The Short Range Structure of Ion-polar Solvent Mixtures. Calculations by the RISM Integral Equations

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The reference hypernetted chain like integral equation of the interaction site model is solved numerically for a solution of ions in a polar solvent. In our model, the ions and the solvent molecules are taken to be charged hard spheres and polar hard dumb-bells, respectively. Calculated pair correlation functions contain a great deal of interesting information on the short range structure of the ionic solutions: a solvated structure around ions and an effect of ionic charges upon the structure of the solvent. It is found that various types of associated structures of constituent species, such as simple ion pairs, ion triplets, and ion pairs separated by one solvent molecule exist in ionic solutions.

One of today's central problems of the physical chemistry of ionic solutions is to develop the theory based on the more realistic model for ionic solutions than the so called primitive model.[1] In the primitive model of ionic solutions, a solvent is considered as a continuum medium, in which ions are immersed, with the same dielectric constant as that of the pure solvent. For the last one decade, several authors proposed theories of ionic solutions in which microscopic structures of solvents were explicitly taken into account.[2-12] Many of these theories were concerned with a mixture of charged hard spheres and dipolar hard spheres.

Taking account of a structure of ions and solvent molecules, we proposed a theory[10] on the static dielectric function and site-site pair correlation functions of ionic solutions composed of polyatomic ions and polar polyatomic molecules based on the interaction site model. In the present paper, we obtain site-site radial distribution functions of ionic solutions composed of charged hard spheres and polar hard dumb-bells using the RISM integral equations.[13,14]

Recently, we proposed an RHNC-like integral equation of RISM-1[15] and solved the equation in the case of fluids composed of dipolar hard dumb-bells. Morriss and Cummings[16,17] presented Monte Carlo simulation results for site-site radial distribution functions and the dielectric constant of the polar hard dumb-bell fluids. A comparison of our results with their simulation results is also made in this paper. An agreement of these two results is fairly good, which encourages us to apply the RHNC-like integral equation of RISM-1 to ionic solutions.

In this paper, we extend the RHNC-like integral equation of RISM-1 to multi-component systems and solved it for ionic solutions composed of charged hard spheres and dipolar hard dumb-bells in order to investigate a short range structure of ionic solutions.

The RHNC-like Integral Equation for Fluid Mixtures

An extension of the RHNC-like integral equation of RISM-1[15] to the case of multi-component systems is made in this section.

We assume here that the molecule of type M has n_M interaction sites and a charge $q_{\alpha M}$ is sited on the α-th site of the molecule of type M. The total potential energy of the fluid mixture is assumed to be the sum over all pairs of the intermolecular potentials. The intermolecular potential between the i-th molecule of type M and the j-th molecule of type M', $U_{MM'}(i_M, j_{M'})$, is given as

$$U_{MM'}(i_M,j_{M'}) = \sum_{\alpha=1}^{n_M}\sum_{\gamma=1}^{n_{M'}} u_{\alpha M\gamma M'}(|\boldsymbol{r}_{iM}^{\alpha}-\boldsymbol{r}_{jM'}^{\gamma}|), \quad (1)$$

where $u_{\alpha M\gamma M'}(|\boldsymbol{r}_{iM}^{\alpha}-\boldsymbol{r}_{jM'}^{\gamma}|)$ is a site-site interaction between the pair of site αM and γM' and $\boldsymbol{r}_{iM}^{\alpha}$ the position of the α-th site of the i-th molecule of type M. The site-site interaction can be divided into two parts,

$$u_{\alpha M\gamma M'}(r) = u^{(0)}_{\alpha M\gamma M'}(r) + u^{(1)}_{\alpha M\gamma M'}(r). \quad (2)$$

Here, $u^{(0)}_{\alpha M\gamma M'}(r)$ is a short range part of the site-site interaction, which is treated as a reference potential, and the perturbation potential $u^{(1)}_{\alpha M\gamma M'}(r)$ is a long range Coulomb potential, that is,

$$u^{(1)}_{\alpha M\gamma M'}(r) = \frac{q_{\alpha M}q_{\gamma M'}}{4\pi\varepsilon_0 r}, \quad (3)$$

where ε_0 is the dielectric constant of vacuum.

The Ornstein-Zernike type equation for a multi-component system is

$$\tilde{\boldsymbol{h}}' = \tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}'\tilde{\boldsymbol{\omega}} + \tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}'\tilde{\boldsymbol{h}}', \quad (4)$$

where $\tilde{\boldsymbol{h}}'$, $\tilde{\boldsymbol{c}}'$, and $\tilde{\boldsymbol{\omega}}$ are matrices with elements $\sqrt{\rho_M\rho_{M'}}\tilde{h}_{\alpha M\gamma M'}(k)$, $\sqrt{\rho_M\rho_{M'}}\tilde{c}_{\alpha M\gamma M'}(k)$, and $\tilde{\omega}_{\alpha M\gamma M'}(k)$, respectively. ρ_M is the number density of molecules of type M. Hereafter, $\tilde{\boldsymbol{A}}'$ denotes a matrix with the element $\sqrt{\rho_M\rho_{M'}}\tilde{A}_{\alpha M\gamma M'}(k)$ and $\tilde{A}_{\alpha M\gamma M'}(k)$ is the Fourier transform of $A_{\alpha M\gamma M'}(r)$,

$$\tilde{A}_{\alpha M\gamma M'}(k) = \int d\boldsymbol{r} A_{\alpha M\gamma M'}(r)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}$$

$h_{\alpha M\gamma M'}(r)$ is the site-site total correlation function, and $c_{\alpha M\gamma M'}(r)$ is the site-site direct correlation function. $\omega_{\alpha M\gamma M'}(r)$ is the intramolecular pair correlation function

and the Fourier transform of $\omega_{\alpha M\gamma M'}(r)$ for rigid molecule is

$$\tilde{\omega}_{\alpha M\gamma M'}(k) = \delta_{MM'}\left\{\delta_{\alpha\gamma} + (1-\delta_{\alpha\gamma})\frac{\sin kl_{\alpha\gamma M}}{kl_{\alpha\gamma M}}\right\}, \quad (5)$$

where δ_{ab} is the Kronecker delta and $l_{\alpha\gamma M}=|r^{\alpha}_{iM}-r^{\gamma}_{iM}|$ the distance between the α-th site and the γ-th site of the same molecule of type M.

The Ornstein-Zernike type equation for a reference system is

$$\tilde{h}^{(0)\prime} = \tilde{\omega}\tilde{c}^{(0)\prime}\tilde{\omega} + \tilde{\omega}\tilde{c}^{(0)\prime}\tilde{h}^{(0)\prime}, \quad (6)$$

where a superscript (0) denotes the reference system quantity. From Eqs. 4 and 6, we obtain

$$\delta\tilde{h}' = \tilde{\chi}\{\boldsymbol{1}-\delta\tilde{c}'\tilde{\chi}\}^{-1}\delta\tilde{c}'\tilde{\chi}, \quad (7)$$

where $\tilde{\chi}=\tilde{\omega}+\tilde{h}^{(0)\prime}$, $\delta\tilde{h}'=\tilde{h}'-\tilde{h}^{(0)\prime}$, and $\delta\tilde{c}'=\tilde{c}'-\tilde{c}^{(0)\prime}$. $\boldsymbol{1}$ is the unit matrix and $\boldsymbol{A}^{-1}$ is the inverse matrix of $\boldsymbol{A}$.

An RHNC-like approximation of RISM-1 for the multi-component system is expressed as

$$\delta c_{\alpha M\gamma M'}(r) = \delta h_{\alpha M\gamma M'}(r) - \ln\frac{g_{\alpha M\gamma M'}(r)}{g^{(0)}_{\alpha M\gamma M'}(r)}e^{\beta u^{(1)}_{\alpha M\gamma M'}(r)}, \quad (8)$$

where $g_{\alpha M\gamma M'}(r)=h_{\alpha M\gamma M'}(r)+1$ is the site-site radial distribution functiion, $\beta=1/k_BT$, k_B the Boltzmann constant and T the absolute temperature. Combining Eq. 7 with Eq. 8, we can solve the integral equation when the reference system quantities are given.

As is shown in the appendix, $h_{\alpha M\gamma M'}(r)$ is a short range function in the case of ionic solutions as well as the case of polar fluids.[18] Then, the RHNC-like approximation, Eq. 8, implies the following asymptotic form of $c_{\alpha M\gamma M'}(r)$ at large r

$$c_{\alpha M\gamma M'}(r) \simeq -\beta q_{\alpha M}q_{\gamma M'}/4\pi\varepsilon_0 r. \quad (9)$$

However, Cummings and Stell[19] showed that Eq. 9 is not correct and the exact asymptotic forms of $c_{\alpha M\gamma M'}(r)$, for example, of a fluid composed of polar diatomic molecules is

$$c_{\alpha M\gamma M'}(r) \simeq -A\beta q_{\alpha M}q_{\gamma M'}/4\pi\varepsilon_0 r, \quad (10)$$

where A is the state dependent constant. All the closure relations of RISM-1 have the same asymptotic form Eq. 9. Thus, it seems that pair correlation functions calculated by the RISM-1 type integral equation have an incorrect long range nature. Nevertheless, the previous calculations showed that the RISM-1 equation gives good results for a short range structure of liquids.[14,20-22] Rossky *et al.*[23] showed that a modification of the asymptotic form of the closure relations produces only very small deviations in the site-site pair correlation functions at a short range region. Since we are interested in a short range structure of ionic solutions, we solve the Ornstein-Zernike type equation with the closure relation Eq. 8.

Applications to Ion-solvent Mixtures.

Model. A system considered is an 1:1 electrolyte solution. Cations(i+) and anions(i−) are charged hard spheres with the same diameter σ_{ii} and have charges $+q_i$ and $-q_i$, respectively. Solvent molecules(s) are fused hard spheres with the same diameter σ_{ss}, on whose center charges $+q_s$ and $-q_s$ are sited. The bond length of solvent molecules is l. An illustration of molecules is shown in Fig. 1. The reference potential is given as

$$u^{(0)}_{\alpha M\gamma M'}(r) = \begin{cases}\infty, & r<\sigma_{MM'}\\ 0, & r>\sigma_{MM'}\end{cases}, \quad (11)$$

where we assume that $\sigma_{is}=(\sigma_{ii}+\sigma_{ss})/2$. The system is electrically neutral, that is, $\rho_{i+}=\rho_{i-}\equiv\rho_i$. Because of the symmetry, we have $g_{i+i+}(r)=g_{i-i-}(r)$, $g_{i+i-}(r)=g_{i-i+}(r)$, $g_{s+s+}(r)=g_{s-s-}(r)$, $g_{s+s-}(r)=g_{s-s+}(r)$, $g_{i+s+}(r)=g_{s+i+}(r)=g_{i-s-}(r)=g_{s-i-}(r)$, $g_{i+s-}(r)=g_{s-i+}(r)=g_{i-s+}(r)=g_{s+i-}(r)$.

Computational Procedures. The function $\delta h_{\alpha M\gamma M'}(r)$ and $\delta c_{\alpha M\gamma M'}(r)$ have a discontinuity at $r=\sigma_{MM'}$, but $H_{\alpha M\gamma M'}(r)=\delta h_{\alpha M\gamma M'}(r)-\delta c_{\alpha M\gamma M'}(r)$ is a continuus function of r.[14,15,20] As is shown in the appendix, $h_{\alpha M\gamma M'}(r)$ for ionic solutions is a short range function. Thus, similar considerations in the previous paper[15] give us the following equations from Eqs. 7 and 8

$$\tilde{H}^{S\prime} = \tilde{\chi}\{\boldsymbol{1}-(\delta\tilde{c}^{S\prime}-\tilde{H}^{L\prime})\tilde{\chi}\}^{-1}(\delta\tilde{c}^{S\prime}-\tilde{H}^{L\prime})\tilde{\chi}-\delta\tilde{c}^{S\prime} \quad (12)$$

and

$$\delta c^{S}_{\alpha M\gamma M'}(r) = g^{(0)}_{\alpha M\gamma M'}(r)[\exp\{H^{S}_{\alpha M\gamma M'}(r)-\psi^{S}_{\alpha M\gamma M'}(r)\}-1] - H^{S}_{\alpha M\gamma M'}(r). \quad (13)$$

Here,

$$\delta c^{S}_{\alpha M\gamma M'}(r) = \delta c_{\alpha M\gamma M'}(r) + H^{L}_{\alpha M\gamma M'}(r),$$
$$H^{S}_{\alpha M\gamma M'}(r) = H_{\alpha M\gamma M'}(r) - H^{L}_{\alpha M\gamma M'}(r),$$
$$H^{L}_{\alpha M\gamma M'}(r) = \frac{\beta q_{\alpha M}q_{\gamma M'}}{4\pi\varepsilon_0 r}(1-e^{-ar}),$$
$$\psi^{S}_{\alpha M\gamma M'}(r) = \frac{\beta q_{\alpha M}q_{\gamma M'}}{4\pi\varepsilon_0 r}e^{-ar},$$

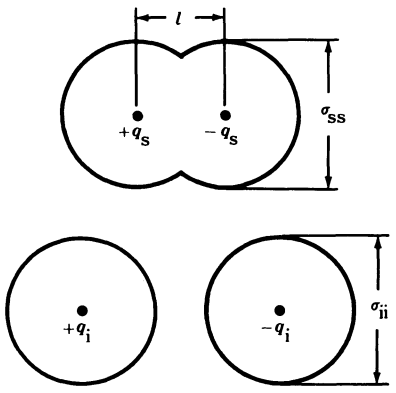

Fig. 1. The shapes of ions and a solvent molecule.

where a is a disposable parameter chosen so as to make the function $\psi^{S}_{\alpha M\gamma M'}(r)$ negligibly small at the termination of the finite range of r. Equations 12 and 13 involve only short range functions that can be numerically handled in the usual way. An iteration calculation is carried out by the use of Eqs. 12 and 13 with an initial guess $H^{S}_{\alpha M\gamma M'}(r)=0$, and is continued until the self consistency of

$$\left|\frac{\exp\{H^{S}_{\alpha M\gamma M'}(r)_{out}\}-\exp\{H^{S}_{\alpha M\gamma M'}(r)_{in}\}}{\exp\{H^{S}_{\alpha M\gamma M'}(r)_{in}\}}\right| < 10^{-6} \quad (14)$$

is satisfied. The site-site radial distribution function is finally obtained as

$$g_{\alpha M\gamma M'}(r) = g^{(0)}_{\alpha M\gamma M'}(r)\exp\{H^{S}_{\alpha M\gamma M'}(r) - \psi^{S}_{\alpha M\gamma M'}(r)\}. \quad (15)$$

Reference System Quantities. Reference system quantities are indispensable for solving the RHNC-like integral equation. It was shown that the PY-like approximation of RISM-1 gives good description of a structure of liquids with short range forces.[14,20] Therefore, a solution of the PY-like integral equation of RISM-1 is used as a reference system quantity. The PY-like approximation of RISM-1 is expressed as[14]

$$c^{(0)}_{\alpha M\gamma M'}(r) = g^{(0)}_{\alpha M\gamma M'}(r)\{1-e^{\beta u^{(0)}_{\alpha M\gamma M'}(r)}\}. \quad (16)$$

We transform Eqs. 6 and 16 into the following equations

$$\tilde{H}^{(0)\prime} = \tilde{\omega}(I-\tilde{c}^{(0)\prime}\tilde{\omega})^{-1}\tilde{c}^{(0)\prime}\tilde{\omega}-\tilde{c}^{(0)\prime}, \quad (17)$$

and

$$c^{(0)}_{\alpha M\gamma M'}(r) = y^{(0)}_{\alpha M\gamma M'}(r)\{e^{-\beta u^{(0)}_{\alpha M\gamma M'}(r)}-1\}, \quad (18)$$

where $y^{(0)}_{\alpha M\gamma M'}(r)=1+H^{(0)}_{\alpha M\gamma M'}(r)$ and $H^{(0)}_{\alpha M\gamma M'}(r)=h^{(0)}_{\alpha M\gamma M'}(r)-c^{(0)}_{\alpha M\gamma M'}(r)$. An interation calculation is carried out by the use of Eqs. 17 and 18 with an initial guess $H^{(0)}_{\alpha M\gamma M'}(r)=0$, and is continued until the self consistency of

$$\left|\frac{y^{(0)}_{\alpha M\gamma M'}(r)_{out}-y^{(0)}_{\alpha M\gamma M'}(r)_{in}}{y^{(0)}_{\alpha M\gamma M'}(r)_{in}}\right| < 10^{-6} \quad (19)$$

is satisfied. The reference system quantities are finally obtained as

$$g^{(0)}_{\alpha M\gamma M'}(r) = y^{(0)}_{\alpha M\gamma M'}(r)e^{-\beta u^{(0)}_{\alpha M\gamma M'}(r)} \quad (20)$$

and

$$\tilde{\chi} = (I-\tilde{\omega}\tilde{c}^{(0)\prime})^{-1}\tilde{\omega}. \quad (21)$$

Results and Discussion

The system considered is characterized by six parameters as follows: the reduced number densities of ions and solvent molecules $\rho_i^*=\rho_i\sigma^3_{ii}$ and $\rho_s^*=\rho_s d^3$, the reduced charge of ions $q_i^*=(\beta q_i^2/4\pi\varepsilon_0\sigma_{ii})^{1/2}$, the reduced dipole moment of solvent molecules $\mu_s^*=(\beta\mu_s^2/4\pi\varepsilon_0 d^3)^{1/2}$, the reduced bond length of solvent molecules $L^*=l/\sigma_{ss}$, and the ratio of σ_{ii} to σ_{ss} $\sigma^*_{ii}=\sigma_{ii}/\sigma_{ss}$. Here, $\mu_s=q_s l$ is the magnitude of the dipole moment of solvent molecules and d, the diameter of the hard sphere whose volume is the same as the solvent molecule, is given by the following equation

$$d^3 = \sigma^3_{ss}(1+3L^*/2-L^{*3}/2). \quad (22)$$

The numerical calculations were carried out with a grid width $\Delta r=0.01\sigma_{ss}$ and the integrals were truncated at $r\approx 10\sigma_{ss}$. Calculations were checked by doubling the cutoff distance, and no meaningfull difference between the two calculations was found.

Comparisons with Monte Carlo Simulation Results for Polar Fluids. Recently, Monte Carlo calculations were carried out for dipolar hard dumb-bell fluids.[16,17] In this subsection, our results are compared with the

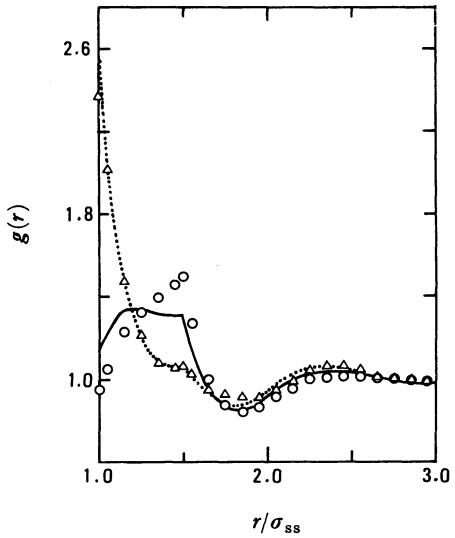

Fig. 2. The site-site radial distribution functions for the polar hard dumb-bell fluid at $\rho_s^*=0.78$, $\mu_s^*=1.17$ and $L^*=0.5$, ——: $g_{++}(r)$ by the RHNC-like equation, ·····: $g_{+-}(r)$ by the RHNC-like equation, ○: $g_{++}(r)$ by the Monte Carlo simulation, △: $g_{+-}(r)$ by the Monte Carlo simulation.

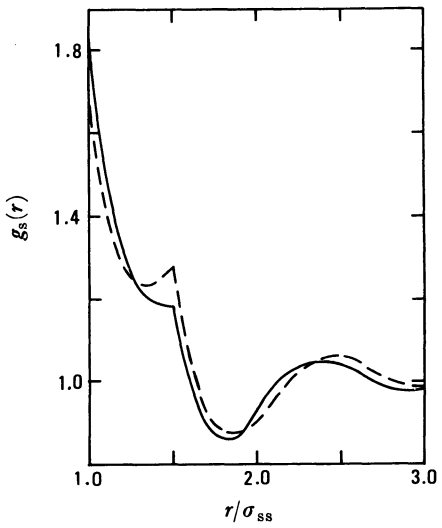

Fig. 3. The radial distribution functions of the centers of atoms. Parameters are the same as Fig. 2. ——: RHNC-like, ·····: Monte Carlo.

simulation results[16] of the polar hard dumb-bell fluid at $L^*=0.5$. $\rho_s^*=0.78$, and $\mu_s^*=1.17$.

Site-site radial distribution functions $g_{++}(r)$ and $g_{+-}(r)$ are shown in Fig. 2. An agreement between the simulation results and ours is good on the whole. Especially, the agreement of $g_{+-}(r)$ is very good except near a contact distance. The radial distribution function of the center of atoms $g_s(r)$ and the radial distribution function of charges $g_d(r)$ are shown in Figs. 3 and 4, respectively. Here, $g_s(r)$ and $g_d(r)$ are defined as

$$g_s(r) = \{g_{++}(r)+g_{+-}(r)\}/2$$

and

$$g_d(r) = \{g_{++}(r)-g_{+-}(r)\}/2.$$

$g_d(r)$ calculated using the interaction site approximation (ISA)[24] is also shown in Fig. 4. The ISA is defined as

$$h_{\alpha M\gamma M'}(r) = -1, \qquad r<\sigma_{\alpha M\gamma M'}$$

and

$$c_{\alpha M\gamma M'}(r) = -\beta u_{\alpha M\gamma M'}(r). \qquad r>\sigma_{\alpha M\gamma M'}$$

This is the molecular fluid analogue of the mean spherical approximation for simple fluids. Though our $g_s(r)$ is qualitatively correct, a small systematic difference between RHNC and Monte Calro results is found from Fig. 3. On the other hand, the agreement of $g_d(r)$ is good. It is said from Fig. 4 that the RHNC-like approximation is superior to the ISA. $\delta g(r)=g_s(r)-g^{(0)}(r)$ are plotted in Fig. 5, where $g^{(0)}(r)$ is the site-site radial distribution function of a nonpolar hard dumb-bell fluid with the same values of L^* and ρ_s^*. It is noted that $g_s(r)$ by ISA is equal to $g^{(0)}(r)$ calculated by the use of the PY-like approximation of RISM-1. Both the $\delta g(r)$ of RHNC and Monte Calro results are nearly equal to zero except at $r/\sigma_{ss}\approx 1-1.7$ where the RHNC result is qualitatively correct. This result shows that most of the disagreement of $g_s(r)$ of RHNC-like results with simulation ones comes from the use of approximate results as the reference system quantities. Thus, it is reasonable to expect that the use of the exact pair correlation functions obtained by computer simulations as reference system quantities gives an excellent result for short range structure of fluids.

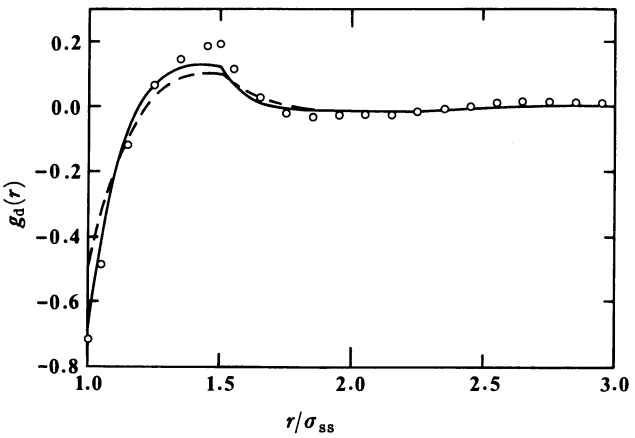

Fig. 4. The radial distribution functions of charges. Parameters are the same as Fig. 2. ——: RHNC-like, ----: ISA, ○: Monte Carlo.

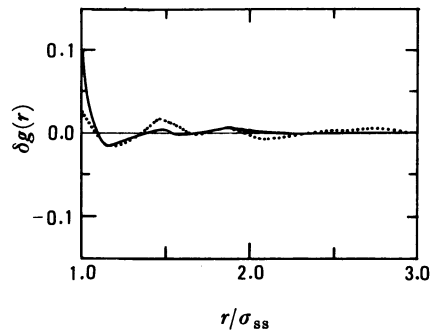

Fig. 5. δg (r). Parameters are the same as Fig. 2. ——: RHNC-like, ·····: Monte Carlo.

Distribution Functions of Ionic Solutions. The figures 6a—6c show the site-site radial distribution functions of an ionic solution. Broken curves in Fig. 6a are ion-ion radial distribution functions by the primitive model for the same state, which are calculated from the RHNC integral equation. The dielectric constant ε of a solvent used in calculations of the primitive model is given by $\varepsilon/\varepsilon_0=1+3y$, where $y=4\pi\beta\rho_s\mu_s^2/9$. This is consistent with the use of the RHNC-like approximation, because the asymptotic form Eq. 9 is obtained from Eq. 10 with $A=1$ and the approximation $A=1$ implies $\varepsilon/\varepsilon_0=1+3y$.[19] It is found from Fig. 6a that the primitive model gives an incorrect description on the short range nature of ion-ion radial distribution functions. The contact value of $g_{i+i-}(r)$ shown in Fig. 6a is large, which indicates that the degree of association of ionic specics is considerably large in this system. $g_{i+i+}(r)$

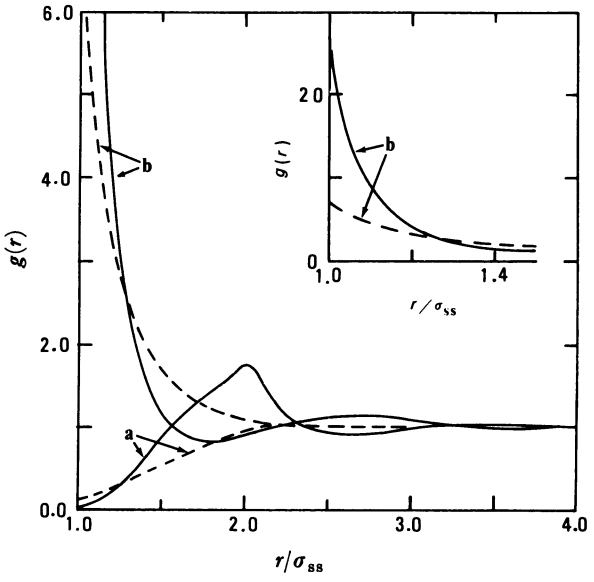

Fig. 6a. The ion-ion radial distribution functions for the ionic solution at $\rho_1^*=0.03$, $\rho_s^*=0.6$, $q_1^*=4.5$, $\mu_s^*=1.0$, $L^*=0.6$ and $\sigma_{11}^*=1.0$. a: $g_{1+1+}(r)$, b: $g_{1+1-}(r)$. ——: the ion-solvent mixture, ----: the primitive model.

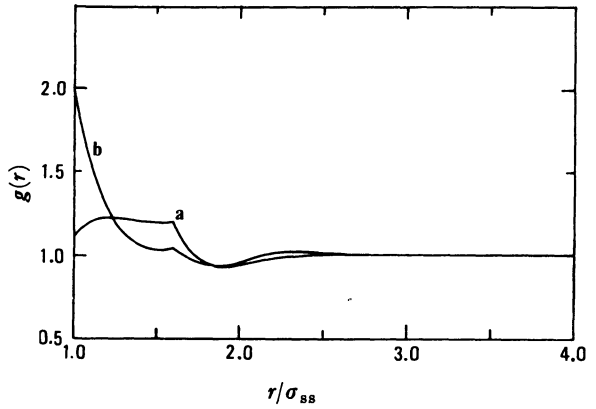

Fig. 6b. The solvent-solvent radial distribution functions for the ionic solution whose parameters are the same as Fig. 6a. a: $g_{s+s+}(r)$, b: $g_{s+s-}(r)$.

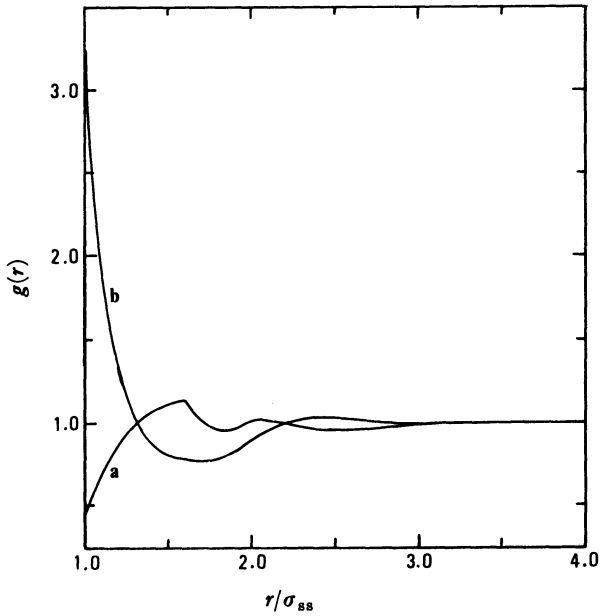

Fig. 6c. The ion-solvent radial distribution functions for the ionic solution whose parameters are the same as Fig. 6a. a: $g_{i+s+}(r)$, b: $g_{i+s-}(r)$.

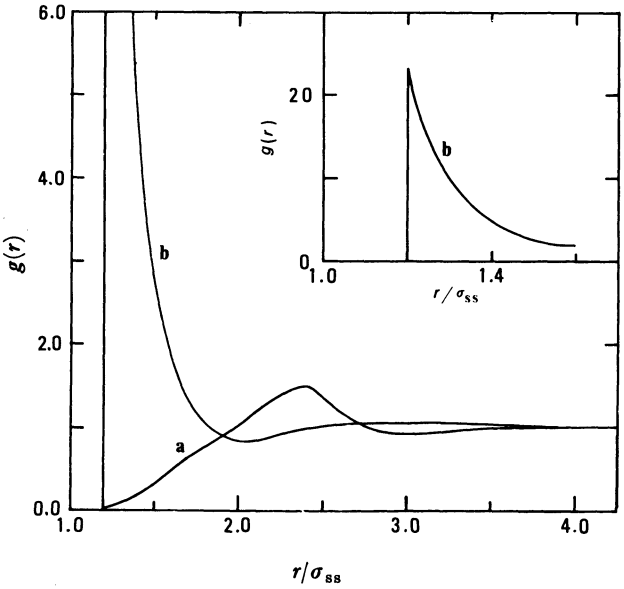

Fig. 7. The ion-ion radial distribution functions for the ionic solution whose parameters are the same as Fig. 6a except $\sigma_{ii}^*=1.2$. a: $g_{i+i+}(r)$, b: $g_{i+i-}(r)$.

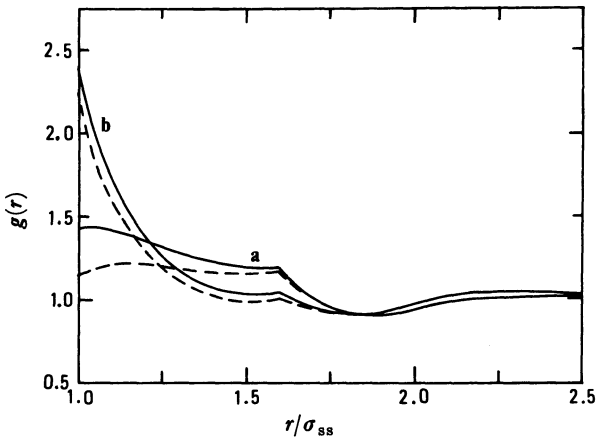

Fig. 8. The solvent-solvent radial distribution functions of the ionic solution at $\rho_i^*=0.05$, $\rho_s^*=0.6$, $\mu_s^*=1.0$, $L^*=0.6$ and $\sigma_{ii}^*=1.0$. a: $g_{s+s+}(r)$, b: $g_{s+s-}(r)$. ——: $q_i^*=4.5$, ----: $q_i^*=0.0$.

has a maximum at $r=2\sigma_{ss}=2\sigma_{ii}$. This maximum suggests the existence of ion triplets shown in Fig. 10a. In order to ascertain this consideration, an effect of the variation of the diameter of ions was investigated. Figure 7 shows the ion-ion radial distribution functions at the same parameters as that of Fig. 6 except $\sigma_{ii}^*=1.2$. The maximum of $g_{i+i+}(r)$ shifts to $r=2.4\sigma_{ss}=2\sigma_{ii}$, which supports the idea that the maximum at $r=2\sigma_{ii}$ comes from ion triplets.

Solvent-solvent radial distribution functions shown in Fig. 6b are similar to those of pure solvents whose details are described in Ref. 15. An effect of ionic charges on the solvent structure is found in Fig. 8. A system with $q_i^*=0$ is the mixture of polar hard dumbbells and neutral hard spheres. The values of solvent-solvent radial distribution functions at $q_i^*=4.5$ are larger than those at $q_i^*=0$ in a small r region. The behavior is explained as follows: ionic charges promote the association of ionic species, and resultantly, a probability that solvent molecules approach each other is enlarged. This effect is small in the case at $\rho_i^*=0.03$.

Ion-solvent radial distribution functions shown in Fig. 6c have cusps at $r/\sigma_{ss}=1+L^*$, which is the same as solvent-solvent radial distribution functions. These cusps come from the structure of solvent molecules and will be rounded off for the system with continuous potentials. The curves of $g_{i+s+}(r)$ and $g_{i+s-}(r)$ intersect each other, and $g_{i+s+}(r)<g_{i+s-}(r)$ at $r/\sigma_{ss}\approx 1$ and $g_{i+s+}(r)>g_{i+s-}(r)$ at $r/\sigma_{ss}\approx 1+L^*$, which is explained in a similar manner to the case of solvent-solvent radial distribution functions for pure solvent. These results imply that an atom of the solvent molecule with an opposite charge to an ion tends to orient toward the ion, that is, a solvated structure is formed around the ion.

It was found that a variation of the polarity of solvent molecules caused an interesting effect upon the short range structure of ionic solutions. $g_{i+i+}(r)$ and $g_{i+s+}(r)$ are shown in Fig. 9, and the contact values of $g_{i+i-}(r)$ and $g_{i+s-}(r)$ are shown in Table 1. With increasing μ_s^*, the maximum at $r/\sigma_{ss}=2$ of $g_{i+i+}(r)$ becomes small and a new maximum arises at $r/\sigma_{ss}\approx1.5$. Further, a shoulder of $g_{i+s+}(r)$ near $r/\sigma_{ss}=1.4$ grows up to a maximum for $\mu_s^*=3$. Simultaneously, the contact value of $g_{i+i-}(r)$ decreases and the contact value of $g_{i+s-}(r)$ increases. These behaviors can be explained as follows. The ion-solvent interaction increases with increasing μ_s^*. As the result, the degree of association of ions themselves will decrease, and so the ion triplets will also decrease. Thus, the contact value of $g_{i+i-}(r)$ and the maximum at $r/\sigma_{ss}=2$ of $g_{i+i+}(r)$ will decrease with increasing μ_s^*. Further, because of the increment of ion-solvent interactions, a new type of ion pairs which, we suppose, has a structure shown in Fig. 10b will be formed, and thus the new maximum of $g_{i+i+}(r)$ and $g_{i+s+}(r)$ will arise near $r/\sigma_{ss}=1.5$. In order to ascertain the consideration, we calculated the Coulombic energy of an associated group of two cations and one solvent molecule which contact each other with an arrangement shown in Fig. 10b in vaccum, and determined the most stable structure of the group energitically. The results are shown in Table 2, where x is the distance between two cations, y the distance between the cation and the positive atom of the solvent molecule, u the electrostatic energy of the group. Parameters used in this calculation are the same as those in the case of Fig. 9, that is, $q_i^*=4.5$, $L^*=0.6$ and $\sigma^*_{ii}=1.0$. The distance x and y is roughly consistent with the position of the maximum of $g_{i+i+}(r)$ and $g_{i+s+}(r)$ at $\mu_s^*=3.0$, respectively. This result supports the consideration that the new maximums of $g_{i+i+}(r)$ and $g_{i+s+}(r)$ come from the ion pairs separated by one solvent molecule as shown in Fig. 10b. In a recent report, Levesque *et al.*[8] expected the existence of ion pairs separated by one solvent molecule as shown in Fig. 10c based on their LHNC and QHNC calculations of mixtures of

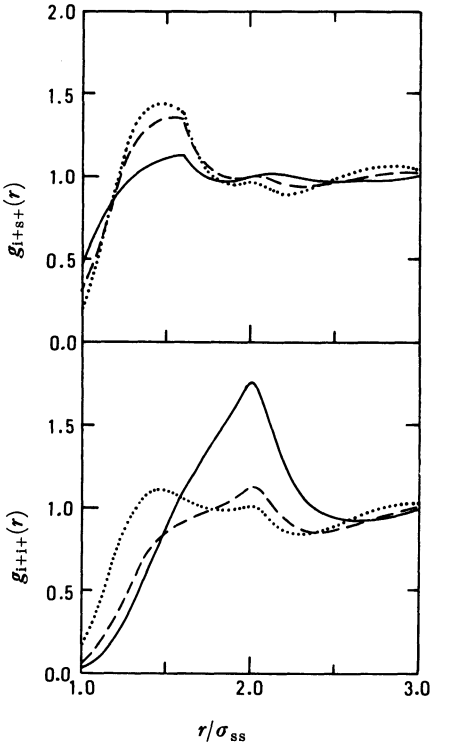

Fig. 9. $g_{i+i+}(r)$ and $g_{i+s+}(r)$ for the ionic solutions at $\rho_i^*=0.03$, $\rho_s^*=0.6$, $q_i^*=4.5$, $L^*=0.6$ and $\sigma^*_{ii}=1.0$. ——: $\mu_s^*=1.0$, ----: $\mu_s^*=2.0$, ·····: $\mu_s^*=3.0$.

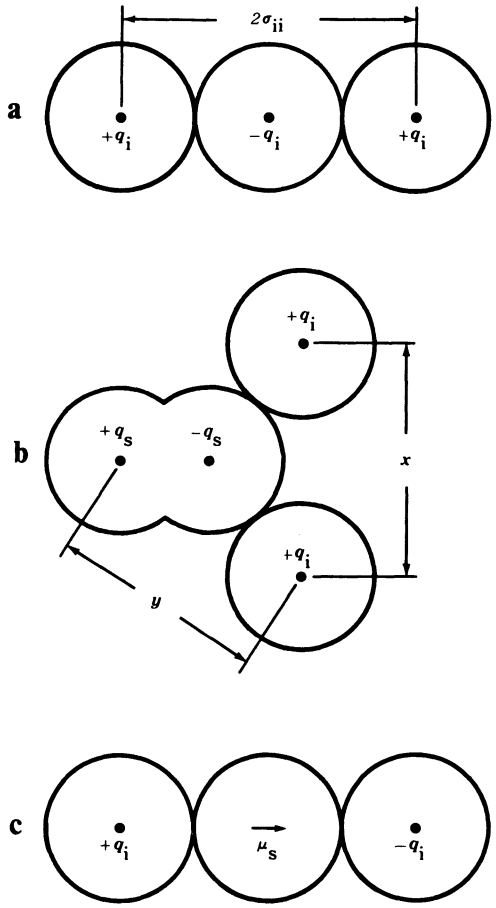

Fig. 10. Illustrations of the ion pairs and the ion triplets. → denotes the point dipole.

Table 1. Contact values of $g_{i+i-}(r)$ and $g_{i+s-}(r)$ at $\rho_s^*=0.6$, $\rho_i^*=0.03$, $q_i^*=4.5$, $L^*=0.6$, and $\sigma^*_{ii}=1.0$

μ_s^*	1	2	3
$g_{i+i-}(r)$	25.26	12.97	9.04
$g_{i+s-}(r)$	3.23	5.39	6.15

Table 2. The most stable structures and energies of the group of two cations and one solvent molecule at $q_i^*=4.5$, $L^*=0.6$, and $\sigma^*_{ii}=1.0$

μ_s^*	x/σ_{ss}	y/σ_{ss}	βu
1	1.85	1.35	5.8
2	1.70	1.41	0.2
3	1.59	1.44	−5.8

charged hard spheres and dipolar hard spheres. The ion pairs expected by Levesque *et al.* have a different structure from ours, which shows that the details of molecular structures must be considered when the short range structures of ionic solutions are investigated.

Concluding Remarks

Site-site radial distribution functions of pure polar fluids calculated with the RHNC-like integral equation of RISM-1 were compared with those of the Monte Carlo calculation. It was found from the comparison that the RHNC-like integral equation gives a fairly good result for the short range structure in polar fluids.

The short range structure in ionic solutions was also investigated by means of the RHNC-like integral equation. It was shown from the calculated site-site radial distribution functions that not only simple ion pairs but also ion triplets (Fig. 10a) and ion pairs separated by one solvent molecule (Fig. 10b) exist in ionic solutions and a solvated structure is formed around ions. The effect of a polarity of solvent molecules on the degree of association of ions and a change of the solvent structure caused by ionic charges have been investigated by the use of the RHNC-like integral equation.

Appendix

It is shown in this appendix that the total correlation functions of ionic solutions are short range functions. Here, we use the same notations as in Ref. 10, hereafter refered to as I.

From Eq. I. 2. 14, we obtain

$$\tilde{\boldsymbol{\chi}} = \tilde{\boldsymbol{\Omega}} + \tilde{\boldsymbol{\Omega}}\tilde{\boldsymbol{\phi}}^{(re)}\tilde{\boldsymbol{\Omega}}, \tag{A. 1}$$

where

$$\chi_{\alpha M \gamma M'}(r) = \rho_M \delta_{MM'}\omega_{\alpha\gamma M}(r) + \rho_M \rho_{M'} h_{\alpha M \gamma M'}(r) \tag{A. 2}$$

Eq. I. 4. 1 is expressed as

$$\tilde{\boldsymbol{\phi}}^{(re)} = -\frac{4\pi\beta}{\varepsilon(k)k^2}\boldsymbol{Z}. \tag{A. 3}$$

Combining Eq. A3 with Eq. A1, we have

$$\tilde{\boldsymbol{\chi}} = \tilde{\boldsymbol{\Omega}} - \frac{4\pi\beta}{\varepsilon(k)k^2}\tilde{\boldsymbol{\Omega}}\boldsymbol{Z}\tilde{\boldsymbol{\Omega}}. \tag{A. 4}$$

By inserting Eqs. I. 3. 11 and I. A. 1 into Eq. A. 4, and by expanding the right hand side of Eq. A4 in power series of k, we find the following equation for ionic solutions at small k

$$\tilde{\boldsymbol{\chi}} = \boldsymbol{\chi}^{(0)} + k^2\boldsymbol{\chi}^{(2)} + \cdots, \tag{A. 5}$$

where

$$\boldsymbol{\chi}^{(0)} = \boldsymbol{\Omega}^{(0)} - \frac{4\pi\beta}{K^2}\boldsymbol{\Omega}^{(0)}\boldsymbol{Z}\boldsymbol{\Omega}^{(0)}, \tag{A. 6}$$

and

$$\boldsymbol{\chi}^{(2)} = \boldsymbol{\Omega}^{(2)} - \frac{4\pi\beta}{K^2}(\boldsymbol{\Omega}^{(0)}\boldsymbol{Z}\boldsymbol{\Omega}^{(2)} + \boldsymbol{\Omega}^{(2)}\boldsymbol{Z}\boldsymbol{\Omega}^{(0)} - \frac{E}{K^2}\boldsymbol{\Omega}^{(0)}\boldsymbol{Z}\boldsymbol{\Omega}^{(0)}). \tag{A. 7}$$

Thus, the existence of $\boldsymbol{\chi}^{(2)}$ is verified, which means that $\boldsymbol{\chi}(r)$ decays faster than r^{-5} at large r. $\omega_{\alpha\gamma M}(r)$ is intrinsically short range. Thus, we find from Eq. A2 that $h_{\alpha M\gamma M'}(r)$ of ionic solutions will decay faster than r^{-5} at large r.

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