

A Model for Weak Electrolytes¹

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The structural and thermodynamic properties of a model electrolyte in which oppositely charged ions bind at a distance L through a delta function interaction are reviewed. The sticky electrolyte model (SEM), as it is called, mimics the behavior of a weak electrolyte and requires a theory (or approximations) for the stickiness (or bonding) between the ions and for the electrical interactions between them. Analytic solutions for charged hard spheres of diameter σ with $L = \sigma/n$ where $n = 1, 2, 3, 4,$ and 5 have been obtained when the hypernetted chain (HNC) approximation was used for the correlation functions inside the hard core and the mean spherical approximation (MS) was employed outside this region. Numerical solutions to the HNC approximation applied to both these regions show only small changes in the internal energy and the degree of association as a function of the concentration. The effect of a solvent on the association of a weak electrolyte is assessed from the analytic solutions to the HNC/MS approximation in the presence of a hard sphere solvent and a dipolar solvent. It is found that the degree of association of the weak electrolyte is considerably enhanced by the packing effect of a solvent and is decreased by ion solvation. In the limit of complete association, the system consists of dumbbells with extended dipoles provided $L < \sigma/2$ when polymerization is averted by the repulsion between the hard cores of like ions. The energies of the systems of extended dipoles are found to have a simple analytic form when they are calculated according to the mean spherical approximation.

KEY WORDS: electrolytes (weak); dipolar dumbbells; hypernetted chain approximation; ion association; mean spherical approximation; sticky electrolyte model.

1. INTRODUCTION

In a weak electrolyte (e.g., an aqueous solution of acetic acid) the solute molecules AB are incompletely dissociated into ions A^+ and B^- according to the familiar chemical equation



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The forces binding the atoms in AB are chemical in nature and must be introduced, at least approximately, in the Hamiltonian in a theoretical treatment of this problem. The binding between A and B in the dimer AB is quite distinct from the formation of ion pairs in higher-valence electrolytes (e.g., aqueous solutions ZnSO_4 at room temperature) where the coulomb interactions between the ions lead to the presence of associated pairs and clusters which account for the anomalous conductance and activity data of these electrolytes at low concentrations [1, 2]. The shielding of the charges on the ions with increasing electrolyte concentration induces the ion pairs to redissociate and the clusters to breakup above a critical composition [2, 3], whereas the population of dimers produced by the chemical bonding represented in Eq. (1) always increases with the concentration of the solution. In this paper I review recent work on weak electrolytes in which dimerization (as opposed to ion pairing) is the result of chemical bonding between oppositely charged ions.

A simple model for a strong electrolyte is the restricted primitive model (RPM) in which the ions are represented as charged hard spheres of the same diameter σ immersed in a structureless solvent of dielectric constant ϵ_0 . The pair potential $u_{ij}(r)$ has the form

$$u_{ij}(r) = u_{ij}^{\text{HS}}(r) + e_i e_j / \epsilon_0 r \quad (2)$$

where $u_{ij}^{\text{HS}}(r)$ is the hard sphere potential, which is infinite for $r < \sigma$ and zero otherwise. The equilibrium properties of the restricted primitive model electrolyte can be calculated quite accurately using the hypernetted chain (HNC) [4] approximation, which assumes that the direct correlation function

$$c_{ij}(r) = -\beta u_{ij}(r) + g_{ij}(r) - 1 - \ln g_{ij}(r) \quad (3)$$

where $g_{ij}(r)$ is the pair correlation function and $\beta = 1/kT$ in which k is Boltzmann's constant and T is the absolute temperature. This equation is solved together with the Ornstein-Zernike equation, which provides another relation between $g_{ij}(r)$ and $c_{ij}(r)$. The effects of ion pairing in higher valence electrolytes and the excluded volume of the ions for all charge types are quite faithfully represented in this approximation [6]; the main drawback of the theory is that the solutions have to be obtained numerically. The mean spherical approximation (MSA) for the RPM electrolyte, on the other hand, can be solved analytically [5]: it assumes that instead of Eq. (3)

$$c_{ij}(r) = -\beta u_{ij}(r) \quad \text{for } r > \sigma \quad (4)$$

This is supplemented with the core condition that

$$g_{ij}(r) = 0 \quad \text{for } r < \sigma \quad (5)$$

Waismann and Lebowitz [5] determined the solution to this approximation and showed that the thermodynamic properties obtained from the energy equation are quite accurate for lower-valence electrolytes [5, 7]. The excess energy E^{ex} is given by

$$\frac{E^{\text{ex}}}{NKT} = \frac{-x[(1+x) - (1+2x)^{1/2}]}{4\pi\rho\sigma^3} \left\{ 1 + \frac{d \ln \epsilon_0}{d \ln T} \right\} \quad (6)$$

where ϵ_0 is the dielectric constant of the solvent, k is Boltzmann's constant, T is the temperature in degrees Kelvin, $x = \kappa\sigma$, where $1/\kappa$ is the Debye length defined by $\kappa^2 = 4\pi\rho e^2/\epsilon_0 kT$, and ρ is the density of the ions. The osmotic coefficient ϕ_E calculated from the energy in the MSA has the form

$$\phi_E = \phi^0 + [3x + 3x(1+2x)^{1/2} - 2(1+2x)^{3/2} + 2]/12\pi\rho\sigma^3 \quad (7)$$

Here ϕ^0 is the osmotic coefficient of the corresponding uncharged hard sphere system. Equation (6) for the energy is related to the heat of dilution of the electrolyte. These are remarkably simple analytic expressions which are directly applicable to solutions in which ion pairing is negligible. Nevertheless, the MSA can also be used to predict the thermodynamic properties of solutions in which ion pairing is significant by making certain assumptions about these pairs; it is assumed, for instance, that the oppositely charged ions within a separation d (greater than the distance of closest approach σ) are paired and that the interactions of the free ions can be treated with sufficient accuracy in the mean spherical approximation (2, 8, 9]. The idea of dividing the system into free ions and associated pairs was first suggested by Bjerrum [10] shortly after the Debye-Huckel theory (11) was proposed. The modern theory of ion pairing or clustering uses a different definition of d from Bjerrum's, employs the MSA instead of the Debye-Huckel theory for the free ions, and determines the number of pairs or clusters by minimizing the free energy. Corti and Fernandez-Prini [2] have used a theory of this type to predict the osmotic coefficients of 2-2 electrolytes in aqueous solution up to concentrations of 3 M .

In what follows we see that the mean spherical approximation is also useful for weak electrolytes and that the excess energy for these solutions in the MSA is given by an equation similar to Eq. (6). An expression of the same form applies for the energies of dipolar dumbbells as well since they can be regarded as fully associated weak electrolytes!

2. A MODEL FOR WEAK ELECTROLYTES

The model calculations that I review are for the sticky electrolyte model (SEM) in which a delta function interaction is introduced into the Mayer f function for the oppositely charged ions at a distance $L \leq \sigma$, where σ is the hard sphere diameter. The model was introduced by Cummings and Stell [12] in their study of dimerization reactions in uncharged systems and is closely related to Baxter's model [13] for adhesive hard spheres. Baxter and also Cummings and Stell solved these models in the Percus–Yevick (PY) approximation using the Wiener–Hopf factorization of $1 - \rho c(k)$, where $c(k)$ is the Fourier transform of the direct correlation function $c(r)$. The technique was introduced earlier by Baxter [14] in his solution of the Percus–Yevick approximation for hard spheres and the extension of the method to study electrolytes was developed independently by Thompson [15] and by Tibavescio [16] and Blum [17].

In the SEM the Mayer f function for ions of opposite sign is defined by

$$f_{+-} = -1 + L\zeta\delta(r-L)/12, \quad r \leq \sigma \quad (8)$$

where ζ is called the sticking coefficient and the delta function in Eq. (8) mimics bonding. The presence of a delta function in the f function induces a delta function in the correlation function $h_{+-}(r)$ with a different coefficient, λ , known as the association parameter:

$$h_{+-} = -1 + L\lambda\delta(r-L)/12, \quad r \leq \sigma \quad (9)$$

The interaction between ions of the same sign is taken to be a pure hard sphere repulsion for $r \leq \sigma$. It follows from simple steric considerations that an exact solution will predict dimerization only if $L < \sigma/2$ but polymerization may occur for $\sigma/2 < L \leq \sigma$. However, an approximate solution may not show the full extent of polymerization that could occur in a more accurate or exact theory when $L \geq \sigma/2$ [18, 19]. This can be exploited to advantage if we wish to suppress association beyond the formation of dimers.

The association ratio K defined by $K = \rho_{AB}/\rho_A\rho_B$ is easily found to be [12]

$$K = \frac{\pi\lambda(L/\sigma)^3}{3(1 - \langle N \rangle)^2} \quad (10)$$

where the average number of dimers $\langle N \rangle = \eta\lambda(L/\sigma)^3$ and $\eta = \pi\rho\sigma^3/6$, in which ρ is the total ionic density. We can now distinguish three different cases [18, 19]:

$\lambda = 0$	No dimers	Strong electrolyte (RPM)
$\lambda = (\sigma/L)^3/\eta$	All dimers if $L < \sigma/2$	Dipolar dumbbells
$0 < \lambda < (\sigma/L)^3/\eta$	Ions + dimers	Weak electrolyte (SEM)

Either the same or different approximations may be used to treat the binding at $r = L$ and the remaining electrical interactions between the ions. The use of PY approximation for the binding in weak electrolytes leads to negative values for λ , prompting Lee *et al.* [18] to employ the HNC approximation for the binding and the MSA for the interactions between the ions. Analytic solutions to this hybrid (HNC/MSA) approximation were obtained by an extension [15] of Wiener–Hopf factorization techniques used for nonionic systems. Numerical solutions to the HNC approximation for both types of interactions present in this model with $n = 2$ and 3 were also obtained by Rasaiah and Lee [19], by a simple modification of the procedure employed for strong electrolytes [3]. Rather surprisingly the association parameters λ obtained from the two approximations are very nearly the same, although the distribution functions (g_{++} and g_{+-}) are quite different, particularly at low concentrations (see Fig. 1). The excess energy of the sticky electrolyte system is given by [18, 19]

$$\frac{E^{\text{ex}}}{NkT} = \frac{\langle N \rangle}{2} \left(\frac{d \ln \zeta}{d\beta} \right) - \left(1 + \frac{d \ln \epsilon_0}{d \ln T} \right) \frac{\kappa H}{2} \quad (11)$$

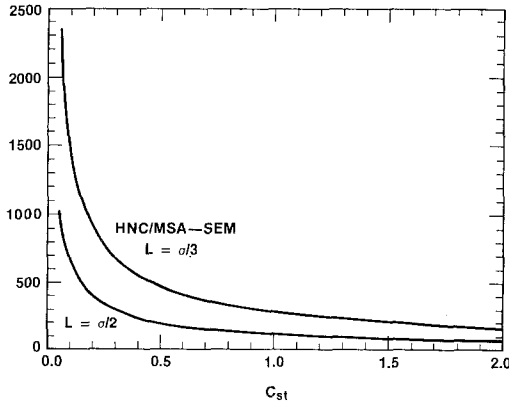


Fig. 1. The association parameter λ as a function of the electrolyte concentration c_{st} in moles per liter for a 2–2 electrolyte using the SEM in the HNC/MS approximation. The dielectric constant $\epsilon_0 = 78.358$, the temperature $T = 298$ K, and the ion diameter $\sigma = 4.2$ Å. The sticking coefficient $\zeta = 1.63 \times 10^6$ and 2.44×10^6 for $L = \sigma/2$ and $\sigma/3$, respectively (from Ref. 19).

where

$$H = \kappa \int_{\sigma}^{\infty} h_D(r) r dr \quad (12)$$

and $h_D(r) = [h_{+-}(r) - h_{++}(r)]/2$. The first term in Eq. (11) is the binding energy and the second is the energy due to the interactions between the charges, which can be determined analytically in the MSA. For any integer $n = \sigma/L$, Rasaiah and Lee [19] have shown that $H' = H/\sigma$ has the form

$$H'(\text{SEM/MSA}) = \frac{(a_1 + a_2 x) - (a_1^2 + 2xa_3)^{1/2}}{24a_4\eta} \quad (13)$$

where $a_i (i=1$ to 4) are functions of the reduced ion concentration η , the association parameter λ , and n . When $\lambda=0$, $a_i=1$, the average number of dimers $\langle N \rangle=0$, and the energy of the RPM electrolyte in the MSA is recovered [see Eq (6)].

The energies of a weak electrolyte calculated analytically from the HNC/MSA approximation (HNC for the binding and MSA for the electrical interactions) and numerically from the HNC approximation alone are very nearly the same. This is illustrated in Fig. 2 for $n=2$ and 3, where comparison is also made with the energy of the corresponding RPM electrolyte ($\lambda=0$). The more negative excess energy of the SEM is due mainly to the additional binding energy. The osmotic coefficients for the same

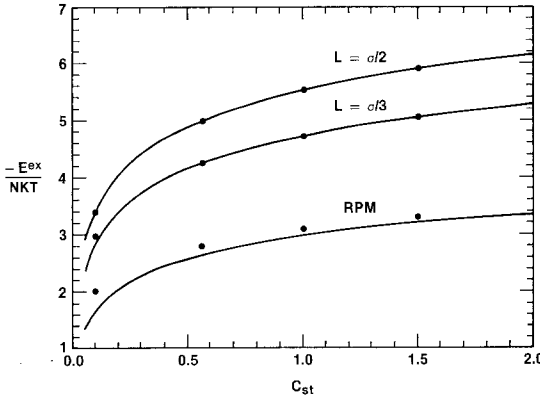


Fig. 2. The excess energy E^{ex} in units of NkT as a function of the electrolyte concentration c_{st} for RPM and SEM 2-2 electrolytes. The lines and points are the results for the HNC/MS and HNC approximations; the other parameters are the same as for Fig. 1 (from Ref. 19).

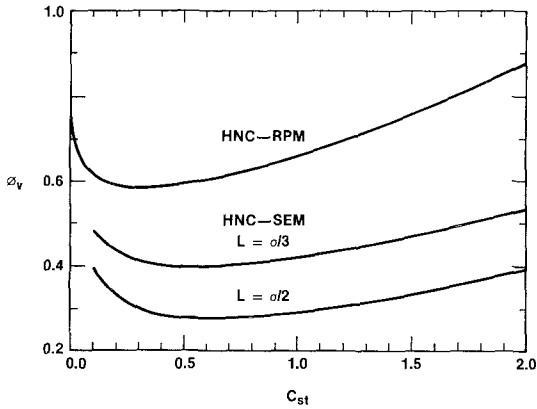


Fig. 3. The osmotic coefficient ϕ calculated from the virial equation as a function of the electrolyte concentration c_{st} for RPM and SEM 2-2 electrolytes using the HNC approximation. The parameters are the same as in Fig. 1 (from Ref. 19).

systems calculated from the HNC approximation using the virial equation are compared in Fig. 3; as expected the weak electrolyte has a lower osmotic coefficient than the strong electrolyte. Note that the excess energies and osmotic coefficients are closer to the RPM results for $n=3$ than for $n=2$. The distribution functions for a 2-2 SEM electrolyte with $L = \sigma/2$ at a electrolyte concentration of 2.0 molar are shown in Fig. 4; the differences between the HNC and the HNC/MSA distribution functions, although

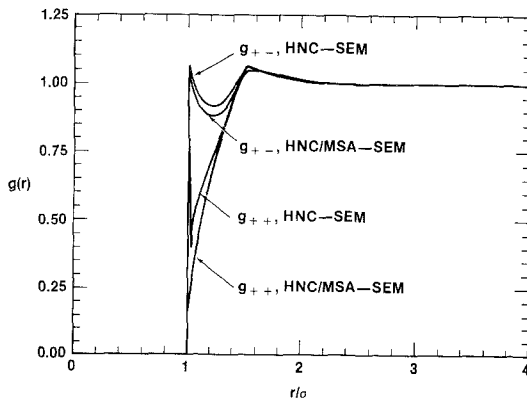


Fig. 4. The ion distribution functions $g_{++}(r)$ and $g_{+-}(r)$ for the 2-2 electrolyte depicted in Fig. 1 at a concentration $c = 2.0 M$ and $L = \sigma/2$ (from Ref. 19).

small at this concentration, become more pronounced as the concentration is decreased [19]. The effects of hard sphere and dipolar solvents on the degree of dissociation of a weak electrolyte have also been studied recently [20] and it is found that the association parameter λ is enhanced by the packing effect of the solvent and decreased by ion solvation.

The use of the PY or HNC approximation to determine the degree of chemical association for electrolytes and nonelectrolytes does not necessarily ensure the equality of the chemical potentials of the products and the reactants in Eq. (1). A better procedure would be to determine λ by minimizing the free energy with respect to the number of dimers in the same that the number of ion pairs is calculated in recent theories of strong electrolytes [2, 8, 10]. This will change λ but leave the analytic expressions for the distribution functions and the thermodynamic properties derived in the MSA for a weak electrolyte unchanged.

3. DIPOLAR DUMBELLS

I have already mentioned the limit $\lambda = (\sigma/L)^3/\eta$ with $L < \sigma/2$ when the system should contain dipolar dumbbells. In the absence of a solvent, the asymptotic form of the direct correlation function (defined through the Ornstein-Zernike (OZ) equation) for this system is given by [19]

$$c_{ij}(r) = -\beta A e_i e_j / r \quad (14)$$

where $A = \varepsilon/(\varepsilon - 1)$ and ε is the dielectric constant of the system of dipolar dumbbells. It follows from Eq. (11) and (13) that the energy of dipolar dumbbells, in the absence of a solvent and excluding the ion binding energy, is given in the MSA by [22]

$$\frac{E^{\text{ex}}}{N_D kT} = \frac{-x[(c_1 + c_2 x') - (c_1^2 + 2c_3 x')^{1/2}]}{24\eta} \quad (15)$$

where x' is the reduced dipole moment defined by

$$x' = \kappa\sigma = 2n(A\pi\rho/kT)^{1/2} \mu \quad (16)$$

in which the dipole moment $\mu = el = e\sigma/n$, c_i ($i = 1$ to 3) are numbers which depend on the dipole elongation L [22] and $N_D = N/2$ is the number of dipoles. The solution for the energy in the MSA should apply to dipolar dumbbells only if $L < \sigma/2$ but calculations of the distribution functions show no evidence of polymerization for $L > \sigma/2$ in this approximation. This MSA solution for dipoles is similar to the analog of the zero-pole approximation (ZPA) [23, 24] for the direct correlation function derived from the site-site Ornstein Zernike (SSOZ) equation for dipolar dumbbells; however, the

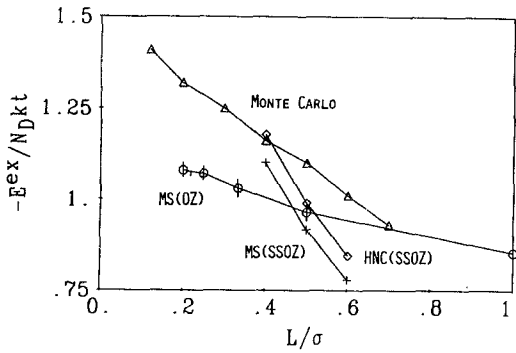


Fig. 5. The excess energy as a function of the elongation L for dipolar dumbbells at constant molecular volume. The reduced dipole moment $\mu^* = (\mu^2/kTd^3)^{1/2}$ and dipole density $\rho_D^* = \rho_D d^3$ are 1.37 and 0.78, respectively. Here d is the radius of the equivalent hard spheres of the same volume (from Ref. 22).

results are different and the excess energy derived from the analog of the ZPA is, unlike our solutions, not equal to zero in the limit of zero charge. Both solutions, however, tend to a small but finite constant in the limit of zero concentration.

The predictions of Eq. (15) are compared in Fig. 5 with the Monte

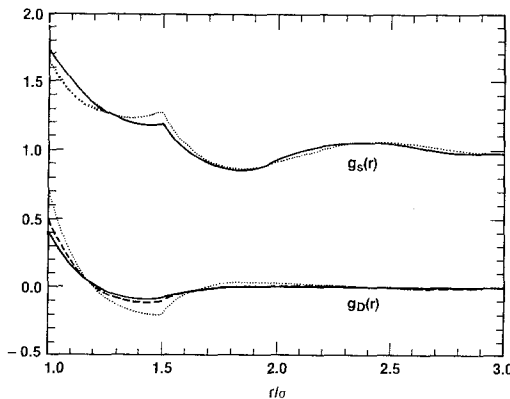


Fig. 6. The sum and difference distribution functions $g_S(r)$ and $g_D(r)$ for dipolar dumbbells with $L = \sigma/2$. The dotted line is the Monte Carlo result and the solid and dashed lines are the MSA calculations with $A = 1.0$ and 1.25, respectively. The model parameters are $T = 253$ K, $\sigma = 3.5$ Å, $\rho_D \sigma^3 = 0.462$, and $\mu = 6.2 \times 10^{-30}$ C m, where ρ_D is the density of the dipoles. $\mu^* = (\mu^2/kT\sigma^3)^{1/2} = 1.52$ (from Ref. 19).

Carlo simulations of the energy of dipolar dumbbells [25]. In the same figure, the energies of dipolar dumbbells using the MSA and HNC approximations for the direct correlation function defined through the SSOZ equation [26] are also shown. It is apparent that all of the calculated energies becomes less negative with increasing elongation, in agreement with the trends shown by the Monte Carlo results. In Fig. 6 the sum and difference functions $g_S(r) = [g_{+-}(r) + g_{++}(r)]/2$ and $g_D(r) = [g_{+-}(r) - g_{++}(r)]/2$ obtained [19] from the MSA and the OZ equation are compared with the Monte Carlo calculations for dipolar dumbbells [27, 28]; the agreement (for $L = \sigma/2$) is seen to be quite satisfactory.

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