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## Mean Field Analysis of an Ion-Dipole Mixture Next to a Plane Charged Wall<sup>†</sup>

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A mean field analysis is made of a single electrolyte against a plane charged wall with the electrolyte modeled by a mixture of unequal radii hard-charged spheres and dipolar hard spheres. The full set of nonlinear equations are solved numerically for ions of equal size while for ions of different size only the linear and linearized dipole theories are treated. For the linearized dipole theory the capacitances are found to have a nonlinear dependence on the surface charge density. The different ion sizes lead to asymmetry in the capacitance curves and nonzero potentials of zero charge.

### Introduction

The electric double layer of a primitive model electrolyte against a uniformly charged plane wall is now fairly well understood.<sup>1-3</sup> Increasing attention is now being paid to treating the solvent at the same theoretical level as the solute rather than introducing the discrete nature of the solvent in an ad hoc manner in the compact layer. The theoretical approaches that have received the most attention are the mean spherical model (MSA) equation<sup>4-7</sup> and the related generalized MSA equation,<sup>8</sup> which treat the electrolyte as a mixture of charged hard spheres and dipolar hard spheres. Attempts are also being made to adopt the successful bulk reference hypernetted-chain integral theory to this double-layer problem.<sup>9</sup> Another promising approach is that based on a potential approach which uses higher order closures in a generalized Poisson equation.<sup>10</sup> This is the modified Poisson-Boltzmann (MPB) theory which has proved to be very successful in the primitive model analysis of the double layer.<sup>1,11</sup> We hope to eventually treat the MPB equation for an ion-dipole mixture, but for the present we look at the predictions of a mean field analysis of the ion-dipole model. Preliminary work has been done in this direction,<sup>12</sup> where it was found for equal ion sizes that the structural form of the capacitance agrees with that predicted by the MSA theory.<sup>4</sup> We extend this work for a single salt to the situation where the two ion species and the dipole species each have different radii. The linear and linear dipole cases are considered in detail and the full nonlinear system solved numerically for equal ion sizes. The theory is flawed through the poor value of the permittivity of the pure solvent and the lack of structure in the singlet distribution functions. However the theory predicts interesting features such as asymmetric capacitance curves,

nonzero potentials of zero charge, and the qualitative behavior of the Parson-Zobel plots and should be useful in the investigation of nonaqueous solutions.

### Theory

The model chosen to represent the electric double layer is the civilized model electrolyte against a uniformly charged plane wall. The civilized model is the simplest electrolyte model giving structure to the solvent and is a mixture of charged hard spheres and dipolar hard spheres. We shall restrict ourselves to a single electrolyte with the two ion species *i* and *j* having charges  $e_i$  and  $e_j$ , respectively, and one solvent species  $\alpha$  of moment  $\mu$ .

The Poisson equation satisfied by the mean electrostatic potential  $\psi(x)$  a distance  $x$  into the solution from the wall is

$$\frac{d^2\psi}{dx^2} = -4\pi \sum_s e_s n_s(x) + 4\pi \int \mu \cdot \nabla n_\alpha(x, \omega) d\omega \quad (1)$$

where  $e_s$  and  $n_s(x)$  are the charge and mean number density,

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respectively, of ions of species  $s$  at  $x$  and  $n_s(x, \omega)$  is the mean number density of the dipoles at  $x$  with rotational coordinates  $\omega$ . In the mean field closure the mean number densities are given by

$$n_s(x) = n_s^\circ H(x - a_s) \exp(-\beta e_s \psi) \quad (2a)$$

$$n_\alpha(x, \omega) = (n_\alpha^\circ / 4\pi) H(x - a_d) \exp(-\beta \mu \cdot \nabla \psi) \quad (2b)$$

where  $H(x)$  is the Heaviside (unit step) function,  $\beta = 1/kT$ ,  $n_s^\circ$  and  $n_\alpha^\circ$  are the bulk number densities of the ions of type  $s$  and the dipoles, respectively, and  $a_s$  and  $a_d$  the ionic and dipolar radii respectively. With the mean field approximation (2) Poisson's equation (1) becomes

$$\frac{d^2\psi}{dx^2} = -4\pi \sum_s e_s n_s^\circ H(x - a_s) \exp(-\beta e_s \psi) - 4\pi H(x - a_d) n_\alpha^\circ \mu \frac{d}{dx} [(\theta \cosh \theta - \sinh \theta) / \theta^2] \quad (3)$$

where

$$\theta = \beta \mu \frac{d\psi}{dx}$$

The generalized Poisson-Boltzmann equation (3) has to be solved with the boundary conditions

$$(i) \psi, \frac{d\psi}{dx} \rightarrow 0, \text{ as } x \rightarrow \infty$$

$$(ii) \frac{d\psi}{dx^+} = -4\pi\sigma, \quad x = 0$$

$$(iii) \frac{d\psi}{dx^+} = \frac{d\psi}{dx^-} \neq 4\pi\mu n_\alpha^\circ [(\theta^+ \cosh \theta^+ - \sinh \theta^+) / \theta^{+2}], \quad x = a_d$$

where  $\sigma$  is the uniform surface charge density on the wall. The mean electrostatic potential  $\psi$  and its derivative  $d\psi/dx$  are continuous for  $x > 0$  except for the nonlinear boundary condition iii for  $d\psi/dx$  at  $x = a_d$ .

If the dipole term is linearized, the generalized Poisson-Boltzmann equation (3) reduces to

$$\frac{d^2\psi}{dx^2} = -(4\pi/\epsilon) \sum_s e_s n_s^\circ H(x - a_s) \exp(-\beta e_s \psi) \quad (5)$$

where  $\epsilon = 1 + 3yH(x - a_d)$  with  $y = 4\pi\beta\mu^2 n_\alpha^\circ / 9$  and the boundary condition (4iii) at  $x = a_d$  becoming the standard:

$$\epsilon \frac{d\psi}{dx^+} = \frac{d\psi}{dx^-} \quad (6)$$

The highly nonlinear character of both eq 3 and the boundary condition 4iii makes it impossible to derive an analytical solution for  $\psi$ . We shall thus consider various simplifying cases such as the linearized dipole situation, eq 5 and 6, in which analytical progress can be made. However, we do note that a first integral of eq 3 can always be found.

### Equal Ion Sizes

We consider first the equal ion size case  $a_i = a_j$ . In this situation the first integral of eq 3 is<sup>12</sup>

$$(d\psi/dx)^2 + (8\pi n_\alpha^\circ / \beta\theta)(\theta \cosh \theta - 2 \sinh \theta + \theta) = (8\pi/\beta) \sum_s n_s^\circ [\exp(-\beta e_s \psi) - 1], \quad x > \max(a_i, a_d) \quad (7)$$

with for  $a_d < a_i$

$$(d\psi/dx)^3 + 4\pi\sigma(d\psi/dx)^2 + (4\pi n_\alpha^\circ / \mu\beta^2)(\theta \cosh \theta - \sinh \theta) = 0, \quad a_d < x < a_i \quad (8)$$

and for  $a_i < a_d$

$$(d\psi/dx)^2 = (8\pi/\beta) \sum_s n_s^\circ [\exp(-\beta e_s \psi) - \exp(-\beta e_s \psi(a_i))] + 16\pi^2\sigma^2, \quad a_i < x < a_d \quad (9)$$

$$\psi = -4\pi\sigma x + \psi(0^+), \quad x < \min(a_i, a_d) \quad (10)$$

If both the ion and dipole terms are linearized, then  $\psi(x)$  can be found; in particular the integral capacitance  $C_I$  and the differential capacitance  $C_D$  are<sup>12</sup>

$$C_D^{-1} = C_I^{-1} =$$

$$\left\{ (4\pi/\epsilon\kappa)[1 + \kappa a_i + \kappa(\epsilon - 1)a_d], \quad a_d \leq a_i \right. \quad (11a)$$

$$\left. \left\{ (4\pi/\kappa_0) \left[ \kappa_0 a_i + \frac{\kappa + \kappa_0 \tanh \kappa_0(a_d - a_i)}{\kappa \tanh \kappa_0(a_d - a_i) + \kappa_0} \right], \quad a_i \leq a_d \right\} \quad (11b)$$

where

$$\kappa_0^2 = \epsilon\kappa^2 = 4\pi\beta \sum_s e_s^2 n_s^\circ, \quad \epsilon = 1 + 3y \quad (12)$$

The capacitances are independent of the surface charge  $\sigma$  and for  $a_d < a_i$  have the same structure as the MSA result.<sup>4</sup> Expanding eq 11b to  $0(\kappa a)$  gives eq 11a, but in general there are not independent contributions from the ions and dipoles to the inverse capacitances for  $a_i < a_d$ . Linearizing only the dipole term in eq 7 and 8, we now have a Gouy-Chapman type problem which can be solved analytically provided the Gouy-Chapman equation is solvable and, if  $a_i < a_d$ , eq 9 is solvable. For a  $z:z$  electrolyte with  $a_d < a_i$  and only linearized dipole terms, the mean electrostatic potential is

$$\psi = -4\pi\sigma[x - a_d + (a_d - a_i)/\epsilon] + \psi(a_i), \quad 0 \leq x \leq a_d \quad (13)$$

$$\psi = -(4\pi\sigma/\epsilon)(x - a_i) + \psi(a_i), \quad a_d \leq x \leq a_i \quad (14)$$

$$\tanh [ze\beta\psi/4] = \tanh [ze\beta\psi(a_i)/4] \exp[-\kappa(x - a_i)], \quad x \geq a_i \quad (15)$$

$$\psi(a_i) = (2/ze\beta) \sinh^{-1} [\sigma(\pi\beta/\epsilon n_t^\circ)^{1/2}] \quad (16)$$

and the capacitances are<sup>13</sup>

$$C_I^{-1} = (4\pi/\epsilon)[a_i + (\epsilon - 1)a_d] + \psi(a_i)/\sigma \quad (17)$$

$$C_D^{-1} = (4\pi/\epsilon)[a_i + (\epsilon - 1)a_d + \kappa^{-1}(1 + \sigma^2\pi\beta/\epsilon n_t^\circ)^{-1/2}] \quad (18)$$

where  $e$  is the absolute value of the electronic charge and  $n_t^\circ = n_i^\circ + n_j^\circ$ .

The general solution for  $\psi(x)$  when  $a_i < a_d$  involves incomplete elliptic integrals stemming from the integration of eq 9 (see eq 49). A solution in terms of elementary functions, corresponding to the case  $B = 1$  in eq 49, occurs when  $\sigma$  satisfies

$$\cosh^{-1} [(2\pi\sigma^2/n_t^\circ) - 1] = 2 \ln \{\tan [\frac{1}{2} \sin^{-1} (\kappa_0/2\pi\sigma ze\beta)]\} \quad (19)$$

giving

$$C_I^{-1} = 4\pi a_i + (ze\beta\sigma)^{-1} \cosh^{-1} [(2\pi\sigma^2\beta/n_t^\circ) - 1] \quad (20)$$

In contrast to the fully linearized theory the capacitances (17, 18) for  $a_d < a_i$  have a nonlinear term in the surface charge. This surface charge contribution is independent of the ion and dipole radii and hence is a contribution to the "diffuse" rather than the "Stern" part of the double layer. The capacitances are symmetrical about  $\sigma = 0$  with the capacitances taking their full linear value at  $\sigma = 0$ , while for  $|\sigma| \rightarrow \infty$ , the surface charge contribution vanishes and

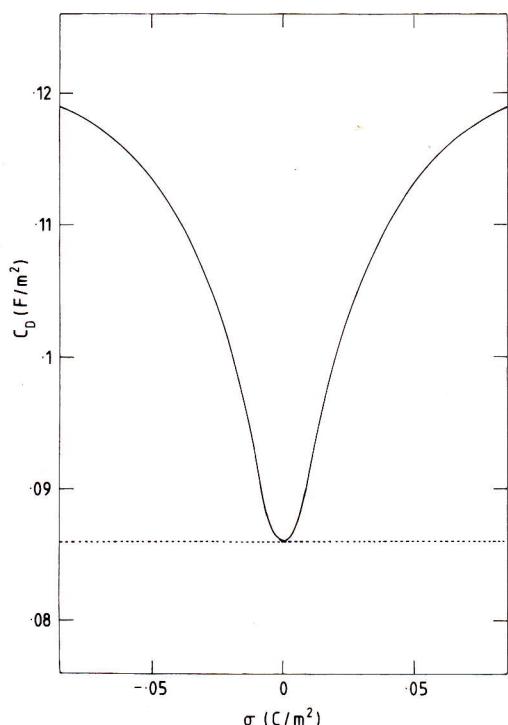
$$C^{-1} = (4\pi/\epsilon)[a_i + (\epsilon - 1)a_d] \quad (21)$$

where  $C = C_I$  or  $C_D$ . The capacitances for a  $a_i < a_d$  are also symmetric about  $\sigma = 0$  with

$$C^{-1} \rightarrow 4\pi a_i \quad (22)$$

as  $|\sigma| \rightarrow \infty$ . The limits (21) and (22) are physically reasonable for a point ion model, as for large surface charge the counterions can accumulate at  $x = a_i$  and essentially balance the wall charge. Thus the capacitances (21, 22) correspond to those for a parallel plate capacitor with a charge  $-\sigma$  at  $x = a_i$ . In the case  $a_d < a_i$  there is a solvent of permittivity  $\epsilon = 1 + 3y$  in  $a_d < x < a_i$ , while for  $a_i < a_d$  the solvent is irrelevant.

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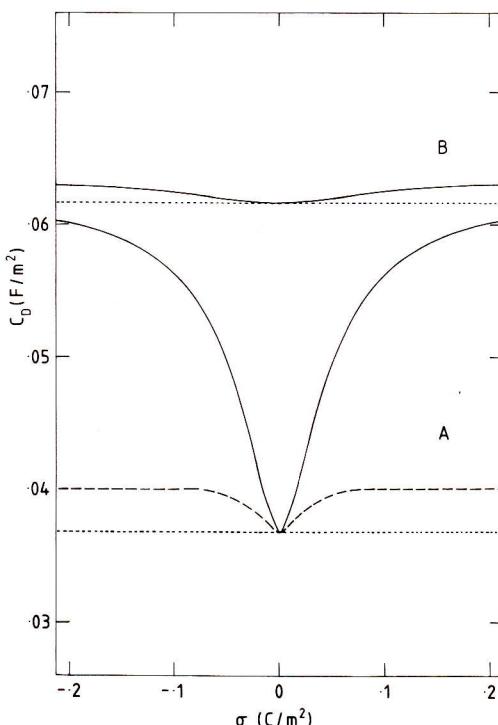
**Figure 1.** Variation of differential capacitance with surface charge at  $c = 1 \text{ M}$  for  $a_i = a_d/2$ ,  $\epsilon = 1.8$ : (—) nonlinear, (---) full linear. The linear dipole and nonlinear curves are almost identical. The curves for  $\epsilon = 78.5$  are marginally greater than those for  $\epsilon = 1.8$ .

The differential capacitances were calculated for a 1:1 electrolyte at a concentration of 1 M ( $\eta_i = \pi(a_i + a_j)^3 n_i^{\circ}/6 = 6.307(a_i + a_j)^3 \times 10^{-4}$ ) with dipole parameters  $a_d = 1.38 \text{ \AA}$ ,  $\eta_d = \pi a_d^3 n_a^{\circ}/6 = 0.04$ , and  $\mu^2/a_d^3 kT = 2.5$  giving  $\epsilon = 1.8$ . The radii of the ions were taken as either  $2a_d$  or  $a_d/2$  while calculations were also performed for  $\epsilon = 78.5$  at the same electrolyte concentration (i.e.,  $\eta_i$  fixed). The permittivities  $\epsilon = 1.8$  and  $\epsilon = 78.5$  correspond to  $\mu = 0.52 \text{ D}$  and  $\mu = 5.12 \text{ D}$ , respectively at  $T = 298 \text{ K}$  and  $\eta_d = 0.04$ .

A numerical solution of the full nonlinear set of equations (7–9) with the boundary conditions (4) was also found to investigate the nonlinear dielectric effects. The numerical solution of eq 7–9 involved a simple iteration scheme based on the finite difference technique. In the case  $a_d < a_i$  the mean electrostatic potential is linear in the region  $x < a_i$ , and hence the solution can be easily found in this region. Equation 8 was solved at a fixed surface charge to derive  $d\psi/dx$  in  $a_d < x < a_i$ . The boundary conditions 4iii then gives  $d\psi(a_i^+)/dx$ , and hence  $\psi(a_i)$  can be derived from eq 7, which specifies  $\psi$  for  $x \leq a_i$ . To calculate  $\psi$  for  $x > a_i$ , the linear solution is used as a first approximation for  $\psi$ , and then the first derivatives at the mesh points calculated from eq 7. The derivatives  $d\psi/dx$  are approximated by the three-point central difference formula with the known left-hand end point  $\psi(a_i)$  and a linear approximation for the right-hand end point. A first approximation to  $\psi$  can now be found at the even mesh points, and an interpolation used for the odd mesh points. With this new  $\psi$  the process is repeated until a suitable convergence is obtained. If only the capacitances are required, the iterated solution in  $x > a_i$  is not needed as  $\psi(a_i)$ , and hence  $\psi(0)$ , is known.

In the case  $a_i < a_d$  the value of  $\psi(a_d)$  at the left-hand mesh point of eq 7 cannot be directly found. To calculate  $\psi(a_d)$ , an approximate  $d\psi(a_d^+)/dx$  is calculated from eq 7 by using the linear value of  $\psi(a_d)$ . The corresponding  $\psi(a_i)$  is now found from the boundary condition 4iii and eq 9. Since eq 9 can be formally integrated, a new  $\psi(a_d)$  corresponding to this  $\psi(a_i)$  can be found numerically. This process is repeated until consistency is achieved between  $\psi(a_d)$  and  $\psi(a_i)$ . When  $\psi(a_d)$  is known the solution for  $x > a_d$  can now be found as for  $a_d < a_i$ .

The variation of the differential capacitance  $C_D$  with surface charge  $\sigma$  at  $c = 1 \text{ M}$  for  $a_d > a_i$  and  $a_d < a_i$  is given in Figures

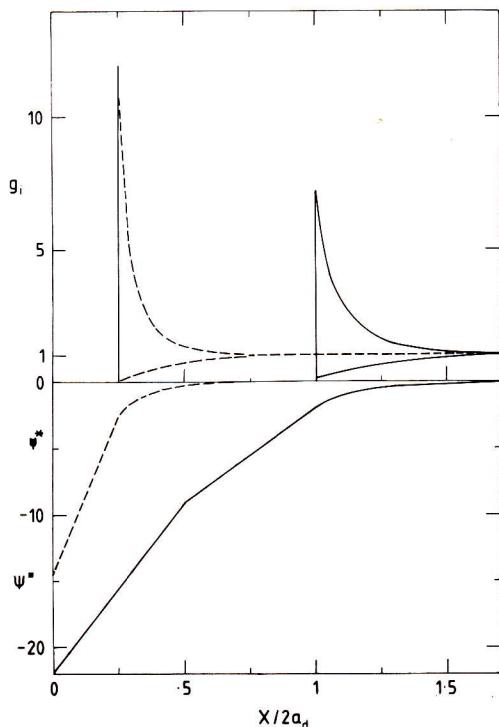


**Figure 2.** Variation of differential capacitance with surface charge at  $c = 1 \text{ M}$  for  $a_i = 2a_d$ : A,  $\epsilon = 1.8$ ; B,  $\epsilon = 78.5$ ; (—) nonlinear; (---) linear dipole; (---) full linear.

1 and 2. As the ionic radii are equal, we have that the differential capacitances are symmetric about the position of zero charge. Also we see that the full linear  $C_D$ , eq 11a,b, are in agreement only with the nonlinear and linear dipole theories at the position of zero charge. In Figure 1 we have  $C_D$  for the nonlinear and linear theory with  $a_d = 2a_i$  and  $\epsilon = 1.8$ . The linear dipole theory gives essentially the same values as the nonlinear theory, while for  $\epsilon = 78.5$  the  $C_D$  of these two theories is again in agreement and also only marginally greater than the  $\epsilon = 1.8$  case. This invariance of the values of  $C_D$  between the two values of  $\epsilon$  and the nonlinear and linear dipole theories indicates that the double-layer behavior is dominated by the smaller ions. In Figure 2 we have the case  $a_i = 2a_d$  for  $\epsilon = 1.8$  and  $\epsilon = 78.5$ . This figure shows the importance of dielectric effects when the dipoles can get closer to the wall than the ions. When  $\epsilon = 1.8$  the response of the nonlinear theory to increasing  $|\sigma|$  from zero is much greater than that for the linear dipole theory. The nonlinear theory predicts a more rapid rise from the position of zero charge and approaches a constant  $C_D$  at a much larger value of  $|\sigma|$ . At  $\epsilon = 78.5$  the nonlinear effects are damped out with the nonlinear and linear dipole values being nearly identical and only a small deviation from the linear  $C_D$  occurring away from the position of zero charge. The nonlinear ion distribution function  $g_i(x)$  and the dimensionless mean electrostatic potential  $\psi^*(x)$  ( $=e\beta\psi(x)$ ) are given in Figure 3 at  $\sigma = -0.021 \text{ C/m}^2$  for the two values of  $a_i$ . The curves display the monotonic behavior found for all values of  $\sigma$  while in the case  $a_d < a_i$  we see the large double layer arising from the lack of shielding of the surface charge by the ions.

#### Unequal Ion Sizes

We now consider the case of unequal ion sizes and always suppose that  $a_i < a_d$ . Depending upon the value of the dipole radius  $a_d$  there are three situations to consider. In all these cases the full linear solution can be found explicitly. We will state only the differential capacitance and the potential of zero charge (pzc) for the linear theory as it is straightforward, although tedious, to derive the full solution. For the linear dipole theory when  $a_d < a_i < a_j$  and  $a_i < a_d < a_j$  an analytical solution can be found by following the analysis of Valleau and Torrie.<sup>14</sup> When  $a_i <$



**Figure 3.** Nonlinear dimensionless mean electrostatic potential  $\psi^*(x)$  ( $=\epsilon\beta\psi(x)$ ) and singlet ion distribution functions  $g_i(x)$  at  $c = 1 \text{ M}$  for  $\sigma = -0.021 \text{ C/m}^2$ : (—)  $a_i = 2a_d$ ; (--)  $a_i = a_d/2$ .

$a_j < a_d$  the solution can be formulated only in terms of incomplete elliptic integrals as in the equal ion size case. The linear dipole results are stated for  $z:z$  valence electrolytes.

$a_d < a_i < a_j$ . The differential capacitance  $C_D$  and the pzc,  $\psi(x=0, \sigma=0)$  for the linear theory are

$$C_D^{-1} = (4\pi/\epsilon\kappa_i) \{1 + \kappa_i a_i + \kappa_i a_d (\epsilon - 1) + [(\kappa_i - \kappa)/D] \exp[-\kappa_i(a_j - a_i)]\} \quad (23)$$

$$\text{pzc} = (c_i/\kappa_i^2)[1 - \kappa/D] \quad (24)$$

where

$$\begin{aligned} D &= \kappa_i \sinh [\kappa_i(a_j - a_i)] + \kappa \cosh [\kappa_i(a_j - a_i)] \\ c_i &= 4\pi n_i^\circ e_i / \epsilon \\ \kappa_i^2 &= 4\pi\beta n_i^\circ e_i^2 / \epsilon \end{aligned} \quad (25)$$

For the linear dipole theory the mean potential is

$$\psi = -4\pi\sigma[x - a_d + (a_d - a_i)/\epsilon] + \psi(a_i), \quad 0 \leq x \leq a_d \quad (26)$$

$$\psi = -(4\pi\sigma/\epsilon)(x - a_i) + \psi(a_i), \quad a_d \leq x \leq a_i \quad (27)$$

$$\begin{aligned} \psi &= (2/\beta e_i) \ln [\sinh (\mp\kappa_i x(B/2)^{1/2} + CB^{1/2})/B^{1/2}], \quad a_i \leq x \leq a_j \\ (28) \end{aligned}$$

$$\tanh [ze\beta\psi/4] = \tanh [ze\beta\psi(a_j)/4] \exp[-\kappa(x - a_j)], \quad x \geq a_j \quad (29)$$

The constants  $C$  and  $B$  and the values of the mean potential at  $a_i$  and  $a_j$  are found from the continuity of  $\psi$  at  $a_i$  and  $a_j$  and from the relations

$$B = -2 + \exp[e_i\beta\psi(a_j)] \quad (30)$$

$$B = y^2 - \exp[-e_i\beta\psi(a_i)] \quad (31)$$

where

$$y^2 = (2\pi\beta/\epsilon n_i^\circ)\sigma^2$$

In particular we can derive the relation

$$y = [scB^{1/2} - B(B+1)(B+2)^{1/2}] / [s^2 - B(B+2)] \quad (32)$$

where

$$s = \sinh [\kappa_i(a_j - a_i)(B/2)^{1/2}], \quad c = \cosh [\kappa_i(a_j - a_i)(B/2)^{1/2}]$$

which gives the  $\sigma$  vs  $\psi(0)$  relation on using eq 26 and 31 to eliminate  $B$  and  $\psi(a_i)$ . As  $-2 < B < \infty$  the results for  $B < 0$  are simply obtained by  $B^{1/2} \rightarrow i|B|^{1/2}$  and using the relations between the harmonic and hyperbolic functions. For a given  $\sigma$ , the constant  $B$  can be calculated and hence  $\psi(x)$  determined. No simple analytical formula can be derived for the pzc or for the differential capacitance. However the value of  $\psi(a_i)$  at the pzc is given by<sup>14</sup>

$$2 \exp[-e_i\beta\psi(a_i)] - \exp[-2e_i\beta\psi(a_i)] = \cos^2[\kappa_i(a_j - a_i)/(2^{1/2} \exp[e_i\beta\psi(a_i)/2])] \quad (33)$$

while for a 1:1 salt we have the following limits for the differential capacitance:

$$\lim_{\sigma \rightarrow \infty} C_D^{-1} = (4\pi/\epsilon)[a_j + (\epsilon - 1)a_d] \quad (34)$$

$$\lim_{\sigma \rightarrow -\infty} C_D^{-1} = (4\pi/\epsilon)[a_i + (\epsilon - 1)a_d]$$

The above results reduce to the primitive model electrolyte results on letting  $a_d \rightarrow 0$  and putting  $\epsilon$  equal to its bulk value.

$a_i < a_d < a_j$ . In this case the differential capacitance and the pzc for the linear theory are

$$C_D^{-1} = (4\pi/\kappa_{i0})\{\kappa_{i0}a_i - D_1^{-1}[(\kappa_{i0} - \epsilon\kappa_i)(\kappa_i c_2 + \kappa s_2) + (\kappa_{i0} + \epsilon\kappa_i)(\kappa_i c_1 + \kappa s_1)]\} \quad (35)$$

$$\text{pzc} = (c_i/\kappa_i^2)[1 + 2\kappa\epsilon/D_1] \quad (36)$$

where

$$D_1 = (\kappa_{i0} - \epsilon\kappa_i)(\kappa_i s_2 + \kappa c_2) - (\kappa_{i0} + \epsilon\kappa_i)(\kappa_i s_1 + \kappa c_1)$$

$$\begin{aligned} s_1 &= \sinh [\kappa_{i0}(a_d - a_i) + \kappa_i(a_j - a_d)], \\ c_1 &= \cosh [\kappa_{i0}(a_d - a_i) + \kappa_i(a_j - a_d)] \end{aligned} \quad (37)$$

$$\begin{aligned} s_2 &= \sinh [-\kappa_{i0}(a_d - a_i) + \kappa_i(a_j - a_d)], \\ c_2 &= \cosh [-\kappa_{i0}(a_d - a_i) + \kappa_i(a_j - a_d)] \end{aligned}$$

$$\kappa_{i0} = \epsilon^{1/2}\kappa_i$$

The mean potential for the linear dipole case is

$$\psi = -4\pi\sigma(x - a_i) + \psi(a_i), \quad 0 \leq x \leq a_i \quad (38)$$

$$\begin{aligned} \psi &= (2/\beta e_i) \ln [\sinh (\mp\kappa_{i0}x(A/2)^{1/2} + K_1)/A^{1/2}], \quad a_i \leq x \leq a_d \\ (39) \end{aligned}$$

$$\begin{aligned} \psi &= (2/\beta e_i) \ln [\sinh (\mp\kappa_{i0}x(B/2)^{1/2} + K_2)/B^{1/2}], \quad a_d \leq x \leq a_j \\ (40) \end{aligned}$$

$$\tanh [ze\beta\psi/4] = \tanh [ze\beta\psi(a_j)/4] \exp[-\kappa(x - a_j)], \quad x \geq a_j \quad (41)$$

with the boundary conditions giving

$$B = -2 + \exp[-e_i\beta\psi(a_j)]$$

$$K_2 = \pm\kappa_{i0}a_d(B/2)^{1/2} + \sinh^{-1} \{B^{1/2} \exp[e_i\beta\psi(a_j)/2]\}$$

$$\psi(a_d) = (2/e_i\beta) \ln [\sinh (\mp\kappa_{i0}a_d(B/2)^{1/2} + K_2)/B^{1/2}] \quad (42)$$

$$A = \epsilon B + (\epsilon - 1) \exp[-e_i\beta\psi(a_d)]$$

$$K_1 = \pm\kappa_{i0}a_i(A/2)^{1/2} + \sinh^{-1} \{A^{1/2} \exp[e_i\beta\psi(a_d)/2]\}$$

$$\psi(a_i) = (2/e_i\beta) \ln [\sinh (\mp\kappa_{i0}a_i(A/2)^{1/2} + K_1)/A^{1/2}]$$

$$\epsilon y^2 = A + \exp[-e_i\beta\psi(a_i)]$$

In the previous linear dipole case we were able to derive eq 32, which gave the relation between  $\sigma$  and  $\psi(a_i)$ . Unfortunately no such simple relation corresponding to eq 32 seems to exist for  $a_i < a_d < a_j$  so that an indirect approach has to be used. Either  $B$  or  $\psi(a_i)$  is specified, and then by use of the relations 42 in succession the corresponding surface charge and mean electrostatic potential can be derived. The limiting values of the differential

capacitance at high surface charge for a 1:1 electrolyte are

$$\lim_{\sigma \rightarrow \infty} C_D^{-1} = (4\pi/\epsilon)[a_j + (\epsilon - 1)a_d] \quad (43)$$

$$\lim_{\sigma \rightarrow -\infty} C_D^{-1} = 4\pi a_i$$

$a_i < a_j < a_d$ . The differential capacitance and the pzc for the linear theory are

$$C_D^{-1} = (4\pi/\kappa_{i0})[\kappa_{i0}a_i + (1 + dt_3)/(d + t_3)] \quad (44)$$

$$\text{pzc} = (c_i/\kappa_i^2)[1 - c_3 + s_3(1 + dt_3)/(d + t_3)] \quad (45)$$

where

$$d = (\kappa_0/\kappa_{i0})(\kappa t_4 + \kappa_0)/(\kappa + \kappa_0 t_4)$$

$$s_3 = \sinh [\kappa_{i0}(a_j - a_i)], \quad c_3 = \cosh [\kappa_{i0}(a_j - a_i)] \quad (46)$$

$$t_3 = \tanh [\kappa_{i0}(a_j - a_i)], \quad t_4 = \tanh [\kappa_0(a_d - a_j)]$$

while for the linear dipole theory the mean electrostatic potential is given by

$$\psi = -4\pi\sigma(x - a_i) + \psi(a_i), \quad 0 \leq x \leq a_i \quad (47)$$

$\psi =$

$$(2/\beta e_i) \ln [\sinh (\mp\kappa_{i0}x(C/2)^{1/2} + K_1)/C^{1/2}], \quad a_i \leq x \leq a_j \quad (48)$$

$$\int_{\psi(a_j)}^{\psi(x)} \frac{d\psi}{[\cosh(z\beta\psi) + B]^{1/2}} = \\ = (8\pi n_t^\circ/\beta)(x - a_j), \quad a_j \leq x \leq a_d \quad (49)$$

$\tanh [ze\beta\psi/4] =$

$$\tanh [ze\beta\psi(a_d)/4] \exp[-\kappa(x - a_d)], \quad x \geq a_d \quad (50)$$

with the boundary conditions giving

$$B = (\epsilon - 1) \cosh [ze\beta\psi(a_d)] - \epsilon$$

$$C = 2B + \exp[ze\beta\psi(a_j)]$$

$$K_1 = \pm\kappa_{i0}a_j(C/2)^{1/2} + \sinh^{-1} [C^{1/2} \exp[e_i\beta\psi(a_j)/2]] \quad (51)$$

$$\psi(a_i) = (2/e_i\beta) \ln \{ \sinh [\mp\kappa_{i0}a_i(C/2)^{1/2} + K_1]/C^{1/2} \}$$

$$\epsilon y^2 = C + \exp[-e_i\beta\psi(a_i)]$$

Unlike the two previous linear dipole situations we do not have an explicit analytical solution for  $\psi(x)$  because of the incomplete elliptic integral occurring in  $a_j < x < a_d$ . To calculate the solution for  $\psi(x)$ , we set  $\psi(a_d)$  and deduce  $B$  from the first of the relations 51. The upper limit of the integral relation 49 is taken at  $x = a_d$  and the equation solved for  $\psi(a_j)$ . The remainder of the relations (51) are now evaluated in sequence to complete the solution. We can again derive the limiting behavior of the differential capacitance at high surface charge, which for 1:1 electrolytes are

$$\lim_{\sigma \rightarrow \infty} C_D^{-1} = 4\pi a_j \quad (52)$$

$$\lim_{\sigma \rightarrow -\infty} C_D^{-1} = 4\pi a_i$$

The analytical results for the differential capacitance and the pzc indicate the complex interplay between the solute and solvent molecules. Only in the case  $a_d < a_i < a_j$  can we identify separate contributions from the solute and solvent molecules. This is surprisingly true for both theories since for the linear dipole theory the relations 32 and 33 are independent of the dipole radius  $a_d$ . Doubtless no independent contributions will occur in the full nonlinear theory. The limits of  $C_D$  as  $|\sigma| \rightarrow \infty$  for the three cases reduce to the capacitances of the parallel plate capacitor as seen in the equal ion size situation. In all the cases these limits are independent of the electrolyte concentration.

#### Numerical Results

In the calculations we take the previous values of the solvent parameters and assume without loss of generality that the smaller

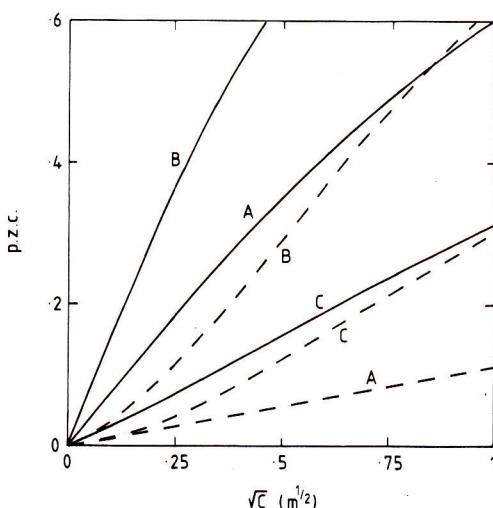
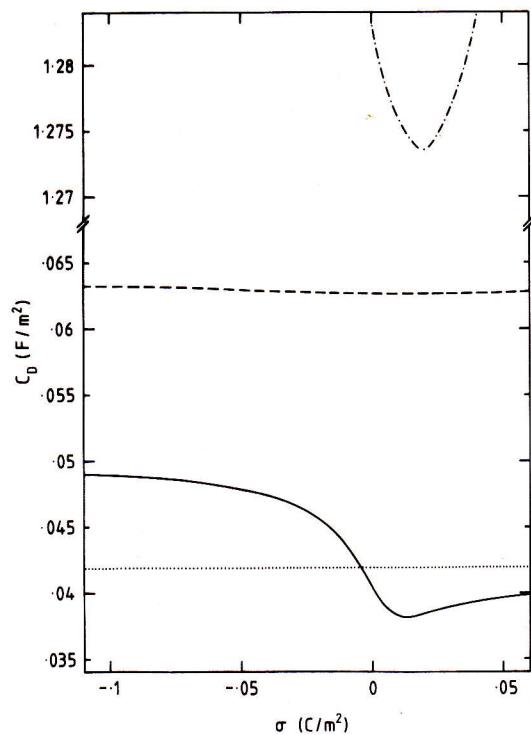


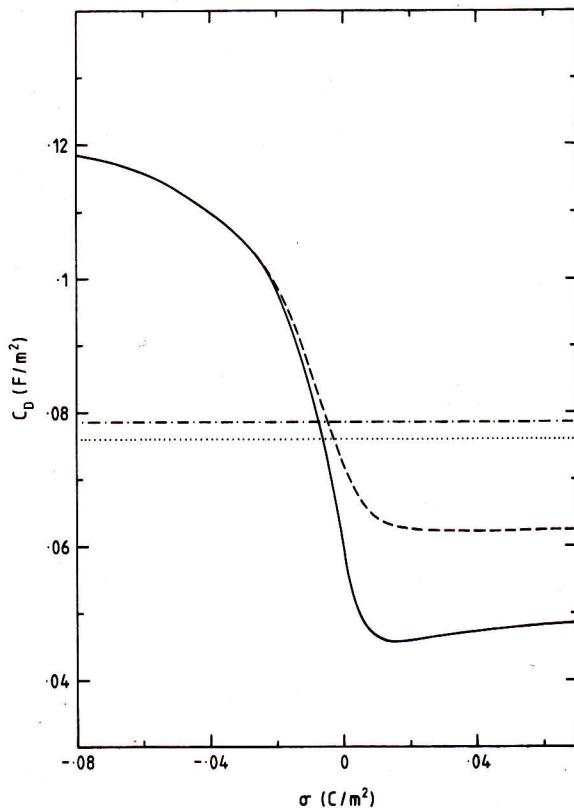
Figure 4. Variation of the dimensionless pzc ( $=e\beta\psi(0,\sigma=0)$ ) with the square root of the electrolyte concentration at differing ionic radii for the linear dipole theory: (—)  $\epsilon = 1.8$ ; (---)  $\epsilon = 78.5$ ; A,  $a_i = 3a_d/2$ ,  $a_j = 2a_d$ ; B,  $a_i = a_d/2$ ,  $a_j = 3a_d/2$ ; C,  $a_i = a_d/2$ ,  $a_j = 2a_d/3$ .

ion is a cation. For the three cases we take the ion radii as (i)  $a_i = 3a_d/2$ ,  $a_j = 2a_d$ , (ii)  $a_i = a_d/2$ ,  $a_j = 3a_d/2$ , and (iii)  $a_i = a_d/2$ ,  $a_j = 2a_d/3$ , where  $a_d = 1.38 \text{ \AA}$ . We also consider again the simple case of a uni-univalent electrolyte. The numerical calculation of the linear dipole solution is fairly straightforward. The square-root sign chosen depends on the surface charge, on the charge of the smaller ion and, when  $\psi(x)$  is not monotonic, on the position of  $d\psi/dx = 0$ . Care also has to be taken in choosing the correct range of the inverse harmonic functions.

In Figure 4 is plotted the variation of the dimensionless pzc with electrolyte concentration at fixed solvent concentration for the linear dipole theory. The behavior of the pzc is similar for both the linear and linear dipole theories, with the theories being identical for low concentrations. For small concentrations the theory predicts a linear variation of the pzc with the square root of the concentration. This linear dependence can be clearly seen, especially for the  $a_d < a_i < a_j$ ,  $\epsilon = 78.5$  situation. Only for the two cases  $a_i < a_d < a_j$ ,  $a_i < a_j < a_d$  with  $\epsilon = 78.5$  is the linear dependence restricted to very small concentrations. Figures 5–7 show the variation of the differential capacitance at an electrolyte concentration of 1 M. In contrast to the equal ion size case the linear dipole  $C_D$  curves show a marked asymmetry. We can also see that the linear theory is totally inadequate in describing  $C_D$ , even in the neighborhood of the pzc. To interpret the  $C_D$  curves, consider in turn the three cases (i)  $a_d < a_i < a_j$ , (ii)  $a_i < a_d < a_j$ , and (iii)  $a_i < a_j < a_d$ . In the first case solvent effects are important as the solvent molecules have the smallest distance of approach to the wall. This importance is reflected in the widely differing results for  $\epsilon = 1.8$  and  $\epsilon = 78.5$  and in the primitive model calculation when  $a_d = 0$ . The actual asymmetry in the capacitance is not as great as we would expect because the dipole terms are linearized in the theory and hence the solvent response to the surface charge is underestimated. For case ii the solvent is relatively unimportant when  $a_i$  is the counterion as the ion can shield the wall charge without the solvents' influence; hence the results for  $\epsilon = 1.8$  and  $\epsilon = 78.5$  are nearly identical. However, when  $a_i$  is the co-ion, solvent effects become important, and because of their inadequate treatment the variation of  $C_D$  is relatively small and the results differ for different  $\epsilon$ . In the third case the solvent molecule has the largest radii so that it has only a small influence on the shielding of the wall charge by the ions. This minor role played by the solvent means that  $C_D$  is identical for both  $\epsilon = 1.8$  and  $\epsilon = 78.5$  except in the neighborhood of the minimum of  $C_D$  where the  $\epsilon = 1.8$  curve lies slightly below that of  $\epsilon = 78.5$ . The change in  $C_D$  with electrolyte concentration at fixed solvent parameters is shown in Figure 8. As the concentration is lowered, the minimum value of  $C_D$  decreases and the value of  $|\sigma|$  at the minimum becomes smaller. The limits of  $C_D$  as  $|\sigma| \rightarrow \infty$  are



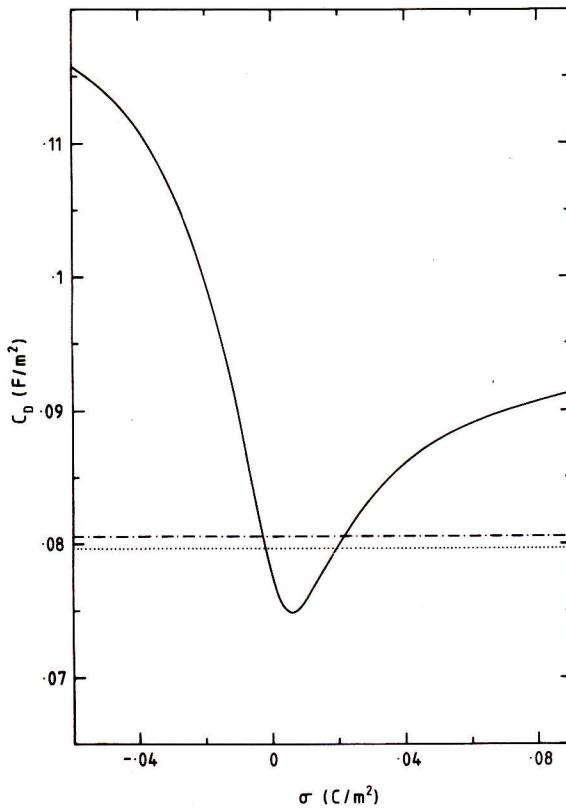
**Figure 5.** Variation of the differential capacitance with surface charge at  $c = 1 \text{ M}$  for  $a_i = 3a_d/2$ ,  $a_j = 2a_d$ : (—) linear dipole  $\epsilon = 1.8$ , (···) full linear  $\epsilon = 1.8$ ; (---) linear dipole  $\epsilon = 78.5$ , (-·-) primitive model  $a_d = 0$ ,  $\epsilon = 78.5$ .



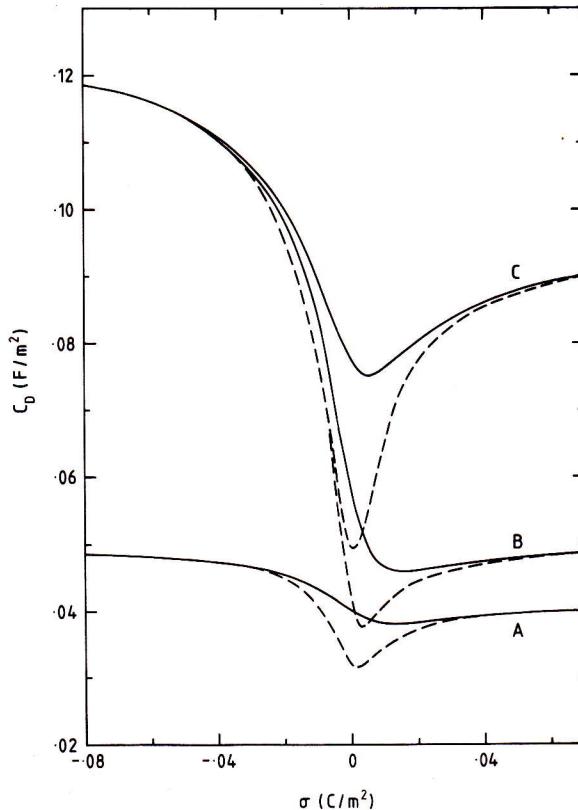
**Figure 6.** Variation of the differential capacitance with surface charge at  $c = 1 \text{ M}$  for  $a_i = a_d/2$ ,  $a_j = 3a_d/2$ : (—) linear dipole  $\epsilon = 1.8$ , (···) full linear  $\epsilon = 1.8$ ; (---) linear dipole  $\epsilon = 78.5$ ; (-·-) full linear  $\epsilon = 78.5$ .

unaltered as they are independent of electrolyte concentration.

The Parson-Zobel<sup>15</sup> plot of the inverse diffuse layer capacitance  $C_d^{-1}$  against the total inverse capacitance at constant  $\sigma$  gives a measure of effects such as specific adsorption. A linear relation

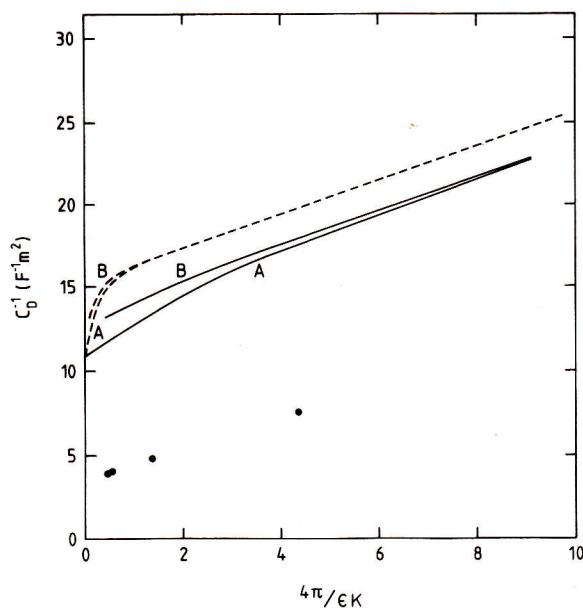


**Figure 7.** Variation of the differential capacitance with surface charge at  $c = 1 \text{ M}$  for  $a_i = a_d/2$ ,  $a_j = 2a_d/3$ : (—) linear dipole  $\epsilon = 1.8$  and  $\epsilon = 78.5$ ; (···) full linear  $\epsilon = 1.8$ ; (-·-) full linear  $\epsilon = 78.5$ .



**Figure 8.** Variation of the differential capacitance with surface charge at different electrolyte concentrations for  $\epsilon = 1.8$ : (—)  $c = 1 \text{ M}$ ; (---)  $c = 0.1 \text{ M}$ ; A,  $a_i = 3a_d/2$ ,  $a_j = 2a_d$ ; B,  $a_i = a_d/2$ ,  $a_j = 3a_d/2$ ; C,  $a_i = a_d/2$ ,  $a_j = 2a_d/3$ .

with unit slope indicates the absence of such effects. In Figure 9 we consider the Parson-Zobel plot at the position of zero charge for the ionic radii corresponding to NaF, namely,  $a_i = 0.97 \text{ \AA}$  and



**Figure 9.** Parson-Zobel plot at  $\sigma = 0$  for  $a_i = 0.97 \text{ \AA}$ ,  $a_j = 1.33 \text{ \AA}$ : (—)  $\epsilon = 1.8$ ; (---)  $\epsilon = 78.5$ ; A, full linear; B, linear dipole; (●) Grahame's<sup>17</sup> experimental points for Hg-aqueous NaF.

$a_j = 1.33 \text{ \AA}$ . Usually the diffuse layer capacitance is calculated from the Gouy-Chapman theory. However, in our work no clear distinction can be made between the inner and diffuse layer capacitance, so from the equal ion size results and the work done with the MSA theory<sup>16</sup> we take  $C_d^{-1} = 4\pi/\epsilon K$ . The Parson-Zobel graphs in Figure 9 have the same structure for both the linear and linear dipole theories. The plots are linear except at high

(16) Blum, L.; Henderson, D.; Parsons, R. *J. Electroanal. Chem.* **1984**, *161*, 389.

electrolyte concentration where the deviations are in the same direction as those observed experimentally. Agreement with Grahame's<sup>17</sup> Hg-aqueous NaF experimental results can be made by adding a concentration-independent term to  $C_d^{-1}$ , arising possibly from the electrode, such as suggested in the MSA approach.<sup>16</sup> A difficulty with comparing the experimental and theoretical results, apart from the inherent approximations in the model and analysis, is that  $C_d$  cannot be consistently specified.

### Conclusion

A limiting feature of the mean field analysis is the dilute gas value of the permittivity of the pure solvent. This low dielectric constant restricts any serious application of the theory to essentially nonaqueous solutions. Irrespective of this restriction some interesting features occur in the theory. The different ionic and dipolar radii lead to asymmetric capacitances and nonzero pzc's, while the nonlinear results for the equal ion size case indicate the importance of dielectric saturation effects when the solvent molecules are smaller than the ions. For the unequal ion size situation the linear dipole theory gives a good representation of the nonlinear theory when the counterions are smaller than the dipoles. The linear theory is inadequate in the unequal ion size case and is only accurate at the pzc for equal ion size. In spite of its shortcomings the linear theory gives the correct qualitative behavior of the Parson-Zobel plot as also seen in the MSA theory. The poor treatment of solvent effects leads to a lack of structure in the singlet distribution functions. Improvements can be made to the model by adding in higher order solvent moments, adsorption, etc. The main improvements though to the theory is in the application of a second-order closure rather than the first-order mean field closure.

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(17) Grahame, D. C. *J. Am. Chem. Soc.* **1954**, *76*, 4819; *Ibid.* **1957**, *79*, 2093.