Cavity functions and association in models for weak electrolytes and sticky hard spheres

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(Received 18 December 1989; accepted 7 March 1990)

Weak electrolytes and other association reactions are modeled as sticky spheres. An analysis of the density expansion, including the bridge diagrams, of the cavity functions $y_{AB}(L)$ for sticky hard spheres (charged or uncharged spheres binding at a distance L) leads to an approximation which provides the degree of association α as the solution to a simple quadratic equation determined by the association constant K_0 and the cavity function $y^0_{AB}(L)$ for the reference system in which the chemical bonding between the reacting species has been turned off. Similar relations are assumed to hold when the bonding is directional and specific enough to lead only to the formation of dimers. Applications to the determination of the reference cavity functions for acetic acid and monochloro acetic acid from experimental data of the degree of association are discussed. In a discrete solvent, the approximation scheme for α remains the same, except that the reference cavity function is scaled differently. Solvent medium effects on the association constant are shown to be related to the cavity function of the undissociated dimer in a pure solvent. An exponential approximation for the reference cavity function $y^0_{AB}(L)$ is derived when the associating species are of the same size and the bonding is spherically symmetric. Expressions for the changes in the thermodynamic functions due to association are obtained analytically in terms of the degree of association and the reference cavity functions. The magnitude of the degree of association, calculated from the exponential approximation for $y^0_{AB}(L)$, and its effect on the thermodynamic properties are different from what was previously observed using the hypernetted chain (HNC) approximation. The thermodynamics of weak 1–1 electrolytes are discussed using the new method and a comparison is made between the new and old methods for 2–2 electrolytes.

I. INTRODUCTION

In recent years there has been renewed interest in the statistical mechanics of chemically reacting systems; for example, chemical association in ionic systems so characteristic of weak electrolytes. Association due to chemical bonding was studied many years ago by Boltzmann[1] and is usually introduced through a strong short range attraction between the reactants as exemplified by the work of Andersen[2] and Høye and Olaussen.[3] The limited range of this interaction, along with the extreme repulsion between overlapping particles, leads to the cancellation of a large number of diagrams in the cluster expansion of the distribution function for the associating species, providing simple expressions for the degree of association and the association constant. More recently, association has also been treated by introducing a delta function interaction between hard spheres[4,5] and between oppositely charged hard sphere ions[6–8] while directional effects have also been considered in a series of papers by Michael Wertheim.[9] In addition, solvent effects on the association of weak electrolytes have been studied by us,[10,11] when it was found that a hard sphere solvent has a strong packing effect which increases dimerization, while a dipolar solvent has both packing and screening effects which compete against each other to enhance or diminish the extent of association. A crucial problem in all of these models is the determination of the degree of association; this paper is concerned with this question for sticky electrolytes and for sticky hard spheres.

Chemical association or bonding is mimicked in this model by introducing a delta function interaction in the Mayer function of the associating species A and B inside the hard core

$$f_{AB}(r) = -1 + \zeta L(1-\delta_{AB})\,\delta(r-L)/12 \quad (r<\sigma) \tag{1.1a}$$

$$= \exp[-\beta e_A e_B/(\epsilon r)] - 1 \quad (r>\sigma) \tag{1.1b}$$

Here $L=\sigma/n$, with n greater than or equal to unity, is the distance at which A and B can bond or stick together and σ is the hard sphere diameter. The strength of the interaction between an A–B pair in isolation is measured by the sticking coefficient ζ, while e_A and e_B are the charges on these ions (which are zero for uncharged hard spheres), ϵ is the dielectric constant of the solvent background, δ_{AB} is a Kronecker delta and $\delta(r-L)$ is a delta function. The presence of a delta function in Eq. (1.1) leads to a pair correlation function for A and B with a delta function inside the hard core,

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

Here λ is an association parameter which is related to ζ in Eq. (1.1a) by

$$y_{AB}(L) = \lambda\tau, \tag{1.3}$$

where $\tau = 1/\zeta$ and $y_{AB}(r)$ is the cavity function defined by

$$y_{AB}(r) = g_{AB}(r)\exp[\beta u_{AB}(r)] \tag{1.4}$$

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in which $u_{AB}(r)$ is the pair potential for A and B and $g_{AB}(r) = 1 + h_{AB}(r)$ is the radial distribution function of the reacting particles. The cavity function is the distribution function for two "ghost" particles which do not interact with each other directly but do so with the other particles; the interaction between two cavities thus occurs only indirectly through the surroundings. It plays a central role in our discussion and its importance in association reactions and many other liquid state phenomena has been recognized earlier by Chandler and Pratt[16] and recently by Chandler and Wolynes in studies of quantum processes (e.g., electron mobility and solvation) in liquids.[17]

The association parameter λ determines the degree of association and the "association constant" K of the reaction

$$A + B \rightarrow AB.$$

The thermodynamic properties of the corresponding unassociated (reference) system are modified by dimerization in proportion to the λ and its determination is important. This has most often been realized by employing the Percus–Yevick (PY)[5] or the hypernetted chain (HNC)[6,7] approximations for the cavity functions $y_{AB}(L)$ of the reactants A and B at the "bonding" distance L. As L becomes shorter, the calculations invariably become much more involved as might be learned from a cursory examination of Refs. 6 and 7 (or 5). Moreover it is not entirely clear that liquid state approximations (PY and HNC) are appropriate for association reactions or are even consistent with the law of mass action.

The association "constant" K for the reaction can be expressed as

$$K = \rho_{AB}/(\rho_A \rho_B) = \alpha/[\rho_0(1-\alpha)^2], \tag{1.5}$$

where α is the degree of the association, ρ_0 is the density of either A or B and the total density is $2\rho_0$. K is strictly a constant only for ideal systems when Eq. (1.5) is known as the law of mass action. The density or concentration of the associated AB pairs

$$\rho_{AB} = \rho_0^2 \int_{L-}^{L+} g_{AB}(r) 4\pi r^2\, dr = \pi\lambda\rho_0^2 L^3/3 \tag{1.6}$$

and the degree of the association

$$\alpha = \langle N \rangle = \pi\lambda\rho_0 L^3/3 = \eta\lambda(L/\sigma)^3, \tag{1.7}$$

where $\eta = \pi\rho_0\sigma^3/3$. The definition of α is identical to the mean number of ion pairs $\langle N \rangle$ defined in our earlier papers.[6–8] Substituting Eqs. (1.6) and (1.7) into Eq. (1.5) leads to

$$K = \pi\lambda L^3/[3(1-\alpha)^2]. \tag{1.8}$$

In the absence of a third component (e.g., a discrete solvent), as the densities of A and B $\rho_0 \rightarrow 0$, the cavity function $y_{AB}(L) \rightarrow 1$, so that $\lambda \rightarrow 1/\tau$, $h_{AB}(r) \rightarrow f_{AB}(r)$, and

$$K \rightarrow K_0 = \pi L^3/3\tau. \tag{1.9}$$

Dividing Eq. (1.8) by K_0 and using Eq. (1.3), provides a relationship between the association constants at a finite concentration and at infinite dilution

$$K/K_0 = \lambda\tau/(1-\alpha)^2 = y_{AB}(L)/(1-\alpha)^2. \tag{1.10}$$

This expression was derived recently by Stell and Zhou[12] who pointed out that it implies that $y_{AB}(L) \rightarrow 1$ like $(1-\alpha)^2$ when the density of the reacting species tends to zero with the stickiness remaining finite. It is a consequence of the law of mass action, but its derivation from the density expansion of the cavity function for reacting molecules has not been discussed before. We consider this problem as well.

When $\alpha = 0$ (no association), $y_{AB}(L) = y^0_{AB}(L)$ which is the cavity function of the corresponding reference system in which the stickiness is absent. In the absence of a discrete solvent, $y^0_{AB}(L) \rightarrow 1$ as the densities of A and B tend to zero. Stell and Zhou[12] suggested the interpolation formula

$$y_{AB}(L) = (1-\alpha)^2 y^0_{AB}(L) \tag{1.11}$$

for the cavity function $y_{AB}(L)$ which implies that

$$K/K_0 = y^0_{AB}(L) \tag{1.12}$$

in which the degree of association is absent. According to this relation the ratio of the two association constants at finite and zero concentrations of A and B is completely determined by the cavity function in the absence of bonding. However, when the bonding is strong (or when the solute packing is great) one expects $\alpha \rightarrow 1$ making the association constant K [see Eq. (1.10)] infinite even when K_0 is finite. This saturation limit has been discussed by us in detail in a series of papers where we consider the ions pairing up to form extended dipoles.[13,14]

In the following pages we discuss a simple approximation for the cavity function $y_{AB}(L)$ which is consistent with all of these limiting conditions and determines α as the solution to a quadratic equation. The paper is organized as follows: in Sec. II, we obtain an expression for the cavity function for the reactants from its cluster expansion which shows explicitly that for $L < \sigma/2$ $y_{AB}(L) \rightarrow (1-\alpha)^2$ as $\rho_0 \rightarrow 0$ for atoms of the same size which suggests a simple approximation for α in terms of the cavity function $y^0_{AB}(L)$ for the reference system obtained by turning off the stickiness. Applications to acetic acid and monochloroacetic acid are considered, assuming a similar relation applies to the dimerization of atoms or ions of different size; Sec. III extends the discussion to association in the presence of a discrete solvent. An exponential type of approximation for the cavity functions of the reference system is considered in Sec. IV, while the modification of the thermodynamic properties due to dimerization are discussed in Sec. V, followed by a discussion of our results in Sec. VI.

II. THE CAVITY FUNCTION AND THE QUADRATIC EQUATION FOR THE DEGREE OF ASSOCIATION

The main difficulty with the use of liquid state approximations (e.g., HNC or PY) to determine the cavity function $y_{AB}(L)$ is that they ignore the bridge diagrams which inevitably lead to expressions for the association constant that are inconsistent with the limiting form of $y_{AB}(L)$. In view of this it seems important to devise a simple but accurate approximation for the cavity function which takes into account the dominant contributions of these diagrams.

The cluster expansion for the cavity function $y_{AB}(L)$ can be expressed as sum of graphs:

$y_{AB}(L) = 1 +$ sum of all topologically distinct irreducible graphs on two white circles labeled A and B, one or more black ρ_A and ρ_B circles with at most one f_{AA}, f_{BB}, or

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f_{AB} bond between each pair of circles but no bond between the pair of white circles. (2.1)

The white circles are root points and the black circles are field points representing either A or B. It follows from the definition of the Mayer function given in Eq. (1.1) that $f_{AB}(r)$ can be separated into two parts: a reference part $f^0_{AB}(r)$, which is the corresponding Mayer function when the stickiness is turned off, and the remainder $f^\delta(r) = \zeta L\delta(r-L)/12$.

$$f_{AB}(r) = f^0_{AB}(r) + f^\delta(r). \tag{2.2}$$

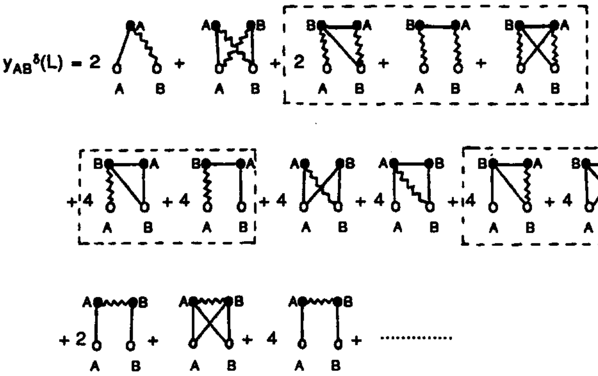
Substituting Eq. (2.2) into Eq. (2.1), we have

$$y_{AB}(L) = y^0_{AB}(L) + y^\delta_{AB}(L), \tag{2.3}$$

where $y^0_{AB}(L)$ is the cavity function for the reference system in the absence of association and $y^\delta_{AB}(L)$ is the change in this function due to association. Each diagram in the f-bond expansion of $y^\delta_{AB}(L)$ contains at least one f^δ bond derived from the $f_{AB}(r)$ bonds present in the expansion of $y_{AB}(L)$. Since there is no bonding among the A's or B's alone but only between an A and a B, we see that

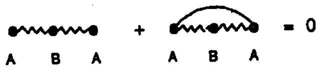
$$f_{AA}(r) = f_{BB}(r) = f^0_{AB}(r) \quad (r<\sigma), \tag{2.4}$$

where, to simplify the notation and graphical representation, we have assumed that A and B are of the same size. Representing these bonds by a dark line (●—●) and $f^\delta(r)$ by a wavy line (●〰●) we see that the density expansion for $y^\delta_{AB}(L)$ in the range $r<\sigma$ can be represented by



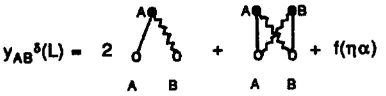
(2.5)

Note that our black circles are labeled and the factor in front of each graph is the number of acceptable graphs with the same value after permuting the labels and the bonds. Acceptability here means that there may be bonding only between an A and a B but not between two A's or two B's. There is also no direct bonding between the root points (white circles) A and B. In addition, since each $f^0_{AB}(r)$ bond will contribute a factor -1 for r inside the hard core, there are no diagrams with two delta bonds in series when $L<\sigma/2$ because for every such diagram there is another one with a $f^0_{AB}(r)$ bond in parallel across the end points which exactly cancels the first i.e.,



(2.6)

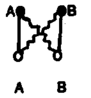
This property is exploited in the cancellation theorem for hydrogen bonding clusters discussed by Andersen[2] and formulated explicitly in the form given in Eq. (2.6) by Høye and Olaussen.[3] In addition, when $L<\sigma/2$, the triangle inequality ensures that some of the diagrams in Eq. (2.5) with an even number of f^0_{AB} bonds will be cancelled by those with an odd number of f^0_{AB} bonds. These are shown as sets of diagrams blocked out in Eq. (2.5); the sum of the diagrams in each block adding up to zero. The leading term in the h bond expansion is an f bond, and we now use a renormalized expansion in terms of h bonds rather than f bonds in the remaining diagrams. The graphs left in Eq. (2.5) can then be written as



(2.7)

where the dark line and the wavy line are $h^0_{AB}(r)$ and h^δ bonds, respectively, which are analogous to the $f^0_{AB}(r)$ bond and f^δ bond defined in Eq. (2.2). The function $f(\eta\alpha)$ contains all the remaining terms in Eq. (2.5) which have a common factor $\eta\alpha$, where α comes from the presence of at least one h^δ bond and η from an $h^0_{AB}(r)$ bond. At low density λ is large,[6,7] and it follows from Eq. (1.7) that α is much greater than η. Therefore we can neglect $f(\eta\alpha)$ in comparison to α^2 at low reactant densities; a similar situation arises in Andersen's study of the hydrogen bonded fluid.[2] We now evaluate the first two diagrams in Eq. (2.7); a direct integration gives

$$= -\pi\rho_0\lambda L^3/3 = -\alpha \tag{2.8}$$



$$= (\pi\rho_0\lambda L^3/3)^2 = \alpha^2 \tag{2.9}$$

Substituting Eqs. (2.8) and (2.9) in Eq. (2.7), we have

$$y^\delta_{AB}(L) = -2\alpha + \alpha^2 + \cdots (L<\sigma/2) \tag{2.10}$$

from which it follows that Eq. (2.3) can be written as

$$y_{AB}(L) = (1-\alpha)^2 + [y^0_{AB}(L) - 1]. \tag{2.11}$$

This is our expression for the cavity function in the absence of a discrete solvent which is different from the assumption of Eq. (1.11). Using Eq. (2.11) in Eq. (1.10) we find, instead of Eq. (1.12), that

$$K/K_0 = 1 + [y^0_{AB}(L) - 1]/(1-\alpha)^2. \tag{2.12}$$

When the reactant density goes to zero, $y^0_{AB}(L)\to 1$, $K\to K_0$ provided $\alpha \neq 1$. When $\alpha = 1$, $K/K_0 = \infty$ and we have saturation.

To calculate the association constant K from K_0, we need the degree of association and the cavity function $y^0_{AB}(L)$ for the reference system. To determine α, combine Eqs. (1.7), (1.9), and (1.10) with Eq. (2.11) when we have

$$\begin{aligned} y^0_{AB}(L) &= \lambda\tau = \alpha/(\rho_0 K_0) \\ &= (1-\alpha)^2 + [y^0_{AB}(L) - 1] \end{aligned} \tag{2.13}$$

which leads to a quadratic equation

$$\alpha^2\rho_0K_0 - \alpha(1 + 2\rho_0K_0)$$

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$$+y^0_{AB}(L)\,\rho_0 K_0 = 0 \tag{2.14}$$

for α. The solution to Eq. (2.14) is

$$\alpha = 1 + \{1 - [(1+2\rho_0 K_0)^2 - 4y^0_{AB}(L) \times (\rho_0 K_0)^2]^{1/2}\}/(2\rho_0 K_0). \tag{2.15}$$

In the limit $\rho_0 \to 0$, $\alpha \to 0$ if K_0 is finite, while in the infinite stickiness limit, when $\tau \to 0$, $K_0 \to \infty$, and $\alpha \to 1$ as $y^0_{AB}(L) \to 1$, which implies that, if the binding force between A and B is very strong, the degree of association will tend to one even at zero density. A convenient feature of the quadratic equation is that to solve for α, we only need to know K_0 (determined by τ and L) and the cavity function $y^0_{AB}(L)$.

Equation (2.14) and its solution (2.15) are the central results of this section derived here for association between two species of the same size. Equation (2.15) provides an explicit relationship between the reference cavity functions and the degree of association α when the association constant K_0 is known

$$y^0_{AB}(L) = \alpha[1 + 2\rho_0 K_0(1-\alpha)]/\rho_0 K_0. \tag{2.16}$$

It should also be applicable to association between atoms or ions whose sizes are different provided polymerization does not occur, i.e., only dimers are formed. In our model the sticky interaction is spherically symmetric, and its extension to atoms or ions of different size does not preclude the association of a large atom with more than one of the smaller atoms; although bonding of more than one large atom with a smaller atom is sterically hindered when L is smaller than the radius of the larger atom.

However, association can be limited to dimerization if we have directional bonding between A and B within a given solid angle Ω subtended by the larger of the species B. The angle Ω must be small enough to enable only one of the other A atoms or ions to bind at a distance L; steric repulsion between the A atoms prevents further polymerization. This model is similar to the one considered by Boltzmann[1] who imagined "sensitive regions" for bonding on the surface of each of the species. Instead of Eq. (1.1a) we will have

$$f_{AB}(r) = -1 + \zeta L\Omega(1-\delta_{AB})\,\delta(\omega-\Omega) \times \delta(r-L)/12 \quad (r<\sigma) \tag{2.17}$$

with a corresponding change in the equations for $h_{AB}(r)$. Introducing this in Eqs. (1.2) and (1.6) we find that K and K_0 are reduced by a factor $\Omega/4\pi$ while the ratio K/K_0 is still given by Eq. (1.10). The cavity function of the reference system now depends on L and Ω. Without further proof, we assume that Eqs. (2.13) with $\{y_{AB}(L,\Omega), y^0_{AB}(L,\Omega)\}$ replacing $\{y_{AB}(L), y^0_{AB}(L)\}$ applies to this model system as well. It follows that Eqs. (2.14) to (2.16) also apply with the substitution of $y^0_{AB}(L,\Omega)$ for $y^0_{AB}(L)$.

The calculation of the reference cavity function $y^0_{AB}(L,\Omega)$ from the Hamiltonian of this system with directional bonding would be very involved. Hence, we take a different point of view and use Eq. (2.16) to calculate $y^0_{AB}(L,\Omega)$ from the experimentally determined degree of dissociation of a weak electrolyte. The examples we consider are acetic acid and monochloroacetic acid in aqueous solution at 25 °C; the degrees of dissociation (our $1-\alpha$) have been determined through conductance measurements by MacInnes and Shedlovsky[19] and by Shedlovsky, Brown, and MacInnes.[20] Each of these acids dissociates into ions of different size and the dissociation constants at this temperature are 1.75×10^5 and 1.49×10^5 M/ℓ, respectively. To illustrate the method (and simplify the calculations) we assume a continuum solvent; the association constants K_0 in Eqs. (2.15) and (2.16) are then simply the inverse of the dissociation constants. Using the data tabulated in their papers we calculate the cavity functions of the reference systems from Eq. (2.16); the results are shown in Fig. 1. The differences between the curves are probably due to the differences between the sizes (and the charge distributions) of the acetate and chloroacetate ions; in either case we expect that the H ions are bonded very close to the surface of the cation so that the bonding distance L is close to the radius of the cation. The reference system for a weak acid has an interesting physical interpretation; it is the corresponding strong acid with the same molecular structure in the same solvent obtained by turning off the short ranged chemical interaction [represented in this model by Eq. (2.17)] between the positive hydrogen ion and anion! The reference cavity function for a weak acid is thus the cavity function for the corresponding strong acid in which chemical association is absent.

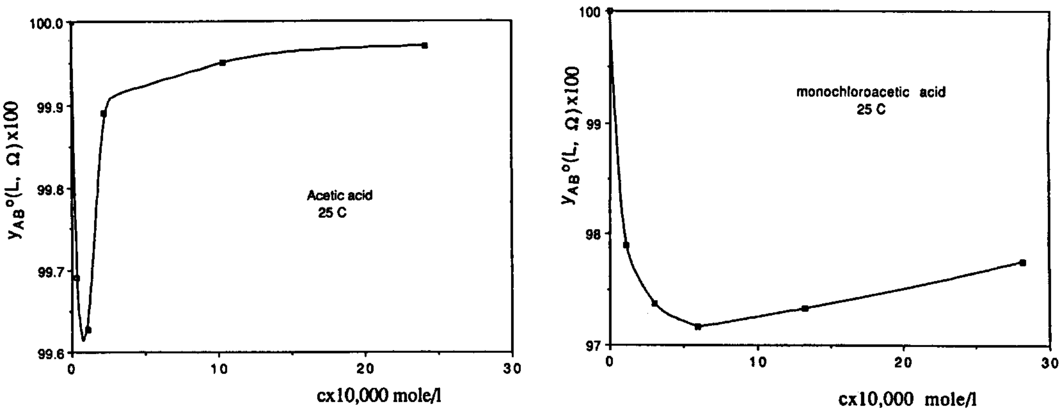

FIG. 1. The reference cavity functions $y^0_{AB}(L,\Omega)$ for acetic acid and monochloroacetic acid as a function of the concentration at 25 °C calculated from Eq. (2.16) and the experimentally determined degree of dissociation.

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III. SOLVENT PACKING EFFECTS ON ASSOCIATION REACTIONS

In this section we show that the effect of a solvent on an association reaction can be treated (at not too high a solvent density) by rescaling the cavity function for the reference system. This leads to a quadratic equation for the degree of association α which is of the same form as the equation derived in the previous section.

In the presence of a discrete molecular solvent, the cavity function $y_{AB}^{s}(L)$ for A and B in the solution (s) may be expressed in the form

$$y_{AB}^{s}(L) = y_{AB}^{u}(L)\, y_{AB}^{v}(L) + y_{AB}^{\mathrm{rem},s}(L), \tag{3.1}$$

where $y_{AB}^{u}(L)$ is the cavity function for two solute particles A and B in the presence of other solute particles only at a density ρ_0, while $y_{AB}^{v}(L)$ is the corresponding cavity function in a pure solvent medium i.e., when the solute density is zero. In Eq. (3.1) the first term corresponds to the product[18] of these cavity functions and the second term $y_{AB}^{\mathrm{rem},s}(L)$ is the remainder which cannot be factorized in this way. The superscripts s, u, and v in these functions imply that we are dealing with a solution (s), solute (u), or solvent (v) medium in which the solute cavity particles are embedded. Note that as the solute density tends to zero, $y_{AB}^{s}(L) \to y_{AB}^{v}(L)$ and hence $\lambda \neq 1/\tau$ in this limit.

Separating out the terms with delta function bonds in the cavity function [cf. Eq. (2.3)], we have

$$y_{AB}^{s}(L) = y_{AB}^{0,s}(L) + y_{AB}^{\delta,s}(L), \tag{3.2}$$

where $y_{AB}^{0,s}(L)$ is the cavity function for the reference solution in which there is no stickiness between A and B. Combining Eqs. (3.2) and (3.1), we find

$$y_{AB}^{\mathrm{rem},s}(L) = y_{AB}^{0,s}(L) - y_{AB}^{v}(L)\, y_{AB}^{0,u}(L) + y_{AB}^{\Delta}(L) \tag{3.3}$$

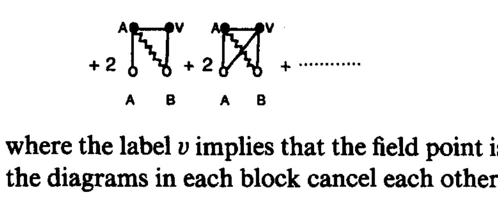
in which we have used Eq. (2.3) (adding a superscript u to the solute cavity function) and

$$y_{AB}^{\Delta}(L) = y_{AB}^{\delta,s}(L) - y_{AB}^{v}(L)\, y_{AB}^{\delta,u}(L). \tag{3.4}$$

Substituting Eqs. (3.3) and (2.11) into Eq. (3.1), we have, when $L < \sigma/2$,

$$y_{AB}^{s}(L) = y_{AB}^{v}(L)\{(1-\alpha)^2 + [y_{AB}^{0,s}(L)/y_{AB}^{v}(L)] - 1\} + y_{AB}^{\Delta}(L). \tag{3.5}$$

In the cluster expansion of $y_{AB}^{\Delta}(L)$, no product diagrams of $y_{AB}^{v}(L)$ and $y_{AB}^{\delta,u}(L)$ occur; also at least one delta function bond and one solvent field point is present in each diagram. An explicit expression of $y_{AB}^{\Delta}(L)$ to first order in the solvent density is



(3.6)

where the label v implies that the field point is a solvent and the diagrams in each block cancel each other when $L \leqslant \sigma/2$. Also, the diagrams left in Eq. (3.6) will partly be cancelled.

When the solvent density is not too high we can neglect $y_{AB}^{\Delta}(L)$. We assume that this is so. Dividing by $y_{AB}^{v}(L)$, and using Eq. (1.7), one finds

$$\begin{aligned} y_{AB}'(L) &= \lambda\tau' = \alpha/(\rho_0 K_0') \\ &= (1-\alpha)^2 + y_{AB}^{0'}(L) - 1, \end{aligned} \tag{3.7}$$

where $y_{AB}'(L)$, τ', K_0', and $y_{AB}^{0'}(L)$ are defined by

$$y_{AB}'(L) = y_{AB}^{s}(L)/y_{AB}^{v}(L), \tag{3.8}$$

$$y_{AB}^{0'}(L) = y_{AB}^{0,s}(L)/y_{AB}^{v}(L), \tag{3.9}$$

$$\tau' = \tau/y_{AB}^{v}(L), \tag{3.10}$$

$$K_0' = K_0 y_{AB}^{v}(L). \tag{3.11}$$

Equation (3.7) is the rescaled form of Eq. (2.13), and leads to a quadratic equation for α similar to Eq. (2.14):

$$\alpha^2\rho_0 K_0' - \alpha(1 + 2\rho_0 K_0') + y_{AB}^{0'}(L)\, \rho_0 K_0' = 0. \tag{3.12}$$

The solution of Eq. (3.12) is the same as Eq. (2.15) except that $y_{AB}^{0}(L)$ and K_0 are replaced by the rescaled quantities $y_{AB}^{0'}(L)$ and K_0'. It follows from Eq. (3.11) that the limiting value of the association constant depends on the density and the nature of the solvent. When the solvent density vanishes, $y_{AB}^{v}(L) \to 1$, Eq. (3.12) reduces to Eq. (2.14). Equation (3.11) provides the theoretical basis for calculating solvent medium effects on the associating constant of a weak electrolyte. Taking the logarithm of this equation

$$\ln K_0' = \ln K_0 + \ln y_{AB}^{v}(L), \tag{3.13}$$

where the last term is the excess chemical potential (divided by kT) of the undissociated AB molecule in the pure solvent which is related to the dielectric constant and other properties of the solvent. We stress again that our discussion in this section applies only when $L \leqslant \sigma/2$ and at not too high densities of the solute and solvent.

IV. THEORETICAL CALCULATION OF THE CAVITY FUNCTIONS FOR REFERENCE SYSTEMS IN THE STICKY ELECTROLYTE MODEL

From the discussion above it is apparent that the degree of association α and the equilibrium properties are determined by K_0 (or K_0') and the cavity functions $y_{AB}^{0}(L)$ and $y_{AB}^{v}(L)$; the second cavity function is needed only in the treatment of association reactions in a discrete solvent. Since stickiness or bonding is absent in these reference and solvent systems, liquid state approximations can be employed to calculate the cavity functions. In this section we discuss one such approximation for the cavity function when the associating species A and B are of the same size.

An exponential type of approximation for the cavity function of ions in a hard sphere solvent of the same diameter follows from our earlier analytic work on the HNC/MS approximation for sticky electrolytes[10] by setting the sticky parameter λ equal to zero

$$y_{AB}^{0,s}(L) = \exp[-1 - c_S(L) - c_D(L)] \quad (L \leqslant \sigma) \tag{4.1}$$

with

$$c_S(L) = \lambda_1 + \lambda_2(L/\sigma) + \lambda_3(L/\sigma)^3 \quad (L \leqslant \sigma) \tag{4.2}$$

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$$\lambda_1 = -(1+2\eta_0)^2/(1-\eta_0)^4 \quad (4.3a)$$

$$\lambda_2 = 6\eta_0(1+\eta_0/2)^2/(1-\eta_0)^4 \quad (4.3b)$$

$$\lambda_3 = \eta_0(1+2\eta_0)^2/[2(1-\eta_0)^4] \quad (4.3c)$$

$$\eta_0 = \eta + \eta_v \quad (4.3d)$$

and

$$c_D(L) = (e^2/\epsilon kT\sigma)\,[2B - B^2(L/\sigma)] \quad (r<\sigma) \quad (4.4)$$

$$B = [1+\kappa\sigma - (1+2\kappa\sigma)^{1/2}]/\kappa\sigma \quad (4.5)$$

$$\kappa^2 = [4\pi e^2/(\epsilon kT)] \sum \rho_i z_i^2. \quad (4.6)$$

Here c_S and c_D are the sum and difference direct correlation functions, η and η_v are the reduced densities of solute and solvent, respectively ($\eta = \pi\rho_0\sigma^3/3$ and $\eta_v = \pi\rho_v\sigma^3/6$, where ρ_v is the solvent density) and κ is the inverse Debye length. On setting η_v equal to zero we have the cavity function for the oppositely charged ions in a continuum solvent; setting, in addition, the charges equal to zero provides the cavity function of the hard sphere reference system. A more accurate expression of the cavity function for a hard sphere system has been given by Henderson and Grundke[15] but we find it more convenient to use the results obtained from Eqs. (4.1)–(4.6) simply by switching off the charge and setting the solvent density equal to zero; the difference between this and the Henderson and Grundke approximation is very small at the solute and solvent densities considered in this study. Using this approximation for the cavity function of the reference system, the degree of association α can be calculated from Eqs. (2.14) or (3.12); while λ and the association constant K are determined using Eqs. (1.7) and (1.10), respectively.

V. THERMODYNAMIC PROPERTIES FOR WEAK ELECTROLYTES IN THE MEAN SPHERICAL APPROXIMATION FOR THE SEM

The excess energy $E^{\rm ex}$ of a weak electrolyte depends on α and is given by[6,7]

$$\beta E^{\rm ex}/N = (d\ln\tau/d\ln\beta)\alpha/2 - xH'/2 \quad (5.1)$$

where Rasaiah and Lee[13] have shown that, in the mean spherical (MS) approximation for associating ions of equal size, $H' = H/\sigma$ has the form

$$H'(\text{MSA}) = [a_1 + a_2 x - (a_1^2 + 2a_3 x)^{1/2}]/(24\,a_4\eta) \quad (5.2)$$

for any integral $n = \sigma/L$, where $x = \kappa\sigma$ and a_i ($i = 1$ to 4) are functions of the reduced ion concentration η, the association parameter λ and n. When $\lambda = 0$ (i.e., the stickiness is removed and the degree of association α is zero), all of the a_i coefficients become unity ($a_i = 1$) and the energy of the RPM electrolyte in the MSA is recovered. For $\lambda \neq 0$ we have[13,14] for

(a) $n = 2$

$$a_1 = 2 - c;\quad a_2 = 2(-3+3c+s)/v$$

$$a_3 = 2(c^2+c-2+2s-cs)/v;\quad a_4 = 4(1-c)/v^2 \quad (5.3)$$

where $v = (\eta\lambda/8)$, $c = \cos(v/2)$ and $s = \sin(v/2)$, while for (b) $n = 3$

$$a_1 = 2(\sqrt{2}-s)v + 6(2\sqrt{2}-2s-\sqrt{2}c);$$

$$a_2 = (-3\sqrt{2}+4s-\sqrt{2}c)v/3 + (5\sqrt{2}-8s-\sqrt{2}c) + 6(-\sqrt{2}+s+\sqrt{2}c)/v,$$

$$a_3 = 6(12-17\sqrt{2}s+3\sqrt{2}cs-4c+12s^2) + 18(-8+7\sqrt{2}s-5\sqrt{2}cs+8c-2s^2)/v,$$

$$a_4 = (3\sqrt{2}-4s+\sqrt{2}c)/3 + 2(-\sqrt{2}+2s+\sqrt{2}c)/v + 3\sqrt{2}(1-c)/v^2, \quad (5.4)$$

where $v = (\eta\lambda/18)$, $c = \cos(\sqrt{2}v/3)$ and $s = \sin(\sqrt{2}v/3)$. The corresponding expressions for $n = 4$ and 5 are quite lengthy and are given in reference 14.

The change (Δ) in the Helmholtz free energy due to stickiness (or bonding) can be expressed as[7]

$$\begin{aligned}\beta\Delta A/N &= -(\eta/2)\,(L/\sigma^3)\int_0^{\zeta} y_{\rm AB}(L,\zeta')\,d\zeta' \\ &= -(L\eta/2\sigma^3)\,[\lambda(1-\ln y_{\rm AB}(L) + \textstyle\int_0^{\lambda}\ln y_{\rm AB}(L,\lambda')\,d\lambda'] \quad (5.5)\\ &= \alpha/2 + (1/2)\ln[y'_{\rm AB}(L)/y^{0'}_{\rm AB}(L)] + I\end{aligned}$$

where N is the total number of solute particles and I is defined by

$$I = [y^{0'}_{\rm AB}(L) - 1]\textstyle\int_0^{\alpha}[(1-\alpha)^2 + y^{0'}_{\rm AB}(L) - 1]^{-1}\,d(1-\alpha). \quad (5.6a)$$

The integrand in Eq. (5.6) is the inverse of the cavity function which, using our exponential approximation for $y^0_{\rm AB}(L)$, is positive (see Figs. 2–4), but the integral depends on whether $y^{0'}_{\rm AB}(L)$ is greater than or less than unity. We find that for the two cases (a) $y^{0'}_{\rm AB}(L) > 1$

$$I = \gamma\{\tan^{-1}[(1-\alpha)/\gamma] - \tan^{-1}(1/\gamma)\} \quad (5.6b)$$

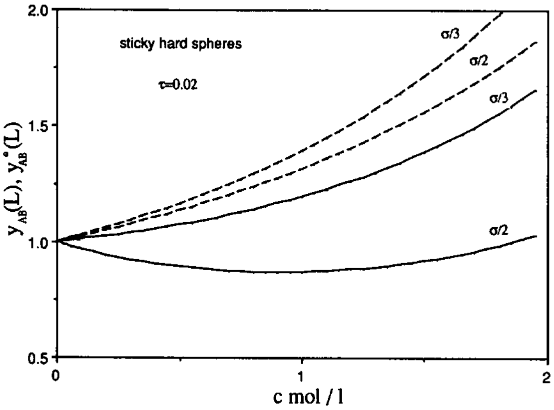

FIG. 2. The cavity functions $y_{\rm AB}(L)$ and $y^0_{\rm AB}(L)$ for the sticky hard spheres at $L = \sigma/2$ and $\sigma/3$ in a continuum solvent plotted as a function of the solute concentration. The connected lines are $y_{\rm AB}(L)$ and the dashed lines $y^0_{\rm AB}(L)$. $y_{\rm AB}(L)$ and $y^0_{\rm AB}(L)$ were calculated from Eqs. (2.11) and (4.1) using Eq. (2.15) for α. The sticky parameter and the molecular diameter are $\tau = 0.02$, $\sigma = 4.2$ A.

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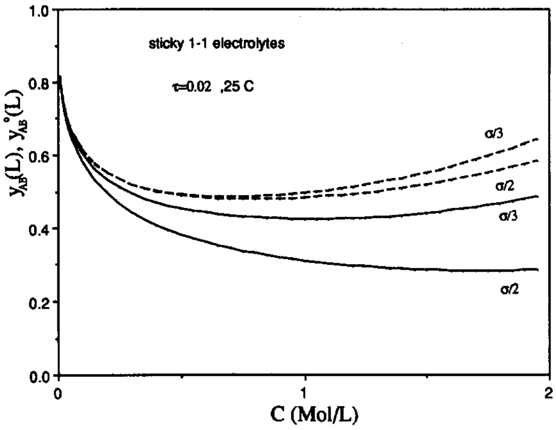

FIG. 3. The cavity functions $y_{AB}(L)$ and $y^0_{AB}(L)$ for the sticky electrolytes at different L in a continuum solvent plotted as a function of the electrolyte concentration. The connected lines are $y_{AB}(L)$ and the dashed lines $y^0_{AB}(L)$. The temperature and dielectric constant are $t = 25\,°C$ and $\varepsilon = 78.358$, the other parameters are $\tau = 0.02$ and $\sigma = 4.2$ A. See caption of Fig. 2 for other details of calculations.

(b) $y^{0'}_{AB}(L) < 1$

$$I = -(1/2)\gamma \ln\{[(1-\alpha-\gamma)(1+\gamma)]/[(1-\alpha+\gamma)(1-\gamma)]\} \tag{5.6c}$$

with

$$\gamma = (|1 - y^{0'}_{AB}(L)|)^{1/2}. \tag{5.6d}$$

In deriving Eqs. (5.5) and (5.6), we have used Eq. (3.7) and the definitions in Eqs. (3.8) and (3.9). As expected, $\Delta A \to 0$ when the stickiness is turned off i.e., when $\alpha \to 0$. The continuum solvent limit is obtained by setting the solvent density equal to zero when $y'_{AB} = y_{AB}(L)$ and $y^{0'}_{AB}(L) = y^0_{AB}(L)$.

As discussed by us in an earlier paper,[10] the osmotic coefficient of the SEM, in the McMillan–Mayer system, can be separated into three parts

$$\phi = 1 + \phi^{hs,ex} + \phi^{el,ex} + \phi^{st,ex}, \tag{5.7}$$

where $\phi^{hs,ex}$ and $\phi^{el,ex}$ are given as[10]

$$\phi^{hs,ex} = (3-\eta_0)/(1-\eta_0)^3 - (3 - 2\eta - 4\eta_v + \eta_0\eta_v)/[(1-\eta_0)^2(1-\eta_v)^2] \tag{5.8}$$

$$\phi^{el,ex} = [2 + 3x - (2+x) \times (1+2x)^{1/2}]/72\eta \tag{5.9}$$

and the sticky part $\phi^{st,ex}$ is found from

$$\phi^{st,ex} = \frac{\mu^{st,ex}}{kT} - \rho^{-1}\int_0^\rho \left(\frac{\mu^{st,ex}}{kT}\right) d\rho. \tag{5.10}$$

The excess chemical potential $\mu^{st,ex}$ is obtained by differentiating ΔA in Eq. (5.5) with respect to N

$$\mu^{st,ex}/kT = \beta\Delta A/N + \eta\frac{\partial(\beta\Delta A/N)}{\partial\eta}. \tag{5.11}$$

Substituting this in Eq. (5.10) and carrying out the integration we have

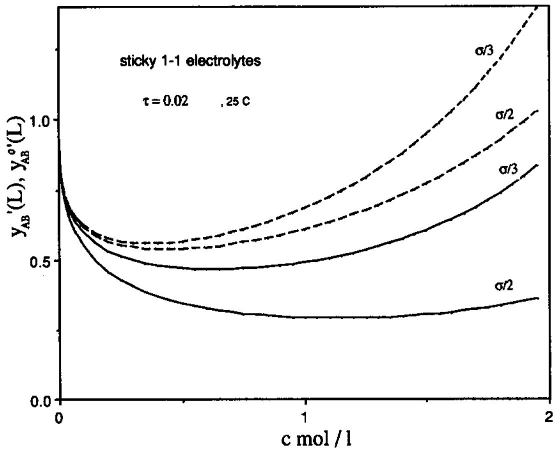

FIG. 4. The rescaled cavity functions $y'_{AB}(L)$ and $y^{0'}_{AB}(L)$ for the sticky electrolytes at different L in a discrete solvent ($\eta_v = 0.1$) plotted as a function of the electrolyte concentration. The connected lines are $y'_{AB}(L)$ and the dashed lines $y^{0'}_{AB}(L)$. $y'_{AB}(L)$ and $y^{0'}_{AB}(L)$ were calculated from Eqs. (3.7), (3.9), and (4.1) using the analog of Eq. (2.15) for α. The model parameters are the same as in Fig. 3.

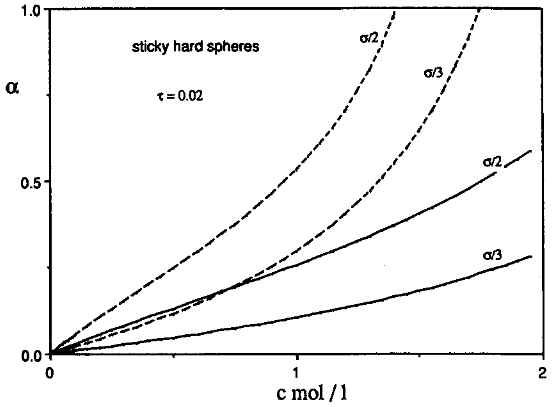

FIG. 5. The degree of association α for different L plotted as a function of the concentration of sticky hard spheres. The full lines are the results in a continuum solvent and the dashed lines are those in a discrete solvent with $\eta_v = 0.1$. For the model parameters and other details, see caption of Fig. 2.

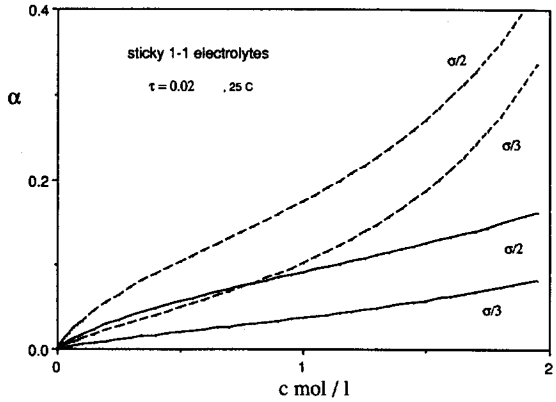

FIG. 6. The degree of association for different L plotted as a function of the electrolyte concentration. The full lines are the results in a continuum solvent and the dashed lines are those in a discrete solvent with $\eta_v = 0.1$. See caption of Fig. 3 for the model parameters and other details.

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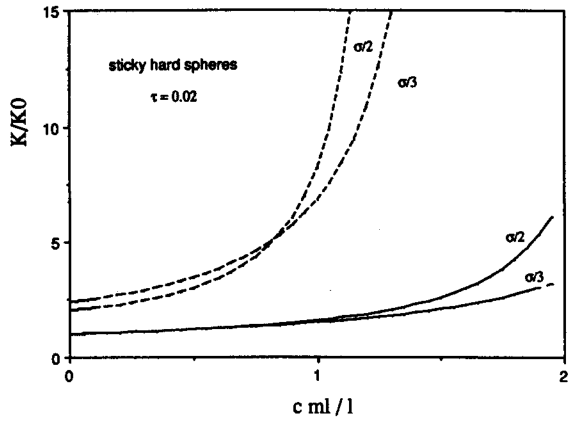

FIG. 7. The ratio K/K_0 for different L plotted as a function of the hard sphere concentration. The full lines are the results in a continuum solvent and the dashed lines are the results in a hard sphere solvent with $\eta_v = 0.1$. The model parameters are the same as in Fig. 2.

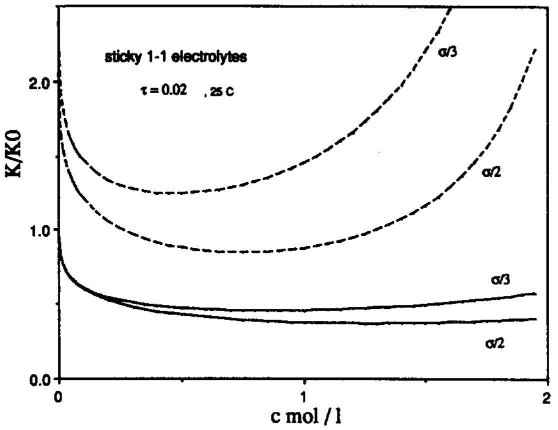

FIG. 8. The ratio K/K_0 for different L plotted as a function of the electrolyte concentration. The full lines are the results in a continuum solvent and the dashed lines are the results in a hard sphere solvent with $\eta_v = 0.1$. The model parameters are the same as in Fig. 3.

$$\begin{aligned}\phi^{\rm st,ex} &= \eta\frac{\partial(\beta\Delta A/N)}{\partial\eta}\\ &= \alpha/2-\alpha(1-\alpha)/y'_{\rm AB}(L)+(\eta^2/2)(L/\sigma)^3\\ &\quad\times\left(\frac{d\lambda}{d\eta}\right)[1-2(1-\alpha)/y'_{\rm AB}(L)]\\ &\quad+(\eta/2)\left[\frac{dy^{0'}_{\rm AB}(L)}{d\eta}\right][1-(1-\alpha)^2]/\\ &\quad[y^{0'}_{\rm AB}(L)\,y'_{\rm AB}(L)]+J \end{aligned}\tag{5.12}$$

with

$$\begin{aligned}\frac{d\lambda}{d\eta} &= \left[\eta\frac{dy^{0'}_{\rm AB}(L)}{d\eta}-2\alpha(1-\alpha)\right]/\\ &\quad\{\eta[\tau'+2\eta(1-\alpha)(L/\sigma)^3]\}\end{aligned}\tag{5.13a}$$

and

$$\begin{aligned}J &= \eta\frac{\partial I}{\partial\eta}\\ &= (\eta/2)\left[\frac{dy^{0'}_{\rm AB}(L)}{d\eta}\right]\{I/[y^{0'}_{\rm AB}(L)-1]\\ &\quad+1/y^{0'}_{\rm AB}(L)-(1-\alpha)/y'_{\rm AB}(L)\}\\ &\quad-[y^{0'}_{\rm AB}(L)-1]\,[\alpha+\eta^2\\ &\quad\times\left(\frac{d\lambda}{d\eta}\right)(L/\sigma)^3/y'_{\rm AB}(L)\Big],\end{aligned}\tag{5.13b}$$

TABLE I. The ratio of the association constants for sticky hard spheres ($\tau = 0.02$) for $L = \sigma/2$ and $\sigma/3$ calculated using two different approximations for the cavity functions.

c mol/l	$K/K_0(\sigma/2)$	$K/K_0(\sigma/3)$	$K/K_0(\sigma/2)$	$K/K_0(\sigma/3)$
	Eq. (2.11) for $y_{\rm AB}(L)$		Eq. (1.11) for $y_{\rm AB}(L)$	
0.100	1.026	1.029	1.024	1.029
0.500	1.179	1.181	1.136	1.164
1.000	1.568	1.487	1.316	1.392
1.500	2.568	2.065	1.580	1.716
1.900	5.320	3.013	1.824	2.083

where I is given by Eq. (5.6b) for $y^{0'}_{\rm AB}(L) > 1$ and by Eq. (5.6c) for $y^{0'}_{\rm AB}(L) < 1$ and τ' is given by Eq. (3.10). $dy^{0'}_{\rm AB}(L)/d\eta$ may be obtained from our approximation for the cavity function of the reference system by differentiating Eqs. (3.9) and (4.1).

$$\begin{aligned}\frac{dy^{0'}_{\rm AB}(L)}{d\eta} &= y^{0'}_{\rm AB}(L)\,[-\lambda'_1-\lambda'_2(L/\sigma)\\ &\quad-\lambda'_3\,(L/\sigma)^3-c'_D(L)]\quad(L<\sigma)\end{aligned}\tag{5.14}$$

where

$$\begin{aligned}\lambda'_1 &= -4(1+2\eta_0)/1-\eta_0)^4\\ &\quad-4(1+2\eta_0)^2/(1-\eta_0)^5,\end{aligned}\tag{5.15a}$$

$$\begin{aligned}\lambda'_2 &= 3(4+8\eta_0+3\eta_0^2)/[2(1-\eta_0)^4]\\ &\quad+6\eta_0(2+\eta_0)^2/(1-\eta_0)^5,\end{aligned}\tag{5.15b}$$

$$\lambda'_3 = \lambda_1+\eta_0\lambda'_1/2,\tag{5.15c}$$

and

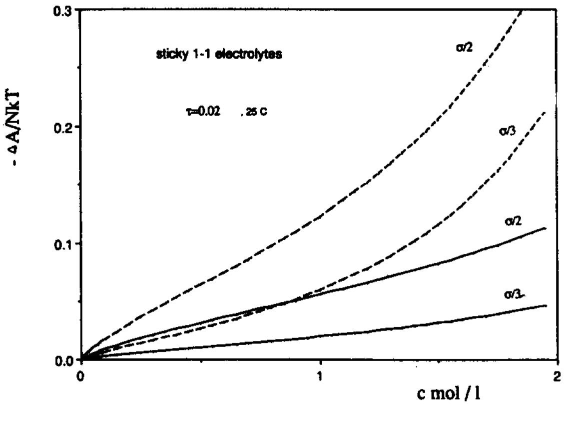

FIG. 9. Plots of the change in the Helmholtz-free energy due to stickiness for different L vs the concentration of a 1–1 electrolyte—see Eq. (5.5). The full lines are the results in a continuum solvent and the dashed lines are the results in a hard sphere solvent $\eta_v = 0.1$. For the model parameters, see caption of Fig. 3.

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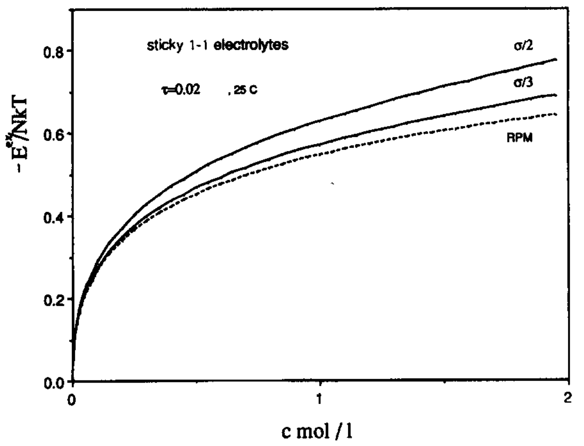

FIG. 10. Plots of the excess internal energy of a sticky 1–1 electrolyte in a continuum solvent for different L vs the electrolyte concentration. The dashed line is for the restricted primitive model (RPM) in which stickiness is absent. The other curves are calculated from Eq. (5.1) using Eq. (2.15) for the degree of association and the MS approximation [Eq. (5.2)] for the electrical interactions. See caption of Fig. 3 for the model parameters.

$$c'_D(L) = (e^2/\epsilon kT\sigma)\,[2B' - 2BB'(L/\sigma)] \quad (r \leqslant \sigma), \tag{5.16}$$

$$B' = [1-(1+2x)^{-1/2} - B]/2\eta. \tag{5.17}$$

Note when the solvent density goes to zero $[\eta_v \to 0, y^{0'}_{\mathrm{AB}}(L) \to y^0_{\mathrm{AB}}(L)$ and $y'_{\mathrm{AB}}(L) \to y_{\mathrm{AB}}(L)]$, the osmotic coefficient given in Eqs. (5.7)–(5.17) reduces to that in a continuum solvent.

VI. RESULTS AND DISCUSSION

The degree of association and the equilibrium properties of associating systems depend critically on the cavity functions $y_{\mathrm{AB}}(L)$ and $y'_{\mathrm{AB}}(L)$; our approximations for these functions for sticky hard spheres and for sticky electrolytes when the associating species are of the same size are plotted against the solute concentration in Figs. 2 and 3 along with the cavity functions $y^0_{\mathrm{AB}}(L)$ and $y^{0'}_{\mathrm{AB}}(L)$ for the reference systems. The parameter $\tau = 1/\zeta$, which determines the strength of the stickiness in the Mayer f bond for AB, is assumed to be the same ($\tau = 0.02$) in each of the systems to make the analysis simpler. It is seen that the addition of an attractive interaction (sticky or electrical) between the associating species A and B decreases the cavity function thereby reducing the probability that two "ghost" particles, which constitute the cavities, can form at a distance $L \lessdot \sigma/2$. This is just the opposite of what is expected of the distribution functions of real particles at $L > \sigma$. Thus, the reference cavity function $y^0_{\mathrm{AB}}(L)$ is always greater than $y_{\mathrm{AB}}(L)$ for the sticky system, and the cavity function for hard spheres (whether sticky or free) is greater than the corresponding cavity function for charged hard spheres. The rescaled cavity functions $y'_{\mathrm{AB}}(L)$ and $y^{0'}_{\mathrm{AB}}(L)$ [see Eqs. (3.8) and (3.9)], which are the relevant ones for association in a dis-

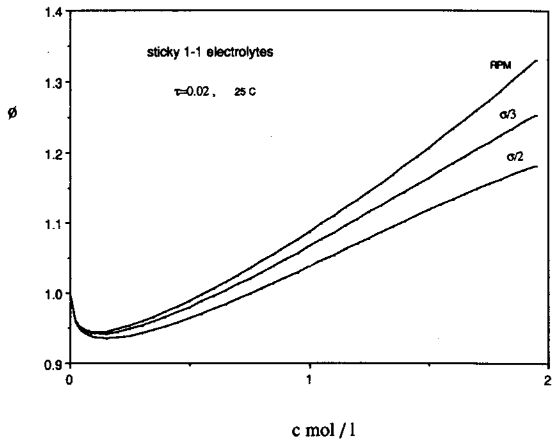

FIG. 11. Plots of the osmotic coefficient of a sticky 1–1 electrolyte in a continuum solvent for different L vs the solute concentration. See caption of Fig. 3 for the model parameters and other details.

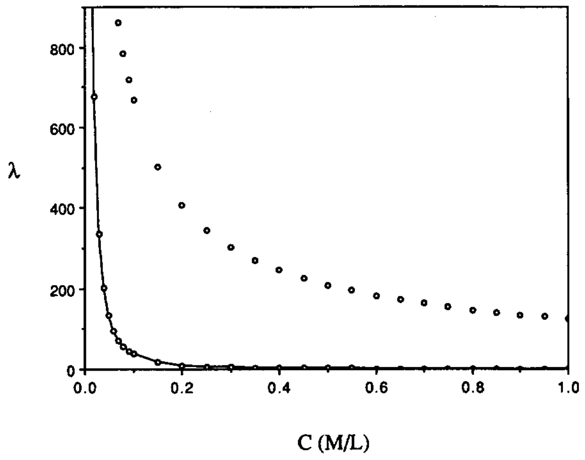

FIG. 12. Plots of the sticky parameter λ for a 2–2 electrolyte with $L = \sigma/2$ vs the solute concentration in a continuum solvent. The unconnected line is the result of Ref. 6 using the HNC approximation, the connected line is the result of our new method for determining the degree of association from Eq. (2.15). Here $t = 25\,^\circ\mathrm{C}$, $z_A = -z_B = 2$, $\epsilon = 78.358$, $\tau = 6.15 \times 10^{-7}$ ($\epsilon_2 = 4000\,k$) and $\sigma = 4.2$ A.

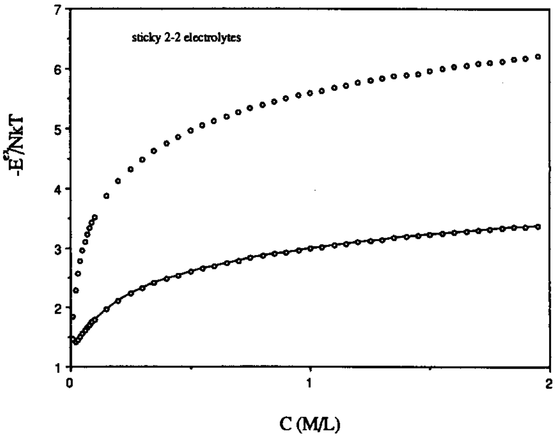

FIG. 13. Plots of the excess energy vs the concentration of a sticky 2–2 electrolyte in a continuum solvent for $L = \sigma/2$. The unconnected curve is the HNC/MS result of reference 6; the connected curve is our new calculation [Eq. (5.1)] using Eq. (2.15) for the degree of association and the MS approximation [see Eqs. (5.2)] for the electrical interactions. See caption of Fig. 12 for the model parameters.

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crete solvent, and plotted as a function of the electrolyte concentration in Fig. 4; the solvent molecules here are hard spheres at a reduced density $\eta_v = 0.1$. The figure shows that the rescaled functions for sticky electrolytes behave similarly to the cavity functions $y_{\rm AB}(L)$ and $y^0_{\rm AB}(L)$ (Fig. 3) in the absence of a hard sphere solvent. Qualitatively the same behavior is also observed for sticky hard spheres in a hard sphere solvent. A comparison of Fig. 1 and Fig. 3 shows that the reference cavity functions calculated from the formula (2.16) by using experimental data for weak acids are similar to those calculated from the exponential approximation (4.1) although the minima occur at much lower concentrations for the weak acids. This may be due to the neglect of size differences and directional bonding in the exponential approximation.

In Figs. 5 and 6 we show our calculations of the degree of association as a function of the solute concentration for sticky hard spheres and sticky electrolytes respectively when $L = \sigma/2$ and $\sigma/3$ with $\tau = 0.02$. The corresponding association constant ratios K/K_0 are displayed in Figs. 7 and 8. As expected α and K/K_0 increase with the solute concentration and are further enhanced by the presence of a hard sphere solvent which exerts a packing effect. We also see that α is greater for $L = \sigma/2$ than for $L = \sigma/3$ at a finite solution concentration, while the order for K/K_0 is reversed for sticky electrolytes at concentrations up to 2 molar both in the presence and in the absence of a hard sphere solvent. The same reversal is also observed for sticky hard spheres in a hard sphere solvent at low concentrations—see Fig. 7. These observations are related to the behavior of the cavity functions. It follows from Eqs. (1.3), (1.5), (1.7), and (1.10) that

$$\frac{\alpha_{\sigma/2}}{\alpha_{\sigma/3}} = \frac{(27/8)y_{\rm AB}(\sigma/2)}{y_{\rm AB}(\sigma/3)}\,, \tag{6.1}$$

$$\frac{(K/K_0)_{\sigma/2}}{(K/K_0)_{\sigma/3}} = \frac{(1-\alpha_{\sigma/3})^2 y_{\rm AB}(\sigma/2)}{[(1-\alpha_{\sigma/2})^2 y_{\rm AB}(\sigma/3)]}\,\cdot \tag{6.2}$$

The larger degree of association at the larger separation (L) is determined by the magnitude of the ratio of the two cavity functions. The relative magnitude of the association constants at the two separations, however, is determined by the ratios of the cavity functions as well as the ratios of the squares of the degrees of dissociation $(1-\alpha)$ which also depend on the cavity functions. It is seen that the approximations for the cavity functions enter critically into this calculation. Using the exponential type of approximation for the cavity function of the reference system, we find $y_{\rm AB}(\sigma/2) < y_{\rm AB}(\sigma/3)$ but $(1-\alpha_{\sigma/3})^2 > (1-\alpha_{\sigma/2})^2$. The order of K/K_0 for sticky hard spheres we find is qualitatively the same as the order found using the PY approximation for the stickiness,[5] but is just the opposite of what is obtained using Eq. (1.11)—see Table I. Another interesting observation is that the association constant and the degree of association are smaller for sticky electrolytes than for the corresponding sticky hard spheres with the same sticking coefficient $1/\tau$. This can be explained in terms of our earlier observation that the cavity function for $L < \sigma/2$ decreases when an attractive interaction is introduced. The same effect is observed in Stell and Zhou's calculation of K/K_0.[12]

The Helmholtz free energy, excess energy and osmotic coefficient are displayed in Figs. 9, 10, and 11 for sticky 1–1 electrolytes. As expected, the addition of a hard sphere solvent makes the free energy due to association more negative. The excess energy and the osmotic coefficients of electrolytes in the absence of a discrete molecular solvent are shown in Figs. 10 and 11. The order of these functions for electrolytes with stickiness at $L = \sigma/2$ and $\sigma/3$ are qualitatively the same as what was found in our earlier work[7] even though the charges and the sticking coefficients are very different.

To compare our new method with the earlier results for weak electrolytes using the HNC/MS approximation (HNC for the stickiness and MS for the electrical interactions), we use the same value for τ ($\tau = 6.15\times10^{-7}$) to calculate the association parameter λ and the excess energy for the 2–2 electrolytes in a continuum solvent ($\eta_v = 0$, $\epsilon = 78.358$) at $L = \sigma/2$. From the results displayed in Figs. 12 and 13 it appears that λ becomes smaller much sooner with increase in concentration than in our earlier calculations using the HNC approximation for stickiness; the same trend appears in the excess energy. The equilibrium constant at this value of τ is large ($K_0/\sigma^3 = 2.12\times10^5$), so that a small uncertainty in the reference cavity function $y^0_{\rm AB}(L)$ will produce a large error in the degree of association α calculated from Eq. (2.15). For this large K_0, our exponential approximation for the cavity function predicts an α that decreases with the concentration for electrolytes while just the opposite behavior is found for sticky hard spheres. This suggests that the exponential approximation for electrolytes may not be accurate enough to use in Eq. (2.15) when the sticking coefficient ζ is large i.e., when K_0 is large. This can be investigated by using integral equation approximations for $y^0_{\rm AB}$ and computer simulation which are beyond the scope of this paper.

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