Investigación *Revista Mexicana de Física* **37** *No. 4 (1991) 648–658*

Thermodynamic properties of sticky electrolytes in the HNC/MS approximation

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(Recibido el 27 de junio de 1990; aceptado el 14 de mayo de 1991)

Abstract. We study an approximation for a model which combines the sticky potential of Baxter and charged hard spheres. In the hypernetted chain (HNC)/mean spherical approximation (MSA), simple expressions for the thermodynamic functions are obtained. These equations should be useful in representing the properties of real electrolytes. Approximate expressions that are similar to those of the primitive model are obtained, for low densities (concentrations) of the electrolyte.

PACS: 61.20.Gy

1. Introduction

In the theory of electrolytes the HNC approximation [1] has played a key role. It is very accurate in representing the properties of model solution, in particular for the primitive model, in which the solvent is a continuum of dielectric constant ϵ. However, it is a difficult theory to handle numerically.

The MSA [2,3], on the contrary, is not as accurate but completely analytic. One way of correcting the shortcomings of the MSA is to combine it with the ideas of Brönsted [4]. This has been done for the first time by Ebeling [5] and Renon [6], and recently studied by Soulahia and Turq [7]. The agreement with the experimental activity and osmotic coefficient is very good.

We like to introduce a model which shares the principle with the above model, but which is analytical and simple. This is the sticky electrolyte model (SEM) which was studied in another context by Lee and co-workers [8].

In Sec. 2 we compute the Baxter function [9] for the model and a scaling parameter Γ'; Sec. 3 contains the analytic expressions of the thermodynamic properties.

2. The distribution function and the sticky electrolyte model (SEM) in the hypernetted chain (HNC)/mean spherical approximation (MSA)

The integral equation approximation for the radial distribution function $g_{ij}(r)$ [10] (proportional to the probability density of finding ions i and j separated by a distance

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$r_{ij} = r$), and the direct correlation function $c_{ij}(r)$, is derived from the Ornstein-Zernike (OZ) equation [11] for mixtures of m species:

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^{m} \rho_k \int c_{ik}(s) h_{kj}(|r-s|)\, ds, \tag{1}$$

with $h_{ij}(r) = g_{ij}(r) - 1$, where ρ_k is the total number density of species k ions. The HNC approximation [2,3] is given by

$$c_{ij}(r) = -\beta\phi_{ij}(r) + h_{ij}(r) - \ln[g_{ij}(r)]; \tag{2}$$

while the MSA for system with hard core potentials is given by [12]

$$h_{ij}(r) = -1 \qquad (r < \sigma_{ij}) \tag{3a}$$

and

$$c_{ij}(r) = \beta\phi_{ij}(r) \qquad (r > \sigma_{ij}), \tag{3b}$$

where σ_{ij} is the diameter for the hard core interaction between species i and j ions and $\beta = 1/k_BT$ (in this case $\sigma_{ij} = \sigma$). For our model, we propose a hybrid approximation obtained by using the HNC approximation inside the core ($r < \sigma$) and the MSA outside the core ($r > \sigma$). Thus

$$c_{ij}(r) = -\beta\phi_{ij}(r) + h_{ij}(r) - \ln[1 + h_{ij}(r)] \qquad (r < \sigma) \tag{4a}$$

and

$$c_{ij}(r) = -\beta\phi_{ij}(r) \qquad (r > \sigma), \tag{4b}$$

which we refer to as the hypernetted-chain/mean spherical approximation (HNC/MSA). A similar approximation called the SMSA (soft MSA) was discussed previously by Blum and Narten [13].

The potential for the sticky electrolyte model (SEM) is

$$\phi_{ij}(r) = \begin{cases} \infty & (r < \sigma) \\ -\log\left[\dfrac{\sigma^- \delta^*_{ij}}{6\tau(\sigma^- - \sigma)}\right] & (\sigma^- < r < \sigma) \\ \displaystyle\sum_{ij} \frac{e^2 z_i z_j}{\epsilon r} & (r > \sigma), \end{cases} \tag{5}$$

where

$$\delta^*_{ij} = \begin{cases} 0 & \text{if } i = j \\ 1 & \text{if } i \neq j, \end{cases}$$

ϵ is the dielectric constant of the continuum solvent and ez_i is the magnitude of charge over the ions. The parameters in this potential are chosen so that τ is a dimensionless temperature, which is zero at zero temperature and large at high temperatures; the factor 6 is introduced purely for convenience in the latter equations.

Equations (4a) and (5) imply that $h_{ij}(r)$ contains a singularity at $r = \sigma$, so that

$$h_{ij}(r) = -1 + \frac{\lambda\sigma^-}{6}\delta^*_{ij}\delta(r-\sigma^-) \qquad (0 < r < \sigma), \tag{6}$$

where

$$\int_a^b dx\, f(x)\delta(x-\sigma) = f(\sigma) \quad \text{if} \quad a < \sigma \le b.$$

The mathematical problem to be solved consist of the mixture OZ equation for $m = 2$ species subject to the closure (4b) and (6). We follow Baxter [9] and define the Mayer f-function:

$$f_{ij}(r) = -1 + \frac{\sigma}{6\tau}\delta^*_{ij}\delta(r-\sigma) \qquad (0 < r < \sigma). \tag{7}$$

The parameter λ which measures the extent of association between oppositely charged ions is related to the parameter τ (a dimensionless measure of the temperature T).

Equations (1) can be rewritten as

$$\begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} - \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix} = \rho \begin{bmatrix} h_{11} & h_{12} \\ h_{21} & h_{22} \end{bmatrix} * \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix}, \tag{8}$$

where $(*)$ denotes the convolution integral and $\rho_{10} = \rho_{20} = \rho/2$.

Equations (8) can be simplified, in the restricted primitive model, where we have the symmetries

$$h_{11} = h_{22}, \quad h_{12} = h_{21} \quad \text{and} \quad c_{11} = c_{22}, \quad c_{12} = c_{21}. \tag{9}$$

We now define

$$h_\mathrm{S}(r) = \frac{h_{12}(r) + h_{11}(r)}{2}, \qquad h_\mathrm{D}(r) = \frac{h_{12}(r) - h_{11}(r)}{2} \tag{10a}$$

and

$$c_\mathrm{S}(r) = \frac{c_{12}(r) + c_{11}(r)}{2}, \qquad c_\mathrm{D}(r) = \frac{c_{12}(r) - c_{11}(r)}{2}. \tag{10b}$$

The OZ equation for the mixture becomes the set of uncoupled equations

$$h_S(r) = c_S(r) + \rho \int c_S(s) h_S(|r - s|)\, ds \tag{11}$$

and

$$h_D(r) = c_D(r) - \rho \int c_D(s) h_D(|r - s|)\, ds, \tag{12}$$

subject to the closures

$$h_S(r) = -1 + \frac{\lambda\sigma^-}{12}\delta(r - \sigma^-) \qquad (0 < r < \sigma^-), \tag{13}$$

$$c_S(r) = 0 \qquad (r > 0) \tag{14}$$

and

$$h_D(r) = \frac{\lambda\sigma^-}{12}\delta(r - \sigma^-) \qquad (0 < r < \sigma^-), \tag{15}$$

$$c_D(r) = \frac{ez\beta}{\epsilon r} \qquad (r > 0) \tag{16}$$

where $\beta = (K_B T)^{-1}$.

The sum equations

Since from Eq.(10*b*) the sum direct correlation function $c_S(r)$ is zero beyond $r = \sigma$, the Baxter [14] factorization of the OZ equation for Eq. (11) is straightforward, yielding

$$r h_S(r) = -q_S'(r) + 2\pi\rho \int_0^\sigma dt\, q_S(t)(r - t) h_S(|r - t|) \tag{17a}$$

and

$$r c_S(r) = -q_S'(r) + 2\pi\rho \int_r^\sigma dt\, q_S(t)(t - r) q_S'(t), \tag{17b}$$

where $q_S(r)$, the Baxter q-function, is zero for $r < 0$ and $r \geq \sigma$ and $q_S'(r)$ is the derivative of $q_S(r)$ with respect to r. Application of closure conditions (10*a*) on $0 < r < \sigma$ results in the following integral equation for $q_S(r)$:

In the range $0 < r < \sigma$,

$$r h_S(r) = r\left[-1 + \frac{\lambda\sigma}{12}\delta(r - \sigma)\right] = -q_S'(r) + 2\pi\rho \int_0^\sigma dt\, q_S(r)(r - t) h_S(r)$$

or

$$q'_{\mathrm{S}}(r) = r\left[1 - 2\pi\rho\int_0^\sigma dt\, q_{\mathrm{S}}(t)\right] + 2\pi\rho\int_0^\sigma dt\, q_{\mathrm{S}}(t) - \frac{\lambda\sigma^2}{12}\delta(r-\sigma). \tag{18}$$

We can define

$$\alpha = 1 - 2\pi\rho\int_0^\sigma dt\, q_{\mathrm{S}}(t) \tag{19}$$

and

$$\beta^* = \frac{1}{\sigma}2\pi\rho\int_0^\sigma dt\, t q_{\mathrm{S}}(t). \tag{20}$$

Then, Eq. (18) is

$$q'_{\mathrm{S}}(r) = r\alpha + \beta^*\sigma - \frac{\lambda\sigma^2}{12}\delta(r-\sigma). \tag{21}$$

Integrating Eq. (21) with respect to r, and using the condition $q_{\mathrm{S}}^0(\sigma) = 0$, gives

$$q_{\mathrm{S}}(r) = \frac{\alpha}{2}(r^2 - \sigma^2) + \beta^*\sigma(r-\sigma) + \frac{\lambda\sigma^2}{12} \tag{22}$$

for $0 < r < \sigma$. Substituting this form for $q_{\mathrm{S}}(r)$ into the Eqs. (19) and (20) gives two linear equations for α and β, which can be solved to give

$$\alpha = \frac{1 + 2\eta - \mu}{(1-\eta)^2}, \quad \beta^* = \frac{1}{2}\frac{-3\eta + \mu}{(1-\eta)^2}, \tag{23}$$

where η is the dimensionless density

$$\eta = \frac{\pi\rho\sigma^3}{6} \tag{24}$$

and

$$\mu = \lambda\eta(1-\eta). \tag{25}$$

These are the results for neutral adhesive spheres of Baxter [9].

The difference equations

The Baxter factorization of Eq. (12) with $c_{\mathrm{D}}(r)$ given by Eq. (16) is somewhat more involved. Following the method of Blum [15,16] we have

$$c_{\mathrm{D}}(r) = c_{\mathrm{D}}^0(r) + \frac{e^2 z^2 \beta}{\epsilon}\frac{e^{-\mu r}}{r}. \tag{26}$$

We then consider the limit $\mu \to 0$, and find in this case that in real space [17]

$$q_{\mathrm{D}}(r) = -A \qquad \text{for} \qquad r \geq \sigma, \tag{27}$$

where

$$A\rho = \kappa \tag{28}$$

and $\kappa^2 = (4\pi\beta e^2/\epsilon)\sum_i z_i^2\rho_i$, κ is the inverse Debye screening length for the electrolyte, and ez_i and ρ_i are the charge and number density, respectively, of ion i. Thus, defining $q_{\mathrm{D}}^0(r)$ by

$$q_{\mathrm{D}}(r) = q_{\mathrm{D}}^0(r) - A \qquad \text{for} \qquad r > 0, \tag{29}$$

so that $q_{\mathrm{D}}^0(r) = 0$ at $r \geq \sigma$, and the boundary conditions on $q_{\mathrm{D}}^0(r)$ are

$$q_{\mathrm{D}}^0(\sigma) = 0 \tag{30}$$

and

$$q_{\mathrm{D}}^0(\sigma^-) = \frac{\lambda\sigma^2}{12}. \tag{31}$$

Following Baxter [14], the factorization

$$[1 + \rho c_{\mathrm{D}}(k)] = q_{\mathrm{D}}(k)q_{\mathrm{D}}(-k)$$

can be written. Here

$$q(k)[1 + \rho h(k)] = [q(-k)]^{-1}, \tag{32}$$

where

$$h(k) = 2\pi \int_{-\infty}^{\infty} dr\, e^{-kr} J(|r|) \tag{33}$$

and

$$J(r) = \int_r^{\infty} dt\, t h(t). \tag{34}$$

Considering the effect of multiplying both sides of (32) by $\exp(-ikr)$ and integrating with respect to k from $-\infty$ to ∞, we have

$$-q(r) + J(r) - 2\pi\rho \int_0^{\sigma} dt\, q(t) J(|r - t|) = 0 \tag{35}$$

for $r > 0$, and $q(r) = 0$ for $r > \sigma$.

In our case

$$J(r) = q_{\mathrm{D}}^{0}(r) - \frac{A}{2} + \rho \int_{0}^{\sigma} dr_1 q_{\mathrm{D}}^{0}(r_1) J(|r - r|) - A\rho \int_{0}^{r} dr_1 J(r - r_1). \tag{36}$$

Now, we take the Stillinger-Lovett zeroth moment (electroneutrality) condition [18]

$$J(r) = 2\pi \int_{r}^{\infty} ds\, s h(s) = b_0' = \text{const.} \tag{37}$$

Substituting Eq. (37) into Eq. (36), we obtain

$$b_0' = q_{\mathrm{D}}^{0}(r) - \frac{A}{2} + \rho b_0' \int_{0}^{\sigma} dr_1\, q_{\mathrm{D}}^{0}(r_1) - \rho A b_0' r \tag{38}$$

and the derivative

$$q_{\mathrm{D}}^{0\prime}(r) = \rho A b_0'.$$

Integrating between r and σ and taking the boundary conditions (Eq. (31)) we have

$$q_{\mathrm{D}}^{0}(r) = \rho A b_0'(r - \sigma) + \frac{\lambda \sigma^2}{12}. \tag{39}$$

Substituting the Eq. (39) into Eq. (38) at $r = 0$, we get

$$\rho A \sigma = -\frac{2\rho\sigma b_0'}{[1 + b_0'\rho\sigma]^2} + \frac{2\rho\lambda\sigma^3/12}{[1 + b_0'\rho\sigma]}, \tag{40}$$

we remember that $\rho A = \kappa$. To make connection with the Debye-Hückel [19] theory (see Blum [15]) we define a new scaling length:

$$\rho b_0' = -\frac{1}{\sigma + \frac{1}{\Gamma'}}. \tag{41}$$

By substitution of this equation into (40) we obtain

$$2\Gamma'\sigma = -\left(1 + \frac{\lambda\eta}{2\pi}\right) + \left[\left(1 + \frac{\lambda\eta}{2\pi}\right)^2 + 2\kappa\sigma\right]^{1/2}, \tag{42}$$

which for $\lambda \to 0$ goes to the correct limit.

Determination of the parameter λ

The solution of the former paragraph is given in terms of the parameters λ, τ and η. These parameters can be related to each other if a closure is given. In fact from (4*a*) we have, defining the function $y_{12}(r)$,

$$g_{12}(r) = \exp[-\beta\phi_{12}(r)]y_{12}(r) \tag{43}$$

and using Eqs. (5) and (7), we find

$$\lambda\tau = y_{12}(\sigma). \tag{44}$$

For the HNC closure (Eq. (2))

$$\ln y_{12}(\sigma) = h_{12}(\sigma) - c_{12}(\sigma). \tag{45}$$

By the definition of $h_{\mathrm{D}}(r)$ and $h_{\mathrm{S}}(r)$, we have

$$h_{12}(r) = h_{\mathrm{S}}(r) + h_{\mathrm{D}}(r) \quad \text{and} \quad c_{12}(r) = c_{\mathrm{S}}(r) + c_{\mathrm{D}}(r) \tag{46}$$

and Eq. (45) can be written as

$$\tau\lambda = \exp[h_{\mathrm{S}}(\sigma) - c_{\mathrm{S}}(\sigma)]\exp[h_{\mathrm{D}}(\sigma) - c_{\mathrm{D}}(\sigma)], \tag{47}$$

where

$$h_{\mathrm{S}}(\sigma) - c_{\mathrm{S}}(\sigma) = \alpha + \beta^* + \lambda\eta q_{\mathrm{S}}(0) - 1 \tag{48a}$$

and

$$h_{\mathrm{D}}(\sigma) - c_{\mathrm{D}}(\sigma) = \frac{\rho A b_0'}{\sigma} + \lambda\eta q_{\mathrm{D}}^0(0), \tag{48b}$$

which together yield

$$\ln[\tau\lambda] = \frac{\eta(\frac{5}{2} - \eta)}{(1-\eta)^2} - \pi\kappa\sigma\left[\frac{\Gamma'}{6\eta(\Gamma'\sigma + 1)}\right] - \lambda\left\{\frac{\eta}{(1-\eta)} + \pi\kappa\sigma\left[\frac{\Gamma'\sigma}{6\eta(\Gamma'\sigma+1)}\right]\right\} + \frac{\lambda^2\eta}{12}, \tag{49}$$

where η and $\Gamma'\sigma$ are defined by Eqs. (24) and (42) respectively. κ is the inverse Debye screening length.

Thus, the analytic solution of the HNC/MSA for the sticky electrolyte reduces to solution of a single nonlinear equation for the parameter λ.

One could argue that if the HNC/MS approximation is used, then in the limit when $\lambda \to 0$, there is a residual effect of the sticky interaction in Eq. (49), which however vanishes at $\eta \to 0$. One would think that a more appropriate closure is

$$\ln[\lambda\tau] = -\lambda\eta\left\{\frac{1}{(1-\eta)} - \pi\kappa\sigma\left[\frac{\Gamma'\sigma}{\Gamma'\sigma + 1}\right]\right\} + \frac{\lambda^2\eta}{12}. \tag{49a}$$

3. Thermodynamic properties

There are different routes to express the thermodynamic properties of a system through its distribution functions [20–23]. The thermodynamic properties by MSA are calculated from the excess internal energy with computer simulation [12,23].

The excess internal energy by the electrostatic part is calculated by means of the relation [23]

$$\Delta E_1 = 2\pi \int_0^\infty dr\, r^2 \sum_{i,j} \rho_i \rho_j g_{ij}(r) \phi_{ij}^c(r), \tag{50a}$$

where $\phi_{ij}^c(r)$ is electrostatic potential and the contribution at the internal energy by the sticky potential is calculated with the expression [24,25]

$$\Delta E_2 = -\frac{V}{2} \sum_{i,j} \rho_i \rho_j \int_0^\infty 4\pi r^2 y_{ij}(r) \frac{\partial(\exp[-\beta \phi_{ij}^s])}{\partial \beta}. \tag{50b}$$

The free energy

$$\frac{\partial(\beta \Delta A)}{\partial \beta} = \Delta E, \tag{51}$$

where ΔA is the excess free energy, can be integrated by parts to yield

$$\beta \Delta A = \beta E - \int_0^\Gamma d\Gamma' \frac{\partial E}{\partial \Gamma'} \beta'. \tag{52}$$

The excess osmotic coefficient is derived from the thermodynamic relation

$$\Delta \phi = \frac{\beta \Delta p}{\zeta_0} \frac{\partial}{\partial \zeta_0} \left(\frac{\beta \Delta A}{\zeta_0} \right), \tag{53}$$

here Δp is the excess pressure, and β is the Boltzmann thermal factor $(1/k_B T)$ and $\zeta_0 = \rho$. Finally, we get the activity coefficient from the thermodynamic formula

$$\frac{\beta \Delta A}{\zeta_0} = -\Delta \phi + \Delta \ln \gamma_\pm, \tag{54}$$

which after a few manipulations gives the thermodynamic properties of a sticky electrolyte system when we take as reference the sticky hard spheres.

The excess internal energy is

$$\Delta E = \Delta E_1 + \Delta E_2 = \frac{\Gamma'^3 + \Gamma'^4 \sigma}{\pi \beta} + 4\pi N \eta \lambda \frac{\partial(\ln \tau)}{\partial \beta}, \tag{55}$$

here N is the total number of particles.

From Eq. (52) and taking $\Delta A = \Delta A^{\mathrm{ex}} - A^{\mathrm{SHS}}$ we have

$$\Delta A = \Delta E_1 + \frac{\Gamma'^3}{3\pi\beta} \tag{56}$$

and the osmotic coefficient is calculated using Eq. (53)

$$\Delta\phi = -\frac{\Gamma'^3}{3\pi\rho}. \tag{57}$$

The activity coefficient is obtained by Eqs. (54), (56) and (57).

The thermodynamic properties are the same as those of MSA when $\lambda = 0$.

The function $\partial(\ln\tau)/\partial\beta$, which appears in (55), can be calculated by different routes, for example Lee and co-workers propose $\partial(\ln\tau)/\partial\beta = -\epsilon_2$, where ϵ_2 is the depth of a deep attractive well; we give a set of trial functions, which are associated with the experimental results [7].

Interesting extensions to include other effects such as localized adsorption can be obtained using the beautiful work of Wertheim [26].

Acknowledgments

This research was supported by the EPSCOR Grant No. NSF RII-8610677 and by the Grant NSF 89.01597. The authors are grateful to D. Glossman for very helpful observations.

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Resumen. En este trabajo estudiamos una aproximación para un modelo que combina el potencial de pegado de Baxter y esferas duras cargadas. En la aproximación HNC/MSA, se obtienen expresiones simples para las funciones termodinámicas. Estas ecuaciones pueden ser utilizadas para representar las propiedades de electrolitos reales. Obtenemos expresiones aproximadas que son similares a las ya conocidas para el modelo primitivo, en el rango de bajas concentraciones.