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Ion-dipole model for electrolyte solutions: Application of the associative mean spherical approximation

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The solution of the associative mean-spherical approximation for ion- dipolar system is reinvestigated and expressed in terms of only five parameters. Three of them have counterparts in the case without association, and the other two are the monomer fractions of ions and dipoles. The explicit expressions for the thermodynamic quantities are represented in a simpler form. Numerical results for thermodynamic properties and phase equilibria are presented.

Key words: *electrolyte solutions, ion-dipole model, association, AMSA, thermodynamic, phase equilibrium.*

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1. Introduction

It is our pleasure to dedicate this article to F. Hirata whose fundamental work in liquid physics yielded a considerable progress in the molecular theory of solvation for many real complex systems and phenomena [1]. Molecular theory of solvation is also important for the development of the microscopic theory of electrolyte solutions which has to be grounded on the explicit consideration of ion-molecular and intermolecular interactions besides the ion-ion ones in continium model case. In the work of Hirata's groups the solvent was treated in the framework of numerical solution of RISM and 3D RISM theory.

The simplest model for electrolyte solution within ion-molecular approach is the ion-dipole model consisting of charged hard spheres (ions) and hard spheres possessing dipole moments (solvent molecules). This model is just rougher than the site-site model used by Hirata groups. However, this model can be analiticaly treated in the framework of the mean spherical approximation (MSA), which may be important for different applications. The simplest ion-dipole model is the mixture of particles of equal sizes. This model has been solved analytically in the MSA by Blum [2,3] and independently by Adelman and Deutch [4]. The analytical expressions for the correlation functions and thermodynamics for this model were obtained and analysed in [5–10]. For a more general case of multicomponent ion-dipolar system with arbitrary sizes of particles and arbitrary valences of ions the MSA solution has been considered in [11–14].

Most recently the ion-dipole model was expanded by association concept [15,16]. As a result, the possibilities of explicit consideration of the effects of ion association, ion solvation and solvent hydrogen bonding have appeared. The description of ion association with an extension MSA has been proposed for pure ionic systems and the associative mean spherical approximation (AMSA) was formulated [17]. In our previous paper [18] we have solved AMSA for the restricted ion-dipole model with only ion association and equal size hard spheres for ions and dipoles. In our next paper [18] this solution was generalized to the case of unequal size of ions and dipoles and for the presented of ion-dipole and dipole-dipole association besides ionic ones. The explicit expressions for thermodynamic properties and dielectric constant have been also presented therein. Unfortunately this solution is rather complicated. In this paper we reinvestigate our previous solution and the present results for thermodynamics in a simpler form, which includes only five parameters. Three of them are of the same sense as in the case without association and two of them are the monomer fractions of ions and dipoles. We also present the numerical investigation of the effect of ion associations on the thermodynamic properties of electrolyte solution.

2. Summary of our previous results

The considered model is a three-component mixture of charged hard spheres density $\rho_{\rm i}$ and hard spheres with embedded point dipoles density $\rho_{\rm s}$. We consider that ions and solvent molecules are characterized by diameters $R_{\rm i}$ and $R_{\rm s}$ correspondly. The model is given by the potentials

$$\begin{aligned}
U_{ij}(r) &= \begin{cases} \infty, & r < R_{\rm i}\,, \\ \frac{Z_{\rm i} Z_j e^2}{r}, & r > R_{\rm i}\,, \end{cases} \\
U_{\rm is}(1,2) &= \begin{cases} \infty, & r < R_{\rm is}\,, \\ \frac{Z_{\rm i} e p_{\rm s}}{r^2}(\hat{r}\hat{p}), & r > R_{\rm is}\,, \end{cases} \\
U_{\rm ss}(1,2) &= \begin{cases} \infty, & r < R_{\rm s}\,, \\ \frac{p_{\rm s}^2}{r^3}\left[3(\hat{r}\hat{p}_1)(\hat{r}\hat{p}_2) - (\hat{p}_1\hat{p}_2)\right], & r > R_{\rm s}\,, \end{cases}
\end{aligned} \tag{1}$$

where $Z_+ = -Z_- = 1$, e is elementary charge, $p_{\rm s}$ is the value of dipole moment of solvent molecule, $\mathrm{R_{is}} = (\mathrm{R_i} + \mathrm{R_s})/2$; $\hat{r}$, $\hat{p}$ are the unit vectors of $\vec{r}_{12}$ and the dipole moment, respectively.

The model considered can be supplemented by association between cations and anions and clusterisation between solvent molecules and between ions and solvent molecules which can disribe the formation chains or network due to hydrogen bonds between solvent molecules and the formation of specific solvation clusters around the ions. For the sake of simplicity we focus here on the dimerisation case characterized by the Mayer function of ion-ion, ion-solvent and solvent-solvent associative interactions

$$f^{as}_{+-}(r) = B_{\rm ii}\delta(r - R_{\rm i}), \qquad f^{as}_{+s} = f^{as}_{-s}(r) = B_{\rm is}\delta(r - R_{\rm is}), \qquad f^{as}_{\rm ss}(r) = B_{\rm ss}\delta(r - R_{\rm s}). \tag{2}$$

In AMSA theory, such dimerization is characterized by the system of two mass action law (MAL) for fraction $\alpha_{\rm i}$ and $\alpha_{\rm s}$ of free ions and solvent molecules respectively:

$$\begin{aligned}
\frac{1-\alpha_{\rm i}}{\alpha_{\rm i}} &= \alpha_{\rm i} 12\eta_{\rm i} B_{\rm ii} g^{00}_{+-}(R_{\rm i}) + \alpha_{\rm s} 24\eta_{\rm s}\frac{R^3_{\rm is}}{R^3_{\rm ss}} B_{\rm is} g^{00}_{\rm is}(R_{\rm is}), \\
\frac{1-\alpha_{\rm s}}{\alpha_{\rm s}} &= \alpha_{\rm i} 24\eta_{\rm i}\frac{R^3_{\rm is}}{R^3_{\rm i}} B_{\rm is} g^{00}_{\rm is}(R_{\rm is}) + \alpha_{\rm s} 24\eta_{\rm s} B_{\rm ss} g^{00}_{\rm ss}(R_{\rm s}),
\end{aligned} \tag{3}$$

where $\eta_{\rm i} = \frac{1}{6}\pi\rho_{\rm i} R^3_{\rm i}$, $\eta_{\rm s} = \frac{1}{6}\pi\rho_{\rm s} R^3_{\rm s}$, are packing fraction for ions and solvent molecules $g^{00}_{\rm ii}(R_{\rm i})$ $g^{00}_{\rm is}(R_{\rm is})$ and $g^{00}_{\rm ss}(R_{\rm s})$ are the contact value of ion-ion, ion-solvent and solvent-solvent pair distribution functions of unbonded particles averaged about orientations of molecules.

In AMSA approach the pair correlation functions $h^{\alpha\beta}_{xy}(12) = g^{\alpha\beta}_{xy} - \delta_{\alpha_0}\delta_{\beta_0}$ satisfy the Wertheim version of the Ornstein-Zernike (WOZ) equations [20,21]. The superscript $\alpha = 0$ shows that the corresponding particle is free and the superscript $\alpha = 1$ shows that it is bonded. Similarly to the usual MSA case, the pair correlation functions can be presented in the form [2–14]

$$\begin{aligned}
h_{\rm ii}(r) &= \frac{1}{2}(h_{++}(r) - h_{+-}(r)), \\
h^s_{\rm ii}(r) &= \frac{1}{2}(h_{++}(r) + h_{+-}(r)), \\
h_{\rm is}(12) &= h^{(s)}_{\rm is}(r) + h^{011}_{\rm is}(r)(\hat{r}\hat{p}), \\
h_{\rm ss}(12) &= h^{(s)}_{\rm ss}(r) + h^{110}_{\rm ss}(r)(\hat{p}_1\hat{p}_2) + h^{112}_{\rm ss}(r)(3(\hat{r}\hat{p}_1)(\hat{r}\hat{p}_2) - (\hat{p}_1\hat{p}_2)).
\end{aligned} \tag{4}$$

Due to the symmetry of the model considered, the WOZ equation decouples into an electrostatic and nonelectrostatic parts. The nonelectrostatic part has the form of WOZ equation for two-component dimerizing mixture [22] in the case considered or dimerizing-chain or network forming mixture with a more correct treatment of hydrogen-bonding effects between solvent molecules. The electrostatic part reduces to the WOZ equation in which the dimerization takes place only between ions. Using the Wertheim-Baxter factorisation technique [23–25] the solution of electrostatic part of WOZ equations was performed in terms of energy parameters

$$
\begin{aligned}
J_\alpha &= 2\pi\rho_{\rm i}R_{\rm i}\int_0^\infty r{\rm d}r\sum_\beta {\rm h}_{\rm ii}^{\alpha\beta}({\rm r}), \qquad {\rm b}_1^\alpha = 2\pi\sqrt{\rho_{\rm i}\rho_{\rm s}}{\rm R_i R_s}\frac{1}{\sqrt{3}}\int_0^\infty {\rm drh}_{\rm is}^{011,\alpha}({\rm r}),\\
b_2 &= 2\pi\rho_{\rm s}R_{\rm s}^3\frac{3}{\sqrt{30}}\int_0^\infty \frac{1}{r}{\rm drh}_{\rm ss}^{112}({\rm r})
\end{aligned}
\tag{5}
$$

connected with the ion and dipole parameters

$$
\kappa_{\rm i}^2R_{\rm i}^2 = 4\pi{\rm e}^2\beta\rho_{\rm i}R_{\rm i}^2, \qquad 3y_{\rm s} = \frac{4}{3}\pi\beta\rho_{\rm s}p_{\rm s}^2, \qquad \delta = R_{\rm s}/R_{\rm i}\,. \tag{6}
$$

The system of equations for parameter (5) should be considered together with equations (3) for fraction $\alpha_{\rm i}$ and $\alpha_{\rm s}$.

Out of the parameters (5), only three of them create the system of coupled nonlinear equations which can be represented in the following form

$$
(a_{\rm i}^0)^2 + 2a_{\rm i}^0a_{\rm i}^1 + a_{\rm s}^2 = \kappa_{\rm i}^2R_{\rm i}^2\,, \tag{7}
$$

$$
a_{\rm i}^0(K_{si}^{00}+K_{si}^{00}) + a_{\rm i}^1K_{si}^{00} + a_{\rm s}(K_{\rm ss}-1) = \kappa_{\rm i}R_{\rm i}\sqrt{3y_{\rm s}}\,, \tag{8}
$$

$$
(K_{si}^{00})^2 + 2K_{si}^{00}K_{si}^{01} + (K_{\rm ss}-1)^2 = 3y_{\rm s} + \beta_6^2/\beta_{12}^4\,, \tag{9}
$$

where

$$
K_{si}^{00} = \frac{\delta}{2\Delta}\left(\Lambda a_{\rm i}^0 + b_1^0\right), \tag{10}
$$

$$
K_{si}^{01} = \frac{\delta}{2\Delta}\left(\Lambda a_{\rm i}^1 + b_1^1 + \rho_{\rm i}z_{\rm ii}b_{\rm i}^0\right), \tag{11}
$$

$$
K_{\rm ss}-1 = \frac{\delta}{2\Delta}\left(\Lambda a_{\rm s} - \frac{2}{\delta}\beta_3\right), \tag{12}
$$

$$
a_{\rm i}^0 = \frac{1}{D}\left[J_0\beta_6^2 - \frac{1}{12}b_1^0\left(b_1^0+b_1^1\right)(\delta\beta_6+3) + \frac{1}{4}b_1^0\left(b_1^1J_0 - b_1^0J_1\right)\right], \tag{13}
$$

$$
\begin{aligned}
a_{\rm i}^1 = \frac{1}{D}\Big\{&\left[\rho_{\rm i}Z_{\rm ii}(1+J_0)+J_1\right]\beta_6^2 - \frac{1}{12}\delta(b_1^0+b_1^1)\rho_{\rm i}z_{\rm ii}b_{\rm i}^0 + b_1^1)\beta_6\\
&+\frac{1}{4}\left(b_1^0(\rho_{\rm i}z_{\rm ii}-1) - b_1^1\right)\left(b_1^1 + b_1^1J_0 - b_1^0J_1\right)\Big\}\,,
\end{aligned}
\tag{14}
$$

$$
a_{\rm s} = \frac{1}{2\delta D}\left\{J_0(b_1^0+b_1^1)\beta_3 + J_1b_1^0\beta_3 + b_1^0 + b_1^1\left[\frac{1}{6}\delta b_1^0(b_1^0+2b_1^1) + \beta_3 + \delta\beta_6\right]\right\}, \tag{15}
$$

$$
\Delta = \beta_6^2 + \frac{1}{4}b_1^0(b_1^0+2b_1^1), \tag{16}
$$

$$
\Lambda = J_1b_1^0 + (1+J_0+\frac{1}{3}\delta\beta_6)(b_1^0+b_1^1), \tag{17}
$$

$$
\begin{aligned}
D = &-\frac{1}{2}(1+J_0)(1+J_0+2J_1)\beta_6^2 + \frac{1}{12}\delta(b_1^0+b_1^1)\left[(b_1^0+b_1^1)(1+J_0)+b_1^0J_1\right]\beta_6\\
&+\frac{1}{8}\left[(1+J_0)b_1^1 - b_1^0J_1\right]^2 - \frac{1}{288}\delta^2b_1^0(b_1^0+b_1^1)^2(b_1^0+2b_1^1),
\end{aligned}
\tag{18}
$$

$$\beta_{3\cdot 2^n} = 1 + \frac{(-1)^n b_2}{3\cdot 2^n}, \tag{19}$$

$$\begin{aligned} J_1 &= -\rho_{\rm i} z_{\rm ii}\left[-\frac{1}{4}\delta^2 (b_1^0)^2 \rho_{\rm i} z_{\rm ii}\,(1+J_0+\frac{1}{3}\delta\beta_6) + \frac{1}{12}\delta J_0 (b_1^0)^2 (2-\delta)(\delta\beta_6+\beta_3)\right.\\ &\left. +\frac{1}{6}\delta (b_1^0)^2(\delta\beta_6+\beta_3) + (1+J_0)^2(\delta\beta_6+\beta_3)^2\right](\delta\beta_6+\beta_3)^{-1}\\ &\times\left(\delta\beta_6+\beta_3+\frac{1}{12}\delta\rho_{\rm i} Z_{\rm ii}(b_1^0)^2(2-\delta)\right)^{-1}, \end{aligned} \tag{20}$$

$$\begin{aligned} b_1^1 &= -\left\{b_1^0 \rho_{\rm i} z_{\rm ii}\left[\frac{1}{12}\delta (b_1^0)^2(2-\delta) + \delta\beta_6(2+J_0)+\beta_3(1+J_0)\right]\right\}\\ &\times\left[\frac{1}{12}\rho_{\rm i} z_{\rm ii}\delta (b_1^0)^2(2-\delta)+\beta_3+\delta\beta_6\right]^{-1}, \end{aligned} \tag{21}$$

$$\rho_{\rm i} z_{\rm ii} = 12\eta_{\rm i} B_{\rm ii}\alpha_{\rm i}^2 g_{+-}^{00}(R_{\rm i}^+). \tag{22}$$

As a result we have shown that the solution of AMSA for ion-dipole model reduces to the system of nonlinear equations for five parameters J_0, b_1^0, b_2, $\alpha_{\rm i}$ and $\alpha_{\rm s}$. This system can be solved numerically, for example, using Newton-Raphson method. For ilustration the dependence of these parameters on ion concentration $c_{\rm i} = \frac{\rho_{\rm i}}{\rho_{\rm i}+\rho_{\rm s}}$ is presented in figure 1. Parameters of the model considered correspond

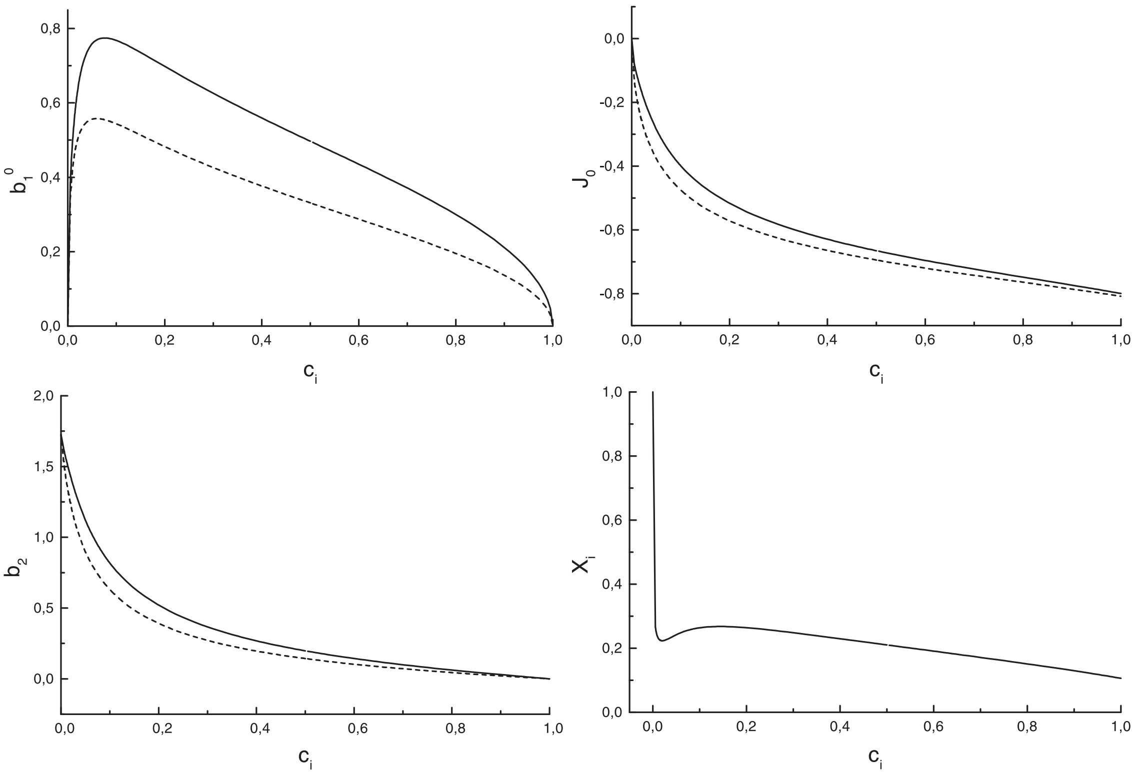

Figure 1. Concentration dependence of the parameters of analytical solution of AMSA for ion dipole model. Solid lines correspond to the model with association parameters $B_{\rm ii} = 10$, $B_{\rm is} = B_{\rm ss} = 0$. Nonassociative case is presented by dotted lines.

to the solution of NaCl in methanol: the dielectric permetivity of pure methanol $\varepsilon = 32.5$, ionic diameters $R_{\rm i} = 2.79$ Å, the diameter of molecules $R_{\rm s} = 4.7$ Å, the parameter of ion association $B_{\rm ii} = 10$ and the parameters $B_{\rm is} = B_{\rm ss} = 0$. For comparison, the results for the case $B_{\rm ii} = 0$ are also presented by dotted line. We can see the importance of ion association for all parameters J_0, b_1^0 and b_2.

3. Thermodynamics

Using the Hoye-Stell scheme [26] for the calculation of thermodynamics in MSA extended by Kalyuzhnyi and Holovko [27] to the AMSA case, the thermodynamic properties of ion-dipolar system in AMSA approach can be calculated [19]. The excess internal energy of the system is equal to

$$\frac{\beta U^{\mathrm{el}}}{V} = \frac{1}{4\pi}\left[\kappa_{\mathrm{i}}^2 R_{\mathrm{i}}^2 (J_0 + J_1) - 2\kappa_{\mathrm{i}} R_{\mathrm{i}} \frac{1}{\delta}\sqrt{3y_{\mathrm{s}}}(b_1^0 + b_1^1) - 6y_{\mathrm{s}} b_2 \frac{1}{\delta^3}\right]. \tag{23}$$

The pressure, the chemical potentials and free energy contain three different contributions: the hard sphere contributions (HS), the contributions from the mass action law (MAL) and electrostatic contribution (el).

For example, the total free energy is equal to

$$\frac{\beta A}{V} = \frac{\beta A^{\mathrm{HS}}}{V} + \frac{\beta A^{\mathrm{MAL}}}{V} + \frac{\beta A^{\mathrm{el}}}{V}. \tag{24}$$

The chemical potentials can be found according to the relation

$$\beta\mu_a = \frac{\partial}{\partial\rho_a}\left(\frac{\beta A}{V}\right) = \beta\mu_a^{\mathrm{HS}} + \beta\mu_a^{\mathrm{MAL}} + \beta\mu_a^{\mathrm{el}}. \tag{25}$$

where $a = i$ or s.

The expression for the pressure can be found according to the relation

$$\beta p = \beta\sum_a \rho_a\mu_a - \frac{\beta A}{V} = \beta p^{\mathrm{HS}} + \beta p^{\mathrm{MAL}} + \beta p^{\mathrm{el}}. \tag{26}$$

For the hard sphere contribution we can use expressions for thermodynamics of mixed hard sphere fluids obtained in the Percus-Yevick approximation [28]

$$\frac{\beta A^{HS}}{V} = -\rho\left(\ln(1-\xi_3) - \frac{3\,\xi_1\xi_2}{\xi_0\,(1-\xi_3)} - \frac{3\,\xi_2^3}{2\,\xi_0\,(1-\xi_3)^2}\right), \tag{27}$$

$$\begin{aligned}\beta\mu_x^{(HS)} = {} & -\ln(1-\xi_3) + \frac{\xi_0\sigma_x^3}{1-\xi_3} + 3\frac{(\xi_2\sigma_x + \xi_1\sigma_x^2)(1-\xi_3) + \xi_1\xi_2\sigma_x^3}{(1-\xi_3)^2} \\ & + \frac{3}{2}\left(\frac{3(1-\xi_3)\xi_2^2\sigma_x^2 + 2\xi_2^3\sigma_x^3}{(1-\xi_3)^3}\right),\end{aligned} \tag{28}$$

$$\beta P^{HS} = \rho\left(\frac{1}{1-\xi_3} + \frac{3\,\xi_1\xi_2}{\xi_0\,(1-\xi_3)^2} + \frac{3\,\xi_2^3}{\xi_0\,(1-\xi_3)^3}\right), \tag{29}$$

where ξ_n is given by

$$\xi_n = \frac{\pi}{6}\sum_x \rho_x\sigma_x^n\,. \tag{30}$$

The MAL contribution for the free energy can be presented in the form [20]

$$\frac{\beta A^{\mathrm{MAL}}}{V} = \left[\rho_{\mathrm{i}}\ln\alpha_{\mathrm{i}} + \frac{1}{2}\rho_{\mathrm{i}}(1-\alpha_{\mathrm{i}})\right] + \left[\rho_{\mathrm{s}}\ln\alpha_{\mathrm{s}} + \frac{1}{2}\rho_{\mathrm{s}}(1-\alpha_{\mathrm{s}})\right]. \tag{31}$$

The electrostatic part of the chemical potentials for ions and dipoles is expressed as

$$\beta\mu_{\mathrm{i}}^{\mathrm{el}} = \frac{1}{4\pi\rho_{\mathrm{i}}}\left[\kappa_{\mathrm{i}}^2 R_{\mathrm{i}}^2 J_0 - \kappa_{\mathrm{i}} R_{\mathrm{i}}\frac{1}{\delta}\sqrt{3y_{\mathrm{s}}}\; b_1^0\right], \tag{32}$$

$$\beta\mu_{\mathrm{s}}^{\mathrm{el}} = -\frac{1}{4\pi\rho_{\mathrm{s}}}\left[\frac{\kappa_{\mathrm{i}} R_{\mathrm{i}}}{\delta}\sqrt{3y_{\mathrm{s}}}\;(b_1^0 + b_1^1) + \frac{1}{\delta^3}6y_{\mathrm{s}} b_2\right]. \tag{33}$$

Electrostatic part for the pressure is given by

$$\beta p^{\rm el} \;=\; \widetilde{J} + \frac{\pi}{3}\sum_{a,b}\rho_a\rho_b R_{ab}^3 Sp\left[h_{ab}(R_{ab})x_b h_{ba}(R_{ab})x_a\right] + \frac{1}{3}\rho_{\rm i}^2 z_{\rm ii}R_{\rm ii}\left(\frac{\partial h_{\rm ii}^{00}(r)}{\partial r}\right)_{r=R_{\rm i}}, \qquad (34)$$

where $x_{\rm s}=1$,

$$\mathbf{x}_{\rm i} = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}, \qquad (35)$$

$$\widetilde{J} = \frac{1}{12\pi}\left[\kappa_{\rm i}^2 R_{\rm i}^2(J_0+J_1) - 4\kappa_{\rm i}R_{\rm i}\frac{1}{\delta}\sqrt{3y_{\rm s}}\;(b_1^0+b_1^1) - 18y_{\rm s}b_2\frac{1}{\delta^3}\right]. \qquad (36)$$

$h_{ab}(R_{ab})$ are the contact values of the corresponding harmonics of the electrostatic part of correlation functions

$$\begin{aligned} h_{\rm ii}^{\alpha\beta}(R_{\rm i}) &= \frac{1}{2\pi\rho_{\rm i}R_{\rm i}}\left[q_{\rm ii}^{\alpha\beta} + (q_{\rm ii}^{0\beta} + a_{\rm i}^{\beta})\delta_{\alpha 1}\rho_{\rm i}z_{\rm ii})\right], \\ h_{\rm is}^{011\alpha}(R_{\rm is}) &= \frac{\sqrt{3}}{2\pi\sqrt{\rho_{\rm i}\rho_{\rm s}}R_{\rm is}}\left[q_{\rm is}^{\alpha} + (q_{\rm is}^0 + a_{\rm s})\delta_{\alpha 1}\rho_{\rm i}z_{\rm ii}\right], \end{aligned} \qquad (37)$$

$$\begin{aligned} h_{\rm ss}^{110}(R_{\rm s}) &= \frac{1}{2\pi\rho_{\rm s}R_{\rm s}}\left(q_{\rm ss} - \frac{2b_2}{R_{\rm s}^2}\frac{\beta_{24}}{\beta_{12}^2}\right), \\ h_{\rm ss}^{112}(R_{\rm s}) &= \frac{1}{2\pi\rho_{\rm s}R_{\rm s}}\left(q_{\rm ss} + \frac{b_2}{R_{\rm s}^2}\frac{\beta_{24}}{\beta_{12}^2}\right), \end{aligned} \qquad (38)$$

where

$$\begin{aligned} q_{\rm ii}^{\alpha\beta} &= \frac{1}{\Delta}\left[(\Delta J_\alpha - \frac{1}{4}\Lambda b_1^\alpha)a_{\rm i}^\beta - \frac{1}{2}b_1^\alpha b_1^\beta + \rho_{\rm i}z_{\rm ii}\delta_{1\beta}b_1^0\right], \\ q_{\rm is}^{\alpha} &= \frac{1}{\Delta}\left[(\Delta J_\alpha - \frac{1}{4}\Lambda b_1^\alpha)a_{\rm s} + b_1^\alpha\frac{1}{\delta}\beta_3\right], \\ q_{\rm ss} &= -\frac{1}{3}(b_1^0+b_1^1)a_{\rm s} - \frac{\Lambda}{2\delta}\beta_3 a_{\rm s} - \frac{2}{\delta^2}(1-\beta_3^2), \end{aligned} \qquad (39)$$

$$\begin{aligned} R_{\rm i}\left(\frac{\partial h_{\rm ii}^{00}(r)}{\partial r}\right)_{r=R_{\rm i}} &= -\frac{1}{2\pi\rho_{\rm i}R_{\rm i}}\left[q_{\rm ii}^{00} + (q_{\rm ii}^{00} + q_{\rm ii}^{01})(q_{\rm ii}^{00} + a_{\rm i}^0)q_{\rm ii}^{00}q_{\rm ii}^{10}\right. \\ &\quad \left. + q_{\rm is}^0\left(R_{\rm s}q_{\rm is}^0 + \frac{1}{2\delta}R_{\rm s}^2\left(b_1^0+b_1^1\right)a_{\rm i}^0 + \frac{\Lambda}{2\Delta\delta}b_2 a_{\rm i}^0 + \frac{1}{\Delta\delta}b_2 b_{\rm i}^0\right)\right]. \end{aligned} \qquad (40)$$

For $g_{+-}^{00}(R_{\rm i})$ in accordance with Bernard-Blum exponential approximation we use the exponential form [29].

$$g_{+-}^{00}(R_{\rm i}) = g_{\rm s}(R_{\rm i})\exp(-h_{\rm ii}^{00}(R_{\rm i})) \qquad (41)$$

$g_{\rm s}(R)$ is the contact value for hard-sphere mixture. For illustration, figure 2 presents the dependence of the ion-ion, ion-solvent and solvent-solvent parts of internal energy and of the total internal energy of ion-dipole systems on ion concentration $c_{\rm i}$ for the parameters

$$\begin{aligned} &\rho^* = \rho_{\rm i}R_{\rm i}^3 + \rho_{\rm s}R_{\rm s}^3 = 0.6, \qquad \gamma = R_{\rm s}/R_{\rm i} = 1, \qquad B_{\rm ii} = 1, \\ &\beta_{\rm i} = \frac{\rm e^2}{kTR_{\rm i}} = 200, \qquad \beta_{\rm s} = \frac{P_{\rm s}^2}{kTR_{\rm s}^3} = 5.6, \qquad B_{\rm is} = B_{\rm ss} = 0. \end{aligned} \qquad (42)$$

For comparison, the results for the nonassociative case ($B_{\rm ii}=0$) are also presented by the dotted lines. As we can see the ion association leads to the increase of ion-ion and ion-solvent parts of

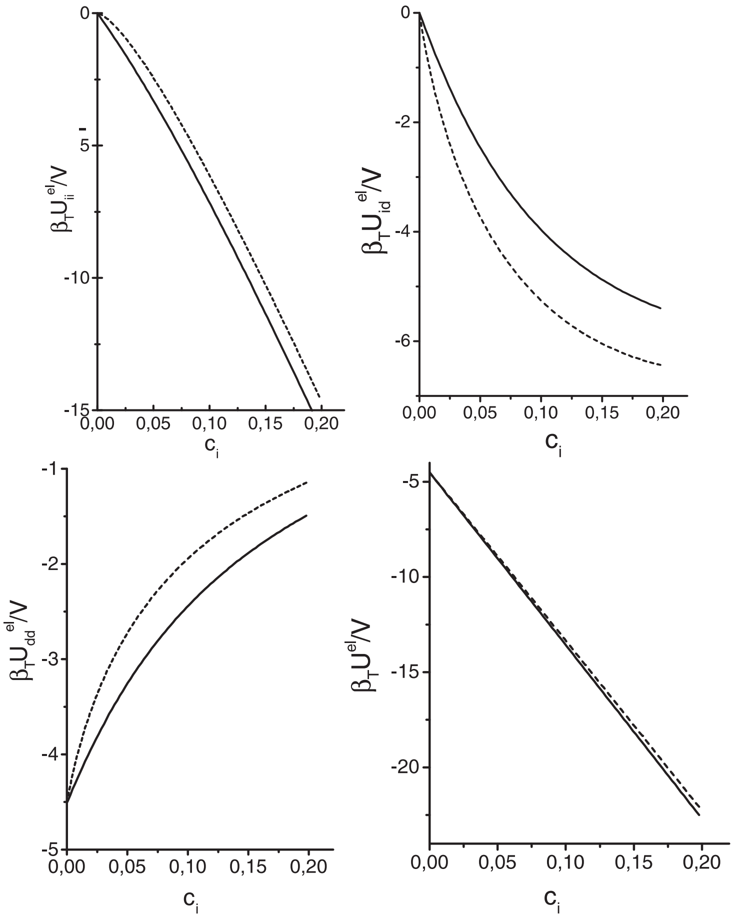

Figure 2. Concentration dependence of the internal energy for ion-dipole model. Solid lines correspond to the model with association parameters $B_{\text{ii}} = 1$, $B_{\text{is}} = B_{\text{ss}} = 0$. Nonassociative case is presented by dotted lines.

internal energy and to the decrease of solvent-solvent part of internal energy. As a result, the changes of the total internal energy are not very significant.

Similar concentrational dependence of pressure, free energy and chemical potentials is illustrated in figure 3. Since the electrostatic part of pressure is negative, the pressure decreases with the increase of ion concentration. The ion association makes this tendency wearker. The free energy also decreases with ion concentration but the effect of ion association has the opposite tendency compaired with the pressure. At the presence of ion association, the free energy is lower than at nonassociative case. The chemical potential of solvent molecules decreases with the increase of ion concentration and the association makes this tendency wearker. The chemical potential for ions has a nonmonotonic concentration dependence showing the maximum at some concentration. It means that for higher concentrations, the electrolyte is nonhomogeneous and separates into two phases with different ion concentrations. The problem of phase equlibria in ion-dipole systems is considered in the next section. Here we only note that the ion association essentially decreases the value of ionic chemical potential.

4. Liquid-liquid coexistence

The problem of phase behaviour of electrolyte solutions has been the subject of considerable effort for the last decade [30,31]. However, the majority of these works were done in the framework

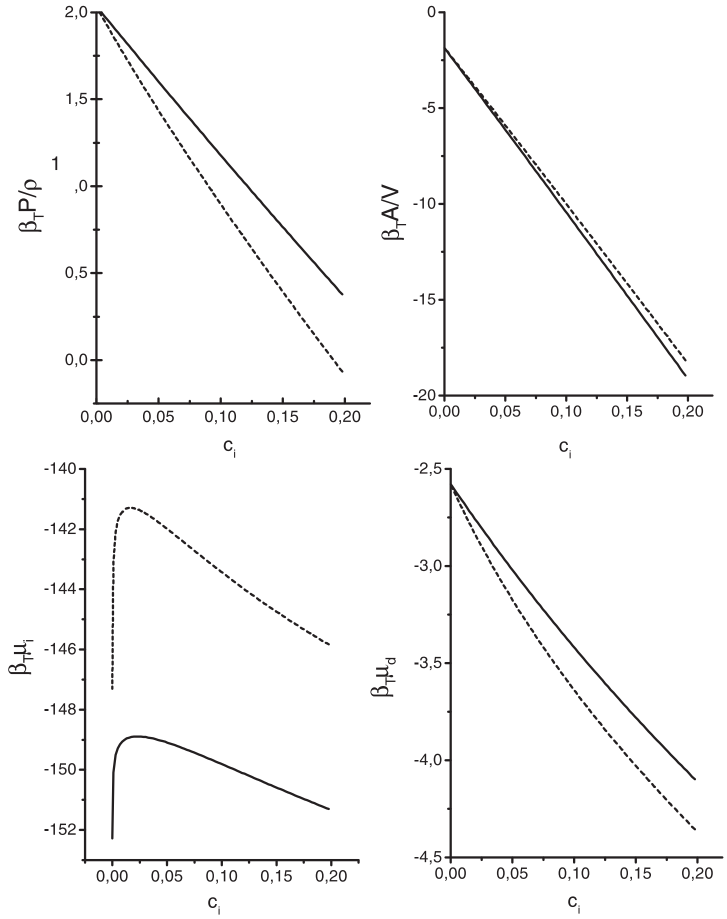

Figure 3. The concentration dependence of the pressure free energy and chemical potentials. Solid lines correspond to the model with association parameters $B_{\rm ii} = 1$, $B_{\rm is} = B_{\rm ss} = 0$. Nonassociative case is presented by dotted lines.

of the restricted primitive model without explicit consideration of solvent molecules. We can select only the papers [9,32] in which the ion-dipole model in MSA approach was used for the description of phase behaviour of electrolyte solutions. The necessity of taking into account the effects of ion association was noted in [33]. For this purpose we can use the analytical expressions for pressure and chemical potentials obtained in the previous section. To calculate the liquid coexistance curve we use the thermodynamical equilibrium condition

$$\begin{aligned} P^{\rm I}(T,\eta^{\rm I},c_{\rm i}^{\rm I}) &= P^{\rm II}(T,\eta^{\rm II},c_{\rm i}^{\rm II}), \\ \mu_{\rm i}^{\rm I} = (T,\eta^{\rm I},c_{\rm i}^{\rm I}) &= \mu_{\rm i}(T,\eta^{\rm II},c_{\rm i}^{\rm II}), \\ \mu_{\rm s}^{\rm I} = (T,\eta^{\rm I},c_{\rm i}^{\rm I}) &= \mu_{\rm s}(T,\eta^{\rm II},c_{\rm i}^{\rm II}), \end{aligned} \tag{43}$$

where $c_{\rm i}^{\rm I}$, $c_{\rm i}^{\rm II}$, $\eta^{\rm I}$ and $\eta^{\rm II}$ are the concentrations of ions and the total packing fractions $\eta = \eta_{\rm i} + \eta_{\rm s}$ in two different phases. The obtained results are presented in figure 4 which shows the effects of ion pairing on liquid-liquid coexistance curve in the ion-dipole model as a function of the ion concentration $c_{\rm i}$ and reduced temperature $T^* = 1/\sqrt{\beta_{\rm i}\beta_{\rm s}}$. The solid line corresponds to the ion-dipole model with the parameter of ion association $B_{\rm ii} = 10$. The dashed line corresponds to the ion-dipole model without ion association [9]. The results are presented for two ratios $\beta_{\rm i}/\beta_{\rm s} = 40$ and 60. As we can see from figure 4, due to the ion association, the critical temperature decreases and the critical concentration increases similarly to the pure ion model in MSA and AMSA treatment [33]. Due to the ion association the coexistance curve is narrower. The effect of ion association

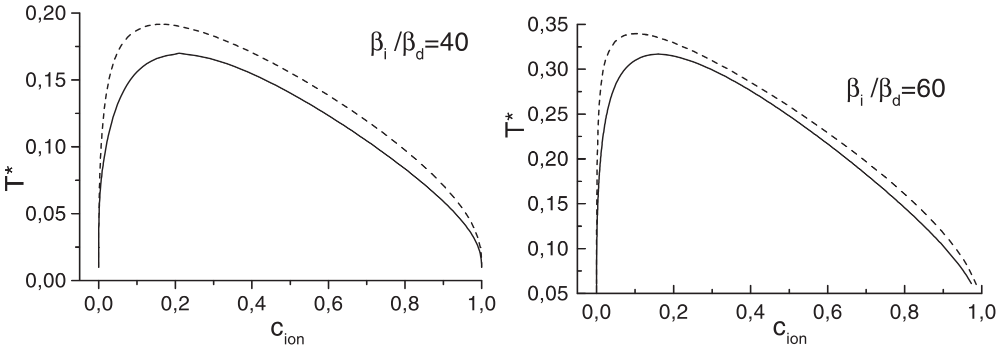

Figure 4. Liquid-liquid coexistance curves for ion-dipole model with fixed total density ρ^*=0.6. Solid lines corresponds the model with association parameters $B_{\mathrm{ii}} = 1$, $B_{\mathrm{is}} = B_{\mathrm{ss}} = 0$. Nonassociative case is presented by dotted lines.

is more important for a more polar solvent (the smaller value of the ratio $\beta_{\mathrm{i}}/\beta_{\mathrm{s}}$). The explicit consideration of solvent molecules leads to a different total density η in two different phases. The total density η is higher in the phase with higher ion concentration compaired to the phase with smaller ion concentration.

5. Conclusions

In this paper we have shown that the analytical solution of AMSA for ion-dipole model reduces to the solution of the systems of nonlinear algebric equations for five parameters. Three of them being similar to the nonassociative case J_0, b_1^1, b_2, are internal energy parameters. Two other parameters α_{i} and α_{s} are monomer fractions of ions and dipole molecules. We have also obtained the analytical expressions for the free energy, pressure and chemical potentials in a simple form. Starting form this expressions the liquid-liquid coexistance is investigated. This result is presented in figure 4. Similar to the van der Waals theory for simple fluids, the presented curves are assymetric with parabolic behaviour in the vicinity of the critical point despite the MSA and AMSA results are not simple mean-field results.

The presented numerical investigation demonstrates the importance of the effect of the associations on the thermodynamical properties. Due to the ion pairing the coexistance curves are narrower, the critical temperature decreases and the critical concentration increases. We have shown that the total density is higher in the phase with higher ion concentration. Since this result is obtained for the fixed total density of systems, further investigations are needed in order to understand the total phase diagram of the model considered. Other aspects are connected with the investigations of the effect of ion-solvent and solvent-solvent association on thermodynamic properties.

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Іонно-дипольна модель розчинів електролітів: застосування асоціативного середньосферичного наближення.

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Розв'язок середньосферичного наближення представлено через п'ять параметрів. Три з них аналогічні для безасоціативного випадку, а два інших є мономерними фракціями іонів та диполів. Точні вирази для термодинамічних величин є представлені в простій формі. Представлені чисельні результати для термодинамічних функцій та фазової рівноваги.

Ключові слова: *розчини електролітів, іонно-дипольна модель, асоціація, AMSA, термодинаміка, фазова рівновага*

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