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Ion-dipole mixture with associative interactions against the charge hard wall

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Ion-dipole mixture with associative interactions against the charge hard wall

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Abstract. A theory for an associative ion-dipolar mixture near a uniformly hard wall is proposed. The Ornstein-Zernike equation for this system is completely solved in the associative mean spherical approximation (AMSA). Analytical expressions for the adsorption coefficient, polarization, potential drop and differential capacitance are obtained.

Іонно-дипольна суміш з асоціативною взаємодією біля зарядженої твердої стінки

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Анотація. Запропоновано теорію для іонно-дипольної суміші біля однорідної твердої стінки. Рівняння Орнштейна-Церніке для цієї системи розв'язане в асоціативному середньо-сферичному наближенні (АССН). Отримані аналітичні вирази для коефіцієнта адсорбції, поляризації, стрибка потенціалу і різницевої ємності.

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1. Introduction

The subject of solvent structure at electrode interfaces has been investigated by many workers in the field of electrochemistry. The well-known Gouy-Chapman-Stern theory [1]-[3] treats the solvent in the diffuse layer as a continuum and consider the structure of the solvent only in monolayer which is adjacent to the electrode (the so-called inner Helmholtz layer). But this theory overestimates the potential difference of the interface. The improvement to the Gouy-Chapman-Stern theory has been proposed by Outwaite, Levine and Bhuiyan [4]-[6]. Their scheme is referred to as the modified Poisson-Boltzmann (MPB) approximation. But in this theory the solvent is also represented as a dielectric continuum.

The most straightforward approach in the theory of fluids is the integral equation method which based on the solution of the Ornstein-Zernike (OZ) equation within different closures: hypernetted chain (HNC), mean spherical approximation (MSA) and others. The OZ equation for a charged hard sphere-dipolar hard sphere mixture near a charged hard wall in the mean spherical approximation has been solved by Blum and Henderson [7]. The same problem has been considered by Carnie and Chan [8]. The MSA correctly predicts the magnitude of the potential drop for aqueous electrolytes [9]. But this model describes only complete dissociated electrolytes. The directed short-range forces can form associative complexes. The theory developed by Wertheim [10],[11] is an effective and powerful tool for the investigation of the thermodynamic and structural properties of the associative liquids. The dimerizing hard spheres near the hard wall have been considered in [12]. The AMSA for the dimerizing hard ions immersed in a dielectric continuum against the charged wall has been solved in [13]. The integral equation theory for the four bonding sites model of associating fluids near a solid surface has been done in [14].

In the present paper we investigate the interfacial properties of the ion-dipole mixture in the AMSA, whose bulk properties have been studied by us previously [15].

2. The associative version of the wall-particle OZ equation

Our system consists the mixture of equal size charged hard spheres and dipolar hard spheres near a charged hard wall. We think of the wall as a hard charged sphere in the limit the density $\rho_w \rightarrow 0$ while the charge z_w and the diameter σ_w go to infinity [16]. Let us call ρ_s, ρ_+, ρ_-

($\rho_+ = \rho_- = \rho_i/2$) the number density of the solvent, cation and anion, respectively, p_s the dipolar moment and $\pm e$ the charge of ions.

The association is due to the attractive interaction of sites located on the surface of each sphere except the wall. But the bonding between ions of the same species is forbidden. And we assume for simplification that dimers are the only association products.

The associative version of the wall-particle OZ equation can be written as

$$h_y^\beta(z, \Omega_2) = c_y^\beta(z, \Omega_2) + \sum_x \sum_{\gamma\delta} \int d3 h_x^\gamma(z', \Omega_3) \rho_x^{\gamma\delta} C_{xy}^{\delta\beta} \quad (1)$$

together with MSA closure relations

$$\begin{aligned} h_y^\beta(z, \Omega_2) &= -\delta_{\beta 0}, & r_{12} < \sigma/2 \\ c_y^\beta(z, \Omega_2) &= -\delta_{\beta 0} \frac{u_y^{el}(z)}{kT}, & r_{12} \geq \sigma/2, \end{aligned} \quad (2)$$

where $h_y^\beta(z, \Omega_2), c_y^\beta(z, \Omega_2)$ are the vectors of the pair and direct wall-particle correlation functions, z is the distance of the particle from the wall surface, Ω_2 orientation of dipolar moment. Subscripts x and y point at the sort of the particle and superscripts α, β, γ and δ at the degree of bonding (0 for unbonded and 1 for bonded particle). $C_{xy}^{\alpha\beta}$ (12) is the matrix of the direct correlation functions for the bulk phase. $d3$ means integration over the positions \vec{r}_3 and possible orientations of dipole.

The wall particle interaction is for ion

$$u_i^{el}(z) = -e E z \quad (3)$$

and for dipole

$$u_s^{el}(z) = -(\vec{p}_s \vec{E}) \quad (4)$$

where \vec{E} is the bare (unscreened) electric field, which is connected with the surface charge density on the wall q_s by

$$E = 4\pi q_s \quad (5)$$

Matrix of density is defined as [10] $\rho_x^{00} = \rho_x, \rho_x^{01} = \rho_x^{10} = \rho_x^0, \rho_x^{11} = 0$, where ρ_x is total density of particles of sort x and ρ_x^0 is density of unbonded particles of sort x , which are connected by self-consistent relations:

$$\rho_i = \rho_i^0 + 2\pi(\rho_i^0)^2 \sigma^3 B_{ii} g_{+-}^{00}(\sigma+) + 4\pi\rho_i^0 \rho_s^0 \sigma^3 B_{is} g_{is}^{00}(\sigma+) \quad (6)$$

$$\rho_s = \rho_s^0 + 4\pi(\rho_s^0)^2 \sigma^3 B_{ss} g_{ss}^{00}(\sigma+) + 4\pi\rho_i^0 \rho_s^0 \sigma^3 B_{is} g_{is}^{00}(\sigma+), \quad (7)$$

where $g_{xy}^{\alpha\beta}(r)$ is the pair correlation function written in (58) and B_{xy} is the strength of the association interaction.

All orientation-dependent functions can be expanded as [17]

$$f_{xy}^{\alpha\beta}(12) = \sum_{mnl} f_{xy}^{\alpha\beta}(r_{12} |^{mnl}) \Phi^{mnl}(\Omega_1, \Omega_2, \Omega_{r_{12}}), \quad (8)$$

where

$$\begin{aligned} \Phi^{000} &\equiv 1, & \Phi^{110}(\Omega_1, \Omega_2) &= \hat{s}_1 \hat{s}_2 \\ \Phi^{011}(\Omega_1, \Omega_r) &= \hat{r} \hat{s}_2, & \Phi^{112}(\Omega_1, \Omega_2, \Omega_{r_{12}}) &= 3(\hat{s}_1 \hat{r})(\hat{s}_2 \hat{r}) - (\hat{s}_1 \hat{s}_2), \end{aligned} \quad (9)$$

The set of OZ equations can be divided into two formally independent sets of equations by introducing the following linear combinations:

$$\begin{aligned} f_i^{(S)\beta}(r) &= \frac{1}{2} \left[f_+^\beta(r |^{000}) + f_-^\beta(r |^{000}) \right] \\ f_i^{(D)\beta}(r) &= \frac{1}{2} \left[f_+^\beta(r |^{000}) - f_-^\beta(r |^{000}) \right] \\ f_s^{(S)\beta}(r) &= f_s^\beta(r |^{000}) \\ f_s^{(D)\beta}(r) &= f_s^\beta(r |^{011}) \end{aligned} \quad (10)$$

In this way we decoupled the ionic and dipolar properties which represented by D-functions from the hard spheres properties which represented by the S-functions. Both subsystems are connected by density relations (6) and (7).

3. The solution of the S-subsystem. The adsoption coefficient

Equation (1) for the subsystem of the S-functions defined by (10) leads to

$$\hat{h}^{(S)}(k) \left[\hat{1} - \hat{\rho} \hat{C}(k) \right] = \hat{c}^{(S)}(k) \quad (11)$$

Vectors $\hat{h}^{(S)}(k)$ i $\hat{c}^{(S)}(k)$ are the one-dimensional Fourier transform of the wall-particle S-functions and matrix $C_{xy}^{\alpha\beta}(k)$ is the the three-dimensional Fourier transform of the direct correlation function of the bulk phase. The bulk system in this case is the mixture of the dimerizing hard spheres.

The direct correlation function for the bulk system is expressible in terms of bulk Baxter functions as

$$\hat{1} - \hat{\rho} \hat{C}(k) = \hat{\rho} \hat{Q}(k) \hat{\rho} \hat{Q}^T(-k), \quad (12)$$

where T denotes matrix transpose.

Taking to account that $\hat{c}^{(S)}(k)$ and $\hat{Q}^T(-k)$ are analytical functions in the lower half-plane of the Fourier space we obtain the following set of equations:

$$g_y^{(S)\beta}(z) - \sum_x \sum_{\gamma\delta} \rho_x \int_0^\infty g_x^{(S)\gamma}(z-r) R_x^{\gamma\delta} Q_{xy}^{\delta\beta}(r) dr = K_y^\beta(0), \quad (13)$$

where

$$g_y^{(S)\beta}(z) = \delta_{\beta 0} + h_y^{(S)\beta}(z) \quad (14)$$

and

$$K_y^\beta(0) = \delta_{\beta 0} - \sum_x \sum_{\delta} \rho_x \int_0^\infty R_x^{0\delta} Q_{xy}^{\delta\beta}(r) dr \quad (15)$$

The matrix $R_x^{\alpha\beta}$ consists from elements $R_x^{00} = R_x^{10} = 1$, $R_x^{11} = 0$.

Baxter functions for bulk phase for S-subsystem can be written in form [18]

$$\begin{aligned} Q_{xy}^{\alpha\beta}(r) &= \frac{1}{2} Q_{xy}^{(2)\alpha\beta}(r^2 - \sigma^2) + Q_{xy}^{(1)\alpha\beta}(r - \sigma) + \Delta_{xy}^{\alpha\beta} & r \leq \sigma \\ Q_{xy}^{\alpha\beta}(r) &= 0 & r > \sigma, \end{aligned} \quad (16)$$

where

$$\begin{aligned} Q_{xy}^{(2)\alpha\beta} &= \left(\frac{2\pi}{1-\eta} + \frac{\pi\rho S_m \sigma_y}{(1-\eta)^2} \right) \delta_{\alpha 0} \delta_{\beta 0} - \frac{2\pi}{1-\eta} \sum_{z\gamma} \rho_z \sigma_z \Delta_{zy}^{\gamma\beta} \delta_{\alpha 0} \\ Q_{xy}^{(1)\alpha\beta} &= -\frac{\pi\rho S_m \sigma^2}{2(1-\eta)^2} \delta_{\alpha 0} \delta_{\beta 0} + \frac{\pi\sigma}{1-\eta} \sum_{z\gamma} \rho_z \sigma_z \Delta_{zy}^{\gamma\beta} \delta_{\alpha 0} \end{aligned} \quad (17)$$

$$\Delta_{xy}^{\alpha\beta} = \delta_{\alpha 1} \delta_{\beta 1} 2\pi\sigma^2 B_{xy} X_x X_y g_{xy}^{00}(\sigma+)$$

$$g_{xy}^{00}(\sigma+) = \frac{1}{1-\eta} + \frac{\rho S_m \sigma}{4(1-\eta)^2} \quad (18)$$

$$X_x = \rho_x^0 / \rho_x \quad \eta = \frac{\pi}{6} \sum_x \rho_x \sigma^3 \quad \rho S_m = \pi \sum_x \rho_x \sigma^2 \quad (19)$$

Substituting (16) and (17) into (15) we obtain

$$K_y^\beta(0) = \frac{1}{2\pi} Q_{xy}^{(2)0\beta} \quad (20)$$

Taking to account continuity of integral convolution in (13) we obtain the contact value of the wall-particle function

$$g_y^{(S)\beta}(\sigma/2+) = K_y^\beta(0) \quad (21)$$

and contact value of the total function

$$g_y^{(S)tot}(\sigma/2+) = g_y^{(S)0}(\sigma/2+) + g_y^{(S)1}(\sigma/2+) = \frac{1+2\eta}{(1-\eta)^2} - \frac{1-X_y}{2(1-\eta)} \quad (22)$$

Equation (13) can be solved using the Laplace transform

$$\tilde{g}_y^{(S)\beta}(s) = \sum_x \sum_{\alpha\gamma} K_x^\alpha(0) \frac{1}{s} \left[\delta_{xy} \delta_{\alpha\beta} - \rho_x R_x^{\alpha\gamma} \tilde{Q}_{xy}^{\gamma\beta}(s) \right]^{-1} \quad (23)$$

The surface density excess is connected with the adsorption coefficient, which is given by [19]

$$\Gamma = \sum_y \rho_y \int_{\sigma/2}^{\infty} dz \left[g_{wy}^{(S)tot}(z) - 1 \right] = \sum_y \rho_y \lim_{s \rightarrow 0} \left[\tilde{g}_{wy}^{(S)tot}(s) - 1/s \right] \quad (24)$$

Performing the calculations defined above we obtain

$$\Gamma = \frac{1}{\pi\sigma^2} \frac{9\eta^2 + (4\eta - 1)\frac{1}{4}\pi\sigma^3 \sum_x \rho_x (1 - X_x)}{1 + 2\eta + \frac{1}{4}\pi\sigma^3 \sum_x \rho_x (1 - X_x)} \quad (25)$$

4. The solution of the D-subsystem

For the D-subsystem using the standard procedure for reduction to Baxter function we obtain an equation

$$\sqrt{\rho_y} h_y^{(D)\beta}(z) - \sum_x \sum_{\gamma\delta} \int_0^{\infty} \sqrt{\rho_x} h_x^{(D)\gamma}(z-r) R_x^{\gamma\delta} q_{xy}^{\delta\beta}(r) dr = -F_y^\beta(z), \quad (26)$$

where

$$F_y^\beta(z) = \sum_x \sum_{\alpha\gamma} \int_0^{\infty} dr \sqrt{\rho_x} \phi_x^\alpha(z+r) P_{xy}^{\alpha\gamma}(r) [R_y^{\gamma\beta}]^{-1}, \quad (27)$$

$$P_{xy}^{\alpha\gamma}(r) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dk e^{ikr} [q^T(-k)]_{xy}^{\alpha\gamma-1}, \quad (28)$$

where $q_{xy}^{\alpha\beta}(r)$ are the Baxter functions for bulk phase defined in the Appendix A, and from (3) and (4) we have

$$\phi_i^0(z) = -\frac{eEz}{kT} \quad (29)$$

$$\phi_s^0(z) = -\frac{p_s E}{\sqrt{3}kT}, \quad (30)$$

where the factor $1/\sqrt{3}$ is a normalization constant arising from the averaging over orientation of dipolar moment.

Using the form of the potentials (29) and (30) we obtain the value $F_y^\beta(z)$ as

$$F_y^\beta(z) = -\lim_{s \rightarrow 0} \sum_\gamma \left[\sqrt{\rho_i} \frac{eE}{kT} \left(z - \frac{\partial}{\partial s} \right) P_{iy}^{0\gamma}(s) [R_y^{\gamma\beta}]^{-1} + \sqrt{\rho_s} \frac{eE}{\sqrt{3}kT} P_{iy}^{0\gamma}(s) [R_y^{\gamma\beta}]^{-1} \right], \quad (31)$$

where $P_{xy}^{\alpha\beta}(s)$ is the Laplace transforms of (28).

Solving the equation (26) we get

$$\sqrt{\rho_y} h_y^{(D)\beta}(s) = -F_x^\alpha(s) P_{xy}^{\alpha\gamma T}(s) [R_y^{\gamma\beta}]^{-1} \quad (32)$$

Let's define $F_1 \equiv F_i^0, F_2 \equiv F_i^1, F_3 \equiv F_s^0$. For small s we can write:

$$\begin{aligned} F_1 &= \frac{E}{\sqrt{4\pi kT} s \delta_{-1}} \left[d_0 P_{12}^{(0)} - d_2 P_{32}^{(-1)} \right] \\ F_2 &= \frac{E}{\sqrt{4\pi kT} s \delta_{-1}} \left[d_0 (P_{11}^{(0)} - P_{12}^{(0)}) - d_2 (P_{31}^{(-1)} - P_{32}^{(-1)}) \right] \\ F_3 &= \frac{E}{\sqrt{4\pi kT} s \delta_{-1}} \left[d_0 P_{13}^{(0)} - d_2 P_{33}^{(-1)} \right], \end{aligned} \quad (33)$$

where d_0 and d_2 are defined by (56), matrices $\hat{P}^{(0)}$ and $\hat{P}^{(-1)}$ are calculated in Appendix B, δ_{-1} is determined as (62).

After some algebra from (66), (67) and (55) we get the very simple expression:

$$F_n = \frac{E a_n}{s d_0 \sqrt{4\pi kT}}, \quad n = 1, 2, 3 \quad (34)$$

Taking to account (34) from (66) and (67) we have two relations:

$$\begin{aligned} F_1 P_{11}^{(0)} + F_2 P_{12}^{(0)} + F_3 P_{13}^{(0)} &= \frac{E \delta_{-1}}{s d_0 \sqrt{4\pi kT}} \\ F_1 P_{31}^{(-1)} + F_2 P_{32}^{(-1)} + F_3 P_{33}^{(-1)} &= 0 \end{aligned} \quad (35)$$

The first one gives the electroneutrality condition:

$$e\rho_i \int_{\sigma/2}^{\infty} dz h_i^{(D) tot}(z) = -\frac{E}{4\pi} \quad (36)$$

We use the second relation of (35) and (68) to calculate of the Laplace transform of $\tilde{h}_s^{(D) tot}(s)$ at $s = 0$:

$$\begin{aligned} \tilde{h}_s^{(D) tot}(0) &= -\frac{E}{\sqrt{4\pi kT} \rho_s d_0 \delta_{-1} \Delta} \left[\frac{1}{2} (b_1^0 (1 - \rho_i z_{ii}) + b_1^1) \beta_3 \right. \\ &\quad \left. * a_1 + \frac{1}{2} b_1^0 \beta_3 a_2 - \beta_6^2 a_3 \right], \end{aligned} \quad (37)$$

where the definitions of Δ and all variables can be found in Appendix A.

From (69),(62) and (63) we get

$$\begin{aligned} -\frac{\partial}{\partial s} \tilde{h}_i^{(D) tot}(0) &= -\frac{eE}{kT d_0^2 \delta_{-1} \Delta} \left[\left(-\frac{[(1 - \rho_i z_{ii})(1 + J_0) + J_1] \beta_3}{2} \right) \right. \\ &\quad \left. * a_1 - \frac{1}{2} (1 + J_0) \beta_3 a_2 + \frac{1}{12} (b_1^0 + b_1^1) \beta_6 a_3 - \beta_3 \right] \end{aligned} \quad (38)$$

We need the two last equations to obtain the total polarization produced by electrode

$$P = \frac{\rho_s P_s}{\sqrt{3}} \tilde{h}_s(0) \quad (39)$$

and the potential difference across the interface

$$\psi = 4\pi \left[\rho_i e \frac{\partial \tilde{h}_i(0)}{\partial s} - \frac{\rho_s P_s}{\sqrt{3}} \tilde{h}_s(0) \right] \quad (40)$$

The differential capacitance is

$$C_D = \frac{E}{4\pi \psi} \quad (41)$$

It is of interest to examine these results in the limit of low concentration of ions. Starting from the Eqs. (55) we can write

$$\begin{aligned} J_0 &= J_0^{(1)} d_0, & J_0^{(1)} &= -\frac{\sqrt{X_i}}{2\sqrt{\epsilon}} \\ b_1^0 &= b_1^{0(1)} d_0, & b_1^{0(1)} &= \frac{\beta_6 \beta_{12} d_2}{2\sqrt{\epsilon}} \\ b_2 &= b_2^{(0)}, \end{aligned} \quad (42)$$

where

$$\beta_{3*2^n} = 1 + (-1)^n \frac{b_2^{(0)}}{3 * 2^n}, \quad n = 0, 1, 2, 3 \quad (43)$$

$b_2^{(0)}$ is obtained from the last equation of (55) which has form

$$\frac{\beta_3^2}{\beta_6^4} - \frac{\beta_6^2}{\beta_{12}^4} = d_2^2 \quad (44)$$

ϵ is Wertheim's dielectric constant

$$\epsilon = \beta_{12}^4 \beta_3^2 / \beta_6^6 \quad (45)$$

The parameters d_0 and d_2 are defined in (56).

Substitution of these results in Eqs. (39) and (40) gives

$$P = \frac{E(\epsilon - 1)}{4\pi d_0 \sqrt{X_i} \epsilon}, \quad (46)$$

$$\psi = \frac{E}{d_0 \sqrt{X_i} \epsilon} + \frac{E}{2\epsilon} \left[1 + \frac{(\epsilon - 1)\beta_6}{\beta_3} - \frac{1 - X_i}{2X_i} \right] \quad (47)$$

5. Results and discussion

To study the effects of the ionic dimerization in the theory of the electrified interface we have solved the associative mean spherical approximation for the ion-dipolar system. The dependences of the ionic monomer fraction, the adsorption coefficient, the polarization and the differential capacitance upon the ionic concentration at the constant density of the mixture are plotted in figures 1-4. We consider the ion-dipolar mixture with the diameter of particles $\sigma = 3\text{\AA}$, the temperature $T = 298K$, the ionic valence $Z = 1$. The pure dipolar subsystem has the dielectric constant $\epsilon = 80$ and the density $\rho_s = 1 \frac{kg}{l}$. The molar mass of the solvent is $M_{solv} = 18 \frac{kg}{kmol}$ and one for the salt is $M_{salt} = 36 \frac{kg}{kmol}$.

The influence the association is investigated in the two regimes which are illustrated on the fig. 1:

- a) no association ($X_i \equiv 1, \tilde{B}_{ii} = 0$);
- b) weak association ($0 \ll X_i < 1, \tilde{B}_{ii} = 10^2$);

$$\tilde{B}_{ii} = B_{ii} \lim_{\rho_i \rightarrow 0} g_{+-}^{00}(\sigma_i +) \quad (48)$$

By the our density of mixture the association leads to decreasing of the adsorption coefficient (fig. 2). It can be easy explained by Eq. (25).

In fig. 3 the curves of the inverse differential capacitance for three cases of association have been plotted. The curve of the weak association is very close to nonassociative one. It is confirmed by eq. (47) which gives

$$C^{-1} \sim \frac{1}{\sqrt{X_i \rho_i}}. \quad (49)$$

The polarization curves are presented in fig. 4. One may observe the behaviours of curves similar to those pertaining to C^{-1} .

6. Appendix A: bulk Baxter functions for the D-subsystem

The matrix Baxter functions for the ion-dipole mixture in the AMSA has been discussed in previous work. For restricted, equal size case we may write

$$q_{xy}^{\alpha\beta} = \frac{1}{2} q_{xy2}^{\alpha\beta} (r - \sigma)^2 + q_{xy1}^{\alpha\beta} (r - \sigma) - \rho_i z_{ii} \delta_{xi} \delta_{yi} \delta_{\alpha 1} \delta_{\beta 1}, \quad (50)$$

where

$$z_{ii} = \pi X_i^2 B_{ii} \sigma^3 g_{+-}^{00}(\sigma +) \quad (51)$$

and

$$\begin{aligned} q_{ii1}^{00} &= \frac{1}{\Delta} (D_1 a_1 - (b_1^0)^2 / 2) \\ q_{ii1}^{01} &= \frac{1}{\Delta} (D_1 a_2 - b_1^0 (b_1^1 + b_1^0 \rho_i z_{ii}) / 2) \\ q_{is1}^{00} &= \frac{1}{\Delta} (D_1 a_3 + b_1^0 \beta_3) \\ q_{ii1}^{10} &= \frac{1}{\Delta} (D_2 a_1 - b_1^0 b_1^1 / 2) \\ q_{ii1}^{11} &= \frac{1}{\Delta} (D_2 a_2 - b_1^1 (b_1^1 + b_1^0 \rho_i z_{ii}) / 2) \end{aligned}$$

$$\begin{aligned} q_{is1}^{10} &= \frac{1}{\Delta} (D_2 a_3 + b_1^1 \beta_3) \\ q_{si1}^{00} &= \frac{1}{\Delta} (D_3 a_1 - b_1^0 \beta_3) \\ q_{si1}^{01} &= \frac{1}{\Delta} (D_3 a_2 - (b_1^1 + b_1^0 \rho_i z_{ii}) \beta_3) \\ q_{ss1}^{00} &= \frac{1}{\Delta} (D_3 a_3 - 2b_2 \beta_{12} - b_1^0 (b_1^0 + 2b_1^1) / 2) \\ q_{si2}^{00} &= \frac{1}{\Delta} (D_4 a_1 - b_1^0 b_2) \\ q_{si2}^{01} &= \frac{1}{\Delta} (D_4 a_2 - b_2 (b_1^1 + b_1^0 \rho_i z_{ii})) \\ q_{ss2}^{00} &= \frac{1}{\Delta} (D_4 a_3 - 2b_2 \beta_3), \end{aligned} \quad (52)$$

and all other elements are equal to zero.

In the previous formulas we have accepted the following definitions:

$$\Delta = \beta_6^2 + \frac{1}{4} b_1^0 (b_1^0 + 2b_1^1) \quad (53)$$

$$\begin{aligned} \beta_{3*2^n} &= 1 + (-1)^n \frac{b_2}{3 * 2^n}, \quad n = 0, 1, 2, 3 \\ D_1 &= J_0 (\beta_6^2 + \frac{1}{4} b_1^0 b_1^1) - \frac{1}{4} J_1 (b_1^0)^2 - \frac{1}{3} b_1^0 (b_1^0 + b_1^1) \beta_{24} \\ D_2 &= J_1 (\beta_6^2 + \frac{1}{4} b_1^0 (b_1^0 + b_1^1)) - \frac{1}{4} J_0 b_1^1 b_1^0 + b_1^1) - \frac{1}{3} b_1^1 (b_1^0 + b_1^1) \beta_{24} \\ D_3 &= -\frac{1}{2} (J_0 (b_1^0 + b_1^1) + J_1 b_1^0) \beta_3 - (b_1^0 + b_1^1) \beta_{12} - \frac{1}{12} b_1^0 (b_1^0 + b_1^1) \\ &\quad * (b_1^0 + 2b_1^1) \\ D_4 &= -\frac{1}{2} (J_0 (b_1^0 + b_1^1) + J_1 b_1^0) b_2 - (b_1^0 + b_1^1) \beta_3 - \frac{1}{4} b_1^0 (b_1^0 + b_1^1) \\ &\quad * (b_1^0 + 2b_1^1) \end{aligned} \quad (54)$$

$$\begin{aligned} a_1 &= \frac{1}{D} \left(J_0 \beta_6^2 + \frac{1}{4} b_1^0 (J_0 b_1^1 - J_1 b_1^0) - \frac{1}{3} b_1^0 (b_1^0 + b_1^1) \beta_{24} \right) \\ a_2 &= \frac{1}{D} \left((\rho_i z_{ii} (1 + J_0) + J_1) \beta_6^2 - \frac{1}{12} (b_1^0 + b_1^1) (b_1^1 + b_1^0 \rho_i z_{ii}) \beta_6 \right. \\ &\quad \left. - \frac{1}{4} (b_1^1 + b_1^0 (1 - \rho_i z_{ii})) ((1 + J_0) b_1^1 - J_1 b_1^0) \right) \end{aligned}$$

$$\begin{aligned}
a_3 &= \frac{1}{2D} \left((J_0(b_1^0 + b_1^1) + J_1 b_1^0) \beta_3 + 2(b_1^0 + b_1^1) \beta_{12} + \frac{1}{6} b_1^0 (b_1^0 + b_1^1) \right. \\
&\quad \left. (b_1^0 + 2b_1^1) \right) \\
D &= -\frac{1}{2} (1 + J_0) (1 + J_0 + 2J_1) \beta_6^2 + \frac{1}{12} (b_1^0 + b_1^1) ((b_1^0 + b_1^1) (1 + J_0) \\
&\quad + J_1 b_1^0) \beta_6 + \frac{1}{8} ((1 + J_0) b_1^1 - J_1 b_1^0)^2 - \frac{1}{288} b_1^0 (b_1^0 + b_1^1)^2 (b_1^0 + 2b_1^1) \\
b_1^1 &= - \left(\frac{1}{2} b_1^0 \rho_i z_{ii} ((1 + J_0) \beta_3 + (2 + J_0) \beta_6 + \frac{1}{12} (b_1^0)^2) \right) / \\
&\quad \left(\frac{1}{24} \rho_i z_{ii} (b_1^0)^2 + \beta_{12} \right) \\
J_1 &= -\rho_i z_{ii} \left(-\frac{1}{16} (b_1^0)^2 \rho_i z_{ii} (1 + J_0 + \frac{1}{3} \beta_6) + \frac{1}{24} (b_1^0)^2 J_0 \beta_{12} \right. \\
&\quad \left. + \frac{1}{12} (b_1^0)^2 \beta_{12} + (1 + J_0)^2 \beta_{12}^2 \right) * \left(\beta_{12} + \frac{1}{24} \rho_i z_{ii} (b_1^0)^2 \right)^{-1} * (\beta_{12})^{-1}
\end{aligned}$$

There are only five independent variables $J_0, b_1^0, b_2, \rho_i^0, \rho_s^0$ which can be found by numerical solving the following set of equations:

$$\begin{aligned}
a_1^2 + 2a_1 a_2 + a_3^2 &= d_0^2 \\
a_1 (K_{si}^{00} + K_{si}^{01}) + a_2 K_{si}^{00} + a_3 (K_{ss}^{00} - 1) &= d_0 d_2 \quad (55) \\
(K_{si}^{00})^2 + 2 K_{si}^{00} K_{si}^{01} + (K_{ss}^{00} - 1)^2 &= d_2^2 + \frac{\beta_6^2}{\beta_{12}^4}
\end{aligned}$$

and the two equations for the monomer densities (6) and (7).

The parameters d_0 and d_2 are the following combinations of charge, dipolar moment, densities and temperature:

$$\begin{aligned}
d_0^2 &= \frac{4\pi e^2 \rho_i \sigma^2}{kT} \\
d_2^2 &= \frac{4\pi p_s^2 \rho_s}{3kT}, \quad (56)
\end{aligned}$$

The expressions $K_{xy}^{\alpha\beta}$ can be written as

$$\begin{aligned}
K_{si}^{00} &= \frac{1}{\Delta} \left[\frac{1}{2} \Lambda a_1 + \frac{1}{2} b_1^0 \right] \\
K_{si}^{01} &= \frac{1}{\Delta} \left[\frac{1}{2} \Lambda a_2 + \frac{1}{2} (b_1^0 \rho_i z_{ii} + b_1^1) \right] \\
K_{ss}^{00} - 1 &= \frac{1}{\Delta} \left[\frac{1}{2} \Lambda a_3 - \beta_3 \right] \quad (57)
\end{aligned}$$

$$\Lambda = \frac{1}{2} (J_0 (b_1^0 + b_1^1) + J_1 b_1^0) + \frac{2}{3} (b_1^0 + b_1^1) \beta_{24}$$

The contact values of the pair functions in (6) and (7) are presented in the exponent form:

$$\begin{aligned}
g_{+-}^{00}(\sigma+) &= \frac{1 + \eta/2}{(1 - \eta)^2} \exp[-h^{00}(\sigma+ |^{000})] \\
g_{is}^{00}(\sigma+) &= \frac{1 + \eta/2}{(1 - \eta)^2} \sinh[h^{00}(\sigma+ |^{011})] / h^{00}(\sigma+ |^{011}) \quad (58) \\
g_{ss}^{00}(\sigma+) &= \frac{1 + \eta/2}{(1 - \eta)^2} \sinh[G_s(\sigma+)] / G_s(\sigma+),
\end{aligned}$$

where

$$\begin{aligned}
h^{00}(\sigma+ |^{000}) &= \frac{q_{ii1}^{00}}{2\pi \rho_i} \\
h^{00}(\sigma+ |^{011}) &= \frac{\sqrt{3} q_{is1}^{00}}{2\pi \sqrt{\rho_i \rho_s}} \quad (59) \\
(G_s(\sigma+))^2 &= 3 \left(\frac{q_{ss1}^{00}}{2\pi \rho_s} \right)^2 + 6 \left(\frac{b_2}{2\pi \rho_s} \frac{\beta_{24}}{\beta_{12}^2} \right)^2
\end{aligned}$$

7. Appendix B: calculation of the Laplace transform of the Baxter functions for the D-subsystem

Let us compute the series expansion of the matrix \hat{P} defined by (), with respect to the variable s

$$\hat{P} = \frac{1}{D(s)} \begin{bmatrix} P_{11}^0 + sP_{11}^1 & P_{12}^0 + sP_{12}^1 & P_{13}^0 + sP_{13}^1 \\ P_{21}^0 + sP_{21}^1 & P_{22}^0 + sP_{22}^1 & P_{23}^0 + sP_{23}^1 \\ P_{31}^{-1}/s + P_{31}^0 & P_{32}^{-1}/s + P_{32}^0 & P_{33}^{-1}/s + P_{33}^0 \end{bmatrix} \quad (60)$$

where

$$D(s) = \frac{\delta_{-1}}{s} + \delta_0 + \dots \quad (61)$$

where

$$\delta_{-1} = -\frac{1}{\Delta} \left(a_1 \beta_3 (1 - \rho_i z_{ii}) + a_2 \beta_3 + a_3 \frac{b_1^0 + b_1^1}{2} \right), \quad (62)$$

$$\delta_0 = \frac{1}{\Delta} \left[a_1 \left(-\frac{1}{2} (J_0 (1 - \rho_i z_{ii}) + J_1) \beta_3 - \frac{1}{12} (b_1^0 + b_1^1)^2 \right) \right]$$

$$\begin{aligned}
& + \frac{1}{12} \rho_i z_{ii} b_1^0 (b_1^0 + b_1^1) + b_2/4 + (9/2 - 5\beta_{12}) \rho_i z_{ii} \Big) \\
& + a_2 \left(-\frac{1}{2} J_0 \beta_3 - \frac{1}{12} b_1^0 (b_1^0 + b_1^1) + b_2/4 \right) \\
& + a_3 \left(\frac{1}{2} (b_1^0 + b_1^1) - \frac{1}{4} \rho_i z_{ii} b_1^0 \right) - \beta_3 \Big]
\end{aligned} \tag{63}$$

Substituting expressions for a_1, a_2 and a_3 into (62) and (63) we have:

$$\delta_{-1} = -\frac{1}{D} \left((J_0 + J_1 + \rho_i z_{ii}) \beta_3 + \frac{1}{6} (b_1^0 + b_1^1)^2 \right) \tag{64}$$

$$\begin{aligned}
\delta_0 = \frac{1}{D} \Big[& (-J_0 \beta_3 - \frac{1}{6} b_1^0 (b_1^0 + b_1^1) + \frac{1}{4} b_2) \rho_i z_{ii} \\
& + (J_0 + J_1) (7\beta_{12} - 6) + \frac{7}{24} (b_1^0 + b_1^1)^2 + \frac{1}{2} \beta_3 \Big]
\end{aligned} \tag{65}$$

Coefficients in (60) have the very interesting structure:

$$\begin{aligned}
P_{31}^{(-1)} &= a_2 p_3^{(-1)} - a_3 p_2^{(-1)} \\
P_{32}^{(-1)} &= a_3 p_1^{(-1)} - a_1 p_3^{(-1)} \\
P_{33}^{(-1)} &= a_1 p_2^{(-1)} - a_2 p_1^{(-1)},
\end{aligned} \tag{66}$$

$$\begin{aligned}
P_{11}^{(0)} &= a_2 p_3^{(0)} - a_3 p_2^{(0)} + \frac{(\rho_i z_{ii} - 1) \beta_3}{\Delta} \\
P_{12}^{(0)} &= a_3 p_1^{(0)} - a_1 p_3^{(0)} + \frac{\beta_3}{\Delta} \\
P_{13}^{(0)} &= a_1 p_2^{(0)} - a_2 p_1^{(0)} + \frac{b_1^0 + b_1^1}{2\Delta}
\end{aligned} \tag{67}$$

$$\begin{aligned}
P_{31}^{(0)} &= a_2 p_3^{(1)} - a_3 p_2^{(1)} + \frac{(b_1^0 + b_1^1 - \rho_i z_{ii} b_1^0) \beta_3}{2\Delta} \\
P_{32}^{(0)} &= a_3 p_1^{(1)} - a_1 p_3^{(1)} + \frac{b_1^0 \beta_3}{2\Delta} \\
P_{33}^{(0)} &= a_1 p_2^{(1)} - a_2 p_1^{(1)} - \frac{\beta_6^2}{\Delta}
\end{aligned} \tag{68}$$

$$P_{11}^{(1)} = a_2 p_3^{(2)} - a_3 p_2^{(2)} + \frac{1}{\Delta} \left[-\frac{1}{12} (b_1^0 + b_1^1)^2 \right]$$

$$\begin{aligned}
& + \frac{1}{12} b_1^0 (b_1^0 + b_1^1) \rho_i z_{ii} + \frac{1}{4} b_2 - \frac{1}{2} \rho_i z_{ii} (1 + \frac{5}{6} b_2) \Big] \\
P_{12}^{(1)} &= a_3 p_1^{(2)} - a_1 p_3^{(2)} + \frac{1}{\Delta} \left[-\frac{1}{12} b_1^0 (b_1^0 + b_1^1) + \frac{1}{4} b_2 \right] \\
P_{13}^{(1)} &= a_1 p_2^{(2)} - a_2 p_1^{(2)} + \frac{1}{\Delta} \left[-\frac{1}{4} b_1^0 \rho_i z_{ii} + \frac{1}{6} (b_1^0 + b_1^1) \beta_{12} \right]
\end{aligned} \tag{69}$$

It means that the sum $\sum_{n=1}^3 = P_{mn}^{(j)} a_n$ ($m=1,2,3$ and $j=-1,0,1$) does not depend on a_n .

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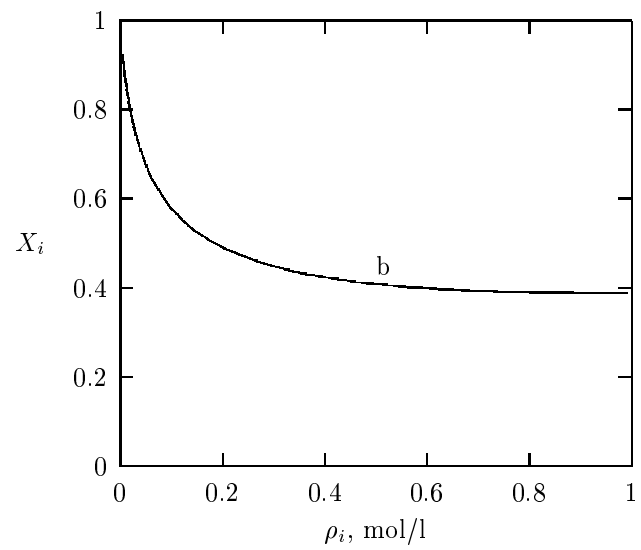


Figure 1. The ionic monomer fraction of an ion-dipolar mixture.

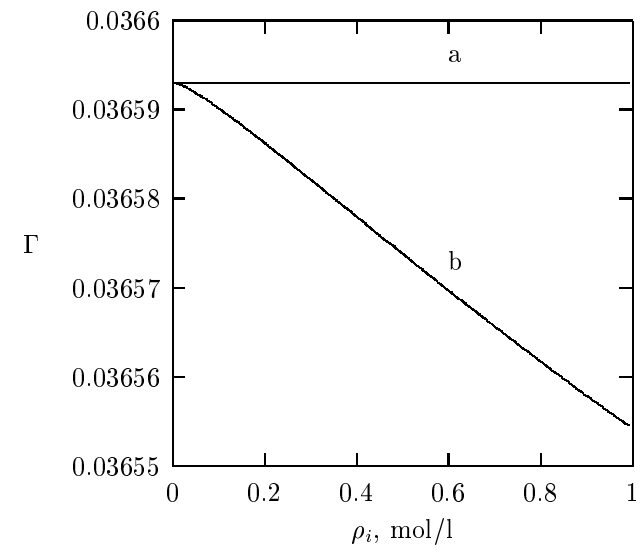


Figure 2. The adsorption coefficient of an ion-dipolar mixture.

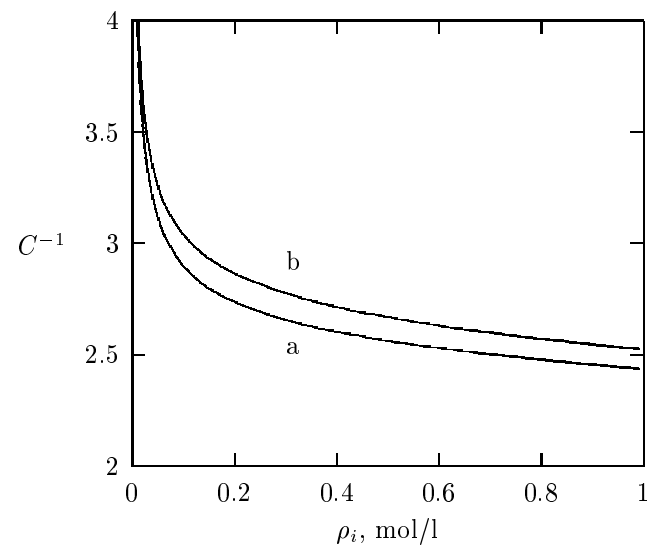


Figure 3. The inverse capacitance of an ion-dipolar mixture.

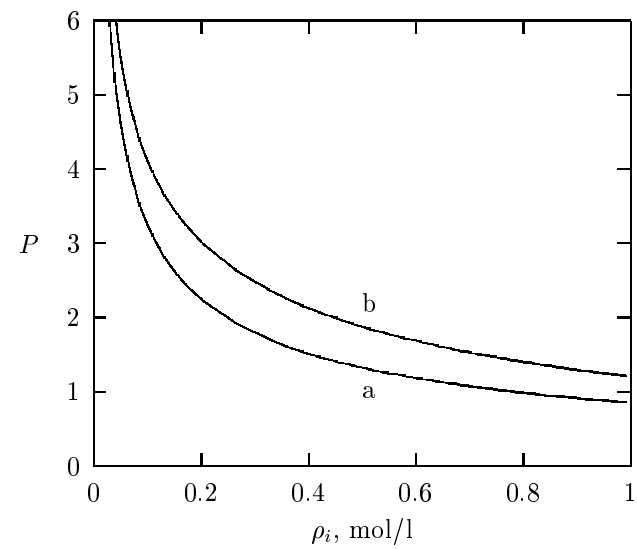


Figure 4. The polarization of an ion-dipolar mixture.

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