Solvent effects in weak electrolytes. I. Effect of a hard sphere solvent on the sticky electrolyte model with $L = \sigma$

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The Ornstein–Zernike (OZ) equations are solved for the sticky electrolyte model (SEM) with a hard sphere solvent using the hypernetted chain (HNC) approximation for the stickiness and the mean spherical (MS) approximation for the electrical interactions. Relations among the coefficients of Baxter's q functions and the equation for the excess internal energy are given in the MS approximation for $L \leqslant \sigma$, where σ is the molecular diameter, and L is the distance at which the oppositely charged ions can stick. The analytical results for $L = \sigma$ in the HNC/MS and PY/MS approximations are presented in detail. When the charges are switched off, the results automatically lead to those of the sticky hard sphere system; when the stickiness is turned off and the discrete solvent is changed to a continuum, the results lead correctly to those of the restricted primitive model (RPM). The thermodynamic properties of the SEM in a hard sphere solvent for $L = \sigma$ are calculated and compared with the properties in a continuum solvent; special attention is paid to the derivation of the osmotic coefficient in the McMillan–Mayer system for the SEM and for the corresponding uncharged system. By switching off the charge and the stickiness, the osmotic coefficient of an isotopic solute–solvent system is also obtained. The numerical results show that the hard sphere solvent has a strong packing effect on the structural and thermodynamic properties of the electrolyte and the association of the oppositely charged ions is greatly enhanced by the hard sphere solvent. The influence of a discrete solvent on the osmotic coefficient is quite subtle: for the charged system, the solvent tends to raise the osmotic coefficient; for the sticky hard sphere system, the solvent has just the opposite effect.

I. INTRODUCTION

The sticky electrolyte model (SEM) for weak electrolytes has been discussed recently in a series of papers[1–4]; similar models have been introduced earlier in the study of association reactions in uncharged systems[5] and in the study of adhesive hard spheres.[6] In this paper we begin a study of the effect of a discrete molecular solvent on weak electrolytes using the sticky electrolyte model. The effect of a hard sphere solvent on the chemical equilibria of nonelectrolytes has already been studied by Pratt and Chandler[7,8] and, in the context of the chemical association model discussed here, by Cummings and Stell[9] and Lee *et al.*[10] Our investigations reveal that the granularity of the solvent has a much more subtle effect on the osmotic coefficient of a weak electrolyte than would have been apparent from the study of solvent effects in uncharged chemically associating systems alone.

We begin our analysis in this paper by considering solvent molecules which, apart from the charges and the stickiness, are in every way identical to the solute species. Our earlier work[1–4] on the SEM assumed a continuum solvent, and much attention was paid in observing how ion association is influenced by the distance L at which binding occurs between oppositely charged ions. However, the solvent will also play an important role in the formation of ion pairs because the ions are distributed in the solvent medium. We expect that different solvents will have varying effects on the association process determined by the density, shape, polarity and polarizability of the solvent molecules to name some of the factors. A hard sphere solvent will enhance ion association considerably, because the hard spheres can pack around the ions squeezing them together and increasing the chances of the ions coming in contact. Things may be quite different for the dipolar solvent; the excluded volume of the dipolar solvent will have an effect similar to that of hard spheres, but the dipoles can also have the opposite effect by approaching close to the ions (solvating them) and creating a barrier to ion association thereby keeping them apart. The enhancement or reduction of ion association will be determined partly by the competition between these two. Moreover the properties of the solvent will also be influenced by the ions immersed in it; all of these effects come from the interactions between the solvent molecules and solute particles with each other.

In order to determine the extent to which the solvent influences the association of oppositely charged ions, we devote some effort to this subject in this and the following papers. In a systemetic way, we start by presenting the results of the SEM with the hard sphere solvent, assuming a finite dielectric constant for the solvent typical of a medium like water at room temperature. In this way we hope to separate the long-range dielectric effect of the solvent from the effects due to solvent granularity. We also confine ourselves here to binding between oppositely charged ions at $L = \sigma$, since the analysis is simplest for this choice, but the physical effect of the solvent remains very much the same as when binding

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occurs at smaller values of L. In the forthcoming papers we intend to consider the consequences of introducing solvent molecules with a finite dipole moment and eventually binding at $L<\sigma$.

Since our results are presented in analytic form, it is a relatively simple matter to investigate the effects of turning off the charges and the stickiness in succession, leaving behind an isotopic mixture of solute and solvent particles. When the charges alone are turned off, we have a mixture of hard spheres A and B of the same size in which there is stickiness between A and B but not between the A's or the B's alone. The effect of a hard sphere solvent on this association reaction has been studied by Cummings and Stell,[9] when the binding between A and B occurs at distances (L) equal to one-half and one-third the molecular diameter σ. Our discussion in this paper also provides the corresponding results for the uncharged system when $L=\sigma$, i.e., when there is surface adhesion between A and B.

The SEM mimics the behavior of a weak acid, for example, by introducing a delta function interaction between the oppositely charged ions leading to the formation of dimers, which increase in number with the electrolyte concentration. This is quite different to the formation of ion pairs in the restricted primitive model (RPM) (charged hard spheres) which is invoked in discussions of the thermodynamics of higher valence aqueous electrolytes, for example, at room temperature. Here the enhanced shielding of the charges with increasing electrolyte concentration causes the electrostatically bound ion-pairs and clusters, present at low concentrations, to break up beyond a critical concentration and to decrease in number as the electrolyte concentration increases.[11–13] This is quite the opposite of what is found in the sticky electrolyte model.

In the SEM, the Mayer f function for the interactions between the ions is given by

$$f_{ij}(r) = \zeta L(1-\delta_{ij})\delta(r-L)/12 - 1, \quad 0<r<\sigma \qquad (1.1)$$

$$= \exp[(e_ie_j/\epsilon kTr)] - 1, \quad r>\sigma \qquad (1.1b)$$

where δ_{ij} is the Kronecker delta, r is the distance between the ions, σ is their diameter, L is the distance at which the oppositely charged ions stick together, e_i is the charge on the ion i, ϵ is the dielectric constant of the medium, and ζ is the sticking coefficient which measures the strength of the bonding between the positive and negative ions; it is the inverse of the parameter τ used by Baxter in his study of adhesive hard spheres.[6] The presence of the delta function in the Mayer f function induces a delta function in the correlation function $h_{ij}(r)$ between the ions with a different coefficient λ called the association parameter. For $r<\sigma$,

$$h_{ij}(r) = -1 + L\lambda(1-\delta_{ij})\delta(r-L)/12, \quad r<\sigma. \qquad (1.2)$$

The average number $\langle N\rangle$ of dimers can be written as $\langle N\rangle = \eta\lambda(L/\sigma)^3$ where $\eta = \pi\rho\sigma^3/6$ and the reduced association constant[5]

$$K = \pi\lambda(L/\sigma)^3/[3(1-\langle N\rangle)^2]. \qquad (1.3)$$

The sticking coefficient ζ and the association parameter λ are related by the equation

$$\lambda = \zeta y_{+-}(L,\zeta), \qquad (1.4)$$

where $y_{+-}(r,\zeta)$ is defined in terms of the radial distribution function by

$$g_{+-}(r,\zeta) = [1+f_{+-}(r,\zeta)]y_{+-}(r,\zeta). \qquad (1.5)$$

The SEM has been solved using the hypernetted chain–mean spherical approximation (HNC/MS) and the Percus–Yevick mean spherical approximation (PY/MS) for the ions in a continuum solvent medium for several distances L, less than or equal to the ion diameter σ, at which the ions of opposite charge can bind or stick to each other.[1–4] The model may be considered to be a modification of the restricted primitive model (RPM) to which stickiness or binding has been introduced in the Hamiltonian. When the stickiness is switched off, all the equilibrium properties for this model obtained in a given approximation must become equal to the corresponding results for the RPM in the same approximation. This serves as a useful test of an analytic theory such as the mean spherical approximation (MSA).

This paper is planned as follows. In Sec. II, the Ornstein–Zernike equations and closures for this problem are discussed for $L=\sigma/n$ where σ is the molecular diameter and n is an integer. In Sec. III, a detailed discussion of the solution of the SEM with the HNC/MS closure and the PY/MS closure is given for $n=1$. In Sec. IV, we derive the thermodynamic properties for this system and the corresponding sticky nonelectrolyte (SN) model. Numerical results for both models are presented and discussed in Sec. V.

II. THE ORNSTEIN–ZERNIKE EQUATIONS AND A GENERAL EXPRESSIONS FOR THE EXCESS ENERGY WHEN $L=\sigma/n$

Our system contains three components: positive ions, negative ions and the hard sphere solvent all of the same diameter σ. We will characterize them with the subscripts 1, 2 and 3, respectively. The Ornstein–Zernike equations for this mixture can be written in the following form

$$h_{11} = c_{11} + \rho_1 c_{11}*h_{11} + \rho_2 c_{12}*h_{12} + \rho_3 c_{13}*h_{31}, \qquad (2.1a)$$

$$h_{12} = c_{12} + \rho_1 c_{11}*h_{12} + \rho_2 c_{12}*h_{11} + \rho_3 c_{13}*h_{31}, \qquad (2.1b)$$

$$h_{13} = c_{13} + \rho_1 c_{11}*h_{13} + \rho_2 c_{12}*h_{13} + \rho_3 c_{13}*h_{33}, \qquad (2.1c)$$

$$h_{31} = c_{31} + \rho_1 c_{31}*h_{11} + \rho_2 c_{31}*h_{12} + \rho_3 c_{33}*h_{31}, \qquad (2.1d)$$

$$h_{33} = c_{33} + \rho_1 c_{31}*h_{31} + \rho_2 c_{31}*h_{31} + \rho_3 c_{33}*h_{33}, \qquad (2.1e)$$

where ρ_i is the density of species i. In the above equations, we have used the relations: $f_{ij} = f_{ji}$, $f_{11} = f_{22}$, $f_{31} = f_{32}$ and $f_{13} = f_{23}$ where f_{ij} represents c_{ij} or h_{ij}. The symbol $*$ represents the convolution integral. The closure equations in the mean spherical approximation (MSA) can be written as

$$c_{11} = c_{22} = -e^2/(\epsilon rkT), \quad r>\sigma \qquad (2.2a)$$

$$c_{12} = c_{21} = -e^2/(\epsilon rkT), \quad r>\sigma \qquad (2.2b)$$

$$c_{13} = c_{23} = c_{31} = c_{32} = c_{33} = 0, \quad r>\sigma \qquad (2.2c)$$

$$h_{11} = h_{22} = -1, \quad 0<r<\sigma \qquad (2.2d)$$

$$h_{12} = h_{21} = -1 + \lambda L\delta(r-L)/12, \quad 0<r<\sigma \qquad (2.2e)$$

$$h_{13} = h_{23} = h_{31} = h_{32} = h_{33} = -1, \quad 0<r<\sigma. \qquad (2.2f)$$

Here, it will be noticed that a delta function, which mimics the stickiness between positive and negative ions, has appeared in the correlation function of the oppositely charged ions. For symmetrically charged electrolytes, we also have

$$\rho_1 = \rho_2 = \rho/2. \tag{2.3}$$

Introducing the following sum and difference correlation functions

$$h_s = (h_{12} + h_{11})/2 \tag{2.4a}$$

$$h_D = (h_{12} - h_{11})/2 \tag{2.4b}$$

with similar definitions for c_s and c_D, allows the set of Eqs. (2.1) to be greatly simplified, leading to

$$h_D = c_D - \rho c_D * h_D, \tag{2.5a}$$

$$h_s = c_s + \rho c_s * h_s + \rho_3 c_{13} * h_{31} \tag{2.5b}$$

$$h_{13} = c_{13} + \rho c_s * h_{13} + \rho_3 c_{13} * h_{33}, \tag{2.5c}$$

$$h_{31} = c_{31} + \rho c_{31} * h_s + \rho_3 c_{33} * h_{31} \tag{2.5d}$$

$$h_{33} = c_{33} + \rho c_{31} * h_{13} + \rho_3 c_{33} * h_{33}. \tag{2.5e}$$

The closure relations can now be rewritten as

$$h_s = -1 + \lambda L \delta(r - L)/24, \quad 0 < r < \sigma \tag{2.6a}$$

$$h_D = L\lambda\delta(r - L)/24, \quad 0 < r < \sigma \tag{2.6b}$$

$$c_s = 0, \quad r > \sigma \tag{2.6c}$$

$$c_D = e^2/(\epsilon r kT), \quad r > \sigma. \tag{2.6d}$$

The difference (2.5a) with the closure equations (2.6b) and (2.6d) is exactly the same as for the SEM in a continuum solvent, which has been solved in earlier papers.[1-4] We only need to solve the remaining four equations which involve the solvent molecules at a density ρ_3. When the solvent density ρ_3 is zero the last three equations and the last term of the second equation vanish, making the sum equation identical to the corresponding relation for a continuum solvent. Following Baxter,[14] we define the integral functions

$$J_s(r) = \int_r^\infty t h_s(t)\,dt, \tag{2.7a}$$

$$J_{ij}(r) = \int_r^\infty t h_{ij}(t)\,dt, \tag{2.7b}$$

$$S_s(r) = \int_r^\infty t c_s(t)\,dt, \tag{2.7c}$$

$$S_{ij}(r) = \int_r^\infty t c_{ij}(t)\,dt. \tag{2.7d}$$

Baxter's Wiener–Hopf factorization[14] of $(1 - \rho c_{ij})$ etc. in Fourier space enables the set of OZ equations (2.5b) to (2.5e) to be replaced by the following equations in real space for the correlation functions:

$$r h_s(r) = -q_s'(r) + 2\pi\rho \int_0^\infty q_s(t)(r - t) h_s(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{13}(t)(r - t) h_{31}(|r - t|)\,dt, \tag{2.8a}$$

$$r h_{13}(r) = -q_{13}'(r) + 2\pi\rho \int_0^\infty q_s(t)(r - t) h_{13}(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{13}(t)(r - t) h_{33}(|r - t|)\,dt, \tag{2.8b}$$

$$r h_{31}(r) = -q_{31}'(r) + 2\pi\rho \int_0^\infty q_{31}(t)(r - t) h_s(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{33}(t)(r - t) h_{31}(|r - t|)\,dt, \tag{2.8c}$$

$$r h_{33}(r) = -q_{33}'(r) + 2\pi\rho \int_0^\infty q_{31}(t)(r - t) h_{13}(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{33}(t)(r - t) h_{33}(|r - t|)\,dt, \tag{2.8d}$$

and

$$r c_s(r) = -q_s'(r) + 2\pi\rho \int_r^\infty q_s(t - r) q_s'(t)\,dt$$
$$+ 2\pi\rho_3 \int_r^\infty q_{31}(t - r) q_{31}'(t)\,dt, \tag{2.9a}$$

$$r c_{13}(r) = -q_{13}'(r) + 2\pi\rho \int_r^\infty q_s(t - r) q_{13}'(t)\,dt$$
$$+ 2\pi\rho_3 \int_r^\infty q_{31}(t - r) q_{33}'(t)\,dt, \tag{2.9b}$$

$$r c_{31}(r) = -q_{31}'(r) + 2\pi\rho \int_r^\infty q_{13}(t - r) q_s'(t)\,dt$$
$$+ 2\pi\rho_3 \int_r^\infty q_{33}(t - r) q_{31}'(t)\,dt, \tag{2.9c}$$

$$r c_{33}(r) = -q_{33}'(r) + 2\pi\rho \int_r^\infty q_{13}(t - r) q_{13}'(t)\,dt$$
$$+ 2\pi\rho_3 \int_r^\infty q_{33}(t - r) q_{33}'(t)\,dt, \tag{2.9d}$$

where $q_s(r)$, $q_{13}r$, $q_{31}(r)$, and $q_{33}(r)$ are the corresponding Baxter q functions which are zero for $r < 0$. Using the MSA closures given in Eqs. (2.2) and (2.6) it follows that each of the q functions are also zero for $r > \sigma$, which allows the upper limit of ∞ in the integrals of the factorized OZ equations to be replaced by σ. These equations are quite general except for the restriction that the solute and solvent molecules are of the same size and together with the difference (2.5a) and the closures given in Eqs. (2.6b) and (2.6d) constitute a complete set of equations for this problem. The integrated forms of Eqs. (2.8) can be written as

$$J_s(r) = q_s(r) + 2\pi\rho \int_0^\infty q_s(t) J_s(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{13}(t) J_{31}(|r - t|)\,dt, \tag{2.10a}$$

$$J_{13}(r) = q_{13}(r) + 2\pi\rho \int_0^\infty q_s(t) J_{13}(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{13}(t) J_{33}(|r - t|)\,dt, \tag{2.10b}$$

$$J_{31}(r) = q_{31}(r) + 2\pi\rho \int_0^\infty q_{31}(t) J_s(|r - t|)\,dt$$
$$+ 2\pi\rho_3 \int_0^\infty q_{33}(t) J_{31}(|r - t|)\,dt, \tag{2.10c}$$

$$J_{33}(r) = q_{33}(r) + 2\pi\rho\int_0^\infty q_{31}(t)J_{13}(|r-t|)dt$$
$$+ 2\pi\rho_3\int_0^\infty q_{33}(t)J_{33}(|r-t|)dt. \tag{2.10d}$$

From Eqs. (2.6a) and (2.8a) it follows that in the region $0<r<\sigma$

$$q_S'(r) + pq_S(r+L)$$
$$= a_1 r + b_1 - \lambda L^2\delta(r-L)/24, \quad 0<r\leqslant L \tag{2.11a}$$
$$q_S'(r) + p[q_S(r+L) - q_S(r-L)]$$
$$= a_1 r + b_1, \quad L<r<\sigma-L \tag{2.11b}$$
$$q_S'(r) - pq_S(r-L) = a_1 r + b_1, \quad \sigma-L<r<\sigma \tag{2.11c}$$

where

$$p = \pi\rho\lambda L^2/12 \tag{2.12}$$
$$a_1 = a_s + a_{13} \tag{2.13a}$$
$$b_1 = b_s + b_{13} \tag{2.13b}$$

and

$$a_s = 1 - 2\pi\rho\int_0^\infty q_s(t)dt, \quad b_s = 2\pi\rho\int_0^\infty tq_s(t)dt \tag{2.14a}$$
$$a_{13} = -2\pi\rho_3\int_0^\infty q_{13}(t)dt, \quad b_{13} = 2\pi\rho_3\int_0^\infty tq_{13}(t)dt. \tag{2.14b}$$

Likewise the differential equations for $q_{31}(r)$ follow from Eqs. (2.2f) and (2.8c):

$$q_{31}'(r) + pq_{31}(r+L) = a_3 r + b_3, \quad 0<r\leqslant L \tag{2.15a}$$
$$q_{31}' + p[q_{31}(r+L) + q_{31}(r-L)]$$
$$= a_3 r + b_3, \quad L<r<\sigma-L \tag{2.15b}$$
$$q_{31}'(r) - pq_{31}(r-L) = a_3 r + b_3, \quad \sigma-L<r<\sigma \tag{2.15c}$$

where

$$a_3 = a_{31} + a_{33} \tag{2.16a}$$
$$b_3 = b_{31} + b_{33} \tag{2.16b}$$

and

$$a_{31} = 1 - 2\pi\rho\int_0^\infty q_{31}(t)dt, \quad b_{31} = 2\pi\rho\int_0^\infty tq_{31}(t)dt, \tag{2.17a}$$
$$a_{33} = -2\pi\rho_3\int_0^\infty q_{33}(t)dt, \quad b_{33} = 2\pi\rho_3\int_0^\infty tq_{33}(t)dt. \tag{2.17b}$$

The absence of stickiness between the solute and solvent accounts for the fact that there is no delta function in the differential equation for $q_{31}(r)$ at $r=L$. The differential equations for $q_{13}(r)$ and $q_{33}(r)$ are similar to each other and involve the same sets of coefficients (a_1, b_1) and (a_3, b_3); in the range $0<r<\sigma$ it follows from Eqs. (2.8b), (2.8d) and 2.2f) that

$$q_{13}'(r) = a_1 r + b_1 \quad 0<r<\sigma \tag{2.18}$$

and

$$q_{33}'(r) = a_3 r + b_3 \quad 0<r<\sigma. \tag{2.19}$$

The last two equations are identical to the differential equations of the q functions in the Percus–Yevick approximation for hard spheres of diameter σ and the solutions are immediate[15]:

$$q_{13}(r) = a_1(r^2-\sigma^2)/2 + b_1(r-\sigma), \quad 0<r<\sigma, \tag{2.20}$$
$$q_{33}(r) = a_3(r^2-\sigma^2)/2 + b_3(r-\sigma), \quad 0<r<\sigma. \tag{2.21}$$

The solutions for $q_{13}(r)$ and $q_{33}(r)$ can be used to eliminate a_{13} and b_{13} from Eqs. (2.13) and a_{33} and b_{33} from Eqs. (2.16). Substituting $q_{13}(t)$ in Eq. (2.14b), $q_{33}(t)$ in Eq. (2.17b) and making use of Eqs. (2.13) and (2.16), we get the following relations between the coefficients:

$$a_1 = [a_s(1+2\eta_3) + 6\eta_3 b_s']/(1-\eta_3)^2, \tag{2.22a}$$
$$b_1' = [b_s'(1-4\eta_3) - 3a_s\eta_3/2]/(1-\eta_3)^2, \tag{2.22b}$$
$$a_3 = [a_{31}(1+2\eta_3) + 6b_{31}'\eta_3]/(1-\eta_3)^2, \tag{2.22c}$$
$$b_3' = [b_{31}'(1-4\eta_3) - 3a_{31}\eta_3/2]/(1-\eta_3)^2, \tag{2.22d}$$

where $b_i' = b_i/\sigma$. These equations apply in the MSA *for arbitrary* $L\leqslant\sigma$ but the details of the solutions for a given $L=\sigma/n$ are determined by the integer n through the coefficients a_s, b_s', a_{31} and b_{31}.

We will next consider the difference equation for *arbitrary* $L=\sigma/n$. It has already been shown[1] that factorization of the difference equation leads to the pair of equations

$$rh_D(r) = q_D^{0'}(r) + 2\pi\rho\int_0^\infty [q_D^0(t)+M]$$
$$\times (r-t)h_D(|r-t|)dt, \tag{2.23}$$
$$rc_D^0(r) = q_D^{0'}(r) + 2\pi\rho[Mq_D^0(r)$$
$$-\int_0^\infty q_D^0(t)q_D^{0'}(t+r)dt], \tag{2.24}$$

where $q_D^0(r)$ is zero for $r<0$, $c_D^0(r)$ is defined by

$$c_D(r) = c_D^0(r) + e^2/\epsilon kTr \tag{2.25}$$

and $M = -\kappa/2\pi\rho$ where κ is the inverse Debye length defined by

$$\kappa^2 = 4\pi e^2\beta\rho/\epsilon. \tag{2.26}$$

The integrated form of Eq. (2.23) is

$$J_D(r) = -q_D^0(r) - M/2 + 2\pi\rho\int_0^\infty dt\, q_D^0(t)J_D(|r-t|)$$
$$-\kappa\int_0^r J_D(t)dt. \tag{2.27}$$

The MSA closure given in Eq. (2.6d) is equivalent to

$$c_D^0(r) = 0 \text{ for } (r>\sigma). \tag{2.28}$$

Substitution in Eq. (2.24) shows that $q_D^0(r)=0$ for $r>\sigma$ enabling the upper limits of integration equal to ∞ in Eqs. (2.23), (2.24), and (2.27) to be replaced by σ.

Because the hard sphere solvent has no interaction with the ions apart from the hard core repulsion, the excess internal energy has the same functional form as the energy of the SEM without the molecular solvent. It can be written as[1–3]

$$\beta E^{ex}/N = -\langle N\rangle(d\ln\zeta/d\ln\beta)/2$$
$$-(1+d\ln\epsilon/d\ln T)\kappa H/2, \tag{2.29}$$

where

$$H=\kappa\int_{\sigma^+}^{\infty} sh_D(s)ds. \qquad (2.30)$$

The first term in Eq. (2.29) comes from the binding of the oppositely charged ions, while the second term arises from the electrical interactions between the ions and is determined by the difference equation. It follows from the analysis in Ref. 3 that in the MSA for the SEM in a hard sphere solvent, $H'=H/\sigma$ has the form

$$H'(\mathrm{SEM/MSA})=[(a_1+a_2x)-(a_1+2xa_3)^{1/2}]/(24a_4\eta) \qquad (2.31)$$

for any integral value of $n=\sigma/L$. The coefficients a_i ($i=1$ to 4) are functions of the ionic concentration, the association parameter λ and n. When $\lambda=0$, $\langle N\rangle=0$, all of the $a_i=1$ and the expression for the excess energy of the restricted primitive model (RPM) in the MSA is recovered. The details of the solution of the SEM for $n=1$ will be discussed next.

III. THE HNC/MSA AND PY/MSA SOLUTIONS OF THE SEM FOR $L=\sigma$

Equations (2.6a) to (2.6d) are the MSA closures for bonding between oppositely charged ions at a distance $L\leqslant\sigma$. In the remainder of this paper we restrict our attention to $L=\sigma-$, which implies that the opposing charges can stick together on contact, i.e., surface adhesion between the positive and negative ions is allowed, and polymerization is not excluded by steric effects.[1-4] The solutions for $L=\sigma/n$ (with $n=2,3\ldots$) can be obtained in a similar way as shown earlier for the SEM in a continuum solvent[1-4] but the analysis is more complicated and will not be given here. However the excess energy in the MSA for arbitrary n is still provided by Eqs. (2.29) and (2.30).

To solve the set of equations (2.8a) and (2.9a) for $L=\sigma$, we need to get the relevant q functions. From the definition of $J_s(r)$ given in Eq. (2.7a) and the closure equation (2.6a), it follows that

$$J_s(\sigma-)=J_s(\sigma+)+\lambda\sigma^2/24. \qquad (3.1)$$

Making use of the fact that $q_s(r)=0$ for $r>0$, it follows from Eqs. (3.1) and (2.10a) that

$$q_s(\sigma-)=\lambda\sigma^2/24. \qquad (3.2)$$

From Eq. (2.11) we find that for $L=\sigma$,

$$q_s'(r)=a_1r+b_1,\quad 0<r<L, \qquad (3.3)$$

where a_1 and b_1 have been defined earlier and are given by Eqs. (2.22a) and (2.22b). Integrating and applying the boundary condition (3.2), we get

$$q_s(r)=a_1(r^2-\sigma^2)/2+b_1(r-\sigma)+\lambda\sigma^2/24. \qquad (3.4)$$

Substituting this in Eqs. (2.14a) we find that

$$a_s=[(1-\eta_3)^2+\eta(2+\eta_3)-(1-\eta_3)(1-\eta_0)\nu]/(1-\eta_0)^2 \qquad (3.5)$$

and

$$b_s'=b_s/\sigma=-[3\eta-(1-\eta_3)(1-\eta_0)\nu]/[2(1-\eta_0)^2]. \qquad (3.6)$$

Combining Eqs. (3.5) and (3.6) with (2.22a) and (2.22b) we have

$$a_1=(1+2\eta_0)/(1-\eta_0)^2-\nu/(1-\eta_0), \qquad (3.7a)$$

$$b_1'=-3\eta_0/[2(1-\eta_0)^2]+\nu/[2(1-\eta_0)], \qquad (3.7b)$$

where $\eta_0=\eta+\eta_3$, $\eta_i=\pi\rho_i\sigma^3/6$, $\nu=\eta\lambda/2$. The solution to Eq. (2.15) for $L=\sigma$ is

$$q_{31}(r)=a_3(r^2-\sigma^2)/2+b_3(r-\sigma),\quad 0<r<\sigma \qquad (3.8)$$

which is the q function in the PY approximation. Substituting in Eqs. (2.17a), solving for a_{31} and b_{31}' and using them in Eqs. (2.22c) and (2.22d) it is found that

$$a_3=(1+2\eta_0)/(1-\eta_0)^2 \qquad (3.9a)$$

$$b_3'=-3\eta_0/[2(1-\eta_0)^2] \qquad (3.9b)$$

which are the coefficients of the PY solution for hard spheres.[6]

The direct correlation function $c_{ij}(r)$ can be obtained from Eqs. (2.9a) and (3.4). Here we give only $c_s(r)$, the one we are most interested in. For $r<\sigma$,

$$c_s(r)=\lambda_1+\lambda_2(r/\sigma)+\lambda_3(r/\sigma)^3+\lambda_4(\sigma/r), \qquad (3.10)$$

where

$$\lambda_1=-(1+2\eta_0-\mu)(1+2\eta_0-\mu\eta_0)/(1-\eta_0)^4+\nu(1+2\eta_0-\mu)/(1-\eta_0)^2, \qquad (3.11a)$$

$$\lambda_2=3\eta_0(2+\eta_0-\mu)^2/[2(1-\eta_0)^4]-\nu(1+2\eta_0-\mu)/(1-\eta_0)^2, \qquad (3.11b)$$

$$\lambda_3=-\eta_0(1+2\eta_0-\mu)^2/[2(1-\eta_0)^4], \qquad (3.11c)$$

$$\lambda_4=-\lambda\nu/24, \qquad (3.11d)$$

where $\mu=\nu(1-\eta_0)$. If the range or r is extended to include $r=\sigma$ a delta function equal to $\lambda\sigma\delta(r-\sigma)/24$ has to be added to the expression for $c_s(r)$. As expected, when the concentration of solvent is set equal to zero ($\eta_3=0$), Eqs. (3.10) and (3.9) reduce to the results of the SEM in a continuum solvent.[16] Also when the stickiness vanishes ($\lambda=0$), all the above results reduce to the PY approximation for hard spheres. The contact value of $h_s(r)$ follows from Eqs. (2.6a), (2.8a) and (3.4):

$$h_s(\sigma+)=-1+(2+\eta_0-2\mu)/[2(1-\eta_0)^2]+\nu\lambda/24. \qquad (3.12)$$

The solution to the difference equation has been obtained earlier.[1-4] For $L=\sigma$ it was found that[3]

$$q_D^0(r)=-\kappa J(r-\sigma)-\sigma\lambda/24, \qquad (3.13)$$

where

$$J=\{(1+\nu+\kappa\sigma)-[(1+\nu)^2+2\kappa\sigma]^{1/2}\}/(2\pi\rho\sigma^2\kappa) \qquad (3.14)$$

is the solution to the following quadratic equation:

$$\pi\rho\sigma\kappa J^2-(\nu+\kappa\sigma+1)J+(\kappa\sigma+2\nu)/(4\pi\rho\sigma)=0. \qquad (3.15)$$

The function $c_D(r)$ for $0<r<\sigma$ is given by

$$c_D(r)=\kappa^2J(1-\pi\rho Jr)+\lambda\nu\sigma/(24r)$$
$$=e^2/(\epsilon kT\sigma)[2B-B^2(r/\sigma)]+\lambda\nu\sigma/(24r),\quad 0<r<\sigma, \qquad (3.16)$$

where

$$B = 2\pi \rho J \sigma = \{(1+\nu+\kappa\sigma) - [(1+\nu)^2 + 2\kappa\sigma]^{1/2}\}/(\kappa\sigma). \qquad (3.17)$$

If the range of r is extended to include $r=\sigma$, a delta function equal to $\lambda\sigma\delta(r-\sigma)/24$ must be added to the expression for $c_D(r)$. From Eqs. (2.6), (2.23) and (3.13) it is found that[3]

$$h_D(\sigma+) = e^2(B-1)^2/(\epsilon kT\sigma) - \lambda\nu/24, \qquad (3.18)$$

where the quadratic equation (3.15) in the form

$$\kappa\sigma(B-1)^2 = 2B(\nu+1) - 2\nu \qquad (3.19)$$

has been used in simplifying the algebra. From the definition of the sum and difference functions given in Eq. (2.4) and the above results for $h_s(\sigma+)$ and $h_D(\sigma+)$, it follows that the contact value of the ion radial distribution function can be written as

$$g_{+-}(\sigma+) = h_{+-}(\sigma+) + 1 = (2+\eta_0-2\mu)/[2(1-\eta_0)^2] + e^2(B-1)^2/(\epsilon kT\sigma), \qquad (3.20)$$

$$g_{++}(\sigma+) = h_{++}(\sigma_+) + 1 = (2+\eta_0-2\mu)/[2(1-\eta_0)^2] - e^2(B-1)^2/(\epsilon kT\sigma) + \lambda\nu/12. \qquad (3.21)$$

The analytic results given above for the direct correlation function and the distribution functions at contact become identical to the MSA solution[11] of the RPM when the stickiness is turned off ($\lambda = 0$) and the solvent density is set equal to zero, i.e., $\eta_3 = 0$. In addition, if we set only the association parameter $\lambda = 0$ in our equations we have the analytic solution of charged hard spheres in a hard sphere solvent in the mean spherical approximation.

Now we are in the position to determine association parameter λ. Making use of Eq. (1.4) and defining $\tau = 1/\zeta$, we have

$$\lambda\tau = y_{+-}(\sigma). \qquad (3.22)$$

The PY/MS approximation leads to

$$\lambda\tau = g_{+-}(\sigma_+) - c_{+-}(\sigma+) = (2+\eta_0-2\mu)/[2(1-\eta_0)^2] + e^2(B^2-2B)/(\epsilon kT\sigma) \qquad (3.23)$$

which can be rearranged, using Eq. (3.17), into the following cubic equation for ν:

$$\nu^3(2c_1-4) + \nu^2(c_1^2+2c_2-6-2x) + \nu(2c_2c_1-4-4x) + (c_2^2-2x-1) = 0, \qquad (3.24)$$

where

$$c_1 = -24\tau + (2-14\eta-2\eta_3)/(1-\eta_0), \qquad (3.25)$$

$$c_2 = 1 + 6\eta(2+\eta_0)/(1-\eta_0)^2 + (2x-x^2)/2, \qquad (3.26)$$

and $x = \kappa\sigma$. This equation can be solved analytically, and we choose the physically acceptable value of λ which must be real and positive. In the HNC/MS approximation, we have

$$\lambda\tau = \exp[h_{+-}(\sigma+) - c_{+-}(\sigma+)] = \exp\{(2+\eta_0-2\mu)/[2(1-\eta_0)^2] + e^2(B^2-2B)/(\epsilon kT\sigma) - 1\}. \qquad (3.27)$$

This equation, however, has to be solved numerically by iteration. In both cases, either in the PY/MS approximation or the HNC/MS approximation, the solution of the SEM with a hard sphere solvent reduces to the solution of a nonlinear algebraic equation.[3]

At zero charge the adhesive electrolyte in a hard sphere solvent becomes an adhesive (or sticky) nonelectrolyte (SN) in the same solvent and the MSA for the RPM electrolyte becomes identical to the PY approximation for hard spheres. The SN system has already been studied by us in the absence of a solvent or when the solvent is treated as a continuum.[3] In the following section we will discuss the thermodynamic properties of an adhesive nonelectrolyte in a hard sphere solvent after an analysis of the corresponding sticky electrolyte model.

IV. THERMODYNAMIC PROPERTIES OF THE STICKY ELECTROLYTE AND STICKY NONELECTROLYTE MODELS FOR $L = \sigma$

Although the hard sphere solvent has no interaction with the ions except for the hard core repulsion, it still has an influence on the excess free energy and the other thermodynamic properties through its effect on the degree of ion association as observed by the magnitude of the association parameter λ. The general expression for the excess energy has already been discussed—see Eqs. (2.29) and (2.30). With binding at $L=\sigma$, $\langle N\rangle = \eta\lambda$ and the solution to the MSA leads to[3]

$$H' = \{(1+\nu) + \kappa\sigma(1-\nu) - [(1+\nu)^2 + 2\kappa\sigma]^{1/2}\}/(12\eta) \qquad (4.1)$$

which is related to the excess energy through Eq. (2.29).

The calculation of the excess Helmholtz free energy has been discussed elsewhere[2,3] for the SEM in a continuum solvent, but in a hard sphere solvent we have additional contributions to the free energy from the hard cores, the stickiness and the electrical interactions between the ions. For the part contributed by the stickiness, we adopt the following formula[2]

$$\beta\Delta A^{\mathrm{ex}}N = -(\eta/2)\int_0^{\zeta} y_{+-}(\sigma,\zeta')d\zeta' = -\nu[1-\ln y_{+-}(\sigma,\zeta)] - (\eta/2)\int_0^{\zeta} y_{+-}(\sigma,\lambda')d\lambda', \qquad (4.2)$$

where ΔA^{ex} is the change in the excess free energy due to the binding between oppositely charged ions. Using Eq. (3.22) for $y_{+-}(\sigma,\zeta)$ in Eq. (4.2) and integrating it out, we have

$$\beta\Delta A^{\mathrm{ex}}N = -\eta/2\{\lambda + \eta\lambda^2/[4(1-\eta_0)] - \lambda^2/24 - \eta\lambda^3/72 + (1+2x)^{3/2}/(18\eta^2) + Y\}, \qquad (4.3)$$

where

$$Y = [(1+\eta\lambda/2)^2 + 2x]^{1/2}(\eta^2\lambda^2 + \eta\lambda - 2 - 4x)/(36\eta^2). \qquad (4.4)$$

When $\lambda = 0$, it is easily verified that ΔA^{ex} is zero; when the solvent concentration decreases to zero we recover the expression for the excess free energy difference in the HNC/MS approximation for the SEM in a continuum solvent.

The free energy difference between a sticky nonelectrolyte and hard spheres can be obtained by turning off the charges in Eqs. (3.23) and (3.27) and making use of Eq. (4.2) when we find that

$$\beta(A^{\rm sn}-A^{\rm hs})/N=(m\eta/2n)\ln[(m-n\lambda)/m]\quad\text{(PY)}\tag{4.5}$$

$$\beta(A^{\rm sn}-A^{\rm hs})/N=-\eta\{\lambda+\eta\lambda^2/[4(1-\eta_0)]\}/2\quad\text{(HNC/PY)},\tag{4.6}$$

where

$$m=(2+\eta_0)/[2(1-\eta_0)^2]\tag{4.7}$$

$$n=\eta/[2(1-\eta_0)].\tag{4.8}$$

The pressure differences in the PY and HNC/PY approximations are obtained by differentiating Eqs. (4.5) and (4.6) with respect to the reduced density:

$$\begin{aligned}(P^{\rm sn}-P^{\rm hs})/\rho kT=&\,(\eta/2n)[m+m'\eta-mn'\eta/n]\\&\times\ln[1-n\lambda/m]\\&+\eta^2(-mn'\lambda-mn\lambda'+nm'\lambda)/\\&[2n(m-n\lambda)],\text{(PY)}\end{aligned}\tag{4.9}$$

where

$$m'=(5+\eta_0)/[2(1-\eta_0)^3],\tag{4.10}$$

$$n'=(1-\eta_3)/[2(1-\eta_0)^2],\tag{4.11}$$

$$\begin{aligned}\lambda'=&\,\lambda[5+\eta_0-\lambda(1-\eta_0)(1-\eta_3)]/\\&[(1-\eta_0)(2+\eta_0)]\end{aligned}\tag{4.12}$$

and

$$\begin{aligned}(P^{\rm sn}-P^{\rm hs})/\rho kT=&-(\eta/2)\{\lambda+\eta\lambda^2(2-2\eta_0+\eta)/\\&[4(1-\eta_0)^2]\\&+\eta\lambda(2-2\eta_0+\eta\lambda)[5+\eta_0\\&-\lambda(1-\eta_0)(1-\eta_3)]/\\&[4(1-\eta_0)^4+2\eta\lambda(1-\eta_0)^3]\}\\&\text{(HNC/PY)}.\end{aligned}\tag{4.13}$$

To determine the osmotic coefficient of the SEM in the McMillan–Mayer system, we have to expend a little more effort since the chemical potential of the solvent is held constant. To realize this requirement, we write the Gibbs–Duhem equation at constant T and constant chemical potential of the solvent in the following form

$$d(P-P^{\rm id})-\rho d(\mu^{\rm s}-\mu^{\rm s,id})=0.\tag{4.14}$$

Here $\mu^{\rm s}$ is the chemical potential of the solute, and the superscript id refers to an ideal system. Intergrating by parts, dividing by kT on both sides and using the following separation of the chemical potential of the solute

$$\mu^{\rm s}-\mu^{\rm s,id}=\mu^{\rm s,hs}+\mu^{\rm s,el}+\mu^{\rm s,st}\tag{4.15}$$

we can write Eq. (4.14) as

$$\begin{aligned}(P-P^{\rm id})/\rho kT=&\,(\mu^{\rm s,hs}+\mu^{\rm s,el}+\mu^{\rm s,st})/kT-\rho^{-1}\\&\times\int_0^\rho[(\mu^{\rm s,sh}+\mu^{\rm s,el}+\mu^{\rm s,st})/kT]d\rho'.\end{aligned}\tag{4.16}$$

This is equivalent to

$$\begin{aligned}\phi-1=\phi^{\rm ex}&=(P-P^{\rm id})/\rho kT\\&=\phi^{\rm hs,ex}+\phi^{\rm el,ex}+\phi^{\rm st,ex}\end{aligned}\tag{4.17}$$

with the excess osmotic coefficients defined by

$$\phi^{\rm hs,ex}=\mu^{\rm s,hs}/kT-\rho^{-1}\int_0^\rho(\mu^{\rm s,hs}/kT)d\rho,\tag{4.18a}$$

$$\phi^{\rm el,ex}=\mu^{\rm s,el}/kT-\rho^{-1}\int_0^\rho(\mu^{\rm s,el}/kT)d\rho,\tag{4.18b}$$

$$\phi^{\rm st,ex}=\mu^{\rm s,st}/kT-\rho^{-1}\int_0^\rho(\mu^{\rm s,st}/kT)d\rho,\tag{4.18c}$$

where the superscript el means the electrical part, st means the sticky interaction part, and hs the hard sphere part. For the hard sphere mixture (hard sphere solute + hard sphere solvent of the same size), the Helmholtz free energy in the Carnahan and Starling[17] approximation is given by

$$A^{\rm hs}=N_0kT[\ln\eta_0+\eta_0(4-3\eta_0)/(1-\eta_0)^2],\tag{4.19}$$

where the total number of particles $N_0=N+N_3$. Differentiating $A^{\rm hs}$ with respect to N gives the chemical potential of the hard sphere part

$$\mu^{\rm s,hs}/kT=(8\eta_0-9\eta_0^2+3\eta_0^3)/(1-\eta_0)^3.\tag{4.20}$$

From the solution of the restricted primitive model (RPM), the electrical interaction part of the chemical potential can be written as

$$\mu^{\rm s,el}/kT=-[3x^2+3x-3x(1+2x)^{1/2}]/72\eta.\tag{4.21}$$

From Eq. (4.3) and the HNC closure (3.27), we can get the chemical potential of the sticky interaction part as

$$\begin{aligned}\mu^{\rm s,st}/kT=&-\eta\{\lambda+3\eta\lambda^2/[8(1-\eta_0)]+\nu^2/\\&[2(1-\eta_0)^2]\}+(\nu+\nu^2)\lambda/12+M_3\lambda/72\\&+(d\lambda/d\eta)[-\eta^2/2-\eta^3\lambda/[4(1-\eta_0)]\\&+\eta M_3/72+\eta(\nu+\nu^2)/12],\end{aligned}\tag{4.22}$$

where

$$\begin{aligned}(d\lambda/d\eta)=&\,\{\lambda(5+\eta_0)-\lambda^2(1-\eta_0)(1-\eta_3)+xM_1\lambda\\&\times(1-\eta_0)^3(2B-2)/12\eta^2\}/\{2(1-\eta_0)^3\\&+\eta\lambda(1-\eta_0)^2+xM_2\lambda(1-\eta_0)^3\\&\times(2B-2)/12\eta^2\}\end{aligned}\tag{4.23}$$

$$M_1=[-1+\nu+\alpha-(2\nu+2\nu^2+x)/\alpha]/2\tag{4.24}$$

$$M_2=[\eta^2-\eta^2(1+\nu)/\alpha]/2\tag{4.25}$$

$$\begin{aligned}M_3=&-\alpha(1+4\nu)+(1+\nu)\\&\times(1+2x-\nu+2\nu^2)/\alpha\end{aligned}\tag{4.26}$$

$$\alpha=[(1+\nu)^2+2x]^{1/2}.\tag{4.27}$$

Substituting Eqs. (4.21) and (4.12), into Eqs. (4.18a) and (4.18b) we have

$$\phi^{\mathrm{hs,ex}} = (3-\eta_0)(1-\eta_0)^{-3} - (3-2\eta-4\eta_3 + \eta_0\eta_3)(1-\eta_0)^{-2}(1-\eta_3)^{-2} \quad (4.28)$$

$$\phi^{\mathrm{el,ex}} = [2+3x-(2+x)(1+2x)^{1/2}]/72\eta. \quad (4.29)$$

Equation (4.29) is the excess osmotic coefficient of the RPM electrolyte in the MSA.[15] The contribution from stickiness to the excess osmotic coefficient $\phi^{\mathrm{st,ex}}$ has to be calculated numerically from Eqs. (4.18c) and (4.22). It is interesting to note that when the solvent density is zero ($\eta_3 = 0$), Eq. (4.28) reduces to the excess osmotic coefficient of a hard sphere solute in a continuum solvent. When the solute density is zero ($\eta = 0$), Eq. (4.28) leads correctly to an excess osmotic coefficient of zero for hard spheres ($\phi^{\mathrm{hs,ex}} = 0$). When $\lambda = 0$ the expressions derived above also provide the osmotic coefficient of an RPM electrolyte in a hard sphere solvent.

The osmotic coefficient of a sticky hard sphere solute in the McMillan–Mayer system in the HNC/PY are obtained by setting the charges equal to zero in Eq. (4.22) when we find

$$\begin{aligned}\mu^{\mathrm{s,st}}/kT = & -\eta\{\lambda + 3\eta\lambda^2/[8(1-\eta_0)] \\ & + \nu^2/[2(1-\eta_0)^2]\} - (\eta^2/4) \\ & \times[2+\eta\lambda/(1-\eta_0)] \\ & \times[\lambda(5+\eta_0) - \lambda^2(1-\eta_0)(1-\eta_3)] \\ & \times[2(1-\eta_0)^3 + \eta\lambda(1-\eta_0)^2]^{-1}. \end{aligned} \quad (4.30)$$

This is the contribution to the chemical potential from the adhesive interaction between the hard sphere solute species A and B immersed in a hard sphere solvent. When the adhesiveness is removed ($\lambda = 0$), the system is similar to a mixture of two isotopes separated from one of the isotopic components (the solvent) by a semipermeable membrane through which the other isotopic species (the solute), which is present on one side of the membrane, cannot pass.

V. RESULTS AND DISCUSSION

In order to compare our work with some of our earlier results,[4] we choose the parameters of the ions and solvent the same as that of the SEM without the molecular solvent. The temperature is taken as 298 K, the diameter is 4.2 A, the solvent dielectric constant is 78.358, and the valences of the ions are + 2 and − 2, respectively.

The association constant λ is obtained by solving Eq. (3.24) or (3.27) at different electrolyte concentrations and the association number $\langle N \rangle$ is determined from $\langle N \rangle = \eta\lambda$. The results in the HNC/MS approximation are shown in Fig. 1. It is apparent from the figure that when the hard sphere solvent is added, both λ and $\langle N \rangle$ increase greatly because of the packing effect of the solvent. In the PY/MS approximation, a negative value of λ is found[1] for the parameters chosen in this study. Since this is physically unacceptable, this approximation will not be considered further.

The excess internal energy $E^{\mathrm{ex}'}$ and the change in the excess Helmholtz free energy ΔA^{ex} due to the stickiness are plotted in Figs. 2 and 3, respectively, with the corresponding results for the same electrolyte in a continuum solvent of the same dielectric constant. In the calculation of the excess internal energy from Eq. (2.29), we have neglected the temperature coefficient of the dielectric constant of the solvent. We see from the figures that both E^{ex} and ΔA^{ex} become more negative in the presence of the solvent. This can be explained by saying that the hard sphere solvent increases the chances of contact between the ions, thereby increasing the average number of dimers, which makes the binding energy and ΔA^{ex} more negative—see Eq. (4.3).

In studying the osmotic coefficients, we first turn off all the charges on the ions and calculate the osmotic coefficients of the solute molecules, initially in a continuum solvent and then in a hard sphere solvent, keeping the chemical potential of the solvent fixed. The results are plotted as a function of the solute concentration in Fig. 4: curve 1 shows the osmotic coefficient of the hard sphere solute, while curve 2 represents

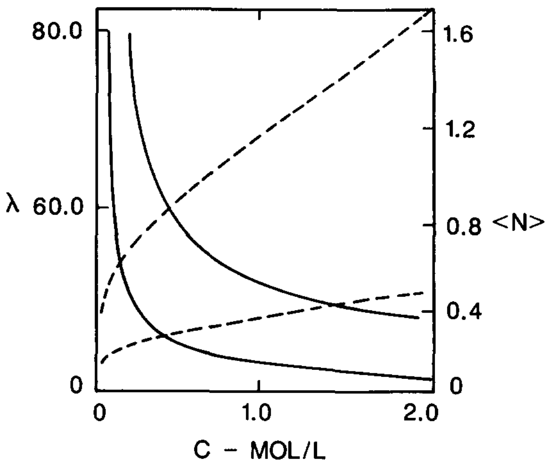

FIG. 1. The association parameter λ (solid line) and the average association number $\langle N \rangle$ (dashed line) for a 2–2 electrolyte in the SEM with, $L = \sigma = 4.2$ Å, $\zeta = 1.098\times 10^3$, ($\tau = 0.000\,91$), $T = 298$ K calculated from the HNC/MS approximation. The upper curve is for the electrolyte in a hard sphere solvent at a reduced density $\eta_3 = 0.376$, the lower curve is for the same electrolyte in a continuum solvent $\eta_3 = 0$. The dielectric constant of the solvent in both systems is the same ($\epsilon = 78.358$).

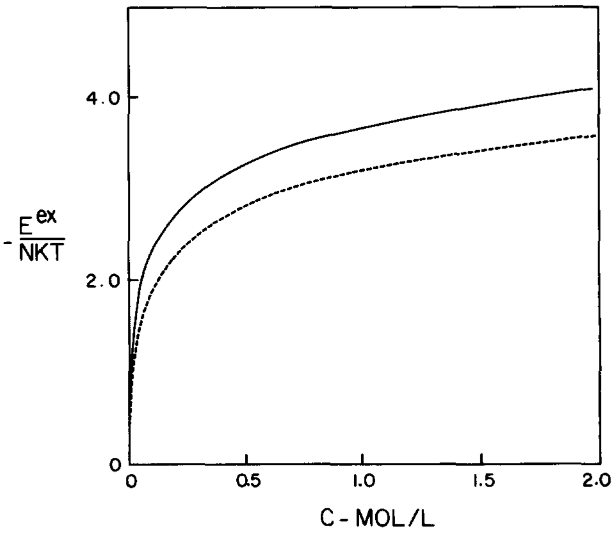

FIG. 2. The excess energy $E^{\mathrm{ex}'}$ plotted as a function of the electrolyte concentration for a 2–2 electrolyte. The solid line is for the continuum solvent ($\eta_3 = 0$), and the dashed line for the hard sphere solvent $\eta_3 = 0.376$. See caption of Fig. 1 for electrolyte and solvent parameters.

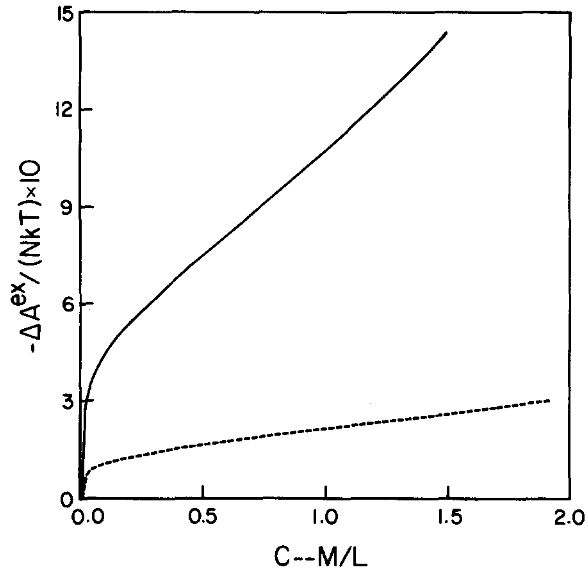

FIG. 3. The change in the excess Helmholtz free energy due to the sticky interaction plotted against the electrolyte concentration for a 2–2 electrolyte. The upper curve is for the electrolyte in a hard sphere solvent ($\eta_3 = 0.376$), the lower curve for the same electrolyte in continuum solvent $\eta_3 = 0$. See caption of Fig. 1 for electrolyte parameters.

the osmotic coefficient of the same solute in a hard sphere solvent of the same size but at a reduced density $\eta_3 = 0.376$. Both sets of osmotic coefficients lie above unity and increase with the solute concentration; the presence of the hard sphere solvent apparently leads to a further increase in the osmotic coefficient of the solute. We emphasize again that, for this system, there is no distinction here between the solute and the solvent except that it is only the solvent molecules that are allowed to pass through the hypothetical semipermeable membrane in the McMillan–Mayer system that is under consideration. Curves 3 and 4 are the osmotic coefficients of the sticky hard sphere solute in a continuum solvent and in the hard sphere solvent, respectively, from which it appears that the osmotic coefficient is lowered in the presence of a hard sphere solvent! It is the opposite of what was found in the absence of stickiness between the solute molecules. This can be explained by assuming that the hard sphere solvent has two opposing effects on a sticky solute—it increases the osmotic coefficient by increasing the density of particles in the system (the packing effect), but it also reduces the osmotic coefficient by increasing the stickiness between the solute molecules thereby increasing the number of dimers and other associated species at the expense of the monomers. The second effect appears to overshadow the first in the present instance. The situation, as we will see, is quite different for the charged system.

In Fig. 5, we have the osmotic coefficients ϕ for the corresponding charged systems; curves 1′ and 2′ are for the restricted primitive model (RPM) in continuum and hard sphere solvents, respectively, while curves 3′ and 4′ are the results of the sticky electrolyte model (SEM) in the same pair of solvents. It is seen that the osmotic coefficient of the SEM is lower than that of the corresponding RPM in the same solvent; this is because of the extra adhesive interaction between the oppositely charged ions in the SEM. The presence of a hard sphere solvent, however, raises the osmotic coefficients of the RPM and SEM electrolytes which is the opposite of what was found for the sticky hard sphere systems with no charges! Here apparently the packing effect due to the hard sphere solvent is the dominant one.

Comparing Figs. 4 and 5 we find that the addition of charge lowers the osmotic coefficient of a nonsticky electro-

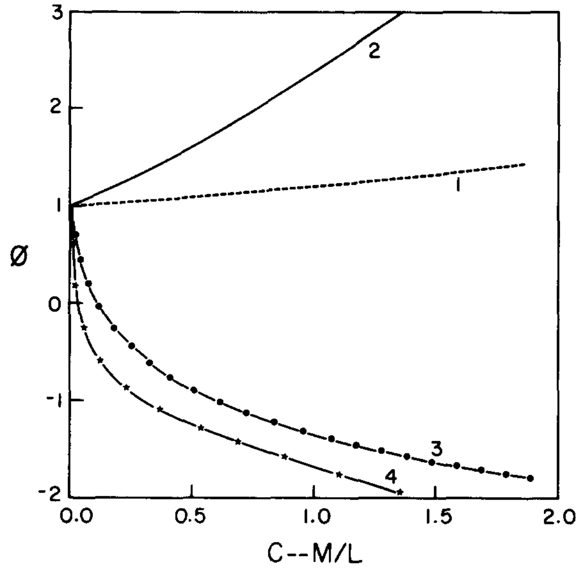

FIG. 4. The osmotic coefficient of a hard sphere solute in a continuum solvent ($\eta_3 = 0$) and in a hard sphere solvent ($\eta_3 = 0.376$) with and without adhesiveness between the solute molecules A and B plotted as a function of the solute concentration. The chemical potential of the solvent is held constant in each case. Curve 1: hard sphere solute, curve 2: hard sphere solute in hard sphere solvent, curve 3: adhesive hard sphere solute, and curve 4: adhesive hard sphere solute in hard sphere solvent.

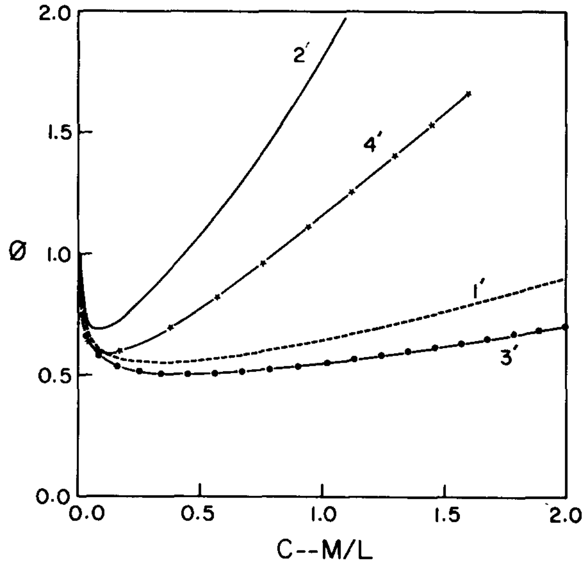

FIG. 5. The osmotic coefficients as a function of the solute concentration for a 2–2 electrolyte. Curve 1 RPM in a hard sphere solvent ($\eta_3 = 0.376$)-HNC/MS approximation; curve 2: RPM in a hard sphere solvent ($\eta_3 = 0.376$)-MS approximation; curve 3:SEM in a continuum solvent-MS approximation. Curve 4: SEM in a hard sphere solvent-HNC/MS approximation. See caption of Fig. 1 for electrolyte parameters and dielectric constant of the solvent.

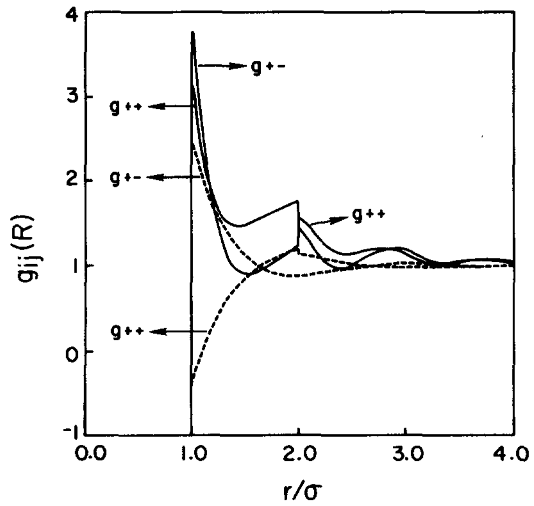

FIG. 6. The ion–ion radial distribution function in the HNC/MS approximation for a 2–2 SEM electrolyte at a concentation of 2 M ($\eta = 0.0934$). The dashed lines are for the electrolyte in a continuum solvent ($\eta_3 = 0$, $\lambda = 5.232$), the full lines for the same electrolyte in a hard sphere solvent ($\eta_3 = 0.376$, $\lambda = 18.60$). See caption of Fig. 1 for electrolyte parameters and solvent dielectric constant.

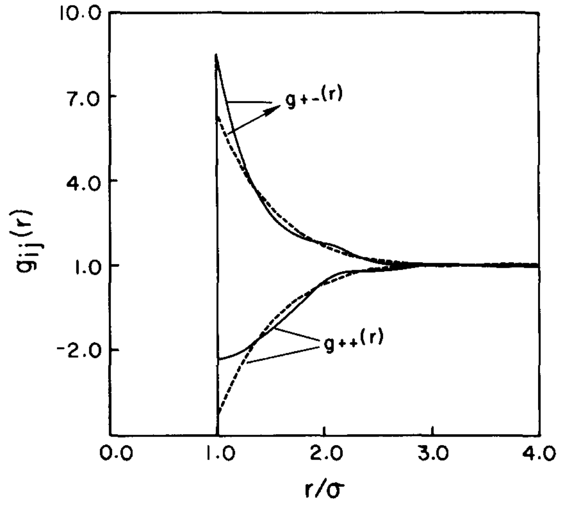

FIG. 7. The ion–ion radial distribution function in the HNC/MS approximation for the 2–2 SEM electrolyte systems described in the caption of Fig. 6 except that the sticking coefficient $\zeta = 24.4$ ($\tau = 0.041$), and the electrolyte concentration is 0.1627 ($\eta = 0.0076$). The dashed line is for the electrolyte in a continuum solvent ($\eta_3 = 0, \lambda = .0315$) and the full line for the electrolyte in a hard sphere solvent ($\eta_3 = 0.376, \lambda = 0.29$).

lyte in a continuum or hard sphere solvent, while just the opposite is true when the ions can stick to one another! The passage from a continuum to a granular solvent influences the osmotic coefficient in two ways: it tends to increase the osmotic coefficient of the system when the solute molecules (charged or uncharged) do not stick or if the solute molecules are charged (ions) and can stick to one another. If, however, the charges are removed from the sticky electrolyte, the change from continuum to a hard sphere solvent decreases the osmotic coefficient. The competition between the stickiness and the packing apparently determines the final outcome.

The ion–ion radial distribution functions of the SEM at concentrations of 2 and 0.1627 M were calculated by Perram's method[18] and are plotted in Figs. 6 and 7, respectively; the dashed lines show the results in a continuum solvent and the full lines depict the situation in a hard sphere solvent ($\eta_3 = 0.376$) which endows the curves with more structure. We see that the contact values of $g_{++}(r)$ and $g_{+-}(r)$ are higher in the hard sphere solvent than in its continuum analog. This is accompanied by an increase in both these distribution functions at $r = 2\sigma$, which is more pronounced at the higher concentration (2 M). At this high end of the concentration scale the discontinuities in the distribution functions at $r = 2\sigma$ are ordered according to the

$$g_{++}(2\sigma-) > g_{+-}(2\sigma-)$$

$$g_{++}(2\sigma+) < g_{+-}(2\sigma+),$$

where − and + in parentheses stand for the subtraction or addition of an infinitesimal quantity. Since our calculations correspond to a sticky interaction at $r = \sigma-$, the changes observed in the distribution functions at $r = \sigma$ and 2σ indicate that the packing effect of the solvent increases the numbers of dimers and triplets over those found in a continuum solvent. For this system, with a dielectric constant of 78.36, the MSA provides no evidence for polymerization beyond the formation of triplets.

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