

Ionic fluids, structure and thermodynamics of ion–dipole mixtures

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Abstract - Pair distribution functions, internal energy, chemical potentials and dielectric constant, as well as solvation interactions of charged hard sphere - hard dipole mixtures have been investigated in the framework of the MSA. The results are discussed with regard to limitations of the model and to the inherent approximations of the MSA.

1. Introduction

The ionic fluid is a model for electrolyte solutions and molten salts. In the framework of this model thermodynamic and structural properties are described on the McMillan-Mayer (MM) level considering the ions as particles in an isotropic dielectric medium representing the solvent [30], or at the Born-Oppenheimer (BO) level treating also the solvent as a system of molecules [18]. The MM mean force potentials at infinite dilution of the ions can be justified by a molecular theory on the BO level, where the short range interactions describe a reference system with separately estimated properties and the long range electrostatic interactions are treated as perturbations in a generalized cluster expansion in combinations with integral equation methods [20, 25].

The Mean Spherical Approximation (MSA) of ion-dipole systems is a first step of such an expansion. Properties of charged hard sphere - hard dipole mixtures such as pair distribution functions, pressure, internal energy, chemical potentials and dielectric constant, as well as solvation energies and excess properties of the ionic subsystem like activity and osmotic coefficients [1, 11, 12, 14, 15, 34] will be discussed with regard to the limitations of the model and of the inherent approximations of the MSA. Higher order corrections to structural and thermodynamic properties are presented for the contributions of various subsystems of the ion-dipole mixture, calculated by nonlinear integral equations of the Reference Hypernetted Chain (RHNC) or similar approximations, and are compared with computer simulations. The ion-ion mean force potential at infinite dilution is discussed for different solvent models, and the connection between MM and BO descriptions is studied by the consideration of the contributions to the solvation interactions [21] of the ions.

All models presented here are based on classical Hamiltonians $H_{N'}$ of N' particles ($(N' - N)$ solvent particles and N solute particles), consisting of a potential energy term $U_{N'}$ (assuming pair interactions only) and a kinetic energy term $K_{N'}$.

$$H_{N'} = K_{N'} + U_{N'} \quad ; \quad U_{N'} = \sum_{\alpha, \beta} \sum_{i < j} u_{\alpha\beta}(ij) \quad (1)$$

The species in the electrolyte solution are represented by subscripts α, β ; the argument i stands for the full set of spatial coordinates of a molecule or an ion of species α (j for β) involving the coordinates of the particle center, and in the case of anisotropic particle interaction an additional orientation vector of the molecule. The grand partition function of this multicomponent system is

$$\Xi[U_{N'}] = \exp(\beta p V) \quad ; \quad \beta = \frac{1}{k_B T} \quad (2)$$

MM models considering ions and the ion aggregates as the only individual particles use the feature that the grand partition function, eq. (2), can be transformed at osmotic equilibrium into an effective grand partition function involving only the solute species (p_{osm} : osmotic pressure)

$$\Xi[\bar{U}_N] = \exp(\beta p_{osm} V) \quad (3)$$

Assuming additivity of the pair potentials $w_{ab}(ij)$ of mean force of the solute particles at infinite dilution yields an Hamilton function H_N of the N solute particle system of species a, b, \dots as the starting point for a theory of excess properties at MM level (subscripts a, b, \dots are used to indicate the MM level, in contrast to α, β, \dots used on the BO level).

$$H_N = K_N + \bar{U}_N \quad ; \quad \bar{U}_N = \sum_{a, b} \sum_{i < j} w_{ab}(ij) \quad (4)$$

The MM theory is conceptually simpler than the BO theory, but it requires additional information on the solvent averaged pair interactions, $w_{ab}(ij)$, of the solute species at infinite dilution.

Characteristic for the description of ionic fluids on both levels, MM as well as BO level, are the long range interaction forces between the particles leading to structural peculiarities such as screening and charge layering.

2. Integral equation methods on the MM level

The crucial point for the estimation of thermodynamic excess properties is the proper calculation of the ionic pair-distribution function $g_{ab}(12)$ from the input potentials.

$$g_{ab}(12) = \frac{V'^2 \int \exp(-\beta \bar{U}_N) d(3) \dots d(N)}{\int \exp(-\beta \bar{U}_N) d(1) \dots d(N)} \quad (5)$$

where V' is a generalized volume, also containing the integration over angular variables.

The calculation is achieved by use of the Ornstein-Zernike (OZ) equation

$$g_{ab}(12) - 1 = h_{ab}(12) = c_{ab}(12) + \sum_c n_c \int c_{ac}(13) h_{cb}(32) d(3) \quad (6)$$

and a general closure relation

$$g_{ab}(12) = \exp[-\beta w_{ab}(12) + h_{ab}(12) - c_{ab}(12) + B_{ab}(12)] \quad (7)$$

where $h_{ab}(12) = g_{ab}(12) - 1$ and $c_{ab}(12)$ are the total and direct correlation functions, respectively. $B_{ab}(12)$ is the sum of so-called elementary diagrams constructed from integrals over h functions (bonds), which are not given by convolution integrals.

An essential step to avoid Coulomb divergencies in the model calculations is screening with the help of renormalized long range potentials. Screening leads to the low density limit

$$W_{ab}^{DEB}(\mathbf{r}) = w_{ab}^{COUL}(\mathbf{r}) \exp(-\kappa r) \quad ; \quad \kappa^2 = \frac{\beta \sum_a \rho_a e_a^2}{\epsilon \epsilon_0} \quad ; \quad \rho_a = \frac{N_a}{V} \quad (8)$$

$$w_{ab}^{COUL}(\mathbf{r}) = \frac{e_a e_b}{4\pi \epsilon \epsilon_0 r} \quad (9)$$

of the potential of mean force

$$W_{ab}(12) = -k_B T \ln[g_{ab}(12)] \quad (10)$$

of a dilute system of classical point charges. $W_{ab}(12)$ is the potential of mean force at finite electrolyte concentrations, in contrast to $w_{ab}(12)$ obtained at infinite dilution.

The input quantity in the interionic theory $w_{ab}(12)$ contains the Coulomb potential and a short range part $w_{ab}^o(12)$

$$w_{ab}(12) = w_{ab}^o(12) + w_{ab}^{COUL}(12) \quad (11)$$

with a short range potential composed of repulsion terms, terms describing the mutual ionic polarization, and the overlap of the ionic solvation shells

$$w_{ab}^o(12) = w_{ab}^{COR}(12) + w_{ab}^{SOLV}(12) \quad (12)$$

The calculation of the pair correlation functions of ions $g_{ab}(12)$ in terms of the $w_{ab}(r)$ is executed with the help of generalized cluster expansions which is a combination of cluster and integral equation techniques. Starting with Debye screening for the Coulomb interaction which corresponds to $\mathbf{c} = -\beta \mathbf{w}^{COUL}$ and $\mathbf{h} = -\beta \mathbf{W}^{DEB}$ (here and in the following text boldface letters are used for matrix representations) one defines the remainder terms

$$\mathbf{c} = -\beta \mathbf{w}^{COUL} + \delta \mathbf{c} \quad ; \quad \mathbf{h} = -\beta \mathbf{W}^{DEB} + \delta \mathbf{h} \quad (13)$$

and the OZ equations for the remainder terms

$$\delta \mathbf{h} - \delta \mathbf{c} = \delta \mathbf{c} * \mathbf{h} - \beta \mathbf{W}^{DEB} * \delta \mathbf{c} - \beta \mathbf{W}^{DEB} * \delta \mathbf{c} * \mathbf{h} \quad (14)$$

A general closure relation follows from the cluster analysis

$$\mathbf{g} = \exp(-\beta \mathbf{w}^o - \beta \mathbf{W}^{DEB} + \delta \mathbf{h} - \delta \mathbf{c} + \mathbf{B}) \quad (15)$$

Setting $\mathbf{B}=0$ leads to screened integral equations (Allnatt-HNC closure)[3]. Numerous algorithms were developed for the solution of such equations. Characteristic features are the use of general matrix integral equation systems, numerical Fourier transformation of the OZ equation, either direct iteration methods or Newton-Raphson methods for the acceleration of iteration [28]. A new feature is the acceleration of iteration by vector extrapolation [22]. These methods are generally used, also in the case of short range interactions. Coulomb interactions require renormalization as given by Allnatt [3] and Ng [31]. Combinations of these methods are in use [23] as well as direct or accelerated iterations with different renormalizations [22].

Thermodynamic excess functions at the MM level are computed along well known formulae such as the osmotic coefficient Φ^{MM}

$$\Phi^{MM}(c) = \frac{p_{osm}}{\rho k_B T} = 1 + \frac{2\pi\rho}{3} \sum_{a,b} x_a x_b \int_0^\infty \frac{\partial[-\beta w_{ab}(r)]}{\partial r} r^3 g_{ab}(r) dr \quad ; \quad x_a = \frac{\rho_a}{\rho} \quad (16)$$

The potentials $w_{ab}^{SO LV}$ can be chosen such as to fit the experimental data in the dilute solution regime. The reproduction of the experimental data is satisfactory on the MM level [8, 10, 17], but the role of the solvation interactions can only be really understood on the BO level.

3. Generalized virial expansions on the BO level

The starting point for a virial expansion is an appropriate model of the intermolecular pair potential $u_{\alpha\beta}(12)$ which may be conceived as a sum of a short range part $u_{\alpha\beta}^{SR}(12)$ and a long range contribution $u_{\alpha\beta}^{LR}(12)$ possibly containing terms from the mutual orientation of the particles. In the present introductory treatment the long range electrostatic interactions are modelled by point charges for ions and by point dipoles for polar molecules. The short range interactions make up the reference system describing the mutual impenetrability of the particles as well as the short range attractive van der Waals forces. The long and short range interactions demand different approaches.

$$u_{\alpha\beta}(12) = u_{\alpha\beta}^{SR}(12) + u_{\alpha\beta}^{LR}(12) \quad (17)$$

The pair interaction potential of a system with only short range interactions $u_{\alpha\beta}^{SR}(12)$, the so-called reference system, may be used to calculate the correlation functions by integral equation approximations derived from the OZ equations of the reference system where $u_{\alpha\beta}^{LR}(12) = 0$.

$$\mathbf{h}^\circ = \mathbf{c}^\circ + \mathbf{c}^\circ * \mathbf{h}^\circ \quad (18)$$

The inclusion of the long range potential $u_{\alpha\beta}^{LR}(12)$ introduces screening, here under the influence of the structure factor of the underlying reference system.

Extraction of the reference system and definition of the remainder

$$\mathbf{c} = \mathbf{C} + \delta\mathbf{c} \quad ; \quad \mathbf{C} = \mathbf{c}^\circ - \beta\mathbf{u}^{LR} \quad (19)$$

$$\mathbf{h} = \mathbf{H} + \delta\mathbf{h} \quad ; \quad \mathbf{H} = \mathbf{h}^\circ + \mathbf{G} \quad (20)$$

first leads to the screening relation

$$\mathbf{H} = \mathbf{C} + \mathbf{C} * \mathbf{H} \quad (21)$$

and then to OZ equation for the remainder:

$$\delta\mathbf{h} - \delta\mathbf{c} = \mathbf{H} * \delta\mathbf{c} + \delta\mathbf{c} * \mathbf{h} + \mathbf{H} * \delta\mathbf{c} * \mathbf{h} \quad (22)$$

We will revert in the following text to this new screening equation with its consideration of short range structure factors as well as to the problem of angular dependent interactions in the case of ion-dipole and dipole-dipole interactions. The general closure relation is as stated in refs. [4, 33]

$$\mathbf{g} = \mathbf{g}^\circ \exp(\mathbf{G} + \delta\mathbf{h} - \delta\mathbf{c} + \delta\mathbf{B}) \quad ; \quad \delta\mathbf{B} = \mathbf{B} - \mathbf{B}^\circ \quad (23)$$

Neglecting the $\delta\mathbf{B}$ term leads to the reference hypernetted chain (RHNC) equation.

4. Ion-dipole mixtures in the MSA

Numerous attempts were carried out to solve the problem of the hard ion - hard dipole mixture [1, 16, 32, 13, 24, 27] containing the interactions sketched in figure 1.

The potentials can be described by the general formulae

$$u_{\alpha\beta}(12) = u_{\alpha\beta}^{000}(r) + u_{\alpha\beta}^{011}(r)\Phi^{011}(12) + u_{\alpha\beta}^{101}(r)\Phi^{101}(12) + u_{\alpha\beta}^{110}(r)\Phi^{110}(12) + u_{\alpha\beta}^{112}(r)\Phi^{112}(12) \quad (24)$$

with the r -dependent coefficients

$$u_{\alpha\beta}^{000}(r) = u_{\alpha\beta}^{HS}(r) + \frac{e_\alpha e_\beta}{4\pi\epsilon_0 r} \quad ; \quad u_{i^*s}^{011}(r) = -\frac{e_i \mu_s}{4\pi\epsilon_0 r^2} \quad ; \quad u_{s^*s}^{112}(r) = -\frac{\mu_s^2}{4\pi\epsilon_0 r^3} \quad (25)$$

and the rotational invariants

$$\Phi^{000}(12) = 1 \quad ; \quad \Phi^{112}(12) = [3(\bar{\mu}_1^0 \bar{r}^0)(\bar{\mu}_2^0 \bar{r}^0) - (\bar{\mu}_1^0 \bar{\mu}_2^0)] \quad (26)$$

$$\Phi^{011}(12) = (\bar{\mu}_1^0 \bar{r}^0) \quad ; \quad \Phi^{101}(12) = (\bar{\mu}_2^0 \bar{r}^0) \quad ; \quad \Phi^{110}(12) = (\bar{\mu}_1^0 \bar{\mu}_2^0)$$

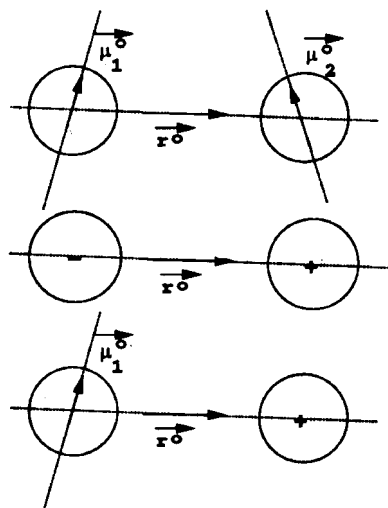


Fig. 1 Dipole - dipole, ion - ion, and ion - dipole interactions

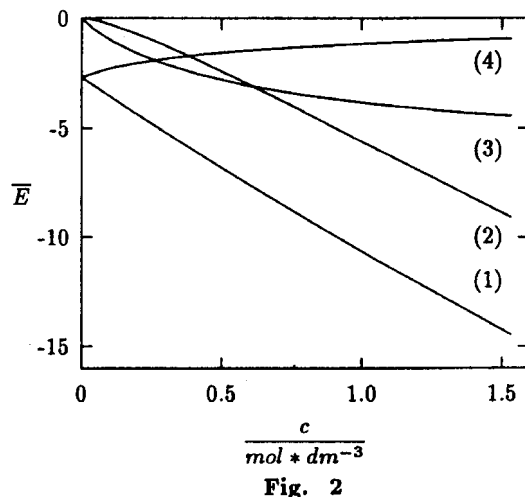


Fig. 2

Fig. 2 The reduced internal energy \bar{E} of a mixture of hard ions and dipoles simulating the solution of a 1-1 electrolyte in methanol at 25°C. Solvent parameters: Effective diameter $\sigma_s = 4.07 \cdot 10^{-10}m$, number density $\rho_s = 1.48 \cdot 10^{28}m^{-3}$, effective dipole moment $\mu^{eff} = 8.3122 \cdot 10^{-30}Cm$, ($\epsilon_{th} = 32.64$). Ion parameters: $|z_+| = |z_-| = 1$, $\sigma_i = 4.07 \cdot 10^{-10}m$. (1): \bar{E} ; (2): \bar{E}_{ii} ; (3): \bar{E}_{is} ; (4): \bar{E}_{ss} .

The angle dependent potential leads to angle dependent correlation functions. A useful representation is the invariant expansion of the correlation functions [11], which is of the same form as the expansion for the potential, eq. (24). The interaction parameters d_0 and d_2 characterize the ion and dipolar subsystems, respectively.

$$d_0^2 = \kappa^2 \epsilon \sigma_i^2 ; \quad d_2^2 = \frac{\rho_s \mu_s^2}{3 \epsilon_0 k_B T} = 3y \quad (27)$$

The discussion of the MSA approximation in the framework of the generalized virial expansions on the BO level, eqs. (22), uses at the lowest step the correlation functions of the Random Phase Approximation (RPA).

$$\delta c = \delta h = 0 ; \quad h = h^0 + G = H \quad (28)$$

The OZ equations for the whole system change into the screening equations (21). The screened potential $G_{\alpha\beta}$ (12) is called the 'chain sum'. If the reference system is a mixture of hard spheres with contact distances $\sigma_{\alpha\beta}$ an optimizing procedure is possible, demanding that $G_{\alpha\beta}(12) = 0$ for $r < \sigma_{\alpha\beta}$. When the direct correlation functions of the reference system c^0 are calculated in the Percus - Yevick approximation for a mixture of hard spheres, the optimized RPA is called the mean spherical approximation (MSA) and can be analytically solved.

$$H = -1 ; \quad r \leq \sigma_{\alpha\beta} ; \quad C = -\beta u^{LR} ; \quad r > \sigma_{\alpha\beta} ; \quad \sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta) \quad (29)$$

The solution is obtained by invariant expansion of the correlation functions and transformation of the OZ equations into a solvable set of matrix equations [11, 12]. Useful forms for the calculations are given in [14, 15]. From these results extensive calculations were carried out on solvation thermodynamics [34]. Some examples will be give here of calculation of thermodynamic properties for the case of equal ionic sizes. Figure 2 shows the reduced internal energy \bar{E} of a mixture of hard ions and dipoles simulating the solution of a 1-1 electrolyte in methanol at 25°C as a sum of ion - ion (\bar{E}_{ii}), ion - dipole (\bar{E}_{is}), and dipole - dipole (\bar{E}_{ss}) - contributions.

$$\bar{E} = \frac{\Delta E'}{N' k_B T} = \bar{E}_{ii} + \bar{E}_{is} + \bar{E}_{ss} \quad (30)$$

In figure 2 the solvent parameter ρ_s was calculated from the molar volume V_m according to $\rho_s = N_A/V_m$ and σ_s as $\sigma_s = (\rho_s)^{-1/3}$, corresponding to a space filling factor $\eta = \pi/6$. An effective dipole moment μ^{eff} was used to produce the experimental dielectric constant ϵ of the solvent according to Wertheim's MSA result [35]. The mean ion diameter was arbitrarily chosen.

Figure 3 shows the concentration dependent dielectric constant $\epsilon_{th}(c)$ [1] of a mixture of hard ions and dipoles simulating NaI and Bu_4NBr solutions in methanol at 25°C. The solvent molecule parameters are those of figure 2, the mean ionic contact distances were arbitrarily chosen. The experimental permittivity data for the comparison are taken from microwave dielectric relaxation experiments [9].

The mean ionic activity coefficient $\gamma_{\pm}(c)$ of a mixture of hard ions and dipoles simulating NaI and Bu_4NBr solutions in acetonitrile at 25°C is given in figure 4. The solvent parameter and the effective dipole moment were calculated as before. The mean ionic contact distances were chosen in such a manner that a qualitative fit of the experimental activity coefficients known from vapor pressure measurements [6, 7] was established.

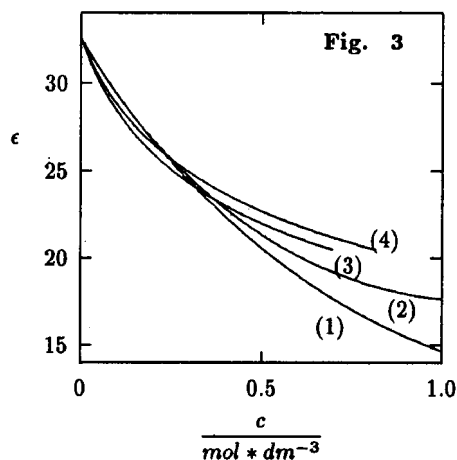


Fig. 3 Concentration dependent dielectric constant ϵ of a mixture of hard ions and dipoles simulating NaI and Bu_4NBr solutions in methanol at $25^\circ C$. Solvent parameters as in figure 2. Ion parameters: Bu_4NBr , $\sigma_i = 6.8 * 10^{-10} m$. (4): ϵ_{th} (MSA), (2): (Experimental data [9]). NaI , $\sigma_i = 6.0 * 10^{-10} m$, (3): ϵ_{th} (MSA); (1): (Experimental data [9]).

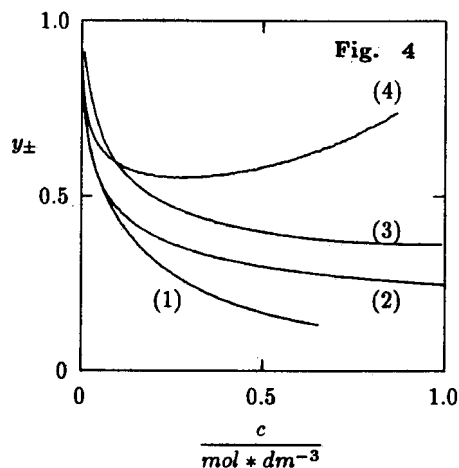


Fig. 4 The mean ionic activity coefficient $y_{\pm}(c)$ of a mixture of hard ions and dipoles simulating NaI and Bu_4NBr solutions in acetonitrile at $25^\circ C$. Solvent parameters: effective diameter $\sigma_s = 4.44 * 10^{-10} m$, number density $\rho_s = 1.14 * 10^{28} m^{-3}$ at $298.15 K$, effective dipole moment $\mu^{eff} = 9.79 * 10^{-30} Cm$, ($\epsilon_{th} = 35.93$). Ion parameters: Bu_4NBr , $\sigma_i = 7.5 * 10^{-10} m$, (4): $y_{\pm}(c)$ (MSA); (3): (Experimental data [7]). NaI , $\sigma_i = 6.0 * 10^{-10} m$, (1): $y_{\pm}(c)$ (MSA); (2): (Experimental data [6]).

The three foregoing examples were chosen to show that already very rough approximations such as fits of the solvent properties by effective dipole moments and radii, and description of the repulsive interactions of the ions by an appropriate mean contact distance σ_i , yield already correlations with the correct tendency of the concentration dependence of the thermodynamic functions.

5. Ion solvation in the BO and MM approaches

The mean force potential at infinite dilution $w_{ab}(r)$ of the ions a and b follows from the infinite dilution limit of the ion-ion radial distribution function

$$\lim_{\rho_i \rightarrow 0} g_{ab}^{BO}(r) = g_{ab}^{BO,\infty}(r) = \exp[-\beta w_{ab}(r)] \quad (31)$$

with the help of direct ionic interaction potentials on the BO level

$$u_{ab}(r) = u_{ab}^{SR}(r) + \frac{e_a e_b}{4\pi\epsilon_0 r} \quad (32)$$

The resulting effective interaction potentials $w_{ab}(r)$ depends in the long range part on a calculated permittivity ϵ_{calc} and on a short range solvation potential

$$w_{ab}(r) = u_{ab}^{SR}(r) + w_{ab}^{SOLV}(r) + \frac{e_a e_b}{4\pi\epsilon_0 r \epsilon_{th}} \quad (33)$$

The solvation potential $w_{ab}^{SOLV}(r)$, in turn, is subdivided into two parts. One part, $w_{ab}^{SOLV,RS}(r)$, is due to the contributions of the reference system, and the other part, $w_{ab}^{SOLV,EL}(r)$, stems from the electrostatic interactions between the ions and the solvent molecules

$$w_{ab}^{SOLV}(r) = w_{ab}^{SOLV,RS}(r) + w_{ab}^{SOLV,EL}(r) \quad (34)$$

$w_{ab}^{SOLV,RS}(r)$ is that part of the solvation potential due to the interaction of the ions a and b in a solvent made up by dielectric nonpolar and nonpolarizable molecules. This quantity is calculable with the help of ion distribution functions $g_{ab}^{BO}(r)$ at ion number density $\rho_i = \rho_+ + \rho_-$ with a potential

$$u_{ab}(r) = u_{ab}^{SR}(r) + \frac{e_a e_b}{4\pi\epsilon_0 \epsilon r} \quad (35)$$

in a dilute solution of number density ρ_s . The reference system interactions (solvent-solvent and ion-solvent potentials

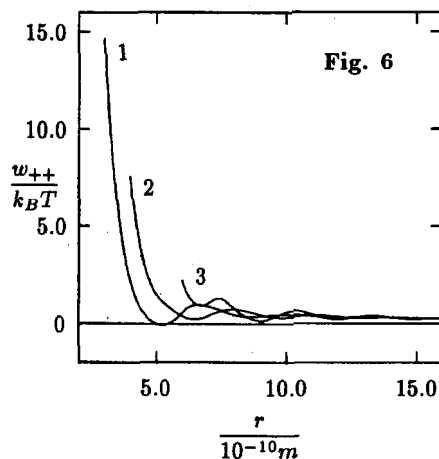
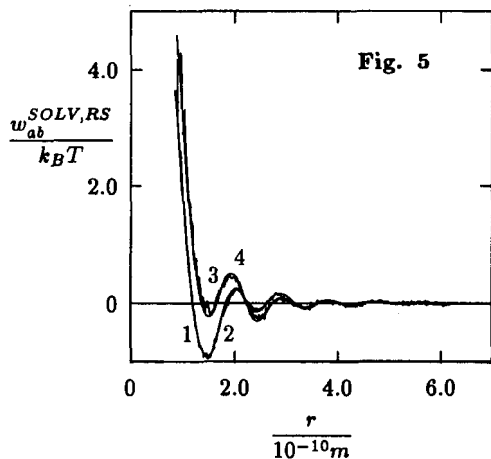


Fig. 5 Reference system contribution to the solvation interaction, $w_{ab}^{SOLV,RS}(r)$, from ion-ion distribution functions of charged soft spheres in a continuous solvent (MM level) and in a soft sphere molecular solvent (BO level). Ion parameters: $\rho_i^* = (\rho_+ + \rho_-)\sigma_i^3 = 0.1$, $b = \beta|z_+z_-|e^2/(4\pi\epsilon_0\epsilon\sigma_i) = 6$. Solvent parameters: $\rho_s^* = \rho_s\sigma_s^3 = 0.85$, $\epsilon^* = \beta\epsilon^{LJ} = 0.5$. $w_{+-}^{SOLV,RS}(r)$: (1):(RHNC); (2):(MC). $w_{++}^{SOLV,RS}(r)$: (3):(RHNC); (4):(MC).

Fig. 6 Influence of the ratio of the ions and solvent dipole radii, σ_i/σ_s , on the potential of mean force between two ions at infinite dilution at 25°C. Parameters of the solvent: $\sigma_s = 3 \times 10^{-10}m$, reduced density $\rho_s^* = 0.8$ and reduced dipole moment $\mu^* = \mu_s/\sqrt{4\pi\epsilon_0k_B T\sigma_s^3} = 1.5$. The dielectric constant in LIN approximation [24] is $\epsilon_{th} = 32.75$. Parameters of the ions: $z_+ = -z_- = 1$. (1): $\sigma_i/\sigma_s = 1$; (2): $\sigma_i/\sigma_s = 4/3$; (3): $\sigma_i/\sigma_s = 2$;

and the short range parts of the ion-ion interactions) are of the Lennard Jones type or, alternatively, of the soft sphere type

$$u_{\alpha\beta}^{SR}(r) = u_{\alpha\beta}^{LJ}(r) = 4\epsilon_{\alpha\beta}^{LJ} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right] ; \quad u_{\alpha\beta}^{SR}(r) = 4\epsilon_{\alpha\beta}^{LJ} \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} \quad (36)$$

In that case Debye screening may be assumed according to eq. (8), and $g_{ab}^{BO}(r)$ takes the form

$$g_{ab}^{BO}(r) = \exp \left[-\beta[u_{ab}^{SR}(r) + w_{ab}^{SOLV,RS}(r) + W_{ab}^{DEB}(r)] \right] \quad (37)$$

On the other hand the ion-ion distribution function $g_{ab}^{MM}(r)$ of a dilute ionic gas with interactions according to eq. (35), may be estimated at equal number density ρ_i to be

$$g_{ab}^{MM}(r) = \exp(-\beta[u_{ab}^{SR}(r) + W_{ab}^{DEB}(r)]) \quad (38)$$

From eqs. (37) and (38) follows the interpretation of $w_{ab}^{SOLV,RS}(r)$ with the help of the BO and MM distribution functions

$$w_{ab}^{SOLV,RS}(r) = -k_B T \ln \left(\frac{g_{ab}^{BO}(r)}{g_{ab}^{MM}(r)} \right) \quad (39)$$

Figure 5 shows the potential $w_{ab}^{SOLV,RS}(r)$ from ion-ion distribution functions of charged soft spheres in a continuous solvent (MM level) and in a soft sphere molecular solvent (BO level). The reliability of the integral equation approximations may be supported with the help of a MC method. The main characteristics of the MC method used are the Metropolis algorithm, periodic boundaries [2], and of a reaction-field corrected cutoff-sphere method [5]. Up to 1.7×10^7 configurations were considered for 2000 particles.

The electrostatic contribution to solvation interactions is obtained from the ion-ion correlation function in the limit of infinite dilution in an ion-dipolar mixture. Various examples can be found in the literature for hard ion-hard dipole mixtures at different levels of approximation [13, 24, 27], and also for related models such as Stockmayer solvents [26]. The contribution of the electrostatic interactions has the general form

$$w_{ab}^{SOLV,EL}(r) = \frac{e_a e_b}{4\pi\epsilon_0\epsilon_{th}} (\epsilon_{th} - 1) F_{ab}(r) \quad (40)$$

with a rapidly decaying oscillating function $F_{ab}(r)$ [16, 24]. Figure 6 shows the role of the relative particle sizes of spherical ions and solvent molecules in a hard particle mixture.

If ions and solvent molecules are of equal size the influence of the electrostatic contribution is dominant. In the case where the ratio of ion to dipole size enlarges, the reference system contribution is of the same magnitude as the electrostatic contribution.

6. Conclusions

Despite the simplicity of the model consisting of polarizable spherical ions dissolved in a system of spherical dipole molecules, it represents the natural complexity of an electrolyte solution with particle interactions between individual ions and solvent molecules of variable sizes. An appropriate treatment of the interaction forces in the interparticle and reference forces gives insight in the nature of solvation and links the BO and MM level models. The very simple BO level model was chosen to illustrate without unnecessary complication the efficient possibilities of the new integral equation method. The hard sphere ion-dipole model already reproduces the thermodynamic and structural properties of electrolyte solutions surprisingly well with the help of meaningful molecular parameters. The underlying mathematical tool for the development of an appropriate MSA method is laborious but the resulting expressions are rather simple and useful for the description of thermodynamic properties such as activity coefficients and also permittivities. Refinement of the solute - solvent model by the use of nonisotropic molecular particles yields better approximations but requires much higher mathematical expenditure.

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