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Dispersion Self-Free Energies and Interaction Free Energies of Finite-Sized Ions in Salt Solutions

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The role for many-body dipolar (dispersion) potentials in ion–solvent and ion–solvent–interface interactions is explored. Such many-body potentials, accessible in principle from measured dielectric data, are necessary in accounting for Hofmeister specific ion effects. Dispersion self-energy is the quantum electrodynamic analogue of the Born electrostatic self-energy of an ion. We here describe calculations of dispersion self-free energies of four different anions (OH[−], Cl[−], Br[−], and I[−]) that take finite ion size into account. Three different examples of self-free energy calculations are presented. These are the self-free energy of transfer of an ion to bulk solution, which influences solubility; the dispersion potential acting between one ion and an air–water interface (important for surface tension calculations); and the dispersion potential acting between two ions (relevant to activity coefficient calculations). To illustrate the importance of dispersion self-free energies, we compare the Born and dispersion contributions to the free energy of ion transfer from water to air (oil). We have also calculated the change in interfacial tension with added salt for air (oil)–water interfaces. A new model is used that includes dispersion potentials acting on the ions near the interface, image potentials, and ions of finite size that are allowed to spill over the solution–air interface. It is shown that interfacial free energies require a knowledge of solvent profiles at the interface.

1. Introduction

Colloidal and model systems in membrane biology can often be described surprisingly well using electrostatic mean-field double-layer theories.¹ The only ionic solution property included in this theory is the ionic charge. Even with extensions to include ion size and other parameters there is nothing in the theory that can explain an almost universal, systematic (Hofmeister) ion specificity. Problems such as, for example, the change in surface tension with added salt, bubble–bubble interactions, and a large number of phenomena that occur in salt solutions depend strongly on the choice of ion pair. They cannot be explained by electrostatic theories however many extra parameters are introduced. These so-called Hofmeister effects are very well-known in the biological sciences. They have remained a mystery for more than 100 years.^{2,3} An important source of ion specificity missed in the classical double-layer theory is the ionic dispersion potential that acts between ions and between an ion and an interface. Ions have in general a different polarizability than the surrounding water (specific for each ion) and, hence, experience very specific dispersion potentials near an interface.^{4,5} At high salt concentrations, where electrostatic potentials become more and more screened, these ionic dispersion potentials dominate the interaction completely. They have not seemed to be important and have not been taken into account in the past. This is because classical theories of interactions such as the Derjaguin–Landau–Verwey–

Overbeek theory of colloid stability treated electrostatic forces via a (nonlinear) double-layer theory and took quantum electrodynamic dispersion interactions into account via the (linear) Lifshitz theory or its extensions. This separation and treatment at different levels of the electrostatic and electrodynamic forces violates both the Gibbs adsorption equation and the gauge condition on the electromagnetic field. The theory is then incorrect.⁴ When the error is corrected, the dispersion forces are seen to have a much more important role and are highly specific.

We have earlier demonstrated the necessity of taking these ionic dispersion potentials into account in calculations that involve interfaces in salt solutions.^{6–12} More recently, extensions have been made to include consistently the dispersion potential that acts between two ions in hypernetted chain (HNC) calculations of bulk electrolyte activity coefficients¹³ and in simulations of the colloid–colloid potential of mean force.¹⁴

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Earlier work^{6–12} that investigated ion specificity did not take care of ion size properly in the calculation of ionic dispersion potentials. We will demonstrate in section 2 how a theory developed by Mahanty and Ninham¹⁵ can be used to calculate dispersion self-free energies of finite-sized ions in water. We will illustrate this with four different anions (OH^- , Cl^- , Br^- , and I^-). Three different examples are considered: the self-free energy of a single ion in water (which influences solubility); the ionic dispersion potential acting between an ion and an air–water interface (important for interfacial tension calculations); and the ionic dispersion potential acting between two ions in water (relevant for activity coefficient calculations). As already remarked, and we wish to emphasize this, earlier estimates of the free energy of ion transfer from water to air (oil) or for considerations of transport across membranes have neglected the dispersion free energy contribution. We demonstrate in section 3 that this ion-specific contribution can be of the same order of magnitude as the electrostatic Born contribution. We shall also investigate ion–interface and ion–ion dispersion potentials in some detail. In section 4 we finally use the calculated ionic dispersion potential acting between ions and the air (oil)–water interface to evaluate the interfacial tension change with added salt. A new model is used that includes dispersion potentials acting on the ions near the interface, image potentials, and ions of finite size that are allowed to spill over the solution–air interface.

2. Theory

The concept of dispersion self-energy in atomic systems was developed by Mahanty and Ninham.¹⁵ It is a quantum electrodynamic dipolar polarization analogue of the Born electrostatic energy of an ion. We will here give the corresponding result for ionic systems in water at finite temperatures. The explicit formulas of Mahanty and Ninham were derived on the assumption that the atomic system is isotropic and that the radial dependence of the polarization cloud around a molecule can be approximated with a Gaussian function. Then the position (\vec{r}) and frequency (ω) dependent polarizability, $\alpha(\vec{r}, \omega)$, has the form

$$\alpha(\vec{r}, \omega) = \alpha(\omega) f(r) \quad (1)$$

$$f(r) = \frac{1}{\pi^{3/2} a^3} e^{-r^2/a^2} \quad (2)$$

where a , the width of the Gaussian, is a measure of the radius of an atomic system. We will here assume that the same approximations can be made for the ions we consider in water. The water is treated within the primitive model as a dielectric continuum; that is, we ignore local water structure and any explicit inclusion of water molecules except through the macroscopic dielectric susceptibility as a function of frequency. (i.e., The theory is at exactly the same level of approximation as the electrostatics.) It is straightforward to extend the result of Mahanty and Ninham to take into account the effect of the surrounding media (here water) with the dielectric function $\epsilon_2(i\omega)$ and finite temperature T . The nonretarded self-free energy of an ion in water is then

$$F_s = \frac{4k_B T}{\sqrt{\pi} a^3} \sum_{n=0}^{\infty} \frac{\alpha^*(i\omega_n)}{\epsilon_2(i\omega_n)} \quad (3)$$

where k_B is Boltzmann's constant, a is the ion radius, and $\alpha^*(i\omega_n)$ is the excess polarizability of the ion in water at an imaginary frequency. The self-free energy is obtained as a summation over discrete frequencies ($i\omega_n$), and the prime on the summation indicates that the $n = 0$ term carries a weight of 1/2. We have assumed room temperature (293 K) throughout this work, which corresponds to a first nonzero frequency of 2.41×10^{14} rad/s. The self-free energy of an ion in water depends in this level of approximation on three quantities: the ion size, the excess ionic polarizability, and the dielectric function of water.

The dispersion self-free energy formalism can also be used to evaluate the dispersion interaction free energy acting on an ion in water a distance z from an interface between water and a second medium with dielectric function $\epsilon_1(i\omega)$. It is

$$F_{\text{ion-int}}(z) = \frac{B}{z^3} = \frac{-2k_B T}{z^3 \sqrt{\pi}} g(z) \sum_{n=0}^{\infty} \frac{\alpha^*(i\omega_n) \Delta_{12}(i\omega_n)}{a^3 \epsilon_2(i\omega_n)} \quad (4)$$

$$g(z) = e^{-z^2/a^2} \left(1 - \frac{a^2}{2z^2} \right) - \frac{\sqrt{\pi} z}{a} \text{erfc}\left(\frac{z}{a}\right) + \frac{\sqrt{\pi} a^3}{4z^3} \text{erf}\left(\frac{z}{a}\right) \quad (5)$$

$$\Delta_{12} = \frac{\epsilon_1(i\omega_n) - \epsilon_2(i\omega_n)}{\epsilon_1(i\omega_n) + \epsilon_2(i\omega_n)} \quad (6)$$

where B is the ion–interface dispersion coefficient and $\text{erf}(z/a)$ and $\text{erfc}(z/a)$ are the error function and the complementary error function, respectively. When we calculate the interfacial tension of electrolytes in section 4, we will consider ions that can spill over the interface. This means that we also need the dispersion interaction free energy acting on an ion in air (oil) a distance z from the interface. It is

$$F_{\text{ion-int}}(z) = \frac{B_2}{z^3} - \Delta F_s \quad (7)$$

$$B_2 = \frac{2k_B T}{\sqrt{\pi}} g(z) \sum_{n=0}^{\infty} \frac{\alpha^*(i\omega_n) \Delta_{12}(i\omega_n)}{a^3 \epsilon_1(i\omega_n)} \quad (8)$$

$$\Delta F_s = F_s(\text{water}) - F_s(\text{air/oil}) \quad (9)$$

where ΔF_s is the change in self-free energy when the ion is brought from water to air (oil). Here, we have assumed that the polarizability and ion size are the same in the air (oil) phase as they are in water. This is clearly not so, but we will still use this approximation for demonstration purposes. There will certainly be an additional change in the self-free energy as a result of the changes in ion polarizability and ion size that we neglect in this way.

For completeness, we will finally consider also two ions a distance r from each other interacting in bulk solution (this potential has recently been included by Kunz et al.¹³ in HNC calculations). The interaction free energy acting between the two ions is

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$$F_{\text{ion-ion}}(r) = \frac{A(r)}{r^6} = \frac{-6k_B T h(r)}{r^6} \sum_{n=0}^{\infty} \frac{\alpha_1^*(i\omega_n) \alpha_2^*(i\omega_n)}{\epsilon_2(i\omega_n)} \quad (10)$$

$$h(r) = \frac{1}{3} \prod_{i=1}^2 \left[\text{erf}\left(\frac{r}{a_i}\right) - \frac{2r}{\sqrt{\pi} a_i} e^{-r^2/a_i^2} \right] + \frac{2}{3} \prod_{i=1}^2 \left[\text{erf}\left(\frac{r}{a_i}\right) - \frac{2}{\sqrt{\pi}} \left(\frac{r}{a_i} + \frac{r^3}{a_i^3} \right) e^{-r^2/a_i^2} \right] \quad (11)$$

where A is the ion–ion dispersion coefficient and $i = 1, 2$ in general corresponds to two different ions (here we take two identical ions).

The dielectric function of water for frequencies below $\omega = 1.32 \times 10^{17}$ rad/s was obtained from tabulated real (n) and imaginary (k) optical constants¹⁶ (the imaginary part of the dielectric function is $\epsilon'' = 2nk$) and the use of a Kramers–Kronig relation according to

$$\epsilon_2(i\omega) = 1 + \frac{2}{\pi} \int_0^{\infty} dx \frac{x \epsilon''(x)}{x^2 + \omega^2} \quad (12)$$

For higher frequencies, we used a model dielectric function for water.¹⁷ The different frequency regimes also take (partial) account of water orientation and hydrogen bonding. The dielectric function of hydrocarbons can be modeled with a simple one-oscillator function,¹⁵

$$\epsilon_1(i\omega) = 1 + \frac{n^2 - 1}{1 + \omega^2/\omega_{uv}^2} \quad (13)$$

where we take the refractive index $n = 1.5$ and the resonance frequency $\omega_{uv} = 1.9 \times 10^{16}$ rad/s from Ederth.¹⁸ We will also briefly consider interactions near a gold–water interface. For that we need the dielectric properties of gold, which are obtained from experimental data.^{19,20}

It is fair to say that the ionic properties required for our calculations are not known in great detail. We assume that we can model the ionic excess polarizability with a single adsorption frequency (ω_1) for each species using the London approximation,

$$\alpha^*(i\omega) = \frac{\alpha^*(0)}{1 + \omega^2/\omega_1^2} \quad (14)$$

The excess polarizability is the excess compared to the polarizability of the surrounding water. A recent calculation by Jungwirth and Tobias²¹ of the ionic polarizability (chloride ion in water) suggests that there will soon be available better data for the polarizability of ions in water. However, the best we can do for now is to use estimated values for the radius, excess polarizability, and ionization potential (adsorption frequency) given in the literature.^{22,23} These data, which are in reasonable agreement with values

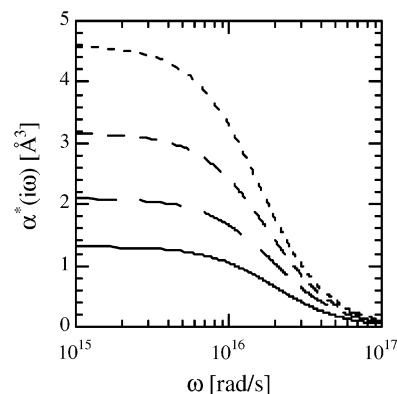


Figure 1. Excess polarizability of ions in water: OH[−] (solid line); Cl[−] (long-dashed line); Br[−] (dashed line); and I[−] (dotted line).

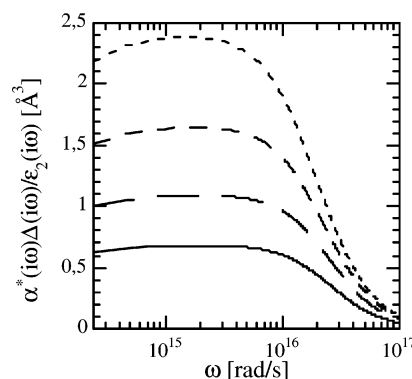


Figure 2. Frequency summand for the interaction free energy between an ion and an air–water interface: OH[−] (solid line); Cl[−] (long-dashed line); Br[−] (dashed line); and I[−] (dotted line). Shown from the lowest nonzero frequency in the frequency summation which at $T = 293$ K is 2.41×10^{14} rad/s.

Table 1. Ion Radius, Ionic Excess Polarizability, and Ionization Potential (Adsorption Frequency)^{22,23} Used in the Calculations of Dispersion Self-Free Energies and Interactions Free Energies

ion	radius [Å]	$\alpha^*(0)$ [Å ³]	adsorption frequency [rad/s]
OH [−]	1.33	1.31	2.00×10^{16}
Cl [−]	1.81	2.10	1.97×10^{16}
Br [−]	1.96	3.17	1.80×10^{16}
I [−]	2.20	4.60	1.59×10^{16}

obtained from refractive index data, are summarized in Table 1 for the four anions considered here (the ionization potential is not well-known but must be in the visible and before the plasma frequency). The available data will be sufficient to demonstrate how we can calculate self-free energies and interaction free energies of finite-sized ions in water. The frequency dependence of the excess polarizability of the four anions considered here is shown in Figure 1. We will first explore in what frequency range the excess polarizabilities and dielectric functions need to be well-known to be able to calculate the self-free energies and interaction free energies accurately. We show as an example the frequency summand for the interaction free energy between an ion and an air–water interface in Figure 2. The lower limit of the relevant frequency range is given by the lowest nonzero frequency in the frequency summation (at $T = 293$ K it is 2.41×10^{14} rad/s). By inspection of Figure 2 we see that the upper limit should be around 10^{17} rad/s. It is clearly not sufficient to know only the static excess polarizabilities.

We will explore in the next section how the difference in excess polarizability can give rise to highly ion-specific self-free energies and interaction free energies.

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Table 2. Dispersion Self-free Energy, Dispersion Self-Free Energy Contribution to the Energy of Ion Transfer, and Born Contribution to the Energy of Ion Transfer^a

anion	F_s (water) [kJ/mol]	ΔF_s (water to air) [kJ/mol]	ΔF_s (water to oil) [kJ/mol]	ΔE_{Born} (water to air) [kJ/mol]	ΔE_{Born} (water to oil) [kJ/mol]
OH ⁻	271	117	-13	516	226
Cl ⁻	169	74	-8	379	166
Br ⁻	182	83	-9	350	153
I ⁻	162	79	-9	312	136

^a The dispersion self-free energy of four anions in water obtained using eq 3 is shown in column 2. The dispersion self-free energy contribution to the energy of ion transfer from water to air is shown in column 3 (and from water to oil in column 4). We furthermore show the Born contribution to the energy of ion transfer from water to air (column 5) and from water to oil (column 6).

3. Numerical Results: Self-Free Energies and Interaction Energies

3.1. Self-Energies of Transfer. The self-free energies from eq 3 of four anions in water are given in Table 2. It can be seen that not only does the excess polarizability influence the self-free energy, but it also depends on the ion radius (a small ion radius is the reason behind the large value for the OH⁻ ion). The ion radius may also be hydrated differently especially near interfaces, so influencing the self-free energy further. The permeation processes by which an ion crosses phospholipid bilayers depends on the free energy of ion transfer. It is of interest to compare the dispersion contribution to the free energy of ion transfer from water to air (oil) with the corresponding contribution from the electrostatic Born energy. The Born energy to transfer an ion from water to air (oil) is²⁴

$$\Delta E_{\text{Born}} = \frac{e^2}{8\pi\epsilon_0 a} \left[\frac{1}{\epsilon_1(0)} - \frac{1}{\epsilon_2(0)} \right] \quad (15)$$

The corresponding dispersion contribution is obtained by subtracting the self-free energy in air (oil) from the self-free energy in water (eq 9). The result is summarized in Table 2. We can immediately see that the previously neglected dispersion self-free energy gives an important contribution. We would like to stress that by dispersion forces we mean the totality of forces with contributions from all frequencies, that is, permanent dipole–permanent dipole (collective many-body Keesom forces) and permanent dipole–induced dipole (Debye forces) as well as dispersion forces proper in visible and UV frequencies. The free energy of ion permeation is typically calculated as a sum of electrostatic, solvophobic, and specific (e.g., hydration) interactions.²⁴ It is clear that to improve earlier calculations of ion permeation one must also include the dispersion contributions.

3.2. Ion Interface Interaction Potentials. The ion–interface dispersion coefficient $B(z)$ and the ion–ion dispersion coefficient $A(r)$ are shown in Figures 3 and 4, respectively. The dispersion potentials acting on the four anions in water are highly ion-specific and follow a Hofmeister series with magnitudes in the order OH⁻ < Cl⁻ < Br⁻ < I⁻. For ion–interface separations that are large compared to the ion size, the B values shown in Figure 3 compare well with our earlier estimates that ignored ion size.⁶ However, it is the short-range behavior that is important, for example, in the evaluation of surface tension changes with added salt. Short-range ionic dispersion potentials and ionic self-energies depend both on ion size and excess polarizability. We have also calculated B values for ions in water near a hydrocarbon–water interface (using eq 13 for the dielectric function of

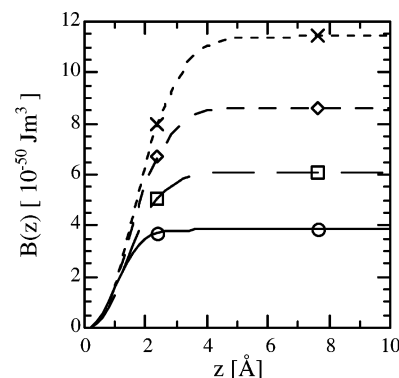


Figure 3. Ion–interface dispersion coefficient $B(z)$ as a function of distance to the air–water interface for four different anions: OH⁻ (○); Cl⁻ (□); Br⁻ (◇); and I⁻ (×).

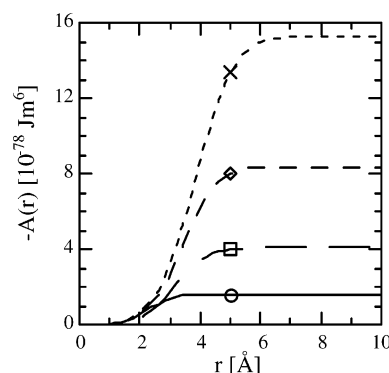


Figure 4. Ion–ion dispersion coefficient $A(r)$ as a function of distance between two ions for four different anions: OH⁻ (○); Cl⁻ (□); Br⁻ (◇); and I⁻ (×).

hydrocarbon). In this case, the dispersion interaction causes a weak attraction of the ions to the interface. Far from the interface, the B values approach the following values (in units of 10^{-50} J m^3): -0.6 (OH⁻), -1.0 (Cl⁻), -1.5 (Br⁻), and -2.0 (I⁻). The sign and magnitude of the ionic dispersion coefficient (B) near a hydrocarbon–water interface depends sensitively on the dielectric function of the hydrocarbon. If we instead take the refractive index $n = 1.43$ and the relaxation frequency $\omega_{\text{uv}} = 1.4 \times 10^{16} \text{ rad/s}$, we would find that the ionic dispersion interaction becomes weakly repulsive for all four anions. Just as for the spreading of oil on water, the matter is one of some delicacy—different frequency regions can make contributions of opposing signs. These reflect the different competing ordering processes induced around ions.²⁵ We have also calculated B values for ions in water near a gold–water interface. In this case, the dispersion interaction strongly attracts the ions toward the interface. Far from the interface, the B values approach the following

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Table 3. Surface Tension Change with Added Salt, Theoretical Result for the Air–Water Interface, and Theoretical Result for the Air–Water Interface when Ionic Dispersion Potentials Are Neglected^a

anion	theor $d(\Delta\gamma)/dc$ (air–water) [10 ⁻³ J m ³ mol ⁻¹ L]	theor $d(\Delta\gamma)/dc$ (no dispersion) [10 ⁻³ J m ³ mol ⁻¹ L]	exptl $d(\Delta\gamma)/dc$ (air–water) [10 ⁻³ J m ³ mol ⁻¹ L]	theor $d(\Delta\gamma)/dc$ (oil–water) [10 ⁻³ J m ³ mol ⁻¹ L]
OH ⁻	1.49	1.19	1.98	1.0
Cl ⁻	1.64	1.24	1.59–1.85	1.1
Br ⁻	1.75	1.25	1.36	1.0
I ⁻	1.86	1.27	1.16–1.24	0.98

^a The surface tension change with added salt at 1 M potassium based salt solutions (with the anions given in column 1). Theoretical and experimental⁶ results for the air–water interface are shown in columns 2 and 4, respectively. For comparison, we show the theoretical result for the air–water interface when ionic dispersion potentials are neglected in column 3 (these values are very similar to the result at the oil–water interface when ionic dispersion potentials are neglected). The theoretical result for one oil–water interface is shown in column 5. The properties of the anions are given in Table 1, and the potassium ion has an expected radius²⁰ of 1.38 Å (we neglect the ionic dispersion potential acting on the cation).

values (in units of 10⁻⁵⁰ J m³): -6.5 (OH⁻), -10.3 (Cl⁻), -14.9 (Br⁻), and -20.3 (I⁻). We have obtained similar results for ions near a mica–water interface. We have in exactly the same way used eq 7 to calculate the dispersion interaction acting on ions in air (hydrocarbon) near an air (hydrocarbon)–water interface. These potentials are required in the calculation of the interfacial tension of electrolytes that will be considered in the next section. It is true in general that the magnitude and sign of the interaction depend sensitively on the ionic excess polarizabilities, the frequency dependence of dielectric susceptibilities, and ion sizes.

4. Numerical Results: Interfacial Tension of Electrolytes

We now go a step further and combine our result with the theory for surface tension changes with added salt of Markin and Volkov. They included factors that allowed ions to spill over the interface and image interactions of finite-sized ions.²⁶ This theory is combined with our theory that includes ionic dispersion potentials⁸ (but is now extended to take finite size effects into account). We use these interaction potentials acting between a finite size ion and the air (oil)–water interface to evaluate the interfacial tension change with added salt. We will see that the result allows us to draw the substantial conclusion that a proper theory of interfacial tension due to dissolved salt requires the interfacial profile of the electrolyte.

The total energy of ion i with charge number z_i includes image (given by Markin and Volkov),²⁶ ionic dispersion, and electrostatic potentials:

$$F_i = F_{i,\text{image}}(z) + F_{i,\text{dispersion}}(z) + z_i e \phi(z) \quad (16)$$

The spatial distributions of the ions are given by the extended Poisson–Boltzmann equation

$$\frac{d^2 \phi}{dz^2} = \frac{-e}{\epsilon_0} \sum_{i=1}^2 z_i \exp\left[-\frac{F_i}{kT}\right] \quad (17)$$

where the dielectric constant takes the value $\epsilon_1(0)$ or $\epsilon_2(0)$ depending on the value of z . For boundary conditions, we assume that the potential and the electrostatic field are 0 far in the bulk solution. We can calculate the increment in the surface tension with added salt from

the Gibbs adsorption equation as

$$\frac{d\gamma}{dc} = \frac{-kT}{c} [\Gamma_1(c) + \Gamma_2(c)] \quad (18)$$

where the surface excess is

$$\Gamma_i(c) = c \int_{-\infty}^{z_G} \exp\left[-\frac{F_i}{kT}\right] dz + c \int_{z_G}^{\infty} \left\{ \exp\left[-\frac{F_i}{kT}\right] - 1 \right\} dz, \quad i = 1, 2 \quad (19)$$

The position of the Gibbs dividing surface (z_G) can be determined in a straightforward manner.²⁶ We assume it to be at 0 (it is different from 0 only at very high salt concentrations).

We consider four salts with potassium as the cation and the anions listed in Table 1. The potassium ion has an assumed radius²⁰ of 1.38 Å, and we neglect the ionic dispersion potential acting on the cation. The result is given in Table 3. We can see that there are important contributions both from image interactions and dispersion interactions. We consider the effect of image potentials and ions spilling over the interface separately in column 4 of Table 3. There is some small degree of ion specificity caused by differences in ion size. There is more ion specificity when we include ionic dispersion potentials. It seems fairly clear that the magnitude of the surface tension change with added salt is of the right order of magnitude if we take ionic dispersion potentials into account. However, it appears that the theoretical Hofmeister sequence is in the wrong order as compared to the experimental result. Although it is not entirely sure that the experimental data itself, widely scattered, is sufficiently credible, especially because it is at least perturbed by the adsorption of atmospheric gas at the interface. One reason for this must be that it is not sufficient to take only image potentials, ionic dispersion potentials, and the effect of ions spilling over the interface into account. Further progress requires inclusion of, for example, hydration forces (the interface profile).²⁷ Nonetheless, the point is that we can no longer ignore dispersion forces. The numbers indicate that the inclusion of electrodynamic fluctuation forces and correlations is clearly important. However, a very important point is that it has the limitation of the primitive model, that is, the assumption that an interface can be modeled by treating the solvent as if it has bulk properties up to the interface. This approximation is shared by standard treatments of electrostatic contributions. The interfacial tension problem requires the inclusion of a profile of solvent, not just by correct treatment of the Gibbs dividing surface but also by the modification through for example, the inclusion of ion-induced surface dipole correlations. The importance

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(27) Manciu, M.; Ruckenstein, E. *Adv. Colloid Interface Sci.* **2003**, *105*, 63. Ruckenstein, E.; Manciu, M. *Adv. Colloid Interface Sci.* **2003**, *105*, 177.

of this has been clearly demonstrated in the simulations of Jungwirth and Tobias.²¹ It is now clear that further progress in the theory will require the taking into account of the change in dielectric properties of water near the interface. The anisotropic surface layer modifies, quite profoundly, the dispersion potential acting on ions near an air–water interface. When this is taken into account, a new understanding emerges. We will show how this key question can be tackled in a subsequent publication.

5. Conclusions

A general method for calculating self-free energies and interaction free energies of ions in salt solutions is presented. We have demonstrated highly ion-specific results that depend on ion size, ionic excess polarizability, and the dielectric functions of the surrounding media.

Ionic free energies and interaction free energies clearly have important roles in ion permeation of thin phospholipid bilayers and interfacial tension changes with added salt. We have highlighted the pressing need for more detailed and accurate data for the frequency-dependent excess polarizability of ions in water. It is hoped that our results will be applied to mean-field calculations, simulations, and other theoretical computations that aim at understanding further the ion specificities that abound and dominate matters found in colloid science, membrane biology, and biochemistry.

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