Solution of the polymer MSA for the polymerizing primitive model of electrolytes

Yu. V. Kalyushnyi

Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996-2300

G. Stell

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400

CEAS Report # 710, March 1995

1Permanent address: Institute for Physics of Condensed Matter, Scientistskoho 1, 290011 Lviv, Ukraine
An analytical solution of the polymer MSA (mean-spherical approximation) for the polymerizing primitive model of electrolytes is obtained. The approximation is an extension of the associative MSA proposed recently [M. Holovko and Yu. Kalyuzhnyi, Mol. Phys., 73, 1145 (1991)] to study the effects of association in ionic systems. The model is defined by adding charges to the totally-flexible sticky two-point model of associating monomers introduced by Wertheim. In the limiting case of an uncharged system, our solution reduces to the solution of the Wertheim polymer PY approximation solved recently [J. Chang and S. I. Sandler, J. Chem. Phys., 102, 437 (1995)].
I. INTRODUCTION

In the last decade a number of studies of model polymer fluids using integral-equation theory have been initiated. These include the polymer EISM theory of Currong and Schweizer [1] and its applications [2] and extensions [3,4], and the Percus-Yevick (PY) theory extended to polymer fluids by Chiew [5]. Recently the Wertheim integral-equation theory for associating fluids [6] and our extension of this theory have also [7] been applied. In [8] the OZ-like equation developed by Wertheim was solved analytically using the polymer PY (PPY) approximation [6] for his totally flexible two-site model [10]. This model is defined by a hard-sphere system with two sticky points placed randomly on a surface of each hard sphere. Concurrently in [9] an analytical solution of the PPY type of the closure [7] for the shielded sticky shell (SSS) model of a polymerizing fluid [11] has been obtained. The method of solution developed in [9] is quite general and is immediately applicable to a number of other models of polymerizing fluids, including the extension of the totally flexible two-site model proposed in [9]. In this extension each sticky point is randomly placed on an attractive shell of diameter \( L < 1 \) with the latter shielded by a repulsive core of unit diameter. We refer to this model as to the shielded sticky two-point (SS2P) model, the limiting version of which, the sticky two-point (S2P) model, coincides with the totally flexible two-site model of Wertheim [10].

In the present study we find an analytical solution of the mean spherical-like approximation for a model of a polymerizing ionic fluid. The approximation is an extension of the associative mean spherical approximation (AMSA) earlier proposed for the description of the effects of dimerization in the ionic fluids [12,13]. We refer to this extension as to the polymer MSA (PMSA). The model is a polymerizing version of the primitive model of electrolytes that is rather straightforward generalization of the S2P model to ionic systems. It consists of an \( n \)-component mixture of charged hard spheres of species \( 1, \ldots, a, \ldots, n \) with number density \( \rho_a \) and charge \( Z_a \). The mixture is electroneutral, so that the following condition is satisfied.
\[ \sum_{i=1}^{n} p_{i} z_{i} = 0 \]  

(1)

As in the case of S2P model, each hard sphere has two sticky points A and B, (regarded as being distinguishable) randomly positioned on its surface. Unlike the version of the S2P model considered in [8] we preserve here the possibility of bonding between any of the two sites which belong to the two particles of any species. Further generalization along the same lines that yield the SS2P generalization of the S2P model is possible; however it is not considered here. For the sake of simplicity we choose an equal diameter for each of the hard-sphere species, although the extension of our theoretical treatment to the more general case with arbitrary diameters is rather straightforward.

Our extension of the AMSA to the case of polymerizing ionic fluids is discussed in Section II of this paper. An analytical solution of the PMSA is obtained via the Baxter factorization technique [14] in Section III. In Section IV the simplified restricted primitive version of the model, in which the association is allowed only between sites of different species belonging to the oppositely charged ions, is considered. It is also demonstrated that in the case of the zero charges on the ions our solution reduces to that obtained in [6] via the single bonding approximation, if the stickiness parameter in our model is chosen to be half of that used in [8]. (This factor of 1/2 is a consequence of the positive and negative ions representing two distinct species, even when they are discharged, whereas in [8] a single-species system is considered.)

II. POLYMER MSA

The pair potential of our primitive model of a polymerizing electrolyte solution is given by

\[ U_{ab}(r) = U_{h,a,b}(r) + U_{ab}^{(C)}(r) + \sum_{KL} U_{ab}^{(KL)}(12) \]  

(2)

where 1 and 2 stand for the spatial and orientational coordinates of two ions, \( a \) and \( b \) are the indexes for the ionic species, \( U_{h,a,b}(r) \) is the hard-sphere potential, \( U_{ab}^{(C)}(r) \) is the Coulomb
potential, and $U_{ab}^{\text{KL}}(12)$ is the short-ranged site-site potential responsible for association. Here $K$ and $L$ take the values $A$ and $B$ and denote the type of site. As usual, the Coulomb interaction has the form

$$U_{ab}^{(C)}(r) = -\frac{e^2 Z_a Z_b}{er}$$

where $e$ is the elementary charge, $Z_a$ is the charge of the ion of a species in electron units, and $\varepsilon$ is the dielectric constant of the continuum.

Due to the site-site interaction $U_{ab}^{\text{KL}}(r)$ the total pair potential is strongly dependent on the orientation of the ions. However, as was already noted in [15,9] the type of the model considered here can be described by an orientationally-averaged version of the Wertheim theory. The latter in conjunction with the S2P model has been discussed in [8]. Its extension to the case of a multicomponent system is rather obvious, and therefore in what follows we shall omit any details, referring the readers to the original publications.

For the present model the Wertheim OZ equation can be written in terms of the orientationally-averaged partial correlation functions $h_{ab}^{\text{KL}}(r)$ and $c_{ab}^{\text{KL}}(r)$ in the form

$$\hat{H}(k) = \hat{C}(k) + \hat{C}(k)\mathbf{\sigma} \hat{H}(k)$$

where $[\mathbf{\sigma}]_{ab} = \delta_{ab} \sigma$, and the matrices $\hat{H}(k)$ and $\hat{C}(k)$ contain the elements which are the Fourier transform of the elements of the matrices $H(r)$ and $C(r)$, respectively. Here $[H(r)]_{ab} = h_{ab}(r)$ and $[C(r)]_{ab} = c_{ab}(r)$. In turn $h_{ab}(r)$, $c_{ab}(r)$, and $\sigma$ are the matrices which take the form

$$h_{ab}(r) = \begin{pmatrix} h_{aa}^a(r) & h_{ab}^a(r) & h_{ab}^b(r) & h_{aa}^b(r) \\ h_{ba}^a(r) & h_{bb}^a(r) & h_{ab}^b(r) & h_{ba}^b(r) \\ h_{bb}^a(r) & h_{ba}^b(r) & h_{bb}^b(r) & h_{bb}^b(r) \\ h_{aa}^b(r) & h_{ba}^a(r) & h_{bb}^a(r) & h_{bb}^b(r) \end{pmatrix}$$

and $\sigma = \begin{pmatrix} \sigma^a & \sigma^b & \sigma^c & \sigma^d \\ \sigma^b & 0 & 0 & 0 \\ \sigma^c & 0 & 0 & 0 \\ \sigma^d & 0 & 0 & 0 \end{pmatrix}$, where the lower indices $\alpha$ and $\beta$ in $\sigma^\alpha$ and in the correlation functions $h_{ab}^{\text{KL}}(r)$ and $c_{ab}^{\text{KL}}(r)$ denote the bonded states of the corresponding particle. The case of $\alpha = 0$ corresponds to
unbonded particle, \( \alpha = A \) or \( \alpha = B \) to the particle with bonded site \( A \) or \( B \), and \( \alpha = \Gamma \) to the particle with both sites, \( A \) and \( B \), bonded. The density parameters \( \sigma_{\alpha}^* \) are related to the densities \( \rho_{\alpha} \) of \( \alpha \)-bonded particles by

\[
\begin{align*}
\sigma_{\alpha}^* &= \rho_{\alpha}, \\
\sigma_{A}^* &= \rho_{A}^* + \rho_{A}, \\
\sigma_{B}^* &= \rho_{B}^* + \rho_{B}, \\
\sigma_{\Gamma}^* &= \rho_{\Gamma}^* + \rho_{A}^* + \rho_{B}^* + \rho_{\Gamma}.
\end{align*}
\] (5)

In our study we are using the MSA-like closure conditions [12,13] which for the present model reads

\[
\begin{align*}
K_{\alpha\beta}^{K}(r) &= -\delta_{\alpha\beta}\delta_{\beta 0}, & \text{for } r < 1 \\
C_{\alpha\beta}^{K}(r) &= -\delta_{\alpha\beta}\delta_{\beta 0}U_{\alpha\beta}^{K}(r) + (1 - \delta_{\alpha\beta})(1 - \delta_{\beta 0})B_{\alpha\beta}^{K}\delta(r - 1), & \text{for } r > 1
\end{align*}
\] (6)

where \( \beta = \frac{1}{r} \) and hereafter we assume the unit diameter for the hard-spheres.

Here, as in [8], the site-site potential is chosen to be infinitesimally short-ranged so that its averaged Mayer function \( f_{K\gamma}^{K}(r) \) takes the form

\[
f_{K\gamma}^{K}(r) = K_{K\gamma}^{K}\delta(1 - r)
\]

where \( \delta \) is the Dirac delta-function and \( K_{K\gamma}^{K} \) is the parameter describing the strength of the stickiness. The constants \( B_{\alpha\beta}^{K} \) are related to the stickiness parameter \( K_{K\gamma}^{K} \) by

\[
B_{KL}^{K} = y_{0L}^{K}K_{KL}^{K}, \quad B_{KA}^{K} = K_{L}^{K}y_{0K}^{K} + K_{AA}^{K}y_{0A}^{K}, \quad B_{KB}^{K} = K_{B}^{K}y_{0B}^{K} + K_{AB}^{K}y_{0A}^{K}, \quad B_{KB}^{K} = K_{B}^{K}y_{0B}^{K} + K_{AB}^{K}y_{0A}^{K}.
\] (7)

where \( y_{0}^{K} \) is the contact value of the function defined by

\[
g_{\alpha\beta}^{K}(r) = \epsilon_{\alpha\beta}(r)[y_{0}^{K}(r) + B_{\alpha\beta}^{K}(1 - \delta_{\alpha\beta})(1 - \delta_{\beta 0})\delta(r - 1)]
\] (8)

and \( \epsilon_{\alpha\beta}(r) = \exp(-\beta U_{\alpha\beta}(r)) \) and \( g_{\alpha\beta}^{K}(r) = K_{\alpha\beta}^{K}(r) + \delta_{\alpha\beta}\delta_{\beta 0}. \)
Finally the relation between the densities $\rho_\alpha$ and parameters $B^\alpha_{\mu\nu}$ are found to be [6,8]

$$
\rho_\alpha = 4\pi \rho_\alpha \sum_i [B^\alpha_{\mu\nu}(\rho_\alpha + \rho_B^i) + B^\alpha_{\mu\nu}(\rho_B^i + \rho_\alpha) + B^\alpha_{\mu\nu}\rho_B^i]
$$

$$
\rho_B^i = 4\pi \rho_\alpha \sum_v [B^\alpha_{\mu\nu}(\rho_\alpha + \rho_B^i) + B^\alpha_{\mu\nu}(\rho_B^i + \rho_\alpha) + B^\alpha_{\mu\nu}\rho_B^i]
$$

$$
\rho_T = \rho_B^i B_T^{\alpha\beta} + 2\pi \sum_v \rho_B^i B_T^{\alpha\beta}
$$

(9)

This completes our PMSA closure conditions for the primitive model of polymerizing electrolytes. Here, in contrast to [8], we do not restrict ourselves to the single-bonding approximation. The latter can be easily introduced into the theory as in [8].

III. SOLUTION OF THE PMSA FOR THE PRIMITIVE MODEL OF POLYMERIZING ELECTROLYTES

Our solution of the OZ equation (4) together with the set of equations (6), which specify the closure conditions and relation between the densities (9) is based upon the Baxter factorization technique [14] and is similar to that developed in [12,13]. We begin by presenting the OZ equation (4) in the form

$$
[\sigma^{-1} - \tilde{\mathbf{C}}(k)][1 + \sigma \tilde{\mathbf{H}}(k)] = \sigma^{-1}
$$

(10)
suitable for factorization

$$
\sigma^{-1} - \tilde{\mathbf{C}}(k) = \tilde{\mathbf{q}}^T(-k)\sigma\tilde{\mathbf{q}}(k)
$$

(11)

$$
\tilde{\mathbf{q}}(k)[1 + \sigma \tilde{\mathbf{H}}(k)] = [\sigma \tilde{\mathbf{q}}^T(-k)\sigma]^{-1}
$$

(12)

In real r-space this set of equations can be written as

$$
-r^T_{\alpha\beta}(r) = \left[ q^T_{\alpha\beta}(r) - 2\pi \sum_{\mu\nu} \sigma_{\mu\nu} \int_0^\infty q^*_{\alpha\beta}(t) q^0_{\mu\nu}(r + t) dt \right]
$$

(13)

$$
-r^T_{\alpha\beta}(r) = \left[ q^T_{\alpha\beta}(r) - 2\pi \sum_{\mu\nu} \sigma_{\mu\nu} \int_0^\infty q^*_{\alpha\beta}(t) q^0_{\mu\nu}(r - t) dt \right]
$$

(14)
where $\sigma_{\alpha}^{\beta}$ is the correspondent element of the matrix $\sigma_\alpha$ and

$$4\pi^2 q_{\alpha \beta}^\delta = \int_{-\infty}^{\infty} \{\sigma^{-1}\}_{\alpha \beta}^{\mu \nu} \delta_{\beta \delta}(k) \exp[-ikr] \, dk \quad (15)$$

Making use of the analytical properties of the function $\delta_{\beta \delta}(k)$ together with the closure conditions (5) yield the following long-range behaviour of the function $q_{\alpha \beta}^\delta(r)$ defined by (15)

$$2r q_{\alpha \beta}^\delta(r) = -\alpha_{\alpha}^{\mu} \xi_{\beta} \exp[-\mu r] \quad (\mu \to 0), \quad \text{for} \quad r > 1 \quad (16)$$

where $\alpha_{\alpha}^{\mu}$ is an unknown constant, which satisfies the set of algebraic equations

$$\sum_{\gamma} \sum_{\gamma} \sigma_{\gamma \alpha}^{\mu} \sigma_{\gamma \beta}^{\mu} \omega_{\gamma} = \frac{4\pi e^2 Z_{\alpha} Z_{\beta}}{\epsilon} \quad (17)$$

obtained by substituting (16) into (13) and studying its long-range asymptotic behaviour.

Using the symmetry property of (17) and following (16) we have

$$\alpha_{\alpha}^{\mu} = 2\omega_{\alpha}^{\mu} \quad (18)$$

where the constants $\omega_{\alpha}^{\mu}$ satisfy the following set of equations

$$\sum_{\gamma} \sum_{\gamma} \omega_{\alpha}^{\mu} \sigma_{\gamma \beta}^{\mu} \omega_{\gamma} = \frac{4\pi e^2}{\epsilon} \quad (19)$$

Next, considering equation (14) in the range $0 < r < 1$ and making use of the electroneutrality condition (1) and relation (18), we arrive at the second order polynomial for the $q$-function

$$q_{\alpha \beta}^\delta(r) = \frac{1}{2} (\delta_{\alpha \beta} + \omega_{\alpha}^{\mu} \omega_{\beta}^{\mu} + \omega_{\alpha}^{\mu} \omega_{\beta}^{\mu} r^2 + \omega_{\alpha}^{\mu} \omega_{\beta}^{\mu} r + \omega_{\alpha}^{\mu} \omega_{\beta}^{\mu} r^2, \quad \text{for} \quad 0 < r < 1 \quad (20)$$

Here

$$a_{\alpha}^* = \delta_{\alpha \beta} - 2\pi \sum_{\gamma} \sum_{\gamma} \sigma_{\gamma \alpha}^{\mu} \int_0^1 q_{\gamma \mu}^\delta(t) \, dt \quad (21)$$

$$b_{\alpha}^* = 2\pi \sum_{\gamma} \sum_{\gamma} \sigma_{\gamma \alpha}^{\mu} \int_0^1 q_{\gamma \mu}^\delta(t) \, dt \quad (22)$$

$$J_{\alpha}^\delta = \sum_{\gamma} \sum_{\gamma} \sigma_{\gamma \alpha}^{\mu} J_{\gamma \alpha}^\delta Z_{\gamma} \quad J_{\alpha}^\delta = \int_{-\infty}^{\infty} b_{\alpha}^* \, dt \quad (23)$$
and the constants $c_{n,m}^t$ follow from the boundary conditions imposed on the function $a_{n,m}^t(r)$

$$a_{n,m}^t(1^+) - a_{n,m}^t(1^-) = -(1 - \delta_{m0})(1 - \delta_{m0})B_{n,m}^t$$

(24)

After some simple algebraic manipulations the set of equations (21), (22) and (24), which define the unknowns $a_{n,m}^t, b_{n,m}^t$ and $c_{n,m}^t$ can be written explicitly as

$$\left(1 + \frac{1}{3} \pi \rho t \right) a_{n,m}^t + \pi \rho t b_{n,m}^t + 2\pi \sum_{\gamma} \sum_{\gamma} \sigma_{n,m}^t c_{n,m}^t = \delta_{n0} - \pi \omega_{n,m}^t \sum_{\gamma} \sigma_{n,m}^t J_{n,m}^\gamma$$

(25)

$$\frac{1}{4} \pi \rho t a_{n,m}^t + \left(\frac{2}{3} \pi \rho t - 1\right) b_{n,m}^t + \pi \sum_{\gamma} \sum_{\gamma} \sigma_{n,m}^t c_{n,m}^t = \frac{2}{3} \pi \omega_{n,m}^t \sum_{\gamma} \sum_{\gamma} \sigma_{n,m}^t J_{n,m}^\gamma$$

(26)

$$\frac{1}{2} \omega_{n,m}^t \delta_{n0} + b_{n,m}^t \delta_{m0} + c_{n,m}^t \delta_{n,m} = -\frac{1}{2\pi} \omega_{n,m}^t Z_{n,m} \delta_{n0} - \omega_{n,m}^t J_{n,m}^t + (1 - \delta_{m0})(1 - \delta_{n0})B_{n,m}^t$$

(27)

where $\rho t = \sum_{\rho} \rho \tau$.

The rest of the $8n - 1$ equations for the unknown parameters $\omega_{n,m}^t$ and $J_{n,m}^t$ can be obtained from (13) considered at $r = 0$. Since the direct correlation functions $c_{n,m}^t(r)$ are finite at $r = 0$, we have

$$b_{n,m}^t \delta_{n0} + \omega_{n,m}^t J_{n,m}^t + \pi \sum_{\gamma} \sum_{\gamma} \sigma_{n,m}^t c_{n,m}^t \delta_{n,m} = (1 - \delta_{m0}) \pi \sum_{\gamma} \sum_{\gamma} \sigma_{n,m}^t (1 - \delta_{m0})(1 - \delta_{n0})B_{n,m}^t B_{n,m}^t$$

(28)

$$b_{n,m}^t + \omega_{n,m}^t \delta_{n0} + \omega_{n,m}^t J_{n,m}^t + 2\pi \sum_{\gamma} \sum_{\gamma} \sigma_{n,m}^t c_{n,m}^t \delta_{n,m}$$

$$+ (1 - \delta_{n0}) \sum_{\gamma} \sum_{\gamma} (1 - \delta_{m0}) \sigma_{n,m}^t Z_{n,m} B_{n,m}^t = 0$$

(29)

The contact values of $y_{n,m}^a(r)$, which appear in the expression (7) for $B_{n,m}^a$, follow from (14) at $r \to 1^+$

$$y_{n,m}^a = \delta_{n0}(b_{n,m}^a + \omega_{n,m}^a J_{n,m}^a) + \delta_{n0}(1 - \delta_{m0}) \sum_{\gamma} \sum_{\gamma} (1 - \delta_{m0}) \sigma_{n,m}^a c_{n,m}^a B_{n,m}^a$$

(30)

Thus the solution of the PMSA for the primitive model of polymerizing electrolyte solution reduces to the solutions of the set of algebraic equations (9) and (25)-(30).
IV. SOLUTION OF THE PMSA FOR THE RESTRICTED PRIMITIVE MODEL OF POLYMERIZING ELECTROLYTES

Substantial simplification occurs in the final equations of the previous section if for the ionic system the restricted primitive model of particles with equal sized cores is used. In addition, if one assume that bonding is taking place only between the sites of different species belonging to the oppositely charged ions,

\[ K^+_{KL} = K^-_{KL} = 0, \quad K^+_{AB} = K^-_{AB} \neq 0 \]  \hspace{1cm} (31)

where + and − denote positively and negatively charged ions, the set of equations (25)-(30) can be presented formally as two independent sets of equations. One of these sets of equations involves the quantities related to the correspondent polymerizing uncharged hard-sphere system, while the other describes the parameters related to the additional effects of the electrostatic interaction. These two sets of equations, as in the case of a dimerizing ionic system [12], are coupled via the relation between the densities (9).

Because of the symmetry of the present model and due to (19) parameters \( a_{a+b}^+ \), which defined the long-range behaviour of the Baxter \( q \)-functions, we have

\[ a_{a+b}^+ = a_{a+b}^- = -a_{a-b}^+ = -a_{a-b}^- = a_b, \quad \text{and} \quad a_A = a_B \]  \hspace{1cm} (32)

For the density parameters we have also

\[ \sigma^+_a = \sigma^-_a = \sigma_a, \quad \text{and} \quad \sigma_A = \sigma_B \]  \hspace{1cm} (33)

Now equation (19) for \( a_b \) takes the form

\[ \sigma \omega^2_b + \sigma \omega \omega \sigma_k + 2\sigma \omega \omega \sigma_t + 2\sigma \omega \omega_k^2 = \frac{4\pi \beta^2 e^2}{\epsilon} \]  \hspace{1cm} (34)

where \( \omega^2_b = -\omega^-_b = \omega_b \).

The set of equations (25)-(30) can be simplified by introducing instead of \( a_{ab}^\pm \) a new set of the unknown parameters \( a_{ab}^{(S)} \) and \( a_{ab}^{(D)} \) defined by
\[ c_{\alpha \beta}^{(S)} = \frac{1}{2} (c_{\alpha \alpha}^{+} + c_{\beta \beta}^{+}), \quad c_{\alpha \beta}^{(P)} = \frac{1}{2} (c_{\alpha \alpha}^{-} - c_{\beta \beta}^{-}). \] (35)

In terms of these parameters the set of equations (25)-(27) can be written as

\[
\begin{align*}
(1 + \frac{1}{\tau} \pi \rho \tau) a_{\alpha} + \pi \rho \tau b_{\alpha} + 4 \pi \sum c_{\alpha \beta}^{(S)} &= \delta_{\alpha 0}, \\
\frac{1}{4} \pi \rho \tau a_{\alpha} + (\frac{3}{4} \pi \rho \tau - 1) b_{\alpha} + 2 \pi \sum c_{\alpha \beta}^{(P)} &= 0, \\
\frac{1}{2} a_{\alpha} \delta_{\alpha 3} + b_{\alpha} \delta_{\alpha 3} + c_{\alpha \beta}^{(S)} &= \frac{1}{2} \{1 - \delta_{\alpha 0} \} \{1 - \delta_{\beta 0} \} B_{\alpha \beta}^{+},
\end{align*}
\] (36)

where \( a_{\alpha} = a_{\alpha}^{+} = a_{\alpha}^{-}, \ b_{\alpha} = b_{\alpha}^{+} = b_{\alpha}^{-} \).

Solution of this set of linear equations gives the following expressions for \( a_{\alpha}, b_{\alpha}, c_{\alpha \beta}^{(S)} \) and the cooscalt values of \( y_{\alpha \beta}^{(S)}(r) = \frac{1}{2} (y_{\alpha \alpha}^{+}(r) + y_{\alpha \beta}^{+}(r)) \)

\[
\begin{align*}
a_{\alpha} &= \frac{1 + 2 \pi \tau}{(1 - \eta \tau)^2}, \quad b_{\alpha} = \frac{-3 \pi \tau}{2 (1 - \eta \tau)^2}, \quad c_{\alpha \alpha}^{(S)} = \frac{-1}{2 (1 - \eta \tau)^2}, \\
a_{\alpha} &= \frac{R_{\alpha}}{1 - \eta \tau}, \quad b_{\alpha} = \frac{-R_{\alpha}}{2 (1 - \eta \tau)}, \quad c_{\alpha \alpha}^{(S)} = 0, \quad \text{for } \alpha \neq 0, \\
\beta \alpha \beta \alpha &= \frac{1}{2} (1 - \delta_{\alpha 0}) B_{\alpha \beta}^{+}, \quad \text{for } \beta \neq 0, \\
y_{\alpha \alpha}^{(S)} &= \frac{2 + \sigma \tau}{2 (1 - \eta \tau)^2}, \quad y_{\alpha \beta}^{(S)} = y_{\beta \alpha}^{(S)} = \frac{R_{\alpha}}{2 (1 - \eta \tau)},
\end{align*}
\] (37) (38) (39)

\[
y_{\alpha \beta}^{(P)} = \pi \alpha (1 - \delta_{\alpha 0}) (1 - \delta_{\beta 0}) B_{\alpha \beta}^{+} B_{\alpha \beta}^{+} + (1 - \delta_{\alpha 0}) (1 - \delta_{\beta 0}) B_{\alpha \beta}^{+} B_{\alpha \beta}^{+},
\] (40)

\[ \text{for } \alpha \neq 0 \text{ and } \beta \neq 0 \]

where \( \eta \tau = \frac{\tau}{\tau} \) and

\[
R_{K} = -2 \pi (\eta K B_{K K}^{+} + \sigma_{0} B_{K K}^{+}), \quad R_{F} = -2 \pi (2 \eta K B_{K K}^{+} + \sigma_{0} B_{K K}^{+})
\]

Here we are using similar notation as that of [6,5], where \( K \) and \( K' \) denote sites of a different type, i.e. if \( K = A \) then \( K' = B \) and vice versa.
One can easily see that the above expressions essentially reduce to those obtained in the PPV approximation in [8] if \( Z_+ = 0 \), \( K_{\text{PPV}}^+ \) and the single bonding approximation is utilized. The only difference is due to the fact that even in the uncharged case we still have here a two-component system in the terminology we are using.

For the set of equations (28), (29) and contact values of the functions \( y_{\text{ab}}^{(D)}(r) = \frac{1}{2} (y_{\text{ab}}^{+}(r) - y_{\text{ab}}^{-}(r)) \), we have:

\[
\begin{align*}
\omega_0 J_0^{(D)} + 2\pi \frac{1}{2\pi} [1 + 2 J_0^{(D)}] &= 0 \\
2(\alpha_{0\sigma} J_0^{(D)} + \alpha_{\sigma} J_0^{(D)}) + 2\pi \frac{1}{2\pi} [1 + 2 J_0^{(D)}] &\left[ 8\pi \sigma B_{K}^{+} + \sigma_0 B_{K}^{-} + \sigma_0 B_{K}^{+} \sigma_0 - \sigma_0 B_{K}^{-} \sigma_0 \right] = 0 \\
2(\alpha_{0\sigma} J_0^{(D)} + \alpha_{\sigma} J_0^{(D)}) - 2\pi \frac{1}{2\pi} [1 + 2 J_0^{(D)}] &\left[ 8\pi \sigma B_{K}^{-} + \sigma_0 B_{K}^{+} + \sigma_0 B_{K}^{-} \sigma_0 - \sigma_0 B_{K}^{+} \sigma_0 \right] = 0 \\
2\alpha_{0\sigma} J_0^{(D)} + 4\pi \sigma B_{K}^{+} + \sigma_0 B_{K}^{-} \sigma_0 - \sigma_0 B_{K}^{+} \sigma_0 &= 0
\end{align*}
\]

Finally, the relation between the densities (2) will take the form:

\[
\begin{align*}
4\pi (B_{K}^{+} + B_{K}^{-}) r_{K}^2 + 4\pi B_{K}^{+} r_{K}^2 + 2\pi B_{K}^{-} r_{K}^2 + 2\pi r_{K}^2 &= 0 \\
2\pi B_{K}^{+} r_{K}^2 + 2\pi B_{K}^{-} r_{K}^2 + 2\pi r_{K}^2 &= 0
\end{align*}
\]
V. CONCLUDING REMARKS

In this paper we present an analytical solution of the mean spherical-like approximation [12,13] for a polymerizing primitive model of electrolytes. The model considered here is an extension of the totally flexible sticky two-point model of Wertheim [10] to the case of systems with ion pairs. We can interpret these upon dissociation with an ion monomer. In our version of the model bonding is allowed between any of two sites which belong to the two particles of any species. By choosing different types of site-site interaction a number of different submodels with different distributions of charge along the polymer chain formed due to the site-site interaction can be generated. The uncharged version of the model with site-site bonding allowed only between the sites of different types reduces to the totally flexible sticky two-site model considered in [8]. The restricted primitive version of the model with sticky interaction possible only between the pair of sites of the same type which belong to two particles of different species, reduces to the dimerizing model studied in [12]. Both cases can be treated as special cases to which the solution presented here applies.

ACKNOWLEDGMENTS

Yu. V. Kalyuzhnyi gratefully acknowledges the support of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy and G. Stell acknowledges NSF support.
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