THE HYPERNETTED CHAIN (HNC) EQUATION FOR HIGHER VALENCE ELECTROLYTES

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The HNC equation is solved for 1-1, 2-1, 3-1 and 2-2 model electrolytes of charged hard spheres of radii 2.1 Å. The thermodynamic properties are presented, the anomalous behaviour of the osmotic coefficients and heats of dilution of 2-2 electrolytes, and oscillations in the charge density about a given ion for different charge types are discussed.

1. INTRODUCTION

The accuracy of the hypernetted chain (HNC) equation has been demonstrated for model 1-1 electrolytes in aqueous solution at 25°C up to a total ionic concentration c of 2M [1-3]. Here we wish to report the results of similar computations for 2-2, 3-1, 2-1 and 1-1 electrolytes up to $c = 4$M for the primitive model (charged hard spheres) in which all ions i have the same radius $r_i^{\mathrm{HS}} = 2.1$ Å. For the other model parameters we take the dielectric constant ϵ of the structureless solvent to be 78.358 with the temperature $T = 298.16$°K. Except when aqueous solutions are being explicitly considered, we also assume in calculating the excess energy per unit volume E^{ex} that $\partial\epsilon/\partial T = 0$.

Our choice of ions of equal size for all of these charged systems has been made with the idea of eliminating the influence of sorting due to differences in ionic radii on oscillations in the charge density per unit volume ρ_i about a central ion i. For a single electrolyte containing c_i ions per unit volume of ionic charge e_i,

$$\rho_i = c_i e_i [g_{ii} - g_{ij}] \quad , \tag{1}$$

where $i, j = +$ or $-$, $i \neq j$ and g_{ij} is the pair correlation function.

We then have

$$\lim_{e_i \to 0,\, e_j \to 0} [g_{ii} - g_{ij}] = 0 \quad , \tag{2}$$

when $r_i^{\mathrm{HS}} = r_j^{\mathrm{HS}}$.

The proof of a second moment condition for the exact pair correlation function has lead Stillinger and Lovett [4] to predict oscillations in the charge density ρ_i when $\kappa a \geqslant 6^{1/2}$, where $1/\kappa$ is the Debye length defined below in eq. (7) and $a \equiv a_{ij}$ is the distance of closest approach. Stillinger and Lowett regard this as an over estimate, and indeed our results for the HNC equation which obeys the second moment condition show oscillations in the charge density at much lower values of κa. Recently Outhwaite [5] has discussed a linear extension of the Debye-Hückel theory in which oscillations are predicted to appear in the case of symmetrical electrolytes (for example 1-1 and 2-2) when $\kappa a \geqslant 1.2412$. Our results for 1-1 and 2-2 electrolytes also appear to support an estimate of κa for the onset of oscillations which is higher than the earlier Kirkwood and Poirier [6] prediction of $\kappa a = 1.03$.

2. THEORY, NUMERICAL PROCEDURE AND RESULTS

In the notation of ref. [1], the integral equation due to Allnatt [7] which we solve is given in matrix form by

$$\tau = X*h + q*X + q*X*h \quad , \tag{3}$$

where

$$h_{ij} = g_{ij} - 1 \quad , \tag{4}$$

$$q_{ij} = -\frac{e_i e_j}{\epsilon r k T} \exp(-\kappa r) \quad , \tag{5}$$

$$X_{ij} = h_{ij} - q_{ij} - \tau_{ij} \tag{6}$$

and

$$\kappa^2 = \frac{4\pi}{\epsilon kT} \sum_{i=1}^{\sigma} c_i e_i^2 \quad . \tag{7}$$

The HNC approximation assumes

$$h_{ij} = (1 + k_{ij}) \exp(q_{ij} + \tau_{ij}) - 1 \ , \tag{8}$$

where k_{ij} is the corresponding Mayer f-bond for the short range potential of the pair of ions i and j. For the charged hard sphere model, with the additional assumption of $\partial\epsilon/\partial T = 0$, the osmotic coefficient ϕ from the virial equation may be written as

$$\phi = \frac{E^{\mathrm{ex}}}{3ckT} + \frac{2\pi c}{3} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} x_i x_j g_{ij}(a_{ij}+) a_{ij}^3 \ , \tag{9}$$

where

$$\frac{E^{\mathrm{ex}}}{ckT} = \frac{1}{2\epsilon ckT} \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i e_j \int_0^{\infty} h_{ij}(r) 4\pi r \mathrm{d}r \tag{10}$$

and x_i is the mole fraction of species i, $a_{ij} = r_i^{\mathrm{HS}} + r_j^{\mathrm{HS}}$ is the distance of closest approach of ions i and j, and $g_{ij}(a_{ij}+)$ is the distribution function for the i,j pair of ions at contact. The two terms which contribute to ϕ are usually of opposite sign.

The numerical Fourier transform procedure for solving the integral equation (3) has been described earlier for 1-1 electrolytes [1]. With certain modifications to obtain convergence below $c = 0.05$M for 2-2 charge types which will be discussed elsewhere, we used the same method except that the number of lattice points N was taken to be 1024 rather than 512. We also required r_{max}, the maximum value of r, to be at least nine times as large as the distance of closest approach a_{ij} with $N = 1024$. At high concentrations, this meant an appropriate increase over the previous choice of $\approx 0.015/\kappa$ for $\hat{r}$, the lattice spacing in real space. At all concentrations the exact value of $\hat{r}$ was adjusted to give a sampling point at $r = a_{ij}$, to enable the distribution functions at contact to be obtained accurately. Due to uncertainties in the asymptotic form of $g_{ij}(r)$ particularly when there are oscillations, the effect of the continuation in $g_{ij}(r)$ for $r > r_{\mathrm{max}}$ on the thermodynamic properties was ignored. The error due to this is discussed below. The number of interations required for convergence increases with the ionic charge, and was as high as 75 for some concentrations of 2-2 electrolytes. We observed the HNC distribution functions for symmetrical (1-1 and 2-2) and unsymmetrical (2-1 and 3-1) electrolytes to obey the self-consistency requirement that $g_{ij}(r) = g_{ji}(r)$ for $i \neq j$. This condition is not met by the solutions to the Poisson-Boltzmann equation for unsymmetrical electrolytes [8].

We define the percentage deviation from the second moment condition by

$$\Delta_2 = 100\left(1 + \frac{4\pi S_2}{6\epsilon kT}\right) \ , \tag{11}$$

where

$$S_2 = \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i e_j \int_0^{\infty} g_{ij}(r)\, 4\pi r^4 \mathrm{d}r \tag{12}$$

and the percentage deviation from electroneutrality (or the zeroth moment condition) by

$$\Delta_0 = 100\left(1 + \frac{4\pi S_0}{\kappa^2 \epsilon kT}\right) \ , \tag{13}$$

where

$$S_0 = \sum_{i=1}^{\sigma} \sum_{j=1}^{\sigma} c_i c_j e_i e_j \int_0^{\infty} g_{ij}(r)\, 4\pi r^2 \mathrm{d}r \quad . \tag{14}$$

Groeneveld has shown that the HNC equation obeys the second moment condition exactly [9]. In our work deviations from this condition must then be due to errors in the numerical procedure from truncation of $g_{ij}(r)$ or from other sources. We consider the effects due to the finite value of r in table 1 by presenting the HNC results for 2-2 systems with $N = 512$ and $N = 1024$ for the same number of iterations and for the same spacing $\hat{r}$. Apparently the effect of truncation is much less severe on the thermodynamic properties than on the moment conditions.

In fig. 1 the osmotic coefficients and the function E^{ex}/ckT when $\partial\epsilon/\partial T = 0$ are plotted against the total ionic concentration c up to $c = 4$M. The HNC results for uncharged systems with the same short range potential are also included. These were also obtained numerically. Since $c = 4$M corresponds to a reduced density ρa^3 of about 0.18, the values of ϕ and E^{ex}/ckT for uncharged systems are very nearly exact. For aqueous solutions in which the solvent is treated as a continuous dielectric, $\partial \ln\epsilon/\partial \ln T = -1.3679$ at 25°C and although ϕ is unaffected, E^{ex}/ckT changes by a factor of $1 + \partial \ln\epsilon/\partial \ln T$ [10].

In fig. 2 ϕ and E^{ex}/I for our model 2-2 and 1-1

Table 1
The effect of the range of integration on the thermodynamic properties and the moment conditions for 2-2 electrolytes in the HNC approximation. $T = 298.16^{\circ}K$, $\epsilon = 78.358$, $\partial\epsilon/\partial T = 0$

N	ϕ		$-E^{ex}/ckT$		Δ_0		Δ_2	
	512	1024	512	1024	512	1024	512	1024
c (moles per litre)								
0.2	0.6206	0.6198	1.939	1.941	2.04	1.40	8.19	0.27
0.8	0.5885	0.5893	2.594	2.591	0.94	1.22	-1.63	0.60
1.6	0.6325	0.6341	2.935	2.929	0.99	1.55	-8.93	1.58
2.0	0.6639	0.6666	3.050	3.041	0.71	1.72	-22.38	2.24
4.0	0.8883	0.8865	3.394	3.396	3.37	2.41	70.99	9.47

electrolytes in aqueous solution are presented as deviations from the Debye-Hückel limiting law for relatively small values of the ionic strength I. The heat of dilution which is directly measurable is equal to E^{ex}/I for 1-1 electrolytes and is four times E^{ex}/I for 2-2 electrolytes. We note that the first deviations for 2-2 electrolytes are the exact opposite of the deviations for 1-1 electrolytes, in agreement with the experimental results of bi-bi valent sulfates and uni-uni valent alkali halides in aqueous solutions [11, 12]. The anomalous behavior of the osmotic coefficients and excess volumes of 2-2 electrolytes has been discussed by others using the limiting law plus second virial coefficient DHLL+B_2 [13, 14] of the Mayer theory of ionic solutions [15]. The Poisson Boltzmann equation [8] and association theories [12] have also been used independently in the interpretation of the osmotic coefficients of 2-2 electrolytes. We find that although the DHLL+B_2 approximation is in close agreement with the HNC calculations for 1-1 electrolytes below $I = 0.04$ M, only qualitative similarity between these approximations is evident for 2-2 electrolytes even at $I = 0.0004$M. However our calculations for both these approximations are, as far as we know, the first to predict the anomaly in the heats of dilution of 2-2 aqueous electrolyte solutions without explicit use of the assumption of association [11].

Oscillations in the distribution functions g_{ij} and in the charge density ρ_i were observed at sufficiently large values of κa. Fig. 3 illustrates oscillations in ρ_i. Estimates of lower and upper bounds for the threshold value of κa for oscillations in ρ_i are given below, for different charge types

$1.235 < \kappa a \leq 1.382$, 1-1 electrolyte ;
$1.381 < \kappa a \leq 1.513$, 2-2 electrolyte ;
$0.53 < \kappa a \leq 0.927$, 2-1 electrolyte ;
$0.34 < \kappa a \leq 0.75$, 3-1 electrolyte .

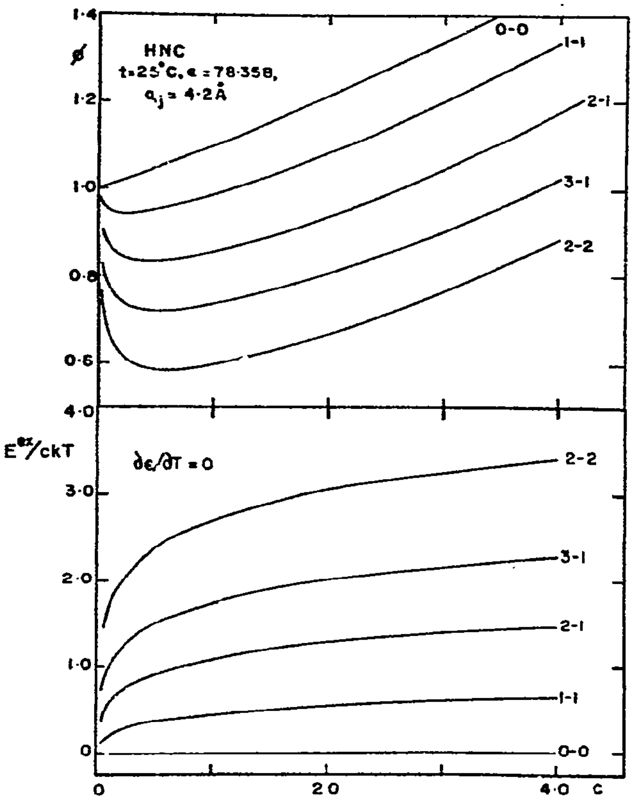

Fig. 1. Thermodynamic properties for charged hard spheres of radii 2.1 Å calculated by the HNC approximation.

While we are certain of the presence of oscillations in ρ_i at the upper estimates for κa, we are much less certain of the absence of oscillations at our estimated lower limits for κa. This is mainly because of the finite range of r in our numerical procedure which denies us information about the charge density outside the maximum

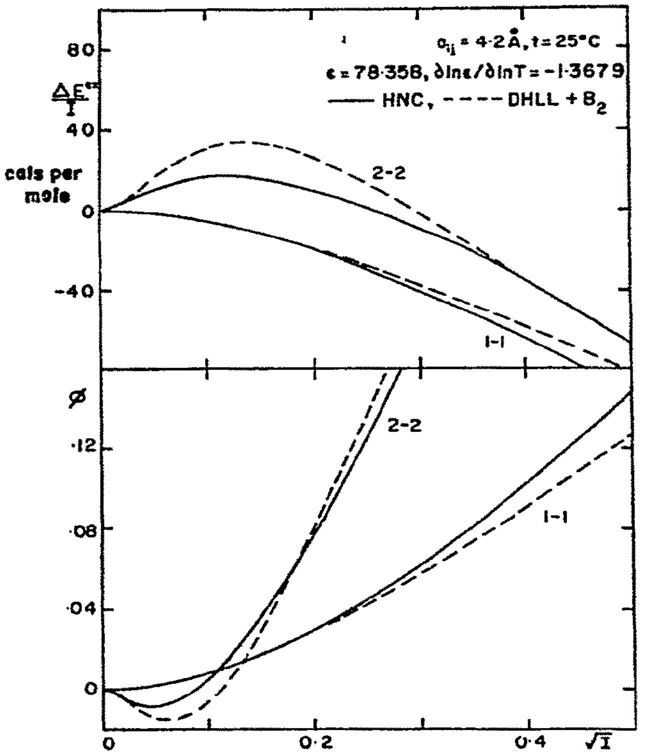

Fig. 2. Deviation of E^{ex}/I and ϕ from the Debye-Hückel limiting law in the DHLL+B_2 approximation and the HNC approximation for 1-1 and 2-2 model electrolytes in aqueous solution at 25°C. $\Delta E^{ex}/I = E^{ex}/I$ (computed) - E^{ex}/I (DHLL), $\Delta\phi = \phi$ (computed) - ϕ (DHLL) .

value of r. The strongest statement that we can make is that there are no oscillations in ρ_i up to r = 40 Å (nearly ten times the distance of closest approach) at the lower limits for κa. We note that for 1-1 electrolytes, our estimate of the range within which the limiting value of κa lies is in excellent agreement with the recent prediction of Outhwaite [5]. His estimate of κa = 1.2412 for the onset of oscillations also applies to 2-2 electrolytes, and is in slight disagreement with our computations for this system in the HNC approximation. This discrepancy may be a reflection of the reduced accuracy of the HNC approximation for highly charged particles i. e. large $e_i e_j/\epsilon kT$. For 2-1 and 3-1 electrolytes the limiting values of κa in the HNC approximation are significantly smaller than the corresponding estimates for symmetrical systems. An extensive discussion of the equilibrium properties of all of these charged systems including self consistency tests and comparisons with experiment will be presented elsewhere.

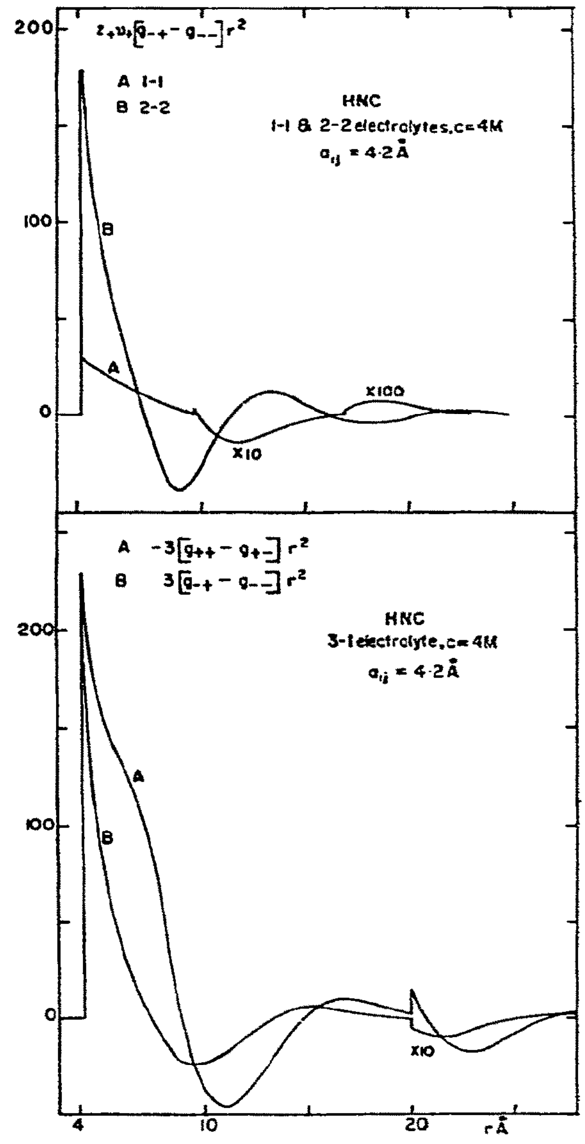

Fig. 3. Oscillations in the charge density for several different charged types in the primitive model. r_i^{HS} = = 2.1 Å at c = 4 M. In the upper figure $\nu_+ z_+$ has the values 1 and 2 respectively for 1-1 and 2-2 electrolytes. × 10 and × 100 denote magnification of the ordinate by 10 and 100 respectively.

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