

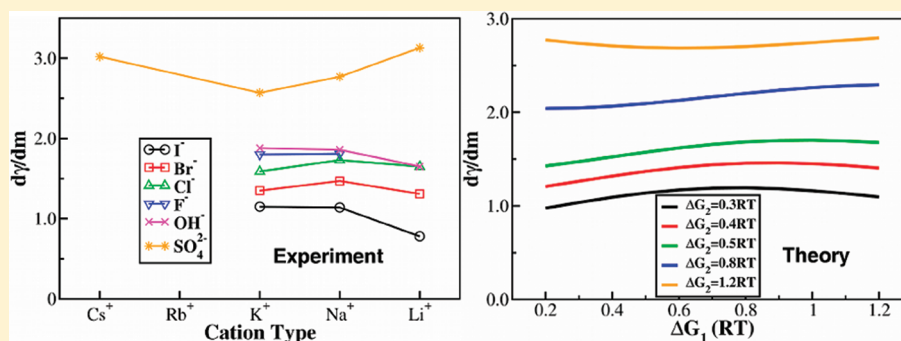
Simple Theoretical Model for Ion Cooperativity in Aqueous Solutions of Simple Inorganic Salts and Its Effect on Water Surface Tension

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S Supporting Information

ABSTRACT:



Careful analysis of experimental data showed that the salt aqueous solution/air surface tension depends on a rather complicated manner of salt composition and points to the importance of ion cooperativity. In this short article, we include the selective binding of anions over cations at interfaces (as revealed from molecular dynamics simulations, spectroscopic measurements, and Record's analysis of the surface tension data) and the anion–cation association (based on the observation of matching water affinity) in a simple theoretical model to understand salt effects on surface tension. The introduction of the surface effect and ion association provides a qualitative explanation of the experimental data, in particular, the strong anion dependence of the cations' rank according to their ability of increasing water surface tension. We hope that the physical insight provided by this study can be used to point to new directions for more detailed studies.

1. INTRODUCTION

How electrolytes, including common inorganic salts, affect liquid water properties has been the subject of many experimental and theoretical studies.^{1–25} The thermodynamics of electrolyte solutions were shown to heavily depend on the type of salts, and various trends were identified.^{1–15} One of the well-known effects of salts on liquid water is their alteration of the water/air surface tension, which is commonly related through the cavity term to their effects on the solvation of other solutes. Following the pioneering work of Franz Hofmeister,⁶ cations and anions are arranged in the so-called Hofmeister series. The ions according to their believed ability to change water structure were classified into kosmotropes, which stabilize and salt-out proteins and are often referred to as water structure makers, and chaotropes, which are thought to break water structure and help salt-in proteins (as well as destabilize the folded proteins).^{1–3,16–18} Most of the common salts, unless at very low concentrations, increase water/air surface tension²⁶ and decrease the solubility of hydrocarbons in water.²⁷ Their effects on water/oil interfacial tension are more complicated but are generally in accordance with their effects on proteins and many other macromolecules.²⁸ Namely, kosmotropes tend to increase and strong chaotropes

(such as KI) decrease the oil/water interfacial tension. Their effects on the solubility of other organic compounds are more complicated and largely dependent on the properties of the solutes, for example, whether it is an acid, a base, an amine, or an acetone.²⁷

The effects of anions on protein solubility and structure as well as a number of other solution properties normally appear to be stronger than those of cations and more importantly, follow more strictly the ranking order $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$, listed here in the order of decreasing ability of salting out proteins or enhancing water surface tension.^{24,26} The rank of the cations, however, is noticeably less strictly followed. One commonly cited peculiar case is Li^+ , which for common salts, is quite often out of sequence. In fact, the entire ranking order for alkali ions can be altered as a result of the change of the counterion in the solution. For example, when ranked by their capability of increasing water/air surface tension²⁶ and when the counterion is Cl^- , the cation

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ranking order is $\text{Na}^+ > \text{K}^+ \sim \text{Li}^+$. When the counterion is SO_4^{2-} , the order becomes $\text{Li}^+ > \text{Cs}^+ > \text{Na}^+ > \text{K}^+$, and for iodide it is $\text{K}^+ \sim \text{Na}^+ > \text{Li}^+$. These results indicate that counterions play an essential role when how cations affect water properties is evaluated. Such an ion-specific counterion effect has also been found in the binding of ions to proteins, micelles, and water/air interfaces.^{13,29–31} All these studies point to the importance of ion cooperativity and maybe ion-pairing in solutions.^{22,32}

For ion-pairing and association, Collins⁴ proposed a law of matching water affinities, which provides a relationship between the tendency of oppositely charged ions to associate in aqueous solutions and their absolute hydration free energies. The model has successfully explained a large variety of phenomena. Extensive computational studies of pairing of ions have been performed, and the results were shown to be generally consistent with Collins' proposal (for example, ref 30). Recently, a simple continuum dielectric extended Debye–Huckel model was used to explain the deduced matching water affinity phenomena.³³ In this model, the change of the solvation environment of smaller ions by the pairing of larger ones prevent the strong association of the two when their sizes (or solvation free energy) are largely different. With more molecular details, earlier dielectric spectra measurements of inorganic salt aqueous solutions were explained by ion associations involving species of contact, single solvent separated, and double solvent separated ion pairs in which most or part of the solvation shell is intact in ion association.²⁹ The effects of cation–anion size difference on their association in molecular simulations were investigated in the companion paper, and it was found that ions of same sizes are more likely to form contact ion pairs (CIP) than ions of different sizes.

From another aspect, using classical molecular dynamics simulations, Jungwirth and Tobias studied the ion distributions at water/air interfaces for inorganic salt solutions.^{13,34} The predictions of these theoretical studies were subsequently verified by the experiments of Saykally and Petersen.³⁵ It was concluded from these investigations that anions, especially the large and highly polarizable ones, are preferred over cations at interfaces. Different proposals were invoked to explain this phenomenon, which included size effects and polarizability. The enhancement of the anion accumulation at interfaces with the introduction of polarizability is in line with Ninham's argument that dispersion forces play essential roles in explaining the Hofmeister series for various systems.⁶ It is important to note here that although polarizability does enhance the selective surface binding of anions over cations, the nonpolarizable model itself is already capable of producing such an effect,³⁶ as tested and discussed in more detail in the companion paper.

Recently, Record and Pegram^{26,37} performed an elegant analysis on the effects of inorganic salts on water/air surface tension. They showed that the distributions of ions are in general agreement with MD simulations: chaotropic anions are enriched, and kosmotropic ones are depleted at such surfaces. They also compared the difference between water/air and water/protein interfaces and suggested that the salting-in/salting-out effects of the cations and anions correlate well with their preferred binding/exclusion at the interfaces. In their study, the preferred binding data were obtained for each cation or anion, and the averaged values over a number of systems with varied counterions were calculated. It is easily seen that the surface adsorption for the same anion can vary greatly when the counter positive ion is changed. Such big differences among the adsorption data again suggest a strong dependence of the anions (cations) on their counterions and are still waiting for explanation.

We introduce in this article a model for the electrolyte effect on surface tension, which unifies the above-mentioned physical properties including the differences in anion and cation surface distribution and the ion-pairing effect (which are investigated by molecular dynamics simulations in the companion paper). We also introduce in the Supporting Information a simple model to rationalize the matching of the solvation free energy effect in ion-pairing. The physical reasoning and thus the results yielded by such a model is similar to that of ref 33, although the derivations are different. Because of the complexity of the problem and the difficulties in obtaining related interacting parameters, we focus on a qualitative explanation of the trend existing in the experimental data.

The article is organized as follows: we presented the simple theory for surface tension in section 2, and in section 3, we give the results calculated from the theory and provide an explanation for the experimental results of the salt effects on surface tension. We also compare the different trends in salt osmotic coefficients and their effects on surface tension. The results are summarized and further discussed in section 4.

2. THEORY

2.1. Simple Theoretical Model for the Effects of Inorganic Salts on Surface Tension. As mentioned earlier, Record and co-workers performed a very insightful analysis of the surface tension data for common salt solutions. In their analysis, the Guggenheim approach was used, and the change of surface tension was related to ion surface adsorption by^{26,37}

$$\left(\frac{d\gamma}{dm}\right)_{\text{G-R}} = -\frac{RTb_w^\sigma\nu}{m_w}(1 + \epsilon^b)\left(\frac{\nu_1K_{p,1} + \nu_2K_{p,2}}{\nu} - 1\right) \quad (1)$$

where R is the gas constant, T the temperature, m_w the molality of water, and b_w^σ the number of water molecules per surface area at the surface. In this equation, $1 + \epsilon^b$ is the factor that converts the concentration derivative to an activity derivative, $\nu = \nu_1 + \nu_2$ is the number of ions per formula unit of the salt, and K_p is the partition coefficient of the ions. The subscript G–R stands for the Guggenheim type of treatment by Record and co-workers.

Using this relationship (eq 1), adsorption of both cations and anions at the interface was investigated based on known surface tension data.²⁶ The results, which vary significantly with the counterions, were averaged for each individual ion and show trends that match their overall effects on surface tension as well as on the solvation of proteins. It was shown that, consistent with MD simulations and experimental studies, anions have a stronger tendency to populate at the interface. In this analysis, the cooperativity between anions and cations was not discussed. However, from both experimental osmotic coefficient and surface tension data and from spectroscopic observations,³² ion cooperativity appears to play a very important role in determining thermodynamic and dynamic properties of electrolyte solutions. For example, in Figures 1a and 2a, we summarize some osmotic coefficient and surface tension data (the experimental data and associated errors are further summarized and analyzed in the Supporting Information). It is clearly seen that the effects of salts on these properties cannot be simply treated as the simple summation of the separate effects of composing anions and cations.

To provide an explanation for the experimental data, we introduce the following simple and speculative model that includes

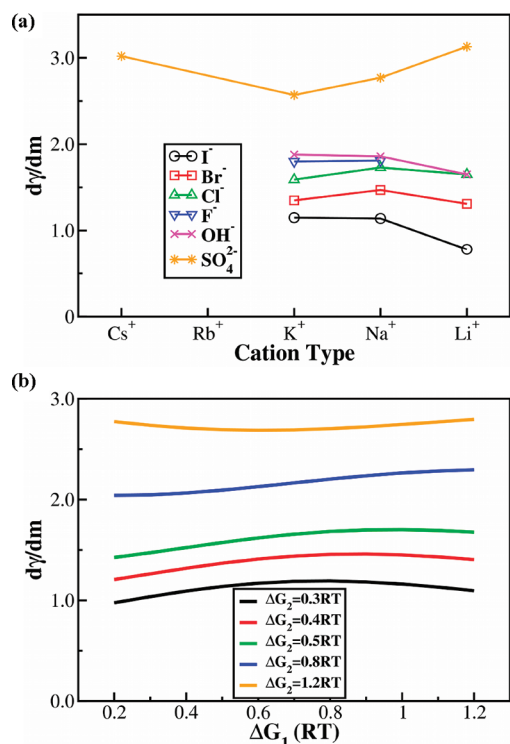


Figure 1. (a) Experimental results (from ref 26) of the salt effect on water surface tension. The curves are used to guide the eyes. For comparison, data for sulfate are also shown. (b) The calculated water surface tension increment (using eq 8, with $A = 2 \text{ dyn} \cdot \text{kg}/(\text{mol} \cdot \text{cm})$, $\lambda = 1$, $B = 1/(k_B T)^2$) showing the dependence of the salt effect on the ΔG values of composing ions. Each curve represents the anion with the indicated ΔG_2 value, and the abscissa is for the ΔG value of the corresponding cations.

ion cooperativity and the effects of an effective surface potential, the latter being used to account for the differentiated surface adsorption of the positively and negatively charged ions. We emphasize here that in this study the surface potential (for more discussions see, for example, ref 38) is an effective one that is used to account for the preferred surface binding of negatively charged ions. First, to the zeroth-order approximation and neglecting the difference brought in by the change of the charge sign, we rewrite eq 1 as

$$\left(\frac{d\gamma}{dm}\right)_{G-R} = -\frac{RTb_w^\sigma \nu}{m_w} \left(\frac{\nu_1 e^{-\beta(\Delta G_1 + \phi q_1)} + \nu_2 e^{-\beta(\Delta G_2 + \phi q_2)}}{\nu} - 1 \right) \quad (2)$$

where $e^{-\beta(\Delta G_i + \phi q_i)}$ in eq 2 is used instead of the $K_{p,i}$ in eq 1, and recognize that ΔG_i bears the meaning of the free energy change associated with an ion moved from the bulk to the surface. In the above equation, ϕ is the effective surface potential that leads to the different surface distributions of positively and negatively charged ions, as stated above. Next, we introduce a term that is a result of the differentiated surface distributions between positive and negative charges, which gives a surface charge density Q at the very top layer of the interface and is in the same spirit as that in the Record treatment.²⁶

$$Q = [m]d\nu_1 q_1 e^{-\beta(\Delta G_1 + \phi q_1)} + [m]d\nu_2 q_2 e^{-\beta(\Delta G_2 + \phi q_2)} \quad (3)$$

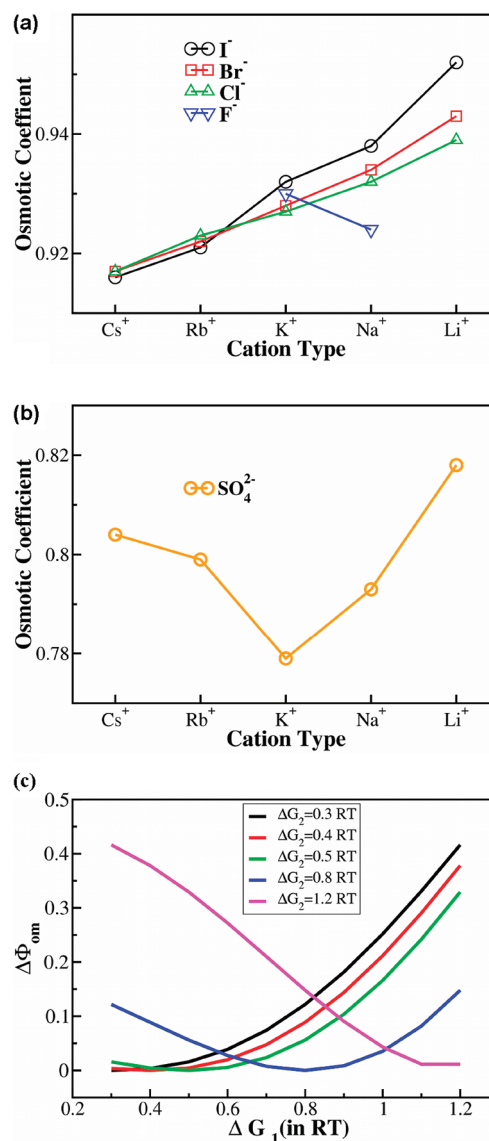


Figure 2. (a) Experimental results on the osmotic coefficients of various inorganic salts (taken from ref 40). (b) For comparison, data for sulfate are also shown. (c) The calculated values of $\Delta\Phi_{om}$ (using eq 9 and $D = 1$). Each curve represents the anion with the indicated ΔG_2 value, and the abscissa is for the ΔG value of the counter cations.

In eq 3, d is the thickness of the surface of interest and brings an additional change to the total surface energy of $Q\phi$ per surface area and may be approximated, following terms given in eq 1 (see also ref 26), by

$$d \approx \frac{b_w^\sigma}{m_w}$$

Next, the effects of ion-pairing, which are expected to reduce the absolute value of Q , are considered. The resulting Q is thus a competition between charge differentiation at the interface and ion-pairing. In the Supporting Information, we provide a simple rationale for the observations consistent with the rule of matching water affinities and show that probabilities of ion association can show a maximum when the solvation energies of the cation and the counterion are close to each other. In this article, we use the empirical eq. S8 (see Supporting Information) to

account for the effects of ion-pairing in reducing the surface net charge,

$$Q = \{[m]d\nu_1q_1 e^{-\beta(\Delta G_1 + \phi q_1)} + [m]d\nu_2q_2 e^{-\beta(\Delta G_2 + \phi q_2)}\} \\ (1 - \lambda e^{-B(\Delta G_2 - \Delta G_1)^2}) \quad (4)$$

Now, adding together $(d\gamma/dm)_{G-R}$ given by eq 2 and the additional contribution resulted from $d(Q\phi)/dm$, making a Taylor expansion, and keeping only the linear term of $\beta\phi q_1$ gives

$$e^{-\beta(\Delta G_1 + \phi q_1)} \approx e^{-\beta\Delta G_1} (1 - \beta\phi q_1) \quad (5)$$

and one finally reaches the following expression for $(d\gamma)/(dm)$:

$$\frac{d\gamma}{dm} = -\frac{RTb_w^\sigma}{m_w} \left\{ \frac{\nu_1 e^{-\beta\Delta G_1} + \nu_2 e^{-\beta\Delta G_2}}{\nu} - 1 \right\} \\ + \frac{b_w^\sigma}{m_w} \{2 - \lambda e^{-B(\Delta G_2 - \Delta G_1)^2}\} \{q_1 \nu_1 e^{-\beta\Delta G_1} \\ + q_2 \nu_2 e^{-\beta\Delta G_2}\} \phi \quad (6)$$

For the systems that are considered in this article, $q_1 = -q_2 = e$, where e is the magnitude of the charge of an electron, eq 6 is reduced to

$$\frac{d\gamma}{dm} = -\frac{RTb_w^\sigma}{m_w} \{e^{-\beta\Delta G_1} + e^{-\beta\Delta G_2} - 2\} \\ + \frac{b_w^\sigma e \phi}{m_w} \{2 - \lambda e^{-B(\Delta G_2 - \Delta G_1)^2}\} \{e^{-\beta\Delta G_1} - e^{-\beta\Delta G_2}\} \quad (7)$$

We finally write

$$\frac{d\gamma}{dm} = -A \{e^{-\beta\Delta G_1} + e^{-\beta\Delta G_2} - 2\} \\ + A \frac{e\phi}{RT} \{e^{-\beta\Delta G_1} - e^{-\beta\Delta G_2}\} \{2 - \lambda e^{-B(\Delta G_2 - \Delta G_1)^2}\} \quad (8)$$

with $A = (RTb_w^\sigma)/(m_w)$. In the following section, we will use eq 8 to discuss qualitatively the dependence of surface tension on ion solvation energies.

3. RESULTS

3.1. Salt Effects on Water Surface Tension. The physical meaning of eqs 7 and 8 is easy to understand: the first term in both equations comes from the (direct) interaction of the two species of ions (anions and cations) with water, and the second term is from the different distributions of positively and negatively charged particles. If the net surface charge is positive, the surface tension is further increased, and when it is negative, the net charge itself has an adverse effect on the surface tension increment. This surface charge effect is reduced by ion-pairing, which appears in eq. S8 of the Supporting Information in a manner of matching water affinity (see also ref 33). The consequences of these equations are also quite obvious, which help further the classification of salts based on their effects on liquid water. For example, four different limiting scenarios (in terms of solvation of anions and cations: strong–strong, weak–weak,

Scheme 1. Classification of Cations and Anions Based on Their Solvation Energy and the Resulting Effects on Water Surface Tension and Osmotic Coefficient^a

	Strongly hydrated	Weakly hydrated	
Ion pairing	Strong	Weak	
Os. Coef.	Small	Large	Strongly hydrated
$d\gamma_i/dm$	+++	++	
$d\gamma_s/dm$	+	-	
$d\gamma/dm$	++++	+	Cation
Ion pairing	Weak	Strong	
Os. Coef.	Large	Small	Weakly hydrated
$d\gamma_i/dm$	++	+	
$d\gamma_s/dm$	++	+	
$d\gamma/dm$	++++	++	

^a γ_i indicates the contribution from individual ions, γ_s is the contribution of the surface charge distribution to the surface tension, and γ is the summation of the former two. The number of + is used to indicate the magnitude of the surface tension increasing effect.

strong–weak, and weak–strong) are given in Scheme 1 and described below.

First, we note that strongly solvated ions (e.g., those with high charge densities; see ref 39 for a survey of data) tend to be buried in the bulk water and strongly increase surface tension (the first terms in eqs 7 and 8, and the opposite is true for weakly solvated ions; see below). However, the combined effects of anions and cations are dependent on specific ion properties. In particular, ion-pairing is prominent for both weak–weak and strong–strong combinations, following the rule of matching water affinity, and can either help increase or decrease the surface tension, depending on the relative solvation energy and the net surface charge resulting from the solvation difference. The combination of weakly solvated anions and strongly solvated cations results in a negative net charge at the interface, and the surface tension increment would be smaller than the opposite combination (strongly solvated anions and weakly hydrated cations). For the latter, although the individual ions affect the surface tension to a lower extent than when both ions are strongly solvated, the higher surface adsorption of positive charges and weak compensating effects from the strongly solvated anions results in a positive net surface charge. The positive net charge thus lends such a salt strong effect of enhancing surface tension.

Lastly, for systems with both weakly solvated anions and cations (e.g., KI), although the individual ions tend to have a small effect on surface tension, the strong ion-pairing effects of cations reduce the surface adsorption of anions and could result in an even larger surface tension than the combination of a strong cation and a weak anion, such as LiI. As a result of such a balance of different effects, the increment of surface tension by different combinations of ions written as (anion solvation energy, cation solvation energy) roughly follows a trend: (strong, strong) \sim (strong, weak) $>$ (weak, weak) $>$ (weak, strong).

In principle, the balancing between the different effects mentioned above leads to a quite complicated situation in the intermediate range of solvation energies (e.g., chlorides and bromides). For example, for chlorides, the individual effects of the counterions on surface tension decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$, following the trend of decreasing solvation energy, whereas the strongest ion-pairing occurs in the middle of the series (the strongest ion-pairing of Cl^- likely

occurs with Na^+ or K^+). The corresponding experimental data was analyzed in the Supporting Information (see Table S1). This competition among the different effects yields a maximum of the $d\gamma/dm$ value in the middle of the alkali series. Such a phenomenon can be seen in Figure 1a for experimental values and in Figure 1b for theoretical results obtained using eq 8.

For the reasons discussed above, the exact prediction of the salt effect on surface tension can be nontrivial. However, a few rules can be obtained and are summarized below. For the same anion, the ranking of cations shows a maximum in its series, the position of which depends on the counterion and roughly follows the rule of matching affinity. If one treats the solvation energy of cations as a continuous function, as the solvation energy of the anion increases, the position for the maximum surface tension shifts gradually from strongly to weakly solvated cations (from the available experimental data, the maximum for iodide is at K; for bromide, between K and Na; and for chloride, between Na and Li). However, for every given alkali cation, the ranking order of the anions remains the same, $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$. These observations again show that cations and anions affect surface tension in quite a different manner, as a result of their different behavior on the surfaces. As discussed below, this difference between positively and negatively charged ions is largely absent in their effects on bulk water activity due to the absence of interfaces, which distinguish ions according to the sign of their charges.

3.2. Simple Argument on Osmotic Coefficient of Salts. Ion-pairing is also expected to affect the water activity coefficient and the osmotic coefficient but in a manner different from the effects on surface tension. Strong ion association reduces the effective number of free nonsolvent particles and is expected to result in a smaller osmotic coefficient.⁴⁰ As shown in Figure 2a, the osmotic coefficient of salts containing Cl^- , Br^- , or I^- increases when the hydration energy of the counterion increases (decrease of the cationic radius). The trend is the opposite for F^- (although there is a lack of data for this latter case. For OH^- , the ranking order of osmotic coefficient is $\text{CsOH} > \text{RbOH} > \text{KOH} > \text{NaOH} > \text{LiOH}$, also opposite to iodides⁴⁰). For comparison, experimental data for SO_4^{2-} are given in Figure 2b.

Deriving a formula for activity coefficients for electrolytes is a difficult task. Various empirical models exist in the literature.⁴⁰ Here, we try to show that a simple qualitative correlation between ion-pairing and the salt osmotic (or water activity) coefficient might exist. For this purpose, we investigate the usage of the following simple function:

$$\Delta\phi_{\text{om}} = D\{\Delta G_1 + \Delta G_2\}\{1 - \lambda e^{-B(\Delta G_2 - \Delta G_1)^2}\} \quad (9)$$

where D is a constant, and other parameters are defined the same as in eq 8. In this equation, the term $\Delta G_1 + \Delta G_2$ is used to approximate the effect that strongly solvated ions tend to have a stronger (direct) effect on water (and thus are prone to increase the salt osmotic coefficient), and the term $\{1 - \lambda e^{-B(\Delta G_2 - \Delta G_1)^2}\}$ is used to include the effect of ion-pairing, which tends to lower the osmotic coefficient, as mentioned above.

Examples of the results from eq 9 are given in Figure 2c, the trend of which shows a reasonable resemblance with the experimentally observed trend in the cation/anion dependence of the osmotic coefficient in salt solutions. (The data are given in Figure 2a for 0.1 M salt concentrations and are taken from ref 40; the data of 1 M salt concentrations are of the same trend.) Both the theoretical curve for $\Delta\phi_{\text{om}}$ and the experimental data for the

salt osmotic coefficient show that for highly solvated anions, the order of decreasing osmotic coefficient is the same as that of increasing atomic mass, while for weakly solvated anions, the order is reversed. However, if the cation remains the same, one sees the opposite ranking order of anions for Li^+ and Cs^+ as an example. This phenomenon is easily seen by the crossing of curves for activity ($\Delta\phi_{\text{om}}$) as a function of the solvation energy of cations drawn for different anions.

On the basis of the argument given above, the explanation of the rather complicated trends in salt osmotic coefficients relies on two contributions: first, the strongly solvated ions tend to have a large osmotic coefficient. However, ion-pairing, which is the most probable for similar but oppositely charged ions (rule of matching water affinity) reduces the osmotic coefficient. As a result, the species with both cations and anions of very different solvation energy tend to have larger osmotic coefficients than those formed by ions with matching water affinities. This effect is the same as that seen in surface tension: strong ions, in general, tend to increase surface tension, and ion-pairing reduces such an effect. The difference between salt effects on osmotic coefficients and surface tension is that anions and cations affect the former in the same way but they affect the latter differently: weakly hydrated anions tend to *decrease* but weakly hydrated cations tend to *increase* the surface tension (ca., eq 8). As a result of this difference, although the ranking order of anions in increasing surface tension remains the same when the counterion is changed, their ranking order according to the osmotic coefficient changes with the cation. The arguments given above for both salt effects on osmotic coefficient are also summarized in Scheme 1.

4. DISCUSSION

In this short article, we tried to rationalize the experimentally observed trends on how different electrolytes affect the water/air surface tension. The models used in this study are rather primitive but do provide simple explanations of several well-known phenomena, some of which have been quite perplexing. In this treatment, we also provided a simplified argument for the rule of water affinity matching and combine this argument with the differentiated cation/anion surface distribution to rationalize the observations on how common inorganic salts increase the water/air surface tension. The inclusion of ion pairing also allows a consistent qualitative explanation of osmotic coefficients of various salts.

For surface tension, the observed salt effects depend on two interplaying factors: the interactions of individual ions with water and the net surface charge as a result of the different propensities of negatively and positively charged ions to adsorb at the surface. The weakly hydrated cations tend to populate at the surface, which increases the surface tension. The enrichment of anions at the interface has an opposite effect. Furthermore, ion-pairing, the extent of which depends on the matching between the solvation energy (which increases roughly reversely to the ion sizes) of the oppositely charged ions, reduces the net surface charges. Therefore, strong ion-pairing has an effect of increasing the surface tension if the anion is weakly hydrated (e.g., I^-). The effect of ion-pairing when the cation is weakly hydrated is to reduce its effect of increasing surface tension. Therefore, as mentioned above, the order of surface tension follows roughly a trend: (strong, strong) \sim (strong, weak) $>$ (weak, weak) $>$ (weak, strong) in the combination of (solvation of anion, solvation of cation).

However, as discussed earlier, strong ion-pairing always reduces salt osmotic coefficients (for ions with matching water affinities, either both are strongly hydrated or both are weakly hydrated) so that the osmotic coefficients are the smallest for (strong, strong) and (weak, weak) systems. As a result, one would expect to observe different trends in surface tension and osmotic coefficient data, e.g., compared to the LiI solution of the same salt concentration, the KI solution has a higher surface tension (due to the higher population of K^+ than Li^+ at the interface) and a smaller osmotic coefficient. Furthermore, following a similar argument, a weak anion/strong cation and a strong anion/weak cation, due to their similar individual ion water interactions (the sum of the effects of cation and anion) and similar ion-pairing, would have comparable effects on water activity, but they would affect surface tension very differently and have anions and cations enriched at the surface, respectively. Therefore, the former (weak anion/strong cation) increases surface tension to a noticeably lower extent than the latter.

For reasons discussed above, different salt-dependence is observed for surface tension and osmotic coefficients. In Figure 1, one sees that for the same cation, the surface tension effect of the salts decreases with the decrease of solvation energy of the anion, and there is no cross between different curves (representing different anions). Whereas, for the osmotic coefficients (Figure 2), the curves representing different anions do cross, with maximum values shown for the combinations of strong anion/weak cation and weak anion/strong cation (the least ion-pairing). On the basis of these arguments, when ion cooperativity is included, the lithium ion does not behave more strangely than other alkali ions. Its off-sequence behavior in chlorides and bromides is a result of different ion-pairing between cations and the Cl^- or Br^- . In fact, all of the following ranking orders, $Li^+ > Na^+ > K^+$, $Na^+ > Li^+ > K^+$, $K^+ > Li^+ > Na^+$, or $K^+ > Na^+ > Li^+$, can be observed for its effect on surface tension, depending on what the counterion exists as in the solution.

For the explanation of salt effects on water surface tension, we introduced in the present study additional effective surface potential terms in the simple continuum model to account for the difference in the solvation of cations and anions of the same magnitude of charges and vdW radii (this difference between anions and cations had been discussed extensively in the literature and was also clearly seen from MD simulations performed for hypothetical ions in the companion paper, although, to the best of our knowledge, had not been considered before in treating water surface tension). The continuum type treatment in this study provides a self-consistent description of the different solvation and bulk/surface partition of cations and anions. This description then led to the very simple understanding of the complex effects of inorganic salts on water/air surface tension as well as on water activity coefficients. The usage of the continuum mode not only leads to an explanation for the perplexing experimental data in simple physical terms but also provides guidance for more detailed studies, such as molecular dynamics simulations and, hopefully, more quantitative experimental measurements.

A number of assumptions were involved in this treatment. These include, most noticeably, the continuum model used in ion solvation and ion–ion interactions, the assumed proportionality between the ionic desolvation energy, the bulk-surface transfer energy, and the use of an effective surface potential in treating the different distribution of positive and negative ions. These assumptions make the theory highly approximate and qualitative rather than quantitative. Nevertheless, simple explanations were

obtained for various phenomena involving the complex behavior of complex salt solutions. We hope that careful analyses and understanding of experimental data can provide new physical insights and help unveil the relationship between ion-pairing and the thermodynamics measurement and thus bring about new opportunities for the understanding of the latter in molecular terms. Detailed molecular dynamics simulations will be used to further test the proposals involving different ion pairs and to understand the physical reasons for their formation. For example, in recent molecular studies and the previous theoretical analysis, it was shown that the intrinsic charge distribution in the water models used is responsible for the partially ordered water orientation at water surfaces⁴¹ and the preferred binding of anions over cations at these surfaces.⁴² Calculations of spectroscopic properties such as that performed in ref 43 are expected to be able to further clarify the molecular detailed effects of ions/counterions on water structure and dynamics.

In summary, although the models are crude and the uncertainties of experimental results are large, the analysis of the experimental data did show the importance of ion cooperativity in understanding the osmotic coefficients of salts and their effects on water surface tension. As discussed earlier, ion cooperativity was seen in a number of simulation studies of ion distributions and spectroscopic study of ion hydration. It was also observed in salt interactions with many other agents including proteins and is expected to play an important role in understanding the salt aqueous solutions and their interfaces. In these more complex systems for which the solute properties are of the main interest, not only the law of matching water affinity but also the law of matching solute affinities might play essential roles and should be analyzed accordingly. We expect the latter to govern the direct binding of the cosolute/cosolvent to the solute of interest, and the ion-pairing might function as a secondary mechanism to the solvation effects. We also expect that such a study can stimulate new experimental and theoretical studies on ionic aqueous solutions that help connect their thermodynamics properties with their structural and dynamics information.

■ ASSOCIATED CONTENT

S Supporting Information. Explanations of the variance in experimental data and of the rule of matching water affinity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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