Osmotic Coefficients and Surface Tensions of Aqueous Electrolyte Solutions: Role of Dispersion Forces

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Osmotic coefficients of a series of 16 aqueous electrolyte solutions are described at concentrations up to about 1 M with the help of HNC calculations and solvent-averaged potentials of charged hard spheres with an additional necessary dispersion potential, omitted from all earlier treatments. The adjusted ionic radii and excess polarizabilities have values of the expected order of magnitude. Whereas the description of the bulk properties is satisfactory, the theory is not so successful in predicting the surface tensions of the corresponding solutions (Hofmeister series). The reasons for this are quite subtle and explored in the text. It is clear now how to make further progress and tackle hydration in a consistent way.

1. Introduction

Since the initial work of Debye and Hückel (DH) in the 1920s[1] much effort has gone into extensions of the theory of activity or osmotic coefficients of electrolyte solutions to higher concentrations beyond the limiting law. Several directions were chosen: some tried to extend the DH equations empirically. These pragmatic ways were based on the ideas of Guggenheim and others.[2] A concatenation of such attempts is embodied in the work of Pitzer,[3] whose equations and parameters are commonly used now in industry and in several disciplines such as geochemistry and biology.

A second group exploited advances in the statistical mechanical theory of liquids. They used integral equations such as the hypernetted chain (HNC)[4] or the mean spherical approximation (MSA) theory.[5,6] The latter is a simple extension of the DH theory. It combines the Coulomb with the hard-sphere interactions. It is interesting to note that in the past few years several attempts to replace the Pitzer phenomenological ansatz by models based on these more physical theories have appeared, but without losing the advantages of the Pitzer equations. These lie in their simplicity and their reasonable predictive capacity.[7,8]

A third direction was chosen starting in the 1970s with the now easier accessibility of sufficient computing power: theories and simulations at the so-called Born−Oppenheimer (BO) level,[9,10] where the solvent (water) was no longer a continuum, but where the solvent molecules were explicitly considered as individual entities. In these calculations the dielectric constant was the result of the calculation rather than an input parameter, in contrast to the traditional solvent-averaged calculations at the McMillan−Mayer (MM) level.[11]

Given the vast literature, the uninitiated might be forgiven for thinking that today everything is known about the behavior of simple ions in solutions. However, a whole range of interesting properties of ions was never described satisfactorily; especially the behavior of ions in complex systems, where interfaces and their interactions are involved. As early as in the 1880s, Hofmeister discovered that ions can be classified according to their salting-in and salting-out behavior of proteins.[12] In the following decades numerous examples of such "Hofmeister series" were found, and scientists tried to explain them with words such as "chaotropic" and "cosmotropic" or "structure-making" and "structure-breaking". It is astonishing that up to now none of the huge theoretical effort undertaken to describe electrolyte solutions was successful in predicting or reproducing such Hofmeister series. The Hofmeister effects stand in the scheme of things in physical chemistry as Mendel's work did in genetics. Except that the former remain unexplained.

What are the reasons? (i) The most careful descriptions of electrolytes are probably those made by Patey and co-workers[9,13] using integral equations and by Heinzinger, Bopp, and others[10,14,15] using simulations at the BO level. However, they had to use ion−ion, ion−solvent, and solvent−solvent potentials and the results, although very comprehensive for the particular systems described, were so complex that it is difficult to draw such general conclusions from them as would be necessary to explain the Hofmeister series. (ii) On the other hand, at the MM level, the potentials of mean force used to describe the activity coefficients did not yield parameters that were physically reasonable enough to show good correlation with expected molecular ion properties. It was argued only that the fitted parameters should have something to do with ion−solvent interactions[16] or with the structure-making and structure-breaking behavior of ions.[17] The most sophisticated work in this direction was probably that of Friedman and co-workers more than thirty years ago.[18,19] These authors combined HNC with a solvent-averaged potential of charged soft-spheres with additional terms for the formation of dielectric cavities and for the interpenetration of the ion hydration spheres (Gurney potential). Unfortunately, the adjusted Gurney parameters did

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Osmotic Coefficients of Aqueous Electrolyte Solutions

J. Phys. Chem. B, Vol. 108, No. 7, 2004 **2399**

not correlate with any molecular property of the ion. Further, their absolute values, of the order of Joules per mole, were too small to be interpreted in terms of hydration.

One of the authors of the present paper has argued for a long time that an important interaction term was neglected up to now in all these theoretical approaches quoted above.[20] Indeed, it is explicitly proven in refs 20 and 21 that within the primitive model continuum solvent (PMCS) approximation, the treatment of dispersion forces in the classical (DLVO) theory of colloidal particle interactions, and in interfacial (double layer) problems in electrolytes is seriously flawed inasmuch as it violates the Gibbs adsorption equation, i.e., thermodynamics and the gauge condition on the electromagnetic field. The same holds true for bulk electrolytes.

The van der Waals interaction derived from dispersion forces are well-known in colloidal chemistry, whereas this type of interaction is never explicitly taken into account for the description of simple ion−ion interactions within the PMCS approximation. The same problem bedevils not just electrolyte correlations but also self-energies. The Born free energy of transfer of an ion from one medium to another is purely electrostatic. The Debye−Hückel and higher order statistical mechanical treatments of solution properties are just the change in this free energy due to electrostatic interactions between the other ions. But corresponding to the Born free energy there is a complementary dispersion free energy due to its polarizible electron cloud distribution. This includes all electromagnetic frequency contributions, microwave (permanent dipole), infrared (permanent dipole−induced dipole correlation), and optical and UV frequency (induced dipole−dipole correlation).[22] This fact was ignored for a long time. The dispersion self-energy is of the same order of magnitude as the Born self-energy.

It is encouraging that in the last years some groups recognized the importance of dispersion forces,[23−25] which they explicitly took into account in their BO simulations of electrolyte solutions and their interfaces. In an outstanding feature article Jungwith and Tobias clearly showed the influence of ion polarizabilities on the properties of electrolyte solutions, especially at the air−water interface.[24] They stated that "...by switching to a non-polarizable force field the surface exposure of chloride drops by a factor of 3, thus demonstrating yet again the dominant role of polarizability in determining the surface propensity of halide anions".

The reason that dispersion forces were neglected in all PMCS approximations is probably because they were considered to be dominated by the Coulomb interaction. It was believed that a small change in the ionic radii would be sufficient to take dispersion forces into account.[17] That appears to be so with empirical approximations. However, it is not true, as will be shown in this paper. One simply cannot treat the statistical mechanics of electrostatic interactions in a correct nonlinear theory like HNC, and the dispersion terms in a lower order linear theory.[26]

At very small salt concentrations <0.02 M dispersion forces are negligible and the combination of short-range (hard or soft core) repulsion and the Coulomb interactions is sufficient to describe the activity coefficients of the ions or the osmotic coefficients of the whole system. However, at concentrations of the order of, e.g., 1 M the long-range Coulomb interactions are screened. This is not the case for the dispersion forces. In fact, as for the interfacial tension in colloidal particle interaction problems dispersion forces play an increasingly important role in electrolyte solutions[20] with increasing concentration. This can

be proved by putting bounds on electrostatic and dispersion forces and will be further demonstrated in the next sections.

From here on we will use "dispersion forces" to mean only that part of Lifshitz−van der Waals interactions that is built into high-frequency (optical and UV) fluctuation correlations.[22,27] The lower frequency (many body) contributions that give rise to hydration of ions are ignored. This is because they are subsumed in the electrostatic and dispersion self-energies that give rise to the assumed "hydrated" or dressed ions that form the primitive model starting point. If such a model fails then we have to consider hydration profiles in more detail.

In a series of papers Bostrom et al.[28] used dispersion forces to describe the behavior of ions at interfaces. These papers demonstrate that when dispersion and electrostatic forces are treated correctly, at the same level in the Gibbs adsorption isotherm, ion specificity emerges. By this we mean that theories based on electrostatics alone can never explain a host of phenomena, e.g., positive adsorption of electrolytes at an oil−water interface.

If dispersion forces are important at surfaces, they should be also important to describe bulk solution properties. A reasonable test for the necessity to invoke the dispersion forces is therefore a comparison of osmotic coefficients and surface tensions, both calculated with the same set of parameters.

2. Theory

2.1. HNC and the Potentials Used. Our interpretation of the experimental osmotic coefficients is based on the hypernetted chain (HNC) approximation at the McMillan−Mayer level (solvent-averaged so-called primitive model)

$$g_{ij}(r) = \exp[-\beta u_{ij}(r) + \gamma_{ij}(r)] \quad (1)$$

where $g_{ij}(r)$ is the radial correlation function of two spherical ions i and j and $u_{ij}(r)$ is their solvent-averaged interaction potential at infinite dilution. The solvent is considered as a continuum. $\beta = 1/(k_B T)$ where k_B is the Boltzmann constant and T is the absolute temperature. The numerical calculation of the quantity $\gamma_{ij}(r)$ is done as usual[29] by combining the HNC approximation with the Ornstein−Zernike equation.

The interaction potential $u_{ij}(r)$ is the sum of a simple hard sphere potential $u_{ij}(r)^{HS}$, the Coulomb potential $u_{ij}(r)^{Coulomb}$, and a dispersion potential $u_{ij}(r)^{DISP}$.

$$u_{ij}(r)^{HS} = \infty \quad \text{if} \quad r \leq a_+ + a_- \quad (2)$$

$$= 0 \quad \text{if} \quad r > a_+ + a_- \quad (3)$$

$$u_{ij}(r)^{Coulomb} = \frac{1}{4\pi\epsilon\epsilon_0} \frac{z_i z_j e^2}{r} \quad (4)$$

The dispersion potential for two molecules which have a finite spread in polarizability is[22]

$$u_{ij}(r)^{DISP} = \frac{-3\hbar}{\pi r^6} \int_0^\infty d\xi \frac{\alpha_i^*(i\xi)\alpha_j^*(i\xi)}{\epsilon_w(i\xi)} F(r) \quad (5)$$

$$\longleftrightarrow$$

$$u_{ij}(r)^{DISP} \approx -\frac{3}{2}\alpha_i^*\alpha_j^* \frac{I_i I_j}{I_i + I_j} \times$$

$$\left[1 + \frac{1 - n_w^2}{n_w} I_w \frac{(n_w I_w + I_i + I_j)}{(n_w I_w + I_i)(n_w I_w + I_j)}\right] \frac{1}{r^6} F(r) \quad (6)$$

TABLE 1: Expected and Adjusted Ion Radii, Reference Ion Polarizabilities α_i Inferred from Experiment, and Excess Polarizabilities and Ionization Potentials Used To Calculate the Dispersion Potentials[a]

ion	expected (ref) radius, Å	adjusted radius, Å	expected (ref) α_i, Å³	expected (ref) α^*, Å³	adjusted α^*, Å³	ioniz pot., kJ/mol
H^+	1.30 (H_3O^+)	2.50	0.0	−0.28	0/−0.3[b]	1312
Li^+	0.69	2.35	0.03	−0.04	−1.7	520.2
Na^+	1.02	2.05	0.26	0.02	1.0	495.8
K^+	1.38	1.89	1.07	0.49	0.5	418.8
Cs^+	1.70	1.81	2.73	1.64	2.0	375.7
NH_4^+	1.48	2.05	1.86	1.14	2.4	456
Cl^-	1.81	1.81	3.42	2.10	4.7	1251.1
Br^-	1.96	1.96	4.85	3.17	6.1	1139.9
I^-	2.20	2.20	7.51	4.60	6.1	1008.4
OH^-	1.33	1.95	1.84	1.31	2.3	1270.5
SCN^-	2.13	2.13	6.74	4.59	6.4	≈970[e]
NO_3^-	1.79	1.79	4.13	2.85	7.0/6.2[c]	≈1000[e]
ClO_4^-	2.40	2.20	5.06	1.99	8.3/7.7[d]	≈1350[e]
CH_3COO^-	2.32	2.20	5.50	2.73	4.2	≈1200[e]

[a] The expected radii, the polarizabilities, and the ionization potential of NH_4^+ are taken from ref 38; the other ionization potentials are taken from ref 40. [b] $HClO_4$ and HNO_3. [c] HNO_3. [d] $KClO_4$ and $HClO_4$. [e] Assumption deduced from similar molecules [40], because no experimental data available.

where

$$F(r) = \frac{1}{3}\prod_{j=1}^{2}\left\{\text{erf}\left(\frac{r}{a_j}\right) - \frac{2r}{\sqrt{\pi}a_j}\exp\left(-\frac{r^2}{a_j^2}\right)\right\} +$$
$$\frac{2}{3}\prod_{j=1}^{2}\left\{\text{erf}\left(\frac{r}{a_j}\right) - \frac{2}{\sqrt{\pi}}\left(\frac{r}{a_j} + \frac{r^3}{a_j^3}\right)\exp\left(-\frac{r^2}{a_j^2}\right)\right\} \quad (7)$$

and

$$\alpha_i^* = \alpha_i - \alpha_{\text{water}}\frac{V_i}{V_{\text{water}}} \quad (8)$$

In the previous equations a_i is the radius of the ion i, which is allowed to be hydrated, ϵ_0 is the permittivity of vacuum, ϵ is the relative permittivity of water (78.3 [30]), z_i is the valence of ion i, e is the charge of an electron, α_i is the polarizability of particle i (ion or water) and V_i is the volume of the bare ion. I_i is the ionization potential of particle i and I_w is the ionization potential of water. n_w is the refractive index of the aqueous solutions ($n \approx 1.34$). The refractive index of the air is set to 1. α_i^* is the excess polarizability of an ion i compared to a hypothetical water molecule of the same size.

To arrive at eq 6, we took a single adsorption frequency for each species, which we took as the ionization potential $I_i = \hbar\omega_i$

$$\alpha_i(i\xi) = \frac{\alpha(0)}{1 + (\xi^2/\omega_i^2)} \qquad \epsilon_w = 1 + 4\pi\rho\alpha_w(i\xi) \quad (9)$$

and ρ is the number density of water molecules.

It should be stressed that $u_{ij}(r)^{\text{DISP}}$ does not diverge at vanishing distances r. The complete expression (6) goes to a constant at zero distance.[22] In this extension to account for the real spread of electron and polarization clouds, the distinction between chemical and physical bonds, strongly and weakly associated electrolytes disappears.[31] Note that, in contrast to the expressions used by Bostrom et al., eq 6 takes into account that the ionization potential of water (1220 kJ/mol) is of the same order of magnitude as the ionization potentials of the ions regarded in this paper; cf. Table 1.

Equation 6 is an approximate expression that deals only with fluctuation correlation contributions in the visible and ultraviolet frequency region. In general, we emphasize that microwave,

infrared, and other frequency regions also contribute. It would be beyond the scope of the present paper to derive the origin of the preceding equations in details. The model, from which the expressions for the dispersion interactions are derived, via the full quantum mechanical expressions for the polarizability, uses a form factor that is a Gaussian (eq 4.21 in Mahanty and Ninham[22]). For a detailed discussion the reader is referred to the literature.[22,31]

2.2. Calculation of Macroscopic Quantities. Osmotic and activity coefficients can be calculated from $u_{ij}(r)$ and $g_{ij}(r)$ in the classical way,[32] for example

$$\phi = 1 - \frac{\rho}{6kT}\int r\frac{\partial u_{ij}(r)}{\partial r}g_{ij}(r)4\pi r^2\,dr \quad (10)$$

where ϕ is the osmotic coefficient and ρ is the analytical particle density. At low salt concentration (<0.1 M) the osmotic coefficient is fitted only with adjusted ion radii. At higher concentrations the increasing deviation of the thus obtained theoretical curve from the experimental values is corrected by the additional fitting of the excess polarizabilities.

In addition, we have calculated the surface tension of the electrolyte solution in the following way:

Once the experimental osmotic coefficients in the MM system[33,34] are correctly described by means of HNC and with adjusted radii a_i and polarizabilities α_i^*, the distribution of the ions near an uncharged interface is calculated, also with HNC. The dispersion interaction between the air and the ions in the aqueous solutions, $u_{i-\text{air}}(r)^{\text{DISP}}$, can be approximated asymptotically by[22]

$$u_{i-\text{air}}(r)^{\text{DISP}} = \frac{\hbar}{4\pi r^3}\int_0^\infty d\xi\,\frac{\alpha_i^*(i\xi)}{\epsilon_w(i\xi)}\frac{\epsilon_w(i\xi) - 1}{\epsilon_w(i\xi) + 1} \quad (11)$$

which is equivalent to

$$u_{i-\text{air}}(r)^{\text{DISP}} \approx \frac{n_w^2 - 1}{16n}\frac{I_iI_w}{(n_wI_w + I_i)} \times$$
$$\left\{1 + \frac{(1 - n_w^2)}{2}\frac{I_w^2}{I_3}\frac{(n_wI_w + I_i + I_3)}{(I_3 + I_i)(I_3 + n_wI_w)}\right\}\alpha_i^*\frac{1}{r^3} \quad (12)$$

where r is the distance between the interface and the center of

Osmotic Coefficients of Aqueous Electrolyte Solutions

J. Phys. Chem. B, Vol. 108, No. 7, 2004 **2401**

the ion, and

$$I_3 = \sqrt{\frac{1 + n_w^2}{2}} I_w$$

With $u_{i-air}(r) = u_{i-air}(r)^{HS} + u_{i-air}(r)^{DISP}$ the $g_{i-air}(r)$ functions can be calculated by HNC. An integration from zero to infinity of these functions allows the calculation of the excess concentration Γ of the ions at the air−water interface.

$$\Gamma = \int_0^\infty (g_{i-air}(r) - 1) 4\pi r^2 \, dr \tag{13}$$

Because of electroneutrality the total excess concentration of the cations Γ_+ must be equal to the total excess concentration of the anions Γ_-: $\Gamma = \Gamma_+ = \Gamma_-$. The verification of this constraint is a good test for the numerical validity of the result.

Finally, the surface tension increment $\Delta\gamma(c)$, which is the difference between the surface tension of the electrolyte solution at salt concentration c and that of pure water, is obtained by the following integration

$$\Delta\gamma(c) = -k_B T \int_0^c \frac{dc'}{c'\chi} \Gamma(c') \tag{14}$$

where χ is the isothermal osmotic compressibility. χ is a direct result of the HNC calculation.

Equation 14 can be derived as follows: according to Gibbs, the surface tension is related to Γ as

$$d\gamma = -\Gamma \, d\mu_{salt} \tag{15}$$

where the chemical potential of a monovalent salt is $\mu_{salt} = \mu_+ + \mu_-$. The statistical mechanics of solutions relates $(\partial\mu_{salt}/\partial c_{salt})$ to the osmotic compressibility and to the partial structure factors of the ions at the origin $S_{ij}(q=0)$ ($S_{++}(q=0) = S_{+-}(q=0) = S_{--}(q=0) = S(0)$) due to electroneutrality; see ref 32. This results in

$$\Delta\gamma = -\frac{\Gamma}{c_{salt}S(0)} \, dc_{salt} \tag{16}$$

and finally in eq 14.

3. Results

3.1. Osmotic Coefficients. The osmotic coefficients of sixteen 1:1 electrolytes are calculated. The experimental data are mostly taken from Hamer and Wu,[35] except for KClO$_4$ solutions, where only data at low concentrations are known.[36] The data are converted to the MM level with the help of the known experimental densities.[37]

The adjusted parameters are given in Table 1 as well as reference data taken or estimated from literature. The reference ionic radii are those proposed by Marcus on the basis of a careful review of all relevant literature data.[38] The reference excess polarizabilities are calculated in the following way:

Experimental molar refractivities (in m^3/mol) of solutions are measured at high frequencies, usually at the sodium D line, $R_\infty = R_D$ via[38]

$$R_\infty = R_D = \lim_{c \to 0} \frac{1}{c} \frac{n_D^2 - 1}{n_D^2 + 2} - \left(\frac{d}{d_0} - \frac{cM}{d_0}\right)\frac{n_{D0}^2 - 1}{n_{D0}^2 + 2} \tag{17}$$

where c is the concentration of the salt, n_D and n_{D0} are the refractive indices of the solution and the pure solvent, respec-
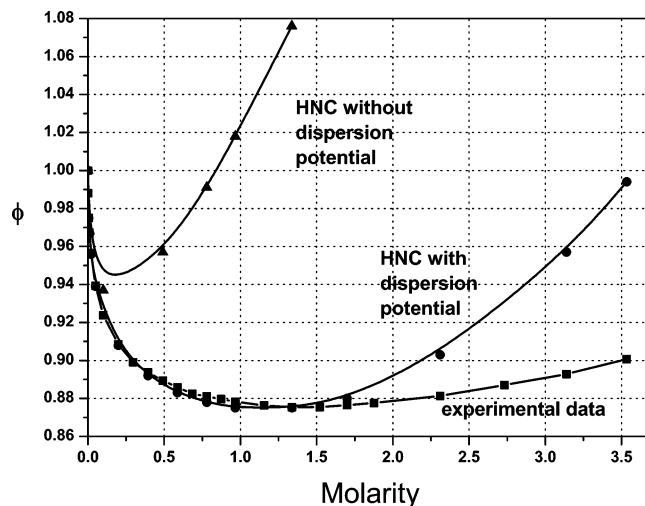

Figure 1. Osmotic coefficients of NaNO$_3$ at 25 °C. Comparison of experimental and calculated values. The quality of fit is comparable to all 16 electrolytes.

tively, and d and d_0 are the corresponding densities. M is the molar mass of the salt. The salt polarizabilities can then by calculated by

$$\alpha = \frac{3}{4\pi N_A} R_\infty \tag{18}$$

To get the ion polarizabilities α_i, α must be split into its ionic contributions. Heydweiller[39] was the first to propose the procedure to do so by taking into account the molar fraction differences of alkali halide ions at infinite dilution and those of isoelectric rare gas atoms. The obtained α_i values are given in Table 1. They are converted into excess polarizabilities with the help of eq 8 assuming that $\alpha_{H_2O} = 1.59$ Å^3 and $V_{water} = 30$ Å^3. The volumes V_i of the ions are calculated according to $V_i = 4/3\pi a_i^3$. a_i are the reference ionic radii given in Table 1. The resulting reference α_i^* are also given in this table.

Note that there is a certain arbitrariness in the calculation of α_i^* The values are taken from measured refractive indices of salt solutions using Clausius−Mosotti. This assumes that the medium is a system of spheres immersed in a continuum solvent. The continuous solvent model is an approximation as well as the assumption of a spherical isotropic polarizability. For ions such as NO$_3^-$ the polarizability within the plane of the atoms is certainly much higher than perpendicular to it.

Another uncertainty comes from the ionization potentials. We took the values for the atoms.[40] Probably a better alternative would be the use of the ionization potentials of the cations, which should be much higher than those of the atoms, and the negative electron affinities for the anions, which are lower by a factor of 2−5 than the ionization potentials of the atoms. However, even in the gas phase they are often not known and nobody knows how they are modified in the solution. Because of all these uncertainties, it is not astonishing that the α_i^* must be adjusted to describe the osmotic coefficients.

Table 1 resumes the values we used keeping in mind that they might significantly differ from the "real" values. Figure 1 shows a typical fit of the experimental values for NaNO$_3$ solutions, where the salt concentrations range from high dilution to approximately 2 M. In Figure 2 the contributions of $u_{NO_3-NO_3}(r)^{HS}$, $u_{NO_3-NO_3}(r)^{Coulomb}$, and $u_{NO_3-NO_3}(r)^{DISP}$ to the total potential $u_{NO_3-NO_3}(r)$ are given for NaNO$_3$ solutions in water. The corresponding pair distribution functions $g(r)$ are shown in Figure 3 for a 1 M solution.
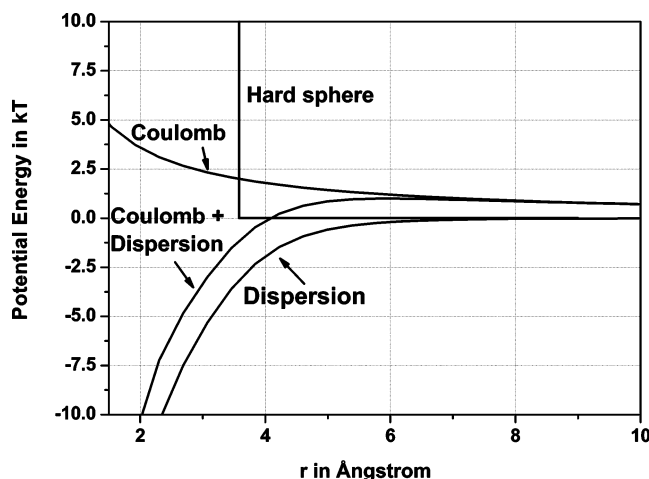
Figure 2. Coulomb, dispersion, and hard-sphere components of the solvent-averaged ion−ion interaction potential between nitrate ions, $u_{NO_3-NO_3}(r)$ in $NaNO_3$. Note that the overall interaction near the contact distance is attractive.
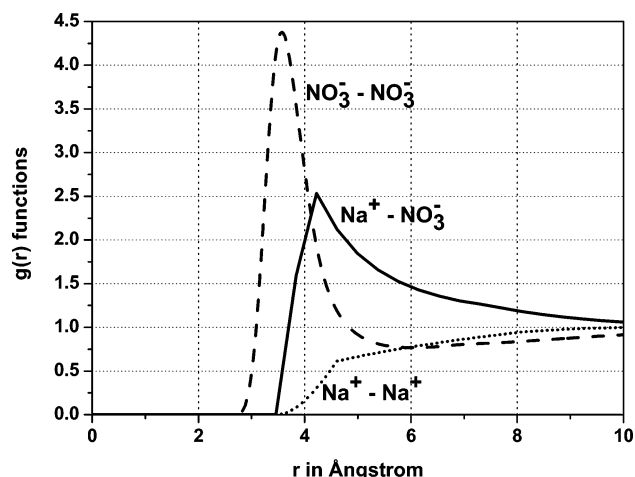

Figure 3. Ion−ion pair distribution functions for $NaNO_3$ at 1 M. Note that the peak in the anion−anion distribution function is a consequence of the attractive dispersion forces.

3.2. Surface Tensions. According to eqs 13 and 14 the surface tension increments $\Delta\gamma(c)$ are calculated for systems where precise experimental data are given in the literature. In contrast to a preceding paper,[28] no parameters are fitted to surface properties. The results, based on the polarizabilities adjusted to the osmotic coefficients, are given in Table 2. Of course, in our approach, changes in hydration forces when two ions come together are not explicitly taken into account. If they are important in the bulk, they are implicitly present both in the hard-sphere terms and in the numerical values of the adjusted excess polarizability parameters. We have also included image forces in our calculations. In the results given in Table 1 their contribution is included. But the contribution is very small.

According to Table 2, the predicted values of the surface tension increments are all between 0.8 and 1.4 (mN/m) × (L/mol). The variation of these values is small given the wide range of ionic radii and excess polarizabilities used for the interaction potentials. The agreement with experimental values is poor. The calculated values do not reflect the Hofmeister series of the surface tension increments. Experimentally, the "softer" the ions, the smaller is the surface tension increment.

Without the dispersion potentials taken into account at the interface, the calculated surface tension increments would be around 0.5−0.7 (mN/m) × (L/mol).

TABLE 2: Experimental and Calculated Surface Tension and Surface Potential Increments[a]

| | surface tension increment $\Delta\gamma/\Delta c$, (mN/m)/(mol/L) | | |
salts	experiment[a]	calculation	$S(0)$
LiCl	1.98 ± 0.09	1.40	0.84
NaCl	2.08 ± 0.08	0.94	0.98
KCl	1.85 ± 0.05	0.88	1.03
CsCl	1.52 ± 0.07	0.89	1.11
NH_4Cl	1.59 ± 0.09	0.97	1.03
HCl	-0.27 ± 0.04	1.10	0.80
NaI	1.23 ± 0.06	1.08	0.84
$NaNO_3$	1.18^b	0.89	1.22
HNO_3	-0.83 ± 0.1	1.04	0.87
CH_3COONa	0.93 ± 0.03	1.02	0.81
NaSCN	$\approx 0.5 \pm 0.1^c$	1.06	0.86
KOH	1.98 ± 0.04	0.83	0.88

[a] $S(0)$ is the structure factor at $k = 0$, resulting from the HNC calculation and used in eq 14. [b] Data from ref 43. [c] Data from ref 44. [d] Data from ref 41.
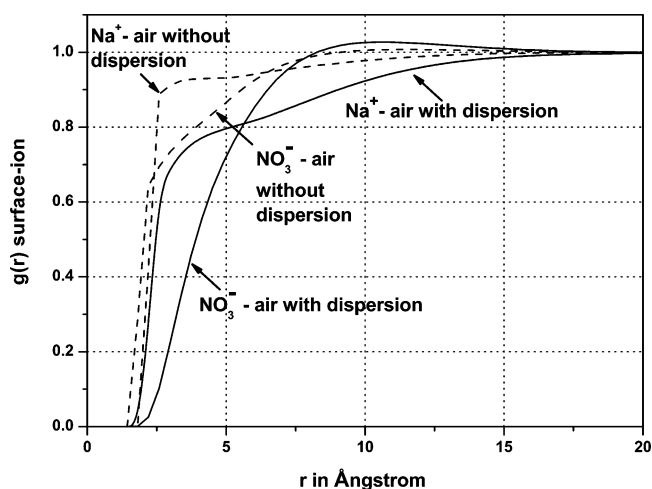

Figure 4. Ion interface distribution of $NaNO_3$ with and without dispersion forces at 1 M.

It should be noted that the use of HNC does not bring noticeable advantages compared to Poisson−Boltzmann (PB) as used in ref 28. At 1 M PB and HNC yield comparable results for the surface tension, provided that the same interaction potentials are used.

Typical $g_{i-air}(r)$ functions are shown in Figure 4. These correlation functions are the result of a subtle interplay between volume effects, electrostatic interactions, and the repulsion or attraction (only in the case of H^+ and Li^+) due to the dispersion forces. For example, if an ion is strongly repelled by the air phase, whereas the counterion is attracted, the electrostatic coupling of the two ions partially equilibrates these two opposing tendencies. Of course, the electroneutrality is not necessarily fulfilled locally. As a consequence, it may happen that near to the interface there is a big excess of one type of ions and in the next layer this excess is balanced by a comparable excess of the counterions.

4. Discussion

4.1. Osmotic Coefficients. At very low concentration it is sufficient to adjust the ionic radii precisely. As can be seen from Table 1, the fitted anionic radii are close or identical to the radii proposed by Marcus. For the cations, they are bigger, reflecting an average hydration sphere. This makes sense, because the cations are expected to be more hydrated than the anions.

Osmotic Coefficients of Aqueous Electrolyte Solutions

J. Phys. Chem. B, Vol. 108, No. 7, 2004 **2403**

For the description of the osmotic coefficients at higher concentrations the same ionic radii are used and the excess polarizabilities are adjusted.

The numerical values of α_i^* have the right order of magnitude. Moreover, as expected, the adjusted excess polarizabilities of the anions are higher than those of the cations. Negative values indicate ion polarizability densities smaller than that of water. Such values are found for Li^+ and H_3O^+. As a result, dispersion forces between these ions and anions are repulsive (cf. eq 6), in contrast to all other dispersion forces, which are attractive.

The quality of all the fits is comparable to Friedman's results,[18] where radii and Gurney parameters were adjusted. If the ions are considered only as charged hard spheres without dispersion interaction, the calculated osmotic coefficients are only in agreement with experiment at very low concentrations, see Figure 1.

To our knowledge, it is for the first time that osmotic coefficients of electrolyte solutions can be quantitatively described at least up to 1 M with physically meaningful parameters. The dispersion forces are more important for anions than for cations, in agreement with the Hofmeister series. They show up at moderate concentrations (>0.1 M) as is also characteristic for Hofmeister series.[41] Beyond 1 or 2 M the MM level description with solvent-averaged pairwise additive potentials is no longer valid. This is because, e.g., at 1 M there are about 30 water molecules per ion, enough to accommodate at most two hydration layers per cation if the anion is unhydrated. This is not bulk water any more. Furthermore, the Coulomb and the dispersion potentials are only the low- and the high-frequency limits of the whole electromagnetic interactions and changes in ion–dipole interactions are neglected. It is certain that the water structure changes at these high concentrations and concentration-dependent potentials are needed. Such an approach is often used,[7] but it is not fully in agreement with the MM model.

It should also be stressed that the adjusted excess polarizability parameters are not completely additive, cf. $\alpha^*(NO_3^-)$. It may be that a more or less counterion independent set of parameters could be found that permits an overall satisfactory fit of all ion pair systems. But such a "pragmatic" fitting procedure is not the objective of the present paper. It seems more physical for the moment to maintain the nonadditivity of polarizabilities.

In Figure 2 the contributions of $u_{NO_3-NO_3}(r)^{HS}$, $u_{NO_3-NO_3}(r)^{Coulomb}$, and $u_{NO_3-NO_3}(r)^{DISP}$ to the total potential $u_{NO_3-NO_3}(r)$ are given for $NaNO_3$ solutions in water. Although the attractive dispersion potential decreases with $1/r^6$, it is more important than the repulsive Coulomb potential close to the contact distance. As a consequence and because of the screening of the electrostatic interactions, the correlation function between the nitrate ions, $g_{NO_3-NO_3}(r)$ exhibits an *attractive peak* near contact with a maximum that is even higher than the plus–minus correlation; see Figure 3. This is a striking demonstration of the importance of dispersion forces. They cannot be taken into account by a simple change of the contact distance.

4.2. Surface Tensions. The interfacial tension problem is rather more complicated than that for bulk thermodynamic properties, for which we have omitted only the hydration shell contribution within the primitive model. The definition of the Gibbs dividing surface is clearly more complicated. Its position depends on the profile of order of water at the air–water interface, and ionic concentration (and dissolved gas). In a more complete calculation we have to allow some part of the ionic

hydration shell to be modified at the Gibbs dividing plane. This is tantamount to involving self-free energies, both Born and van der Vaals dispersion self-energies (cf. ref 22, eqs 4.69 and 4.70). Because this complication is ignored, we cannot expect quantitative agreement.

The hydration shells in the bulk and at the interface are certainly different. Ions may come together without losing their hydration shell in the bulk. But if they come into direct contact with the air–water interface, they can and will lose their hydration shell. The opposite is also possible. Furthermore, it was shown by Jungwirth and Tobias[24] that the asymmetric ion hydration at the surface causes a net dipole. It is the dispersion interaction between water and the polarizable ions that yields the major contribution to the surface tension increments. Compared to that, the direct ion–surface interaction, as considered in this paper, and without self-energies is a minor effect. As a consequence, the surface tension increment of a 1 M $NaNO_3$ solution is much smaller than the surface tension increment of a 1 M NaCl solution, in contrast to our calculations where both are similar. Besides, the experimentally determined surface potential of these solutions are negative. This result cannot be reproduced by our calculations.

The primitive (hard hydrated core) model does not allow the inclusion of important terms due to interpenetrating or asymmetric hydration shells or overlapping ionic wave functions. By retaining the usual hard core ansatz for electrostatics we are allowed to see the importance of these Gurney or civilized model corrections to the potential. The older analysis of electrolytes that does not include dispersion forces suffers from the same effects as the older DLVO theory of colloid science.

In particular, the assumption of a hard hydration core is a source of artifact. It does not allow partial dehydration of a positively adsorbed ion. If the hard core restriction is relaxed, a different situation obtains. For those ion pairs that exhibit positive adsorption at the air–water interface, the apparent qualitative descrepancies even in sign may then be removed if we use the complete dispersion force expressions (eq 4.6.9 in ref 22). In principle it would be also possible to take the polarizability values proposed by Bostrom et al.[28] However, the fitted polarizabilities in Bostrom's paper are just in the wrong order: softer ions have lower polarizabilities, which is physically not realistic. The explanation is clear now: water–ion dispersion interactions and the incomplete hydration at the surface are not taken into account.

Nonetheless, we remark again that without dispersion forces, which can change in sign depending on the frequency dependent dielectric properties of the medium in contact with water, it is impossible to explain even the sign of adsorption excesses at difference interfaces. For example, potassium bromide adsorbs negatively at the air–water interface, positively at a hexadecane–water interface, and negatively at a hexane–water interface. This is predicted by the dispersion force potential. In addition, the sign of the excess polarizabilities can explain why some ions such as H^+ ar Li^+ are adsorbed positively at the air–ion water interface in contrast to most other ions.

Although it is clear now that high-frequency dispersion forces between ions alone are not sufficient to explain in fine detail the ion specificity of the surface tensions of electrolyte solutions, it is interesting to have a look at the ion distribution functions perpendicular to the surface, as predicted by the present model. According to Figure 4 nitrate ions experience an additional repulsion at the surface due to dispersion forces. In reality, by taking into account the ion self-energy and the incomplete

2404 *J. Phys. Chem. B, Vol. 108, No. 7, 2004*

Kunz et al.

hydration, the dispersion forces will lead to an additional *attractive* term.

Karraker and Radke[42] argued that the solution−air interface attracts OH⁻ ions. In light of our results this is definitely possible, however, the excess of anions at the interface will crucially depend on the counterion. Furthermore, according to Karraker and Reke the excess concentration of OH⁻ is rather low (≈one excess charge per 65 nm²). Such a small amount of charge is insignificant for the calculated surface tension.

5. Conclusion

There are two important conclusions that can be drawn from this analysis.

(i) The recognition of apparently counterintuitive attractive like charge interactions between ions in the bulk will drastically modify our interpretation of potentials at interfaces. Dispersion forces responsible for interfacial phenomena at charged interfaces implicate anions as well as cations in phenomena beyond ordinary electrochemistry; pH and buffers,[21,45,46] but also for sodium, calcium, and proton pumps where the role of anions is ignored.

(ii) To explain quantitatively specific ion effects (various Hofmeister series) at interfaces, it is necessary to include the dispersion forces in full generality. Such a theory including electrostatics and electrodynamic fluctuation forces is consistent and includes all many body interactions in principle through its reliance on measured dielectric properties. But this is not sufficient. Hydration forces, incomplete hydration at the interface, and the resulting net dipoles must also be taken into account. This can be tackled now with much more confidence.

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