

Unsymmetrical electrolytes with adhesive interactions

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The sticky electrolyte mode for a weak unsymmetrical electrolyte is solved in the mean spherical approximation (MSA) when there are adhesive interactions between oppositely charged ions. The distribution functions at contact and the thermodynamic properties in this approximation are derived; the solutions reduce to those of corresponding symmetrical adhesive electrolyte studied by Rasaiah and Lee [J. Chem. Phys. **83**, 6396 (1985)] when the sizes of the ions and the magnitudes of the charges are made the same and to those of adhesive nonelectrolytes when the charges are removed. When the stickiness is turned off the solutions of the primitive model electrolyte in the MSA are recovered.

I. INTRODUCTION

The sticky electrolyte model (SEM) has been studied by us in a series of papers.¹⁻⁶ In this model for weak electrolytes, ion association is introduced in the Hamiltonian through a delta function interaction between oppositely charged ions at a L distance which is less than the sum of the radii of the ions. All of our studies so far have been confined to symmetrical electrolytes in which the ions have the same charge magnitudes and their sizes are the same. The Ornstein-Zernike equations were solved analytically in the mean spherical approximation (MSA) and numerically in the hypernetted chain (HNC) approximation for different values of L . The solvent effect in this model has also been investigated^{5(a),5(b)} when it was found that a hard sphere solvent has a strong packing effect on association while a dipolar solvent has both a packing effect due to the hard cores and a screening effect attributed to the dipoles. When $L < \sigma/2$, where σ is the hard core diameter, the hard core repulsion between ions of the same sign ensures that polymerization is sterically inhibited so that the only associated species present are expected to be dimers. By adjusting the coefficient of the delta function interaction it is possible to ensure that all of the ions are paired; then the theory already developed for weak electrolytes can be applied to these dimers, which are extended dipoles, as well. In particular the analytic solutions for the energy of these dipolar fluids in the mean spherical approximation have obtained for $L = \sigma/n$ with $n = 2, 3, 4$ and 5 .

In this paper we begin the study of sticky electrolytes in which the sizes of the associating ions may be different and the magnitudes of the charges on them are not necessarily the same. This is a more realistic model for weak electrolytes but the mathematical development is more complicated than it is for symmetrical sticky electrolytes. We begin our discussion in general terms with the bonding distance $L < R_i + R_j$, where R_i and R_j are ionic radii, but our detailed analysis is confined only to adhesion between oppositely charged ions. This is similar to the model first introduced by Baxter^{7(a)} and studied by Barboy and Tenne^{7(b)} for a mixture of adhesive hard spheres of unequal size; the difference lies in the presence of charges on the spheres and the allowance for adhesion only between unlike ions. The special case of adhesion between oppo-

sitely charged ions of the same size has already been studied by us^{4,5} in the MSA and the results for the more general case presented here reduce to those found earlier in the limit of equal ion sizes. The extension of our studies to mixtures of charged ions, aside from its immediate relevance to the aggregation of charged particles and colloids, also provides the means to investigate the properties of the double layer at charged surfaces when preferential adsorption or adhesion of one or more ions plays an important role.⁸ This may be realized by taking the "wall limit" of our model in which the density of one species (the aspiring electrode or charged surface) is allowed to tend to zero while its radius becomes infinitely large.

Our system consists of at least two kinds of ions of opposite charge; ion i has density ρ_i , diameter σ_i and charge $z_i e$, where z_i is the valence and e is the magnitude of the electronic charge. Throughout this paper, we also use subscripts 1 or 2 to denote the two species of a single electrolyte. Electroneutrality implies that

$$\sum_i \rho_i z_i = 0. \quad (1.1)$$

In the SEM, the interaction energy between i and j is given as the sum of two terms:

$$u_{ij}(r) = u_{ij}^0(r) + u_{ij}^b(r), \quad (1.2a)$$

with

$$u_{ij}^0(r) = \infty, \quad r < \sigma_{ij} \quad (1.2b)$$

$$= -z_i z_j e^2 / \epsilon r, \quad r > \sigma_{ij} \quad (1.2c)$$

$$u_{ij}^b(r) = -\epsilon_2(1 - \delta_{ij}), \quad L + \delta < r < L - \delta. \quad (1.2d)$$

In Eq. (1.2a), $u_{ij}^0(r)$ is the pair potential of the reference system in which there is no adhesion or "chemical bonding" and ϵ is the dielectric constant of the solvent medium. The second term $u_{ij}^b(r)$ introduces bonding (or adhesion) between ions with binding energy $-\epsilon_2$ at a distance $L < \sigma_{ij}$ where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ is the contact distance between two ion centers. The Kronecker delta δ_{ij} in this expression allows bonding to occur only between oppositely charged ions.

The Mayer f -function for the interactions between the ions is given by

$$f_{ij}(r) = -1 + \zeta L(1 - \delta_{ij})\delta(r - L)/12, \quad 0 < r < \sigma_{ij} \quad (1.3a)$$

$$= \exp(-\beta z_i z_j e^2 / \epsilon r) - 1, \quad r > \sigma_{ij} \quad (1.3b)$$

where ζ is the sticking coefficient which is the inverse of the parameter τ introduced by Baxter^{7(a)} in his study of the adhesive hard spheres, $\beta = 1/k_B T$, k_B is Boltzmann constant and T is the absolute temperature. Combining (1.3a) and (1.2d), we have

$$\exp[\beta \epsilon_2(1 - \delta_{ij})] = \zeta L(1 - \delta_{ij})\delta(r - L)/12, \quad 0 < r < \sigma_{ij} \quad (1.3c)$$

The presence of the delta function in Mayer function induces a delta function in the correlation function $h_{ij}(r)$ with a different coefficient λ called the association parameter:

$$h_{ij}(r) = -1 + \lambda L(1 - \delta_{ij})\delta(r - L)/12, \quad 0 < r < \sigma_{ij} \quad (1.4)$$

The association number $\langle N_{ij} \rangle$, which is the average number of j ions around an i ion, is given by

$$\langle N_{ij} \rangle = \rho_j \int_0^{L+\sigma_{ij}} g_{ij}(r) 4\pi r^2 dr = \pi \lambda \rho_j L^3 / 3 \quad (i \neq j), \quad (1.5)$$

where

$$g_{ij}(r) = h_{ij}(r) + 1 \quad (1.6)$$

is the radial distribution function. The density of i, j pairs is then

$$\rho_{ij} = \rho_i \langle N_{ij} \rangle = \rho_j \langle N_{ji} \rangle \quad (i \neq j). \quad (1.7)$$

Note that $\langle N_{ij} \rangle$ is just the degree of association α for a symmetrical electrolyte. The equilibrium ratio K for the association reaction $i + j \rightarrow ij$ can be written as

$$\begin{aligned} K &= \rho_{ij} / (\rho_i^* \rho_j^*) \\ &= \rho_i \langle N_{ij} \rangle / [(\rho_i - \rho_{ij})(\rho_j - \rho_{ij})] \\ &= \pi \lambda L^3 / [3(1 - \langle N_{ij} \rangle)(1 - \langle N_{ji} \rangle)] \quad (i \neq j), \end{aligned} \quad (1.8)$$

where ρ_i^* is the equilibrium density of component i . Therefore, once the sticky parameter λ is known, the degree of association $\langle N_{ij} \rangle$ and the association constant K can be calculated. It is easily verified that Eqs. (1.5) and (1.9) reduce to the known results for symmetric sticky electrolytes¹⁻⁵ and for sticky hard spheres⁹ when the sizes are equal. The sticking coefficient ζ is related to the association parameter λ by^{3,5}

$$\lambda = \zeta v_{ij}(L, \zeta) \quad (i \neq j), \quad (1.9)$$

where the cavity function $v_{ij}(L, \zeta)$ is defined by

$$g_{ij}(r, \zeta) = [1 + f_{ij}(r, \zeta)] v_{ij}(r, \zeta). \quad (1.10)$$

In our earlier work on this model for weak electrolytes the degree of association α , which is related to the sticky parameter λ , was calculated using either the hypernetted chain (HNC) approximation or the Percus-Yevick (PY) approximation for the cavity function $v_{ij}(L)$ at the bonding distance L . While these liquid state approximations may be

suitable for adhesive interactions between the associating species, doubts have arisen about whether they are directly applicable to the cavity functions of the associating ions in weak acids and other dimerization reactions where polymerization is precluded by steric or directional effects. Stell and Zhou¹⁰ have suggested a simple interpolation formula for the cavity function $v_{AB}(L)$, namely,

$$v_{AB}(L) = v_{AB}^0(L) (1 - \alpha)^2, \quad (1.11)$$

where α is the degree of association and $v_{AB}^0(L)$ is the cavity function of the corresponding reference system in which the interaction term [Eq. (1.2d)] in the Hamiltonian leading to bonding has been deleted. It has been shown by us⁶ that there is extensive cancellation of the diagrams in the density expansion of the cavity function when the dominant bridge diagrams, (which are ignored in most liquid state approximations) are included and when steric effects limit association to dimerization. This analysis⁶ also suggests the approximation

$$v_{AB}(L) = v_{AB}^0(L) - 1 + (1 - \alpha)^2. \quad (1.12)$$

Since there is no bonding term in the Hamiltonian of the reference system, $v_{AB}^0(L)$ can be safely calculated with one of the liquid state (HNC or PY) approximations. The degree of association is then obtained as the solution to a quadratic equation determined by $v_{AB}^0(L)$ and the association constant at infinite dilution $K_0 = \pi \zeta L^3 / 3$.

The method that we use to solve the Ornstein-Zernike equation (OZ) equation for adhesive electrolytes in the MS approximation is similar to the one used by Blum^{11,12} for the primitive model electrolyte and is an extension, to unsymmetrical electrolytes, of Baxter's Wiener-Hopf factorization of the direct correlation function for hard spheres of unequal size. Throughout this paper we will use Blum's notation as far as possible to facilitate comparison with his results when the stickiness is turned off. Wei and Blum¹³ have studied mixtures of ions and point dipoles in which there is stickiness between all species which makes the analysis, as far as it can be carried, far more complicated than what we present here for a single unsymmetrical weak electrolyte. Their discussion also does not include calculations of the association parameter λ and the correlation functions. This paper is planned as follows: in Secs. II and III we discuss the solution in detail for unsymmetrical adhesive electrolytes in the mean spherical approximation. In Sec. IV we consider the equal size limit of our solution that reduces to the analytic solutions for symmetrical sticky electrolytes. Section V is devoted to the thermodynamics of adhesive electrolytes.

II. THE METHOD OF SOLUTION

As stated in the Introduction we make use of Blum's extension^{11,12} to electrolytes of the Baxter's Wiener-Hopf factorization of the direct correlation functions for mixtures [see Eq. (2.12)]. We will summarize the method and important relations before discussing the solution for adhesive electrolytes.

The Ornstein-Zernike (OZ) equation for the system considered is

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k c_{ik}(r) * h_{kj}(r), \quad (2.1)$$

where $c_{ij}(r)$ is the direct correlation function and $*$ represents a convolution. The closure equations are

$$h_{ij}(r) = -1 + \lambda L(1 - \delta_{ij})\delta(r - L)/12 \quad (0 < r < \sigma_{ij}), \quad (2.2a)$$

$$c_{ij}(r) = \lim_{\mu \rightarrow 0} -\beta z_i z_j (e^2/\epsilon r) \exp(-\mu|r|/r) \quad (r > \sigma_{ij}). \quad (2.2b)$$

The first relation is exact while the second applies only to the mean spherical approximation. Except for a delta function at $L < \sigma_{ij}$, the closure equations in the MSA are the same when there is no stickiness (i.e., in the primitive model electrolyte). Therefore, the theoretical analyses of the two should be similar.

Defining the Fourier transforms

$$\begin{aligned} \tilde{C}_{ij}(k) &= (\rho_i \rho_j)^{1/2} \int c_{ij}(r) \exp(ik \cdot r) dr \\ &= 4\pi (\rho_i \rho_j)^{1/2} \int_0^\infty c_{ij}(r) \left(\frac{k}{r}\right) \sin(kr) dr, \end{aligned} \quad (2.3a)$$

$$\begin{aligned} \tilde{H}_{ij}(k) &= (\rho_i \rho_j)^{1/2} \int h_{ij}(r) \exp(ik \cdot r) dr \\ &= 4\pi (\rho_i \rho_j)^{1/2} \int_0^\infty h_{ij}(r) \left(\frac{k}{r}\right) \sin(kr) dr, \end{aligned} \quad (2.3b)$$

the OZ equation (2.1) can be transformed into

$$\delta_{ij} = \sum_k [\delta_{ik} + \tilde{H}_{ik}(k)] [\delta_{kj} - \tilde{C}_{kj}(k)]. \quad (2.4)$$

The direct correlation function is now split into two parts, a short ranged part $c_{ij}^0(r)$ and a remainder equal to the long ranged contribution with an exponential damping factor containing the parameter μ , which is introduced to avoid the divergence of the integrals like (2.3). Thus

$$\begin{aligned} c_{ij}(r) &= c_{ij}^0(r) - \lim_{\mu \rightarrow 0} \beta z_i z_j (e^2/\epsilon r) \exp(-\mu|r|/r) \quad (r > \sigma_{ij}), \end{aligned} \quad (2.5)$$

where

$$c_{ij}^0(r) = 0 \quad (r > \sigma_{ij}). \quad (2.6)$$

Taking the Fourier transform of (2.5) we have

$$\tilde{C}_{ij}(k) = \tilde{C}_{ij}^0(k) - \lim_{\mu \rightarrow 0} \alpha_{ij}/(k^2 + \mu^2) \quad (r > \sigma_{ij}), \quad (2.7)$$

where $\tilde{C}_{ij}^0(k)$ is defined in the same way as Eq. (2.3a) and α_{ij} is given by

$$\alpha_{ij} = 4\pi (\rho_i \rho_j)^{1/2} z_i z_j \beta e^2/\epsilon = \alpha_0^2 (\rho_i \rho_j)^{1/2} z_i z_j \quad (2.8a)$$

with

$$\alpha_0^2 = 4\pi \beta e^2/\epsilon. \quad (2.8b)$$

Substituting (2.7) into (2.4) leads to

$$\delta_{ij} = \sum_k [\delta_{ik} + \tilde{H}_{ik}(k)] \{ \delta_{kj} - \tilde{C}_{kj}^0(k) + \alpha_{kj}/(k^2 + \mu^2) \}, \quad (2.9)$$

which is the OZ equation for this problem in Fourier space. Integrating Eqs. (2.3a) and (2.3b) by parts, one finds

$$\tilde{C}_{ij}^0(k) = 2(\rho_i \rho_j)^{1/2} \int_0^\infty c_{ij}^0(r) \cos(kr) S_{ij}(r) dr, \quad (2.10a)$$

$$\tilde{H}_{ij}(k) = 2(\rho_i \rho_j)^{1/2} \int_0^\infty h_{ij}(r) \cos(kr) J_{ij}(r) dr, \quad (2.10b)$$

where

$$S_{ij}(r) = 2\pi \int_r^\infty c_{ij}^0(t) dt, \quad (2.11a)$$

$$\begin{aligned} J_{ij}(r) &= 2\pi \int_r^\infty h_{ij}(t) t dt \\ &= J_{ij} - 2\pi \int_0^r h_{ij}(t) t dt, \end{aligned} \quad (2.11b)$$

and

$$J_{ij} = 2\pi \int_0^\infty h_{ij}(t) t dt. \quad (2.11c)$$

The derivatives of (2.11) give

$$J'_{ij}(r) = -2\pi r h_{ij}(r); \quad S'_{ij}(r) = -2\pi r c_{ij}(r). \quad (2.11d)$$

The second factor in Eq. (2.9) is factorized by extending the method introduced by Baxter to coulomb systems:^{11,12}

$$\delta_{ij} - \tilde{C}_{ij}^0(k) + \alpha_{ij}/(k^2 + \mu^2) = \sum_k \tilde{Q}_{ik}(k) \tilde{Q}_{jk}(-k), \quad (2.12)$$

where the $Q(k)$ functions are defined by

$$\begin{aligned} \tilde{Q}_{ij}(k) &= \delta_{ij} - (\rho_i \rho_j)^{1/2} \int_{\lambda_{ji}}^{\sigma_{ji}} Q_{ij}(r) \exp(ikr) dr \\ &\quad + A_{ij} (\rho_i \rho_j)^{1/2} \int_{\lambda_{ji}}^\infty \exp[r(-\mu + ik)] dr, \end{aligned} \quad (2.13)$$

in which A_{ij} is a constant that will be determined later and

$$\lambda_{ji} = (\sigma_j - \sigma_i)/2, \quad (2.14a)$$

$$\sigma_{ji} = (\sigma_j + \sigma_i)/2. \quad (2.14b)$$

Substituting Eq. (2.12) into Eq. (9), one finds

$$\sum_k [\delta_{ik} + \tilde{H}_{ik}(k)] \tilde{Q}_{kj}(k) = [\tilde{Q}^T(-k)]_{ij}^{-1}, \quad (2.15)$$

where $\tilde{Q}^T(-k)$ is the transpose of Q_{ij} matrix. The inverse Fourier transform of Eqs. (2.12) and (2.15) gives

$$\begin{aligned} J_{ij}(r) &= Q_{ij}(r) - \frac{A_{ij}}{2} + \sum_k \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} J_{ik}(|r-t|) Q_{kj}(t) dt \\ &\quad - \sum_k \rho_k \int_{\lambda_{jk}}^r J_{ik}(|r-t|) A_{kj} dt, \end{aligned} \quad (2.16a)$$

$$\begin{aligned}
S_{ij}(r) = & \alpha_{ij} \exp(-\mu r) / [2\mu(\rho_i \rho_j)^{1/2}] + [Q_{ij}(r) - A_{ij}] \theta(r - \lambda_{ji}) + [Q_{ji}(r) - A_{ji}] \theta(-r - \lambda_{ji}) \\
& - \sum_k \rho_k (\rho_i \rho_j)^{1/2} \int_{\sup(\lambda_{ki} r + \lambda_{kj})}^{\inf(\sigma_{ki} r + \sigma_{kj})} Q_{ik}(t) Q_{jk}(t - r) dt + \sum_k \rho_k A_{ik} \int_{\sup(\lambda_{ki} r + \lambda_{kj})}^{\sigma_{jk}} Q_{jk}(t) dt \\
& + \sum_k \rho_k A_{jk} \int_{\sup(\lambda_{ki} r + \lambda_{kj})}^{\sigma_{ki}} Q_{ik}(t) dt - \sum_k \rho_k A_{ik} A_{jk} \exp[-\mu(|r| + 2\lambda_{ki})] / 2\mu,
\end{aligned} \tag{2.16b}$$

where θ is a Heaviside step function, $\sup(x, y)$ means the maximum number is to be chosen and $\inf(x, y)$ means the minimum number is to be chosen between x and y . In deriving (2.16a), the electroneutrality condition in the form

$$\sum_k \rho_k \int_0^\infty J_{ik}(t) A_{kj} dt = -A_{ij}/2, \tag{2.17a}$$

has been used. To derive this start by equating the charge on ion i with the charge in its atmosphere:

$$-z_i = 4\pi \sum_k z_k \rho_k \int_0^\infty h_{ik}(t) t^2 dt. \tag{2.17b}$$

An integration by parts of $\int_0^\infty J_{ik}(t) dt$ and the use of Eq. (2.18), which is derived below, leads to Eq. (2.17a). Taking the limit $\mu \rightarrow 0$, we find from Eq. (2.16b)

$$\alpha_{ij} = (\rho_i \rho_j)^{1/2} \sum_k \rho_k A_{ik} A_{jk}. \tag{2.17c}$$

Comparing this with Eq. (2.8), one sees that

$$A_{ik} = z_i a_{ki}, \tag{2.18}$$

where

$$\sum_k \rho_k a_k^2 = \alpha_0^2. \tag{2.19}$$

This implicitly defines a_k . The relations (2.16) and (2.19) are the same as the ones obtained for unsymmetrical electrolytes in the absence of stickiness.^{11,12} In the MSA the Q functions are zero just beyond the contact distance:

$$Q_{ij}(r) = 0 \quad (r > \sigma_{ij}^+). \tag{2.20}$$

We now study the case $L = \sigma_{ij}$, which means the stickiness occurs just short of the contact distance. In the SEM we find from Eqs. (2.11b) and (2.2a) that

$$J_{ij}(\sigma_{ij}^-) = J_{ij}(\sigma_{ij}^+) + \pi \lambda \sigma_{ij}^2 (1 - \delta_{ij}) / 6. \tag{2.21}$$

But from Eqs. (2.16a) and (2.20), it is seen that

$$J_{ij}(\sigma_{ij}^-) - J_{ij}(\sigma_{ij}^+) = Q_{ij}(\sigma_{ij}^-), \tag{2.22}$$

which implies that

$$Q_{ij}(\sigma_{ij}^-) = \pi \lambda \sigma_{ij}^2 (1 - \delta_{ij}) / 6 = Q_{ij}^1, \tag{2.23}$$

where Q_{ij}^1 is a shorthand for $Q_{ij}(\sigma_{ij}^-)$ which is a constant. From Eq. (2.11b) it is seen that

$$J_{ij}'''(r) = 0 \quad (r < \sigma_{ij}^-), \tag{2.24a}$$

which, by using Eq. (2.16a), leads to

$$Q_{ij}'''(r) = 0 \quad (r < \sigma_{ij}^-). \tag{2.24b}$$

Integrating Eq. (2.24) with the boundary conditions (2.20) and (2.23), one finds

$$Q_{ij}(r) = (r - \sigma_{ij}) Q_{ij}' + (r - \sigma_{ij})^2 Q_{ij}'' / 2 + Q_{ij}^1 \quad (r < \sigma_{ij}^-). \tag{2.25}$$

The problem now is to determine the coefficients in the Q functions and the constants A_{ij} which appear in the definitions of the Fourier transforms of these functions [see Eq. (2.13)]. Differentiating Eq. (2.16a) with respect to r when $r < \sigma_{ij}^-$, we have

$$\begin{aligned}
2\pi r = & Q_{ij}'(r) + 2\pi \sum_k \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} (r - t) Q_{kj}(t) dt - \sum_k \rho_k J_{ik} A_{kj} \\
& - 2\pi \sum_k \rho_k \int_{\lambda_{jk}}^r (r - t) A_{kj} dt,
\end{aligned} \tag{2.26}$$

where $Q_{ij}'(r)$ is the derivative with respect to r and the constant J_{ij} is defined by Eq. (2.11c). Differentiation again of Eq. (2.26) with respect to r leads to

$$\begin{aligned}
2\pi = & Q_{ij}''(r) + 2\pi \sum_k \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} Q_{kj}(t) dt - 2\pi \sum_k \rho_k \\
& \times A_{kj} (r - \lambda_{jk}).
\end{aligned} \tag{2.27}$$

Define

$$K_{ij}^0 = \int_{\lambda_{ji}}^{\sigma_{ji}} Q_{ij}(t) dt, \tag{2.28}$$

$$B_i = \sum_k \rho_k z_k J_{ki}. \tag{2.29}$$

To solve Eqs. (2.26) and (2.27), we need to fix r and we choose $r = \sigma_j/2$. (Any other choice of r between 0 and σ_{ij} is permissible, but it leads to solutions too complicated to be easily manipulated). Substituting $r = \sigma_j/2$ into Eqs. (2.26) and (2.27) and making use of Eqs. (2.18), (2.28), and (2.29) gives us two relations:

$$\begin{aligned}
\pi \sigma_i \sigma_j = & -Q_{ij}(\lambda_{ji}) - a_j \sigma_i (B_i + \pi x_2 / 4) \\
& + (\pi \sigma_i / 6) \sum_k \rho_k \sigma_k^2 Q_{kj}(\lambda_{jk}) + Q_{ij}^1 \\
& - (\pi \sigma_i / 6) \sum_k \rho_k \sigma_k^2 Q_{kj}^1
\end{aligned} \tag{2.30}$$

and

$$\begin{aligned}
2\pi = & (6/\sigma_i^2) Q_{ij}(\lambda_{ji}) - (12/\sigma_i^3) K_{ij}^0 + (6/\sigma_i^2) Q_{ij}^1 \\
& + 2\pi \sum_k \rho_k K_{kj}^0 - \pi a_j x_1,
\end{aligned} \tag{2.31}$$

where we have used

$$Q_{ij}(\lambda_{ji}) = -\sigma_i Q'_{ij} + (\sigma_i^2/2) Q''_{ij} + Q_{ij}^3 \quad (2.32)$$

and the definition

$$x_i = \sum_k \rho_k z_k \sigma_k^i \quad (2.33)$$

Multiplying (2.31) by $\sigma_i^3/12$, we get after rearrangement

$$\begin{aligned} \pi\sigma_i^3/6 = (\sigma_i/2) Q_{ij}(\lambda_{ji}) - K_{ij}^0 + (\pi\sigma_i^3/6) \sum_k \rho_k K_{kj}^0 \\ - \pi a_j x_1 \sigma_i^3/12 + (\sigma_i/2) Q_{ij}^3 \end{aligned} \quad (2.34)$$

Using Eq. (2.25) in Eq. (2.28) and combining this with Eq. (2.33), we have

$$Q'_{ij} = (2/\sigma_i) Q_{ij}(\lambda_{ji}) - (6/\sigma_i^2) K_{ij}^0 + (4/\sigma_i) Q_{ij}^3 \quad (2.35)$$

$$Q''_{ij} = (6/\sigma_i^2) Q_{ij}(\lambda_{ji}) - (12/\sigma_i^3) K_{ij}^0 + (6/\sigma_i^2) Q_{ij}^3 \quad (2.36)$$

Therefore, once $Q_{ij}(\lambda_{ji})$ and K_{ij}^0 are known, Q'_{ij} and Q''_{ij} can be easily calculated.

Equations (2.30) and (2.34) generate two sets of linear equations for $Q_{ij}(\lambda_{ji})$ and K_{ij}^0 which are

$$\begin{aligned} (1 - \pi\rho_1\sigma_1^3/6) Q_{11} - (\pi\rho_2\sigma_1\sigma_2^2/6) Q_{21} \\ = -\pi\sigma_1^2 - a_1\sigma_1(B_1 + \pi x_2/4) - (\pi\rho_2\sigma_1\sigma_2^2/6) Q_{ij}^3 \end{aligned} \quad (2.37a)$$

$$\begin{aligned} (1 - \pi\rho_1\sigma_1^3/6) Q_{12} - (\pi\rho_2\sigma_1\sigma_2^2/6) Q_{22} \\ = -\pi\sigma_1\sigma_2 - a_2\sigma_1(B_1 + \pi x_2/4) + (1 - \pi\rho_1\sigma_1^3/6) Q_{ij}^3 \end{aligned} \quad (2.37b)$$

$$\begin{aligned} (-\pi\rho_1\sigma_2\sigma_1^2/6) Q_{11} + (1 - \pi\rho_2\sigma_2^3/6) Q_{21} \\ = -\pi\sigma_1\sigma_2 - a_1\sigma_2(B_2 + \pi x_2/4) + (1 - \pi\rho_2\sigma_2^3/6) Q_{ij}^3 \end{aligned} \quad (2.37c)$$

$$\begin{aligned} (-\pi\rho_1\sigma_2\sigma_1^2/6) Q_{12} + (1 - \pi\rho_2\sigma_2^3/6) Q_{22} \\ = -\pi\sigma_2^2 - a_2\sigma_2(B_2 + \pi x_2/4) - (\pi\rho_1\sigma_2\sigma_1^2/6) Q_{ij}^3 \end{aligned} \quad (2.37d)$$

and

$$\begin{aligned} (1 - \pi\rho_1\sigma_1^3/6) K_{11}^0 - (\pi\rho_2\sigma_1^3/6) K_{21}^0 \\ = -\pi\sigma_1^3/6 + (\sigma_1/2) Q_{11} - \pi x_1 a_1 \sigma_1^3/12, \end{aligned} \quad (2.38a)$$

$$\begin{aligned} -(\pi\rho_1\sigma_2^3/6) K_{11}^0 + (1 - \pi\rho_2\sigma_2^3/6) K_{21}^0 \\ = -\pi\sigma_2^3/6 + (\sigma_2/2) Q_{21} - \pi x_1 a_1 \sigma_2^3/12 + (\sigma_2/2) Q_{ij}^3, \end{aligned} \quad (2.38b)$$

$$\begin{aligned} (1 - \pi\rho_1\sigma_1^3/6) K_{12}^0 - (\pi\rho_2\sigma_1^3/6) K_{22}^0 \\ = -\pi\sigma_1^3/6 + (\sigma_1/2) Q_{12} - \pi x_1 a_2 \sigma_1^3/12 + (\sigma_1/2) Q_{ij}^3, \end{aligned} \quad (2.38c)$$

$$\begin{aligned} -(\pi\rho_1\sigma_2^3/6) K_{12}^0 + (1 - \pi\rho_2\sigma_2^3/6) K_{22}^0 \\ = -\pi\sigma_2^3/6 + (\sigma_2/2) Q_{22} - \pi x_1 a_2 \sigma_2^3/12, \end{aligned} \quad (2.38d)$$

where we have used 1 and 2 to represent the two components explicitly and the fact that

$$Q_{12}^3 = Q_{21}^3 = Q_{ij}^3 = \pi\lambda\sigma_{12}^2/6 \quad (2.39)$$

as well as the short hand $Q_{ij} = Q_{ij}(\lambda_{ji})$.

The solution to the set of Eqs. (2.37) is

$$Q_{ij}(\lambda_{ji}) = -\pi\sigma_i\sigma_j/\Delta - a_j\sigma_i N_i + (1 - \delta_{ij}) Q_{ij}^3, \quad (2.40)$$

where

$$\Delta = 1 - (\pi/6) \sum_k \rho_k \sigma_k^3 \quad (2.41)$$

and

$$N_i = B_i + \pi x_2/(4\Delta) + (\pi/6\Delta) \sum_k \rho_k B_k \sigma_k^3 \quad (i=1,2). \quad (2.42a)$$

The above equation can be solved for B_i when we find

$$B_i = N_i - \pi x_2/4 - (\pi/6) \sum_k \rho_k N_k \sigma_k^3 \quad (i=1,2). \quad (2.42b)$$

Substitution of Eq. (2.40) in Eq. (2.38) leads to the solution

$$K_{ij}^0 = K_{ij}^{00} + K_{ij}^{0\lambda}, \quad (2.43)$$

where K_{ij}^{00} is given by

$$\begin{aligned} K_{ij}^{00} = -(\pi\sigma_i^2/2\Delta) [\sigma_j + \sigma_i/3 + \pi\xi_2\sigma_i\sigma_j/6\Delta] - (a_j\sigma_i^2/2) \\ \times [N_i + (\pi\sigma_i/6\Delta)(x_1 + \sum_k \rho_k N_k \sigma_k^2)], \end{aligned} \quad (2.44)$$

in which ξ_i is defined by

$$\xi_i = \sum_k \rho_k \sigma_k^i \quad (2.45)$$

The second term of (2.43), which depends explicitly on the stickiness, has two expressions

$$K_{ij}^{0\lambda} = (\sigma_i/\Delta) (1 - \pi\rho_j\sigma_j^3/6) Q_{ij}^3 \quad (i \neq j), \quad (2.46a)$$

$$K_{ii}^{0\lambda} = (\pi\rho_j\sigma_j\sigma_i^3/6\Delta) Q_{ij}^3 \quad (i \neq j). \quad (2.46b)$$

Using these in Eqs. (2.35) and (2.36), we have for the coefficients in the Baxter Q -functions

$$\begin{aligned} Q'_{ij} = (2\pi/\Delta) [\sigma_{ij} + \pi\xi_2\sigma_j\sigma_i/(4\Delta)] \\ + a_j [N_i + \pi\sigma_i P_n/(2\Delta)] + \Lambda_{ij} \end{aligned} \quad (2.47)$$

and

$$Q''_{ij} = (2\pi/\Delta) [1 + \pi\xi_2\sigma_j/(2\Delta)] + \pi a_j P_n/\Delta + (2/\sigma_i) \Lambda_{ij} \quad (2.48)$$

where the sticky contribution

$$\Lambda_{ij} = (6/\sigma_i) Q_{ij}^3 (1 - \delta_{ij}) - (6/\sigma_i^2) K_{ij}^{0\lambda} \quad (2.49)$$

P_n is defined by

$$P_n = \sum_k \rho_k \sigma_k (z_k + N_k \sigma_k), \quad (2.50)$$

and a_j (or A_{ij}/z_i) is defined by Eqs. (2.18) and (2.17). To determine a_j we go back to Eq. (2.16a), set $r = 0$ multiply by $\rho_i z_i$ and sum over i on both sides to get

$$\begin{aligned} B_j = \sum_i \rho_i z_i Q_{ij}(0) - (a_j/2) \sum_i \rho_i z_i^2 + \sum_i \rho_i z_i B_i a_j \lambda_{ji} \\ + \sum_i \rho_i B_i K_{ij}^0 \end{aligned} \quad (2.51)$$

Combining this with Eqs. (2.43)–(2.51) we find, after much algebra, that

$$a_j = -(2/D) [N_j + \pi\sigma_j P_n/(2\Delta) - \tau_j], \quad (2.52)$$

with

$$D = \sum_k \rho_k (z_k + N_k \sigma_k)^2, \quad (2.53)$$

$$T_{ij} = T_{ij}^0 + (B_i/z_i) K_{ij}^{\alpha\lambda}, \quad (2.54)$$

$$T_{ij}^0 = (1 - \delta_{ij}) (-1 + 3\sigma_j^2/\sigma_i^2) Q^\lambda/2 + 3(\sigma_i^2 - \sigma_j^2) K_{ij}^{\alpha\lambda}/(2\sigma_i^3), \quad (2.55)$$

$$\tau_j = \sum_i \rho_i z_i T_{ij}, \quad (2.56)$$

Note that when the stickiness is zero T_{ij} , T_{ij}^0 and τ_j are zero. What has been done so far is to express the constants Q'_{ij} , Q''_j , and a_j in terms of N_j , λ , and τ_j , the determination of which is discussed in the next section.

III. THE DETERMINATION OF Γ , THE CONTACT VALUE $g_{ij}(\sigma_j^+)$ AND λ .

The symmetry of the direct correlation function $c_{ij}(r)$ and $S_{ij}(r)$ requires

$$Q_{ij}(\lambda_{ji}) - A_{ij} = Q_{ji}(\lambda_{ij}) - A_{ji}, \quad (3.1)$$

which can be seen from Eq. (2.16b). Substitution of Eqs. (2.40) and (2.18) in (3.1) produces another symmetric relation

$$a_i(z_i + \sigma_i N_i) = a_i(z_j + \sigma_j N_j), \quad (3.2)$$

which suggests the relation

$$(z_i + \sigma_i N_i)/a_i = D/(2\Gamma), \quad (3.3)$$

where D and N_i are defined by Eqs. (2.53) and (2.42a), respectively, and Γ is a new constant. A similar scaling assumption has been used earlier by Blum^{11,12} to solve the primitive model electrolyte (charged hard spheres) in the MSA; it is preserved here in the MSA solution of the SEM because of the symmetry of the sticky interaction. It follows that

$$a_i = (2\Gamma/D)(z_i + \sigma_i N_i). \quad (3.4)$$

Inserting this in Eq. (2.19) and making use of Eq. (2.53) we get.

$$4\Gamma^2 = D\alpha_0^2 = \alpha_0^2 \sum_i \rho_i (z_i + N_i \sigma_i)^2 = \alpha_0^2 \sum_i \rho_i z_i'^2, \quad (3.5a)$$

with a modified valence $z_i' = z_i + N_i \sigma_i$. Comparing this with κ defined by

$$\kappa^2 = (4\pi\beta e^2/\epsilon) \sum_i \rho_i z_i'^2 = \alpha_0^2 \sum_i \rho_i z_i'^2, \quad (3.5b)$$

where $1/\kappa$ is the Debye screening length: it is seen that $2\Gamma \rightarrow \kappa$ as the density $\rho_i \rightarrow 0$. From Eqs. (3.5a) and (2.52) we have

$$-\Gamma(z_i + \sigma_i N_i) = N_i + \pi\sigma_i P_n/(2\Delta) - \tau_i \quad (3.6)$$

or

$$z_i' = z_i + N_i \sigma_i = \{z_i - \pi\sigma_i^2 P_n/(2\Delta) + \sigma_i \tau_i\}/(1 + \Gamma\sigma_i). \quad (3.7)$$

Also P_n defined in Eq. (2.50) can be written as in terms of Γ and τ_i . To do this start with Eq. (3.7) multiply by $\rho_i \sigma_i$ and sum over i which leads to another expression for P_n :

$$P_n = P_n^0 + \Omega^{-1} \sum_i \rho_i \sigma_i^2 \tau_i (1 + \Gamma\sigma_i)^{-1}, \quad (3.8)$$

where

$$P_n^0 = \Omega^{-1} \sum_i \rho_i z_i \sigma_i (1 + \Gamma\sigma_i)^{-1}, \quad (3.9)$$

$$\Omega = 1 + (\pi/2\Delta) \sum_k [\rho_k \sigma_k^3 / (1 + \Gamma\sigma_k)]. \quad (3.10)$$

Note that τ_i is zero when there is no stickiness and the expressions for Γ and P_n then reduce to Blum's results for unsymmetrical electrolytes. Substituting B_i from Eq. [2.42(b)] and T_{ij} from Eq. (2.54) into Eq. (2.56), we can get a rather simple expression for τ_i :

$$\tau_i = 2\nu_j(z_j + \sigma_j N_j)/\sigma_{ij} = 2\nu_j z_j'/\sigma_{ij} \quad (j \neq i), \quad (3.11)$$

with

$$\nu_j = \pi\lambda\rho_j \sigma_j^3/12 \quad (j \neq i). \quad (3.12)$$

Combining Eqs. (3.11) with (3.7) leads to the solution for z_j' for a single electrolyte:

$$z_1' = [(1 + \Gamma\sigma_2)(z_1 - \pi\sigma_1^2 P_n/2\Delta) + (2\nu_2\sigma_1/\sigma_{12})(z_2 - \pi\sigma_2^2 P_n/2\Delta)]/\Pi, \quad (3.13a)$$

$$z_2' = [(1 + \Gamma\sigma_1)(z_2 - \pi\sigma_2^2 P_n/2\Delta) + (2\nu_1\sigma_2/\sigma_{12})(z_1 - \pi\sigma_1^2 P_n/2\Delta)]/\Pi, \quad (3.13b)$$

where

$$\Pi = (1 + \Gamma\sigma_1)(1 + \Gamma\sigma_2) - 4\sigma_1\sigma_2\nu_1\nu_2/\sigma_{12}^2. \quad (3.14)$$

Substituting Eq. (3.11) into P_n , we get the final solution for z_i' :

$$z_1' = \{(1 + \Gamma\sigma_2)z_1^0 + 2\nu_2 z_2^0 \sigma_1/\sigma_{12} + \pi\rho_1 \sigma_1^2 \nu_2 Z_\sigma / [\Delta\Omega\sigma_{12}(1 + \Gamma\sigma_1)]\}/\Omega_0, \quad (3.15a)$$

$$z_2' = \{(1 + \Gamma\sigma_1)z_2^0 + 2\nu_1 z_1^0 \sigma_2/\sigma_{12} - \pi\rho_2 \sigma_2^2 \nu_1 Z_\sigma / [\Delta\Omega\sigma_{12}(1 + \Gamma\sigma_2)]\}/\Omega_0, \quad (3.15b)$$

where

$$\Omega_0 = \Pi + (\pi\sigma_1^2 \sigma_2^2 / \Delta\Omega\sigma_{12}) \sum_{i,j} \rho_i \nu_j (1 - \delta_{ij}) + (2\pi\sigma_1 \sigma_2 \nu_1 \nu_2 / \Delta\Omega\sigma_{12}^2) \sum_i \rho_i \sigma_i^3 / (1 + \Gamma\sigma_i) \quad (3.16)$$

and

$$z_i^0 = z_i - \pi P_n^0 \sigma_i^2 / 2\Delta, \quad (3.17)$$

$$z_\sigma = z_1 \sigma_2^2 - z_2 \sigma_1^2. \quad (3.18)$$

Equations (3.15) together with Eq. (3.5a) give a self-contained set of equations for the parameter Γ , which can be solved by iteration once the sticky parameter λ is known. To determine λ we need another closure equation, which is discussed following the calculation of the contact value of the correlation function.

This is obtained by differentiating Eq. (2.16a) with respect to R and setting $r = \sigma_{ij}^+$:

$$\begin{aligned} & -2\pi\sigma_{ij}^+ h_{ij}(\sigma_{ij}^+) \\ & = -B_i a_j + \sum_k \rho_k \int_\lambda J'_{ik}(|\sigma_{ij}^+ - t|) Q'_{kj}(t) dt \\ & \quad - \sum_k \rho_k \int_\lambda J'_{ik}(|\sigma_{ij}^+ - t|) A_{kj} dt, \end{aligned} \quad (3.19)$$

which can be rewritten as

$$\begin{aligned}
 -2\pi\sigma_{ij}h_{ij}(\sigma_{ij}^+) &= -a_j[B_i + \pi\sum_k \rho_k z_k \sigma_{ik}^2 - 2\nu_j z_j/\sigma_{ij}] - 2\nu_j \sigma_j/\sigma_{ij}[Q_{jj} - \sigma_j Q_{jj}'/2] - 2\pi\sum_k \rho_k \sigma_k^2 [(\lambda_{ik}/2 + \sigma_k/3)Q_{kj}' \\
 &\quad - \sigma_k(\lambda_{ik}/6 + \sigma_k/8)Q_{kj}''] + 2\pi\sigma_i^2 \nu_i/\sigma_{ij} - \pi\lambda\sigma_{ij}\nu\delta_{ij}/3, \quad (3.20)
 \end{aligned}$$

where we have used Eqs. (1.4), (2.11d), and (2.25). Substituting Eqs. (2.47), (2.48) for Q_{ij}' and Q_{ij}'' and Eqs. (2.52) for a_i we find, after much algebra, that

$$\begin{aligned}
 g_{ij}(\sigma_{ij}^+) &= (\sigma_{ij} + \pi\xi_2\sigma_j \sigma_i/4\Delta)/(\Delta\sigma_{ij}) - Da_i a_j/(4\pi\sigma_{ij}) \\
 &\quad + g_{ij}^\lambda(\sigma_{ij}^+), \quad (3.21a)
 \end{aligned}$$

where

$$g_{ij}^\lambda(\sigma_{ij}^+) = -(1/(\Delta\sigma_{ij}^2))\sum_k \nu_k \sigma_k^2 \quad (i \neq j) \quad (3.21b)$$

or

$$\begin{aligned}
 g_{ii}^\lambda(\sigma_{ii}^+) &= -(1/(\Delta\sigma_{ii}^2))\sum_k \nu_k \sigma_k^2 \\
 &\quad + \lambda\sigma_{ij}\nu_j/(6\sigma_{ii}) \quad (i \neq j) \quad (3.21c)
 \end{aligned}$$

arises from the adhesive interactions determined by λ . It is seen that $g_{ij}(\sigma_{ij}^+) = g_{ji}(\sigma_{ji}^+)$ as required by symmetry. The first term in Eq. (3.21a) is a pure hard sphere contribution while the second term $Da_i a_j/2$ is the electrical contribution in the MSA to the distribution function at contact which also depends on λ . This term vanishes when the charges are zero. Thus Eq. (3.21) also provides the distribution functions at contact for adhesive nonelectrolytes when there is adhesion only between different species. When the stickiness is removed ($\nu_j = \nu_i = 0$) we get the known contact value for an unsymmetrical electrolyte.¹⁴ It is shown in Sec. IV that the earlier results for charged and uncharged systems are recovered in the equal size limit.

To determine the sticky parameter λ , make use of Eq. (1.10) and the definition $\xi = 1/\tau$, when we have

$$\lambda\tau = y_{12}(\sigma_{12}), \quad (3.22)$$

where stickiness is present only between oppositely charged ions. Here, $y_{12}(\sigma_{12}^+)$ can be determined by using different approximations.^{3,5} In the PY/MS and HNC/MS approximations,

$$y_{12}(\sigma_{12}) = g_{12}(\sigma_{12}^+) - c_{12}(\sigma_{12}^+) \quad (\text{PY/MS}), \quad (3.23a)$$

$$y_{12}(\sigma_{12}) = \exp[h_{12}(\sigma_{12}^+) - c_{12}(\sigma_{12}^+)] \quad (\text{HNC/MS}), \quad (3.23b)$$

where we have used the subscripts 1, 2 to express the two species explicitly and the correlation functions $g_{12}(\sigma_{12}^+)$ and $c_{12}(\sigma_{12}^+)$ are determined in the MS approximation. In either case since Γ is a function λ , Eq. (3.22), with (3.23a) or (3.23b), and Eq. (3.5a) have to be solved numerically for λ . Another way to determine λ , which makes use of liquid state approximations for the corresponding non-sticky reference system [see Eq. (1.12)] is discussed by us in Ref. 6.

In summary, the final solution of the unsymmetric SEM in the MSA is obtained from the simultaneous solution of Eq. (3.5a) and Eq. (3.22) for Γ and λ , in which z_i' are given in Eqs. (3.15a) and (3.15b).

IV. THE EQUAL SIZE LIMIT

Before we continue with the study of the thermodynamics of the adhesive electrolyte, we will check what happens when the ion sizes and valences are equal in magnitude. First recall for the totally symmetric electrolyte that $\sigma_i = \sigma_j = \sigma$, $z_i = -z_j$, $\rho_i = \rho_j = \rho$. Using these conditions, we have

$$\sigma_{ij} = \sigma, \quad \lambda_{ij} = 0, \quad (4.1)$$

$$\eta = \pi\rho\sigma^3/6, \quad x_i = 0, \quad (4.2)$$

$$\Delta = 1 - 2\eta, \quad (4.3)$$

$$\nu = \nu_1 = \nu_2 = \lambda\eta/2. \quad (4.4)$$

From Eqs. (3.15), it also follows that

$$z_1' + z_2' = 0, \quad (4.5)$$

which, together with Eq. (3.8), shows that

$$P_n = 0, \quad N_1 + N_2 = 0. \quad (4.6)$$

Substituting Eqs. (4.1)–(4.6) into Eq. (3.13), we are led to the simple expressions

$$z_i' = [z_i(1 + \Gamma\sigma) + 2\nu z_j]/[(1 + \Gamma\sigma)^2 - 4\nu^2] \quad (i \neq j) \quad (4.7a)$$

or

$$\begin{aligned}
 N_i \sigma = -z_i[\Gamma\sigma(1 + \Gamma\sigma) + 2\nu - 4\nu^2]/[(1 + \Gamma\sigma)^2 \\
 - 4\nu^2] \quad (4.7b)
 \end{aligned}$$

which, when substituted into Eq. (2.53), leads to

$$D = \sum_k \rho_k (z_k + N_k \sigma_k)^2 = (1 + \Gamma\sigma + 2\nu)^{-2} \sum_k \rho_k z_k^2 \quad (4.8)$$

Also substituting Eq. (4.8) and (2.8b) in (3.5), we have

$$2\Gamma\sigma(1 + \Gamma\sigma + 2\nu) = \sigma\alpha_0[\sum_k \rho_k z_k^2]^{1/2} = \kappa\sigma, \quad (4.9)$$

where κ is the Debye screening length defined by

$$\kappa^2 = (4\pi\beta e^2/\epsilon)\sum_k \rho_k z_k^2 \quad (4.10)$$

Equation (4.9) is a quadratic equation whose solution is

$$2\Gamma\sigma = -(1 + 2\nu) + [(1 + 2\nu)^2 + 2\kappa\sigma]^{1/2}, \quad (4.11)$$

where the sign in front of the root is the one which gives the known result in the MSA when the stickiness is turned off ($\nu = 0$). Combining Eqs. (2.42b), (2.29), (1.1), and (4.6), we have

$$N_i = B_i = \sum_k \rho_k z_k J_{ki} = -\rho_i z_i J_D \quad (i=1,2), \quad (4.12)$$

where we have used $z_i = -z_j$, $\rho_i = \rho_1 + \rho_2$ and the definition

$$J_D = (J_{12} - J_{11})/2. \quad (4.13)$$

The relation between J_D and Γ , from Eq. (4.12), (4.7), and (4.11), is

$$\rho_i \sigma J_D = (\Gamma \sigma + 2\nu)/(1 + \Gamma \sigma + 2\nu) \quad (4.14)$$

Combining (4.9) and (4.14) produces a quadratic equation for $\rho_i \sigma J_D$; the solution of which is

$$\rho_i \sigma J_D = \{(1 + \kappa \sigma + 2\nu) - [(1 + 2\nu)^2 + 2\kappa \sigma]^{1/2}\} / \kappa \sigma. \quad (4.15)$$

Except for a factor of 2π in the definition of J_D and a factor of 2 in the definition of ν , this is identical to the result given earlier by Rasaiah and Lee³ for an adhesive symmetrical electrolyte.

It follows from Eq. (3.21), that the distribution functions at contact, for the equal ion size case, are given by

$$g_{ij}(\sigma^+) = (1 + \eta)/\Delta^2 - (z_j/z_i)\Gamma^2/(\pi\rho_i\sigma) - (2\nu/\Delta) + \lambda\nu\delta_{ij}/6, \quad (4.16)$$

where we have used the fact that for the symmetrical case

$$a_j D = 2z_j \Gamma / (1 + \Gamma \sigma + 2\nu) \quad (4.17)$$

and

$$D = \rho_i z_i^2 (1 - \rho_i \sigma J_D)^2. \quad (4.18)$$

This result is also identical to the solution given earlier by Rasaiah and Lee.³

V. THERMODYNAMICS OF THE MODEL ADHESIVE ELECTROLYTE

We will now discuss the thermodynamics of the unsymmetric adhesive electrolyte. The excess energy per unit volume has the form

$$\begin{aligned} E^{\text{ex}} &= - \left(\frac{1}{2} \right) \sum_{i,j} \rho_i \rho_j \int_0^\infty \frac{d \exp[-\beta u_{ij}(r)]}{d\beta} \\ &\quad \times [y_{ij}(r) 4\pi r^2 dr] \\ &= - \left(\frac{1}{2} \right) \sum_{i,j} \rho_i \rho_j \int_0^{\sigma_{ij}^+} \frac{d \exp[-\beta u_{ij}(r)]}{d\beta} \\ &\quad \times [y_{ij}(r) 4\pi r^2 dr] \\ &\quad + \left(\frac{1}{2} \right) \sum_{i,j} \rho_i \rho_j \int_{\sigma_{ij}^+}^\infty u_{ij}(r) g_{ij}(r) 4\pi r^2 dr \\ &= E^{\text{ex},b} + E^{\text{ex},a}, \end{aligned} \quad (5.1)$$

where $u_{ij}(r)$ is defined in Eq. (1.2), $E^{\text{ex},a}$ is the excess energy of the charge interaction part given by

$$\begin{aligned} E^{\text{ex},a} &= \left(\frac{2\pi e^2}{\epsilon} \right) \sum_{i,j} \rho_i \rho_j z_i z_j \int_{\sigma_{ij}^+}^\infty r g_{ij}(r) dr \\ &= E^{\text{ex},c} - \left(\frac{2\pi e^2}{\epsilon} \right) \sum_{i,j} \rho_i \rho_j z_i z_j \int_0^{\sigma_{ij}^+} r g_{ij}(r) dr, \end{aligned} \quad (5.2a)$$

with

$$E^{\text{ex},c} = \left(\frac{2\pi e^2}{\epsilon} \right) \sum_{i,j} \rho_i \rho_j z_i z_j \int_0^\infty r g_{ij}(r) dr, \quad (5.2b)$$

and $E^{\text{ex},b}$ is the binding energy caused by the stickiness:

$$\begin{aligned} E^{\text{ex},b} &= - \left(\frac{1}{2} \right) \sum_{i,j} \rho_i \rho_j \\ &\quad \times \int_0^{\sigma_{ij}^+} \frac{d \exp[-\beta u_{ij}(r)]}{d\beta} y_{ij}(r) 4\pi r^2 dr \end{aligned} \quad (5.2c)$$

Substituting Eqs. (1.2d) and (1.10) into Eq. (5.2b), we have

$$\begin{aligned} E^{\text{ex},b} &= - 2\pi \epsilon_2 \sum_{i,j} \rho_i \rho_j (1 - \delta_{ij}) \\ &\quad \times \int_0^{\sigma_{ij}^+} \exp[\beta \epsilon_2 (1 - \delta_{ij})] y_{ij}(r) r^2 dr \\ &= - 2\pi \epsilon_2 \sum_{i,j} \rho_i \rho_j (1 - \delta_{ij}) [\sigma_{ij}^3 \zeta y_{ij}(\sigma_{ij}^+) / 12] \\ &= - (\epsilon_2 / 2) \sum_{i,j} \rho_i \rho_j \langle N_{ij} \rangle (1 - \delta_{ij}), \end{aligned} \quad (5.3)$$

where we have used Eqs. (1.3c) and (1.5). To derive the $E^{\text{ex},a}$, we rewrite (5.2a) in the more convenient form

$$\begin{aligned} E^{\text{ex},a} &= \left(\frac{e^2}{\epsilon} \right) \sum_i \rho_i z_i B_i - \left(\frac{2\pi e^2}{\epsilon} \right) \sum_{i,j} \rho_i \rho_j z_i z_j \int_0^{\sigma_{ij}^+} r g_{ij}(r) dr \\ &= \left(\frac{e^2}{\epsilon} \right) \sum_i \rho_i z_i N_i - \left(\frac{e^2}{2\epsilon \sigma_{ij}} \right) \sum_{i,j} \rho_i \rho_j z_i z_j \langle N_{ij} \rangle (1 - \delta_{ij}). \end{aligned} \quad (5.4)$$

From Eq. (3.6), we have

$$N_i = - [\Gamma z_i + \pi \sigma_i P_n / (2\Delta) - \tau_i] / (1 + \Gamma \sigma_i). \quad (5.5)$$

Substituting Eq. (5.5) into Eq. (5.4), we have

$$\begin{aligned} E^{\text{ex},a} &= - (e^2/\epsilon) \sum_i \rho_i z_i (1 + \Gamma \sigma_i)^{-1} [\Gamma z_i + \pi \sigma_i P_n / 2\Delta \\ &\quad - \tau_i] - (e^2/(2\epsilon \sigma_{ij})) \sum_{i,j} \rho_i \rho_j z_i z_j \langle N_{ij} \rangle (1 - \delta_{ij}). \end{aligned} \quad (5.6)$$

Finally, we have

$$\begin{aligned} E^{\text{ex}} &= - \sum_{i,j} \rho_i \rho_j \langle N_{ij} \rangle (1 - \delta_{ij}) [e^2 z_i z_j / (2\epsilon \sigma_{ij}) \\ &\quad + \epsilon_2 / 2] + E^{\text{ex},c}, \end{aligned} \quad (5.7a)$$

with

$$\begin{aligned} E^{\text{ex},c} &= - (e^2/\epsilon) \sum_i \rho_i z_i (1 + \Gamma \sigma_i)^{-1} [\Gamma z_i \\ &\quad + \pi \sigma_i P_n / (2\Delta) - \tau_i]. \end{aligned} \quad (5.7b)$$

It is seen from Eq. (5.7) that Blum's result for the primitive model electrolyte is recovered when the stickiness is taken away.

As discussed in many places,²⁻⁶ the change in Helmholtz free-energy caused by turning on the stickiness is given by

$$\begin{aligned} \Delta A^{\text{ex,st}}/(Nk_B T) &= [A^{\text{ex}}(\text{SEM}) - A^{\text{ex},0}(\text{PM})]/(Nk_B T) \\ &= - \left(\frac{\pi \rho_1 \rho_2 \sigma_{12}^3}{3 \rho_t} \right) \int_0^\xi y_{12}(\xi') d\xi' \\ &= - \left(\frac{4 \rho_1 \nu_2}{\rho_t} \right) [1 - \ln y_{12}(\lambda)] \\ &\quad - \left(\frac{\pi \rho_1 \rho_2 \sigma_{12}^3}{3 \rho_t} \right) \int_0^\lambda \ln y_{12}(\lambda') d\lambda', \end{aligned} \quad (5.8)$$

where $A^{\text{ex},0}$ (PM) is the excess Helmholtz free-energy of the corresponding charged system without stickiness which is the primitive model (PM) electrolyte. Here, $y_{12}(\lambda)$ can be found either from PY/MS or HNC/MS approximation or from our approximation.⁶ In HNC/MS approximation [see Eq. (3.23b)], we find using Eqs. (3.21), (2.5), and (2.6) that

$$\begin{aligned} \Delta A^{\text{ex,st}}/Nk_B T &= - \left(\frac{4 \rho_1 \nu_2}{\rho_t} \right) \left\{ 1 + \frac{1}{2 \Delta \sigma_{12}^2} \sum_k \nu_k \sigma_k^2 + \frac{D a_j}{4 \pi \sigma_{12}} \right\} \\ &\quad + \frac{\rho_1 \rho_2 \sigma_{12}^2}{12 \rho_t} \int_0^\lambda [D(\lambda') a_2(\lambda') a_1(\lambda') d\lambda', \end{aligned} \quad (5.9)$$

while in the PY/MS approximation, no simple expression is obtained for Eq. (5.8). The total excess Helmholtz free-energy can now be expressed as

$$\Delta A^{\text{ex}}/(Nk_B T) = [\Delta A^{\text{ex},0}(\text{PM}) + \Delta A^{\text{ex,st}}]/(Nk_B T), \quad (5.10)$$

where $\Delta A^{\text{ex},0}$ (PM) is known analytically in the mean spherical approximation and is given by¹¹

$$\begin{aligned} \Delta A^{\text{ex},0}(\text{PM})/(Nk_B T) &= (A - A^{\text{hs}})/(Nk_B T) \\ &= E^{\text{ex},0}/(Nk_B T) + \Gamma^0/(3 \pi \rho_t) \end{aligned} \quad (5.11)$$

and $E^{\text{ex},0}$ and Γ^0 are the energy and shielding parameter for the primitive model electrolyte.¹¹

When the charges are turned off, the MS approximation becomes identical to the PY approximation and we

can determine the excess free-energy difference between sticky nonelectrolytes (sn) and hard spheres (hs) analytically in the two approximations that have been considered! From Eq. (5.9) we have in the HNC/PY approximation

$$\frac{A^{\text{ex,sn}} - A^{\text{ex,hs}}}{Nk_B T} = - \frac{4 \rho_1 \nu_2}{\rho_t} \left\{ 1 + \frac{1}{2 \Delta \sigma_{12}^2} \sum_k \nu_k \sigma_k^2 \right\} \quad (\text{HNC/PY}) \quad (5.12)$$

and from Eqs. (3.23) and (5.8) we find that in the PY approximation

$$\frac{A^{\text{ex,sn}} - A^{\text{ex,hs}}}{Nk_B T} = \frac{m \pi \rho_1 \rho_2 \sigma_{12}^3}{3 n \rho_t} \ln \frac{m - n \lambda}{m} \quad (\text{PY}), \quad (5.13)$$

where $m = (1/(\sigma_{12} \Delta)) [\sigma_{12} + \pi \xi_2 \sigma_2 \sigma_1 / (4 \Delta)]$ and $n = (\pi \sigma_{12} / (12 \Delta)) \sum_k \rho_k \sigma_k^2$. When the sizes are the same, the corresponding results for sticky nonelectrolytes are recovered.⁵ The osmotic coefficient and activity coefficient can now be obtained in the usual way by differentiation with respect to the electrolyte concentration.²⁻⁵

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