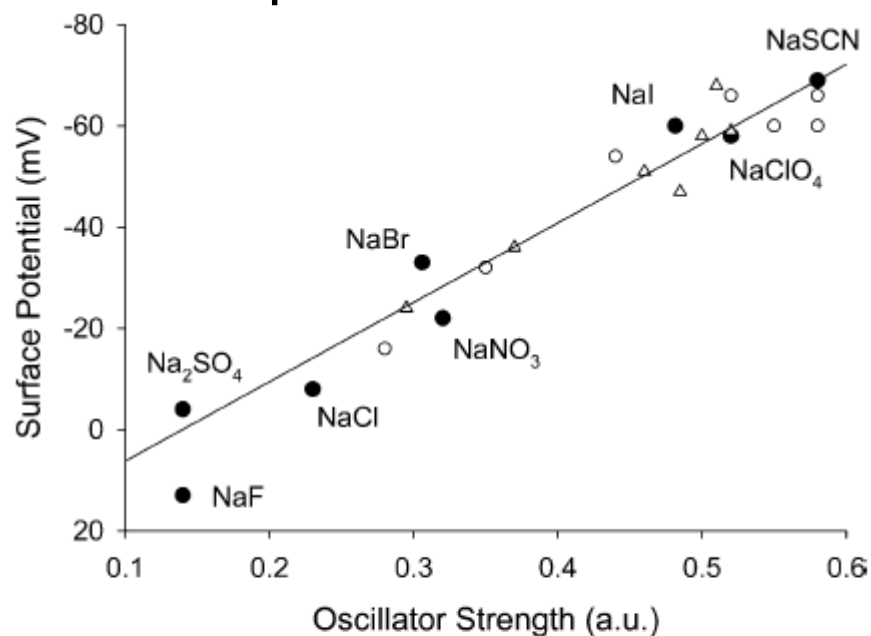
**Figure 5.** The relative oscillator strength of the 3200  $\text{cm}^{-1}$  peak vs anion concentration in the subphase. The lines are Langmuir isotherm fits to the data. The fit for perchlorate is denoted by a dashed line as it is obviously not as good as for the other anions.

**Table 1.** Dissociation Constants of Anions to PNIPAM

	$\text{SCN}^-$	$\text{ClO}_4^-$	$\text{I}^-$	$\text{NO}_3^-$	$\text{Br}^-$	$\text{Cl}^-$
$K_{D,app}$ (M)	0.031	0.016	0.048	0.20	0.30	0.76
$B_{\max}$ (au)	0.43	0.37	0.35	0.22	0.22	0.15
$K_{D,intrinsic}$ (M)	0.19	0.15	0.50	3.8	4.0	15

# Results

## Surface potential



**Figure 6.** Correlation between the surface potential and the oscillator strength for the  $3200\text{ cm}^{-1}$  peak. The solid circles are 1 M salt concentrations of the Hofmeister salts except for sulfate and fluoride which were  $\sim 0.8\text{ M}$ . The open circles and open triangles represent various concentrations of NaSCN and NaClO<sub>4</sub>, respectively. The average error bar for each data point is  $\pm 14\text{ mV}$ .

**Table S1.** Oscillator Strengths of Water Peaks as well as Relative Surface Potential Values for Air/PNIPAM/Aqueous Systems with 1 M Salt ( $\sim 0.8\text{ M}$  for NaF and Na<sub>2</sub>SO<sub>4</sub>)

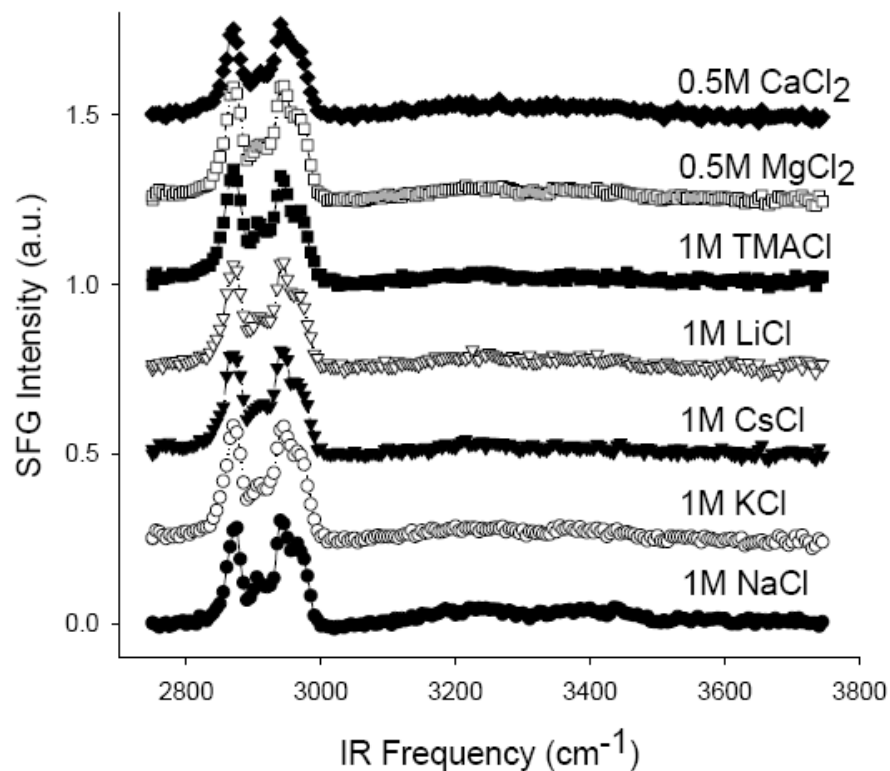
		NaSCN	NaClO <sub>4</sub>	NaI	NaNO <sub>3</sub>	NaBr	NaCl	NaF	Na <sub>2</sub> SO <sub>4</sub>
Oscillator	$3200\text{ cm}^{-1}$	0.58	0.52	0.48	0.32	0.30	0.23	0.14	0.14
Strength (a.u.)	$3400\text{ cm}^{-1}$	0.35	0.31	0.30	0.22	0.24	0.22	0.15	0.15
$\Delta$ Surface Potential (mV)		-69 ( $\pm 8$ )	-58 ( $\pm 12$ )	-60 ( $\pm 23$ )	-22 ( $\pm 10$ )	-33 ( $\pm 15$ )	-8 ( $\pm 12$ )	13 ( $\pm 19$ )	4 ( $\pm 17$ )

**Table S2.** Relative Surface Potential Values of the Air/PNIPAM/Aqueous System with Varying Concentrations of NaSCN and NaClO<sub>4</sub> in the Subphase. (unit: mV)

	0.01M	0.03M	0.1M	0.3M	0.6M	1M	1.5M	2M
NaSCN	-16 ( $\pm 18$ )	-35 ( $\pm 15$ )	-54 ( $\pm 13$ )	-66 ( $\pm 12$ )	-60 ( $\pm 12$ )	-69 ( $\pm 9$ )	-60 ( $\pm 13$ )	-66 ( $\pm 11$ )
NaClO <sub>4</sub>	-24 ( $\pm 13$ )	-36 ( $\pm 18$ )	-51 ( $\pm 12$ )	-68 ( $\pm 18$ )	-59 ( $\pm 14$ )	-58 ( $\pm 12$ )	-58 ( $\pm 16$ )	-47 ( $\pm 9$ )

# Results

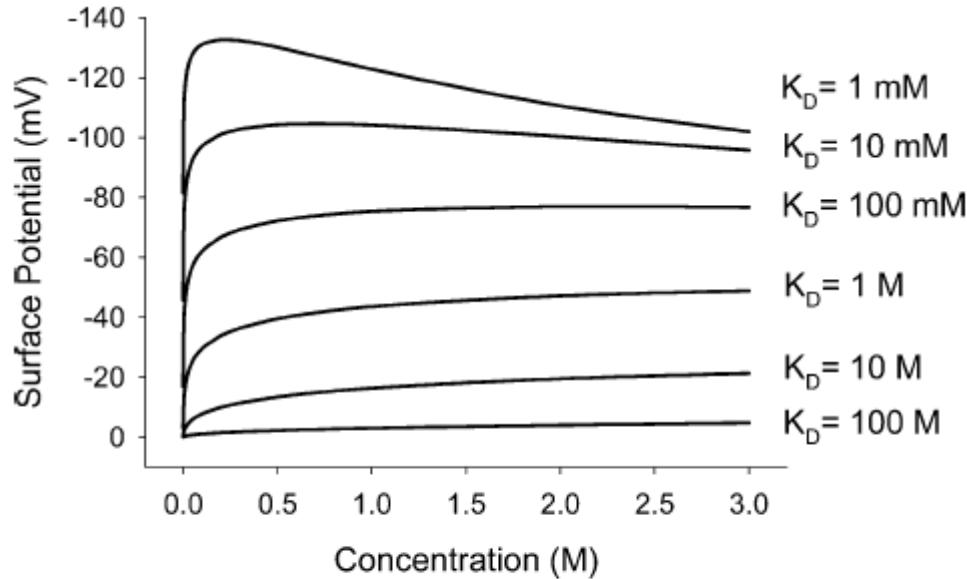
## Effect of Cations



**Figure S2. VSFS spectra of the air/PNIPAM/Aqueous interface as a function of cation identity. All experiments were conducted with 1 M Cl<sup>-</sup>. This dictated using lower molar concentrations of MgCl<sub>2</sub> and CaCl<sub>2</sub>. Other choices such as keeping the cation concentration or the ionic strength constant would, of course, have been possible. However, these were judged to be less desirable because changes in Cl<sup>-</sup> concentration have a non-negligible effect on the water structure (Figure 4a). It would have also been possible to use F<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> salts; however, many of these salts have only limited solubility in aqueous solution. The spectra are offset to avoid crowding**

# Results

## Ion Adsorption Isotherms and Gouy-Chapman-Stern Theory



**Figure 7.** Concentration dependence of the surface potential predicted by Gouy–Chapman–Stern theory for anion adsorption.  $N_s$  is set at  $5 \times 10^{14} \text{ cm}^{-2}$ . The solution is assumed to contain only the anion and its counterion, both of which are monovalent.

$$\sigma_{ads} = \frac{zeN_s \frac{C}{K_D} \exp \frac{ze\phi(0)}{kT}}{1 + \frac{C}{K_D} \exp \frac{ze\phi(0)}{kT}}$$

$\sigma_{ads}$  : surface charge density due to anion adsorption

$N_s$  : number density of binding sites

$\phi(0)$  : surface potential

$K_d$  : equilibrium dissociation constant

$$\sigma_d = (8I\epsilon_r\epsilon_0kT)^{1/2} \sinh \frac{ze\phi(0)}{2kT}$$

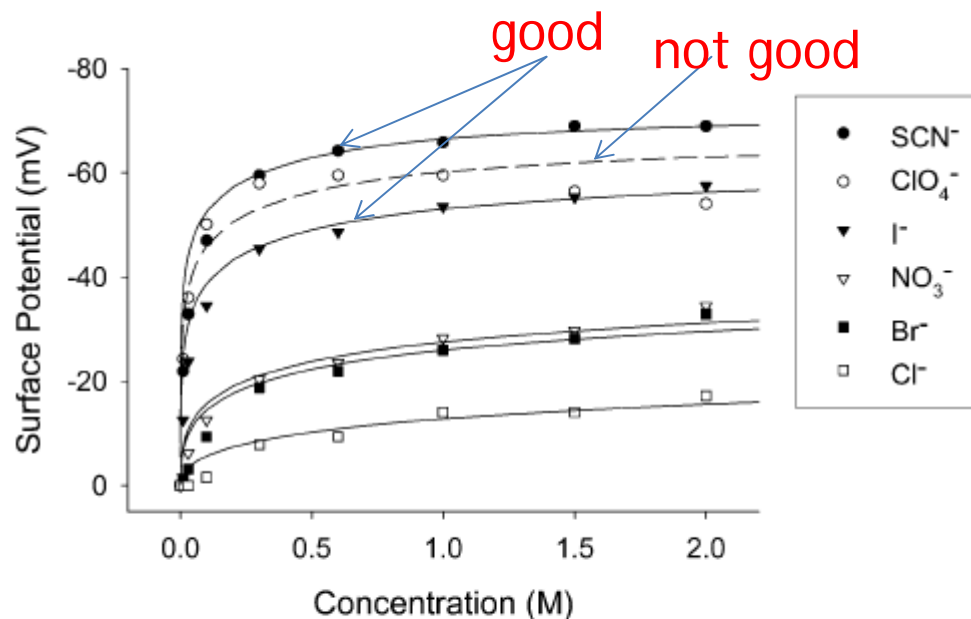
$\sigma_d$  : net charge density in the diffuse double layer

$$\sigma_d + \sigma_{ads} = 0$$



# Results

## Ion Adsorption Isotherms and Gouy-Chapman-Stern Theory



**Figure 8.** Changes in the surface potential as a function of salt concentration in the subphase. The lines represent fits using the Gouy–Chapman–Stern model. The fit for perchlorate is represented by a dashed line to emphasize the fact that it does not fit nearly as well.

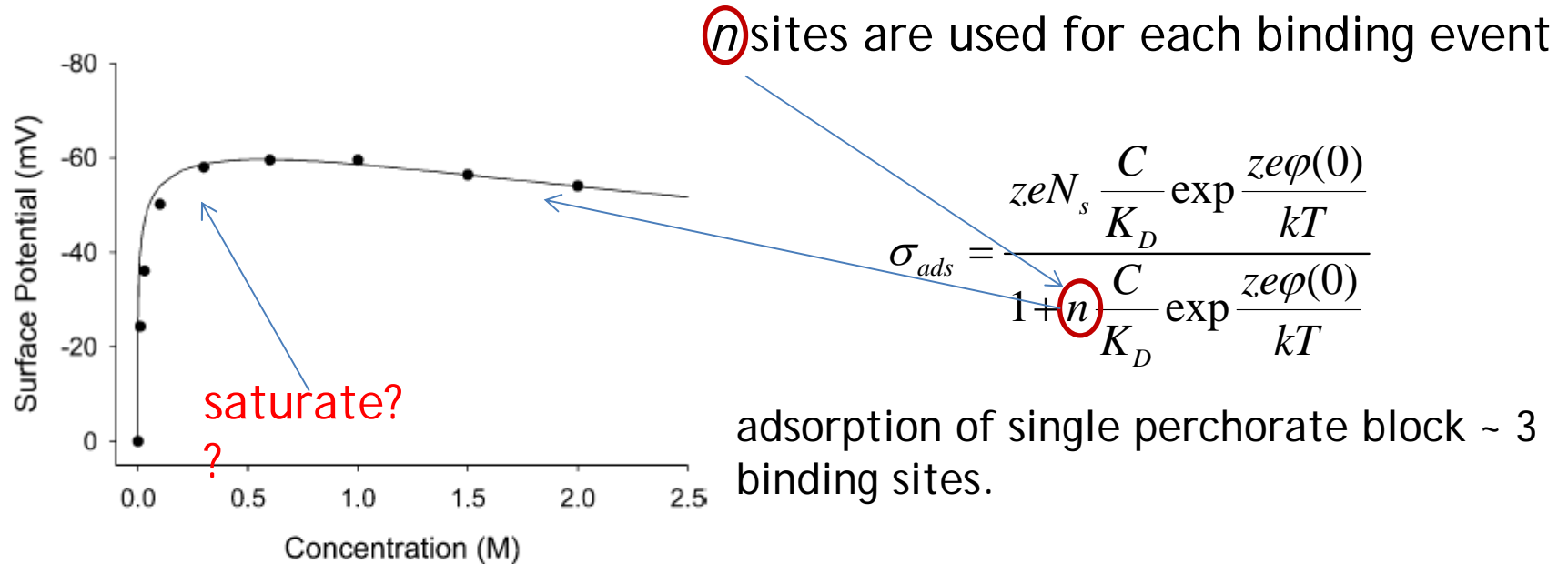
**Table 1.** Dissociation Constants of Anions to PNIPAM

	SCN <sup>-</sup>	ClO <sub>4</sub> <sup>-</sup>	I <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	Br <sup>-</sup>	Cl <sup>-</sup>
$K_{D,app}$ (M)	0.031	0.016	0.048	0.20	0.30	0.76
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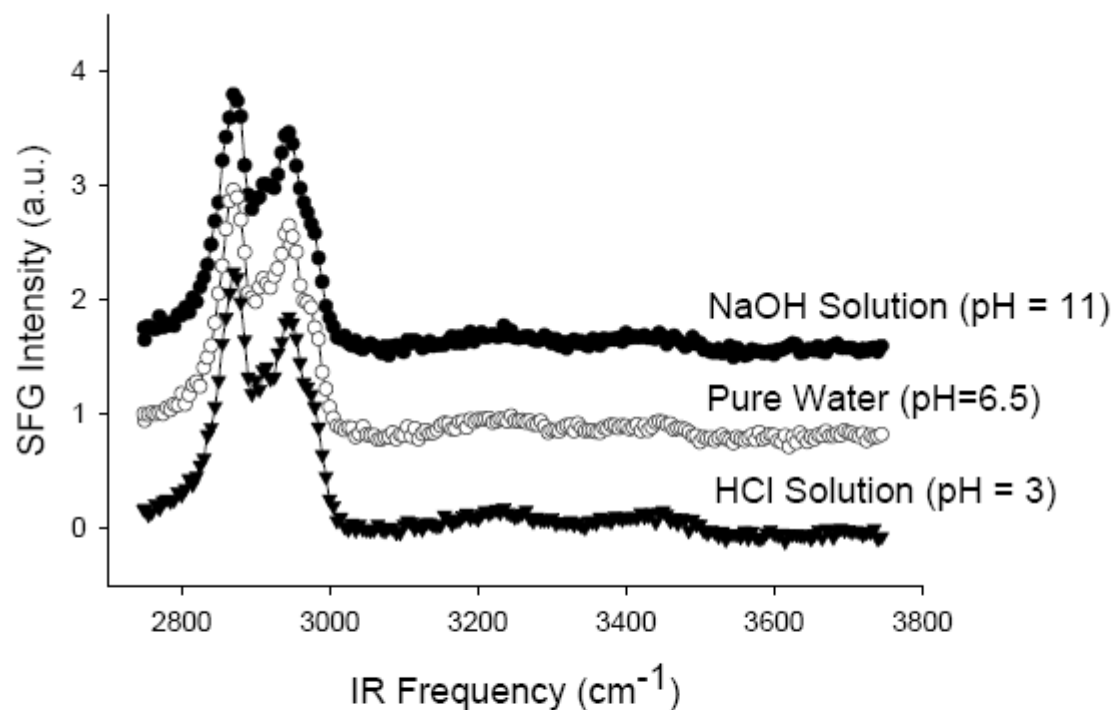


# Results

## Ion Adsorption Isotherms and Gouy-Chapman-Stern Theory



**Figure 9.** Change in surface potential as a function of NaClO<sub>4</sub> concentration in the aqueous subphase. The solid line is a fit to the modified Gouy-Chapman-Stern model from eq 5, 6, and 7.



**Figure S1.** VSFS spectra of the air/PNIPAM/aqueous interface as a function of pH. The acidic and basic solutions were prepared by adding HCl and NaOH, respectively, with no additional salts. The spectrum of pure water is the same as the one in Figure 2b. The spectra are offset for clarity.