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A treatment of the exclusion volume term in the inhomogeneous Poisson-Boltzmann theory for an ion-dipole mixture

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The exclusion volume approximation in the Poisson-Boltzmann theory is analysed at the mean field level for an ion-dipole mixture against a plane, uniformly charged hard wall. An earlier treatment is extended to take account of the deviation of the exclusion volume term from the uncharged wall – uncharged hard sphere distribution function. Preliminary numerical results are presented for a 1:1 electrolyte at $c = 1.0$ mole/dm^3 with unequal ion and dipole sizes.

Key words: *excluded volume term, Poisson-Boltzmann, ion-dipole mixture, electric double layer*

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1. Introduction

The electric double layer, in the neighbourhood of a charged surface in an electrolyte solution, plays a key role in understanding the behaviour of many physical, chemical and biological phenomena. The classical treatment of the electrical double layer is based on the mean field Poisson-Boltzmann (PB) equation where the electrolyte solution is modelled by a system of point ions moving in a dielectric continuum. Many attempts have been made to improve both the electrolyte model and the theory of this classical approach. A basic reference electrolyte model is the primitive model (PM) where the ions in the dielectric are given finite size by being represented as charged hard spheres. More realistic models treat the solvent on an equal footing with the solute, the solvent having dipoles and higher order multipoles.

Theoretical improvements have been based on improved or modified PB equations, integral equations and simulation [1,2].

We consider here a PM electrolyte or an ion-dipole mixture against a uniformly charged plane hard wall. The emphasis will be upon examining the influence of ion or solvent size upon the structure of the electric double layer within a mean electrostatic potential framework. Various attempts have been made to account for the steric effect of the ions and the solvent. The earliest work was that of Stern [3] who introduced the idea of an inner compact layer to correct the Gouy-Chapman [4,5] theory which overestimated ionic adsorption. Stern's approach has led to many different models and theories for the structure of the solution next to an electrode [6–8], but there are difficulties in reconciling many of these approaches with an overall consistent statistical mechanical picture of the double layer. An important related aspect is a realistic model of the electrode in assessing its influence on ionic distribution and adsorption [9,10].

The first formal statistical mechanical analysis detailing the deficiences of the PB equation was due to Kirkwood [11]. He showed that the two approximations in the theory were the neglect of the exclusion volume term and of the fluctuation potential. The exclusion volume term arises from the discharged ion in the formal charging process, and in the double layer it plays a major role in controlling the surface concentration of the ions. The various treatments and relative importance of the two approximations within the mean electrostatic framework for the restricted PM (RPM) are given in [1,12]. There has been a recent resurgence of interest in incorporating steric effects into the PB equation in a simple fashion. These attempts are based on lattice model [13–15] and functional [16–18] approaches. The derivation in [13,18] of these improved PB equations invokes solvent exclusion volume effects and the new theories impose an upper limit on the surface concentration of the counterions. No treatment is made of fluctuation effects and the solvent is solely considered as neutral hard spheres. The underlying electrolyte model, when the solvent is uncharged hard spheres moving in a dielectric continuum, is the solvent primitive model (SPM). The modified Poisson-Boltzmann (MPB) theory [1,12,19–21] treats both the exclusion volume and the fluctuation potential term and formally prevents unphysical counterion surface coverage at high surface charge. By neglecting the fluctuation term, we show here how the MPB exclusion volume term reduces to expressions analogous to the recent improved PB results. Preliminary results are also presented for the ion-dipole mixture with different sizes which extends earlier work [22] on a corrected PB theory incorporating exclusion volume terms.

2. Theory

The electric double layer is modelled by a mixture of charged hard spheres and dipolar hard spheres moving in a medium of background relative electric permittivity ε_∞ in the neighbourhood of a uniformly charged plane hard wall. At a normal distance x_1 from the electrode into the solution, Poisson's equation for the mean electrostatic potential $\psi = \psi(1)$ is

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x_1^2} = -\frac{1}{\varepsilon_0\varepsilon_\infty}\sum_k e_k n_k g_k + \frac{1}{\varepsilon_0\varepsilon_\infty}\frac{\mathrm{d}P}{\mathrm{d}x_1}, \tag{1}$$

where

$$P = n_d \int \mu \cdot \hat{x}_1\, g_d\, \mathrm{d}\omega. \tag{2}$$

Here $P = P(1)$ is the polarization with $\mathrm{d}\omega$ the dipole rotational elements, e_k the charge on an ion of species k, μ the dipole moment, n_t the bulk number density of species t and g_k, g_d the singlet distribution functions for an ion k or dipole d at x_1 respectively. The labels s and t are for either ions or dipoles while k and d signify ions and dipoles respectively. For both the PM and SPM, P vanishes and ε_∞ is replaced by the bulk relative electric permittivity (bulk dielectric constant) ε. However, in the PM, exclusion volume effects only arise through ion size while the SPM also incorporates hard sphere solvent effects.

Neglecting the fluctuation term [23],

$$g_k = \zeta_k \exp(-\beta e_k \psi), \tag{3}$$

$$g_d = (\zeta_d/4\pi)\exp(-\beta\mu\cdot\nabla\psi), \tag{4}$$

where $\zeta_k = g_k(e_k = 0)$, $\zeta_d = g_d(\mu = 0)$ are the exclusion volume terms. For high values of the surface charge σ, the exclusion volume terms will impose a limit on the surface concentration of the ions and solvent. The mean field approximation is given by replacing ζ_k, ζ_d by the appropriate unit step functions.

To treat the exclusion volume terms, consider the exact equation (2.11) of [24],

$$\ln g_s = -\beta\phi_s + \int_0^1 \int \sum_t n_t\, c_{st}\, \frac{\partial g_t}{\partial\lambda}\, \mathrm{d}2\, \mathrm{d}\lambda, \tag{5}$$

where ϕ_s is the interaction between the particle s and the field due to the electrode, $c_{st} = c_{st}(1,2|\lambda)$ is the nonuniform direct correlation function and λ is the coupling parameter for the electrode field. Although developed for the PM, equation (5) also holds for the hard sphere ion-dipole mixture when d2 includes the rotational elements for t running over the dipole species.

The exclusion volume term from equation (5) is

$$\ln\zeta_s = -\beta\phi_s(s=0) + \int_0^1 \int \sum_t n_t\, c_{st}(s=0)\, \frac{\partial g_t}{\partial\lambda}\, \mathrm{d}2\, \mathrm{d}\lambda, \tag{6}$$

where $s = 0$ means that the ion or dipole at x_1 is discharged.

A formal decomposition of c_{st} into a short and long range part means we expect the long range term to vanish and $c_{st}(s = 0)$ to be of short range, independent of λ. Also $\phi(s = 0)$ is simply the hard sphere – hard wall interaction. So integrating with respect to λ,

$$\ln\zeta_s = \int \sum_t n_t\, c_{st}(s=0)[g_t - 1]\mathrm{d}2, \tag{7}$$

with $\zeta_s = 0$ when x_1 is less than the distance of closest approach of s to the electrode. Now putting the surface charge zero in equation (7), and then subtracting the result from equation (7), gives

$$\ln(\zeta_s/\zeta_s^0) = \int \sum_t n_t \left\{ [c_{st}(s=0)g_t - c_{st}^0 g_t(\sigma=0)] + [c_{st}^0 - c_{st}(s=0)] \right\} \mathrm{d}2, \qquad (8)$$

where $\zeta_s^0 = \zeta_s(\sigma = 0)$ and c_{st}^0 indicates that in c_{st} both the molecule s at x_1 and surface charge are discharged. Setting $c_{st}(s = 0) = c_{st}^0$, which is true for the bulk, gives

$$\ln(\zeta_s/\zeta_s^0) = \int \sum_t n_t c_{st}^0 [g_t - g_t(\sigma = 0)] \,\mathrm{d}2. \qquad (9)$$

Equations similar to equation (9) can be derived from the other standard statistical mechanical theories [1, p. 188–189], although now c_{st}^0 takes its bulk value rather than the inhomogeneous value in equation (9). Given a value for c_{st}^0, such as the bulk Percus-Yevick (PY) value for a mixture of uncharged hard spheres [25], the equations (1), (3), (4), (9) form a consistent set of equations for ψ. We shall not consider the full solution here but only analyse how the exclusion volume term given by equation (9) may alter the PB equation. A solution of the system for ζ_s given by the PY uncharged hard sphere singlet distribution function has been treated elsewhere [22].

Alternatively an equation analogous to equation (8) for the PM can be derived from the BBGY hierarchy [19]

$$\ln(\zeta_s/\zeta_s^0) = \int_{x_1}^{\infty} \sum_t n_t \int_{S_{12}} \hat{x}\cdot\hat{r}_{12}\,[g_t g_{st}(e_s = 0) \\ - g_t(\sigma=0) g_{st}(e_s = \sigma = 0)] \,\mathrm{d}S_2 \mathrm{d}x_2. \qquad (10)$$

We first show how equation (7) in conjunction with equations (3), (4) relates to the earlier work of Borukhov *et al.* [14,15]. Consider a single electrolyte with charges e_i, e_j, with all the ions and dipoles having the same diameter R and $c_{st}(s = 0)$ given by the bulk uncharged direct correlation function. In this special case we write ζ and c^0 for ζ_s and c_{st}^0 respectively as they are the same for all the species.

Equation (7) then simplifies to

$$\ln\zeta = \int \sum_k n_k\, c^0[\zeta \exp(-\beta e_k \psi) - 1] \,\mathrm{d}2 \\ + \int (n_d/4\pi)\, c^0[\zeta \exp(-\beta\mu\cdot\nabla\psi) - 1]\mathrm{d}2. \qquad (11)$$

We now assume that the exclusion volume term only deviates slightly from its bulk value of unity, and write $\zeta = 1 + \delta$ where $|\delta| < 1$. So expanding to the first order in δ and approximating δ in the integrand by its mean value $\overline{\delta}$ at x_1, gives

$$\delta = \overline{\delta} X + X - X^b, \qquad (12)$$

where

$$X = n_i F_i + n_j F_j + n_d G_d, \tag{13}$$

$$X^b = \sum_s n_s \int c^0 \, \mathrm{d}2, \tag{14}$$

$$F_k = \int c^0 \exp(-\beta e_k \psi) \, \mathrm{d}2, \tag{15}$$

$$G_d = \int c^0 D \, \mathrm{d}2, \tag{16}$$

$$D = (1/4\pi) \int \exp(-\beta \mu \cdot \nabla\psi) \, \mathrm{d}\omega = \sinh\Theta/\Theta, \tag{17}$$

$$\Theta = \mu\beta \mathrm{d}\psi/\mathrm{d}x_2. \tag{18}$$

Equating $\overline{\delta}$ to δ and solving equation (12) gives

$$\zeta = \frac{1 - X^b}{1 - X}, \tag{19}$$

which is implicit in the RPM work of Bell and Levine [26]. To see if (19) may predict a finite counterion g_i for a large surface charge, we use the approximation $c^0 = -1 + O(n)$, $r < R$, and zero elsewhere, and so for $x_1 > R/2$, $F_k \sim -v\exp(-\beta e_k \psi)$, $G_d \sim -v\exp(-\beta\mu \cdot \nabla\psi)$, where $v = 4\pi R^3/3$ or the truncated sphere for $R/2 < x_1 < R$. With these approximations

$$\zeta = \frac{1 + v\sum_s n_s}{1 + v\left[\sum_k n_k \exp(-\beta e_k \psi) + n_d \exp(-\beta\mu \cdot \nabla\psi)\right]}, \tag{20}$$

thus for $|\beta e_i \psi| \gg 1$ with $-\beta(\mu \cdot \nabla\psi - e_i\psi) \ll 0$

$$g_i \to \frac{1}{v n_i}\left(1 + v\sum_s n_s\right), \tag{21}$$

which is finite. Multiplying numerator and denominator of equation (20) by $1 + X^b$ and neglecting terms of order n^2, then putting $n_d = 0$ or $\mu = 0$ gives the special cases of [14]. The corrected PB equation is given by equations (1), (3), (4), (19) and when $n_d = 0$ we are working with the PM so that the correction arises solely from the ion sizes, and when $\mu = 0$ the correction is within the SPM and comes from the solvent size. As stressed by Kralji-Iglic and Iglic [13], Borukhov *et al.* [14], an exclusion volume term imposes a limit on the surface ion concentration. The present formulation of the MPB theory [1,20] for the RPM utilizes approximations to equation (10) and would be expected to prevent unphysical counterion adsorption. As yet there are no MPB numerical results for high surface charge.

A failure of result (19) or (20) is that when the ions and dipole are discharged the exclusion volume term is unity, as in the PB theory, rather than the uncharged hard sphere-hard wall distribution function. Indeed this uncharged distribution function must contain important steric effects at high electrolyte concentrations. To overcome this deficiency we generalize the derivation of (19) by writing $\zeta_s = \zeta_s^0(1+\delta_s)$ where we assume $|\delta_s|$ is small. So, substituting in equation (9) for ζ_s, using (3), (4) for the singlet distribution functions, expanding to first order in δ_s, and approximating δ_s under the integral sign by its mean value $\overline{\delta}_s$ at x_1 gives

$$\delta_s = \sum_k \overline{\delta}_k n_k F_{sk} + \overline{\delta}_d n_d G_{sd} + X_s - X_s^0, \tag{22}$$

where

$$X_s = \sum_k n_k F_{sk} + n_d G_{sd}, \tag{23}$$

$$X_s^0 = X_s(\sigma = 0), \tag{24}$$

$$F_{sk} = \int c_{sk}^0 \zeta_k^0 \exp(-\beta e_k \psi)\,\mathrm{d}2, \tag{25}$$

$$G_{sd} = \int c_{sd}^0 \zeta_d^0 D\,\mathrm{d}2. \tag{26}$$

If we approximate $\overline{\delta}_s$ by δ_s then equation (22) becomes a system of linear equations which can readily be solved for δ_s. When $\sigma \to 0$, $\delta_s \to 0$ and so as required $\zeta_s \to \zeta_s^0$. For a single electrolyte with equal size ions of charge e_i and e_j, simplifications occur as then for $c_{ii}^0 = c_{ij}^0 = c_{jj}^0$, $F_{ii} = F_{ji}$, $F_{jj} = F_{ij}$ and $G_{id} = G_{jd}$. Furthermore if the dipoles are also the same size as the ions, $F_{di} = F_{ii}$, $F_{dj} = F_{jj}$, $G_{id} = G_{jd} = G_{dd}$. In particular for a $z:z$ electrolyte for equisized ions and dipoles,

$$\zeta = \zeta^0 \frac{1 - n(F_{ii}^0 + F_{jj}^0) - n_d G_{dd}^0}{1 - n(F_{ii} + F_{jj}) - n_d G_{dd}}, \tag{27}$$

where $n_i = n_j = n$; and for the $1:z$ case with equal sizes,

$$\zeta = \zeta^0 \frac{1 - n(zF_{ii}^0 + F_{jj}^0) - n_d G_{dd}^0}{1 - n(zF_{ii} + F_{jj}) - n_d G_{dd}}, \tag{28}$$

where $n_i = zn_j = zn$ and $\zeta = \zeta_s$, $\zeta^0 = \zeta_s^0$. As before these two results are analogous to those of Borukhov *et al.*. In any investigation of the influence of the exclusion volume term given by equation (9), we would expect equation (22) to provide a reasonable first approximation to ζ_s for the numerical solution of the corrected PB equation, or the corresponding MPB theory in the RPM. In (22) the ζ_s^0 and c_{st}^0 can be estimated by any appropriate uncharged hard wall – hard sphere distribution function and bulk hard sphere direct correlation function respectively.

3. Results and discussion

We now present some preliminary results for the unequal size ion-dipole mixture based on equation (9) for ζ_k and equation (22) for ζ_d. From equation (22), with

$\delta_k = 0$, we obtain

$$\zeta_d = \zeta_d^0 \frac{1 + \sum_k n_k (F_{dk} - F_{dk}^0) - n_d G_{dd}^0}{1 - n_d G_{dd}}. \tag{29}$$

For consistency the dipole exclusion volume term should also be calculated from equation (9). The present numerical procedure needs to be adapted to solve this consistent situation, but we expect equation (29) to be a good approximation to ζ_d for the considered parameter range. The exclusion volume term for zero surface charge ζ_s^0, and the uncharged bulk direct correlation function, are approximated by the corresponding Percus-Yevick values for uncharged hard sphere mixtures [25]. The three component PY g_s^0 has been given elsewhere [22] and the PY c_{st} can be derived from Baxter's work [27], namely

$$rc_{ij} = \begin{cases} -\alpha_i r - \beta_i + 2\pi \sum_s n_s I_s, & r < R_{ij} \\ 0, & r > R_{ij}, \end{cases} \tag{30}$$

where

$$I_s = I_b = -\frac{R_i^2}{24}\left[12\beta_s^2 + 12\alpha_s\beta_s(r + R_s) + \alpha_s^2(2R_i r + 6R_s r + 3R_s^2)\right], \quad r < S_{ji}\,, \tag{31}$$

$$I_s = I_b + (S_{ij} + r)^2 \left\{\frac{\beta_s^2}{2} + \frac{\alpha_s\beta_s}{2}(R_{is} + R_{js}) + \frac{\alpha_s^2}{24}\left[r(2S_{ij} - r) + 3(R_{ij} + R_s)^2\right]\right\}, \quad R_{ij} > r > S_{ji}\,, \tag{32}$$

and

$$\alpha_i = \frac{1 - \xi_3 + 3R_i\xi_2}{(1 - \xi_3)^2}, \quad \beta_i = -\frac{3R_i^2\xi_2}{2(1 - \xi_3)^2}, \quad \xi_j = \frac{\pi}{6}\sum_i n_i R_i^3 R_i^j. \tag{33}$$

Here R_i is the diameter of i with $R_{ij} = (R_i + R_j)/2$, and $S_{ij} = (R_i - R_j)/2$.

The numerical solution of Poisson's equation (1), in conjunction with equations (3), (4) and exclusion volumes given by equation (9) for the ions and (29) for the dipoles, was obtained by a modification of the quasi-linearization technique of [22]. Calculations were performed for a 1:1 electrolyte at concentration $c = 1.0\,\text{mole/dm}^3$ with $R_+ = 3.6\,\text{Å}$, $R_- = 3.0\,\text{Å}$ while the solvent parameters were $R_d = 2.4\,\text{Å}$, $\mu = 1.84\,\text{D}$ and concentration $c_d = 45\,\text{mole/dm}^3$. The background permittivity ε_∞, which reflects the atomic and electronic polarization of solute and solvent, was taken to be 2 and temperature $T = 298.15\,\text{K}$.

In the figures, comparisons are made with the case when the exclusion volume term is simply given by the PY uncharged singlet distribution function g_s^0, this situation being denoted by g_s^*. Figure 1 indicates a large reduction in the value of ζ_k from the PY g_k^0 at $\sigma = 0.1\,\text{C/m}^2$ in the vicinity of the electrode. In contrast there is only a small reduction in ζ_d, so now it is the largest, not the smallest, exclusion volume term near the electrode. The small reduction in ζ_d is significant as it indicates a correlation with the surface charge which will become more important as σ increases. A similar overall picture occurs for $\sigma = -0.1\,\text{C/m}^2$.

The variation of the contact values of ζ_s and g_s for σ varying from -0.15 to $0.15\,\text{C/m}^2$ are given in figures 2–4. For the ions ζ_k is less than the PY g_k^0, except

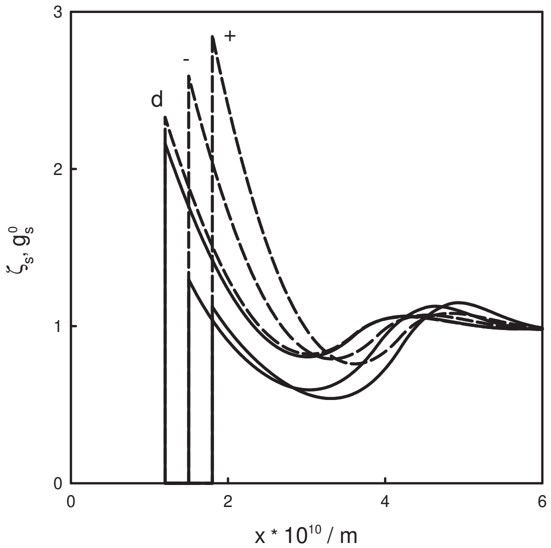

Figure 1. Exclusion volume term ζ_s (solid line) and PY g_s^0 (dashed line) at $\sigma = 0.1\,\mathrm{C/m^2}$. Other parameters as in text. The solvent, anion and cation functions are denoted by d, $-$, $+$ respectively.

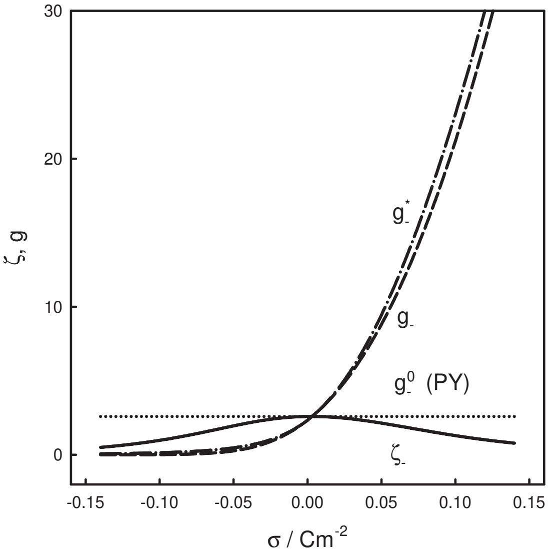

Figure 2. Contact value of the anion exclusion volume term and singlet function for $|\sigma| < 0.15\,\mathrm{C/m^2}$. The singlet functions g_-, g_-^* are calculated using ζ_- and PY g_-^0 respectively.

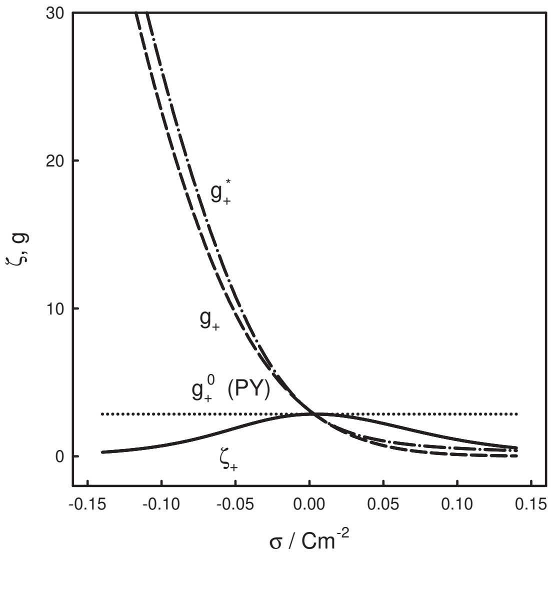

Figure 3. Contact value of the cation exclusion volume term and singlet function for $|\sigma| < 0.15\,\mathrm{C/m^2}$. The singlet functions g_+, g_+^* are calculated using ζ_+ and PY g_+^0 respectively.

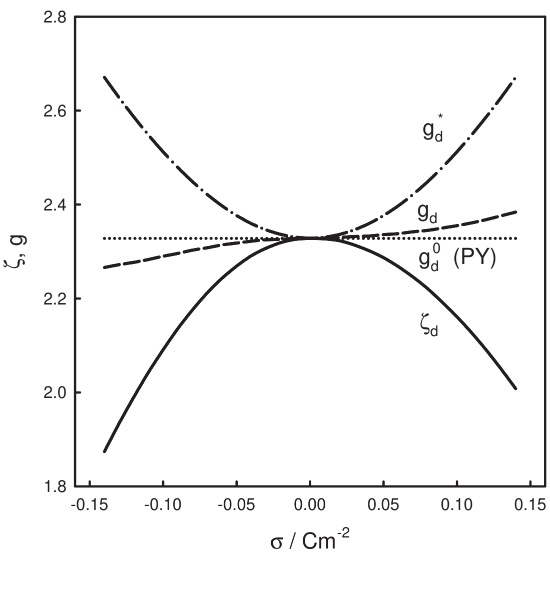

Figure 4. Contact value of the solvent exclusion volume term and singlet function for $|\sigma| < 0.15\,\mathrm{C/m^2}$. The singlet functions g_d, g_d^* are calculated using ζ_d and PY g_d^0 respectively.

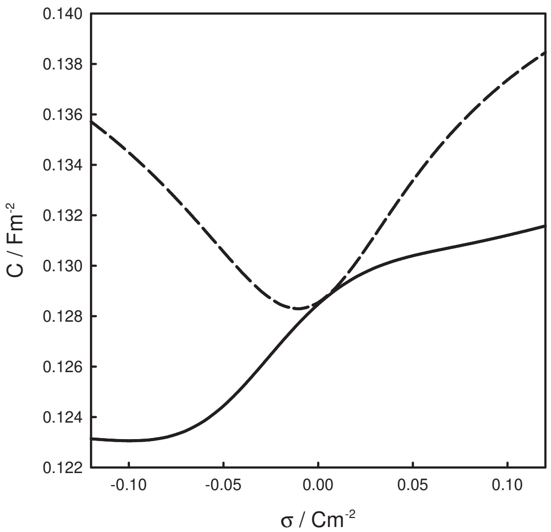

Figure 5. The differential capacitance C. The dashed line is the capacitance when the exclusion volume term is given by the PY g_s^0.

when $\sigma = 0$. This in turn reduces the contact value of g_k for $\sigma \neq 0$ from g_k^*. However for the solvent when $\sigma > 0$, the contact value of g_d is larger than that of g_d^* in contrast to its lower value when $\sigma < 0$. This is a reflection of the different molecular sizes, with the dipole being the smallest. At these low surface charges the larger counterion (cation for $\sigma < 0$) reduce the adsorption of the solvent molecules relative to the g_d^0, and the smaller counterion (anion for $\sigma > 0$) increase the solvent adsorption. The effect is clearly seen in figure 5 for the differential capacitance. Rather than an asymmetric 'U' shape from the g_s^* as found in [22], the capacitance begins to adopt a shape reminiscent of group 2 of Parson's classification [28].

The absolute values of the capacitance are too low, and this can be attributed to many factors, two of the most probable being the poor representation of the solvent and the neglect of the fluctuation term in the distribution functions. However it appears that the formulation of the exclusion volume terms presented here which takes into account surface charge correlations, married with treating solute and solvent molecules on an equal footing, may prove fruitful. Work is in progress studying the implication of various parameter variations.

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Трактування члена виключеного об'єму в неоднорідній теорії Пуассона-Больцмана для іонно-дипольної суміші

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Наближення виключеного об'єму в теорії Пуассона-Больцмана аналізується на рівні середнього поля для іонно-дипольної суміші біля плоскої, однорідно зарядженої твердої стінки. Попередній розгляд є розширений до врахування відхилення члена виключеного об'єму від функції розподілу незаряджена стінка – незаряджена тверда сфера. Попередні числові результати є представлені для електроліту 1:1 при c=1.0 моль/дм^3 з нерівними розмірами іонів і диполів.

Ключові слова: *член виключеного об'єму, Пуассон-Больцман, іонно-дипольна суміш, електричний подвійний шар*

PACS: *68.08.-p*