

Some recent developments in the statistical mechanical theory of ionic solvation

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Abstract— Solvation forces in electrolyte solutions may advantageously be treated with statistical mechanical methods from a unique point of view on the Born–Oppenheimer (BO) level. Integral equation techniques of the RHNC type are used and the potentials of mean force and the correlation functions yielding the excess functions are estimated for typical model solvents such as nonpolar and polar hard spheres or Lennard–Jones particles etc. The solvation contributions (Gurney potentials) to the effective interactions are presented and their effects in real solutions are discussed.

INTRODUCTION

Information on ion solvation commonly is accessible from the excess functions of thermodynamic or transport properties such as osmotic and activity coefficients, heats of dilution or electrolyte conductivity obtained as the functionals of solvent averaged mean force potentials. This treatment at the McMillan–Mayer (MM) level represents ions as moving particles interacting by average forces in a structureless solvent characterized by its viscosity and relative permittivity. At MM-level solvation effects can only be indirectly reflected by the parameters of the ionic mean force potentials which commonly are subdivided into the contributions from the long-range Coulomb interactions and the short-range repulsive and attractive interactions. The form and relative magnitude of these contributions strongly affect the ion distributions and the structural and thermodynamic excess quantities. Ion association (ref. 1), ‘coulombic unmixing’ (ref. 2) and ‘hydrophobic unmixing’ (ref. 3) are interpreted in the framework of such interionic theories in terms of effective interactions at infinite dilution.

It is advantageous for the understanding of the short-range effects usually described by ‘overlapping of Gurney spheres’ to investigate the leading potential terms at the BO-level where both the solvent molecules and the ions are structured interacting particles of the electrolyte solution; for the volume and surface properties see (refs. 4–8).

The model calculations as well as the experiments (ref. 9) at BO-level reflect a variety of features affecting the molecular pair distribution functions. The results from BO calculations and those of the solvent averaging description at the McMillan–Mayer level may be compared with the help of integral equation techniques based on the Ornstein–Zernike equation and a Reference Hypernetted Chain (RHNC) closure relation. The underlying theory and the numerical procedures are given in (refs. 7, 10–12). In the present study the defining equations for the mean force potentials at BO- and MM-level are discussed. It is shown how the Gurney term of the ion–ion interactions reproduces the properties of the solvent structure at the MM-level and how the solvent structure influences the Coulomb interaction via the solvent permittivity ϵ . In a first step the contribution of solvent averaged short-range non electrostatic interactions (we call them reference system (RS) interactions) to the solvation forces is studied with the help of hard and soft spheres and Lennard–Jones particles. In a second step we introduce electrostatic interactions between the ions and the solvent molecules considered as polar hard spheres and Stockmayer particles.

EFFECTIVE IONIC INTERACTION IN A MOLECULAR SOLVENT

The effective interaction between two ions a and b at position 1 and 2 in a solution is given by the mean force potential (pmf) $w_{ab}(12)$ related to the ion–ion radial distribution function $g_{ab}(12) = 1 + h_{ab}(12)$ in the mixture by the relationship

$$w_{ab}(12) = -k_B T \ln(1 + h_{ab}(12)); \quad a, b = +, - \quad (1)$$

where $h_{ab}(12)$ is the so-called total correlation function. The pmf w_{ab} can be split into three parts

$$w_{ab}(12) = v_{ab}^{\text{RS}}(12) + w_{ab}^{\text{SOLV}}(12) + w_{ab}^{\text{LR}}(12) \quad (2)$$

In eq. (2) $v_{ab}^{\text{RS}}(12)$ is the contribution of direct short-range interactions between ions a and b containing isotropic or anisotropic repulsive and attractive contributions, e.g. interaction potentials of the hard sphere, Lennard–Jones, dumbbell, tetrahedron etc. types. In dilute ionic systems the long-range contribution to the pmf, w_{ab}^{LR} , is a Debye-type interaction, i.e. a Coulomb interaction between the ions, screened by the permittivity $\epsilon(n_s, n_i)$ of the solution and by a Debye shielding exponent κ_D

$$w_{ab}^{\text{LR}}(r) = \frac{z_a z_b e^2}{4\pi\epsilon_0\epsilon(n_s, n_i)r} \exp(-\kappa_D r); \quad \kappa_D^2 = \frac{e^2 \sum_a n_a z_a^2}{\epsilon_0\epsilon(n_s, n_i)k_B T} \quad (3a, b)$$

In eqs. 3a and b k_B is the Boltzmann constant and T is the Kelvin temperature; z_a , z_b are the valences of the ions a and b, e is the elementary charge; n_s and n_i are the number densities of the solvent molecules and the ions, respectively; ϵ_0 and $\epsilon(n_s, n_i)$ are the permittivity of vacuum and the relative permittivity of the solution at the particle densities n_s and n_i ; r is the interionic distance. In the case of infinitely dilute solutions ($n_i \rightarrow 0$, $\kappa_D \rightarrow 0$) w_{ab}^{LR} is the Coulomb interaction $w_{ab}^{COUL}(r)$ with $\epsilon(n_s)$ as the relative permittivity of the pure solvent

$$w_{ab}^{COUL}(r) = \frac{z_a z_b e^2}{4\pi\epsilon_0\epsilon(n_s)r} \quad (4)$$

The relative permittivity $\epsilon(n_s, n_i)$ must be calculated with the help of the statistical mechanical theory of the model solvent or solution, including the electrostatic interactions between solvent molecules and between ions and solvent molecules, or else be treated as an experimental input parameter.

The solvation interaction contribution w_{ab}^{SOLV} in eq. (2) can be subdivided into two parts, one resulting from the short-range interactions of all constituents of the system, the reference interaction $w_{ab}^{SOLV,RS}(12)$, the other one stemming from the long-range electrostatic interactions between all species, $w_{ab}^{SOLV,EL}(12)$

$$w_{ab}^{SOLV}(12) = w_{ab}^{SOLV,RS}(12) + w_{ab}^{SOLV,EL}(12) \quad (5)$$

On the other hand the main contribution at the MM-level to the radial distribution function $g_{ab}^{MM}(12)$ of a dilute system of ions in a structureless solvent is given by

$$g_{ab}^{MM}(12) = \exp\left(-\beta(u_{ab}^{RS}(12) + w_{ab}^{LR}(12))\right); \quad \beta = 1/k_B T \quad (6)$$

with $\epsilon(n_s, n_i)$ as a given input parameter. The comparison of eqs. (1) and (6) shows that in the case of infinite dilution

$$\lim_{n_i \rightarrow 0} g_{ab}(12) = \lim_{n_i \rightarrow 0} \left(g_{ab}^{MM}(12) \exp(-\beta w_{ab}^{SOLV}(12))\right) = g_{ab}^0(12) \quad (7)$$

$$g_{ab}^0(12) = \exp\left(-\beta(u_{ab}^{RS}(12) + w_{ab}^{SOLV,0}(12) + w_{ab}^{COUL}(12))\right) \quad (8)$$

showing that the solvation interactions calculated at BO-level in the case of infinitely dilute solutions are equivalent to the ad hoc introduced Gurney cosphere interactions at MM-level. These cosphere interactions are often estimated by fit procedures from a comparison with thermodynamic and transport excess functions of electrolyte solutions (ref. 11).

SOLVENT MODELS WITHOUT ELECTROSTATIC INTERACTIONS

Our first model calculations concern the influence of the contribution $w_{ab}^{SOLV,RS}$ to the solvation of a diluted gas of charged particles in a molecular model solvent.

This can be studied by the comparison of the ion-ion radial distribution functions in a homogeneous structureless solvent of permittivity ϵ (MM-level) with the distribution of an equal number of ions in the mixture with solvent molecules (BO-level). The solvent molecules exert no electrostatic interactions on the ions. However, for the sake of formal consistency with the MM-calculations we introduce the factor $1/\epsilon(n_s)$ of the Coulomb ion-ion interactions also for the BO-calculations.

The calculations of ion-ion radial distribution functions at BO- and MM-level are established with the help of a reference-HNC-technique based on a method of generalized virial expansions (ref. 12).

The simple assumption of equal reference interactions for ions and solvent molecules yields $w_{ab}^{SOLV,RS}$ as the difference of the mean force potential of the system composed only of reference interactions and direct short-range interactions $u_{ab}^{RS}(12)$

$$w_{ab}^{SOLV,RS}(12) = -k_B T \ln(1 + h_{ab}^{RS}(12)) - u_{ab}^{RS}(12) \quad (9)$$

Fig. 1a shows the contribution $w_{ab}^{SOLV,RS}$ for reference systems where $u_{ab}^{RS}(12)$ is a Lennard-Jones potential $u^{LJ}(r)$ for all particles

$$u^{LJ}(r) = 4\epsilon_{LJ} \left((\sigma/r)^{12} - (\sigma/r)^6 \right) \quad (10)$$

at reduced distance r/σ , reduced interaction strength of $\epsilon_{LJ}^* = \epsilon_{LJ}/k_B T = 0.5$, and three reduced particle densities $n^* = N\sigma^3/V = 0.5, 0.7, 1.0$; N is the number of molecules, and V is the volume of the system; σ is the distance parameter of the Lennard-Jones potential, where it has zero value. The position of the potential minimum $u_{min}^{LJ}(r_{min}) = -\epsilon$ is given by $r_{min} = 2^{1/6}\sigma$.

Fig. 1a shows that the potential contribution $w_{ab}^{SOLV,RS}(12)$ is negative for small r and of damped oscillating form, and yields an additional attraction between the ions if their center-to-center distance r is less than 1.2σ . This effect

is independent of the attractive part of the Lennard-Jones interaction. It stems from a probability force due to the 'granularity' of the solvent yielding the repulsive short-range interactions between all particles in the solution; equal contributions to the ion-ion interactions also are produced in the hard and soft sphere model solvents. This is shown in Fig. 1b, where the solvation potentials $w_{ab}^{\text{SOLV,RS}}$ (12) of Lennard-Jones type are compared with those derived from a soft sphere reference system described by a n -12-potential of the form

$$u^{n-12}(r) = 4\epsilon_{n-12}(\sigma/r)^{12} \quad (11)$$

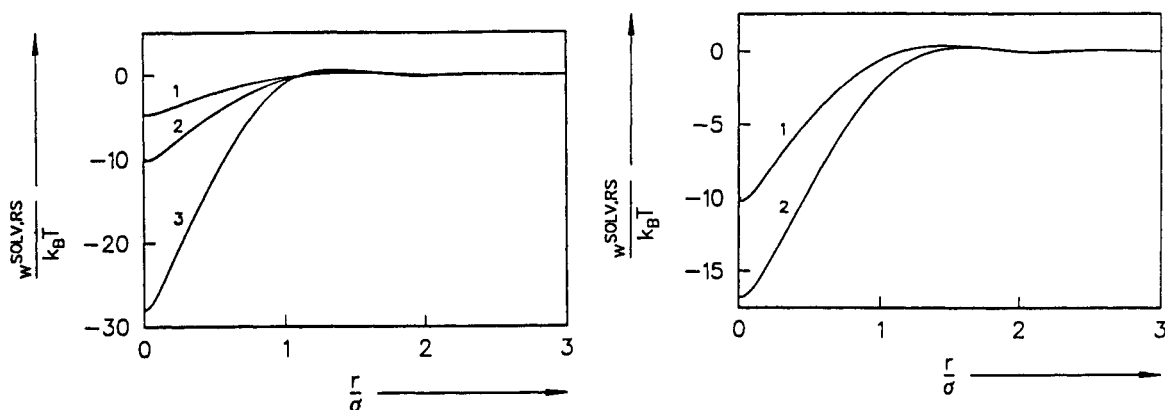


Fig. 1. Solvation contribution $w_{ab}^{\text{SOLV,RS}}/k_B T$ to the mean force potential. a: Lennard-Jones systems ((1), (2), (3) $n^* = 0.5, 0.7, 1.0$); b: a comparison of (1) Lennard-Jones and (2) soft sphere systems (see the text).

In eq. (11) ϵ_{n-12} is the potential strength and σ is a distance parameter. With $n^* = N\sigma^3/V$ and $\epsilon_{n-12}^* = \epsilon_{n-12}/k_B T$, $w_{ab}^{\text{SOLV,RS}}$ (12) is given in Fig. 1b for a reduced density $n^* = 0.7$ and for $\epsilon_{n-12}^* = \epsilon_{LJ}^* = 0.5$.

In the next figures it is shown, how these contributions $w_{ab}^{\text{SOLV,RS}}$ (12) change the ion-ion distributions of a dilute ion gas imbedded in a nonpolar molecular model solvent. Figs. 2a and 2b show the ion-ion radial distribution functions (rdf) of charged hard spheres in a continuous solvent (MM-level) for an aqueous 2-2 model electrolyte solution of moderate concentration. The coupling strength for the Coulomb interactions is given by the Bjerrum parameter $b = l_B/R = 6.8166$ ($l_B = (ze)^2/(4\pi\epsilon_0 k_B T)$ is the Bjerrum length). The system has a reduced ion density $n_i^* = (N_+ + N_-)R^3/V = 0.06$; N_+ and N_- are the numbers of positive and negative ions, R is the hard sphere diameter, and V is the volume of the solution.

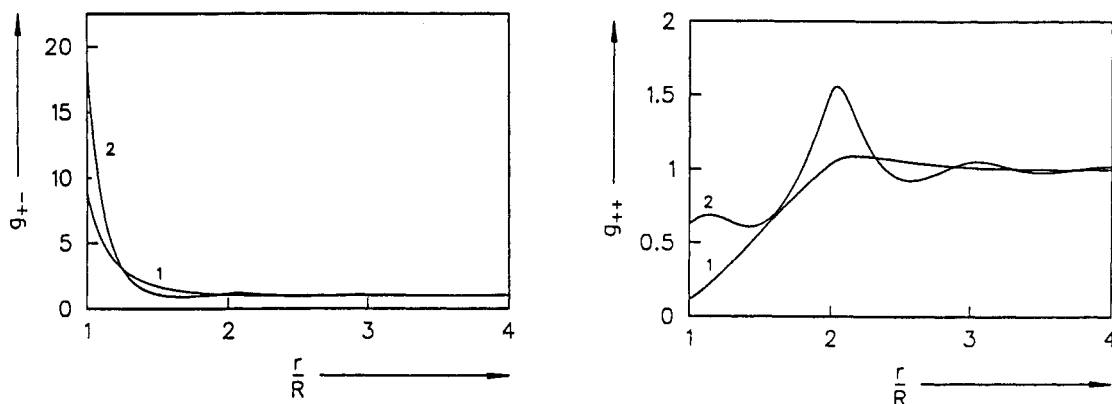


Fig. 2. Radial ion-ion distribution functions a: (+-) and b: (++) of charged hard spheres in a continuous solvent ((1) MM-level) and in a hard sphere solvent ((2) BO-level).

These curves may be compared with the results of a calculation where the ions are imbedded in a hard sphere solvent of equal permittivity $\epsilon(n_s)$ in such a way, that the total reduced number density is $n^* = n_s^* + n_i^* = 0.7534$ (rdf on BO-level). The reduced number density of the solvent is $n_s^* = N_s R^3/V$, and N_s is the number of solvent molecules.

Adding the contribution $w_{ab}^{\text{SOLV,RS}}$ to the mean force potential between the ions already leads to a pronounced increase of contact probabilities of pairs (+-) and contact of pairs (++), and oscillations around the long-range continuum contribution w_{ab}^{LR} with a remarkable peak at $r/R \approx 2$ in the rdf (++) due to the second minimum in $w_{ab}^{\text{SOLV,RS}}$.

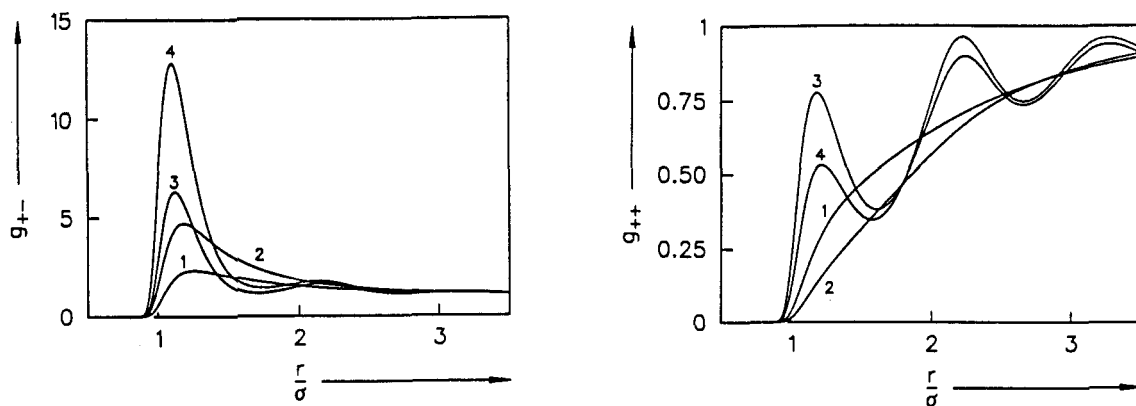


Fig. 3. Radial ion-ion distribution functions a: (+-) and b: (++) of charged soft spheres in a continuous solvent ((1), (2) $b = 2, 4$; MM-level) and in a soft sphere solvent ((3), (4) $b = 2, 4$; BO-level).

When the ions and solvent molecules undergo soft sphere reference interactions a similar behaviour of the ion-ion rdf is observed at the BO-level shown in Figs. 3a and b for a soft sphere model with short-range interactions given by eq. (11) where $\epsilon_{n-12}^* = 0.5$. The comparison is made of the radial distribution functions of ions in a continuum (MM-level) and in a molecular solvent with a reduced number density $n_i^* = 0.69$ (BO-level); b again is the Bjerrum parameter, $b = l_B/\sigma$. Two ionic subsystems with different Coulomb interactions are presented, characterized by values of $b = 2$ and $b = 4$. The reduced number density is $n_i^* = N_i\sigma^3/V = 0.01$ in both cases.

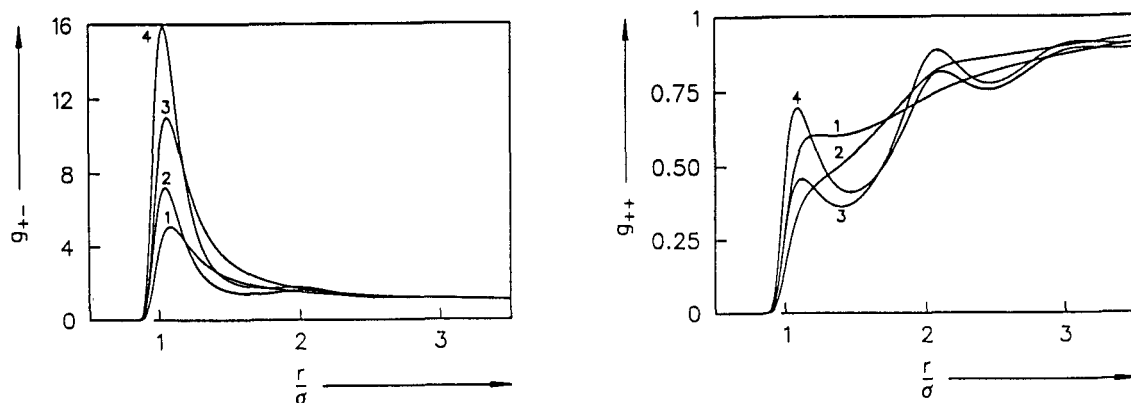


Fig. 4. Radial ion-ion distribution functions a: (+-) and b: (++) of charged Lennard-Jones particles in a continuous solvent ((1), (2) $b = 2, 4$; MM-level) and in a Lennard-Jones solvent ((3), (4) $b = 2, 4$; BO-level).

The reference system interactions of more realistic models of the solution contain contributions from attractive dispersion forces, such as modelled by a Lennard-Jones potential (eq. (10)). The corresponding radial ion-ion distribution functions are shown in Figs. 4a and 4b, where the ion-ion rdf of mixtures of Lennard-Jones (LJ)- and Lennard-Jones-Coulomb (LJC)-particles are shown under equal conditions as for molecules and ions with only soft repulsive core interactions. The Bjerrum parameter for the LJC-interactions (the sum of the contributions w_{ab}^{COUL} (eq. (4)) and u^{LJ} (eq. (10))) uses σ as the distance parameter defined by eq. (10). According to eq. (7) the differences between both kinds of rdf are caused by the solvation interaction term given by eq. (9) shown in Figs. 1. A comparison of Figs. 4a and 4b with Figs. 2 and 3 further shows that the repulsive part of the reference interactions determines the shape and strength of the contribution $w_{ab}^{\text{SOLV,RS}}$ of the solvation potential.

Fig. 5 shows the pmf in the case of a very dilute solution of an aqueous 1-1 model electrolyte ($b = 2$ and $n_i^* = 0.001$). Structural oscillations of the solvation potential due to the reference system contribution occur 'in phase' for the (++) and (+-) potentials. Additional attraction between ions of unlike and equal charge appears at distances $r < 1.2\sigma$. A secondary potential maximum occurs in both cases for $r > 1.5\sigma$. These effects increase at increasing ion size and decreasing charge density and at high solvent densities.

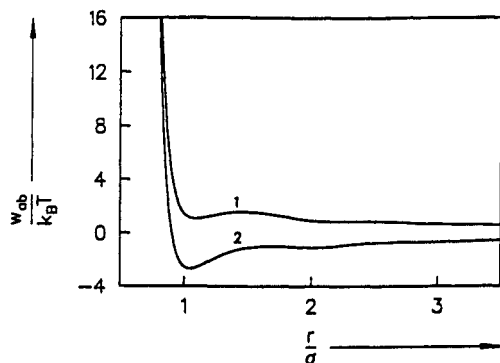


Fig. 5. Effective ionic interaction of a dilute solution of charged Lennard-Jones particles in a Lennard-Jones solvent: (1) (++); (2) (+-).

INFLUENCE OF THE ELECTROSTATIC CONTRIBUTION

Solvent molecules exert electrostatic forces on the ions leading to the static permittivity $\epsilon(n_s, n_i) > 1$ and to the term $w_{ab}^{\text{SOLV,EL}}$ of the solvation potential.

In the framework of a statistical mechanical theory at BO-level the permittivity of the solvent $\epsilon(n_s)$ must be calculated from the properties of the solvent molecules. This is not a trivial problem. The angle-dependent interactions between the solvent molecules lead to two-particle distribution functions in terms of rotational invariants from which the static permittivity $\epsilon(n_s)$ is accessible, usually with the help of MC- or MD-calculations or numerical solution of nonlinear integral equations for the correlation functions (see e.g. ref. 8 and the references quoted there). For a model solution of charged hard spheres (ions) imbedded in a solvent of hard spheres with central point dipoles the pair correlation functions and consequently also its thermodynamic properties may be calculated via mean spherical approximation (MSA) (refs. 4-6 and references quoted there). The MSA is based on a system of integral equations linearized with respect to the long-range interactions; it does not account for the complete effect of ion pairing and does not yield the correct value of the permittivity of a highly polar solvent. However, an important feature of the MSA is its simplicity. As an example, the internal excess energy E^{ex} and the permittivity $\epsilon(n_s)$ of a dipolar hard sphere solvent are given by the relationships (ref. 19).

$$(E^{\text{ex}}/N_s k_B T)^{\text{MSA}} = -(3y\eta_D)/(2\eta_{\text{HS}}) \quad (12)$$

$$\text{and } \epsilon(n_s)^{\text{MSA}} = q(\eta_D)/q(-\eta_D/2); \quad q(x) = (1+2x)^2/(1-x)^4. \quad (13a,b)$$

In these equations the parameter η_{HS} is the packing fraction, related to the reduced number density $n_s^* = N_s R^3/V$ of the solvent: $\eta_{\text{HS}} = \pi n_s^*/6$. R is the diameter of the dipolar hard spheres. The parameter η_D depends on the dipolar coupling parameter y which in turn is connected with the dipolar moment μ of the solvent molecules

$$3y = q(\eta_D) - q(-\eta_D/2); \quad y = 4\pi n_s^*(\mu^*)^2/9; \quad (\mu^*)^2 = \mu^2/(R^3 k_B T) \quad (14a,b,c)$$

The mean force potential between two charged hard spheres in an infinitely dilute solution of dipolar hard spheres is also calculable. The electrostatic contribution to the solvation potential derived from this calculation has the general form (refs. 5-7)

$$w_{ab}^{\text{SOLV,EL}} = w_{ab}^{\text{LR}}(\epsilon(n_s) - 1)G_{ab}(r, \eta_D) \quad (15)$$

At infinite dilution w_{ab}^{LR} is given by the Coulomb potential (eq. (4)) and $\epsilon(n_s)$ is the permittivity of the solvent, eq. (13). The function G_{ab} is of damped oscillating form, tending to zero after several solvent diameters. From eqs. (2), (5), (9) and (15) follows the effective interionic interaction in an infinitely dilute solution

$$w_{ab}(r) = -k_B T \ln(1 + h_{ab}^{\text{RS}}(r)) + w_{ab}^{\text{LR}}(r) \left(1 + (\epsilon(n_s) - 1)G_{ab}(r, \eta_D) \right) \quad (16)$$

The MSA calculation of $w_{ab}(r)$ according to eq. (16) is shown in Fig. 8a for the packing fraction of the solvent of $\eta_{\text{HS}} = 0.4$ and the reduced dipole moment $\mu^* = 2$, leading to $\epsilon(n_s)^{\text{MSA}} = 73.04$. The strength of the ion-ion interaction is given by the modified Bjerrum parameter $b_0 = b\epsilon(n_s) = 33.33$. The MSA results may be used as the starting point for the calculation of higher approximations to the correlation functions in the hard sphere ion-dipole mixture with the help of generalized virial expansions (refs. 7,8).

Another possibility is the use of the MSA results of the correlation functions of dipolar hard spheres as the input of a perturbation theory for the calculation of the effective interaction of two Lennard-Jones ions in a Stockmayer-fluid. For this model system the packing fraction η_{LJ} , the reduced dipole moment μ^* and the Bjerrum parameter b are defined just as in the case of hard spheres, replacing R by σ . Fig. 6b shows the corresponding mean force potential calculated with the parameters $\eta_{\text{LJ}} = 0.4$, $\mu^* = 2$ and $b_0 = 33.33$. Other calculations of ionic mean force potentials were carried out with more refined solvent models (refs. 15-17) and with more elaborate numerical integral equation techniques (ref. 8). The common feature of all these calculations is that increasing electrostatic forces between the ions and the molecules change the character of the ionic solvation interactions. The oscillations in the region of penetration of the first solvation shells become 'antiphase'; an additional repulsion between positive and negative ions at distances

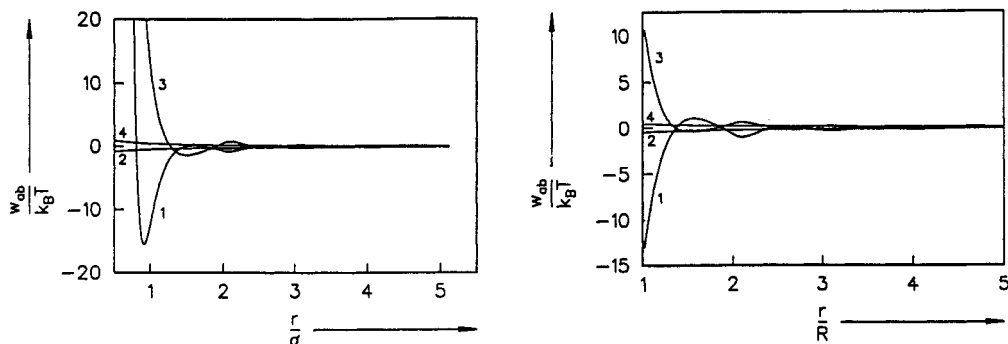


Fig. 6. Mean force potential of two ions in a dipolar fluid at infinite dilution. a: charged hard spheres in a dipolar hard sphere solvent; b: Lennard-Jones ions in a Stockmayer solvent: (1) (+-), (3) (++), (2) and (4) Coulomb interaction.

$1 < x < 2$ corresponds to an additional attraction between two positive (or negative) ions. The magnitude of these effects strongly depends on the relations between the radii of ions and molecules, on the charges and dipole moments, and on solvent temperature and density (refs. 7,11,13). This in turn leads to a peculiar thermodynamic behaviour of the electrolytes including various forms of phase transitions (refs. 3,6).

CONCLUSIONS

Dense solvents with strongly repulsive core interactions and relatively weak electrostatic contributions to the mean force potentials produce at low ion concentrations a remarkable increase of ion pairing compared with continuous solvents of equal permittivity (MM-level description without specific solvation interaction between the ions). This may be understood as a tendency to 'Coulombic unmixing', i.e., phase separation of the ion distributions to yield ion pairs and other clusters in solution. The effect increases with increasing ion charges and decreasing solvent permittivity. An example is the solution of Bu_4NI in benzene, where ion pairing and unmixing are observed (ref. 18).

When short-range and electrostatic forces contribute to the mean force potentials, such constellations also are found for the ion-ion pmf in infinitely dilute solutions, leading to the phenomenon of 'hydrophobic unmixing' (ref. 3). Phase separations in electrolyte solutions were reported in ref. 14 for several aqueous tetraalkylammonium halide solutions, among them also solutions of Bu_4NI . The potential model proposed in ref. 3 for ion-ion interactions at MM-level explains this type of phase separation by special solvation contributions to the ionic interaction potentials. The form of the solvation potentials connected with 'hydrophobic unmixing' permit the simultaneous occurrence of (+-) and of (++) ion pairs (so-called Kauzmann pairs) in the solution. The comparison of the behaviour of Bu_4NI in water and benzene shows that the solvent is responsible for the different types of phase transitions. Our calculations show that the account of the solvent and solute properties at the molecular scale may explain the diversity of effective ionic interactions in solutions and stimulate the use of Gurney potentials calculated at BO-level for an improved estimation of thermodynamic properties of electrolyte solutions.

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