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1991 J. Phys.: Condens. Matter 3 7907

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Hypernetted chain theory for electrolyte solutions: a new approach between continuous and discrete solvent models

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Received 12 April 1991, in final form 20 June 1991

Abstract. A new type of HNC calculation is proposed in which the variation of the solvation energies with salt and solvent concentration is taken into account. This is done by means of a self-consistent calculation of the distance dependent permittivity function around a central ion. The theory yields ion-ion as well as ion-solvent correlation functions and concentration dependent permittivities. In contrast to HNC calculations with a completely discrete-solvent model, the program requires only a small amount of computing power.

1. Introduction

Integral equation techniques are often used for calculating structural and thermodynamical properties of electrolyte solutions [1]. As far as numerical methods are concerned, the hypernetted chain (HNC) equation is considered to be the most convenient closure to the classical Ornstein-Zernike equation. Up to the present, two levels of description have been used in the framework of integral equations.

At the so-called Born-Oppenheimer (BO) level, the structure of the solvent is explicitly taken into account, and HNC provides us not only with ion-ion, but also with ion-solvent and solvent-solvent correlation functions [2]. However, the amount of numerical and mathematical problems is considerable.

At the so-called McMillan-Mayer (MM) level, the solvent is 'averaged out' and, as a result, we obtain 'only' solvent-averaged ion-ion pair correlation functions [3]. At this level, HNC is significantly simpler to resolve but information about ion-solvent interactions is lost ('primitive model' HNC).

For both types of HNC calculations, potentials are needed which describe the interactions between two particles. At the BO level these potentials are inferred from *ab-initio* calculations or from more qualitative atomic models [4]. At the MM level, the potentials are derived from BO calculations [5] or from intuitive physico-chemical models such as the Gurney-Friedman 'vanilla' model [6].

In fact, the resulting correlation functions depend critically on the choice of the potential model. At the MM level, adjustable parameters are introduced into the potentials in order that the result is as close to experimental data as possible [6].

Normally, osmotic or activity coefficients serve as a thermodynamic reference. More recently, the calculated correlation functions could be directly compared with

neutron scattering data [7]. This comparison allowed us to obtain a set of potential parameters which produce realistic solvent-averaged ion-pair correlation functions by means of the 'primitive-model' HNC.

However, the parameters are difficult to interpret. Therefore HNC figures mainly as a fitting algorithm for the description of experimental data.

In this paper we will present an alternative approach at a level which is placed somewhere between MM and BO. The theory should fulfill the following conditions.

- (i) The amount of computing costs should not considerably exceed that of HNC-MM.
- (ii) Nevertheless the calculation of ion-solvent correlation functions should be possible.
- (iii) The adjustable parameters should have a precisely defined physical sense.

A convenient starting point is given by one of the authors [8] in the framework of Poisson-Boltzmann equations. The method described in the following can be regarded as a translation of the ideas given there to integral equation techniques. We briefly repeat these ideas.

At the MM level, the calculated ion-ion correlation functions depend only on the solvent-averaged potentials, the temperature and the *salt* concentration. In our present approach the correlation functions depend also on the concentration of the solvent and the change of ion-solvent interactions as a function of solute and solvent concentrations. In this way we take into account a change in the energy of solvation of the ions when the concentrations vary. Thus the salt activity coefficient γ_{\pm} can be written formally as

$$\ln \gamma_{\pm} = B_{ij} + \Delta B_{i_s} \quad (1)$$

where B_{ij} represents the free energy change due to ion-ion interactions and ΔB_{i_s} is the free energy change of solvation between a given concentration c and infinite dilution: $\Delta B_{i_s} = B_{i_s}(c) - B_{i_s}(c \rightarrow 0)$. ΔB_{i_s} cannot be calculated at the MM level.

One of the features of the present approach is the calculation of a permittivity function $\epsilon(r)$ around a central ion so as to reflect the molecular and dipolar character of the solvent. The distance dependent dielectric function is calculated with the help of ion-ion pair correlation functions $g_{ij}(r)$ which come from HNC. The function $\epsilon(r)$ is inserted into the ion-ion interaction potential, which is then used for a new 'primitive model' HNC calculation. The resulting ion-pair correlation functions yield a new function $\epsilon(r)$ and the iteration cycle continues until $\epsilon(r)$ and $g_{ij}(r)$ are self-consistent. From the correlation functions thermodynamic properties like activity coefficients can be calculated as well as $\epsilon(c)$ for a given concentration. However, the change of the reference state and the variation of the ion-solvent interactions with concentration require a modification of the relations used to calculate thermodynamic quantities. Besides the thermodynamic quantities, $\epsilon(r)$ and $g_{ij}(r)$ allow us to calculate the ion-solvent correlation functions $g_{i_s}(r)$.

The method was tested by comparing the theoretical results with experimental data for two aqueous electrolyte solutions, namely NaCl/H₂O and KBr/H₂O.

As will be discussed later, the model for the ion-ion potentials was chosen to be as simple as possible. This has the advantage that the typical features of the new approach are not hidden by the choice of a sophisticated potential model; however, the price to be paid for this is that the calculated results cannot be expected to be in perfect agreement with experiment.

In the next section we will describe the applied technique in detail.

2. Theory

2.1. The algorithm of the classical 'primitive model' HNC

Since our theory is based on the algorithm of the solvent-averaged model HNC (HNC-MM, 'primitive model' HNC) we briefly repeat the basic equations.

The HNC equation (2) provides a link between the interaction potentials $u_{ij}(r)$ of two isolated ions i and j and their radial correlation functions $g_{ij}(r)$

$$g_{ij}(r) = \exp[-\beta u_{ij}(r) + S_{ij}(r)] \quad (2)$$

where $\beta = 1/kT$. k is Boltzmann's constant. The quantity $S_{ij}(r)$ can be regarded as the difference between the direct potential $u_{ij}(r)$ and the concentration-dependent potential of mean force $W_{ij}(r)$ resulting from the influence of all other particles

$$S_{ij}(r) = \beta[u_{ij}(r) - W_{ij}(r)]. \quad (3)$$

In the HNC approximation $S_{ij}(r)$ is given by

$$S_{ij}(r) = h_{ij}(r) - c_{ij}(r) \quad (4)$$

where

$$h_{ij}(r) = g_{ij}(r) - 1 \quad (5)$$

is the total correlation function and $c_{ij}(r)$ is the direct one involved in the Ornstein-Zernike equation

$$h_{ij}(r_{12}) = c_{ij}(r_{12}) + \sum_k \rho_k \int c_{ik}(r_{13}) h_{kj}(r_{32}) d\mathbf{r}_3 \quad (6)$$

where ρ_k is the number density of particles of type k . Equations (2) and (4-6) can iteratively be solved for given potentials $u_{ij}(r)$. Since we deal with charged ions, the algorithm must be modified because of the long-range part of the solvent-averaged potential due to Coulombian interactions. Reference [9] contains a discussion of this problem.

In our case the potential model is chosen as simple as possible. It consists of a hard-sphere term $u_{ij}^{\text{HS}}(r)$ and an electrostatic term $u_{ij}^{\text{ele}}(r)$.

$$u_{ij}(r) = u_{ij}^{\text{HS}}(r) + u_{ij}^{\text{ele}}(r). \quad (7)$$

$$u_{ij}^{\text{HS}}(r) = \begin{cases} \infty & \text{if } r < a_{ij} \\ 0 & \text{if } r > a_{ij} \end{cases} \quad (8)$$

where $a_{ij}(r)$ is the sum of the ionic radii a_i and a_j , and u_{ij}^{ele} is given by

$$u_{ij}^{\text{ele}} = \frac{z_i z_j e^2}{4\pi\epsilon(r)\epsilon_0 r} \quad (9)$$

in which z_i and z_j are the valencies of ions i and j , e is the charge of an electron, ϵ_0 is the permittivity of vacuum and $\epsilon(r)$ is a distance-dependent permittivity function of the solution. Therefore, as far as the HNC algorithm is concerned, one of the main differences between HNC-MM and our approach is the distance dependence and, as we will see, the concentration dependence of ϵ .

2.2. The distance and concentration dependence of the permittivity

The calculation of $\epsilon(r)$ is based on the following model.

We consider a central ion i . At infinite dilution the displacement field $D_i(r)$ created by the ion i is

$$D_i(r) = \frac{z_i e}{4\pi\epsilon_0 r^2} \quad (10)$$

When the concentration of ions increases, additional charges appear in the neighbourhood of the central ion i

$$D_i(r) = \frac{z_i e}{4\pi\epsilon_0 r^2} + \frac{4\pi \int_0^r (\rho_i g_{ii}(r) z_i e + \rho_j g_{ij}(r) z_j e) dr}{4\pi\epsilon_0 r^2} \quad (11)$$

Thus, $D_i(r)$ can be calculated from known ion-ion correlation functions $g_{ij}(r)$. In the next step we calculate the electric field $E_i(r)$. For this purpose a model has to be introduced. We chose a model which is based on the work of Booth [10] and Grahame [11] and which is discussed in details by Liszi *et al* [12]. It is assumed that the permittivity ϵ of a liquid depends on the electric field strength E in the following way:

$$\epsilon = n^2 + \frac{4\pi N \mu}{E} L \left(\frac{\beta \mu 3 \epsilon E}{2\epsilon + n^2} \right) \quad (12)$$

Here N is the number of molecules in unit volume, μ is the actual dipole moment of a molecule, n is the refractive index of water ($n = 1.3342$) and $L(x) = \coth(x) - 1/x$ is Langevin's equation. By introducing further approximations explained in [12], equation (12) can be rewritten as follows:

$$\epsilon = n^2 + \frac{\epsilon' - n^2}{E\sqrt{b}} \tan^{-1} E\sqrt{b} \quad (13)$$

where b is the Booth-Grahame coefficient (for water $b = 1198.3 \text{ \AA}^2 \text{ V}^{-2}$) and ϵ' is the static relative permittivity under weak fields. The relation $E = D/\epsilon$ immediately yields the desired relation between the electric field and the displacement field which can be written in our case as

$$E_i = \left(D_i - \frac{(\epsilon(\infty) - n^2) \tan^{-1}(E_i \sqrt{b})}{\sqrt{b}} \right) \frac{1}{n^2} \quad (14)$$

$\epsilon(\infty)$ is equal to the value $\epsilon(c)$ which will be discussed in section 3.

Equation (14) is solved iteratively starting with an estimated value for $E(r)$. The function $\epsilon_i(r)$ is then immediately calculated by

$$\epsilon_i(r) = D_i(r)/E_i(r) \quad (15)$$

With the knowledge of $D_i(r)$ and $E_i(r)$ it is easy to calculate the polarization field $P_i(r)$ from

$$P_i(r) = \epsilon_0(D_i(r) - E_i(r)) \quad (16)$$

It should be stressed that like the hard-sphere potential model, our model for the variation of ϵ with the distance r is very simple. Other models suggest a more complicated structure of $\epsilon(r)$ [13], which may lead to different results for the calculated correlation functions.

2.3. The change of the reference state

2.3.1. The reference at infinite dilution. As indicated in subsection 2.2, the displacement field at infinite dilution is only due to the central ion (equation (10)). Nevertheless, the Booth-Grahame equation gives a variation of $E(D(r))$ and hence a distance dependent $\epsilon(r)$ which is related to the solvation of ions at infinite dilution (cf equation (1)).

$$B_{i,s}(c \rightarrow 0) = \frac{1}{4\pi} \int_0^\infty 4\pi r^2 dr \int_0^{E(r)} E(r)\epsilon(r) dE \quad (17)$$

Of course, for infinite dilution—which is our reference state— $\epsilon(\infty)$ is equal to the dielectric constant of the pure solvent, for water: $\epsilon(\infty) = 78.3$. But in the neighbourhood of the ions $\epsilon(r)$ decreases down to values of $n^2 = 1.78$ due to the high electric field. For finite salt concentrations $D(r)$, $E(r)$, and $\epsilon(r)$ will change (for a given distance r) in comparison with their corresponding values for $c \rightarrow 0$. Therefore the solvation energy $B_{i,s}$ will differ from the reference state value $B_{i,s}(c \rightarrow 0)$.

In section 2.5 we will discuss the calculation of activity coefficients derived from the potential function at the contact of two ions. It is important to note that this calculation is always relative to the corresponding calculation at infinite dilution.

2.3.2. The covolume correction.

HNC calculations take the covolumes of the ions into account. At the MM level the covolume of the solvent is neglected. In our present work, we intend to calculate also ion-solvent correlation functions. This has two consequences for the calculation of covolumes.

(i) The punctual ion-solvent correlation functions must be corrected by the covolume of the ions and the solvent itself in order to get 'real' correlation functions.

(ii) The HNC ion-ion correlation functions must also be corrected by the covolume of the solvent.

The reference system of state differs now from the MM system. However we will stress that the covolume corrections have only a small influence on the ion-ion correlation functions. As far as the activity coefficients are concerned the solvent covolume effects are very small for concentrations less than 1 m. Nevertheless, the calculation of the covolumes is important for the calculation of ion-solvent correlation functions.

The basic ideas of the covolume corrections [14] are already given in [8]. The only modification to the corrections of Poisson-Boltzmann equations is that in a HNC calculation the influence of the covolume of the ions on the ion-ion correlation functions is already included in the hard sphere term of the ion-ion interaction potential.

The covolumes of an ion i , b_i and of a solvent molecule s , b_s are defined as

$$b_i = \frac{16\pi}{3} a_i^3 \quad b_s = \frac{16\pi}{3} a_s^3 \quad (18)$$

where b_i and a_i are given in \AA^3 and \AA , respectively (cf tables 1 and 2).

Furthermore we define

$$\beta^{(1)} = 1 + \rho_+ b_+ + \rho_- b_- \quad (19)$$

$$\beta^{(2)} = \beta^{(1)} + \rho_s b_s \quad (20)$$

$$\rho_i = C_i N_A \times 10^{-27} \quad (21)$$

where C_i is the macroscopic concentration of particle i in mol l⁻¹ and N_A is Avogadro's number.

In the next section we explain how the covolume correction is carried out simultaneously with the calculation of the ion-solvent correlation functions.

2.4. The calculation of the ion-solvent correlation functions

The polarization field $P_i(r)$ is related to the number of solvent dipoles *between the ions* per unit volume. In order to obtain the real polarization $P_i^*(r)$ relative to the *total* unit volume, it is necessary to take the volume occupied by the ions into account.

$$P_i^*(r) = P_i(r)/\beta_i^{(3)} \quad (22)$$

$$\beta_i^{(3)} = 1 + \rho_i g'_{ii}(r) b_i + \rho_j g'_{ij}(r) b_j \quad (23)$$

The ion-ion correlation functions $g'_{ij}(r)$ are corrected by the covolume of the solvent. They will be defined in (27) and (28). The punctual ion-solvent correlation function $g_{is}(r)$ is then given by

$$g_{is}(r) = \exp \frac{(P_i^*(r) E_i(r))}{c_{is}(r) kT}. \quad (24)$$

$c_{is}(r)$ is the real concentration profile of the ion-solvent correlation

$$c_{is}(r) = g_{is}(r) \rho_s \frac{\beta^{(2)}}{(c_{is}(r) b_s) + \beta_i^{(3)}}. \quad (25)$$

$c_{is}(r)$ is used now for the calculation of $g'_{ii}(r)$

$$T_i(r) = \frac{\beta_i^{(3)}}{(c_{is}(r) b_s) + \beta_i^{(3)}} \frac{\beta^{(2)}}{\beta^{(1)}} \quad (26)$$

$$g'_{ii}(r) = g_{ii}(r) T_i(r) \quad (27)$$

$$g'_{ij}(r) = g_{ij}(r) T_i(r) \quad (28)$$

Equations (22)–(28) form a closed set of equations. There is one set of equations for the cation ($i \equiv +, j \equiv -$) and one for the anion ($i \equiv -, j \equiv +$). Details of the computation are discussed in section 3.

2.5. The calculation of the activity coefficient

At the MM level, correlation functions from HNC can be directly related to activity coefficients y_{\pm} in units of molarity [15, 16]

$$\ln y_i = \sum_j \left(-\sqrt{\frac{\rho_i}{\rho_j}} \bar{c}_{ij}(0) + 2\pi\rho_j \int_0^{\infty} h_{ij}(r) S_{ij}(r) r^2 dr \right) \quad (29)$$

$$\ln y_{\pm} = \sum_i \frac{\rho_i}{\rho} \ln y_i \quad \rho = \sum_i \rho_i. \quad (30)$$

($\hat{c}(0)$ is the Fourier transform of the direct correlation function $c(r)$ at $k = 0$.) In our case the situation is more complicated because the reference state has changed (cf subsection 2.3.1). We chose the following decomposition similar to MSA calculations [17]

$$\ln y_i = \ln y_i^{\text{HS}} + \ln y_i^{\text{ele}} \quad (31)$$

A simple HNC-MM calculation with $z_+ = 0$ and $z_- = 0$ gives $\ln y_i^{\text{HS}}$, the contribution of uncharged hard spheres for a given concentration.

The term $\ln y_i^{\text{ele}}$ is calculated from the potential $V_i(a_{ij})$ at the contact of two ions i and j ,

$$V_i(a_{ij}) = \int_{\infty}^{a_{ij}} E_i(r) dr \quad (32)$$

which yields the free energy of the electrostatic interaction between the ions

$$kT \ln y_i' = \frac{1}{2} V_i(a_{ij}) z_i e. \quad (33)$$

Taking into account the corresponding expression for the reference state at infinite dilution $\ln y_i^\infty$ yields

$$\ln y_i^{\text{ele}} = \ln y_i' - \ln y_i^\infty \quad (34)$$

$$= \frac{z_i e}{2kT} (V_i(a_{ij}) - V_i^\infty(a_{ij})) \quad (35)$$

$\ln y_i^{\text{ele}}$ reflects both the interionic electrostatic interaction B_{ij}^{ele} and the change of the solvation energy ΔB_{is} . The precision of (31) can be estimated by comparing its result with (29) for the special case where $\epsilon(r) = \text{constant} = 78.3$ for all concentrations. For this special case we tested the resulting activity coefficients for NaCl in water up to concentrations of 2 M. Between the y_i values calculated in the two ways, the deviations are less than 1%. This difference comprises the errors which are made in the numerical calculation of $D_i(r)$, $E_i(r)$ and $V_i(a_{ij})$. As far as our present work is concerned the precision is regarded to be sufficient.

For comparison with experiment we further converted the calculated molar activity coefficients to units of molality.

3. Computational Aspects

3.1. The algorithm

3.1.1. First iteration cycle. The program starts with a classical HNC-MM calculation where $\epsilon(r) = \text{constant} = \epsilon(c)$ is an estimated value for a given concentration, e.g. about 70 for 1 M KBr/H₂O. From the obtained $g_{ij}(r)$ functions $D_i(r)$, $E_i(r)$ and $\epsilon_i(r)$ are calculated according to (11), (14) and (15). The resulting $\epsilon_+(r)$ and $\epsilon_-(r)$ functions are introduced in the interaction potentials $u_{++}(r)$ and $u_{--}(r)$. For the $u_{+-}(r)$ potential the average values $(\epsilon_+(r) + \epsilon_-(r))/2$ are used. With these new potentials a new HNC calculation is performed, then $\epsilon_i(r)$ functions are calculated and the iteration cycle continues until the $g_{ij}(r)$ function of two iterations are identical.

The variation of ϵ with concentration is only important near the contact of the ions. At greater distances ($r > 10 \text{ \AA}$) $\epsilon(r)$ rapidly tends to $\epsilon(\infty) = \epsilon(c)$. Therefore the long-range part of HNC is not touched and the conventional HNC algorithms can be applied as described in [18]. Furthermore the variation of ϵ does not dramatically change the ion-ion correlation functions of classical HNC-MM. As a consequence, the $g_{ij}(r)$ from HNC-MM are always a good starting point so that the iteration cycles easily converge.

3.1.2. Second iteration cycle. When this convergence is achieved we simultaneously calculate the ion-solvent correlation function $g_{is}(r)$ (equation (24)), and the covolume correction function $T_i(r)$ (equation (26)). This simultaneous calculation starts at high r values where the functions $T_i(r)$, $g_{ii}(r)$, $g_{ij}(r)$ are very close to 1. For the calculation of these functions at smaller particle distances we made, in (23), the assumption that $g'_{ii}(r - \Delta r) \approx g'_{ii}(r)$ and $g'_{ij}(r - \Delta r) \approx g'_{ij}(r)$ and, in equations (24) and (25) the assumption that $c_{is}(r - \Delta r) \approx c_{is}(r)$. Since Δr is small (cf subsection 3.2) this approximation is justified. A new HNC iteration cycle (subsection 3.1.1) starts now but this time the HNC equation (2) is modified to read

$$g_{ij}(r) = \{ \exp [-\beta u_{ij}(r) + S_{ij}(r)] \} T_{ij}(r) \quad (36)$$

$$T_{ij}(r) = \frac{1}{2}(T_i(r) + T_j(r)). \quad (37)$$

In general T_{ij} has values close to 1, except at distances close to the contact distance of the particles, so convergence is rapidly obtained. The $T_i(r)$ coefficients have an effect similar to an additional short-range potential. They slightly modify the values of the $g_{ij}(r)$ functions at the contact distance of ions i and j . For the systems discussed in this paper, the maxima of the $g_{\pm}(r)$ functions are thus slightly increased by about 1%. Since the long-range part of the correlation functions are not influenced by $T_i(r)$, equation (37) is in agreement with the Stillinger and Lovett conditions.

From the corrected $g_{ij}(r)$ the ion-solvent correlation functions can immediately be calculated. Furthermore a new set of T_{ij} values can be obtained which is in general so close to the first one that no further iteration cycle is necessary.

A different run is performed for infinite dilution in order to obtain $V_i^{\infty}(a_{ij})$. In y_{\pm} can then be calculated for a given concentration and a given value of $\epsilon(c)$ according to (31)–(35).

3.2. Numerical problems

As usual, HNC calculations are partially carried out in Fourier space. This means that the spacing Δr in real space cannot be arbitrarily diminished for a given number of grid points without loss of precision in Fourier space. Furthermore the contact distance a_{+-} divided by Δr should give an integer. This is a consequence of the hard-sphere model.

In order to get reliable numerical results we chose Belloni's HNC algorithm [16, 18] which allows the introduction of non-equidistant grid points in the region where the correlation functions and the permittivity function vary rapidly. The application of very fine grid points in this region considerably improved the numerical integration and differentiation. However, for non-equidistant grid points the fast Fourier algorithm cannot be used. A good compromise between computing time and numerical precision is obtained when using 1024 points with $\Delta r = a_{\pm}/10$ and 400 additional grid points with $\Delta r = a_{\pm}/100$ in the low-distance region.

4. Results and discussion

4.1. The activity coefficient and $\epsilon(c)$

The theory presented here—we will call it HNC-BIS—was tested for two types of solutions: NaCl/H₂O and KBr/H₂O. Between 0.1 m and 1 m we adjusted the calculated activity coefficients to experimental ones by varying the values of $\epsilon(\infty)$. Furthermore we carried out two other series of calculations. Classical HNC at the MM level with $\epsilon(r) = \epsilon(c) = 78.3$ for all values of r and c (HNC-MM) and HNC with $\epsilon(r) = \epsilon(c) = \epsilon_{\text{exp}}$ (HNC-C) where ϵ_{exp} are concentration—but not distance dependent—permittivities derived from dielectric measurements [20,21]. The results and the potential parameters used are given in tables 1 and 2.

Table 1. Experimental and calculated properties of NaCl solutions at 25 °C. $\epsilon_{\text{calc}}(\infty)$ are permittivities which yield the experimentally obtained values of activity coefficients γ_{exp}^m by means of HNC-BIS and equation (33) after conversion into the molality scale. Units: m , mol (kg solvent)⁻¹; c , mol l⁻¹; c_w , water concentration in mol l⁻¹. $a_{\text{Na}^+} = 0.98$ Å; $a_{\text{Cl}^-} = 1.81$ Å; $a_{\text{H}_2\text{O}} = 1.39$ Å.

m	c	c_w	$\ln \gamma_{\text{exp}}^m$ [19]	$\ln \gamma_{\text{HS}}^m$	ϵ_{exp} [21]	$\epsilon_{\text{calc}}(\infty)$		$\ln \gamma_{\text{calc}}^m$	
						HNC-BIS	HNC-MM	HNC-MM	HNC-C
0.1	0.09952	55.29	-0.109	0.003	76.7	74.5	-0.127	-0.130	
0.3	0.2975	55.08	-0.149	0.012	73.4	67.0	-0.185	-0.203	
0.5	0.4939	54.88	-0.167	0.019	70.5	60.5	-0.214	-0.249	

Table 2. Experimental and calculated properties of KBr solutions at 25 °C. Units: m , mol (kg solvent)⁻¹; c , mol l⁻¹; c_w , water concentration in mol l⁻¹. $a_{\text{K}^+} = 1.33$ Å; $a_{\text{Br}^-} = 1.96$ Å; $a_{\text{H}_2\text{O}} = 1.39$ Å.

m	c	c_w	$\ln \gamma_{\text{exp}}^m$ [19]	$\ln \gamma_{\text{HS}}^m$	ϵ_{exp} [20]	$\epsilon_{\text{calc}}(\infty)$		$\ln \gamma_{\text{calc}}^m$	
						HNC-BIS	HNC-MM	HNC-MM	HNC-C
0.1	0.0994	55.20	-0.112	0.007	77	76.8	-0.118	-0.119	
0.3	0.2960	54.82	-0.159	0.020	75	73.8	-0.164	-0.175	
0.5	0.4899	54.44	-0.182	0.033	72.4	72.0	-0.183	-0.216	
1.0	0.9630	53.50	-0.210	0.067	66.9	71.0	-0.198	-0.257	

A comparison between the experimental values of the activity coefficients of NaCl and KBr shows that $\ln \gamma_{\text{exp}}^m$ (KBr) is more negative than $\ln \gamma_{\text{exp}}^m$ (NaCl) for comparable concentrations. This feature cannot be ascribed to the different ion sizes of KBr and NaCl since this would have a - small—effect in the opposite direction (cf $\ln \gamma_{\text{HS}}^m$). Therefore we believe that the different activity coefficients result from a different change of the solvation energy $\Delta B_{i,s}$ in both solutions.

In Friedman's HNC-MM calculations [6] this effect is globally reflected in the Gurney soft sphere potential by Gurney parameters which are two times more negative for KBr ($A_{++} = -100$ cal mol⁻¹, $A_{+-} = -86$ cal mol⁻¹) than for NaCl solutions ($A_{++} = -50$ cal mol⁻¹, $A_{+-} = -47$ cal mol⁻¹). This means that an additional attractive potential was used which is two times more attractive for KBr solutions than for NaCl solutions.

HNC-MM with the simple charged hard sphere potential and $\epsilon = 78.3$ for all concentrations predicts activity coefficients which are either too small (NaCl) or in rough agreement with experiment (KBr), cf tables 1 and 2. At the MM level, a decrease of ϵ_c with increasing concentrations (HNC-C) leads to calculated activity coefficients which are, in both cases, by far too small when compared with experiment.

In contrast, in HNC-BIS calculations the variation of $\epsilon(c)$ is a natural consequence of the variation of $B_{i,s}(c)$. It should be noted that a decrease of $\epsilon(c)$ in HNC-BIS calculations can either produce higher γ values than the ones obtained by HNC-MM (cf NaCl 0.5 m) or lower values (cf KBr 1.0 m). This is a consequence of the competition between ion-ion (B_{ij}) and ion-solvent ($B_{i,s}$) interactions in our model. It is equivalent to a competition between ionic association and ionic solvation. In any case, a decrease of $\epsilon(c)$ with concentration is in qualitative agreement with values ϵ_{exp} deduced from experiment (cf figure 1). In the HNC-BIS calculations the fitted $\epsilon(c)$ values of NaCl solutions are smaller than the ones obtained in the fitting process of γ_{KBr} . This is also in qualitative agreement with experiment [20]. However, we must remark that the adjusted $\epsilon(c)$ values of the NaCl solutions are too low when compared with experiment and that it is difficult to obtain self-consistency of HNC-BIS calculations for low $\epsilon(c)$ values. Therefore we restricted our present calculations to concentrations not higher than 0.5 m in the case of NaCl solutions. It is interesting to note that the approach of Kusalik and Patey [2] also gives a too strong decrease of ϵ (NaCl) with salt concentration for $c < 1$ M.

In order to compare the accuracy of our approach with that of HNC-MM and HNC-C we also carried out HNC-BIS calculations with $\epsilon(\infty) = \epsilon_{\text{exp}}$. The $\ln \gamma_{\pm}$ values obtained in this way are -0.122 , -0.178 , and -0.206 for NaCl concentrations of 0.1 m, 0.3 m and 0.5 m, respectively. Although these values are not in agreement with the experimental values, they are better than the results from HNC-MM and HNC-C (cf table 1). The same tendency was found for the KBr solutions.

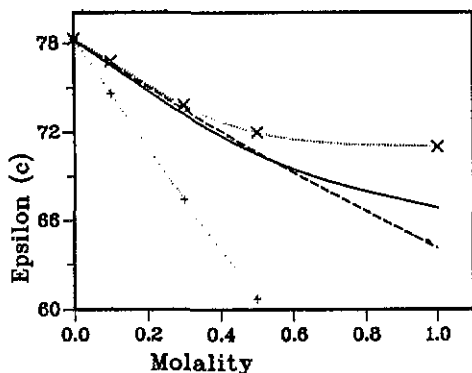


Figure 1. The concentration dependence of $\epsilon(c)$ at 25 °C. Values derived from experiment for KBr (—) [20] and NaCl (---) [21], and calculated values which give the correct activity coefficients for KBr (x) and NaCl (+).

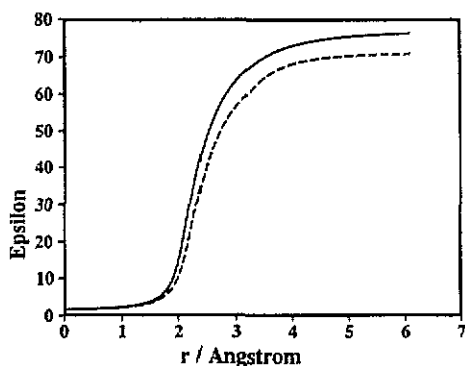


Figure 2. The variation of the permittivity function $\epsilon(r)$ with distance r to a central ion at 25°C for 0.1 m (—) and 1 m (---) KBr.

4.2. The distance dependence of $\epsilon(r)$

In figure 2 two typical examples of the distance dependence of $\epsilon(r)$ are displayed as obtained by HNC-BIS. As given by the Booth-Grahame equation $\epsilon(r)$ varies between the square of the refraction index ($n^2 = 1.78$) and $\epsilon(\infty)$. The variation is spectacular between 2 and 4 Å, i.e. at distances similar to the diameter of small ions. Beyond 8 Å $\epsilon(r)$ is almost identical with $\epsilon(\infty)$.

For dilute solutions (0.1 m) $\epsilon(r)$ is not significantly influenced by the ion-ion correlation functions. The second term of (11) is small. In contrast, at 1 m, the contribution of this term is visible beyond the contact distance of cation and anion (for KBr 3.29 Å). The dielectric function is shifted to higher values. The situation is similar for NaCl but the contact distance is smaller, 2.79 Å.

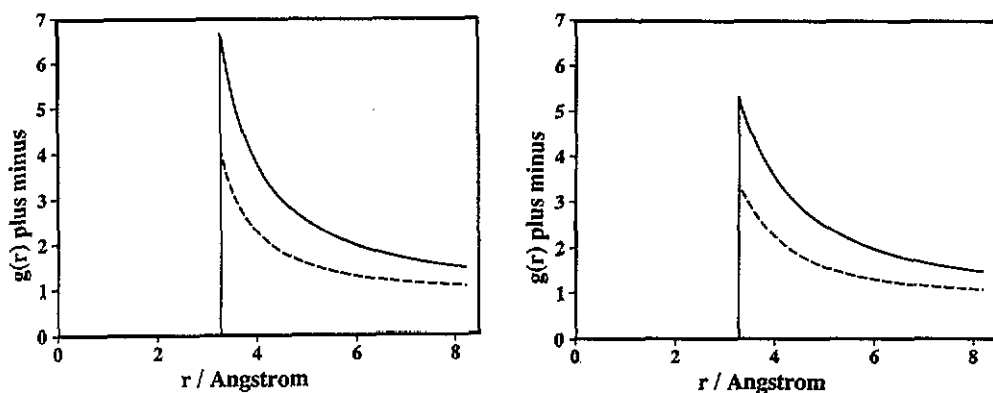


Figure 3. (a) The cation-anion correlation functions $g_{+-}(r)$ for KBr solutions at 0.1 m (—) and 1 m (---) as derived from HNC calculations with variable $\epsilon(r)$. (b) The cation-anion correlation functions $g_{+-}(r)$ for KBr solutions at 0.1 m (—) and 1 m (---) as derived from HNC-C ($\epsilon(c) = 76.8$ and 71.0, respectively).

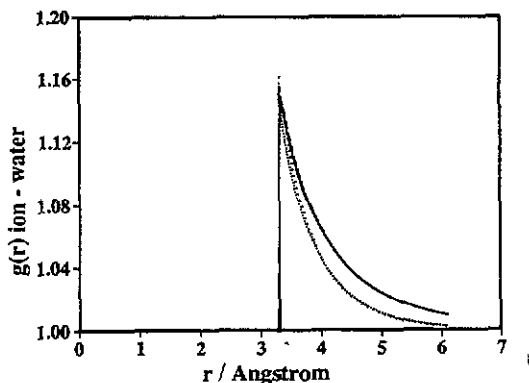


Figure 4. Ion-solvent correlation functions of KBr solutions at two different concentrations: $g_{+-s}(r)$ (—) and $g_{--s}(r)$ (---) at 0.1 m; $g_{+-s}(r)$ (· · · · ·) and $g_{--s}(r)$ (· · · · ·) at 1 m.

4.3. Correlation functions

In figure 3(a) the resulting correlation functions $g_{K+B\tau^-}(r)$ are given for 0.1 m and 1 m. For comparison we display the analogous result, obtained by HNC-C, in figure 3(b). As expected, the lower values of $\epsilon(r)$ (HNC-BIS) near contact considerably enhance the $g_{+-}(r)$ functions at contact. Their general shape, however, is not changed.

The behaviour of the ion-solvent correlation functions is more instructive (figure 4). Near contact the correlation functions around cation and anion are somewhat different up to centre-to-centre distances of about 4 Å. When the concentration is increased, not only the absolute concentration of water in the solution diminishes but also the relative concentration, represented by the ion-water correlation functions, has smaller values near the ion-water contact distance. Speaking in physical terms, more and more water molecules are pushed back out of the first solvation shells. Corresponding calculations based on the Poisson-Boltzmann equations [8] show that at very high concentrations the solvation of the ions is progressively weakened by the presence of counterions. This exemplifies the competition of solvation and association in concentrated solutions. The extension of HNC calculations to high concentrations or even saturation conditions will be the topic of a future work.

Acknowledgment

One of the authors (WK) is grateful to the Commission of the European Communities for a grant.

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