Ion Binding by Charged Particles in their Diffuse Layer based on a Symmetrized Poisson–Boltzmann Approach

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The collective interactions in a four-component mixture of charged particles, the ions whose dissociation generates the charge of the particles, and the ions of a binary electrolyte are described by a symmetrized Poisson–Boltzmann (SPB) equation. The ion excesses in the diffuse layer are considered to be bound to the particles. The computations show that the binding numbers in the SPB approximation can differ considerably from those obtained on the basis of the conventional Poisson–Boltzmann equation. The structure of the mixture described by the SPB equations is examined and it is found that there are conditions under which the collective interactions generate an effective attraction among particles.

Several kinds of ion binding to charged particles in electrolyte solutions are possible. One can consider bound ions to be those attached to specific sites on the surface. This type of binding may involve some covalent bonding between the ion and the site. However, other ions that are not attached in this way may still not be completely free. Indeed, the closer the counterions are to the surface of the particle, the more the electrostatic interactions will restrict their motion parallel to its surface. They can be considered to be bound to the extent that they move with the particle and are not osmotically active. In the present paper the ion excesses present in the diffuse layer of the particles are considered to be bound to the particle and their number is calculated on the basis of various approximations.

Ion binding in the diffuse layer plays a role in electrolyte solutions of proteins and was calculated in the literature by means of the Poisson–Boltzmann (PB) equation or even by its linear Debye–Hückel (DH) approximation (see ref. 1 and 2, and references therein). The PB equation

$$\Delta\psi_p = -\frac{4\pi}{\varepsilon}\, e \sum n_\alpha \exp(-ez_\alpha\psi_p/k_B T) \qquad (1)$$

describes the electrical potential, ψ_p, around a charged particle immersed in an electrolyte. In eqn. (1), n_α and ez_α are the concentration and electrical charge of an electrolyte ion of species α, respectively, ε is the relative permittivity of the solvent, $k_B T$ is the temperature in energetic units and the charged particles are not included in the summation. For the binary symmetrical electrolytes usually considered, $\alpha = +$ or $-$, $z_+ = -z_- = z$, $n_+ = n_- = n/2$, and the PB equation acquires the form

$$\Delta\psi_p = \frac{4\pi n e z}{\varepsilon k_B T}\, \sinh\!\left(\frac{ze\psi_p}{k_B T}\right) \qquad (2)$$

Let us introduce the pair correlation function, $g_{\alpha\beta}$, which characterizes the probability of finding a particle β at a distance r from the central particle α and which is normalized by

$$g_{\alpha\beta}(\infty) = 1 \qquad (3)$$

The diffusive ion-binding numbers around the spherical particle (p) can be defined by the expressions

$$d_\alpha = 4\pi n_\alpha \int_{R_{p\alpha}}^{\infty} [g_{p\alpha}(r) - 1] r^2 \, dr \qquad (4)$$

where $R_{p\alpha}$ is the minimum distance between the centres of a particle and an ion, α. In the case of repulsion among particles and ions, $g_{p\alpha}(r) < 1$ and $d_\alpha < 0$, which means that there is a deficit of ions in comparison with their average concentration. Similarly, the attraction among particles and ions leads to an excess of the latter around the particles ($d_\alpha > 0$). Within the PB approximation, the pair correlation functions are given by

$$g_{\alpha\beta} = \exp(-ez_\beta\psi_\alpha/k_B T) \qquad (5)$$

and the values of d_α can be calculated in terms of the PB solution. However, eqn. (5) does not satisfy the symmetry condition imposed by the definition of $g_{\alpha\beta}$

$$g_{\alpha\beta} \equiv g_{\beta\alpha} \qquad (6)$$

since the PB solution depends on the ion species that is placed in the centre of the coordinates.[3] Indeed, $z_\alpha\psi_\beta \neq z_\beta\psi_\alpha$ when the species α and β have unequal charges and/or sizes. In addition, the interactions among the electrolyte ions and among the colloidal particles are neglected in this approach.

In principle, full consideration of all the interactions in a mixture can be provided by the different closures of the Ornstein–Zernike (OZ) equation (see ref. 4 for a review). For M-component mixtures, the latter represents a system of $0.5M(M + 1)$ non-linear integral equations difficult to solve. A more simple way to satisfy eqn. (6) and to account for the interactions among ions and particles is to use the symmetrized PB (SPB) equation. The SPB equation was proposed by Feat and Levine[5] and applied by them to electrical double layers and later extended to binary asymmetrical electrolytes.[6–11] It has been shown[7,12] that the SPB equation represents the zero-order term of a virial expansion of the OZ equation. The SPB equation for a ternary mixture was used for the description of a system containing colloidal particles in a binary electrolyte.[12]

A comparison between the SPB equation, the hypernetted chain closure (HNC) of the OZ equation, and Monte Carlo data for 1 : 2 and 1 : 3 binary electrolytes has shown that the results of SPB and HNC are very close up to a concentration of 1 mol dm^{-3}, and the Monte Carlo data differ by less than 20% for concentrations smaller than 0.5 mol dm^{-3}.[8–10]

In this paper, we derive the SPB equation for a four-component mixture containing charged particles, the ions whose dissociation generates the charge of the particles and the anions and cations of a binary electrolyte. The SPB equation is employed to calculate the ion-binding numbers to the particles and the results are compared with those obtained using the PB and DH approximations.

Symmetrized Poisson–Boltzmann Equation for a Four-component Mixture

Within the SPB approximation, the pair correlation functions are given by[7,12]

$$g_{\alpha\beta} = \gamma_{\alpha\beta} \exp(-\psi_{\alpha\beta}); \quad \gamma_{\alpha\beta} = \exp(-\phi_{\alpha\beta}) \qquad (7)$$

where $\phi_{\alpha\beta}$ is the short-range pair potential in $k_B T$ units, $\psi_{\alpha\beta} = ez_\beta\psi_\alpha/k_B T$ is the dimensionless potential given by the SPB equations[12]

$$\Delta\psi_{\alpha\alpha} = -\kappa^2 \sum_\beta v_\beta \lambda_{\alpha\beta}\gamma_{\alpha\beta} \exp(-\psi_{\alpha\beta});$$

$$\psi_{\alpha\beta} = \frac{\lambda_{\alpha\beta}}{2}\left(\frac{\psi_{\alpha\alpha}}{\lambda_{\alpha\alpha}} + \frac{\psi_{\beta\beta}}{\lambda_{\beta\beta}}\right) \qquad (8)$$

$\kappa = (4\pi n e^2 I/\varepsilon k_B T)^{1/2}$ is the reciprocal Debye length, $n = \sum n_\alpha$ is the total concentration of ions and particles in a mixture, $I = \sum v_\alpha z_\alpha^2$ is the dimensionless ionic strength, $v_\alpha = n_\alpha/n$ and $\lambda_{\alpha\beta} = z_\alpha z_\beta/I$.

The SPB equation satisfies the boundary condition

$$\psi_{\alpha\beta}(\infty) = 0 \qquad (9)$$

which is a consequence of the electroneutrality condition. The second boundary condition depends on the charge distribution within the ions. If one employs the primitive model of electrolytes,[13] i.e. spherical ions with point charges in their centres located in a dielectric continuum of the same permittivity or with a charge uniformly smeared upon the ion surface, then this condition acquires the form

$$r^2 d\psi_{\alpha\alpha}/dr = -Xz_\alpha^2; \quad \text{for } r = R_{\alpha m} \qquad (10)$$

where $X = e^2/\varepsilon k_B T$ is the Bjerrum length and $R_{\alpha m}$ is the sum of the radii of the ion α and the smallest ion present in a mixture

$$R_{\alpha m} = 0.5_{\min\beta}[R_\alpha + R_\beta] \qquad (11)$$

Let us consider a four-component mixture of particles (p) with negative charge, $-Ze$, monovalent ions (h) whose dissociation from the particles generates their charge, and the anions ($-$) and cations ($+$) of a binary 1 : 1 electrolyte, say KCl. Obviously, $n_+ = n_-$, $n_h = Zn_p$. It is convenient to measure the distance in units of the cation diameter of the electrolyte, R_+. Then the SPB equations acquire the forms

$$\Delta\psi_{pp} = \kappa_+^2 Z\left\{\gamma_{p+}\exp\left[\left(\frac{\psi_{pp}}{Z} + Z\psi_{++}\right)\middle/2\right]\right.$$

$$- N_-\gamma_{p-}\exp\left[-\left(\frac{\psi_{pp}}{Z} + Z\psi_{--}\right)\middle/2\right]$$

$$+ N_h\gamma_{ph}\exp\left[\left(\frac{\psi_{pp}}{Z} + Z\psi_{hh}\right)\middle/2\right]$$

$$\left. - N_p Z\gamma_{pp}\exp(\psi_{pp})\right\} \qquad (12)$$

$$\Delta\psi_{++} = \kappa_+^2\left\{N_-\gamma_{+-}\exp[(\psi_{++} + \psi_{--})/2]\right.$$

$$- N_h\gamma_{+h}\exp[-(\psi_{hh} + \psi_{++})/2]$$

$$- \gamma_{++}\exp(-\psi_{++}) + N_p Z\gamma_{p+}$$

$$\left. \times \exp\left[\left(\frac{\psi_{pp}}{Z} + Z\psi_{++}\right)\middle/2\right]\right\} \qquad (13)$$

$$\Delta\psi_{--} = \kappa_+^2\left\{\gamma_{+-}\exp[(\psi_{++} + \psi_{--})/2]\right.$$

$$- N_p\gamma_{p-}\exp\left[-\left(\frac{\psi_{pp}}{Z} + Z\psi_{--}\right)\middle/2\right]$$

$$- N_-\gamma_{--}\exp(-\psi_{--})$$

$$\left. + N_h\gamma_{-h}\exp[(\psi_{hh} + \psi_{--})/2]\right\} \qquad (14)$$

$$\Delta\psi_{hh} = \kappa_+^2\left\{N_-\gamma_{h-}\exp[(\psi_{hh} + \psi_{--})/2]\right.$$

$$+ N_p\gamma_{ph}\exp\left[\left(\frac{\psi_{pp}}{Z} + Z\psi_{hh}\right)\middle/2\right]$$

$$\left. - \gamma_{h+}\exp[-(\psi_{hh} + \psi_{++})/2] - N_h\gamma_{hh}\exp(-\psi_{hh})\right\} \qquad (15)$$

where $\kappa_+ = (4\pi n_+ e^2 R_+^2/\varepsilon k_B T)^{1/2}$ is the dimensionless Debye parameter of the electrolyte cations, $N_- = n_-/n_+$, $N_h = n_h/n_+$, $N_p = n_p/n_+$,

$$\gamma_{++} = \gamma_{--} = \gamma_{+-} = \begin{cases} 0; & \text{for } r' < 1 \\ 1; & \text{for } r' \geqslant 1 \end{cases}$$

$$\gamma_{p+} = \gamma_{p-} = \begin{cases} 0; & \text{for } r' < R'_{p\alpha} \\ 1; & \text{for } r' \geqslant R'_{p\alpha} \end{cases}$$

$$\gamma_{ph} = \begin{cases} 0; & \text{for } r' < R'_{ph} \\ 1; & \text{for } r' \geqslant R'_{ph} \end{cases} \qquad (16)$$

r' is the dimensionless distance r in units of R_+, $R'_{\alpha\beta} = 0.5(R'_\alpha + R'_\beta)$, R'_α is the dimensionless radius of ion α in units of R_+ and $R_- = R_+$. Considering that the ions generated by the dissociation of the particles are the smallest ones in the mixture, the values of R_{pm} in the boundary conditions [eqn. (10)] are equal to R_{ph}.

Diffusive Ion Binding by Particles

In the PB approximation, only anions and cations are considered and their binding numbers satisfy the relation

$$d_+ - d_- = Z \qquad (17)$$

where the d_α are defined by eqn. (4). Note that the ions generated via the dissociation of the particle are included among the counterions. A very simple expression is provided by DH theory. Within the latter approximation, $g_{\alpha\beta} = 1 - \psi_{\alpha\beta}$, and the linear PB approximation provides the equation

$$\psi_{p\alpha} = \frac{XZz_\alpha}{(1 + \kappa R_{p\alpha})r}\exp[-\kappa(r - R_{p\alpha})] \qquad (18)$$

This approximation allows the following analytical expression to be obtained

$$d_+ = -d_- = Z/2 \qquad (19)$$

The SPB equation takes into account the interactions among all the species as well as the effect of the excluded volume. The relation among the d_α has the following form (see Appendix)

$$d_+ + d_h - Zd_p - d_- + \frac{4\pi}{3}[n_p Z(R_{pp}^3 - R_{ph}^3)$$

$$+ n_+(R_{p-}^3 - R_{p+}^3)] = Z \qquad (20)$$

Computations of the binding numbers were performed

using the following values for the parameters. R_h for the ions present in water generated *via* the dissociation of the particles is taken as 1.5 Å (as for H^+ ions), and the diameters of the hydrated anions and cations, R_+ and R_-, are taken to be 4.2 Å.[14,15] Using these values, one obtains, at room temperature, $X_0 = X/R_+ = 1.68$ and $\kappa_+ = 1.1\sqrt{c}$, where c is the molar concentration of the binary electrolyte.

The iterative procedure in the numerical calculations has been carried out as follows: Eqn. (12)–(15) have been rewritten in the form

$$\Delta\psi_{\alpha\alpha} = \sum_\beta f_\beta(\psi_{\alpha\alpha}, \psi_{\beta\beta}) \tag{21}$$

For the ith iteration, the right-hand side of eqn. (21) was linearized

$$f_\beta(\psi_{\alpha\alpha}^i, \psi_{\beta\beta}^i) \cong f_\beta(\psi_{\alpha\alpha}^{i-1}, \psi_{\beta\beta}^{i-1})$$
$$+ \left(\frac{\partial f_\beta}{\partial \psi_{\alpha\alpha}}\right)_{i-1} (\psi_{\alpha\alpha}^i - \psi_{\alpha\alpha}^{i-1}) \tag{22}$$

and eqn. (21) was solved independently for each $\psi_{\alpha\alpha}^i$. The iteration was continued until the difference between $\psi_{\alpha\alpha}^i$ and $\psi_{\alpha\alpha}^{i-1}$ became smaller than 0.1%. The numerical solutions of the PB and SPB equations were obtained using a grid of 1000 points with a mesh size $\Delta r' = 0.025$. This provides an error for the binding numbers of *ca.* 1%.

The binding numbers for $\kappa_+ = 0.25$ and $\kappa_+ = 0.5$ are plotted in Fig. 1 A–D, which show that the PB equation always overestimates the values of d_+ and $|d_-|$ ($d_- < 0$). The difference between the PB and SPB solutions increases dramatically with increasing fraction of colloidal particles, N_p.

Eqn. (19) overestimates significantly $|d_-|$ but is closer than the PB solution to the SPB solution for d_+. Hence the DH expression can be used for estimation of the counterion binding numbers at least for $Z < 10$ and $N_p < 0.01$, but is inaccurate for the evaluation of the coion binding number.

Eqn. (19) is independent of κ_+ (*i.e.* the concentration). Both the PB and SPB results for d_+ have a very weak dependence on κ_+. Only for $Z > 10$, there is a more significant difference between the values of d_- obtained for $\kappa_+ = 0.25$ and $\kappa_+ = 0.5$.

Structure of the Ionic Mixture

The structure of the ionic atmosphere surrounding a charged particle is determined by the pair correlation functions, $g_{\alpha\beta}$. The PB equation provides a monotonic behaviour for $g_{p\alpha}(r)$ with the limit given by eqn. (3). These functions have a maximum or a minimum value at $r = R_{p\alpha}$ depending on whether the species p and α have opposite or the same type of charges. For small concentrations of colloidal particles and electrolyte, the solutions of the PB and SPB equations are
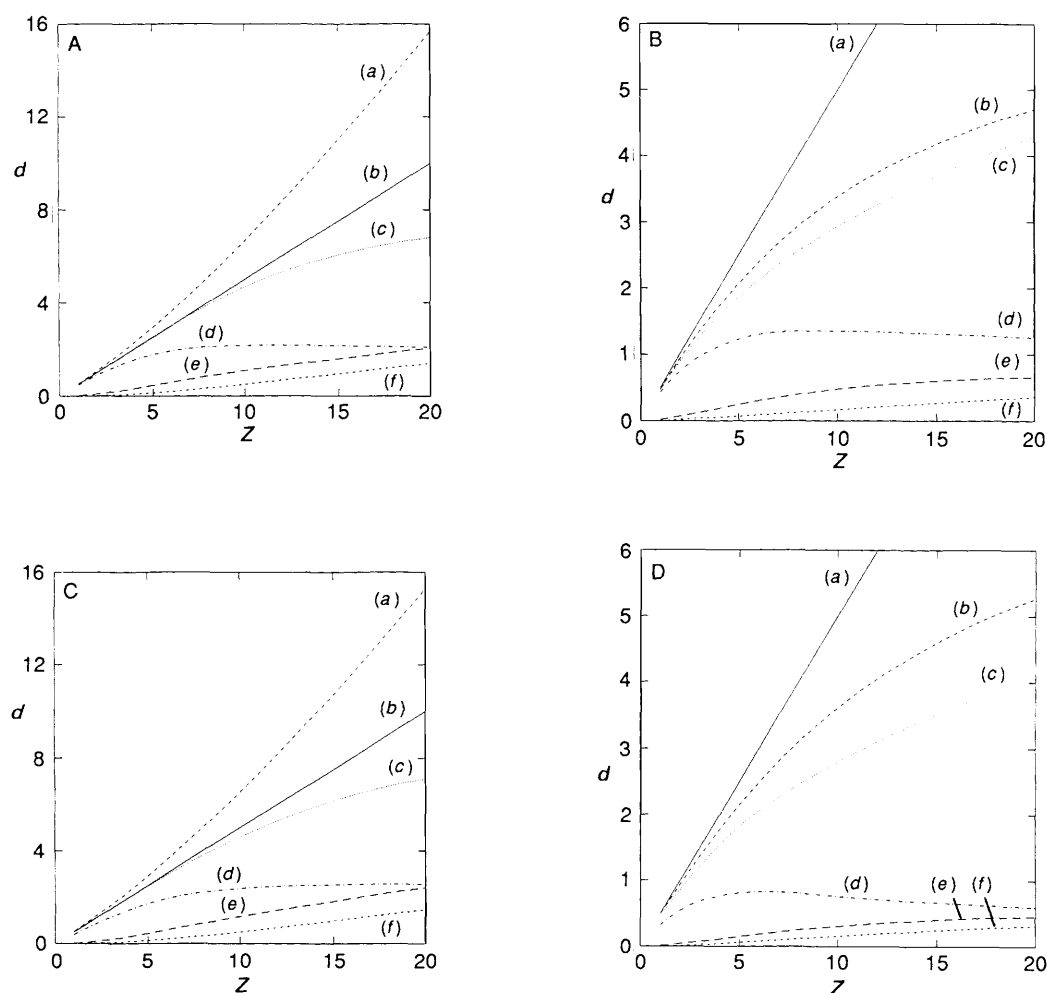

Fig. 1 Diffusive ion-binding numbers for $X_0 = 1.68$ and $R'_p = 5$. A, d_+ for $\kappa_+ = 0.25$: (a) d_+, PB; (b) d_+, DH; (c) d_+, $N_p = 0.01$; (d) d_+, $N_p = 0.05$; (e) d_H, $N_p = 0.05$; (f) d_H, $N_p = 0.01$. B, d_- for $\kappa_+ = 0.25$: (a) $-d_-$, DH; (b) $-d_-$, PB; (c) $-d_-$, $N_p = 0.01$; (d) $-d_-$, $N_p = 0.05$; (e) $-d_p$, $N_p = 0.05$; (f) $-d_p$, $N_p = 0.01$. C, d_+ for $\kappa_+ = 0.5$: (a) d_+, PB; (b) d_+, DH; (c) d_+, $N_p = 0.01$; (d) d_+, $N_p = 0.05$; (e) d_H, $N_p = 0.05$; (f) d_H, $N_p = 0.01$. D, d_- for $\kappa_+ = 0.5$: (a) $-d_-$, DH; (b) $-d_-$, PB; (c) $-d_-$, $N_p = 0.01$; (d) $-d_-$, $N_p = 0.05$; (e) $-d_p$, $N_p = 0.05$; (f) $-d_p$, $N_p = 0.01$. The PB and DH results imply $N_p \to 0$
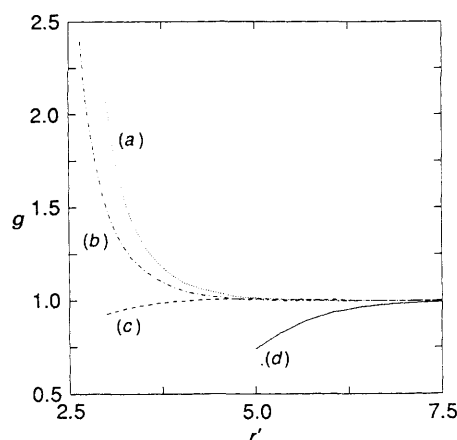
Fig. 2 Pair correlation functions $X_0 = 1.68$, $Z = 5$, $R'_p = 5$, $\kappa_+ = 0.5$, $N_p = 0.05$. (a) g_{p+}, (b) g_{ph}, (c) g_{p-}, (d) g_{pp}

similar at least qualitatively.[12] However, the advantage of the SPB equation is that it allows ions of various sizes to be distinguished (see Fig. 2). Since the ions whose dissociation generates the charge of the particles are considered here to be smaller than the other counterions, the former are attracted more strongly by the particles than the latter.

With increasing N_p and small values of $X_0 Z^2/R'_p$, the SPB solution provides a new qualitative behaviour of the pair correlation functions. In particular, the particle–ion correlation functions become non-monotonic and, what is most interesting, the particle–particle correlation function indicates an effective attraction among charged particles since $g_{pp}(r) > 1$ (see Fig. 3). The same behaviour has been found and discussed previously for a ternary system.[12] A possible explanation for this attraction is as follows: Let us consider two charged particles at a distance r. The repulsion of the left-hand particle due to the particles located at its left and of the right-hand particle due to the particles located at its right tend to decrease the distance between the two. If this effect dominates, then an apparent attraction is observed between the two particles. This attraction is, in this case, a result of the collective behaviour of the particles. Note that computer simulations led, under some circumstances, for ensembles of identical charged particles, to radial distribution functions $g_{pp}(r) > 1$,[16,17] and hence to effective attractions. In ref. 16 an ensemble of particles with pair potentials of the Yukawa form was considered, while in ref. 17 a binary mixture of hard-sphere macro-ions and point counterions was investigated.
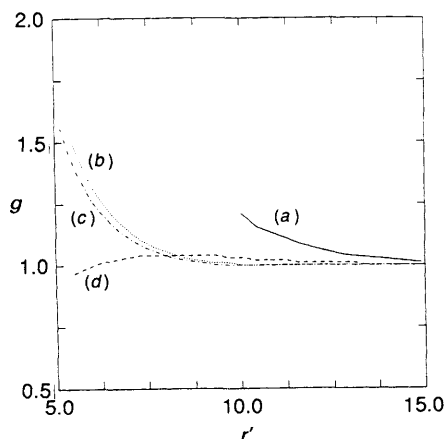

Fig. 3 Pair correlation functions for $X_0 = 1.68$, $Z = 5$, $R'_p = 10$, $\kappa_+ = 0.25$, $N_p = 0.1$. (a) g_{pp}, (b) g_{p+}, (c) g_{ph}, (d) g_{p-}

Appendix

Diffusive Binding Numbers within the DH, PB and SPB Approximations

According to the definition,

$$d_\alpha = 4\pi n_\alpha \int_{R_{p\alpha}}^\infty [g_{p\alpha}(r) - 1] r^2 \, dr \tag{A1}$$

where $R_{p\alpha} = 0.5(R_p + R_\alpha)$ is the sum of the radii of the colloidal particles and ions of species α. The Poisson equation around a colloidal particle can be written in the form

$$\Delta\psi_p = \frac{-4\pi}{\varepsilon} e \sum z_\alpha n_\alpha (g_{p\alpha} - 1) \tag{A2}$$

where the functions $g_{p\alpha}$ are replaced by the differences $g_{p\alpha} - 1$, since $\sum z_\alpha n_\alpha = 0$. Let us integrate eqn. (A2) over the volume within the limits $[R_{pm}, \infty]$, where R_{pm} is the shortest distance between the colloidal particle and the smallest ion present in the mixture. Integration of the left-hand side of eqn. (A2) leads to a relation which is equivalent to the boundary condition [eqn. (10)] obtained as a consequence of the Gauss law:

$$\int_{R_{pm}}^\infty \Delta\psi_p r^2 \, dr = \int_{R_{pm}}^\infty r^{-2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial\psi_p}{\partial r}\right) r^2 \, dr$$

$$= -r^2 \frac{\partial\psi_p}{\partial r}\bigg|_{r = R_{pm}} = z_p e/\varepsilon \tag{A3}$$

For the four-component model considered here, $z_p = -Z$ and $R_{pm} = R_{ph}$, and integration of the right-hand side of eqn. (A2) leads to

$$\frac{-4\pi}{\varepsilon} e \sum n_\alpha z_\alpha \int_{R_{ph}}^\infty [g_{p\alpha}(r) - 1] r^2 \, dr$$

$$= \frac{e}{\varepsilon}\left\{ d_+ + d_h - Zd_p - d_- \right.$$

$$\left. + \frac{4\pi}{3}[n_p Z(R_{pp}^3 - R_{ph}^3) + n_+(R_{p-}^3 - R_{p+}^3)] \right\} \tag{A4}$$

where the relations, $n_+ = n_-$, and $g_{\alpha\beta}(r) = 0$ at $r < R_{\alpha\beta}$, have been employed. Eqn. (A3) and (A4) lead to

$$d_+ + d_h - Zd_p - d_-$$

$$+ \frac{4\pi}{3}[n_p Z(R_{pp}^3 - R_{ph}^3) + n_+(R_{p-}^3 - R_{p+}^3)] = Z \tag{A5}$$

The latter equation has general validity, irrespective of the way in which the functions $g_{\alpha\beta}$ are calculated, and consequently can also be used within the SPB approximation. In the PB equation, the value of n_p is neglected and n_h is included in n_+. In addition, the differences between the anion and cation sizes are not taken into account. Therefore, eqn. (A5) reduces to eqn. (17): $d_+ - d_- = Z$.

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