vibrational structure and still more extensive calculations are needed to confirm this one way or the other.

Conclusions

We have seen that the QRHF-CC and MR-CC schemes are capable of calculating molecular IPs to a high accuracy. In deciding which method to use one must strike a balance between cost and accuracy. The QRHF-CCSD method, as presently implemented, requires separate CCSD calculations on the molecule and the lowest cationic states, although this is not necessary, as discussed below. The QRHF-CCSD method is reasonably accurate, although because it does not account for any effects of connected triple excitations, it may give poorer values for certain IPs than the QRHF-CCSDT-1 and MR-CC methods, as we have shown. Currently, the QRHF-CCSDT-1 method is also implemented by performing separate CCSDT-1 calculations on the molecule and cations of interest, and the iterative inclusion of triple excitations is 1 order of magnitude more expensive than a CCSD calculation.

For both QRHF-CCSD and QRHF-CCSDT-1 it is not necessary to do separate calculations, since in a slightly modified formulation the energy difference may be computed directly.[50] The direct calculation is, essentially, what would be done in the MR-CC scheme provided that a single determinant dominates the "model" function of the MR-CC procedure, which is usually the case.

The MR-CC method requires a CCSD calculation on the neutral molecule and then the determination of the amplitudes of those excitations which are not possible in the neutral molecule but which may occur in the cations (a much smaller number of amplitudes than in the initial CCSD calculation on the neutral molecule). Consequently, the total cost of an MR-CC calculation is less than that of two CC calculations. As we mentioned earlier, a single MR-CC calculation furnishes the whole set of IPs that may be obtained from the orbitals chosen to be active. It follows that the MR-CC method is the most economical of the three methods (and more economical than the HF-MBPT/CC methods), even if one wants only a single IP. The MR-CC method appears to be more accurate than the QRHF-CCSD method but not quite as accurate as the QRHF-CCSDT-1 approach, although except for the 5a′ IP of CH_2NH they give virtually identical results for the two molecules studied here. Extension of the MR-CC scheme to introduce "shake-up" effects requires consideration of additional sectors in the hierarchical Fock space approach.

We have reported valence IPs of methylenimine, methylenephosphine, and P_2. The results have been compared with data obtained from other theoretical techniques and experiment. In general, agreement is very good, showing that the new CC schemes are capable of a balanced treatment of the correlation energies of the neutral molecule and cations, suggesting that they should be valuable techniques for predicting and interpreting photoelectron spectra. Particular attention should be drawn to the MR-CC method, which is more economical than the other CC schemes, yet is almost as accurate as the separate state CCSDT-1 methods.

The work presented here represents a complete and accurate calculation of the principal valence IPs of methylenimine and methylenephosphine. Larger basis sets have been used than in previous work; highly accurate correlated methods have been employed; the 3a′ and 4a′ IPs of these molecules have been accurately calculated for the first time; and an accurate calculation of the separation of the lowest two cationic states of CH_2PH has been achieved. The experimental discrepancy of 0.1–0.3 eV should be further analyzed.

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Highly Asymmetric Electrolytes: A Comparison of Monte Carlo Simulations and the HNC Integral Equation

V. Vlachy,[†] Christopher H. Marshall, and A. D. J. Haymet*

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received July 20, 1988*

Abstract: Computer simulation results are presented for a model electrolyte solution in which the ions are asymmetric in both charge and size. The asymmetry in size is 10:1, and in charge from 10:1 to 15:1. The ions are modeled in two different ways: (i) as charged hard spheres embedded in a dielectric continuum and (ii) using more realistic, "soft" potentials to model short-range interactions. In both cases the solvent is not present explicitly. The computer simulations are performed on a relatively large sample of particles and permit quantitative comparison with the integral equation approximations. Specifically, the accuracy of the hypernetted chain equation is examined. This approximate integral equation provides reasonable estimates for both the pair correlation functions and thermodynamic properties, even up to the region in which converged solutions disappear. However, systematic discrepancies with the simulation results are found as the charge asymmetry is increased. In brief, the hypernetted chain approximation places counterions too close to each other and also too close to the highly charged polyion. This leads to an underestimate of the polyion–polyion correlation and allows the polyions to come too close to each other. This affects the interpretation of intermicellar structure factors obtained by neutron scattering experiments. A second consequence is that the hypernetted chain approximation misplaces the region of phase separation.

1. Introduction

Polyelectrolytes, solutions of colloids, micelles, and globular proteins, which are a set of classical topics in physical chemistry and currently also popular areas of research, can be viewed as electrolytes asymmetric in both charge and size. Their properties in solution are dominated by the Coulombic interactions between the highly charged polyions and the small counterions. The mobility and activity of these counterions are reduced considerably below their values in a bulk simple electrolyte. When an external electric field is applied to such a solution, a fraction of the counterions is thought to move as an integral part of a polyion.

[†] Permanent Address: Department of Chemistry, University E. Kardelj, Ljubljana 61000, Yugoslavia.

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There are two, approximate theoretical models which are used frequently to study these solutions. The first is motivated by the difference in the mobility of interacting species caused by the size and charge asymmetry, and leads naturally to a cell model of the solution.[1,2] The second class of models treats the solution as an effective one-component fluid of macroions interacting via a screened Coulomb potential,[3,4] in which the effects of both counterions and solvent are included only in a continuum approximation, via the so-called "screening length". Although incomplete, both models yield fair agreement with selected experiment data, albeit with the help of adjustable parameters.

In this work we adopt a more microscopic point of view,[2] although the solvent is still not treated at a fully molecular level. One result of this work is the prediction of adjustable parameters in the above models. More importantly, microscopic properties of the asymmetric electrolyte are predicted. A much more realistic starting point for the study of these solutions is the so-called "primitive model", which has been used successfully in the study of *simple* electrolyte solutions.[5] In this model, the electrolyte is treated as a mixture of charged hard spheres immersed in a dielectric continuum representing a solvent. Several integral equation approximations have been applied to this model,[2,6–19] and by comparison with experimental data the most accurate seems to be the hypernetted chain (HNC) equation.

Unfortunately, there is a crucial range of parameters, corresponding to dilute solutions of colloids, where the hypernetted chain equation cannot be solved. This effect has been noticed first in studies of symmetric electrolytes at low concentration and reduced temperatures,[20] and for asymmetric electrolytes it has been investigated recently by Belloni.[21] In a system containing highly charged polyions and counterions, as the concentration is decreased, the osmotic compressibility may diverge (erroneously) at a certain concentration, and therefore no solution of the hypernetted chain equation can be obtained beyond this point. This has been interpreted by some as indicating spinodal decomposition. In order to avoid this pathology, several other ad hoc closure approximations have been introduced recently.[14–18] In this way, convergent solutions of approximate theories have been obtained for several models of interest in the chemistry and physics of micellar solutions.[19]

Because of approximations introduced into the *model* (rather than the theory), further development of integral equation techniques is difficult without reliable computer simulations against which to test the approximations. Despite recent progress, a number of central questions remain unanswered. For example, (i) how accurately do the theories reproduce the structure of the solution; (ii) is the concentration of counterions close to the polyion predicted accurately, and (iii) to what extent is the "spinodal decomposition" actually an artifact of the integral equation approximation? These are the main questions addressed in our study. We use both Monte Carlo simulations and the HNC integral equation to obtain accurate structural and thermodynamic predictions. The number of molecules needed for a computer simulation of a polyelectrolyte solution is necessarily large, and such a computation can best be performed efficiently with a vectorized code on a vector computer. The only other simulations of which we are aware are those by Linse and Jonsson,[2] but the number of particles included in their seminal calculation is perhaps too small to permit critical comparison of different integral equation approximations.

In this study, we present accurate results for the various correlation functions in an asymmetric electrolyte. Systems have been studied with the asymmetry from 10:1 to 15:1 in charge and of 10:1 in size. Note that micelles such as sodium *n*-octanoate and sodium sulfonate micelles are modeled by a surface charge of 15 or 20 units, and a sphere from 3.0 to 4.0 nm in diameter. One important industrial application of polyelectrolytes is due to the fact that they can enhance (or inhibit) chemical reactions between ions,[22] and in turn this "catalytic effect" can be used to probe the ionic correlations about more complicated polyions.[23] To understand these processes, a more microscopic picture of ion correlations is needed. In this work, all three correlation functions, polyion–polyion, counterion–polyion, and counterion–counterion, are calculated as functions of both the polyion charge and concentration of the solution.

Although the charged hard-sphere model is a useful starting point for the study of polyelectrolyte solutions, it has major drawbacks. Most importantly, it yields an unrealistically high concentration of counterions in the first layer next to the polyion.[23] (This effect also contributes to the instability of the numerical algorithm used to solve the integral equation.) Ramanathan and Friedman[24] proposed a more realistic, "soft-sphere" model to describe electrolyte solutions. This model has been applied successfully to strongly associating solutions, such as 2:2 electrolytes[25] and cylindrical polyelectrolyte models of DNA solutions.[23,26] The "soft-core" model has been found to be a more realistic representation of these systems, and this is also true for micellar solutions since it allows some counterions to penetrate the short-range part of the potential energy which models the hydrocarbon core. In addition to being more realistic, continuous potentials are frequently easier to implement in integral equation and simulation studies. In this work we use these models, together with the HNC equation and Monte Carlo technique, to evaluate structural and thermodynamic properties in the range of parameters modeling spherical polyelectrolytes.

The models and numerical methods used in this study are described in section 2. The simulation and integral equation results are presented in the section 3. We include the thermodynamic and structural properties of both the hard- and the soft-sphere models as predicted by both numerical techniques. Since our simulations are performed on a relatively large sample, they are accurate enough to allow assessment of the validity of the hypernetted chain equation in this region of parameters and concentrations. A major part of this section is devoted to this comparison. We also address some implications for experimentally measurable properties, and the deficiencies of the hypernetted chain equation are discussed briefly. From a technical viewpoint, a simplified model of the so-called "bridge graph" yields some improvement over the hypernetted chain equation. Our conclusions are summarized in section 4.

2. Models and Methods

In this paper we study only two-component systems, which are salt-free solutions in which the free amphiphiles present in real

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Table I. Parameters Used in the Monte Carlo Simulations and in the Hypernetted Chain Calculations[a]

model	z_p	concn of polyions, mmol/dm^3	r_p^*, nm	r_c^*, nm	A_{pp}, nm	A_{pc}, nm	A_{cc}, nm	reduced energy per particle $-\beta E/N$
			(i) Hard-Sphere Model					
1.	12	8.299	1.0	0.1		infinite for $r < (r_i^* + r_j^*)$, zero elsewhere		2.83 ± 0.05
2.	12	2.083	1.0	0.1				2.30 ± 0.05
			(ii) Soft-Sphere Model, Eq 2					
3.	12	8.299	0.9	0.07	1.804	1.804	1.804	2.80 ± 0.05
4.	10	8.299	0.915	0.07	1.804	1.804	1.804	2.14 ± 0.05 [2.143 ± 0.002]
			(iii) Soft-Sphere Model, Eq 3					
5.	15	0.804	1.625	0.175	0.715	10.725	0.715	1.50 ± 0.04 [1.514 ± 0.002]

[a] The integral equation results are shown in square brackets.

micellar solutions are neglected. In such systems, the interactions are very strong and they represent a rigorous test for approximate theories. In addition, the solution to the hypernetted chain integral equation is generally easier to obtain when some simple electrolyte is added to the system. The interactions between the ions are given by the following pairwise additive potential energy:

$$\beta u_{ij}(r) = \beta u_{ij}^*(r) + \frac{z_i z_j e^2 \beta}{4\pi\epsilon_0\epsilon_r r} \tag{1}$$

where i and j label either counterions (c) or polyions (p), and z_p is the number of elementary charges e on a polyion, $z_c e$ is the charge on a counterion, and $\epsilon_0\epsilon_r$ is the (uniform) permittivity throughout the system. All properties of the solvent are subsumed into this dielectric continuum. As usual, $\beta = 1/kT$; T is the absolute temperature, and k is Boltzmann's constant. For the hard-sphere model, $u_{ij}^*(r)$ is infinite for distances less than $(r_i^* + r_j^*)$, where r_i^* and r_j^* are the hard-sphere radii.

For the soft-sphere model, two different short-range functions have been used. Both have been implemented in previous studies of electrolyte[25] and cylindrical polyelectrolyte solutions.[23,26] In the first model, the short-range part of the interaction potential is given by:

$$\beta u_{jj}^*(r) = \frac{A_{ij}}{r_i^* + r_j^*}[(r_i^* + r_j^*)/r]^9 \tag{2}$$

The parameters r_i^* and r_j^* are chosen to reproduce the first peak of the polyion–counterion pair correlation function, in order to produce a similar clustering of the counterions at approximately the distance of the closest approach of the corresponding hard-sphere model. The second potential function, given by eq 3,[26] has shorter range and is suitable for modeling more rigid macromolecules such as micelles

$$\beta u_{ij}^*(r) = \frac{A_{ij}}{r_i^* + r_j^*}\exp[(r_i^* + r_j^* - r)/\lambda] \tag{3}$$

where λ has the units of length and here is set equal to 0.1 nm. Our calculations are summarized by the data collected in Table I. All calculations are for aqueous solutions at 298 K, with a Bjerrum length $\beta e^2/4\pi\epsilon_0\epsilon_r = 0.715$ nm.

In the Metropolis Monte Carlo method,[27] a sequence of configurational states (called a Markov chain) is generated according to the condition

$$f \leq \min[1, \exp(-\beta\Delta u)] \tag{4}$$

where f is a random number selected from a uniform distribution on the interval [0,1], and Δu is the difference in internal energy between the trial configuration and the previously accepted configuration. The average of any configurational property becomes the canonical average in the limit of infinite chain length. For the model solutions described above, we have used this procedure to evaluate various correlation functions, configurational energies, and osmotic coefficients.

There are several problems routinely associated with the simulation of Coulombic systems, and these are encountered in the present study. In an initial examination of this system we found substantial size dependence in the polyion–polyion correlation function $g(r)$, just as found by Linse and Jonsson (see Figure 2 of ref 2). The simulation method allows reliable evaluation of $g(r)$ up to the half the edge of the basic cell, if a simple cubic box is used. In this work, we found empirically that the correlation functions are not distorted by boundary effects if three maxima of the correlation function can be found within half the box length. Hence the total number of polyions included in the simulation must necessarily be large, as must be the number of counterions included to satisfy electroneutrality. We choose to work with 128 polyions in the basic cell and use periodic boundary conditions. While many calculations on Coulombic systems have used Ewald summation to approximate the periodicity, the minimum image approximation used in this work has been found to be acceptable for dilute solutions.[28]

A second problem in the simulation of an asymmetric electrolyte is a low acceptance ratio for attempted moves of the polyions. As expected, the polyions are always enclosed by several counterions, and this makes them hard to move.[2] We have found that the displacement parameter, which optimizes the simulation, should exceed several times the diameter of the small ions in order to give the polyions a chance to "escape" from entrapment by the counterions. The acceptance ratios in our simulations vary from 0.15 to 0.3. At higher concentrations than reported here, and also for lower reduced temperatures, we have found that the convergence is very slow. As noticed previously,[2] an anisotropic structure persists throughout the simulation and the resulting $g(r)$ for polyions does not appear to be liquid-like. The simple Metropolis Monte Carlo method becomes inefficient under these conditions. This prevents immediate extension of our calculation to even more asymmetric electrolytes (for example, 1:40), where in addition a large number of particles, of the order of 10 000, are needed in the basic simulation cell. It is interesting to note, however, that the other correlation functions, both polyion–counterion and counterion–counterion, seem to be unaffected by this convergence problem. The large difference in the mobilities between the species in this region lends credence to the use of the cell model for studying polyion–counterion interactions.

The results of the computer simulations are collected in Table I and in the figures below. The figures show raw data: no smoothing procedures have been applied. One important piece of information for future work is the number of passes (that is, Monte Carlo moves per particle) needed to obtain reasonably good statistics. In this work we have found the 2000–3000 passes are enough for equilibration. The statistics have been collected over an additional 4000 passes.

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The numerical procedure for solving the hypernetted chain equation is relatively new, and has been used in several recent studies.[29,41] In summary, the basis set method of Gillan,[30] subsequently modified by Labik and co-workers,[31] has been generalized for multicomponent mixtures. The long-range Coulomb terms are renormalized as proposed previously.[32,33] One may start the derivation with the Ornstein–Zernike equation, which for a mixture reads

$$h_{ij}(r_{ij}) = c_{ij}(r_{ij}) + \sum_k \rho_k \int \mathrm{d}r_k c_{ik}(r_{ik}) h_{kj}(r_{kj}) \qquad (5)$$

where $g_{ij} = h_{ij} + 1$ is the pair correlation function, ρ_k is the number density of component k, and $c_{ij}(r_{ij})$ is the direct correlation function which is defined by this equation. It is useful to write the equation in the matrix form

$$\rho + \rho\hat{h}\rho = [\rho^{-1} - \hat{c}]^{-1} \qquad (6)$$

where the caret denotes the Fourier transform. The pair potential energy $u_{ij}(r)$ may be separated into a short-range part and a long-range (Coulombic) part u'_{ij}, where $\Psi = -\beta u'_{ij}$. The long-range part of the direct correlation function is then subtracted, to yield a well-behaved function of shorter range:

$$\hat{c}_s = \hat{c} - \hat{\Psi} \qquad (7)$$

Further, we introduce

$$\hat{V}^{-1} = \rho^{-1} - \hat{\Psi} \qquad (8)$$

and

$$\rho\hat{q}\rho = \hat{V} - \rho \qquad (9)$$

where V is the new hypervertex function. The renormalized Ornstein–Zernike equation can be obtained from these equations as:

$$\hat{V} + \rho\hat{h}_s\rho = [\hat{V}^{-1} - \hat{c}_s]^{-1} \qquad (10)$$

where $h_s = h - q$ and the function $q_{ij}(r_{ij})$ is the screened Coulomb potential. Equation 10 is merely a definition, and needs to be supplemented by yet another equation. The exact closure is

$$c_{ij} = \exp[-\beta u_{ij} + h_{ij} - c_{ij} + B_{ij}] - 1 - h_{ij} + c_{ij} \qquad (11)$$

where B_{ij} is the bridge function. Frequently this quantity is set to be zero, to yield the hypernetted chain (HNC) approximation.

We have used an efficient algorithm for solving the Ornstein–Zernike equation, developed from ideas proposed by Labik and co-workers[31] and Gillan.[30] The function $r[h - c]$ is expanded in a sine function basis and obtained numerically, first by the Newton–Ralphson method and then by direct iteration. A one-component version of such algorithm was recently applied to study the structure and thermodynamics of the Yukawa fluid, and it was found efficient and stable.[34] The multicomponent, renormalized version has been used to study the central force model of liquid water,[29] in which further details of the implementation of the method may be found. In all solutions of the HNC equation, the numerical accuracy was monitored carefully by checking the Stillinger–Lovett moment conditions. Both the zero and second moment defects were less than 0.001 in all calculation reported below. Thermodynamic properties, such as the excess energy per particle and the osmotic coefficient, were evaluated using the standard equations.[35]

3. Results and Discussion

In this section we present the results of the computer simulations and comparisons with the hypernetted chain equation. First, we have repeated some of the calculations for the hard-sphere models of ref 2. The polyions and counterions are charged hard spheres of radius 1.0 and 0.1 nm, respectively (see models 1 and 2 in Table I). The polyions have 12 negative charges while the counterions are monovalent, so we have +1/−12 electrolyte with a concentration of polyions equal to 8.299 mmol/dm^3. The correlation functions at two different concentrations are shown in Figures 1 and 2, and should be compared with Figures 2 and 8 of ref 2. Our simulations are performed with 128 polyions in the basic cell, which gives a polyion–polyion correlation function which is accurate to approximately the third maximum. It is interesting that there is very good agreement for the excess energy in the two calculations, especially considering that a much smaller number of particles was used in the previous study. The figures show strong clustering of the counterions around the polyion (contact values are indicated in the graph), especially at lower concentrations, as shown by the polyion–counterion and the counterion–counterion correlation functions. The latter is especially interesting, and it will be discussed more thoroughly in connection with the integral equation results. These results pertain to a relatively low reduced temperature, $T^* = 0.128$, defined in the usual way as ratio of the thermal energy kT to the potential energy of the polyion and counterion at contact. The hypernetted chain integral equation results for this particular set of parameters have been presented earlier.[2]

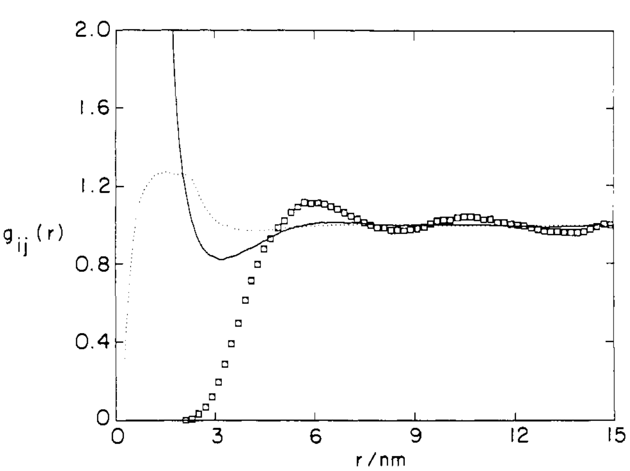

Figure 1. The pair correlation functions for the +1/−12 electrolyte obtained by Monte Carlo simulation. The ions are modeled as charged hard spheres (model 1: $r_p = 1.0$ nm and $r_c = 0.1$ nm), and the concentration of polyions is 8.299 mmol/dm^3. The symbols represent the polyion–polyion correlation function, the solid line is the counterion–polyion, and the dotted line is the counterion–counterion correlation function. The "contact" values of the correlation functions are $g_{pc}(r = 1.15) = 14.1$ and $g_{cc}(r = 0.25) = 0.27$.

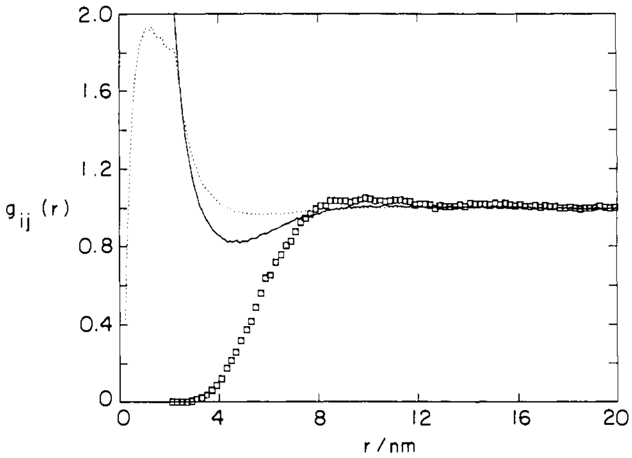

Figure 2. The pair correlation functions for the +1/−12 electrolyte. The concentration of polyions is 2.083 mmol/dm^3. All other data are the same as for Figure 1. The "contact" values of the correlation functions are $g_{pc}(r = 1.15) = 40.7$ and $g_{cc}(r = 0.25) = 0.43$.

New results are presented here for the soft-sphere model of polyelectrolyte solutions. In Figure 3 we present a comparison

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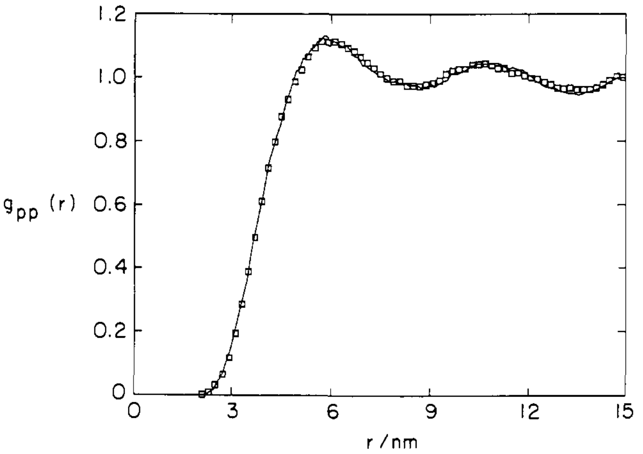

Figure 3. The polyion–polyion correlation functions, obtained from computer simulations, for (a) the "hard sphere" electrolyte (model 1, symbols), and (b) the "soft sphere" electrolyte (model 3, solid line). The concentration of polyions is 8.299 mmol/dm^3.

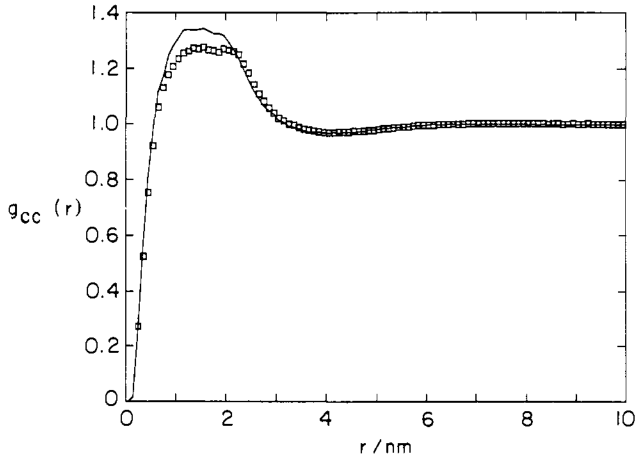

Figure 4. Comparison of the counterion–counterion correlation functions. All data are the same as in Figure 3.

of "hard" versus "soft" sphere +1/−12 electrolyte solution. The concentration and hard-sphere radii are the same as above, and the parameters for the soft spheres are listed under "model 3" in Table I. The symbols are the results for the hard-sphere model, and the line is obtained by using eq 2 to describe the short-range repulsive interactions. The agreement between two models is good, since the minimum of the potential energy has been chosen to lie near the sum of hard-sphere radii of the corresponding hard-sphere model. The counterion–counterion correlation functions displayed in Figure 4 reflect the fact that "soft" counterions may be more closely packed than their hard-sphere analogues. This correlation function is also much more sensitive to the choice of the parameters describing the short-range interactions between counterions.

Of most interest is the comparison of the computer simulations with the predictions of the hypernetted chain equation. This is a definitive test of the accuracy of the HNC approximation. We can also determine whether the structure factor of the solution, which can be measured experimentally by neutron scattering techniques,[36] is predicted accurately and whether the concentration of the counterions in contact with polyion, relevant for some spectroscopic properties, can be predicted correctly. The answers to these questions, for the range of parameters investigated here, are given in Figures 5 through 7.

First we present the results for a +1/−10 electrolyte solution at the polyion concentration 8.299 mmol/dm^3. The parameters for the short-range potential function are listed under "model 4" in Table I. The polyion–polyion correlation functions (Figure 5a) are in a fair agreement, but it is clear that the repulsive potential of mean force between the polyions is underestimated by the integral equation. On the given scale, the polyion–counterion correlation functions (Figure 5b) seem to be in good agreement (it is difficult to see the disagreement for a rapidly varying function), except for a small overshoot in the HNC prediction. However, there is a significant discrepancy in results for the counterion–counterion correlation function. The shape of these

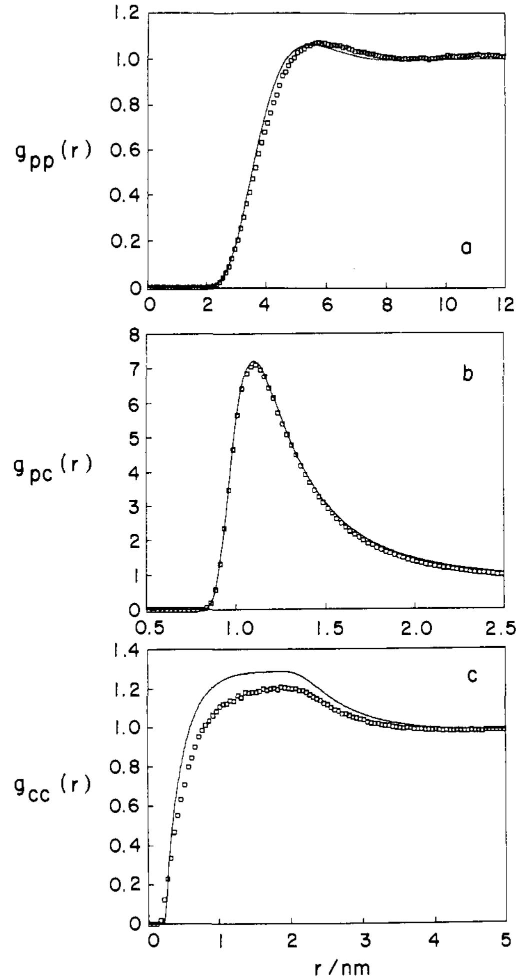

Figure 5. The (a) polyion–polyion, (b) counterion–polyion, and (c) counterion–counterion correlation functions for the +1/−10 electrolyte (model 4 in Table I), at the polyion concentration 8.299 mmol/dm^3. The symbols denote the Monte Carlo data and the solid lines are obtained from the HNC approximation.

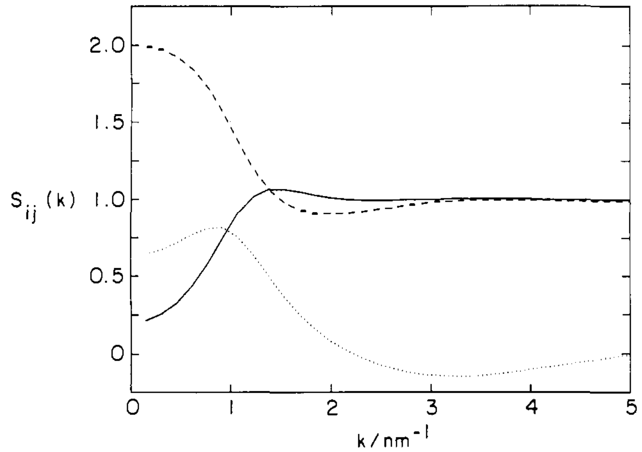

Figure 6. The partial structure factors of a +1/−10 electrolyte solution obtained from the HNC equation for model 4: polyion–polyion (solid line), counterion–counterion (dashed), and counterion–polyion (dotted) partial structure factors.

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(36) Chen, S.-H. *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*; Degiorgio, V., Corti, M., Eds.; Elsevier: New York, 1985.

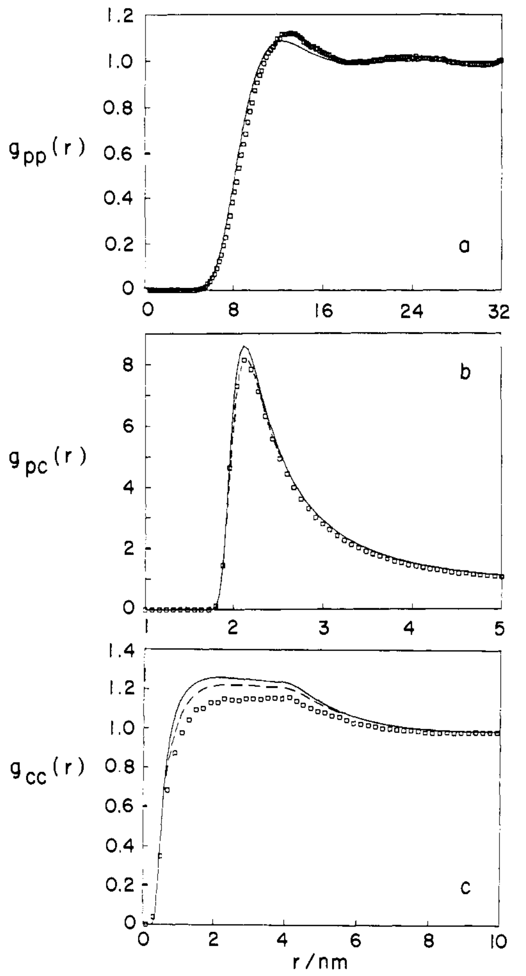

Figure 7. The (a) polyion–polyion, (b) counterion–polyion, and (c) counterion–counterion correlation functions, obtained for the +1/−15 electrolyte solution (model 5 in Table I), and at polyion concentration 0.804 mmol/dm^3. The symbols denote the Monte Carlo data, the solid lines are the HNC results, and the dashed lines are obtained using a hard-sphere bridge function model to correct the counterion–counterion correlation function, as explained in the text.

correlation functions, as shown in Figures 1, 2, 4, and 5c, reflects the fact that counterions meet most probably on the "surface" of a polyion. Furthermore, the maximum around 2.0 nm in Figure 5c reflects the effect of two counterions distributing themselves on opposite sides of a polyion. This local maximum persists also for highly charged polyions, namely, in the range of charge density relevant to colloids. The counterion–counterion correlation function is sensitive to the charge on the polyion, and especially to the concentration of solution, as seen by comparison of Figures 1 and 2. The partial structure factors of the solution are displayed in Figure 6.

The thermodynamic properties, energy, osmotic coefficient, and compressibility (HNC only) have also been calculated. The good agreement in excess thermal energy is shown in Table I. Fair agreement has also been found for the osmotic coefficients. For example, in +1/−10 electrolyte solution (model 4), the Monte Carlo result is 0.625 ± 0.02, and the hypernetted chain result (virial route) for the osmotic coefficient is 0.635 ± 0.002.

Polyelectrolytes are often used to enhance the rate of the chemical reaction between counterions, and to inhibit reaction between coions.[22] The rate of an activation controlled reaction may be related to the quantity $g_{ij}(a)$, where "a" is the distance of collision of the two particles.[37] For this reason it is important to determine accurate correlation functions. This rate can be modified considerably by introducing a polyelectrolyte as an additional species. Counterions and coions get (in loose terminology) spatially separated from each other by the field of the polyions. When particles i and j have charge of the same sign (both counterions), an increase of the rate is observed. However, the reaction is inhibited when the charges on ions i and j differ in sign, for example, in the reaction between counterions and coions. Specifically, for the 0.0121 M 1:1 electrolyte the value of $g_{cc}(0.4\text{ nm})$ is 0.06, whereas the same quantity in the +1/−15 electrolyte, with the same concentration of counterions, is the much larger value 0.15.

Mean field theories of polyelectrolyte solutions,[38] based on the Poisson–Boltzmann equation, may overestimate grossly the increase of the rate of chemical reaction for highly charged polyelectrolytes. Counterion–counterion correlations are ignored in these studies [see, for example, eq 2 of ref 23] by implicitly setting $g_{cc}(r) = 1$ for all distances. As shown by Wensel and co-workers,[23] this may lead to a huge discrepancy with the experimental data, and it may also provoke unrealistic conclusions concerning the ionic correlations in the polyelectrolyte soltuion. Hence, it is important to test integral equation approaches for the calculation of this quantity.

The deficiencies of the hypernetted chain equation are most clearly displayed in Figure 7, in which the results for the +1/−15 electrolyte solution ("model 5" of Table I) are shown. The HNC correlation functions for this model are in only semiquantitative agreement with the computer simulation data. The integral equation overestimates the concentration of counterions close to each other, and also (to a lesser degree) to the surface of a polyion. This in turn affects the polyion–polyion correlation function, which is underestimated. This leads to the erroneous prediction that polyions can approach each other more closely than predicted by the simulation study. In addition, the first peak of the polyion–polyion correlation function is underestimated. The osmotic compressibility, evaluated from the hypernetted chain equation, strongly increases in this region of parameters, as a result of the less repulsive potential of mean force between polyions.

Finally, above a certain charge on the polyion, or below a certain concentration, no solution of the hypernetted chain equation can be obtained, due the intrinsic, mathematical approximations in the theory. This effect has been investigated recently by Belloni,[21] who was able to map the region in which the hypernetted chain equation diverges and to estimate the critical temperature and concentration as a function of the charge on the polyion. In contrast, our computer simulations show *no* indication of any phase transition or spinodal decomposition in the region of parameters studied by Belloni.[21] In fact, with the Monte Carlo method it is easy to obtain results well within the "prohibited" range of parameters predicted by HNC (eq 2 of ref 21). Actually, the results presented in Figure 2 (and previously obtained by Linse and Jonsson[2]) pertain to the packing fraction 0.0053 and to the reduced temperature 0.128, while the HNC estimates of the critical values of the parameters are 0.006 and 0.192, respectively.

Similar deficiencies in the HNC integral equation have been noted for other strongly interacting systems, such as the electrical double layer[39] and 2:2 electrolytes.[40] In fact the double-layers studies already observed that the HNC approximation overestimates the number of counterions next to the charged surface, just as observed in this work. The overestimate of the larger clusters of charged species has been observed previously in studies of 2:2 electrolyte solutions.[25,40,41] This effect has been explained satisfactorily on the basis of the leading bridge graphs missing from the HNC approximation. Bacquet and Rossky[40] have estimated the corrections to the hypernetted chain equation, and they found much better agreement with the simulations of 2:2 electrolyte when the corrections are included in the integral equation. In this work, especially for $g_{++}(r)$, there is an analogy with simple electrolytes, and a similar analysis may apply. The counterion–counterion correlation function $g_{++}(r)$ is affected by the geometrical situation

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where four particles, two counterions and two polyions, are close together. This situation, which is unphysical in our case, is included in the hypernetted chain equation (see Figure 11 of ref 25), while, in fact, it may be largely canceled by the next bridge graph, as explained previously.[25,40,41] Even without doing the elaborate calculation, one can see that the contribution of this graph will extend beyond the distance $2(r_p^* + r_c^*)$, where r_p^* and r_c^* are the radii of the polyion and coion. This is consistent with the results of 2:2 electrolytes[40] and with our computer results for the counterion–counterion correlation function. These "collective interactions" between a polyion and several counterions may also explain why the "nearly universal" behavior of the bridge function seems to break down in this case. Because the counterions interact mainly on the surface of the polyion, and at the same time avoid contact with each other, there seems little reason to expect a faithful hard-sphere model bridge function for the counterion–counterion interaction in the usual range of packing fractions.

Nevertheless, we have attempted to improve the HNC calculation with a model, hard-sphere bridge function chosen empirically. Since the counterion–counterion correlation function is in most serious disagreement with the computer simulation, we have chosen to apply the corrections to this one function. In accordance with our computer simulations, we have chosen the reference hard-sphere diameter for the bridge function model to be $2(r_p^* + r_c^*) = 4.4$ nm. This is the range in which the counterion–counterion correlation function is affected by the presence of a polyion. With a choice of the reduced density of the reference hard-sphere liquid $\rho^* = 0.125$, we obtain the agreement displayed in Figure 7. It is interesting that a correction to $g_{cc}(r)$ also corrects $g_{pc}(r)$, while the improvement to $g_{pp}(r)$ is less significant and is not shown here. This example is designed to show only that a more serious study, similar to our electrolyte work,[29,41] is likely to yield a measurable improvement over the hypernetted chain approximation.

4. Conclusions

The comparison between the Monte Carlo simulations and the hypernetted chain integral equation indicates that HNC approximation is useful for asymmetric electrolytes in the range of parameters examined here. However, since its thermodynamic predictions are intrinsically inconsistent, it yields different results for the virial and the compressibility pressure. The essential defect is that the HNC theory overestimates the concentration of counterions close to the polyion, and moreover it substantially overestimates $g_{cc}(r)$ in a wide range of distances. This leads to an underestimate of the degree of structure in the solution. The position of the first peak in the polyion–polyion correlation function is at too short a distance, and its magnitude is too small. This fact should be considered when intermicellar structure factors, obtained from small-angle neutron scattering, are analyzed using the hypernetted chain equation. In addition, the HNC equation erroneously predicts spinodal decomposition in the region of complete mixing. The hypernetted chain approximation may be useful for studying the catalytic effect of the micelles on certain chemical reactions, where a substantial improvement over the traditional meanfield approach is needed.

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Ab Initio Study of Destabilized π-Conjugated Systems with Large π-Overlap: Sulfur Trimethylene and Chlorine Trimethylene Cation. Electrostatics as a Dominant Factor in Multiple Bonding for Second-Row Elements

Andrzej Rajca*,[1] **and Kee Hag Lee**[2]

Contribution from the Department of Chemistry, University of California,
Berkeley, California 94720. *Received July 28, 1988*

Abstract: Ab initio calculations at the MP2/6-31G**//HF/6-31G*/ZPVE level of theory indicate that conjugative stabilization in 6π-electron Y-conjugated systems, $X(CH_2)_3$ and XO_3 (X = P (anion), S (neutral), and Cl (cation)), is dominated by electrostatic interactions; that is, increasing the X–C overlap and decreasing X–C charge separation via change in electronegativity of X *decreases* stability of the D_{3h}-symmetric structures versus the structures with lower symmetry (less π-overlap). These energy patterns are reflected in properties of the electron densities (ellipticities at bond critical points, integated atomic populations, etc.) at the HF/6-31G* level for the D_3- and D_{3h}-symmetric structures; the more the atomic charges (relative electronegativities) approach or even exceed the formal charges of "no formal double bond" resonance structure, $X^{n+}(Z^-)_3$, the greater is the preference for the geometries where π-conjugation is feasible. $S(CH_2)_3$ (D_3), which is most predisposed to π-overlap, shows signs of a very weak bonding; it possesses a "pseudoatom" (local maximum of the electron density) and two bond critical points along each SC bond axis. For the ylide $S(CH_2)_3$, a double-well potential energy surface (PES) is found with two D_3-symmetric local minima that are 9 kcal mol^{-1} below the D_{3h}-symmetric transition structure for methylene rotation; 47 kcal mol^{-1} below the D_3-symmetric structure, a very flat fragment of the PES, which corresponds to the methylene thirane structure, is located. Preparation of the Y-conjugated $S(CH_2)_3$ (D_3) may be quite difficult but feasible in view of the fact that the barrier for its collapse to the global minimum is estimated as close to 6.0 kcal mol^{-1} (MP3/6-31G*//HF/6-31G*/ZPVE); IR and Raman spectra calculated at the HF/6-31G* level may aid the experiment.

Recent years have witnessed proliferation of multiple-bonded molecules containing elements beyond the first row.[3] Such molecules are generally quite unstable and, therefore, isolated either in a matrix or stabilized by sterically bulky substituents. Both experimental and theoretical works are predominantly confined to systems with just one multiple bond.[4] The next logical

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(1) Address correspondence to this author at the Department of Chemistry, Kansas State University, Manhattan, KS 66506. Miller Fellow, 1985–1987. Presented, in part, at the 196th National American Chemical Society Meeting, Los Angeles, 1988.

(2) On leave from Won Kwang University, Republic of Korea.

(3) Recent examples. C═Sn: Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546. C═Ge: Couret, C.; Escudie, J.; Satge, J.; Lazraq, M. *J. Am. Chem. Soc.* **1987**, *109*, 4411.

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