Solvent effects in weak electrolytes. II. Dipolar hard sphere solvent and the sticky electrolyte model with $L = \sigma$

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The sticky electrolyte model in a dipolar solvent is studied in this paper. A detailed separation of the Ornstein–Zernike (OZ) equations and their solution in the mean spherical (MS) approximation for binding (or stickiness) at $L = \sigma$ are given. The results derived earlier by Adelman and Deutch, Blum *et al.* and by Høye *et al.* in this approximation are reproduced when the stickiness is switched off. Also when the density of the solvent goes to zero, the results reduce to those of the sticky electrolyte model (SEM) in a continuum solvent. It is found that the PY/MS approximation gives negative solutions for the association parameter λ, while the HNC/MS approximation works in a narrow interval of the sticky potential well depth ϵ_2 between the positive and negative ions. As expected, the ion association increases when sticky potential well becomes deeper, but the dipole moment of the solvent is found to have a strong screening effect on this association. The study of the radial distribution functions of this system shows that the probability of a free ion appearing near a counter ion is greatly decreased when binding occurs between the oppositely charged ions at the contact; the opposite happens for ions of the same sign. The absolute value of the ion solvation energy becomes smaller as the electrolyte concentration increases and when stickiness between oppositely charged ions is introduced.

I. INTRODUCTION

The sticky electrolyte model (SEM) first discussed by Lee, Rasaiah, and Cummings, has been studied in a series of papers.[1–4] Recently this model has been extended to noncontinuous solvent media by us[5] (hard sphere solvent) and by Wei and Blum[6] (dipolar solvent). In this model, a delta function is introduced in the interaction between oppositely charged ions in the range $0 < r \leqslant \sigma$, where σ is the diameter of the ions. In this way, ion association in a weak acid is mimicked and the extent of this association can be calculated. The model is a modification of the restricted primitive model (RPM), which has been studied, in a dipolar solvent, by a number of authors.[7–12] The Hamiltonians for the SEM and the RPM, in a given solvent, are different only inside the hard core, outside the range $r > \sigma$, the Hamiltonians for the two models are the same. When the stickiness is switched off in the SEM, all the results of the RPM should be recovered. This serves as a useful check on the solutions of the SEM, particularly when they can be obtained analytically as in the mean spherical approximation (MSA) which is used in this paper.

In the previous paper,[5] we studied solvent effects on ion association in the SEM with a hard sphere solvent. It was found that the ion association was considerably enhanced and the excess internal energy and free energy of the ions became more negative in the presence of this solvent. The question arises—what will happen if this model was studied in a dipolar solvent? At least two effects can be expected; the solvent will tend to increase the extent of the association due to packing of the solvent molecules around the bonded ion pairs or clusters. Also the dipoles of the solvent molecules should screen the charges on the ions tending to decrease the extent of ion association. We will study these effects in detail in this paper.

Even though a general solution for the (SEM) in a dipolar solvent has been discussed by Wei and Blum,[6] we still feel there is much left to be done. The work of Wei and Blum is very general with allowance for stickness between all of the species of different sizes that are present in solution. This also makes their theoretical analysis more complicated than necessary to understand the physical chemistry of weak electrolytes. Moreover their discussion does not include a calculation of the association parameter λ and the correlation functions. Therefore, we will carry out our analysis in the following pages limiting ourselves essentially from the beginning to the case of ions and solvent molecules of the same size with the prospect of stickiness or adhesion only between oppositely charged ions. Our results include the determination of the assocation parameter λ and the thermodynamic properties, as well as the calculation of the correlation functions. We will also discuss the solvation energy of the ions as a function of the ion concentration in the presence and in the absence of the stickiness between oppositely charged ions. This is of great interest to chemists and has been studied by Chan *et al.*[13] in the limit of infinite dilution when there is no stickiness between the ions. Wherever possible we also make contact with the analysis by Wei and Blum[6] as well as with previous work by others on ion–dipole mixtures.[7–12]

This paper is planned in the following way: in Sec. II the decomposition and solution of the Ornstein–Zernike equation in the SEM in a dipolar solvent are presented in detail and in Sec. III the thermodynamic properties of this system and the solvation energy at the low ion concentration are calculated. The numerical results are discussed in Sec. IV.

II. SOLUTION OF THE ORNSTEIN–ZERNIKE EQUATIONS FOR THE SEM IN THE MEAN SPHERICAL APPROXIMATION

A. Decomposition of the Ornstein–Zernike equations

Our system is composed of three components: positive and negative ions with a charge $e_i = z_i e$ on each ion i where

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z_i is the valence and e is the electronic charge, and dipolar hard sphere solvent molecules with a dipole moment μ. All of the species have the same diameter σ. Although a number of papers have been contributed to the solution of the MSA for the ion–dipole system, to our knowledge, the details of the decomposition of the Ornstein–Zernike equation are only given by Chan *et al.*[13] in Fourier space. We will first discuss the decomposition in r space. For this system, the interaction energy can be written as

$$u_{ij} = z_i z_j e^2/r, \tag{2.1a}$$

$$u_{id} = -z_i e\mu\phi^{011}/r^2, \tag{2.1b}$$

$$u_{dd} = -\mu^2\phi^{112}/r^3, \tag{2.1c}$$

where the subscript i,j represents a positive or negative ion, the subscript d signifies a dipole and r is the distance between two particles. The angular functions have the following definitions:

$$\phi^{011} = \hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{s}}_2, \tag{2.2a}$$

$$\phi^{112} = 3(\hat{\mathbf{s}}_1\cdot\hat{\mathbf{r}}_{12})(\hat{\mathbf{s}}_2\cdot\hat{\mathbf{r}}_{12}) - \hat{\mathbf{s}}_1\cdot\hat{\mathbf{s}}_2, \tag{2.2b}$$

where $\hat{\mathbf{r}}_{12}$ is the unit vector in the direction of $\mathbf{r}$ and $\hat{\mathbf{s}}_i$ is the unit vector along the dipole i. The several Ornstein–Zernike equations can be written as

$$h_{++} = c_{++} + \rho_+ c_{++} * h_{++} + \rho_- c_{+-} * h_{-+} + \rho_d \int c_{+d} \times (\mathbf{r}-\mathbf{r}',\omega) h_{d+}(\omega,\mathbf{r}') d\mathbf{r}' d\omega/4\pi, \tag{2.3a}$$

$$h_{+-} = c_{+-} + \rho_+ c_{++} * h_{+-} + \rho_- c_{+-} * h_{--} + \rho_d \int c_{+d} \times (\mathbf{r}-\mathbf{r}',\omega) h_{d-}(\omega,\mathbf{r}') d\mathbf{r}' d\omega/4\pi, \tag{2.3b}$$

$$h_{+d} = c_{+d} + \rho_+ c_{++} * h_{+d} + \rho_- c_{+-} * h_{-d} + \rho_d \int c_{+d} \times (\mathbf{r}-\mathbf{r}',\omega) h_{dd}(\omega,\mathbf{r}',\omega') d\mathbf{r}' d\omega/4\pi, \tag{2.3c}$$

$$h_{-d} = c_{-d} + \rho_+ c_{-+} * h_{+d} + \rho_- c_{--} * h_{-d} + \rho_d \int c_{-d} \times (\mathbf{r}-\mathbf{r}',\omega) h_{dd}(\omega,\mathbf{r}',\omega') d\mathbf{r}' d\omega/4\pi, \tag{2.3d}$$

$$h_{dd} = c_{dd} + \rho_+ c_{d+} * h_{+d} + \rho_- c_{d-} * h_{-d} + \rho_d \int c_{dd} \times (\omega',\mathbf{r}-\mathbf{r}',\omega) h_{dd}(\omega,\mathbf{r}',\omega'') d\mathbf{r}' d\omega/4\pi, \tag{2.3e}$$

where $*$ represents a convolution integral, $d\omega = \sin\phi\, d\phi\, d\theta$ and $\mathbf{r}$ represents a vector coordinate. In the SEM a delta function interaction is present inside the hard core at a distance $r = L$ and the closure equations can be put in the following form

$$h_{++}(r) = h_{--}(r) = -1, \quad 0 < r < \sigma \tag{2.4a}$$

$$h_{+-}(r) = h_{-+}(r) = -1 + \lambda L\delta(r-\sigma)/12, \quad 0 < r < \sigma \tag{2.4b}$$

$$h_{id}(r,\omega) = h_{di}(\omega,r) = -1, \quad 0 < r < \sigma \tag{2.4c}$$

$$h_{dd}(r,\omega,\omega') = -1, \quad 0 < r < \sigma. \tag{2.4d}$$

In the MSA, the direct correlation functions outside the hard core are approximated by their asymptotic forms

$$c_{ij}(r) = -\beta z_i z_j e^2/r, \quad r > \sigma \tag{2.5a}$$

$$c_{id}(r,\omega) = c_{di}(\omega,r) = \beta e\mu\phi^{011}/r^2, \quad r > \sigma \tag{2.5b}$$

$$c_{dd}(r,\omega,\omega') = \beta\mu^2\phi^{112}/r^3 \quad r > \sigma \tag{2.5c}$$

where $\beta = (kT)^{-1}$ in which k is Boltzmann's constant and T is the absolute temperature. To decompose Eq. (2.3), we follow Chan *et al.*[13] and introduce the following functions:

$$f_{ij} = f_{ii}^{\text{hs}} + z_i z_j f^{000}(r), \tag{2.6a}$$

$$f_{id} = f_{id}^{\text{hs}} + z_i f^{011}(r)\phi^{011}, \tag{2.6b}$$

$$h_{di} = f_{id}^{\text{hs}} - z_i f^{011}(r)\phi^{011}, \tag{2.6c}$$

$$f_{dd} = f_{dd}^{\text{hs}} + f^{110}(r)\phi^{110} + f^{112}(r)f^{112}, \tag{2.6d}$$

where f_{ij} represents c_{ij} or h_{ij}, $f_{ii}^{\text{hs}} = (f_{++} + f_{+-})/2$ and $f_{id}^{\text{hs}} = (f_{id} + f_{di})/2$, which correspond to the usual definitions of sum functions for oppositely charged ions.[3,5] A similar ansatz was used by Chan *et al.*[13] in their discussion of ion–dipole mixtures (without stickiness) in the MSA and provides the crucial step in making the decomposition of the Ornstein–Zernike equations. Taking the sum of Eqs. (2.3a) and (2.3b), the sum of Eqs. (2.3c) and (2.3d), and carrying out the corresponding angular integrations leads us to the following two equations:

$$h_{ii}^{\text{hs}} = c_{ii}^{\text{hs}} + \rho c_{ii}^{\text{hs}} * h_{ii}^{\text{hs}} + \rho_d c_{id}^{\text{hs}} * h_{di}^{\text{hs}}, \tag{2.7a}$$

$$h_{id}^{\text{hs}} = c_{id}^{\text{hs}} + \rho c_{ii}^{\text{hs}} * h_{id}^{\text{hs}} + \rho_d c_{id}^{\text{hs}} * h_{dd}^{\text{hs}}. \tag{2.7b}$$

Substracting Eq. (2.3b) from Eq. (2.3a) and Eq. (2.3d) from Eq. (2.3c) and doing the corresponding angular integrations, we have

$$h^{000} = c^{000} + z_+^2 \rho c^{000} * h^{000} - (\rho_d/3) c^{011} * h^{011}, \tag{2.8a}$$

$$h^{011} = c^{011} + z_+^2 \rho c^{000} * h^{011} + (\rho_d/3) c^{011} * (h^{110} + 2h^{112}). \tag{2.8b}$$

In deriving the above equations, we have used the assumption implied in Eqs. (2.6) and the definition that $\rho = \rho_+ + \rho_-$. Substituting Eq. (2.6) into the last equation of (2.3) and carrying out the convolution integrations lead to

$$h_{dd}^{\text{hs}} = c_{dd}^{\text{hs}} + \rho c_{di}^{\text{hs}} * h_{id}^{\text{hs}} + \rho_d c_{dd}^{\text{hs}} * h_{dd}^{\text{hs}}, \tag{2.8c}$$

$$h^{110} = c^{110} - z_+^2 (\rho/3) c^{011} * h^{001} (\rho_d/3) \times [c^{110} * h^{110} + 2c^{112} * h^{112}], \tag{2.8d}$$

$$h^{112} = c^{112} - z_+^2 (\rho/3) c^{011} * h^{011} + (\rho_d/3) \times [c^{112} * h^{110} + c^{110} * h^{112} + c^{112} * h^{112}]. \tag{2.8e}$$

Up to now, we have separated the hard sphere part from the electrostatic part. To simplify Eq. (2.8) further, let us define

$$\rho_0 = \rho z_+^2 = \rho_+ z_+^2 + \rho_- z_-^2, \tag{2.9}$$

$$h^{+dd} = h^{110} + 2h^{112}, \tag{2.10a}$$

$$h^{-dd} = h^{110} - h^{112} \tag{2.10b}$$

with corresponding definitions for the c functions. Equations (2.8) can then be put into the following form with the help of Eqs. (2.9) and (2.10)

$$h^{000} = c^{000} + \rho_0 c^{000} * h^{000} - (\rho_d/3) c^{011} * h^{011}, \tag{2.11a}$$

$$h^{011} = c^{011} + \rho_0 c^{000} * h^{011} + (\rho_d/3) c^{011} * h^{+dd}, \tag{2.11b}$$

$$h^{+dd} = c^{+dd} - \rho_0 c^{011} * h^{011} (\rho_d/3) c^{+dd} * h^{+dd}, \tag{2.11c}$$

$$h^{-dd} = c^{-dd} + (\rho_d/3) c^{-dd} * h^{-dd}. \tag{2.12}$$

Because the ion–diople correlation function is symmetric, Eq. (2.11b) can also be written as

$$h^{011} = c^{011} + \rho_0 c^{011} * h^{000} + (\rho_d/3) c^{+dd} * h^{011}. \quad (2.11\text{d})$$

Now the Ornstein–Zernike equations have been decomposed into three groups in r space: the hard sphere part given in Eqs. (2.7) and (2.8c), the electrical interaction part shown in Eq. (2.11) and the pure dipolar part displayed in Eq. (2.12) which correspond to the results given in Chan *et al.*'s paper[13] in k space. It should also be noticed that the electrical interaction part in Eq. (2.11) reduces to the difference equation of the SEM in the continuum solvent when the dipole density $\rho_d \to 0$. Because of the ansatz introduced in Eq. (2.6), the closure equations (2.4) and (2.5) of the SEM in the MSA can also be separated into three groups:

(a) The hard sphere closures:

$$h^{\text{hs}}_{ii} = -1 + \lambda L \delta(r-L)/24, \quad 0<r<\sigma \quad (2.13\text{a})$$

$$h^{\text{hs}}_{id} = -1, \quad 0<r<\sigma \quad (2.13\text{b})$$

$$h^{\text{hs}}_{dd} = -1, \quad 0<r<\sigma \quad (2.13\text{c})$$

$$c^{\text{hs}}_{ii} = c^{\text{hs}}_{id} = c^{\text{hs}}_{dd} = 0, \quad r>\sigma. \quad (2.13\text{d})$$

(b) The ion–ion, ion–dipole and part of the dipole–dipole closures

$$h^{000} = -\lambda L \delta(r-L)/(24 z_+^2), \quad 0<r<\sigma \quad (2.14\text{a})$$

$$h^{011} = h^{110} = h^{112} = h^{+dd} = 0, \quad 0<r<\sigma \quad (2.14\text{b})$$

$$c^{000} = -\beta e^2/r, \quad r>\sigma \quad (2.14\text{c})$$

$$c^{011} = \beta e\mu/r^2 \quad r>\sigma \quad (2.14\text{d})$$

$$c^{110} = 0 \quad r>\sigma \quad (2.14\text{e})$$

$$c^{112} = \beta\mu^2/r^3 \quad r>\sigma \quad (2.14\text{f})$$

$$c^{+dd} = 2\beta\mu^2/r^3, \quad r>\sigma. \quad (2.14\text{g})$$

(c) The remainder of the dipole–dipole closures:

$$h^{-dd} = 0, \quad 0<r<\sigma \quad (2.15\text{a})$$

$$c^{-dd} = -\beta\mu^2/r^3, \quad r>\sigma. \quad (2.15\text{b})$$

At this point we see that the hard sphere part shown in Eqs. (2.7) and (2.8c) with the closures given in Eqs. (2.13) are exactly the same as that of the SEM with hard sphere solvent which we have solved earlier.[5] The dipolar part Eq. (2.12) with the closure given in Eq. (2.15) is the same as that of the pure dipole case and its solution is a well known result obtained by Wertheim.[14] Therefore, we only need to solve the electrostatic part of the interactions shown in Eq. (2.11) with the closures displayed in Eq. (2.14).

B. Solution of the SEM in the PY/MS and HNC/MS approximations

The solution of the OZ equations in the mean spherical approximation for the ion–dipole system has been discussed by Adelman and Deutch,[7] Blum,[8–10] and by Høye and Lomba.[12] Adelman and Deutch used the method of Laplace transforms to solve the OZ equation while Baxter's adaptation of Wiener–Hopf factorization was employed by Blum[8–10] and Høye *et al.*[12] In the following we use Baxter's method to solve the set of OZ equation in the SEM. Defining the three-dimensional Fourier transform

$$f(k) = \int e^{i\mathbf{k}\cdot\mathbf{r}} f(r)\,d\mathbf{r}, \quad (2.16)$$

Eqs. (2.6) can be written in Fourier space as

$$f_{ij}(k) = f^{\text{hs}}_{ii}(k) + z_i z_j f^{000}(k), \quad (2.17\text{a})$$

$$f_{id}(k) = f^{\text{hs}}_{id}(k) + z_i f^{011}(k)\phi^{011}(k), \quad (2.17\text{b})$$

$$f_{di}(k) = f^{\text{hs}}_{id}(k) - z_i f^{011}(k)\phi^{011}(k), \quad (2.17\text{c})$$

$$f_{dd}(k) = f^{\text{hs}}_{dd}(k) + f^{110}(k)\phi^{110}(k) + f^{112}(k)\phi^{112}(k), \quad (2.17\text{d})$$

where

$$f^{000}(k) = 4\pi \int_0^\infty r^2 j_0(kr) f^{000}(r)\,dr, \quad (2.18\text{a})$$

$$f^{011}(k) = 4\pi i \int_0^\infty r^2 j_1(kr) f^{011}(r)\,dr, \quad (2.18\text{b})$$

$$f^{110}(k) = 4\pi \int_0^\infty r^2 j_0(kr) f^{110}(r)\,dr, \quad (2.18\text{c})$$

$$f^{112}(k) = -4\pi \int_0^\infty r^2 j_2(kr) f^{112}(r)\,dr. \quad (2.18\text{d})$$

Here $j_i(kr)$ is spherical Bessel function of ith order and the Fourier transforms of the angular functions are given by

$$\phi^{001}(k) = \hat{\mathbf{s}}\cdot\hat{\mathbf{k}}, \quad (2.19\text{a})$$

$$\phi^{110}(k) = \hat{\mathbf{s}}_1\cdot\hat{\mathbf{s}}_2, \quad (2.19\text{b})$$

$$\phi^{112}(k) = 3(\hat{\mathbf{s}}_1\cdot\hat{\mathbf{k}})(\hat{\mathbf{s}}_2\cdot\hat{\mathbf{k}}) - \hat{\mathbf{s}}_1\cdot\hat{\mathbf{s}}_2, \quad (2.19\text{c})$$

in which all the hatted functions are unit vectors. In order to use Baxter's factorization method,[15] we have to transform the three dimensional Fourier transform back into one dimension, i.e., define

$$F_{ij}(r) = [(\rho_i\rho_j)^{1/2}/2\pi] \int e^{-ikr} f^{lmn}(k)\,dk. \quad (2.20)$$

The one-dimensional correlation functions in r space can be written as

$$F_{ii}(r) = 2\pi\rho_0 \int_r^\infty r' p_0(r/r') f^{000}(r')\,dr', \quad (2.21\text{a})$$

$$F_{id}(r) = -F_{di}(r) = 2\pi(\rho_d\rho_0/3) \times \int_r^\infty r' p_1(r/r') f^{011}(r')\,dr', \quad (2.21\text{b})$$

$$F_{dd}(r) = (2\pi\rho_d/3) \int_r^\infty r' p_2(r/r') f^{112}(r')\,dr', \quad (2.21\text{c})$$

$$F'_{dd}(r) = (2\pi\rho_d/3) \int_r^\infty r' p_0(r/r') f^{110}(r')\,dr', \quad (2.21\text{d})$$

$$F^+_{dd}(r) = F'_{dd} + 2F_{dd} = (2\pi\rho_d/3) \int_r^\infty r' [p_0(r/r') f^{110}(r') + 2p_2(r/r') f^{112}(r')]\,dr', \quad (2.21\text{e})$$

where $p_i(r/r')$ is the Legendre polynomial of the ith order: $p_0(x) = 1, p_1(x) = x, p_2(x) = 0.5(3x^2 - 1)$. These F functions correspond to Baxter's J and S functions. If $f^{lmn}(r) = h^{lmn}(r)$, then $F_{ij}(r) = J_{ij}(r)$ and if $f^{lmn}(r) = c^{lmn}(r)$, then $F_{ij}(r) = S_{ij}(r)$.

We can also put the set of Eqs. (2.11) into Fourier space:

$$h^{000}(k)=c^{000}(k)+\rho_0c^{000}(k)h^{000}(k)-(\rho_d/3)c^{011}(k)h^{011}(k), \tag{2.22a}$$

$$h^{011}(k)=c^{011}(k)+\rho_0c^{000}(k)h^{011}(k)+(\rho_d/3)c^{011}(k)h^{+dd}(k), \tag{2.22b}$$

$$=c^{011}(k)+\rho_0c^{011}(k)h^{000}(k)+(\rho_d/3)c^{+dd}(k)h^{011}(k), \tag{2.22c}$$

$$h^{+dd}(k)=c^{+dd}(k)-\rho_0c^{011}(k)h^{011}(k)+(\rho_d/3)c^{+dd}(k)h^{+dd}(k). \tag{2.22d}$$

These equations have been given earlier by Chan *et al.*[13] Changing the set of equations back into r space by one-dimensional inverse Fourier transformations and using Eq. (2.21), we have

$$J_{ii}(r)=S_{ii}(r)+S_{ii}(r)*J_{ii}(r)+S_{id}(r)*J_{di}(r), \tag{2.23a}$$

$$J_{id}(r)=S_{id}(r)+S_{ii}(r)*J_{id}(r)+S_{id}(r)*J^{+}_{dd}(r), \tag{2.23b}$$

$$J_{di}(r)=S_{di}(r)+S_{di}(r)*J_{ii}(r)+S^{+}_{dd}(r)*J_{di}(r), \tag{2.23c}$$

$$J^{+}_{dd}(r)=S_{dd}(r)+S_{di}(r)*J_{id}(r)+S^{+}_{dd}(r)*J^{+}_{dd}(r), \tag{2.23d}$$

which can be represented collectively in k space by

$$J(k)=S(k)+S(k)J(k), \tag{2.23e}$$

where $J(k)$ and $S(k)$ are 2×2 matrices. These equations are similar to Baxter's original form for mixtures of molecules with central forces.[15] His factorization implies that

$$\delta_{ij}-S_{ij}(k)=\sum_l Q_{il}(k)Q_{jl}(-k), \tag{2.24}$$

where the Fourier transform of the Q function is defined as

$$Q_{ij}(k)=\delta_{ij}-\int_0^\infty Q_{ij}(r)e^{ikr}dr. \tag{2.25}$$

It follows from Eqs. (2.23) and (2.24) that

$$S_{ij}(r)=Q_{ij}(r)-\sum_k\int_0^\infty Q_{ki}(r+t)Q_{kj}(t)dt. \tag{2.26a}$$

Similarly from Eqs. (2.23), (2.24), and (2.25), one finds that

$$J_{ij}(r)=Q_{ij}(r)+\sum_k\int_0^\infty Q_{ik}(t)J_{kj}(|r-t|)dt. \tag{2.26b}$$

In the remainder of this paper, we will assume a univalent electrolyte ($z_+=-z_-=1$) with stickiness between oppositely charged ions at a distance $L=\sigma-$, which means the bonding takes place only just inside the contact distance of σ. Before we give the Q functions explicitly, let us determine the functions $J_{ij}(r)$ for $r<\sigma$ and $S_{ij}(r)$ for $r>\sigma$. Combining Eq. (2.21) with the closure of (2.14), we see that $J_{ij}(r)$ is a polynomial of r in the range $r<\sigma$.

$$J_{ii}(r)=2\pi\rho_0\int_\sigma^\infty rh^{000}(r)dr-\pi\rho_0\lambda\sigma^2/12=b_0-\nu/\sigma, \tag{2.7a}$$

$$J_{id}(r)=-J_{di}(r)=2\pi(\rho_d\rho_0/3)^{1/2}r\int_\sigma^\infty h^{011}(r)dr=b_1r, \tag{2.27b}$$

$$J^{+}_{dd}(r)=(2\pi\rho_d/3)\left\{\int_\sigma^\infty rh^{011}(r)dr-\int_\sigma^\infty rh^{112}(r)dr\right\}+2\pi\rho_dr^2\int_\sigma^\infty h^{112}(r)r^{-1}dr=b'_0r+b_2r^2. \tag{2.27c}$$

The constants are

$$b_0=2\pi\rho_0\int_\sigma^\infty rh^{000}(r)dr, \tag{2.28a}$$

$$b_1=2\pi(\rho_d\rho_0/3)^{1/2}\int_\sigma^\infty h^{011}(r)dr, \tag{2.28b}$$

$$b'_0(r)=(2\pi\rho_d/3)\int_\sigma^\infty r[h^{011}(r)-h^{112}(r)]dr, \tag{2.28c}$$

$$b_2=2\pi\rho_d\int_\sigma^\infty h^{112}(r)r^{-1}dr, \tag{2.28d}$$

where

$$\nu=\eta_0\lambda/2, \tag{2.28e}$$

$$\eta_0=\pi\rho_0\sigma^3/6. \tag{2.28f}$$

and the electroneutrality condition implies that

$$\int_0^\infty J_{ii}(t)dt=-1/2 \tag{2.28g}$$

Here, in order to make an easy comparison with the known facts, we have used the same notation as Blum[8,9] and Hoye and Lomba[12] for the constants b_i which play an important role in determining the excess internal energy and the same definition for ν as that in our earlier paper. We can calculate $S_{ij}(r)$ for $r>\sigma$ in a similar way by combining Eqs. (2.21) and Eqs. (2.14c)–(2.14f) when it is found that

$$S_{ii}(r)=-d_0^2e^{-zr}/2z,\quad r>\sigma \tag{2.29a}$$

$$S_{id}(r)=-S_{di}(r)=d_0d_2e^{-zr}/2,\quad r>\sigma \tag{2.29b}$$

$$S^{+}_{dd}(r)=0,\quad r>\sigma \tag{2.29c}$$

with the definition

$$d_0^2=4\pi\beta\rho e^2, \tag{2.30}$$

$$d_2^2=4\pi\beta\rho_d\mu^2/3. \tag{2.31}$$

In deriving Eq. (2.29), a screening function e^{-zr} has been attached to $c_{ii}(r)$ and $c_{id}(r)$. Actually, Eqs. (2.29) are the same for ion–dipole mixtures because, in the MSA, the stickiness only appears at contact. It is well known that Baxter's Q functions are second-order polynomials of r, for $r<\sigma$, in the mean spherical approximation, and we expect it to keep the same form when we add the stickiness. Therefore we write

$$Q_{ij}(r)=\delta_{ij}Q^{\lambda}_{ij}+Q^{0}_{ij}(r)-A_{ij}e^{-zr}, \tag{2.32}$$

$$Q^{0}_{ij}(r)=(r-\sigma)Q'_{ij}+(r-\sigma)^2Q''_{ij}/2,\quad r<\sigma \tag{2.33a}$$

$$=0,\quad r>\sigma \tag{2.33b}$$

where the first term in Eq. (2.32) comes from the stickiness, $Q^{0}_{ij}(r)$ is defined in Eq. (2.33) and the coefficients Q'_{ij}, Q''_{ij}, and A_{ij} are as yet undetermined. Hereafter we will use reduced units by putting $\sigma=1$. Since there is no stickiness assumed between the ions and dipoles or between dipoles, $Q^{\lambda}_{dd} = Q^{\lambda}_{id} = 0$. To determine the sticky term Q^{λ}_{ii}, we have to make use of the fact

$$J_{ii}(1-) = J_{ii}(1+) - \nu = b_0 \tag{2.34}$$

which can be seen from Eq. (2.27a). Substituting this in Eq. (2.23a) for $J_{ii}(r)$ and comparing it to the case without stickiness, one finds that the sticky term Q^{λ}_{ii} for the ions can be written as

$$Q^{\lambda}_{ii} = -\pi\rho_0\lambda/12 = -\nu, \tag{2.35}$$

where the last equality shows that ν is the negative of Q^{λ}_{ii}. From the asymptotic form of the $S_{ij}(r)$ in Eq. (2.29) and $Q_{ij}(r)$ in Eq. (2.32), we can get the Fourier transforms $S_{ij}(k)$ and $Q_{ij}(k)$, substitute them into Eq. (2.24) and put $k=0$, when the following set of equations is obtained:

$$a_1^2 + a_2^2 = d_0^2, \tag{2.36a}$$

$$-a_1K_{di} + a_2(1-K_{dd}) = -d_0d_2, \tag{2.36b}$$

$$(1-K_{dd})^2 + K^2_{di} = y_1 + d_2 \tag{2.36c}$$

with

$$a_1 = A_{ii}, \tag{2.37a}$$

$$a_2 = A_{id}, \tag{2.37b}$$

$$K_{ij} = \int_0^\infty Q^0_{ij}(r)dr, \tag{2.37c}$$

$$y_1 = (1-b_2/6)/(1+b_2/12)^2, \tag{2.37d}$$

where we have used the fact that $A_{di} = A_{dd} = 0$, which will become clear later. Our K_{dd} and K_{di} correspond to Blum's K_{11} and K_{10}. Substituting the Q functions defined in Eq. (2.32) into Eq. (2.26b) and taking the limit $z=0$, leads to the following set of equations:

$$J_{ii}(r) = Q^0_{ii}(r) - A_{ii} - \nu + \sum_k \int_0^\infty J_{ik}(r-t)Q^0_{ki}(t)dt - \sum_k \int_0^r J_{ik}(r-t)A_{ki}dt - \sum_k \int_0^\infty J_{ik}(-t)A_{ki}dt, \tag{2.38a}$$

$$J_{id}(r) = Q^0_{id}(r) - A_{id} + \sum_k \int_0^\infty J_{ik}(r-t)Q^0_{kd}(t)dt - \sum_k \int_0^r J_{ik}(r-t)A_{kd}dt - \sum_k \int_0^\infty J_{ik}(-t)A_{kd}dt, \tag{2.38b}$$

$$J_{dd}(r) = Q^0_{dd}(r) - A_{dd} + \sum_k \int_0^\infty J_{dk}(r-t)Q^0_{kd}(t)dt - \sum_k \int_0^r J_{dk}(r-t)A_{kd}dt - \sum_k \int_0^\infty J_{dk}(-t)A_{kd}dt, \tag{2.38c}$$

$$J_{di}(r) = -J_{id}(r), \tag{2.38d}$$

where the summations range over k from i (ion) to d (dipole). Substituting Eq. (2.33) for $Q^0_{ij}(r)$ and combining Eqs. (2.38) and (2.27), a set of algebraic equations is realized. After much algebra, the constants A_{ij} in Baxter's Q function and K_{ij} defined in Eq. (2.37c) can be expressed in terms of b_0, b_1, b_2, and λ. The final results are

$$a_1 = A_{ii} = [b_0\beta_6^2 - b_1^2\beta_{24}/3 + \nu\Delta(1+b_0)]/D_1, \tag{2.39a}$$

$$a_2 = A_{id} = b_1[b_0\beta_3/2 + 1 + b_2/12 + b_1^2/12]D_1, \tag{2.39b}$$

$$A_{di} = A_{dd} = 0, \tag{2.39c}$$

$$K_{ii} = -Q'_{ii}/2, \tag{2.39d}$$

$$K_{id} = -Q'_{id}/2, \tag{2.39e}$$

$$K_{di} = b_1\{1 + a_1\Lambda\}/2\Delta, \tag{2.39f}$$

$$1 - K_{dd} = [2\beta_3 - a_2b_1\Lambda]/(2\Delta), \tag{2.39g}$$

where

$$D_1 = -[(1+b_0)\beta_6 - b_1^2/12]^2/2, \tag{2.40a}$$

$$\Delta = \beta_6^2 + b_1^2/4, \tag{2.40b}$$

$$\Lambda = b_0/2 + 2\beta_{24}/3, \tag{2.40c}$$

$$\beta_3 = 1 + b_2/3; \quad \beta_6 = 1 - b_2/6, \tag{2.40d}$$

$$\beta_{24} = 1 - b_2/24; \quad \beta_{12} = 1 + b_2/12 \tag{2.40e}$$

and we have followed Blum's notation[8–11] as far as possible. Meanwhile, we find that the coefficients of the Baxter's function in Eq. (2.33) have the same form when there is no stickiness, and agree with those given by Høye and Lomba,[12] except for some small disagreements which may be due to typographical or other errors:

$$Q'_{ii} = [a_1(b_0\Delta - b_1^2\Lambda/2) - b_1^2/2]/\Delta, \tag{2.41a}$$

$$Q'_{id} = [a_2(b_0\Delta - b_1^2\Lambda/2) - b_1\beta_3]/\Delta, \tag{2.41b}$$

$$Q'_{di} = -b_1[(1+a_1\Lambda)\beta_3 + a_1\Delta/3]/\Delta, \tag{2.41c}$$

$$Q'_{dd} = -2 + 2\beta_3^2/\Delta - a_2[b_1\Delta/3 + b_1\Lambda\beta_3]/\Delta, \tag{2.41d}$$

$$Q''_{ii} = Q''_{id} = 0, \tag{2.41e}$$

$$Q''_{di} = -b_1b_2(1+a_1\Lambda)/\Delta - a_1b_1, \tag{2.41f}$$

$$Q''_{dd} = [2b_2\beta_3 - a_2b_1b_2\Lambda]/\Delta - a_2b_1. \tag{2.41g}$$

Here we pause to check the limiting condition ($\rho_d \to 0$) and to make contact with our earlier results.[3,5] The definition of $h^{000}(r)$ in Eq. (2.6a) can be written as

$$h^{000}(r) = [h_{++}(r) - h_{+-}(r)]/2 \tag{2.42}$$

which is the negative of the difference function $h_D(r)$ appearing in our earlier paper.[1–5] When the density of the solvent goes to zero ($\rho_d \to 0$), we see from Eqs. (2.36), (2.39), and (2.28) that $a_2 \to 0$, $b_1 \to 0$, $b_2 \to 0$, $b_0 \to -2\pi\rho_0 J_D$ and $a_1 \to \kappa$ where $\kappa = d_0$ is Debye screening constant and J_D is defined by

$$J_D = \int_r^\infty h_D(r)rdr. \tag{2.43a}$$

It follows from Eq. (2.39a) that

$$J_D = \{(1+\kappa+\nu) - [(1+\nu)^2 + 2\kappa]^{1/2}\}/\kappa. \tag{2.43b}$$

This is the result given by Rasaiah and Lee[3] for the SEM in the continuum solvent. Also it can be seen that $Q'_{ii} \to -2\pi\rho_0\kappa J_D$ and $Q^0_{ii}(r) \to 2\pi\rho_0 q^0_D(r)$ for the SEM in a continuum solvent.[5] From the above solutions, we will see that all of the equilibrium properties can be expressed in terms of four parameters b_0, b_1, b_2, and ν or λ, which can be derived from Eqs. (2.36a)–(2.36c) and the following relation for λ.

So far we have not considered the approximation for stickiness. As discussed elsewhere,[1,4,5] the dissociation parameter λ is related to the parameter τ introduced by Baxter in his study of sticky hard spheres by

$$\lambda\tau = y_{+-}(\sigma). \tag{2.44a}$$

τ is the inverse of the sticking coefficient ζ ($\tau = 1/\zeta$) which is defined by the Mayer f function for oppositely charged ions

$$f_{+-}(r) = \zeta L\delta(r-L)/12 - 1 \quad 0<r<\sigma \tag{2.44b}$$

$$= \exp(-e_+e_-/kTr) - 1 \quad r>\sigma. \tag{2.44c}$$

In the PY/MS approximation, we have

$$\begin{aligned}\lambda\tau &= g_{+-}(\sigma^+) - c_{+-}(\sigma^+)\\ &= 1 + h^{\text{hs}}_{ii}(\sigma^+) - h^{000}(\sigma^+) - [c^{\text{hs}}_{ii}(\sigma^+) - c^{000}(\sigma^+)]\end{aligned} \tag{2.45}$$

while the HNC/MS approximation,

$$\begin{aligned}\lambda\tau &= \exp[h_{+-}(\sigma^+) - c_{+-}(\sigma^+)]\\ &= \exp\{h^{\text{hs}}_{ii}(\sigma^+) - h^{000}(\sigma^+)\\ &\quad - [c^{\text{hs}}_{ii}(\sigma^+) - c^{000}(\sigma^+)]\}.\end{aligned} \tag{2.46}$$

When the stickiness occurs at contact, as in the present case, τ can be determined from an equivalent square-well potential with the same second virial coefficient as adhesive hard spheres through the relation[1,3]

$$\tau = \sigma^3 \exp(-\epsilon_2/kT)/(12w\sigma^3 + w^3). \tag{2.47}$$

This method was first proposed by Cummings and Stell[16] in their treatment of chemical reactions of uncharged systems. Here ϵ_2 is the depth of the potential well where the binding occurs between the oppositely charged ions and w, which is the width of this well, is chosen as 0.1σ. Thus the determination of b_0, b_1, b_2 and λ reduces to the solution of four nonlinear algebraic equations.

Following Hernandez and Blum's[11] analysis of a mixture of ions and dipoles, we can set up a cubic equation for b_1^2 [see Eq. (2.50) below] with b_0, b_2 represented in the coefficients. Starting from Eqs. (2.36), (2.39), and (2.40) the following equation can be derived after some algebra

$$a_1\beta_3 + a_2b_1/2 = d_0y_1\Delta. \tag{2.48}$$

Substituting a_1 and a_2 from Eq. (2.39a) and (2.39b), we have

$$b_0\beta_3 + b_1^2/6 + \nu\beta_3(1+b_0) = y_1d_0D_1. \tag{2.49}$$

Squaring this and replacing d_0^2 with $a_1^2 + a_2^2$ we get a cubic equation

$$c_0 + c_2b_1^2 + c_4b_1^4 + c_6b_1^6 = 0, \tag{2.50}$$

where

$$\begin{aligned}c_0 = &-b_0^2\beta_3^2 + y_1b_0^2\beta_6^4 - 2\nu b_0\beta_3^2(1+b_0)\\ &+ 2\nu b_0\beta_6^4(1+b_0)y_1^2 + \nu^2(1+b_0)^2(-\beta_3^2 + y_1^2\beta_6^4),\end{aligned} \tag{2.51a}$$

$$\begin{aligned}c_2 = &\, y_1^2(1 + b_2/12 + b_0^2\beta_3^2/4) + b_0y_1^2\\ &\times\{\beta_3(1+b_2/12) - 2\beta_6^2\beta_{24} - \nu\beta_3(1+b_0)/3\\ &+ [\beta_6^2(1+b_0)^2\nu^2/2 + \beta_6^2(1+b_0)\nu b_0]y_1^2\} - b_0\beta_3,\end{aligned} \tag{2.51b}$$

$$\begin{aligned}c_4 = &\{y_1^2[6(1+b_2/12) + 3b_0\beta_3 + 4\beta_{24}^2] - 1\}/36\\ &+ \nu^2(1+b_0)^2y_1^2/16,\end{aligned} \tag{2.51c}$$

$$c_6 = y_1^2/144. \tag{2.51d}$$

It is easily verified that this equation reduces to Hernandez and Blum's result[11] when the stickiness vanishes ($\lambda = 0$). The solution of this equation requires knowledge of b_0 and b_2, which comes from the solution of Eq. (2.36).

C. The correlation functions

In deriving the above results, we mainly employed the factored equations for $J_{ij}(r)$ in Eq. (2.26b). From Eq. (2.26a), the direct correlation functions can be calculated analytically for $r<\sigma$ since the Q functions are known. Equations (2.26a) can be put into the derivative form by direct differentiation with respect to r

$$\begin{aligned}S'_{ii}(r) = &\, Q^{0\prime}_{ii}(r) - a_1Q^0_{ii}(r) - a_2Q^0_{id}(r) + (a_1^2 + a_2^2)/2\\ &- \int_r^\infty Q^{0\prime}_{ii}(t)[Q^0_{ii}(t-r) - \nu]dt\\ &- \int_r^\infty Q^{0\prime}_{id}(t)Q^0_{id}(t-r)dt + a_1\nu\end{aligned} \tag{2.52a}$$

$$\begin{aligned}S'_{id}(r) = &\, Q^{0\prime}_{id}(r) - \int_r^\infty Q'_{ii}(t)Q_{di}(t-r)dt\\ &- \int_r^\infty Q'_{id}(t)Q^0_{dd}(t-r)dt,\end{aligned} \tag{2.52b}$$

$$\begin{aligned}S'_{dd}(r) = &\, Q^{0\prime}_{dd}(r) - \int_r^\infty Q^{0\prime}_{di}(t)Q_{di}(t-r)dr\\ &- \int_r^\infty Q^{0\prime}_{dd}(t)Q^0_{dd}(t-r)dr.\end{aligned} \tag{2.52c}$$

Making use of the definition for $S_{ij}(r)$ in Eq. (2.21) and carrying out the above integrations, we have

$$\begin{aligned}C^{000}(r) = &\,(2\pi\rho_0)^{-1}[(a_1Q'_{ii} + a_2Q'_{id})\\ &+ (Q'^2_{ii} + Q'^2_{id})r/2 - \nu^2/r],\end{aligned} \tag{2.53a}$$

$$\begin{aligned}C^{011}(r) = &\,(2\pi)^{-1}(\rho_d\rho_0/3)^{-1/2}[-\nu Q'_{di} + (Q'_{ii}Q'_{di}\\ &+ Q'_{id}Q'_{dd} + \nu Q''_{di})r/2\\ &- (Q'_{ii}Q''_{di} + Q'_{id}Q''_{dd})r^2/6],\end{aligned} \tag{2.53b}$$

$$\begin{aligned}C^{+dd}(r) = &\,(2\pi\rho_d)^{-1}\{(Q'^2_{dd} + Q'^2_{di})r/2\\ &- (Q''^2_{dd} + Q''^2_{di})/24\\ &- [Q''_{dd} - (Q''^2_{dd} + Q''^2_{di})/6\\ &+ (Q'_{dd}Q''_{dd} + Q'_{di}Q''_{di})/2]\}\end{aligned} \tag{2.53c}$$

with three relations among the coefficients

$$Q'_{ii} = -[(Q'_{ii} + a_1)^2 + (Q'_{id} + a_2)^2]/2 - Q'_{ii}\nu - a_1\nu, \tag{2.54a}$$

$$\begin{aligned}Q'_{id} = &-(Q'_{ii}Q'_{di} + Q'_{id}Q'_{dd})/2\\ &+ (Q'_{ii}Q''_{di} + Q'_{id}Q''_{dd})/6,\end{aligned} \tag{2.54b}$$

$$Q''_{dd} = Q'_{dd} + [(Q''_{di}/2 - Q'_{di})^2 - (Q''_{dd}/2 - Q'_{dd})^2]/2. \tag{2.54c}$$

Again it can be seen that when we take the limit $\rho_d \to 0$, we have

$$Q'_{ii} \to -2\pi\rho_0 \kappa J_D, \tag{2.55a}$$

$$-rc^{000}(r) \to \kappa^2 J_D r(1 - \pi\rho_0 J_D r) + \lambda\nu/24 \tag{2.55b}$$

which is the result for $-rc_D(r) \equiv -r[c_{+-}(r) - c_{++}(r)]/2$ of the SEM in a continuum solvent.[3] Also when we take the limit $\lambda = 0$, i.e., on turning off the stickiness, Eqs. (2.53) and (2.54) reduce to the equations for ion dipole mixtures given by Vericat and Blum.[10] With the help of Eq. (2.21), the contact value of the correlation functions can be calculated directly from Eqs. (2.38). The results are

$$-2\pi\rho_0 h^{000}(1+) = -\nu(\nu + Q'_{ii}) - a_1(b_0 + \nu) \tag{2.56a}$$

$$-2\pi(\rho_0\rho_d/3)^{1/2} h^{011}(1+) = -\nu Q'_{id} - a_2(b_0 + \nu) \tag{2.56b}$$

$$-2\pi(\rho_d/3) h^{+dd}(1+) = a_2 b_1 \tag{2.56c}$$

Here again Eq. (2.56a) reduces to our earlier result when the density of the solvent ρ_d goes to zero.[5]

III. THERMODYNAMICS

As discussed elsewhere,[1–5] the number of associated ion pairs in the SEM is directly related to the association constant λ and the density of the electrolyte, which can be expressed as

$$\langle N \rangle = \eta_0 \lambda \tag{3.1}$$

Because we have added the stickiness just inside the hard core of oppositely charged ions at contact and used the MSA outside the hard cores, the excess interaction energy per unit volume can be written as[3,8,9,12]

$$E^{\text{ex}}/kT = [d_0^2 b_0 - 2d_0 d_2 b_1 - 2d_2^2 b_2]/4\pi - \rho_0 \langle N \rangle \beta\epsilon_2/2. \tag{3.2}$$

Here the last term is the contribution from the stickiness, while the others have a similar form in the absence of stickiness.[7–9,12] If we are interested in the excess internal energy due to the interaction between the ions, we have

$$E_i^{\text{ex}}/\rho_0 kT = d_0^2 b_0/24\eta_0 - \langle N \rangle \beta\epsilon_2/2 \tag{3.3}$$

here E_i^{ex} is the ion–ion excess interaction energy per unit volume. If we choose the pure dipolar liquid as the reference system, Eq. (3.2) can be written as

$$\Delta E^{\text{ex}} = \rho_0 e^2 b_0 - \rho_0 \langle N \rangle \epsilon_2/2 - 2(\rho_0\rho_d/3)^{1/2} e\mu b_1 - 2\rho_d \mu^2 [b_2 - b_2(\rho = 0)]/3. \tag{3.4}$$

As $\rho = 0$, $b_1 = 0$ and b_2 is related to the dielectric constant of the dipolar solvent. As discussed by Blum,[8] the excess chemical potential due to the electrical interactions in the MSA can be expressed as

$$\mu^{\text{ex}} - \mu^{\text{ex},0} = (1/\rho_0)[\Delta E^{\text{ex}}] \tag{3.5a}$$

and the mean activity coefficient of the electrolyte is given by[17]

$$kT \ln \gamma_\pm = kT \ln \gamma^0 + \rho_0 \Delta E^{\text{ex}}, \tag{3.5b}$$

where γ^0 is the activity coefficient of the uncharged solute.

From the discussion in Sec. II, it follows that to get the complete solution to this problem, we have to solve the set of nonlinear algebraic equations given in Eqs. (2.36) and (2.45) or (2.46) for b_0, b_1, b_2 and λ. Even though they could be solved on a computer, they are still too complicated because the nonanalytic form of the solutions obscures their relationship to the thermodynamic properties. So at first, we wish to see what happens analytically in the limit of infinite dilution of the ions. When ρ_0 is very small, $b_0^2 \ll 0$ and $b_1^4 \ll b_1^2$. Making use of these facts and substituting D_1 defined in Eq. (2.40a) into Eq. (2.49), we have

$$b_0[-\beta_3 - y_1 d_0 \beta_6^2 + y_1 d_0 \beta_6 b_1^2/12 - \nu\beta_3] = y_1 d_0 \beta_6^2/2 + b_1^2/6 - y_1 d_0 \beta_6 b_1^2/12 + \nu\beta_3. \tag{3.6}$$

From the solution of Eq. (2.12), the dielectric constant ϵ determined by Wertheim in the MSA can be expressed as[14]

$$\epsilon = q_+/q_- = (1 + 4\xi)^2 (1 + \xi)^4 (1 - 2\xi)^{-6} = \beta_3^2 \beta_{12}^4 \beta_6^{-6}, \tag{3.7}$$

where we have used

$$\xi = \eta_d \int_\sigma^\infty h^{112}(t) t^{-1} dt = b_2/12, \tag{3.8a}$$

$$q_- = \beta_6^2 \beta_{12}^{-4}, \tag{3.8b}$$

$$q_+ = \beta_3^2 \beta_6^{-4}. \tag{3.8c}$$

Using Eqs. (2.37d) and (3.7) in Eq. (3.6) and expanding the denominator leads to the following expression for b_0:

$$b_0 = -(\kappa + 2\nu)/[2(1 + \kappa + \nu)] + b_1^2 \times [2\beta_6^{-1} - 4\beta_3^{-1} - \kappa\beta_6^{-1}/(1 + \kappa + \nu)]/[24(1 + \kappa + \nu)]. \tag{3.9}$$

Here κ is the Debye screening constant defined by $\kappa = d_0/\epsilon^{1/2}$ and ϵ is dielectric constant in the MSA. At low concentrations, near the infinite dilution limit, the ion–ion interaction energy can be expressed as

$$\begin{aligned} E_{ii}^{\text{ex}} &= \rho_0 e^2 b_0 - \rho_0 \langle N \rangle \epsilon_2/2 \\ &= -\rho_0 e^2 (\kappa + 2\nu)/[2(1 + \kappa + \nu)] + b_1^2 \\ &\quad \times [2\beta_6^{-1} - 4\beta_3^{-1} - \kappa\beta_6^{-1}/(1 + \kappa + \nu)]/ \\ &\quad [24(1 + \kappa + \nu)] - \rho_0 \langle N \rangle \epsilon_2/2. \end{aligned} \tag{3.10}$$

We will next discuss the calculation of the solvation energy, which is defined as the interaction energy of a single ion with solvent molecules around it, and can be expressed in the following form

$$\begin{aligned} E_i &= \rho_d \int u_{id}(\mathbf{r},\omega) g_{id}(\mathbf{r},\omega) d\mathbf{r} d\omega \\ &= -(4\pi/3)\rho_d z_i^2 e\mu \int_\sigma^\infty h^{011}(r) dr \\ &= -2(\rho_d/3\rho_0)^{1/2} z_i^2 e\mu b_1 \end{aligned} \tag{3.11}$$

which relates the solvation energy to b_1. This definition is identical to Chan *et al.*'s E_{Born}.[13] At $r = 1$, Eq. (2.38b) can be written as

$$b_1 = -a_2/2 - a_2 b_0 + b_0 \int_0^1 Q_{id}^0(t)dt + \int_0^1 J_{id}(1-t)Q_{dd}^0(t)dt \quad (3.12)$$

which enables the solvation energy at finite ion concentration to be calculated in the SEM.

In the following we confirm the expectation that the solvation energy at infinite dilution in the SEM is identical to the solvation energy of free ions since the electrolyte should be completely dissociated in this limit. As the density of the electrolyte goes to zero, $b_0 \to 0$, $K_{di} \to 0$, which can be seen from Eqs. (2.28a) and (2.39f). Now Eqs. (2.36b) and (2.36c) can be written as

$$a_2(1-K_{dd}) = -d_0 d_2 = -4\pi\beta\mu e(\rho_d\rho_0/3)^{1/2}, \quad (3.13)$$

$$(1-K_{dd})^2 = y_1^2 + d_2^2. \quad (3.14)$$

From Wertheim's solution for the pure dipolar system,[14] we have

$$q_+ - q_- = \beta_3^2\beta_6^{-4} - \beta_6^2\beta_{12}^{-4} = -4\pi\beta\mu^2\rho_d/3 = d_2^2. \quad (3.15a)$$

Substituting Eqs. (3.15a) and (2.37d) in Eq. (3.14) leads to

$$(1-k_{dd})^2 = q_+ \quad (3.15b)$$

and Eq. (3.13) becomes

$$a_2 = -4\pi\beta\mu e(\rho_d\rho_0/3q_+)^{1/2}. \quad (3.16)$$

Now substituting Eq. (3.16) back into Eq. (2.36a)

$$\begin{aligned} a_1 &= [4_\pi\beta\rho_0 e - (4\pi\beta\mu e)^2\rho_d\rho_0/3q_+]^{1/2} \\ &= [4\pi\beta\rho_0 e^2 q_-/q_+]^{1/2} = [4\pi\beta\rho_0 e^2/\epsilon]^{1/2} = \kappa, \end{aligned} \quad (3.17)$$

where κ is defined by $\kappa = d_0/\epsilon^{1/2}$ and ϵ is Wertheim's dielectric constant. From here we can see that a_1 also goes to zero as $\rho_0 \to 0$. Now Eq. (3.12) can be put into the following form

$$b_1(1-M) = -a_2/2, \quad (3.18)$$

where M is defined by

$$M = \int_0^1 (1-t)Q_{dd}^0(t)dt. \quad (3.19a)$$

At infinite dilution $Q_{dd}^0(t)$ can be expressed analytically as[13,19]

$$Q_{dd}^0 = 24\xi\,[\,\beta_3\beta_6^{-2}(r^2-1) - 3\xi\beta_6^{-2}(r-1)\,], \quad (3.19b)$$

where ξ is given by Eq. (3.8a). Integrating Eq. (3.19a) with the help of Eqs. (3.19b) leads to

$$M = 1 - q_+^{1/2} + 3\xi/(1-2\xi)^2. \quad (3.20)$$

Combining Eqs. (3.20), (3.16), and (3.18), the solvation energy of a single ion immersed in a infinitely dilute solution can be written as

$$E_i = -e^2[(1-\epsilon^{-1})[1 - 3\xi q_+^{-1/2}(1-2\xi)^{-2}]^{-1}. \quad (3.21)$$

This is the result given by Chan *et al.*[13] in their discussion of the Born energy of free ions at infinite dilution. If the electrolyte has a finite concentration, however, Eq. (3.11) is expected to give a more accurate result. We will compare this with Eq. (3.21) in Sec. IV.

IV. RESULTS AND DISCUSSION

The equilibrium properties are determined by four functions b_0, b_1, b_2, and λ which are related by four nonlinear equations as indicated earlier in Sec. II. The problem therefore reduces to solving these Eqs. (2.36) and (2.45) or (2.46). To do this we need the contact value of $h_{ii}^{\text{hs}}(1+)$, which can be written as[5]

$$h_{ii}^{\text{hs}}(1+) = -1 + (2+\eta_0+\eta_d-2\mu)/[2(1-\eta_0)^2] + \nu\lambda/24. \quad (4.1)$$

τ is determined from Eq. (2.47) and ϵ_2 is chosen as the electrostatic interaction energy at the contact between the positive and negative ions. In all the following calculations, we assume the reduced density of the dipolar solvant $\eta_d = 0.37$, the dipole moment of the solvent $\mu = 1.85$ D, the temperature $T = 298.15$ K and the diameter of the particles $\sigma = 2.76$ Å. The dielectric constant of the vacuum background is taken to be unity. We also assume that the electrolyte has charges $+1$ and -1, respectively, on the positive and negative ions. If the PY/MS approximation is used, a negative solution for λ is obtained, which is unrealistic and similar to what was found earlier[1–5] in the SEM and a hard sphere or continuum solvent. Therefore all the results given in the following discussion are for the HNC/MS approximation which leads to positive value of λ.

Figures 1 and 2 are the plots of the association parameter λ and the average ion association number $\langle N \rangle$ versus the

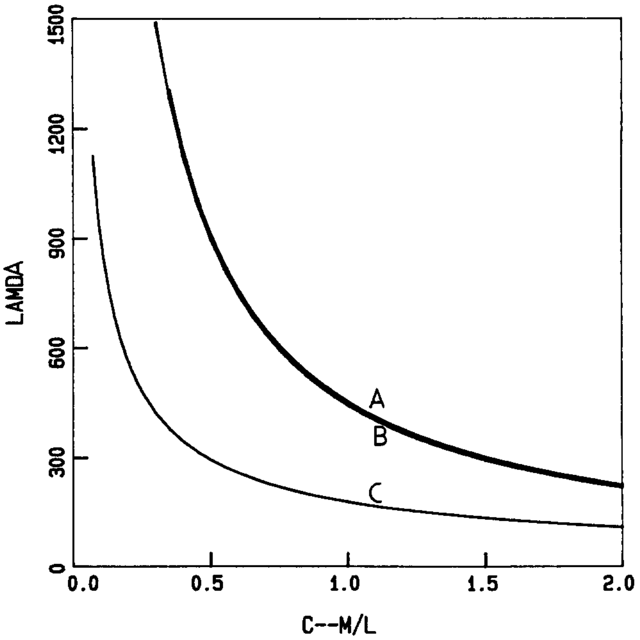

FIG. 1. The association number λ plotted as a function of the concentration of a 1-1 electrolyte in the SEM with $\sigma = 2.7$ A, $T = 298.15$ K, $\epsilon_2 = 200.3kT$. Curve A is for the electrolyte in a hard sphere solvent of reduced density $\eta_s = 0.37$, curves B and C are the corresponding results in a continuum solvent and a dipolar solvent, respectively. The dipolar solvent density is the same as the density of the hard sphere solvent.

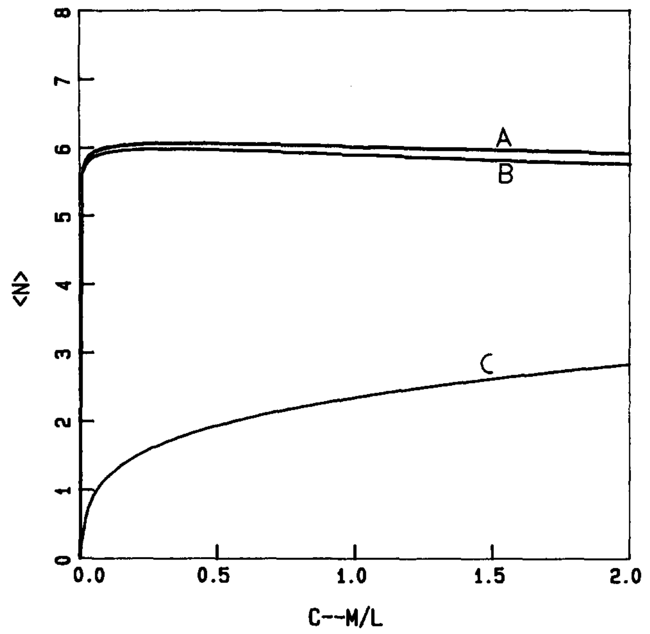

FIG. 2. The average association number $\langle N \rangle$ of the oppositely charged ions plotted as a function of the electrolyte concentration. Curve A is the result of the SEM in a hard sphere solvent, curves B and C are the corresponding results in a continuum solvent and a dipolar solvent, respectively. See caption of Fig. 1 for the details of the electrolyte parameters.

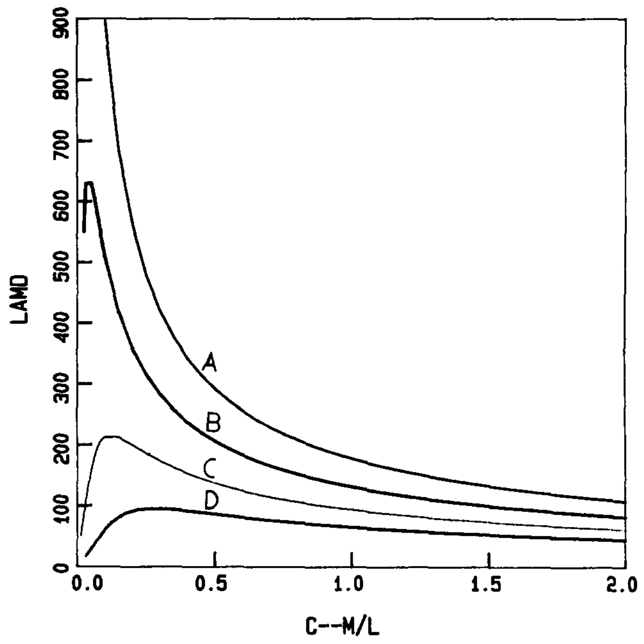

FIG. 3. The change of the association parameter λ with the electrolyte concentration and the model parameter ϵ_2. A: $\epsilon_2 = 200.3kT$, B: $\epsilon_2 = 198.3kT$, C: $\epsilon_2 = 196.3\ kT$,D: $\epsilon_2 = 194.0kT$. See caption of Fig. for the other parameters.

concentration of the electrolyte. To make a comparison, we calculated λ for three different systems using the same model parameter τ for stickiness. Curves A, B, and C are results of the SEM in hard sphere, continuum and dipolar solvents, respectively. We see that the hard sphere solvent has a small packign effect on the ion association, which makes λ and $\langle N \rangle$ slightly larger than in a continuum solvent while the dipolar solvent mainly has a screening effect on ion association, separating the ions one from another making λ and $\langle N \rangle$ smaller than their values in a continuum solvent. With a dielectric constant of unity it is seen that the association number $\langle N \rangle$ of the ions reaches six in both the continuum solvent (or vacuum) and the hard sphere solvent, which may be due to the formation of an octahedral or other clusters. We will not pursue this aspect of our work any further here because we wish to concentrate our efforts on the effect of a dipolar solvent on the equilibrium properties of a weak electrolyte.

To determine how the model parameter ϵ_2 influences the ion association in this solvent, we have solved the four equations (2.36) and (2.46) at different values of ϵ_2 (or τ) to determine λ and $\langle N \rangle$; the results are shown in Figs. 3 and 4. It can be seen that the extent of the ion association decreases as ϵ_2 becomes smaller, which is reasonable because ϵ_2 characterizes the extent of the sticky interaction (weak or strong) between the oppositely charged ions.

The results of b_0, b_1 and b_2 with and without stickiness are plotted in Figs. 5, 6, and 7 for $\epsilon_2 = 200.3\ kT$. The figures show that b_0 becomes more negative and b_1 less positive when stickiness is added between the positive and negative ions with the opposite being true for b_2. It is apparent from Eq. (3.2) that b_0, b_1, and b_2 are *related closely to the energies of ion–ion, ion–dipole, and dipole–dipole interactions*; the addition of stickiness to the oppositely charged ions increases the ion–ion interaction strength and decreases the ion–dipole interaction strength making b_0 more negative and b_1 less positive. Since b_2 becomes more positive when the stickiness is added to the ions this implies that the dipole–dipole interactions are enhanced concurrently. The approximation for b_0, given in Eq. (3.9), is also plotted in Fig. 5 (curves A

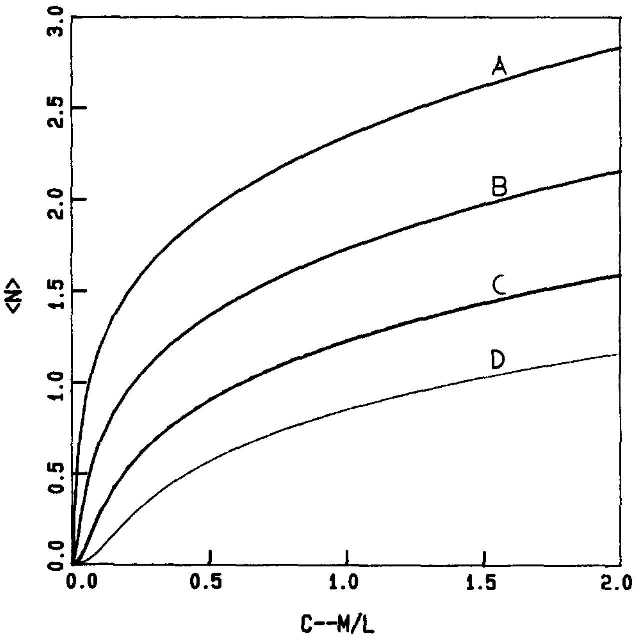

FIG. 4. The change of the average association number $\langle N \rangle$ with the electrolyte concentration and the model parameter ϵ_2. A: $\epsilon_2 = 200.3kT$, B: $\epsilon_2 = 198.3kT$, C: $\epsilon_2 = 196.3kT$, D: $\epsilon_2 = 194.0kT$. See caption of Fig. 1 for the other parameters.

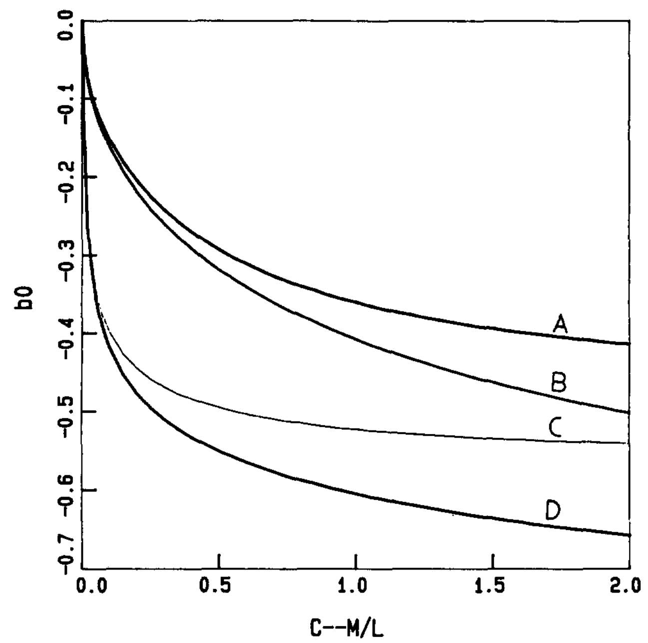

FIG. 5. The plot of b_0 [see Eq. (2.28a)] as a function of the electrolyte concentration. Curves A and C are the approximate solutions [Eq. (3.9)] in the absence and in the presence of stickiness, respectively; curves B and D are the corresponding exact solutions to the MSA. See caption of Fig. 1 for the details of the electrolyte parameters. b_0 is related to the ion–ion interactions.

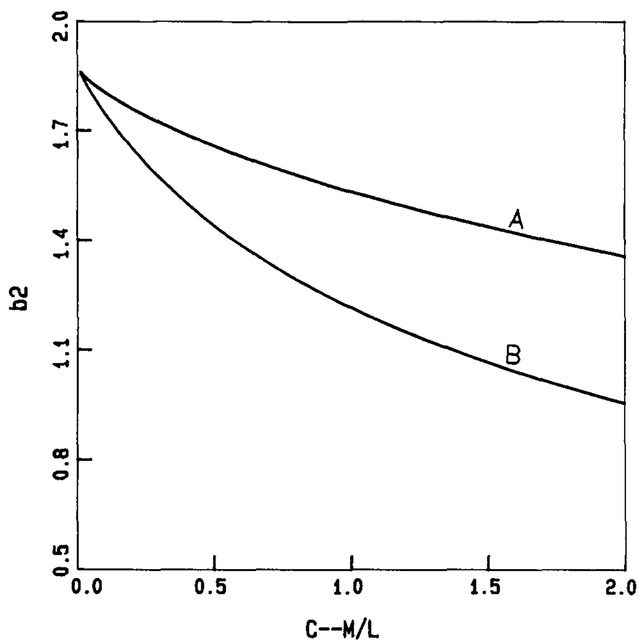

FIG. 7. The plot of b_2 as a function of the electrolyte concentration. Curve A: the result for the SEM, curve B: the result without stickiness. See caption of Fig. 1 for the details of the electrolyte parameters. b_2 is related to the dipole–dipole interactions.

and C) which shows that the departure from the exact solution is small at low concentrations, but becomes larger as the concentration of the electrolyte increases.

The excess ion–ion interaction energies (including the binding energy) given in Eq. (3.3) are plotted in Fig. 8—curve A is the result for the SEM in a dipolar solvent, curve B and curve C are the results for the same electrolyte without stickiness in a hard sphere solvent and in a dipolar solvent, respectively. Note that the dielectric constant of the continuum and hard sphere solvents are taken as unity. We have not plotted the energy for the SEM in a hard sphere solvent in Fig. 8 because the binding energy equal to $\rho_0\langle N\rangle\epsilon_2/2$ is too large on the scale of this figure—see also Fig. 2. Figure 8

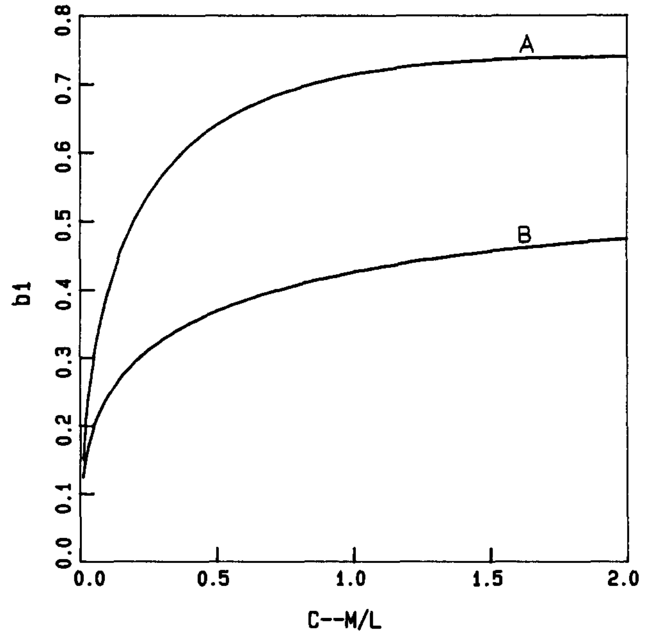

FIG. 6. The plot of b_1 as a function of the electrolyte concentration. Curve A: the result without stickiness, curve B: the result for the SEM. See caption of Fig. 1 for the details of the electrolyte parameters. b_1 is related to the ion–dipole interactions.

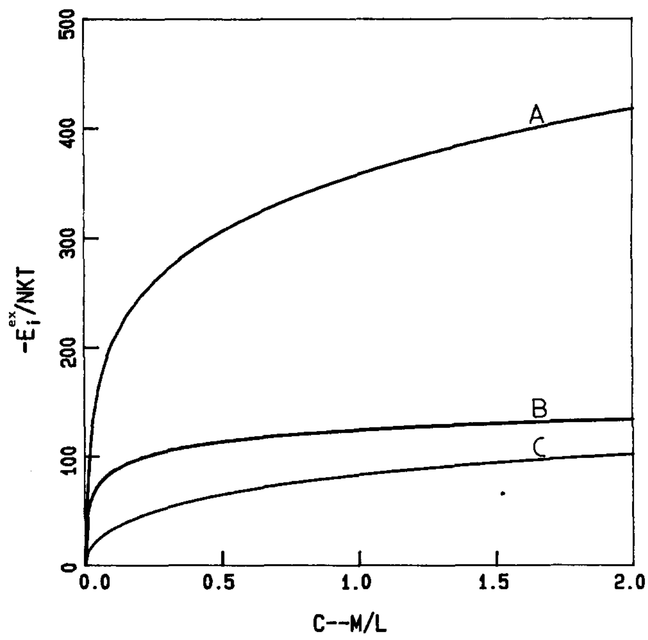

FIG. 8. The ion–ion interaction energy plotted as a function of the electrolyte concentration. A: the SEM in a dipolar solvent, B: electrolyte without stickiness in a hard sphere solvent, C: electrolyte without stickiness in a dipolar solvent. See caption in Fig. 1 for the parameters.

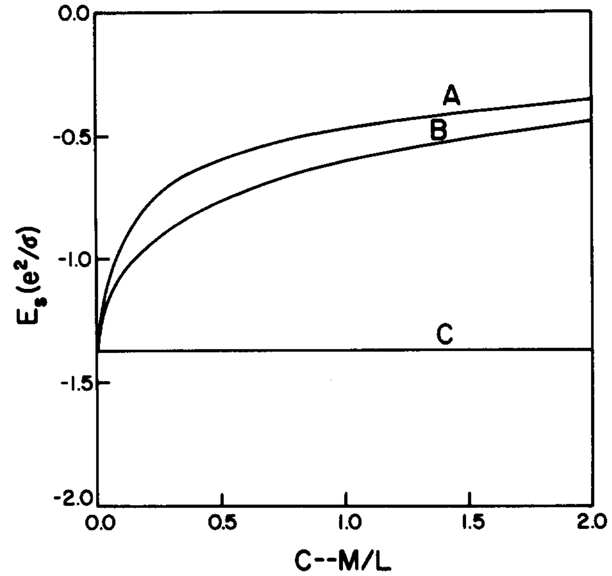

FIG. 9. The change of the ion solvation energy with the concentration of the electrolyte. A: the SEM, B: electrolyte without stickiness, C: both electrolytes at infinite dilution, $\epsilon_2 = 196.3kT$. See caption of Fig. 1 for the other parameters.

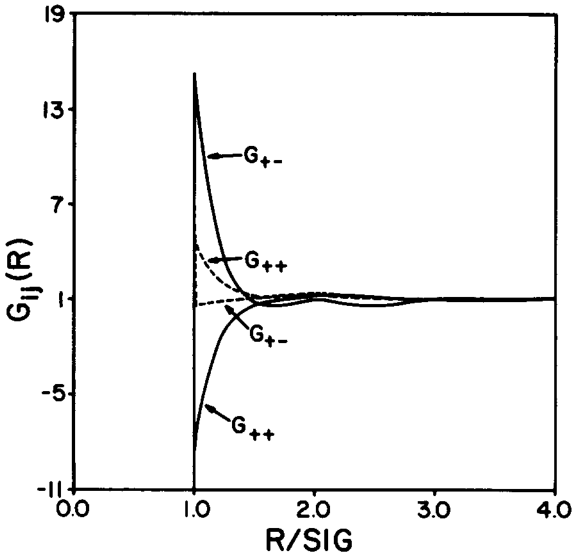

FIG. 11. The ion–ion radial distribution function in the HNC/MS approximation for a 1–1 electrolyte at a concentration 1.0 M, $\epsilon_2 = 196.3kT$, $\eta_d = 0.37$, $T = 298$ K in a dipolar solvent. The dashed line shows the results for the SEM in a dipolar solvent; the full line the corresponding results for the same system in the absence of stickiness.

shows that the ion–ion interaction energy in the absence of stickiness is greater in a hard sphere solvent than in a dipolar solvent because of the absence of screening. However, the addition of a sticky interaction between the ions in a dipolar solvent makes the ion–ion interaction energy more negative.

In Fig. 9, the solvation energy is plotted according to Eq. (3.11). The horizontal line C shows Chan's result at infinite dilution given in Eq. (3.21), while curves A and B are the results of Eq. (3.11) with and without stickiness, respectively. In both cases, the energies reduce correctly to the same limiting value at infinite dilution. It will be noticed that the solvation energy becomes less negative with increasing ion concentration. This may be understood as follows—when the ion concentration increases, each ion is not surrounded by fewer solvent molecules than at infinite dilution; that is to say the solvation number of the ion decreases leading to a smaller solvation energy. When the stickiness is added to the oppositely charged ions, the solvation shell of each ion is reduced further by association making the solvation energy even smaller.

Finally, we will discuss the radial distribution functions for this system; they were calculated by Perram's method.[18] We have plotted the ion–ion radial distribution function at two different concentrations (0.1 and 1.0 M) in Figs. 10 and

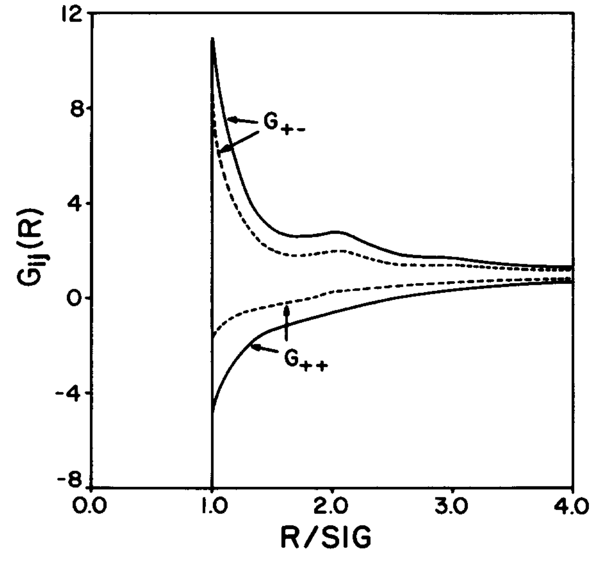

FIG. 10. The ion–ion radial distribution function in the HNC/MS approximation for the 1–1 electrolyte at a concentration 0.1 M, $\epsilon_2 = 196.3kT$, $\eta_d = 0.37$, $T = 298$ K. The dashed line corresponding to the SEM in a dipolar solvent. The full line corresponding to the electrolyte in the same system without stickiness.

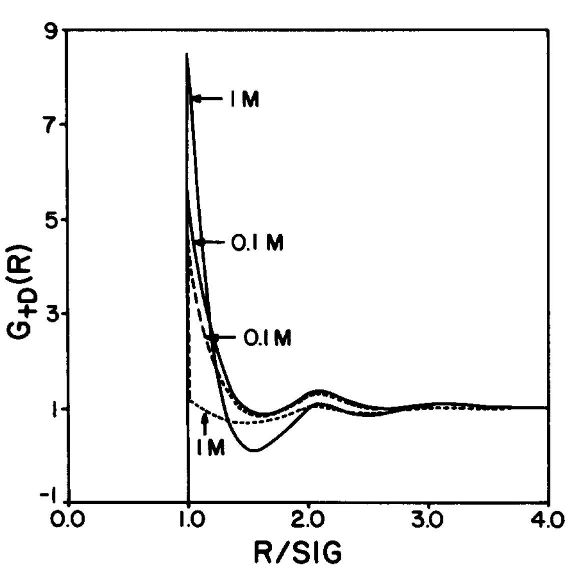

FIG. 12. The ion–dipole radial distribution function in the HNC/MS approximation for a 1–1 electrolyte at two concentrations 0.1 and 1.0 M, $\epsilon_2 = 196.3kT$, $\eta_d = 0.37$, $T = 298$ K. See caption of Fig. 1 for other details.

11, and the ion–dipole distribution functions at the same electrolyte concentrations in Fig. 12. The full lines are the results for charged hard spheres in a dipolar solvent, and the dashed lines are the calculations for the SEM in a dipolar solvent. The addition of a sticky interaction between oppositely charged ions reduces the contact value of $g_{+-}(r)$ and alters the distribution functions beyond this distance especially at high concentrations (~ 1.0 M—see Fig. 11). The smaller contact value at $r = \sigma +$ implies that the binding between oppositely charged ions at $r = \sigma -$ reduces the probability that a free ion appears in the vicinity of its counter ion. At higher concentrations a steep reduction in $g_{+-}(r)$ just beyond $r = \sigma +$ is also observed. The opposite is true for the $g_{++}(r)$. Figure 12 for the ion–dipole radial distribution functions, shows that the contact value of $g_{+d}(r)$ also drops sharply when the oppositely charged ions stick to each other.

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[19] This follows from Wertheim's (Ref. 14) demonstration that dipolar hard spheres in the MSA can be mapped on to hard spheres in the PY approximation at positive and negative densities. Equation (3.19b) is the PY solution for the hard sphere Q functions obtained by Baxter (Ref. 15).