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Thermodynamic Properties of Aqueous Solutions: Non-symmetric sticky electrolytes with overlap between ions in the HNC and mean-spherical approximation

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Based on a sticky-electrolyte model, the Ornstein-Zernike integral equation is solved for non-symmetric electrolytes with stickiness between ions at various distances equal to or less than the collision diameter. The HNC approximation is used for the closure inside the hard core, while the mean-spherical approximation for electrostatic interactions is used for the closure outside the hard core. Expressions for correlation functions and thermodynamic properties in term of the sticky parameters are derived. Numerical results are presented for various cases.

I. INTRODUCTION

Blum and coworkers[1-3] have extensively studied application of the mean-spherical approximation (MSA) for symmetric and non-symmetric electrolytes. By adopting Baxter's factorization procedure, the Fourier-transform of the Ornstein-Zernike equation was decomposed into two fundamental equations: one for the total correlation function and the other for the direct correlation function. After a lengthy and tedious derivation, they were able to relate analytically all configurational thermodynamic functions to a scaling parameter that was solved by a simple iteration procedure for given conditions. Blum's theory is the basis of several engineering-oriented models (e.g. Ball, Planche, Furst and Renon[4]). The approximate

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explicit solution for the scaling parameter presented by Harvey, Copeman and Prausnitz[5] significantly simplifies the calculation.

To take into account ion-pairs and other cluster formation, a more realistic model called sticky-electolyte model (SEM) was developed by several authors[6-8]. For symmetric electrolytes, Lee, Rasaiah, Cummings and Zhu[9-14] introduced ion association in the Hamiltonian through a delta-function interaction between oppositely charged ions at a distance equal to or less than the collision diameter. The analytical expressions for the internal energy and the Helmholtz function were obtained through the cavity correlation function. Excess internal energies, excess Helmholtz functions, osmotic coefficients and pair correlation functions were calculated for some electrolyte solutions.

For non-symmetric electrolytes, Herrera and Blum[15,16] and Zhu and Rasaiah[17] derived equations based on a sticky-electrolyte model. However, the sticky position is restricted to adhesion between oppositely charged ions at the hard-core surface. Regrettably, no numerical results were shown. Recently, Blum and Bernard[18,19] have reported further efforts for mixtures of charged hard spheres using Wertheim's formalism with a new exponential approximation.

Because ion pairs formed by strong (chemical) forces always exhibit overlap between ions, a contact-sphere model provides only an approximation. In this work, we solve the Ornstein-Zernike equation for sticky non-symmetric electrolytes based on a more general model in which the sticky position can be equal to or less than the collision diameter $\sigma_{ij}=(\sigma_i+\sigma_j)/2$, where σ_i and σ_j are the hard-core diameters of ions i and j. The sticky distance L_{ij} for an i-j pair may select any value between the limits:

$$\sup(\sigma_i/2, \sigma_j/2) < L_{ij} \le \sigma_{ij} \tag{1.1}$$

where sup(x,y) means that the maximum of either x or y is chosen.

In Sec.II, we briefly introduce the two fundamental equations obtained by factorizing the Ornstein-Zernike equation with results similar to those given by Herrera, Blum, Zhu and Rasaiah[15,16,17]. In Sec.III, we discuss in detail the solution of the fundamental equations for SEM. Because the sticky distance L_{ij} may be less than the collision diameter σ_{ij}, the symmetry conditions will not yield a simple scaling parameter. For a multicomponent system containing K ions, characteristic parameters N_i (i=1,2,...,K) are obtained by solving a set of non-linear equations. An expression for calculating the direct correlation function is also derived; this expression allows us to obtain the total correlation function inside the hard core by using either

the PY or the HNC closure condition. We then derive expressions for thermodynamic properties in Sec. IV: the excess internal energy is expressed analytically through N_i (i=1,2,...,K); the excess Helmholtz function is expressed through the cavity correlation function at the sticky position. The cavity correlation function is determined analytically by N_i (i=1,2,...,K). Expressions for other thermodynamic properties are also given. Finally, Sec.V presents results of numerical calculations, followed by a short discussion.

II. FUNDAMENTAL EQUATIONS FROM FACTORIZATION OF THE ORNSTEIN-ZERNIKE INTEGRAL (OZ) EQUATION

We consider a non-symmetric-electrolyte solution containing K ions with different sizes σ_i and charges $Z_i e$ (i=1,2,...,K) in a solvent medium. Here e is the unit charge. In the framework of the sticky-electrolyte model (SEM), the interaction potential $u_{ij}(r)$ comprises three contributions: the hard-sphere contribution (hs), the sticky contribution (st) and the electrostatic contribution (el):

$$u_{ij}(r) = u_{ij}^{\mathrm{hs}}(r) + u_{ij}^{\mathrm{st}}(r) + u_{ij}^{\mathrm{el}}(r) \tag{2.1}$$

where r is the center-to-center interion distance.

$$u_{ij}^{\mathrm{hs}}(r) = \infty \qquad r < \sigma_{ij}, \quad r \neq L_{ij}$$

$$= 0 \qquad r > \sigma_{ij}, \quad r = L_{ij} \tag{2.2}$$

$$u_{ij}^{\mathrm{st}}(r) = -\beta^{-1} \ln\left[L_{ij}\,\delta(r - L_{ij}) / 12\tau_{ij}\right] \tag{2.3}$$

$$u_{ij}^{\mathrm{el}}(r) = Z_i Z_j e^2 / 4\pi\varepsilon r \tag{2.4}$$

Here, $\beta = 1/kT$; τ_{ij} is the inverse of the sticky coefficient ξ_{ij} which measures the strength of the stickiness, $\tau_{ij}^{-1} = \xi_{ij}$; ε is the permittivity of the solvent medium. Eq.(2.3) indicates that there is a Dirac δ function interaction at L_{ij} , that is, a stickiness at this position. Electroneutrality demands that

$$\Sigma_k \rho_k Z_k = 0 \tag{2.5}$$

where ρ_k is the number density of ion k. The state of the electrolyte solution is fixed by all ρ_i , σ_i and τ_{ij}.

For this system, the OZ integral equation is

$$h_{ij}(r) - c_{ij}(r) = \Sigma_k \rho_k \int dr'\, c_{ik}(|r - r'|) h_{kj}(r') \tag{2.6}$$

where the total correlation function $h_{ij}(r)$ is defined by the pair correlation function $g_{ij}(r)$, $[h_{ij}(r) = g_{ij}(r) - 1]$, $c_{ij}(r)$ is the direct correlation function. In terms of a virial expansion, the total correlation function for SEM has the form[9-12],

$$h_{ij}(r) = -1 + \Lambda_{ij} L_{ij} \delta(r - L_{ij}) / 12 \qquad r < \sigma_{ij} \qquad (2.7)$$

where Λ_{ij} is a sticky parameter (yet to be determined) that is a function of σ_i, ρ_i and τ_{ij}.

However, eq.(2.3) is not closed, i.e., it is insufficient. An independent relation between $h_{ij}(r)$ and $c_{ij}(r)$ is needed to solve the equation. Two closure relations are commonly used inside the hard core: the Percus-Yevick (PY) approximation and the Hypernetted Chain (HNC) approximation,

$$y_{ij}(r) = g_{ij}(r) - c_{ij}(r) \qquad \text{(PY)} \qquad r < \sigma_{ij} \qquad (2.8)$$

$$y_{ij}(r) = \exp[h_{ij}(r) - c_{ij}(r)] \qquad \text{(HNC)} \qquad r < \sigma_{ij} \qquad (2.9)$$

where $y_{ij}(r)$ is the cavity correlation function defined by

$$y_{ij}(r) = g_{ij}(r) \exp[\beta u_{ij}(r)] \qquad (2.10)$$

Outside the hard core, the mean-spherical approximation (MSA) is usually adopted; it is a first-order approximation of HNC, i.e.

$$c_{ij}(r) = -\beta u_{ij}(r) = -\beta u_{ij}^{\text{el}}(r) \qquad r > \sigma_{ij} \qquad (2.11)$$

To avoid divergence of the integrals that will appear in the Fourier transform, the long-range electrostatic interaction is revised with the use of a parameter μ,

$$u_{ij}^{\text{el}}(r) = \lim_{\mu \to 0} \left[Z_i Z_j e^2 / (4\pi r \varepsilon) \exp(-\mu |r|) \right] \qquad r > \sigma_{ij} \qquad (2.12)$$

Thus, the direct correlation function for all r can be expressed as

$$c_{ij}(r) = c_{ij}^{o}(r) + \lim_{m \to 0} \left[-Z_i Z_j \beta e^2 / (4\pi r \varepsilon) \exp(-\mu |r|) \right] \qquad (2.13)$$

where $c_{ij}^{o}(r)$ is the short-range contribution, that is equal to zero outside the hard core.

The Fourier transforms of $c_{ij}(r)$ and $h_{ij}(r)$ are

$$\tilde{C}_{ij}(k) = \sqrt{\rho_i \rho_j} \int c_{ij}(r) \exp(i\mathbf{k} \cdot \mathbf{r}) \mathrm{d}\mathbf{r} = 4\pi \sqrt{\rho_i \rho_j} \int_0^\infty c_{ij}(r) \sin(kr)(r/k) \mathrm{d}r \qquad (2.14)$$

$$\tilde{H}_{ij}(k) = \sqrt{\rho_i \rho_j} \int h_{ij}(r) \exp(i\mathbf{k} \cdot \mathbf{r}) \mathrm{d}\mathbf{r} = 4\pi \sqrt{\rho_i \rho_j} \int_0^\infty h_{ij}(r) \sin(kr)(r/k) \mathrm{d}r \qquad (2.15)$$

Eq. (2.6) is then transformed into:

$$\delta_{ij} = \Sigma_k \left[\delta_{ik} + \tilde{H}_{ik}(k) \right] \left[\delta_{kj} - \tilde{C}_{kj}(k) \right] \qquad (2.16)$$

Taking the Fourier transform of eq.(2.13), we have

$$\tilde{C}_{ij}(k) = \tilde{C}_{ij}^{o}(k) - \lim_{\mu \to 0} \alpha_{ij} / (k^2 + \mu^2) \qquad (2.17)$$

where $\tilde{C}_{ij}^{o}(k)$ is defined as in eq. (2.14); α_{ij} is given by:

$$\alpha_{ij} = \sqrt{\rho_i \rho_j} Z_i Z_j \beta e^2 / \varepsilon = \alpha_0^2 \sqrt{\rho_i \rho_j} Z_i Z_j \tag{2.18}$$

$$\alpha_0^2 = \beta e^2 / \varepsilon \tag{2.19}$$

Substitution of eq.(2.17) into eq.(2.16) yields the corresponding OZ equation in Fourier space:

$$\delta_{ij} = \Sigma_k \left[\delta_{ik} + \tilde{H}_{ik}(k)\right]\left[\delta_{kj} - \tilde{C}_{kj}^{o}(k) + \alpha_{kj} / (k^2 + \mu^2)\right] \tag{2.20}$$

Integrating eqs.(2.14) and (2.15) by parts, we find

$$\tilde{C}_{ij}^{o}(k) = 2\sqrt{\rho_i \rho_j} \int_0^\infty \cos(kr) S_{ij}(r) \mathrm{d}r \tag{2.21}$$

$$\tilde{H}_{ij}(k) = 2\sqrt{\rho_i \rho_j} \int_0^\infty \cos(kr) J_{ij}(r) \mathrm{d}r \tag{2.22}$$

where

$$S_{ij}(r) = 2\pi \int_r^\infty c_{ij}^{o}(t) t \, \mathrm{d}t \tag{2.23}$$

$$J_{ij}(r) = 2\pi \int_r^\infty h_{ij}(t) t \, \mathrm{d}t \tag{2.24}$$

The right-hand side of eq.(2.20) can be factorized following the method of Baxter[20] via the Wiener-Hopf factorization method extended by Blum[1-3] to coulombic systems with a function $\tilde{Q}_{ij}(k)$ (called Baxter function) defined as:

$$\tilde{Q}_{ij}(k) = \delta_{ij} - \sqrt{\rho_i \rho_j} \int_{\lambda_{ji}}^{\sigma_{ji}} Q_{ij}(r) \exp(ikr) \mathrm{d}r + A_{ij} \sqrt{\rho_i \rho_j} \int_{\lambda_{ji}}^{\infty} \exp[r(ik - \mu)] \mathrm{d}r \tag{2.25}$$

where A_{ij} is determined later. We define

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \tag{2.26}$$

$$\lambda_{ij} = (\sigma_i - \sigma_j)/2 \tag{2.27}$$

The OZ equation, eq.(2.20), is then decomposed into two separate equations, one for $c_{ij}(r)$ and the other for $h_{ij}(r)$:

$$\delta_{ij} - \tilde{C}_{ij}^{o}(k) + \alpha_{ij} / (k^2 + \mu^2) = \sum_k \tilde{Q}_{ik}(k) \tilde{Q}_{jk}(-k) \tag{2.28}$$

$$\sum_k \left[\delta_{ik} + \tilde{H}_{ik}(k)\right] \tilde{Q}_{kj}(k) = \left[\tilde{Q}^T(-k)\right]_{ij}^{-1} \tag{2.29}$$

The inverse Fourier transforms of eqs. (2.28) and (2.29) are

$$\begin{aligned} S_{ij}(r) = {} & \alpha_{ij} \exp(-\mu|r|) / 2\mu\sqrt{\rho_i \rho_j} - \Sigma_k \rho_k A_{ik} A_{jk} \exp(-\mu|r| - 2\mu\lambda_{kj}) / 2\mu \\ & + [Q_{ij}(r) - A_{ij}] H(r - \lambda_{ji}) + [Q_{ji}(-r) - A_{ji}] H(-r - \lambda_{ij}) \\ & - \Sigma_k \rho_k \int_{\sup(\lambda_{ki},\, r+\lambda_{kj})}^{\inf(\sigma_{ki},\, r+\sigma_{kj})} Q_{ik}(t) Q_{jk}(t - r) dt \\ & + \Sigma_k \rho_k A_{jk} \int_{\sup(\lambda_{ki},\, r+\lambda_{kj})}^{\sigma_{ki}} Q_{ik}(t) dt + \Sigma_k \rho_k A_{ik} \int_{\sup(\lambda_{kj},\, -r+\lambda_{ki})}^{\sigma_{kj}} Q_{jk}(t) dt \end{aligned} \tag{2.30}$$

$$J_{ij}(r)=[Q_{ij}(r)-A_{ij}/2]H(r-\lambda_{ji})+\sum_k \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} J_{ik}(|r-t|)\,Q_{kj}(t)\mathrm{d}t$$
$$-\sum_k \rho_k \int_{\lambda_{jk}}^{r} J_{ik}(|r-t|)\,A_{kj}\mathrm{d}t \tag{2.31}$$

where H is the Heaviside function; sup means that the maximum is chosen; inf means that the minimum is chosen. Eq.(2.30) is responsible for solving the direct correlation function $c_{ij}(r)$ through $S_{ij}(r)$, while eq.(2.31) is responsible for solving the total correlation function $h_{ij}(r)$ through $J_{ij}(r)$. If $r>\lambda_{ji}$, eq.(2.31) becomes

$$J_{ij}(r)=[Q_{ij}(r)-A_{ij}/2]+\sum_k \rho_k \int_{\lambda_{jk}}^{\sigma_{jk}} J_{ik}(|r-t|)\,Q_{kj}(t)\mathrm{d}t$$
$$-\sum_k \rho_k \int_{\lambda_{jk}}^{r} J_{ik}(|r-t|)\,A_{kj}\mathrm{d}t \tag{2.32}$$

From eq.(2.30), when μ approches zero, we obtain:

$$\alpha_{ij}=\sqrt{\rho_i\rho_j}\sum_k \rho_k A_{ik}A_{jk} \tag{2.33}$$

Compared with eqs.(2.18) and (2.19), we have

$$A_{ij}=a_j Z_i \tag{2.34}$$
$$\sum_k \rho_k a_k^2=\alpha_0^2=\beta e^2/\varepsilon \tag{2.35}$$

From these two equations we can see that, instead of A_{ij}, another characteristic parameters a_i (i=1,2,...,K) must be determined. Eq.(2.35) provides a normalization constraint for parameters a_i. Applying electroneutrality for an ion and its ion atmosphere, we also have

$$4\pi\sum_k \rho_k Z_k \int_0^\infty h_{ik}(t)t^2dt=-Z_i \tag{2.36}$$
$$\sum_k \rho_k A_{kj}\int_0^\infty J_{ik}(t)dt=-A_{ij}/2 \tag{2.37}$$

These two equations have been used in the derivation of eq.(2.31).

Eqs.(2.30) and (2.31) are two fundamental equations for SEM similar to those given by Herrera, Blum, Zhu and Rasaiah[2,15,16,17]. However, there are minor differences between eq.(2.30) of this work and those published previously, probably because of misprints.

III. SOLUTION OF THE TWO FUNDAMENTAL EQUATIONS FOR SEM

When state conditions σ_i, ρ_i and τ_{ij} are fixed for a solution containing K ions, we have to find $2K^2$ functions $J_{ij}(r)$ and $S_{ij}(r)$, K^2 Baxter functions $Q_{ij}(r)$ and K parameters a_j, as shown in the fundamental equations, eqs.(2.30) and (2.31), as well as by eq.(2.34) which relates the A_{ij}'s to those a_j's. However, this task can be simplified. We first focus attention on

the solution of the second fundamental equation, eq.(2.31). We then solve the first fundamental equation, eq.(2.30). Finally, we use the cavity correlation function to obtain a self-consistent result for the sticky parameter Λ . The calculational procedure consists of six parts.

1. Polynomial Expansion of the Baxter function

Considering the continuity of $S_{ij}(r)$ at $r=\sigma_{ij}$, in the MSA the Baxter functions $Q_{ij}(r)$ are zero beyond the contact distance:

$$Q_{ij}(r)=0 \qquad r>\sigma_{ij} \qquad (3.1)$$

On the other hand, from eq.(2.7), $h_{ij}(r) = -1$ when $r<\sigma_{ij}$ (except $r=L_{ij}$ because of the stickiness). Therefore, we have from eq.(2.24),

$$J_{ij}'''(r)=0 \qquad r<\sigma_{ij},\ r\neq L_{ij} \qquad (3.2)$$

The third-order derivative of $Q_{ij}(r)$ should also be zero as shown by eq.(2.31):

$$Q_{ij}'''(r)=0 \qquad r<\sigma_{ij},\ r\neq L_{ij} \qquad (3.3)$$

From eqs.(2.7) and (2.24) we obtain

$$J_{ij}(L_{ij}^{-})-J_{ij}(L_{ij}^{+})=\pi\Lambda_{ij}L_{ij}^{2}/6 \qquad (3.4)$$

By using eq.(2.31),

$$J_{ij}(L_{ij}^{-})-J_{ij}(L_{ij}^{+})=Q_{ij}(L_{ij}^{-})-Q_{ij}(L_{ij}^{+}) \qquad (3.5)$$

Therefore, we can write a second-order polynomial expansion for $Q_{ij}(r)$ with respect to $r=\sigma_{ij}$,

$$Q_{ij}(r)=(r-\sigma_{ij})Q_{ij}'+(r-\sigma_{ij})^2Q_{ij}''/2+Q_{ij}^{\lambda}H(-r+L_{ij}) \qquad \lambda_{ji}\le r\le\sigma_{ij} \qquad (3.6)$$

where Q_{ij}^{λ} stands for the contribution to $Q_{ij}(r)$ at L_{ij} owing to stickiness, determined by the (as yet) unknown sticky parameter Λ_{ij},

$$Q_{ij}^{\lambda}=Q_{ij}(L_{ij}^{-})-Q_{ij}(L_{ij}^{+})=\pi\Lambda_{ij}L_{ij}^{2}/6 \qquad (3.7)$$

Q_{ij}'' is independent of ion i (indicated in the details of the derivation) and therefore replaced by Q_{j}''. From the above analysis, the K^2 Baxter functions $Q_{ij}(r)$ can be determined by (K^2 +K) expansion coefficients Q_{ij}' and Q_{j}''.

2. Expressions for polynomial coefficients of the Baxter function

When we take the first and second derivatives of eq.(2.32) in the range $\lambda_{ji} < r < \sigma_{ij}$, we have

$$-2\pi r\, h_{ij}(r) = Q_{ij}^{'}(r) - 2\pi\Sigma_k \rho_k \int_{\lambda_{ji}}^{\sigma_{ij}} (r-t) h_{ik}(|r-t|) Q_{kj}(t)dt$$
$$+ 2\pi\Sigma_k \rho_k A_{kj} \int_{\lambda_{ji}}^{r} (r-t) h_{ik}(|r-t|)dt - \Sigma_k \rho_k J_{ik} A_{kj} \tag{3.8}$$

$$-2\pi[h_{ij}(r) + r\, h_{ij}^{'}(r)] = Q_j^{''}(r)$$
$$-2\pi\Sigma_k \rho_k \int_{\lambda_{ji}}^{\sigma_{ij}} \left[h_{ik}(|r-t|) + |r-t| h_{ik}^{'}(|r-t|)\right] Q_{kj}(t)dt \tag{3.9}$$
$$+ 2\pi\Sigma_k \rho_k A_{kj} \int_{\lambda_{ji}}^{r} \left[h_{ik}(|r-t|) + |r-t| h_{ik}^{'}(|r-t|)\right] dt$$

where superscripts ′ and ″ represent first-order and second-order derivatives with respect to r, respectively.

$$J_{ij} = J_{ij}(0) = 2\pi \int_0^{\infty} h_{ij}(t)\, t\, \mathrm{d}t \tag{3.10}$$

Substituting $r = \sigma_j / 2$ and remembering that $L_{ij} > \sup(\sigma_i / 2,\ \sigma_j / 2)$, we obtain

$$\sigma_{ij} Q_j^{''} = Q_{ij}^{'} - 2\pi\Sigma_k \rho_k K_{kj}^1 - a_j (B_i + \frac{\pi}{4}\chi_2 - \frac{\pi}{2}\sigma_j \chi_1) \tag{3.11}$$

$$Q_j^{''} = 2\pi + \pi a_j \chi_1 - 2\pi\Sigma_k \rho_k K_{kj}^0 \tag{3.12}$$

where

$$K_{ij}^0 = \int_{\lambda_{ji}}^{\sigma_{ij}} Q_{ij}(t)dt \tag{3.13}$$

$$K_{ij}^1 = \int_{\lambda_{ji}}^{\sigma_{ij}} Q_{ij}(t)\, t dt \tag{3.14}$$

$$\chi_n = \Sigma_k \rho_k \sigma_k^n Z_k \tag{3.15}$$

$$B_i = \Sigma_k \rho_k Z_k J_{ki} \tag{3.16}$$

Substitution of eq.(3.6) into eqs.(3.11) and (3.12) yields

$$Q_{ij}^{'} = -\frac{2}{\sigma_i^2} K_{ij}^0 + \frac{\sigma_i}{3} Q_j^{''} + \frac{2}{\sigma_i^2} Q_{ij}^{\lambda}(L_{ij} - \lambda_{ji}) \tag{3.17}$$

$$K_{ij}^1 = \frac{3\sigma_j - \sigma_i}{6}\left[K_{ij}^0 - Q_{ij}^{\lambda}(L_{ij} - \lambda_{ji})\right] - \frac{\sigma_i^4}{72} Q_j^{''} + \frac{1}{2} Q_{ij}^{\lambda}(L_{ij}^2 - \lambda_{ji}^2) \tag{3.18}$$

After tedious algebra, we obtain

$$K_{ij}^0 = K_{ij}^{00} + K_{ij}^{0\lambda} \tag{3.19}$$

$$K_{ij}^{00} = \frac{\sigma_i^2}{2}\left\{\frac{\pi}{\nabla}\left[\frac{\sigma_i}{3}\left(1 + \frac{\pi\sigma_j \zeta_2}{2\nabla}\right) + \sigma_j\right] + a_j (N_i + \frac{\pi\sigma_i}{6\nabla} P_n)\right\} \tag{3.20}$$

$$K_{ij}^{0\lambda} = Q_{ij}^{\lambda}(L_{ij} - \lambda_{ji}) - \frac{\pi\sigma_i^2}{2\nabla}\left[(\Omega_2^{(j)} - \sigma_j\Omega_1^{(j)}) - \sigma_i\Omega_1^{(j)}/3\right]$$
$$-\frac{\pi^2\sigma_i^3\zeta_2}{12\nabla^2}(\Omega_2^{(j)} - \sigma_j\Omega_1^{(j)}) \tag{3.21}$$

where

$$\zeta_n = \sum_k \rho_k \sigma_k^n \tag{3.22}$$

$$\nabla = 1 - \frac{\pi}{6}\zeta_3 \tag{3.23}$$

$$N_i = B_i + \frac{\pi}{4\nabla}[\chi_2 + \frac{2}{3}\sum_k \rho_k \sigma_k{}^3 B_k] \tag{3.24}$$

$$P_n = \sum_k \rho_k \sigma_k (N_k\sigma_k + Z_k) \tag{3.25}$$

$$\Omega_n{}^{(j)} = \sum_k \rho_k Q_{kj}^{\lambda}(L_{kj}{}^n - \lambda_{jk}{}^n) \tag{3.26}$$

Substituting eqs.(3.18) and (3.19) into eqs.(3.11) and (3.12), we have

$$Q_j^{''} = 2\pi + \pi a_j \chi_1 - 2\pi\sum_k \rho_k K_{kj}^0 = Q_j^{''0} + Q_j^{''\lambda} \tag{3.27}$$

$$Q_j^{''0} = \frac{2\pi}{\nabla}(1 + \frac{\pi}{2\nabla}\sigma_j\zeta_2) + \frac{\pi a_j P_n}{\nabla} \tag{3.28}$$

$$Q_j^{''\lambda} = \frac{2\pi}{\nabla}\left[-\Omega_1{}^{(j)} + \frac{\pi\zeta_2}{2\nabla}(\Omega_2{}^{(j)} - \sigma_j\Omega_1{}^{(j)})\right] \tag{3.29}$$

$$Q_{ij}^{'} = -\frac{2}{\sigma_i^2}K_{ij}^0 + \frac{\sigma_i}{3}Q_j^{''} + \frac{2}{\sigma_i^2}Q_{ij}^{\lambda}(L_{ij} - \lambda_{ji}) = Q_{ij}^{'0} + Q_{ij}^{'\lambda} \tag{3.30}$$

$$Q_{ij}^{'0} = \frac{\pi}{\nabla}\left[\sigma_i\left(1 + \frac{\pi\sigma_j\zeta_2}{2\nabla}\right) + \sigma_j\right] + a_j(N_i + \frac{\pi\sigma_i}{2\nabla}P_n) \tag{3.31}$$

$$Q_{ij}^{'\lambda} = \frac{\pi}{\nabla}\left[(\Omega_2{}^{(j)} - \sigma_j\Omega_1{}^{(j)}) - \sigma_i\Omega_1{}^{(j)} + \frac{\pi\sigma_i\zeta_2}{2\nabla}(\Omega_2{}^{(j)} - \sigma_j\Omega_1{}^{(j)})\right] \tag{3.32}$$

For Baxter functions at λ, we have

$$Q_{ij}(\lambda_{ji}) = -\sigma_i Q_{ij}^{'} + \frac{1}{2}\sigma_i{}^2 Q_j^{''} + Q_{ij}{}^{\lambda}$$
$$= -a_j\sigma_i N_i - \pi\sigma_i\sigma_j/\nabla + Q_{ij}{}^{\lambda} - \pi\sigma_i(\Omega_2{}^{(j)} - \sigma_j\Omega_1{}^{(j)})/\nabla \tag{3.33}$$

$$Q_{ji}(\lambda_{ij}) = -\sigma_j Q_{ji}^{'} + \frac{1}{2}\sigma_j{}^2 Q_i^{''} + Q_{ji}{}^{\lambda}$$
$$= -a_i\sigma_j N_j - \pi\sigma_j\sigma_i/\nabla + Q_{ji}{}^{\lambda} - \pi\sigma_j(\Omega_2{}^{(i)} - \sigma_i\Omega_1{}^{(i)})/\nabla \tag{3.34}$$

From eqs.(3.27) and (3.30) we see that, by using eqs.(3.8) and (3.9) (the numbers of these equations are K^2 and K, respectively), all (K^2 +K) expansion coefficients $Q_{ij}^{'}$ and $Q_j^{''}$ are finally expressed as functions of 2K characteristic parameters N_j and a_j (j =1,2,...,K).

3. Relations between N_j and a_j

From eq.(2.31) at $r=\sigma_j/2$, combined with eqs.(3.16) and (3.24), we find the relation between N_j or B_j and a_j :

$$a_j = -\tfrac{2}{D}(N_j + \pi\sigma_j P_n / 2\nabla + \psi_j^{\lambda}) \tag{3.35}$$

where

$$D = \sum_k \rho_k (N_k\sigma_k + Z_k)^2 \tag{3.36}$$

$$\psi_j^{\lambda} = -\sum_k \rho_k Q_{kj}^{\lambda}[N_k(L_{kj} - \lambda_{jk}) + Z_k] + \tfrac{\pi}{2\nabla} P_n(\Omega_2^{(j)} - \sigma_j\Omega_1^{(j)}) \tag{3.37}$$

Further,

$$B_j = \sum_k \rho_k Z_k\left[(\frac{\sigma_j}{2} - \sigma_{kj})Q_{kj}' + (\frac{\sigma_j}{2} - \sigma_{kj})^2 Q_j'' / 2 + Q_{kj}^{\lambda}\right] \tag{3.38}$$
$$- a_j\sum_k \rho_k Z_k^2 / 2 + \sum_k \rho_k B_k K_{kj}^0 + \sum_k \rho_k B_k A_{kj}(\lambda_{jk} - \sigma_j / 2) \quad .$$

By using eq.(3.35), the only remaining unknown parameters are K characteristic parameters N_j, where $j = 1,2,...,K$.

4. Set of K equations to obtain N_j

We use the symmetry property of the direct correlation function $c_{ij}(r)$ and the corresponding function $S_{ij}(r)$. According to eq.(2.30), symmetry gives

$$A_{ij} - Q_{ij}(\lambda_{ji}) = A_{ji} - Q_{ji}(\lambda_{ij}) \quad . \tag{3.39}$$

Substitution of eqs.(2.34), (3.33), (3.34) and (3.35) into eq.(3.39) yields

$$a_j(N_i\sigma_i + Z_i) + \pi\sigma_i(\Omega_2^{(j)} - \sigma_j\Omega_1^{(j)}) / \nabla = a_i(N_j\sigma_j + Z_j) + \pi\sigma_j(\Omega_2^{(i)} - \sigma_i\Omega_1^{(i)}) / \nabla \tag{3.40}$$

where all the variables other than N_j can be expressed as functions of N_j and state conditions σ_i, ρ_i and τ_{ij}. Therefore the only unknown parameters are N_j, (j=1,2,...,K). For symmetric electrolytes, $\sigma_i = \sigma_i = \sigma$; for non-symmetric electrolytes with ion association occuring only at the contact surface, $L_{ij} = \sigma_{ij}$. For such systems, the second terms on both sides of eq.(3.40) vanish. A scaling parameter can then be introduced as shown by Lee, Rasaiah, Cummings and Zhu[9-14] for symmetrical electrolytes; and by Herrera and Blum[15,16] and Zhu and Rasaiah[17] for non-symmetric electrolytes. In this work, we must solve a set of K non-linear equations to obtain all N_j (j=1,2,...,K). The number of eqs.(3.40) is K-1. With the additional normalization constraint, eq.(2.35), altogether we have K independent equations which permit us to solve for K parameters N_j, (j=1,2,...,K). The solution of the second fundamental equation, eq.(2.31), is then finally completed.

5. Direct correlation functions

We solve the first fundamental equation, eq.(2.30), to obtain the direct correlation function inside the hard core, as required for obtaining the cavity correlation function $y_{ij}(L_{ij})$ at the sticky position. We then take the derivative of eq.(2.30) in the range $\lambda_{ji} \le r < \sigma_{ji}$ when $\sigma_j \ge \sigma_i$, or in the range of $\lambda_{ij} \le r < \sigma_{ij}$ when $\sigma_j \le \sigma_i$. We obtain

$$
\begin{aligned}
2\pi r c_{ij}{}^{o}(r) &= -Q'_{ij}(r) + \Sigma_k \rho_k A_{jk}\, Q_{ik}(r+\lambda_{kj}) \\
&\quad - \Sigma_k \rho_k Q_{ik}(\sigma_{ki}) Q_{jk}(\sigma_{ki} - r) + \Sigma_k \rho_k \int_{r+\lambda_{kj}}^{\sigma_{ki}} Q'_{ik}(t) Q_{jk}(t-r)dt \\
&= -Q'_{ij} - (r-\sigma_{ij})Q''_j - Q^{\lambda}_{ij}\,\delta(r-L_{ij}) + \Sigma_k \rho_k A_{jk}\, Q_{ik}(r+\lambda_{kj}) \\
&\quad - \Sigma_k \rho_k Q_{ik}(\sigma_{ki}) Q_{jk}(\sigma_{ki} - r) \\
&\quad + \Sigma_k \rho_k Q^{\lambda}_{ik} Q_{jk}(L_{ki} - r) H(L_{ki} - \lambda_{kj} - r) \\
&\quad + \Sigma\Big[\rho_k \varpi^1_{ij} Q'_{ik} Q'_{jk} + (\varpi^2_{ij} Q'_{ik} + \varpi^3_{ij} Q'_{jk}) Q''_k \\
&\quad + \varpi^4_{ij} (Q''_k)^2 + (\varpi^5_{ij} Q'_{ik} + \varpi^6_{ij} Q''_k) Q^{\lambda}_{kj} H(r - \sigma_{ki} + L_{kj})\Big]
\end{aligned}
\tag{3.41}
$$

where

$$
\begin{aligned}
\varpi^1_{ij} &= \frac{r^2}{2} - \frac{\sigma_i - \sigma_j}{2} r + \frac{\sigma_i^2 - 2\sigma_i\sigma_j - 3\sigma_j^2}{8} \\
\varpi^2_{ij} &= -\frac{r^3}{6} + \frac{\sigma_i - \sigma_j}{4} r^2 - \frac{\sigma_i^2 - 2\sigma_i\sigma_j + \sigma_j^2}{8} r + \frac{\sigma_i^3 - 3\sigma_i^2\sigma_j + 3\sigma_i\sigma_j^2 + 7\sigma_j^3}{48} \\
\varpi^3_{ij} &= \frac{r^3}{6} - \frac{\sigma_i - \sigma_j}{4} r^2 + \frac{\sigma_i^2 - 2\sigma_i\sigma_j - 3\sigma_j^2}{8} r - \frac{\sigma_i^3 - 3\sigma_i^2\sigma_j - 9\sigma_i\sigma_j^2 - 5\sigma_j^3}{48} \\
\varpi^4_{ij} &= -\frac{r^4}{24} + \frac{\sigma_i - \sigma_j}{12} r^3 - \frac{\sigma_i^2 - 2\sigma_i\sigma_j + \sigma_j^2}{16} r^2 + \frac{\sigma_i^3 - 3\sigma_i^2\sigma_j + 3\sigma_i\sigma_j^2 + 7\sigma_j^3}{48} r \\
&\quad - \frac{\sigma_i^4 - 4\sigma_i^3\sigma_j + 6\sigma_i^2\sigma_j^2 + 28\sigma_i\sigma_j^3 + 17\sigma_j^4}{384} \\
\varpi^5_{ij} &= -r + \frac{\sigma_i + \sigma_j}{2} \\
\varpi^6_{ij} &= -\frac{r^2}{2} + \frac{\sigma_i + \sigma_j}{2} r - \frac{\sigma_i^2 + 2\sigma_i\sigma_j + \sigma_j^2}{8}
\end{aligned}
\tag{3.42}
$$

From the direct correlation function inside the hard core, eq.(3.41), we see that, similar to the pair correlation function and the total correlation function, there is a Dirac function, that is, a discontinuity at the sticky position. However, as shown in the next section, the cavity correlation function is not discontinuous because the Dirac function is subtracted in the expression. Eq.(3.41) also gives the direct correlation function for the "usual" MSA without stickiness. Hirioke[21] has given detailed numerical results.

6. Cavity correlation function and sticky parameter

In the final step, we calculate the sticky parameter Λ_{ij}. In terms of the cavity correlation function at the sticky position, the sticky parameter Λ_{ij} in the expression for the total correlation function, eq.(2.7), can be evaluated through the sticky coefficient ξ_{ij},

$$\Lambda_{ij} = \xi_{ij}\, y_{ij}(L_{ij}) \tag{3.43}$$

where ξ_{ij} is defined by $\xi_{ij} = \tau_{ij}^{-1}$. Eq.(3.43) is derived by combining eqs.(2.3), (2.7) and (2.10).

The degree of stickiness, α_{ij}°, that is, the average number of ion j around ion i, is calculated by

$$\alpha_{ij}^{\circ} = \rho_j \int_{L_{ij}^-}^{L_{ij}^+} g_{ij}(r)\, 4\pi r^2 dr = \frac{\pi}{3}\rho_j \Lambda_{ij} L_{ij}^3 \tag{3.44}$$

At the sticky position, $h_{ij}(L_{ij})$ has a Dirac function as shown in eq.(2.7). On the other hand, $c_{ij}(L_{ij})$ also has a Dirac function. In the PY or HNC approximation, eqs.(2.8) and (2.9), we have the difference between $h_{ij}(L_{ij})$ and $c_{ij}(L_{ij})$; the Dirac functions then cancel. Therefore, we can use the PY or HNC approximation to estimate the cavity correlation function at the sticky position, $y_{ij}(L_{ij})$. To do so, we use the direct correlation function $c_{ij}(L_{ij})$ obtained by eq.(3.41) and the total correlation function $h_{ij}(L_{ij})$ by eq.(2.7). We can then estimate the sticky parameter Λ_{ij}.

When we solve the second fundamental equation, we tacitly assume that the sticky parameter Λ_{ij} is known. We then can solve a set of K equations to obtain N_j's; in turn, we obtain all other desired parameters and functions. Now we obtain Λ_{ij} again. Therefore, we have an iteration process. The objective is self-consistent results for the sticky parameter Λ_{ij} in eq.(3.43).

VI. THERMODYNAMIC PROPERTIES

If we select a hard-sphere mixture without stickiness as the reference system, the excess internal energy can be found using the potential function and the correlation function by the well-known relations:

$$E^{\mathrm{ex}} = E(\mathrm{SEM}) - E(\mathrm{hs}) = -\frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_0^\infty \frac{d\exp[-\beta\, u_{ij}(r)]}{d\beta} y_{ij}(r) 4\pi r^2 dr$$

$$= -\frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_0^{\sigma_{ij}} \frac{d\exp[-\beta\, u_{ij}(r)]}{d\beta} y_{ij}(r) 4\pi r^2 dr$$

$$+\frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_{\sigma_{ij}}^\infty u_{ij}(r) g_{ij}(r) 4\pi r^2 dr$$

$$= E^{\mathrm{ex,st}} + E^{\mathrm{ex,el}} \quad . \tag{4.1}$$

As shown in eq.(4.1), the excess internal energy can be separated into two parts, the electrostatic contribution and the sticky contribution:

$$E^{\mathrm{ex,el}} = \frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_{\sigma_{ij}}^\infty u_{ij}^{\mathrm{el}}(r) g_{ij}(r) 4\pi r^2 dr$$

$$= \frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_0^\infty u_{ij}^{\mathrm{el}}(r) g_{ij}(r) 4\pi r^2 dr - \frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_0^{\sigma_{ij}} u_{ij}^{\mathrm{el}}(r) g_{ij}(r) 4\pi r^2 dr$$

$$= \frac{\mathrm{e}^2 V}{4\pi\varepsilon}\left[\sum_i \rho_i Z_i N_i - \sum_{i,j}\rho_i\rho_j Z_i Z_j Q_{ij}^\lambda\right] \tag{4.2}$$

$$E^{\mathrm{ex,st}} = \frac{V}{2}\sum_{i,j}\rho_i\rho_j\int_0^{\sigma_{ij}} kU_{ij}^{\mathrm{st}}(r) g_{ij}(r) 4\pi r^2 dr$$

$$= V\sum_{i,j}\rho_i\rho_j\, kU_{ij}^{\mathrm{st}} L_{ij} Q_{ij}^\lambda \tag{4.3}$$

where $U_{ij}^{\mathrm{st}} = -T\ln(L_{ij}/12\tau_{ij})$ is a measure of the sticky energy, expressed in temperature units.

If we select a hard-sphere mixture with stickiness as the reference system,

$$E^{\mathrm{ex}} = E^{\mathrm{ex,el}} = \frac{\mathrm{e}^2 V}{4\pi\varepsilon}\left[\sum_i \rho_i Z_i N_i - \sum_{i,j}\rho_i\rho_j Z_i Z_j Q_{ij}^\lambda\right] \quad . \tag{4.4}$$

As indicated by the above equations, the excess internal energy can be calculated analytically when we have all N_j's and the Q_{ij}^λ which contain the sticky parameter Λ_{ij}. Those N_j's can be obtained by solving a set of K nonlinear equations.

For the Hemholtz function, we use a relation based on the cavity correlation function[10,22],

$$\frac{\delta(\beta A/V)}{\delta f_{ij}(r,\xi_{ij})} = -\rho_i\rho_j\, y_{ij}(r,\xi_{ij}) \quad . \tag{4.5}$$

From the definition of the Mayer function

$$f_{ij}(r) = \exp[-\beta u_{ij}(r)] - 1 \quad , \tag{4.6}$$

we have

$$f_{ij}(r) = L_{ij}\,\delta(r - L_{ij})\xi_{ij}/12 - 1 \qquad 0 < r < \sigma_{ij}$$

$$= \exp(-Z_i Z_j \beta e^2/4\pi\varepsilon r) - 1 \qquad r > \sigma_{ij} \quad . \tag{4.7}$$

The change of Mayer function resulting from the change of stickiness is:

$$\partial f_{ij}(r) = L_{ij}\delta(r - L_{ij})\partial\xi_{ij} / 12 \qquad 0 < r < \sigma_{ij} \quad . \tag{4.8}$$

For convenience, we select as a reference an eletrolyte mixture with no stickiness, i.e., the normal MSA. The excess Helmholtz function, i.e., the change in the Helmholtz function between SEM and MSA, can be calculated by:

$$\begin{aligned} \beta A^{ex} / N &= \beta[A(\mathrm{SEM}) - A(\mathrm{MSA})] / N \\ &= -\frac{\pi}{3\sum_k \rho_k}\sum_i\sum_j \rho_i \rho_j L_{ij}^3 \int_0^{\xi_{ij}} y_{ij}(L_{ij}, \xi'_{ij}) d\xi'_{ij} \\ &= -\frac{\pi}{3\sum_k \rho_k}\sum_i\sum_j \rho_i \rho_j L_{ij}^3 \left[\Lambda_{ij}[1 - \ln y_{ij}(L_{ij})] + \int_0^{\Lambda_{ij}} y_{ij}(L_{ij}, \Lambda'_{ij}) d\Lambda'_{ij}\right] \end{aligned} \tag{4.9}$$

where N is the total number of ions.

If we select a hard-sphere mixture without stickiness as the reference system, the excess Helmholtz function of the system is

$$A^{ex} = A(\mathrm{SEM}) - A(\mathrm{hs}) = A(\mathrm{SEM}) - A(\mathrm{MSA}) + A^{ex}(\mathrm{MSA}) \tag{4.10}$$

where

$$A^{ex}(\mathrm{MSA}) = E^{ex}(\mathrm{MSA}) + (\Gamma^3 / 3\pi)VkT \quad . \tag{4.11}$$

Here Γ is the scaling parameter in Blum's[1-3] "normal" MSA,

$$4\Gamma^2 = \alpha_0^2 \sum_k \rho_k \left[(Z_k - \frac{\pi}{2\nabla} P_n \sigma_k^2) / (1 + \Gamma\sigma_k)\right]^2 \quad . \tag{4.12}$$

The excess osmotic pressure can be obtained by differentiating the excess Helmholtz function,

$$p^{ex} = -\left(\frac{\partial A^{ex}}{\partial V}\right)_T \quad . \tag{4.13}$$

The osmotic coefficient and the activity coefficient are calculated by

$$\phi^{ex} = \beta p^{ex} / \zeta_0 \tag{4.14}$$

$$ln\gamma_{\pm}^{ex} = \beta G^{ex} / N = \beta A^{ex} / N + \phi^{ex} \quad . \tag{4.15}$$

V. RESULTS AND DISCUSSION

The method discussed above can be used to calculate thermodynamic properties such as excess internal energies, excess Helmholtz functions, osmotic coefficients and activity coefficients in the framework of SEM. In this section, we present results for the reduced excess internal enerny $-E^{ex} / NkT$ with a hard-spheres mixture as a reference; the reduced excess Helmholtz function $-A^{ex} / NkT$ with the "normal" MSA as a reference; the sticky

parameter Λ and the degree of stickiness α° for 2-2 eletrolyte solutions. We consider only stickiness between oppositely charged ions.

If we take the PY approximation inside the hard core, the cavity correlation function $y_{ij}(r)$ is negative. Because of this unrealistic result, we adopt the HNC approximation.

First, we present calculations for the RPM model ($\sigma_1 = \sigma_2 = \sigma$). The results are summarized in Figs.1-3. Figure 1 shows the sticky parameter as a function of concentration c(mol/dm^3). The state properties for the system are the same as those used by Rasaish and Lee[11]. Here $D=\varepsilon/\varepsilon_0$ is the dielectric constant of the solvent. Sticky parameter Λ decreases when the concentration increases. However, the degree of stickiness α° and $-E^{ex}/NkT, -A^{ex}/NkT$ increase, as expected. Comparison with Rasaish and Lee's work indicates that agreement is nearly perfect. In Fig.2, we plot the sticky properties against the

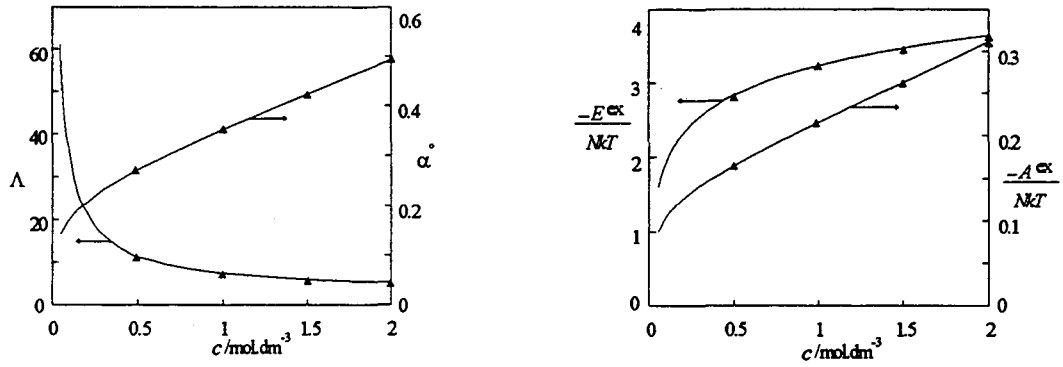

Fig.1. Λ, α° and $-E^{ex}/NkT, -A^{ex}/NkT$ as functions of concentration for sticky charged hard-sphere 2-2 electrolyte. $T = 298$K, $D = 78.358$, $\sigma = 0.42$ nm, $\xi = 1.1\times10^3$, $L_{st} = \sigma$.
♠: Rasaish and Lee[11]; —:this work.

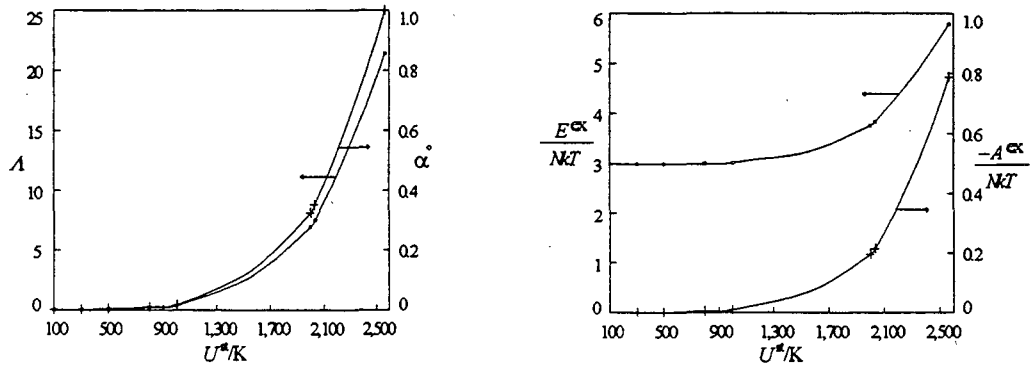

Fig.2. Λ, α° and $-E^{ex}/NkT, -A^{ex}/NkT$ as functions of sticky energy for sticky charged hard-sphere 2-2 electrolyte when c=1.0mol.dm^{-3}. T=298K, $D = 78.358$, $\sigma = 0.42$ nm, $L_{st} = \sigma$.

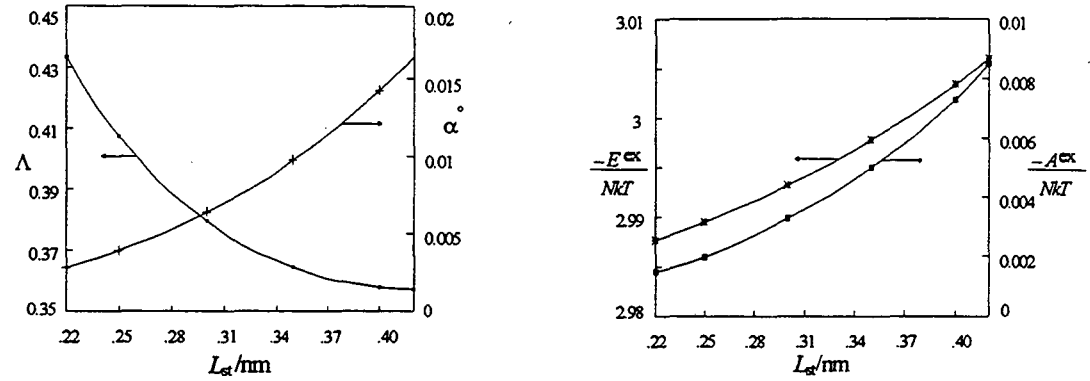

FIG.3. Λ , α° and $-E^{ex}/NkT$, $-A^{ex}/NkT$ as functions of sticky position for sticky charged hard-sphere 2-2 electrolyte, c=1.0mol.dm^{-3}. T=298K, $D = 78.358$, $\sigma = 0.42$ nm, $U^{st} = -1000$K.

sticky energy U^{st}. We see that Λ, α° and $-E^{ex}/NkT$, $-A^{ex}/NkT$ all increase as the reduced sticky energy rises. Fig.3 shows relations between the sticky properties and the sticky position L_{st}. The sticky position studied in this work is in the range $\sigma > L_{st} > \sigma/2$. Λ, α° , $-E^{ex}/NkT$ and $-A^{ex}/NkT$ show the same behavior as those in Fig.1. As for the influence of the sticky distance, shown in Fig.3, when the two ions are closely associated (smaller L_{st}), although the sticky parameter Λ increases, ΛL_{st} still reduces because Λ increases more slowly. The sticky probability represented by correlation function h, shown in eq.(2.7), declines. The degree of stickiness α° also falls because a wider region of infinite repulsive energy barrier must be overcome before the ions can associate. The excess internal energy and the excess Helmholtz function decrease.

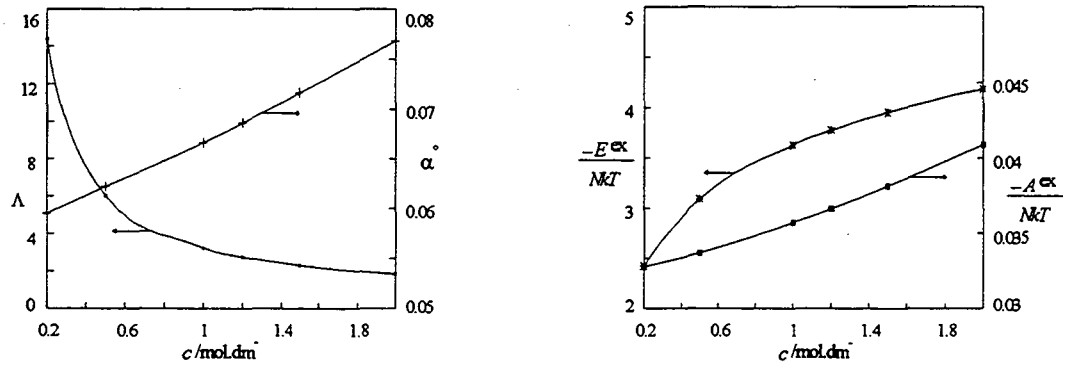

FIG.4. Λ , α° and $-E^{ex}/NkT$, $-A^{ex}/NkT$ as functions of concentration for sticky charged hard-sphere 2-2 electrolyte. T=298K, $D = 78.358$, $\sigma_1 = 0.22$ nm, $\sigma_2 = 0.42$ nm, $U^{st} = -2000$K, $L_{st} = \sigma_{12}$.

Now we turn to non-symmetric electrolytes. The results are summarized in Figs.4–6. The sticky properties are plotted as functions of concentration c(mol/dm^{-3}) in Fig.(4). Results are

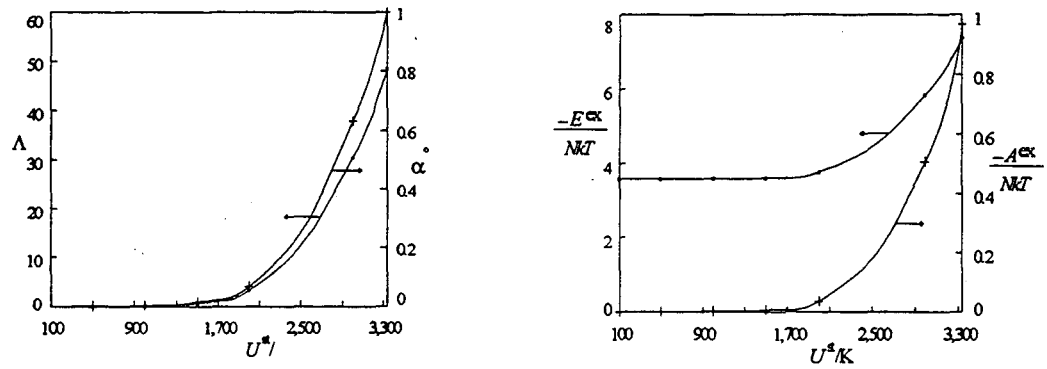

FIG.5. Λ, α° and $-E^{ex}/NkT$, $-A^{ex}/NkT$ as functions of sticky energy for sticky charged hard-sphere 2-2 electrolyte when c=1.0mol.dm-3. T=298K, $D=78.358$, $\sigma_1=0.22$ nm, $\sigma_2=0.42$ nm, $L_{st}=\sigma_{12}$.

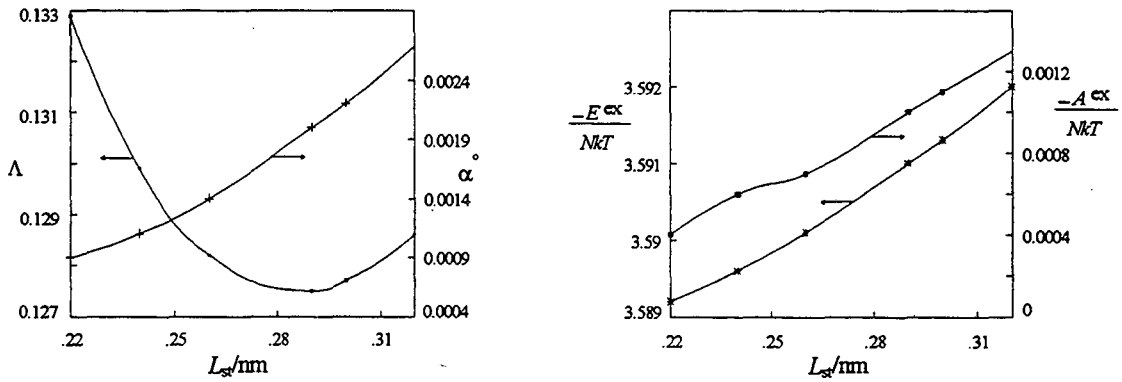

FIG.6. Λ, α° and $-E^{ex}/NkT$, $-A^{ex}/NkT$ as functions of sticky position for sticky charged hard-sphere 2-2 electrolyte when c=1.0mol.dm^{-3}. T=298K, $D=78.358$, $\sigma_1=0.22$ nm, $\sigma_2=0.42$ nm, $U^{st}=-1000$K.

similar to those in Fig.1 for the RPM model. The dependence of the sticky properties on the sticky energy are shown in Fig.5 which is also similar to Fig.2.

Fig.6 shows the relation between the sticky properties and the sticky position L_{st}. The range is: $\sigma_{12} > L_{st} > \sup(\sigma_1/2, \sigma_2/2)$. As shown in Fig.6, α°, $-E^{ex}/NkT$ and $-A^{ex}/NkT$ show similar behavior as in Fig.4. However, as for Λ, it shows a minimum.

The above results indicate that the method developed here is applicable to symmetric and non-symmetric electrolytes with stickiness between ions at various sticky positions. Although the derivation is tedious, the final equations are clear and intuitive. The main difference

between this work and those for simpler cases reported by Lee, Rasaiah, Cummings and Zhu[9-14], by Herrera and Blum[15,16], and by Zhu and Rasaiah[17], lies in the parameter estimation. In the earlier publications, a single scaling parameter Γ is estimated numerically. However, in this work, K parameters N_j, (j=1,2,...,K) must be obtained by solving a set of K nonlinear equations. Here K is the number of ion species. This additional calculation is the cost we have to pay for increasing the complexity of the systems. For a single non-symmetric electrolyte, where K=2, the numerical task is not heavy. For mixed electrolytes, the computation time increases appreciably.

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