Theory of the electrical double layer: Ion size effects in a molecular solvent

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Recent application of the reference hypernetted-chain theory to the calculation of the structure of electrical double layers in wholly molecular models of aqueous electrolytes [J. Chem. Phys. **90**, 4513 (1989)] is extended to NaCl solutions. The strong interaction of the small Na$^+$ ion with the solvent molecules leads to a number of novel features, notably a very high adsorption of Na$^+$ into a region about 4 Å from the surface next to the first solvent layer. This is sufficient to produce a positive potential of zero charge of about 29 mV and to cause the effective surface charge experienced by the diffuse layer to be positive even when the surface carries a substantial negative charge. In most cases, however, the surface potential is found to be remarkably insensitive to the details of the structure of the double layer for a given surface charge.

I. INTRODUCTION

In this paper we continue our recent development[1-3] of a wholly molecular description of the electrical double layer based on the reference hypernetted-chain (RHNC) theory of multipolar hard sphere models of electrolyte solutions. For double layers, as for any aspect of the behavior of electrolyte solutions, a wide variation in experimentally measured properties for different ionic species is superimposed upon an underlying universal behavior arising from the presence in the system of long-range Coulombic forces between the ions. This commonality is ordinarily manifest at low concentrations where such forces dominate the behavior of the system, the molecular nature of the solvent is not apparent and a dielectric continuum model is appropriate. In the case of the double layer a mean-field treatment of this primitive model leads to the Gouy–Chapman theory which gives a good account of the behavior of the differential capacitance of double layers at very low concentrations and surface charges.[4] This is precisely the regime in which this property would be expected to be dominated by the contribution of an extended diffuse layer that would be much the same in shape and extent for all salts. More recent theoretical and computer simulation work has shown that the Gouy–Chapman theory continues to give a reasonably accurate description of double layers in a continuum solvent, at least for 1:1 aqueous systems, to quite high concentrations and surface charges[5] even though such models are altogether incapable of accounting for the observed behavior of real systems in this regime. To go beyond a theory of this universal behavior in order to describe the properties of particular systems (or even to construct a theory capable of *ab initio* prediction of the absolute magnitude of diffuse layer effects) it is necessary to take into account the differences in the way various ions interact with the solvent and the surface. Since the inter-

actions in both these cases are characterized by distance scales of molecular dimensions this necessitates the use of a Hamiltonian model in which the solvent is treated as a distinct molecular species.

Recently, we have been using the RHNC theory to investigate the properties of double layers in such a model[1-3] in which the solvent molecules are hard spheres with embedded point multipole moments chosen to represent the effective charge distribution in molecules of liquid water and the ions are charged hard spheres of varying diameters. In such a highly simplified model the variation in solvation properties with ion size arises only from the resulting change in the location of the hard sphere cutoff of the charge-multipole forces. Nevertheless, at infinite dilution this is already sufficient to generate a remarkable variety in the behavior of single ions in the vicinity of a surface,[2] apparently as a result of high sensitivity to ion size of the local solvation properties of the very specific water structure that is established near a flat surface.[1] Previously, we have reported the extension of these infinite dilution studies to the full double layer problem for a single salt KCl in which both ions are slightly larger than the solvent particles.[3] However, the most dramatic of the infinite dilution effects occurred for smaller ions[2] such as Na$^+$ and so we here extend that work to consider double layers in NaCl solutions at finite concentration.

II. MODEL AND RESULTS

As before, the solvent molecules are hard spheres of diameter $d_s = 2.8$ Å carrying a point dipole and a point quadrupole of tetrahedral symmetry with magnitudes appropriate to polarized bulk liquid water. The Na$^+$, K$^+$, and Cl$^-$ ions are singly charged hard spheres of diameter $0.84d_s$ (2.35 Å), $1.08d_s$ (3.02 Å), and $1.16d_s$ (3.25 Å), respectively. We also discuss a few results for the salt "Eq$^+$ Eq$^-$" in which both ions are the same size as the water molecules. The surface at which the double layer is formed is introduced as a single macroion of diameter d_m ranging from

$10d_s$ (28 Å) to $30d_s$ (84 Å) carrying up to several hundred elementary charges. Following the convention used in our earlier work we describe the resulting surface charge density σ for all values of d_m in terms of the number of elementary charges necessary to produce it on a macroion of diameter $20d_s$. In these units we consider values for σ of -28 and -108 corresponding, respectively, to 352 and 91 Å² per electron. The RHNC closure is applied to the Ornstein–Zernike equations for the isotropic mixture of solvent, ions and the macroion and is solved to obtain the correlation functions between the macroion and the other species in the system. These describe the structure of the double layer that forms at the macroion surface. The theory and all technical aspects of its numerical solution are unchanged from our earlier work on similar systems[1-3] and in what follows we make use of notation and conventions introduced in those earlier papers.

A. Small macroions

Three generalizations emerged from our previous application of the RHNC theory to systems similar to those we consider here: Most of the short-range response of the solvent to the surface is independent of surface charge and is therefore most easily examined at a neutral surface; this solvent response is very sensitive to surface curvature, even for rather large macroions; and the short-range component of the ionic structure near the surface, while very sensitive to ion size, is largely controlled by this solvent structure without affecting it greatly. With this in mind we begin with a comparison of the structures of NaCl and KCl solutions close to uncharged macroions of diameters $10d_s$ and $20d_s$. In Fig. 1(a) are shown the macroion–ion radial distribution functions (i.e., the ion density profiles) for Na⁺ and Cl⁻ near an uncharged $10d_s$ macroion in 0.1 M NaCl and for K⁺ near the same macroion in 0.1 M KCl. (The Cl⁻ profile in this latter system is only very slightly different from that shown in the figure for NaCl.) In all figures the origin is the contact distance of a *solvent* molecule and distances are expressed in solvent diameters so that the macroion surface is at -0.5 and the Na⁺ profile begins at -0.08. The short-range structural features extend only about 3 or 4 solvent diameters from the surface and are evidently very sensitive to the size of the ion. Thus, the K⁺ and Cl⁻ profiles have much fine structure but are very similar since these two ions are about the same size in our model. (In fact, because of the tetrahedral symmetry of the solvent model we use, equal sized cations and anions have identical profiles against a neutral surface.[2]) There is a depletion of all three ionic species in the immediate vicinity of this uncharged surface in a manner consistent with conventional notions about the relationship between high solubility of these ions and their lack of affinity for the macroion "impurity." This effect is evidently much larger for the smaller Na⁺ ion and results in a noticeable charge separation in which the immediate surface region is characterized by a small negative charge with a correspondingly small positive surface potential of a couple of millivolts. This is just the reverse of what occurs in a continuum solvent model[6] in which the smaller contact distance of the Na⁺ ion determines the sign of the charge separation and illustrates again the supremacy of ion–solvent
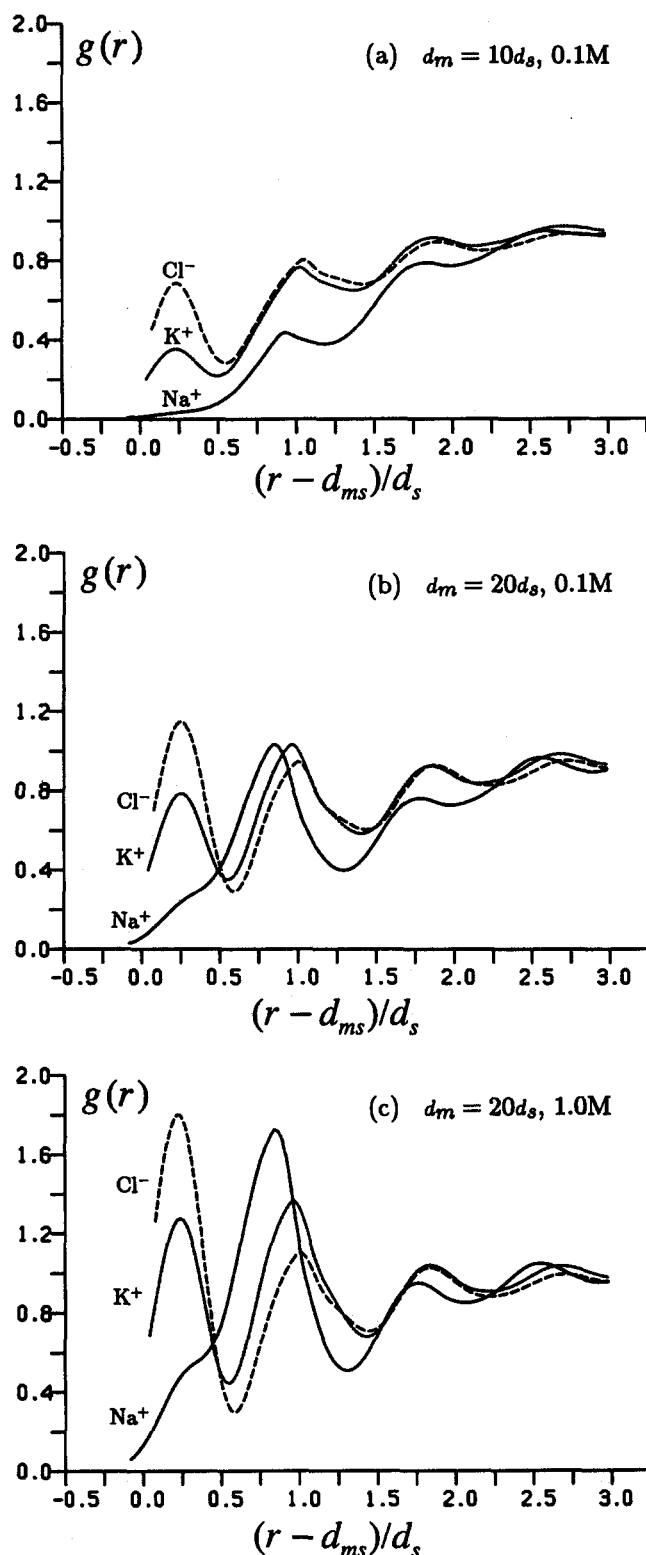

FIG. 1. The density profiles of small ions next to the surface of a neutral macroion of diameter d_m for two electrolyte concentrations; (—) Na⁺ in NaCl; (---) Cl⁻ in NaCl; (···) K⁺ in KCl. (a) $d_m = 10d_s$, 0.1 M; (b) $d_m = 20d_s$, 0.1 M; (c) $d_m = 20d_s$, 1.0 M.

interactions, at least in a model which contains no specific ion–surface interactions. However, the precise nature of the local ion–solvent structures near the surface that give rise to the one-body profiles of Fig. 1 is not obtainable from the kind of theory we have used.

Generally, the features of the short-range ion–surface structure become more pronounced as the surface becomes flatter or as the concentration increases. The same three ion–surface profiles next to a $20d_s$ macroion are shown in Fig. 1(b) for 0.1 M solutions and in Fig. 1(c) for 1.0 M salts. The peaks near contact for the K^+ and Cl^- ions become larger in both cases while the deficiency of Na^+ ions in this region persists. One consequence of this in the 1.0 M NaCl case is a much larger charge separation at the surface with an associated potential of zero charge of about 13 mV. The most prominent feature of Fig. 1(c) is the large peak in the Na^+ profile near $0.8d_s$ from contact. This appears to be the precursor of a much larger effect that we discuss later for the case of a $30d_s$ macroion where the Na^+ ion is responding to a very specific solvent structure that has only just begun to form in the present $20d_s$ case.

In Fig. 2 we show how the counterion (cation) profiles of Fig. 1(a) are modified when the $10d_s$ macroion carries a surface charge of -28 [Fig. 2(a)] and -108 [Fig. 2(b)].
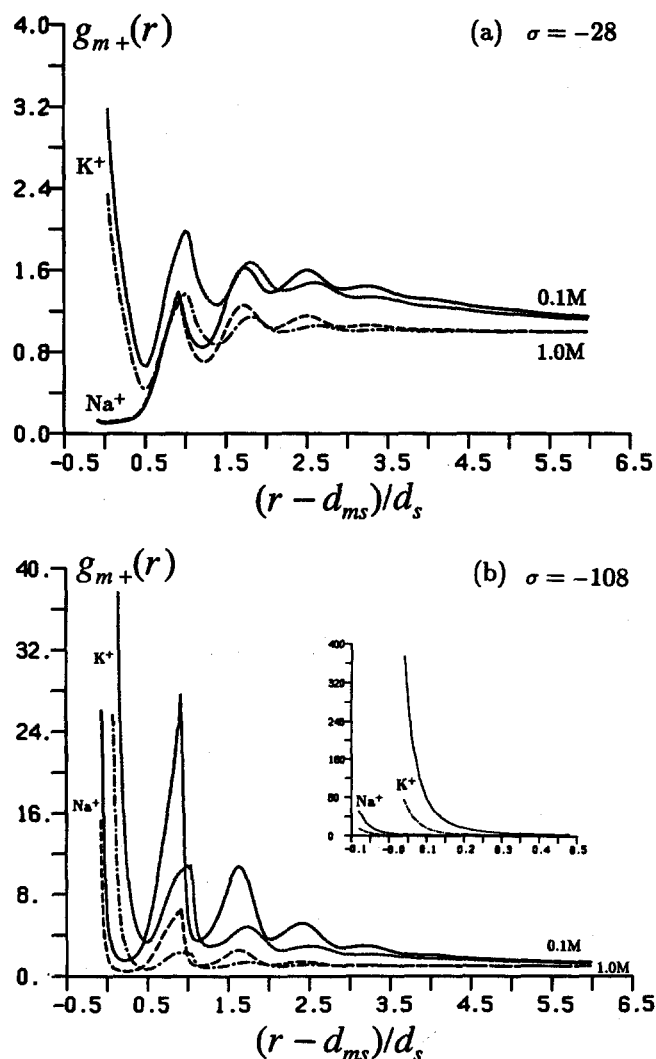

FIG. 2. Counterion density profiles near a $10d_s$ macroion in KCl and NaCl solutions; (—) Na^+ in 0.1 M NaCl; (---) Na^+ in 1.0 M NaCl; ($\cdots$) K^+ in 0.1 M KCl; ($-\cdot-$) K^+ in 1.0 M KCl. (a) surface charge density $\sigma = -28$; (b) $\sigma = -108$.

In both cases the short-range structure still extends the same 3 or 4 diameters from the surface. In the 0.1 M systems a smooth decay typical of a continuum solvent model is visible beyond this region but at 1.0 M the screening is essentially complete at this distance so that the surface effects are entirely short ranged in nature. A notable feature of our earlier RHNC results for KCl solutions at charged surfaces[3] was the prediction of a very high concentration of counterions virtually in contact with the surface resulting in an extremely rapid neutralization of the surface charge. The steep K^+ profiles at contact in Fig. 2 are typical examples. The Na^+ profiles, particularly in Fig. 2(a), are striking counterexamples to the idea that this fast screening is a universal feature of the model arising from the unscreened interactions of contact ions with the full macroionic charge. Even this smaller surface charge of -28 is quite substantial (nearly 5 μC cm^{-2}) and yet has no effect at all on the Na^+ deficiency already present immediately next to a neutral surface. At the highest surface charge, Fig. 2(b), a contact peak has developed for the Na^+ ion but it is much smaller than the corresponding feature for K^+ and at 0.1 M represents far less charge than the large secondary peak near $0.9d_s$. These very different short-range structures in the two salts naturally mean that the more distant parts of the interface will be responding to quite different effective surface charges; this is especially evident in the differing amplitudes of the counterion profile decay beyond $4d_s$ at 0.1 M in Fig. 2(a).

A quantity we have used previously[3] to characterize the ionic structure of the interface is $f_Q(r)$, the fraction of the macroionic charge Q that has been neutralized by free charges within a distance r of the center of the macroion. A comparison of the behavior of this quantity in NaCl and KCl solutions for $10d_s$ macroions is made in Fig. 3(a) for 0.1 M solutions and in Fig. 3(b) for 1.0 M solutions. The solid line in each figure is $f_C(r)$ the single curve that would result for all Q if the ion profiles had no short-range structure at all but assumed instead their asymptotic form $e^{-\kappa r}/r$ at all distances [cf. Eq. (6) of Ref. 3]. At 0.1 M the neutralization is slower than this continuum result at low surface charge for both salts. This is because the deviations from continuum solvent behavior here are still dominated by the short-range structure of a *neutral* surface at which the Cl^- ion suffers the least depletion [cf Fig. 2(a)]. Again, for both salts the screening is eventually faster than the continuum result at high surface charges, but in the case of NaCl this is due to the large counterion peak near one diameter from contact whereas in KCl it is the Coulombic adsorption of K^+ ions onto the surface that is responsible. As we saw in Fig. 2(c) for a $20d_s$ macroion, at high concentration the features of the short-range structure in the ion density profiles tend to be amplified. This is reflected in the various $f_Q(r)$ for the $10d_s$ macroion at 1.0 M in Fig. 3(b). For example, the field of a small negative surface charge is not sufficient to reverse the large differences between the Cl^- and Na^- profiles right next to a neutral surface so that this region continues to carry a negative space charge and $f_Q(r)$ is initially small and negative. At high surface charge the fast screening in KCl is still more rapid than was the case at 0.1 M, with a full 60% of the macroion charge being neutralized by ions virtually in con-
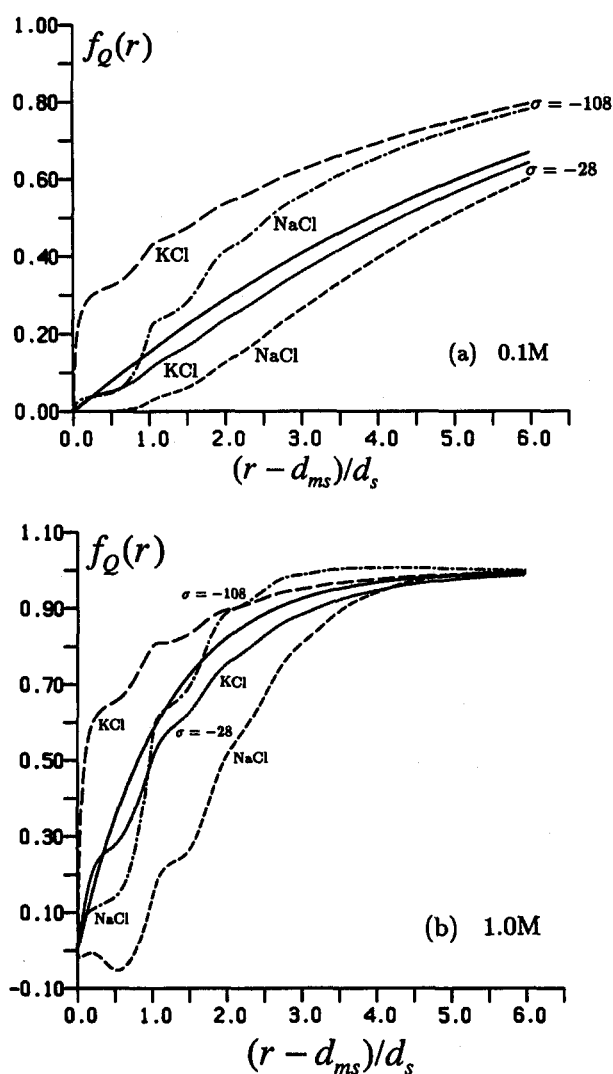
FIG. 3. $f_Q(r)$, the fraction of macroion charge neutralized within r of macroions with $d_m = 10d_s$; (—) $f_c(r)$ "continuum" result for all σ; (–––) NaCl, $\sigma = -28$; ($\cdots$) KCl, $\sigma = -28$; (–·–) NaCl, $\sigma = -108$; (– – –) KCl, $\sigma = -108$. (a) 0.1 M; (b) 1.0 M.

FIG. 4. Solvent polarization per particle $\langle \cos \theta_\mu \rangle$ about $10d_s$ macroions, symbols as in Fig. 3. (a) 0.1 M; (b) 1.0 M.

tact with the surface. The initial screening in NaCl is much slower but the large counterion density near one diameter has grown to the point that the neutralization eventually exceeds not only the continuum and KCl results but also exceeds very slightly the total macroion charge itself so that $f_Q(r)$ decays to unity from above.

The consequences for the solvent of these differences in the ionic structure are most visible in $\langle \cos \theta_\mu \rangle$, the profile of the mean polarization per particle (θ_μ is the angle between the molecular dipole of a solvent molecule and the surface normal pointing into the fluid.[1]) As shown in Fig. 4 this quantity has a very deep negative well at contact at both 0.1 M [Fig. 4(a)] and 1.0 M [Fig. 4(b)] regardless of the counterion, indicating the very strong polarization of the contact layer of solvent molecules. At the lower concentration the superposition of short-range oscillatory structure upon the smooth decay ($e^{-\kappa r}/r^2$) characterizing the large-r behavior is apparent and the differences between the NaCl and KCl results appear rather smaller than might have been expected on the basis of Figs. 2 and 3. Notice that the actual
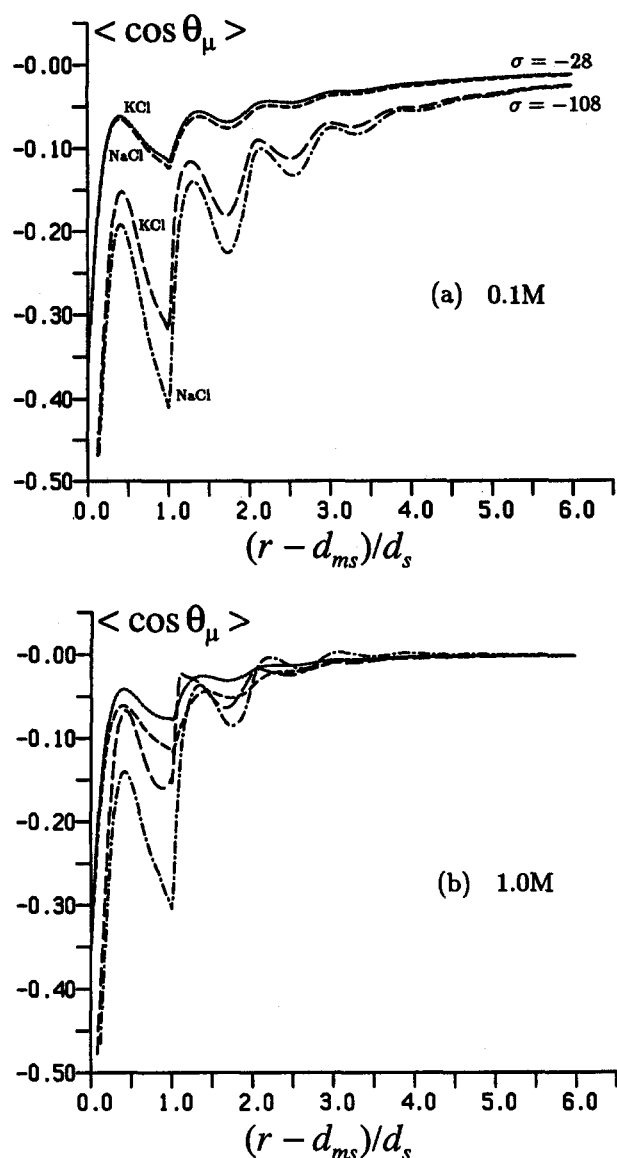
magnitude of the polarization for both salts at large r has only doubled with the near quadrupling of the surface charge density from -28 to -108. This is because the neutralization rate shown in Fig. 3(a) is so much higher at the higher surface charge and shows again that a complete and accurate description of the short-range surface structure of the double layer would be a prerequisite to a predictive theory of the magnitudes of effects even in the distant regions of the diffuse layer. At 1.0 M [Fig. 4(b)] the polarization, like the rest of the interfacial structure, is entirely short ranged and the effects of high surface charge are more extreme. The highly localized peak in the Na^+ density near $1d_s$ from contact is echoed by a virtual singularity in the curvature of $\langle \cos \theta_\mu \rangle$ at the same point for both surface charges; the structure in this same quantity for KCl solutions is less extreme. In both cases, however, there are regions (just beyond $1d_s$, for example) where the stronger oscillatory behavior induced by the larger surface charge results in a *smaller* degree of solvent polarization than for the lower sur-

face charge. For NaCl the numerical values of $\langle \cos \theta_\mu \rangle$ at high surface charge show the opposite sign to the surface charge at large r, consistent with the small excess neutralization mentioned above in the discussion of Fig. 3(b), though this effect is scarcely discernible in Fig. 4(b).

One of the most interesting aspects of double layers in a molecular solvent has turned out to be the behavior of the mean electrostatic potential about the macroion, $\psi(r)$. As one would expect of a molecular solvent model, the $\psi(r)$ predicted by the theory is highly oscillatory and much larger than in the corresponding continuum solvent.[1,3] In addition, however, it exhibits a very large maximum at contact with a sign *opposite* to that of the surface charge and generally appears little correlated with the ionic structure throughout the interface.[3] One might still expect the differences in the short-range structure of the interfaces in NaCl and KCl we have been describing to be reflected in $\psi(r)$ and this is, in fact, the case for the separate ionic and solvent contributions to the total potential as shown in Fig. 5(a). (ψ is expressed in dimensionless form defined by $\psi^* \equiv \psi e/kT$; $\psi \approx \psi^* \times 25.7$ mV.) The lower two curves are the total ionic (macroion,
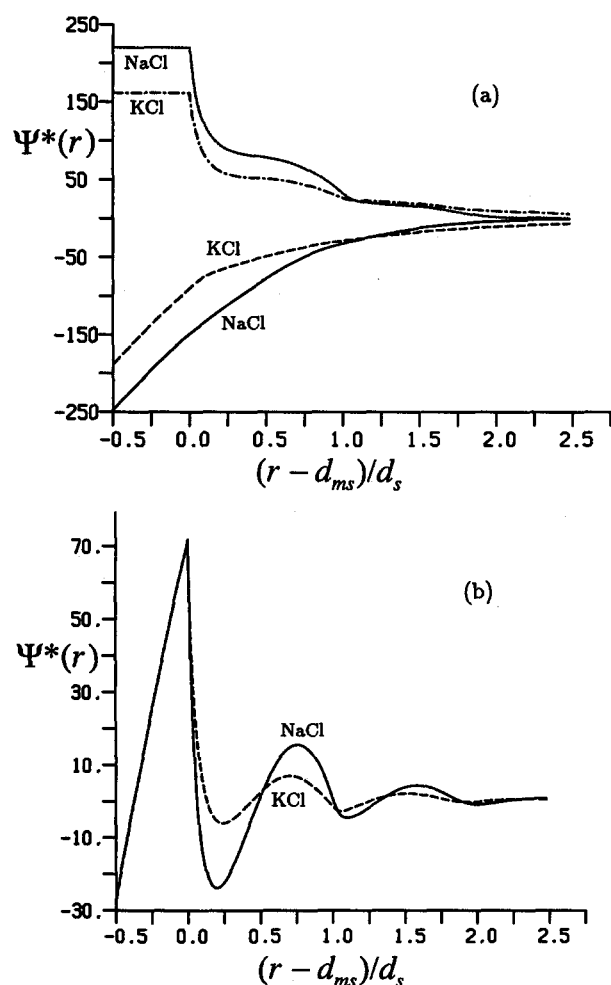

FIG. 5. (a) Ionic and solvent contributions to the mean electrostatic potential $\psi(r)$ for a macroion with $d_m = 10d_s$ and $\sigma = -108$ at 1.0 M; (—) ionic contribution in NaCl; (---) ionic contribution in KCl; ($\cdots$) solvent contribution in NaCl; (—·—) solvent contribution in KCl. (b) Total $\psi(r)$ for this same macroion; (—) in NaCl; (---) in KCl.

anion, and cation) contributions to $\psi(r)$ about a $10d_s$ macroion with surface charge -108 at 1.0 M in KCl and NaCl while the upper two curves are the total solvent contributions to the potential in the same two systems. [The latter contributions are due almost entirely to the field of the solvent dipoles although there is a small quadrupole term; explicit expressions for the components of $\psi(r)$ are given in Eq. (9) of Ref. 3.] In both systems the kink in the ionic component at the counterion contact distance is relatively inconspicuous owing to the dominant contribution made by the large macroion charge. The strong polarization of the contact layer of solvent, on the other hand, leads to the nearly vertical rise in the solvent contribution that terminates abruptly at contact and hence to the large positive spike at this point in the total potential. Of course, there is a large cancellation between these ionic and solvent contributions to $\psi(r)$ at all points [at large distances, the two terms will differ in magnitude by $O(1/\epsilon)$ or about 1%]. Nevertheless, when the two pairs of curves in Fig. 5(a) are added to form the total potential for each of these systems an extraordinary cancellation of a different sort occurs, as shown in Fig. 5(b). Despite differences of $60kT$ (more than 1.5 V) between the two salts in the components of $\psi(r)$ the resulting total potential on the surface of the macroion is the same for both to within $0.1kT$. This is a very general phenomenon that occurs to a greater or lesser degree in all systems we have investigated. In the present instance, the difference between the two surface potentials is probably not significant given the numerical means by which it must be determined but in other systems the difference, though still small, seems to be numerically significant. We are, in any case, skeptical of the possibility of any heretofore undiscovered exact result, especially since it would apparently have to be independent of counterion size and this seems quite implausible for, say, very large counterions.

The surface potential can be interpreted as the work required to bring a test charge that does not affect the system up to the surface from infinity; it is also proportional to the energy of interaction of the single macroion with the solution. Both of these interpretations are grounds for expecting it not to depend strongly on the nature of the salt at low concentration and surface charge where the long-range interactions of an extended diffuse layer must dominate. But the almost total lack of dependence on the significant differences in the short-range structures for different salts even at high surface charges and concentrations is still surprising. If corroborated, it obviously has serious implications for methods of inferring double layer structure from the behavior of the electrostatic potential.

B. Large macroions

All indications from our earlier work on these models[1-3] are that the solvent structure at a flat surface is quite different from that at highly curved surfaces and that the very specific "ice-like" ordering that characterizes flat surfaces is fully established in the macroion model only once the macroion diameter exceeds $20d_s$. Since the small Na^+ ion is especially sensitive to the solvent structure, large changes in the double layer structure of NaCl are expected to accompany the development of this solvent ordering at flatter sur-

faces. We have already seen indications of this at infinite dilution[2] where the potential of mean force between a neutral $30d_s$ macroion and a single Na^+ ion showed a very deep attractive well centered at about $0.7d_s$ beyond contact. This phenomenon manifests itself dramatically at finite concentration as we see in Fig. 6(a) which shows the cation density profiles at the surface of a neutral $30d_s$ macroion for a series of 0.1 M salts with a variety of cation sizes. The Na^+ ion is unique in showing a very high absorption into the region just adjacent to the maximum in the solvent density profile, the solid line in the figure. Even in the absence of so-called specific adsorption forces small highly polarizing cations such as Na^+ are expected to respond differently in the double layer because they are thought to retain a tightly bound solvation shell that prevents them from coming into direct contact with the surface.[7] Although the net result in Fig. 6(a) is similar in some respects to this, we believe quite a different mechanism may be responsible, one which takes into account the evident role of solvent ordering with decreasing surface curvature in inducing the dramatic change in Na^+

FIG. 6. Ion density profiles next to a neutral macroion with $d_m = 30d_s$ in various 0.1 M salts; (—) solvent density profile for all systems; (·−·−) KCl; (···) Eq^+ Eq^- salt; (---) NaCl. (a) cation density profiles; (b) anion density profiles.

response evident between Figs. 1(b) and 6(a). The interactions between solvent molecules in this and other models of liquid water are very strong and highly directional and impose a very specific local orientational order in the bulk solvent. This order is really not compatible with the spherical field of an ion and the high solubility of salts with a small ion such as Na^+ could be thought of as due to the large ion–solvent energy of solvation in spite of a considerable cost in solvent–solvent interactions. At a flat surface the situation is quite different. The same strong and highly directional forces between the solvent molecules now lead to the establishment of an ice-like orientational order in the immediate surface layer.[1,8,9] An interesting property of this layer is that it may be easily polarized in the direction normal to the surface without any significant disruption of the favorable orientations between the solvent molecules comprising it.[1] This may then account for the predisposition of a small ion exerting a high field, such as Na^+, for the region immediately adjacent to this surface layer in preference to the bulk, as indicated by the large peak in Fig. 6(a). Details on the local solvent structure about a Na^+ ion in this surface region, as could be obtained from computer simulation or a fully inhomogeneous theory of the interface, would obviously be helpful in deciding the validity of this hypothesis. The present theory describes only the average effect of this ionic structure on the solvent layer near the surface. This is quite small, as we would expect based on the robustness of the solvent ordering in this region observed previously even with large surface charges.[1] In particular, the angular probability densities which characterize the structure of the pure solvent at a neutral surface[1] are scarcely changed at all in the presence of 0.1 M NaCl.

In Fig. 6(b) we show the anion density profiles that accompany each of the cations in Fig. 6(a). By symmetry, the profile of the Eq^- ion in this figure is identical to that for the Eq^+ cation in Fig. 6(a) and for this salt there can be no charge separation or potential at this neutral surface. The small differences between the lower Cl^- profile here and the K^+ profile in Fig. 6(a) represent a very small charge separation for KCl and the resulting (positive) potential on the surface is extremely small. The large Na^+ peak in NaCl, however, induces a significant increase in the Cl^- density close to the surface so that the Cl^- profiles in NaCl and KCl are quite different here in contrast to the situation for smaller neutral macroions. Obviously, there is a substantial charge separation in the NaCl system; the total charge within one diameter of contact corresponds to a positive surface charge density σ of about 14 and the surface potential of zero charge is nearly 29 mV. Indeed, all of the correlation functions beyond $4d_s$ from the surface in this system resemble those of a diffuse layer with this positive surface charge.

NaCl solutions with a $30d_s$ macroion differ from those with larger cations in another way: The regime in which we can find solutions to the RHNC equations is much reduced. With considerable care and effort we were able to obtain a solution for $\sigma = -28$ in 0.1 M NaCl. The resulting ion profiles are shown in Fig. 7(a). There is no indication of the formation of a second peak in the counterion density closer to contact with the surface; instead, the additional Na^+ pop-
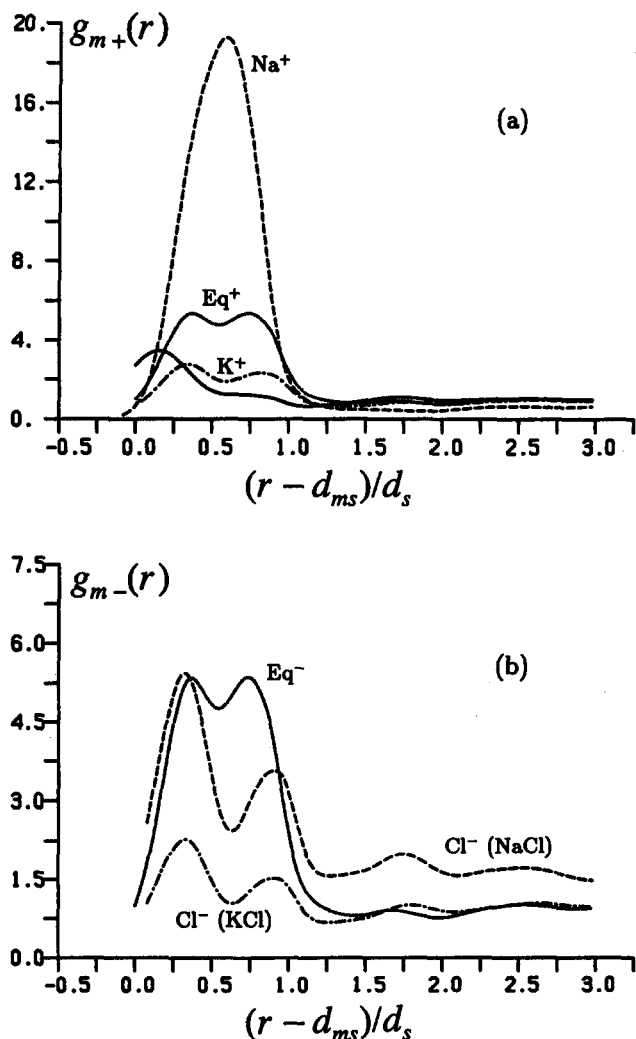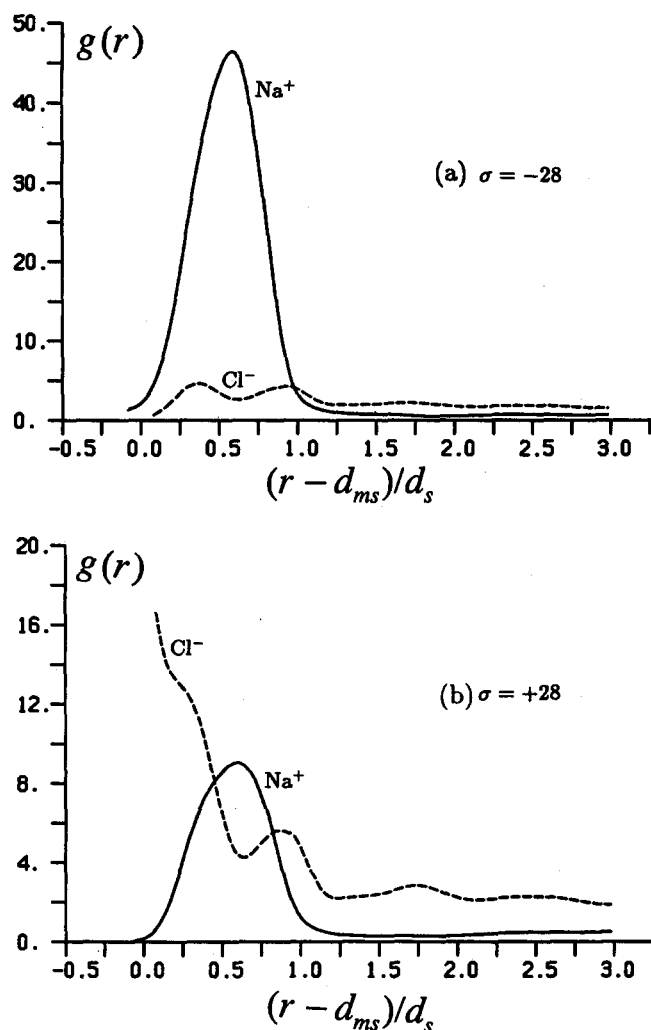
FIG. 7. Ion density profiles next to a charged $30d_s$ macroion in 0.1 M NaCl; (—) Na^+ profile. (---) Cl^- profile. (a) $\sigma = -28$; (b) $\sigma = +28$.

trations which may well be related to our failure to find solutions in the high concentration regime.

The notable asymmetry of the cation and anion profiles at a neutral surface in NaCl makes it the first system we have considered where the behavior at a positively charged surface is also of interest and here solutions to the RHNC equations are relatively easy to obtain. Figure 7(b) shows the ion profiles for 0.1 M NaCl at a $30d_s$ macroion with a surface charge of $+28$. The Na^+ peak has been reduced to half its height at a neutral surface but there is still a region where it exceeds the density of the Cl^- counterion and the neutralization of the macroion charge is temporarily reversed. At still higher positive surface charges the Na^+ is expelled from the surface region and, except for a change of sign, the behavior of the system comes to resemble that of KCl at a negatively charged surface.[3]

A recurring characteristic of our various RHNC results for these macroion systems has been the frequent emergence of a surprisingly simple additivity of effects, particularly those of charged surfaces to short-range effects already present at a neutral surface.[2,3] Something of this nature occurs even for the NaCl system at the $30d_s$ macroion surface which we illustrate in Fig. 8. In this figure we have plotted $f_Q(r)$, the fraction of macroion charge neutralized within a given distance of the macroion, for three 0.1 M systems: KCl and NaCl with $\sigma = -28$ and NaCl with a positive surface charge of $+28$. The most interesting of these is $f_Q(r)$ for NaCl at the negatively charged surface which shows a large excess neutralization of about 50% of the macroion charge coming, of course, from the large Na^+ density peak. (A smaller excess neutralization phenomenon has been observed for this large macroion in KCl also,[3] but only at much higher concentration and arising from quite a different structure in which the strong contact adsorption of K^+ plays a crucial role.) The fourth curve in the figure, the dotted line, represents similar information about the charge near the

ulation has been absorbed into the large peak near $0.7d_s$ whose maximum is now nearly 50 times the bulk density. (This still corresponds to a relatively modest absolute local density, of course, since the reference bulk density for the 0.1 M salt is several hundred times smaller than the solvent density.) This enhanced peak contains more than enough charge to neutralize the negative surface and the behavior of the ion density profiles beyond $1d_s$ in the figure clearly shows that the system is responding as though to a *positive* surface charge even though the surface potential is negative, about -156 mV. From the behavior of the iterative process by which this solution was obtained we believe that this surface charge of -28 is very close to the largest for which the RHNC equations can be solved for a $30d_s$ macroion in 0.1 M NaCl, at least by the methods we have used. We have also been unable to obtain stable solutions to the RHNC equations for even a neutral $30d_s$ macroion in NaCl solutions more concentrated than about 0.1 M. As pointed out above, the general effect of increasing concentration is to enhance whatever short-range structural features are present at low concentration. On this basis, we would expect the Na^+ density peak in Fig. 6(a) to become still larger at high concen-
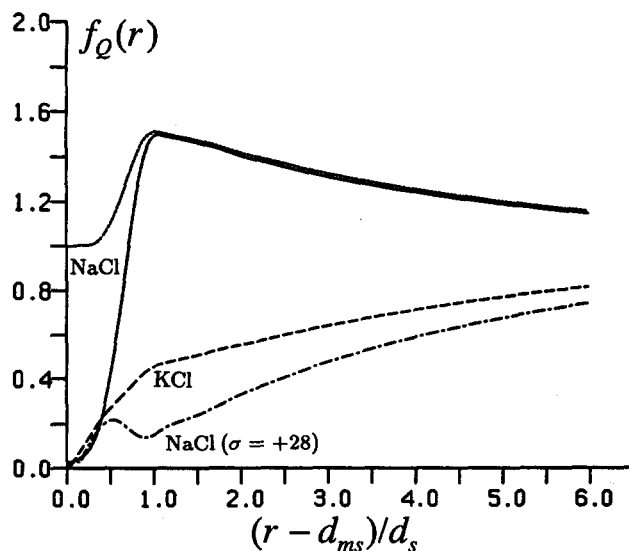

FIG. 8. $f_Q(r)$, the fraction of macroion charge neutralized within r of a $30d_s$ macroion for 0.1 M salts; (—) NaCl, $\sigma = -28$; (---) KCl, $\sigma = -28$; ($\cdots$) $f_0(r)$ (see the text) for NaCl, $\sigma = 0$; (-·-) NaCl, $\sigma = +28$.

neutral macroion for NaCl. $f_Q(r)$ would be meaningless for this system; what we have plotted instead is the quantity $f_0(r) \equiv 1 + Q(r)/28$ where $Q(r)$ is the total charge within a distance r of the neutral macroion. Thus, both $28[f_Q(r) - 1]$ and $28[f_0(r) - 1]$ represent the *total* charge, macroion, anion and cation, within a distance r of the macroion center (expressed as a surface charge density in reduced units). The merging of these two lines just beyond the maximum in $f_Q(r)$ implies that all of the additional cation density required to neutralize the macroion charge resides within, and is merely added to, the density peak of the Na^+ ion for the neutral surface. All parts of the system more than $2d_s$ from the surface see the *same* effective surface charge density of about + 14 in both cases. This is demonstrated in Fig. 9 where we have plotted $\langle \cos \theta_\mu \rangle$ for both these NaCl systems as well as for 0.1 M KCl. Clearly, the polarization per particle beyond two diameters from contact is the same in both NaCl systems. Note also that the small positive peak in the polarization at $1d_s$ is consistent with our speculation above as to the mechanism for the strong adsorption of Na^+ ions into this region.

The excess neutralization phenomenon exhibited by the NaCl system in Fig. 8 has two interesting consequences for the components of the electrostatic potential which we show in Fig. 10(a). First, the ionic contribution (solid line) is not a monotone function of r; second, because the distant regions of the interface experience the field of an effective surface charge that is positive, the ionic contribution to $\psi(r)$ lies *above* the solvent component (dotted line). The contrast with the more conventional behavior of the components of $\psi(r)$ for the same macroion in 0.1 M KCl, also shown in Fig. 10(a), is quite striking. Once again, however, when these pairs of components are added to give the total $\psi(r)$ for each system an astonishing cancellation occurs as shown in Fig. 10(b). The surface potentials for these two entirely different structures differ by about 28 mV (one unit in the dimension-
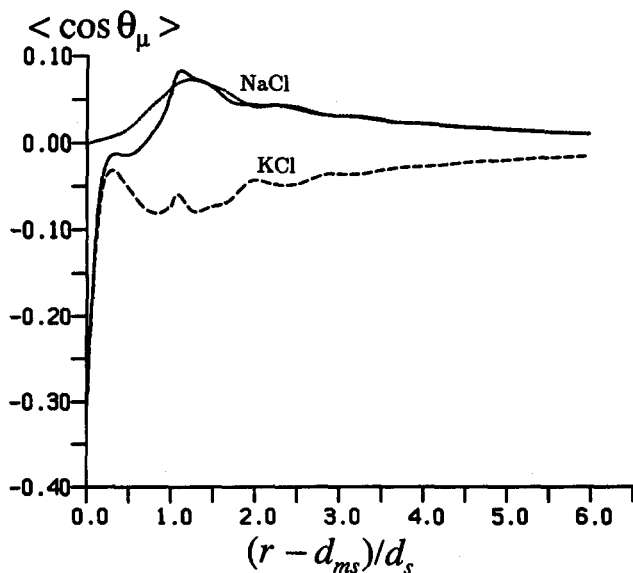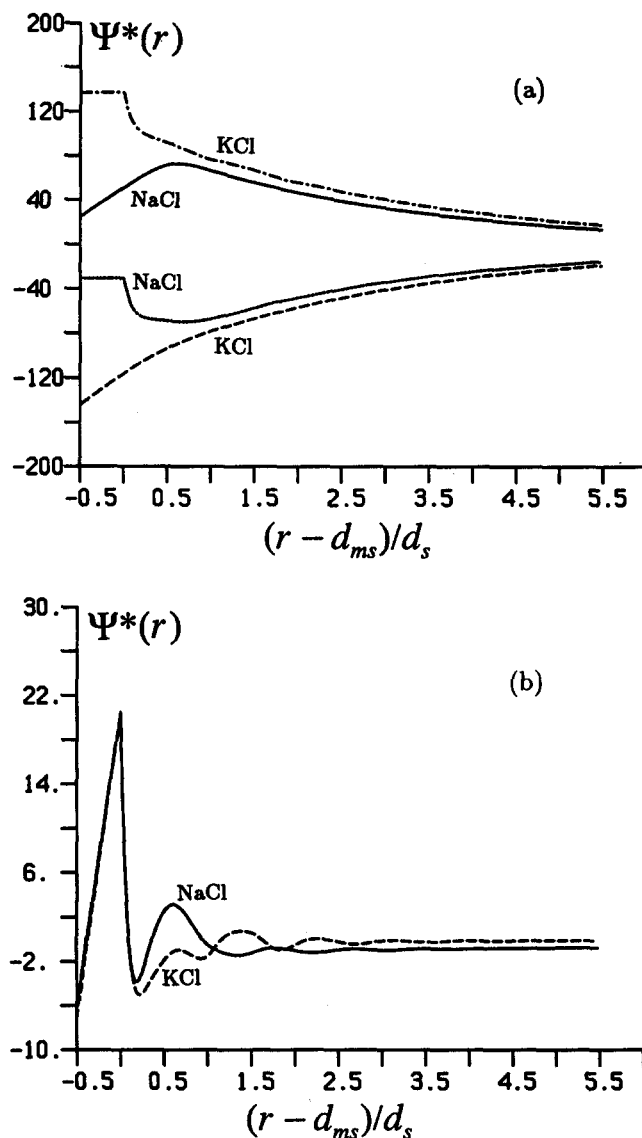

FIG. 10. (a) Ionic and solvent contributions to the mean electrostatic potential $\psi(r)$ for a macroion with $d_m = 30d_s$ and $\sigma = -28$ at 0.1 M; (—) ionic contribution in NaCl; (---) ionic contribution in KCl; (···) solvent contribution in NaCl; (-·-) solvent contribution in KCl. (b) Total $\psi(r)$ for this same macroion; (—) in NaCl; (---) in KCl.

FIG. 9. Solvent polarization per particle $\langle \cos \theta_\mu \rangle$ about a $30d_s$ macroion for 0.1 M salts; symbols as in Fig. 8.

less scale used for ψ in the figures) which is just the difference in the potential of zero charge for these two salts. The only discernible microscopic effect of the rich asymmetry in the structure of the NaCl interface appears to be the addition of this pzc to the value of the potential at charged surfaces in the nearly symmetric KCl and this, of course, produces no effect whatsoever in the differential capacitance relative to that for the same model of a KCl double layer.

III. CONCLUSION

Although the only difference between our models of KCl and NaCl is a reduction of the cation hard sphere diameter from 3.02 to 2.35 Å, the RHNC theory predicts completely different structures for the two salts in the vicinity of a surface. This is not entirely unexpected in view of the large differences in the structure of bulk solutions for these same

models[10] and the strong dependence on ion size of the response to the surface of single ions (i.e., at infinite dilution) which we reported previously.[2] The common principle underlying this variety of behavior near surfaces remains the tyranny of the solvent ordering immediately next to a neutral surface in determining the short-range structure of the charged interface. For NaCl this takes the form of a large, highly localized peak in the Na^+ concentration just outside this ordered solvent layer; we believe this may be interpreted as showing preferential solvation of small ions here due to the ease of polarization of the adjacent surface layer of solvent. At a neutral surface this Na^+ peak produces a potential of zero charge of 29 mV and a positive polarization of the solvent in the resulting diffuse layer. When the surface is negatively charged this peak acquires just enough additional charge to neutralize that on the surface. Consequently, the diffuse region of the interface continues to experience the same effective positive charge as for a neutral surface and responds identically. This is reminiscent of a similar saturation effect at higher surface charges that we found previously in KCl double layers[3] and emphasizes the futility of predicting the sign, much less the magnitude, of diffuse layer properties in a molecular solvent model without an accurate knowledge of the short-range structure near the surface.

The effect of these extremes of ion behavior near the surface on the overall short-range structure of the solvent there is very small, but this is in large part a numbers game in which the absolute ion densities are too small to have much impact on the average solvent behavior. There may well be significant restructuring of the surface layer of solvent in the immediate vicinity of a counterion which would be described in our homogeneous mixture of macroion plus solution by many-body correlation functions, or by a solution of the inhomogeneous Ornstein–Zernike equations for electrolyte and solvent at a planar wall.

More difficult to rationalize is the degree to which the mean electrostatic potential remains unchanged despite this great variety in the ionic structure near the surface. The surface potential in particular seems in these models to be reduced to little more than an indirect measure of the applied surface charge density. Questions about the appropriateness of our highly simplified models and the accuracy of the RHNC theory aside, the fact that nearly identical values of this quantity can mask such disparate surface structures raises some troubling questions about the reliability of inferring such microscopic structure in real systems from measurements of macroscopic properties such as the differential capacitance. In this respect, the status of wholly molecular theories of the double layer is comparable to that of similar theories of bulk electrolyte solution behavior. For the surface problem, however, the lack of experimental methods capable of directly probing the interfacial region on a molecular distance scale is now being keenly felt by theorists.

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