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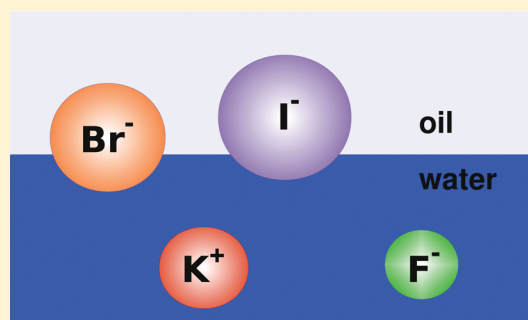
Ions at the Water–oil Interface: Interfacial Tension of Electrolyte Solutions

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S Supporting Information

ABSTRACT: A theory, based on a modified Poisson–Boltzmann equation, is presented that allows us to calculate the excess interfacial tension of an electrolyte–oil interface accurately. The chaotropic (structure-breaking) ions are found to adsorb to the water–oil interface as the result of large polarizability, weak hydration, and hydrophobic and dispersion interactions. However, kosmotropic (structure-making) anions as well as potassium and sodium ions are found to be repelled from the interface. The adsorption of Γ^- and ClO_4^- is found to be so strong as to lower the interfacial tension of the water–oil interface, in agreement with the experimental data. The agreement between the calculated interfacial tensions and the available experimental data is very good. The theory is used to predict the interfacial tensions of six other potassium salts, for which no experimental data is available at the moment.



INTRODUCTION

Although the bulk thermodynamics of electrolyte solutions has been reasonably well understood since the pioneering work of Debye and Hückel almost a century ago, electrolyte surface properties remain an outstanding challenge. Experimental measurements of the surface tensions of electrolyte solutions indicate that ions, in general, are depleted from the interfacial region.¹ This is consistent with the classical ideas of Langmuir, Wagner, Onsager, and Samaras.^{2–5} The fundamental insight of this early work was that a strong dielectric discontinuity between air and water results in induced surface charge at the air–water interface. This surface charge produces exactly the same electric field in water as an image charge placed across the dielectric interface. The electrostatic repulsion of ions from their images leads to ion depletion near the Gibbs dividing surface (GDS). The predictions of the Wagner–Onsager–Samaras (WOS) theory are in good agreement with the experimental measurements of the surface tensions of NaCl solutions at very low concentrations. The theory, however, can be brought into quantitative agreement with experiments of up to 1 M concentration if ionic hydration is taken into account.⁵ However, if the same theory is then applied to a NaI solution, then one finds qualitatively incorrect behavior. The theory predicts that at the same concentration of electrolyte the surface tension of NaI should be larger than that of a NaCl solution, whereas experiments find the opposite behavior.¹ The fact that there might be something fundamental missing from WOS theory was indicated by the electrostatic surface potential measurements of Frumkin⁶ performed in 1924. Frumkin observed that, in general, surface potentials of solutions containing alkali metal salt are negative, signifying that anions penetrate further toward air than do cations. The formation of

such a double layer cannot be accounted for within the WOS formalism, even if the hydration of ions is taken into account. For close to a century, Frumkin's measurements have failed to find a plausible theoretical explanation. The situation started to change when a new generation of polarizable force field simulations showed that contrary to WOS theory and in agreement with Frumkin's measurements strongly polarizable halogen ions such as Γ^- and Br^- could actually become adsorbed to the air–water interface.^{7–11} The conclusion that some ions are present at the air–water interface has been also confirmed by spectroscopic¹² and photoelectron emission experiments.^{13–15} Nevertheless, the situation remains unclear. State of the art force fields for polarizable ions produce too much adsorption,¹⁶ resulting in a negative excess surface tension for NaI solution, contrary to the experimental data. Furthermore, sum-frequency spectroscopy (VSFS) indicates a significantly diminished anion population in the topmost layer of the electrolyte solution compared to that in the bulk concentration.¹²

There have been a number of theoretical attempts to account for the ionic distribution at the air–water interface.^{17,18} One interesting proposal, which has been extensively discussed in the literature, is that the dispersion (van der Waals) interaction between ions and water is responsible for the ionic adsorption.¹⁸ This, however, contradicts both experiments and simulations. Dispersion forces are proportional to the ionic polarizability. Because heavy halide ions such as Γ^- and Br^- are much more polarizable than small alkali metal cations such as

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Na^+ or K^+ , their van der Waals interaction energy with water is much more favorable than that of metal cations. Therefore, dispersion forces, if they play any role in the interfacial geometry, should favor the bulk solvation of iodide and bromide. This, however, is not what is observed experimentally or in the polarizable force field simulations, which find that large halide anions prefer interfacial solvation much more than do metal cations, which are completely absent from the GDS.

A different theory has recently been proposed by Levin,¹⁹ who argued that polarizable ions are driven toward the air–water interface by their hydrophobic cavitation energy. When an ion is solvated in water, a cavity is formed from which water molecules are excluded. For small cavities, the energy penalty of creating a hole in water is purely entropic and is proportional to the number of water molecules excluded from the hole. The prefactor of the volumetric dependence is known from the bulk simulations.²⁰ When an ion is at the interface, its cavitation energy is diminished proportionally to the fraction of ionic volume exposed to air. For hard ions of Debye–Hückel theory, the cavitation energy, however, is too small to compensate for the electrostatic self-energy penalty of exposing the ionic charge to the low dielectric environment of air. The polarizable ions, however, can shift the electronic density so that it remains mostly hydrated. In fact, for an ideal polarizable ion sitting exactly on the interface 99% of its charge remains hydrated.¹⁹ The electrostatic self-energy penalty of moving a soft polarizable ion toward the GDS is relatively small and is comparable to the gain in cavitation energy. It is possible to use the theoretically derived ion–interface interaction potentials to calculate quantitatively the excess surface tensions of different electrolyte solutions by integrating the Gibbs adsorption isotherm equation. Excellent agreement between the theory^{21,22} and experiment^{23–25} is found for 10 different sodium salts with concentrations ranging from 0 to 1 M. The theory also predicts that for an extended air–water interface there should be significantly less adsorption than is observed in the polarizable force fields simulations. The concentration of adsorbed anions remains below their bulk value, consistent with the VSFS measurements.¹² Furthermore, the sequence of surface tensions and surface potentials obtained theoretically follows precisely the famous Hofmeister lyotropic series.²² The picture that emerges from this theoretical work is that near the air–water interface ions can be divided into two categories: kosmotropes and chaotropes.^{22,26} Kosmotropes are strongly hydrated and are repelled from the air–water interface. However, chaotropes lose their hydration sheath and, as a result of their large polarizability and cavitation forces, become adsorbed to the surface. The classification of ions into kosmotropes and chaotropes correlates precisely with their Jones–Dole viscosity B coefficient:²⁷ ions with positive B are kosmotropes, and ions with negative B are chaotropes. When we consider the almost perfect agreement between theory and experiment, dispersion (van der Waals) interactions between ions and water do not seem to play any role in the ionic adsorption to the air–water interface. For kosmotropic ions, this is easily understood. These ions never cross the GDS; therefore, they remain as well hydrated near the interface as they were in the bulk, interacting with the same number of water molecules. For chaotropic ions, the absence of the dispersion interaction is not so simply understood. One possible explanation is that as a chaotropic ion crosses the GDS its electronic charge density concentrates on the high dielectric side of the interface, producing an intense electric

field that attracts nearby water molecules. The part of the ion that stays in water, therefore, remains as well hydrated as the whole ion was in the bulk, interacting with the same number of water molecules. The dispersion energy of such a chaotropic ion will then be similar to that of an ion in the bulk solution. The picture presented above was confirmed by the subsequent *ab initio* simulations of Γ^- adsorption. The theoretically predicted ion–interface interaction potential was found to be in almost perfect agreement with the potential of mean force (PMF) obtained using the *ab initio* simulations.²⁸ Unfortunately, at the moment there is no way to predict *a priori* which ions are kosmotropes and which are chaotropes. The hydration properties of ions are determined by quantum mechanics and are still not well understood.²⁹ In our theory, the information indicating which ion is a kosmotrope and which one is a chaotrope is taken as an external input and is based on the ionic viscosity B coefficient that is measured experimentally.

One of the most promising directions for the present research is to help understand the stability of protein solutions.^{26,30} Over a century ago, Hofmeister³¹ measured the concentrations of various salts needed to precipitate egg white proteins, organizing them into the famous lyotropic series that now bears his name. Hofmeister ions are particularly interesting because they show a large degree of universality. The same sequence has been observed in a variety of different contexts, not only with proteins but also with DNA,³² collagen,³³ critical micelle concentrations,³⁴ the stability of hydrophobic colloids,^{35,36} and so forth. The universality seems to arise from the interaction of Hofmeister ions with nonpolar groups. In this respect, a theory that can quantitatively account for the effect of Hofmeister salts on the interfacial tension of the oil–water interface might prove to be especially illuminating in understanding the underlying mechanisms of this universality. The construction of such a theory and its comparison with the experimental data is the goal of this article.

■ MODEL AND THEORY

Consider an electrolyte solution with cations of charge q and anions of charge $-q$ confined to a mesoscopic drop of water³⁷ of radius R that is surrounded by oil. Water and oil will be treated as uniform dielectrics with permittivities of $\epsilon_w = 80.36$ and $\epsilon_o = 2$ (dodecane), respectively, with a sharp interface at $r = R$ corresponding to the GDS. The Bjerrum length, defined as $\lambda_B = \beta q^2 / \epsilon_w$, is 7.09 Å for water at 20 °C. The adsorption (ion excess per unit area) is defined as

$$\Gamma_{\pm} = \frac{\left[\int_0^{\infty} \rho_{\pm}(r) 4\pi r^2 dr - \frac{4\pi R^3}{3} c_b \right]}{4\pi R^2} \quad (1)$$

where $\rho_{\pm}(r)$ represents the ionic density profiles at a distance r from the center of the drop and $c_b = \rho_+(0) = \rho_-(0)$ is the electrolyte bulk concentration that must be calculated theoretically. If N ion pairs are inside the drop, then the expression simplifies to $\Gamma_{\pm} = (N/4\pi R^2) - (c_b R/3)$. The surface tension can be obtained by integrating the Gibbs adsorption isotherm equation

$$d\gamma = -\Gamma_+ d\mu_+ - \Gamma_- d\mu_- \quad (2)$$

where μ_{\pm} represents the chemical potentials. For the mesoscopic drops that we study, there is no dependence of the surface tension on the radius of curvature R . The excess

interfacial tension that is calculated is therefore that of the thermodynamic interface.

Previous work showed that near an electrolyte–air interface kosmotropic anions remain hydrated whereas chaotropic anions lose their hydration sheath and partially cross the GDS.²² The electrostatic self-energy of a chaotropic ion of radius a and relative polarizability α at a distance $z = R - r$ from the GDS (toward the electrolyte) was found to be¹⁹

$$\beta U_{\text{pol}}(z) = \frac{\lambda_B}{2a} \left[\frac{\pi x^2}{\theta(z)} + \frac{\pi[1-x]^2 \epsilon_w}{[\pi - \theta(z)] \epsilon_o} \right] + g \left[x - \frac{1 - \cos[\theta(z)]}{2} \right]^2 \quad (3)$$

where $\theta(z) = \arccos[-z/a]$ and $g = (1 - \alpha)/\alpha$. The fraction of charge that remains hydrated, x , is obtained by minimizing eq 3:

$$x(z) = \frac{\left[\frac{\lambda_B \pi \epsilon_w}{a \epsilon_o [\pi - \theta(z)]} + g[1 - \cos[\theta(z)]] \right]}{\left[\frac{\lambda_B \pi}{a \theta(z)} + \frac{\lambda_B \pi \epsilon_w}{a \epsilon_o [\pi - \theta(z)]} + 2g \right]} \quad (4)$$

The driving force for a chaotropic ion to move toward the GDS is the decrease in its hydrophobic cavitation energy. For small ions, the cavitation energy is mostly entropic and is proportional to the average number of water molecules excluded from the region occupied by the ion (or to the ionic volume).³⁸ When a chaotropic ion crosses the GDS, the cavitation hydrophobic energy drops proportionally to the volume of the ion exposed to air¹⁹

$$U_{\text{cav}}(z) = \begin{cases} \nu a^3 & \text{for } z \geq a \\ \frac{1}{4} \nu a^3 \left(\frac{z}{a} + 1 \right)^2 \left(2 - \frac{z}{a} \right) & \text{for } -a < z < a \\ < a \end{cases} \quad (5)$$

where $\nu \approx 0.3 k_B T / \text{\AA}^3$ is obtained from bulk simulations.²⁰ When ions penetrate oil, there is also a lipophobic cavitation energy penalty. However, because the molecular weight of oil (dodecane) is 10 times larger than that of water and its mass density is similar to that of water, the cavitation energy of the ion in oil is 10 times smaller than it is for the same ion in water—on average, there are 10 times fewer oil molecules excluded from a cavity inside oil than water molecules excluded from the same size cavity in water—and can be safely ignored.

When either a chaotropic or a kosmotropic ion approaches an interface, it induces a polarization charge that repels it from the GDS. This potential was calculated to be

$$\beta U_{\text{im}}(z) = \frac{\beta W_c a}{z} e^{-2\kappa(z-a)} \quad (6)$$

where $\kappa = (8\pi\lambda_B c_b)^{1/2}$ is the inverse Debye length. The work done to bring an ion from infinity to the contact distance $z = a$ is given by⁵

$$\beta W_c = \frac{\lambda_B}{2} \int_0^\infty dk \frac{k[s \cosh(ka) - k \sinh(ka)]}{s[s \cosh(ka) + k \sinh(ka)]} \quad (7)$$

where $s = (\kappa^2 + k^2)^{1/2}$.

For the air–water interface, dispersion forces do not play any role in determining the excess surface tension. This, however, is not necessarily the case for the oil–water interface. It is very difficult to account for the dispersion interaction in a complicated interfacial geometry. However, using typical Hamaker constants³⁹ and a scaling ansatz, we will attempt to derive an order of magnitude estimate for the dispersion energy of a chaotropic anion at the oil–water interface.

We first note that the dispersion energy is proportional to the ionic polarizability and the polarizability is proportional to the ionic volume. We shall then assume that the dispersion energy of an ion sitting at the oil–water interface is proportional to the volume that is exposed to the low dielectric environment (oil),

$$U_{\text{dis}}(z) = \begin{cases} 0 & \text{for } z \geq a \\ A_{\text{eff}} \alpha \left[1 - \frac{\left(\frac{z}{a} + 1 \right)^2 \left(2 - \frac{z}{a} \right)}{4} \right] & \text{for } -a < z < a \end{cases} \quad (8)$$

where A_{eff} is the effective interaction constant. We next recall that for an ion sitting at the air–water interface the dispersion energy was found to be null, $A_{\text{eff}} = 0$. This means that a chaotropic ion moving across the air–water interface does not pay any dispersion energy penalty. As far as the dispersion interaction goes, it is as if the interface did not exist. We argued earlier that this was a consequence of the shifted electron density, which preserved the average number of water molecules in the first hydration shell of a chaotropic ion as it partially penetrated the interface. We can now make an order of magnitude estimate of the coupling constant A_{eff} for the oil–water interface, $A_{\text{eff}} \approx A_{\text{mw}}^v - A_{\text{mo}}^v$, where A_{mo}^v is the metal–oil Hamaker constant in vacuum and A_{mw}^v is the metal–water Hamaker constant in vacuum. Using the standard relations for the Hamaker constants, we find $A_{\text{mo}}^v = (A_{\text{mm}}^v A_{\text{oo}}^v)^{1/2}$ and $A_{\text{mw}}^v = (A_{\text{mm}}^v A_{\text{ww}}^v)^{1/2}$. The Hamaker constants³⁹ for metal–metal, oil–oil (dodecane), and water–water interactions are $A_{\text{mm}}^v = 35 \times 10^{-20}$, $A_{\text{oo}}^v = 5 \times 10^{-20}$, and $A_{\text{ww}}^v = 3.77 \times 10^{-20}$ J, respectively. With these values, we expect the coupling constant at the oil–water interface to be $A_{\text{eff}} \approx -4.4 k_B T$. Note that we are using a metal Hamaker constant because ionic nonideality has already been taken into account through the relative polarizability α that was introduced in eq 8. We should stress that this is only an order of magnitude estimate of the coupling constant. In practice, we will determine the precise value of A_{eff} by fitting the interfacial tension of the KI solution.

For monovalent ions in water at room temperature, the interionic correlations are weak and the mean-field treatment is justified. The ionic density profiles inside the water drop are obtained from the numerical solution of the modified Poisson–Boltzmann (PB) equation

$$\nabla^2 \phi(r) = -\frac{4\pi q}{\epsilon_w} [\rho_+(r) - \rho_-(r)]$$

$$\rho_+(r) = c_1 e^{[-\beta q \phi(r) - \beta U_{\text{im}}(z)]}$$

$$\rho_-^{\text{kos}}(r) = c_2 e^{[\beta q \phi(r) - \beta U_{\text{im}}(z)]}$$

$$\rho_-^{\text{cha}}(r) = c_3 e^{[\beta q \phi(r) - \beta U_{\text{im}}(z) - \beta U_{\text{pol}}(z) - \beta U_{\text{cav}}(z) - \beta U_{\text{dis}}(z)]} \quad (9)$$

where $\phi(r)$ is the electrostatic potential and c_1 , c_2 , and c_3 are the normalizations. Superscript kos and cha denote kosmotropic and chaotropic anions, respectively. In Table 1, we summarize

Table 1. Ion Classification into Chaotropes (c) and Kosmotropes (k)^a

anions	chao/kosmo	radius (Å)	polarizability (Å ³)
F ⁻	k	3.52	*
Cl ⁻	k	2	*
Br ⁻	c	2.05	5.07
I ⁻	c	2.26	7.4
IO ₃ ⁻	k	3.74	*
BrO ₃ ⁻	k	2.41	*
NO ₃ ⁻	c	1.98	4.48
ClO ₃ ⁻	c	2.16	5.3
ClO ₄ ⁻	c	2.75	5.45

^aEffective radii (hydrated or partially hydrated) for kosmotropes and (bare) for chaotropes, for which we have also include the polarizabilities.⁴⁰

the values of the ionic radii, polarizabilities, and ionic classification into kosmotropes and chaotropes.

We now proceed to calculate the excess interfacial tensions of the water–oil interface for different potassium salts. We will assume that K⁺ is partially hydrated and adjust its radius of hydration to fit the interfacial tension of the KCl electrolyte–oil interface correctly. All of the anionic radii and polarizabilities are exactly the same as in our previous work on the excess surface tension of an electrolyte–air interface.^{21,22} The bulk hydration radii were taken from Nightingale,⁴² and the polarizabilities were taken from Pyper et al.⁴⁰ Note that both K⁺ and Cl⁻ are kosmotropes and are repelled from the GDS so that neither cavitation nor dispersion interactions play any role in the KCl solution. By solving eq 9 iteratively, we obtain the bulk concentration c_b . The surface tension is calculated by integrating the Gibbs adsorption isotherm (eq 2) with the chemical potentials given by $\beta\mu_{\pm} = \ln(c_b\Lambda_{\pm}^3)$, where Λ_{\pm} represents the de Broglie thermal wavelengths. The use of the ideal gas chemical potential is consistent with the PB equation, which also neglects the interionic correlations. We find that to fit the experimental data for KCl (Figure 1) the radius of K⁺ must be adjusted to be 2 Å. For large concentrations, the nonideality affects both adsorption and the excess chemical potential. Compared to the Monte Carlo simulations,³⁷ we see however that these effects can be absorbed into a slight renormalization of the cation radius, which in any case is used as a fitting parameter. In this way, good agreement between the theory and experiments extends up to a 1 M concentration. We next study the KI solution. I⁻ is a chaotrope, so both cavitation and dispersion forces play an important role at the oil–water interface. Using the same radius

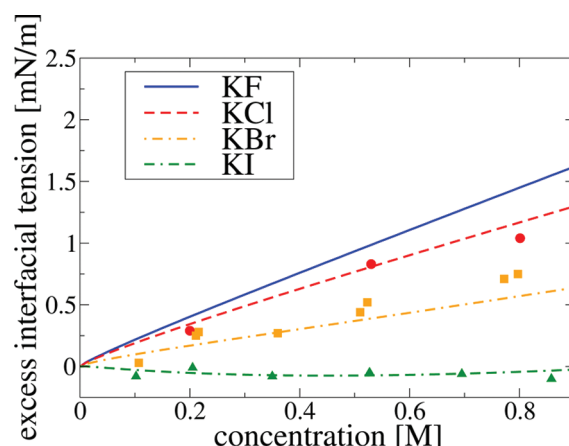


Figure 1. Excess interfacial tensions for solutions containing KF, KCl, KBr, and KI. Symbols are the experimental data,⁴¹ and lines are the present theory. Circles represent experimental data for KCl, squares represent experimental data for KBr, and triangles represent experimental data for KI. No experimental data is available for KF.

of K⁺, we find a good fit of the experimental data with $A_{\text{eff}} = -4k_B T$, which is surprisingly close to our theoretical estimate. Figure S1, in Supporting Information, shows the ion–interface interaction potentials for K⁺ and I⁻. Figure S2, in Supporting Information, separates the total interaction potential into its different contributions.

With the two free parameters now determined, we can calculate the interfacial tensions for the other halide salts, KF and KBr. Unfortunately, no experimental data is available for KF; however, we do find good agreement between the experimentally measured interfacial tension of KBr and the present theory (Figure 1). Furthermore, the agreement would be even better if we could use a somewhat smaller polarizability of Br⁻. The fact that the polarizability of Br⁻ quoted in the literature seems to be overestimated has already been noticed in our work on the stability of hydrophobic colloidal suspensions.³⁶ This conclusion seems to be also consistent with the recent ab initio simulations.⁴³ In Figure 2, we plot the ionic

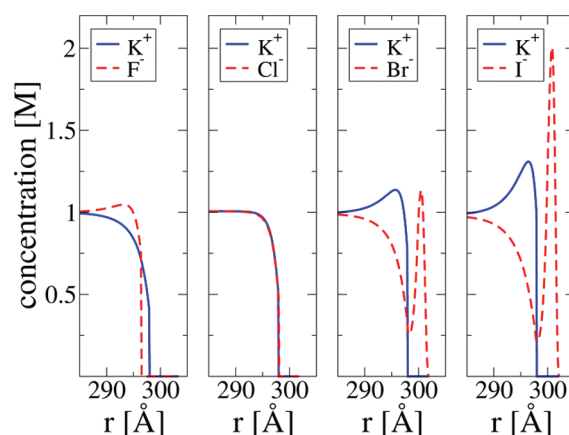


Figure 2. Ionic density profiles for KF, KCl, KBr, and KI at 1 M. The GDS is at $r = 300$ Å.

density profiles of potassium halide salts at 1 M concentration, which show a strong adsorption of iodide at the water–oil interface. Finally, in Figure 3 we calculate the surface tensions of potassium salts containing oxyanions. We hope that the

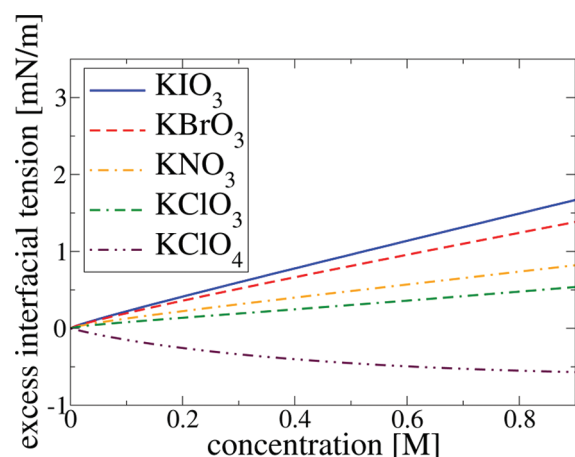


Figure 3. Theoretically calculated excess interfacial tensions for solutions of KIO_3 , KBrO_3 , KNO_3 , KClO_3 , and KClO_4 .

experimental data for these salts will become available in the near future.

CONCLUSIONS

We have presented a theory that allows a quantitatively accurate calculation of the excess interfacial tension of an electrolyte–oil interface. The theory shows that the kosmotropic anions remain hydrated near the GDS whereas the chaotropic anions loose their hydration sheath and become adsorbed to the interface as a result of their large polarizability, cavitation, and dispersion forces. The excess interfacial tensions follow the Hofmeister series precisely. Unlike the air–water interface, dispersion interactions play an important role at the oil–water interface, resulting in the strong adsorption of highly polarizable ions such as I^- and ClO_4^- . This explains why these two ions are such strong denaturants of proteins.

ASSOCIATED CONTENT

Supporting Information

Total ion–interface potentials for K^+ and I^- at 1 M. Different contributions to the ion–interface potentials for K^+ and I^- at 1 M. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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