

ION PAIRING AND RELATED TOPICS

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Abstract - The Bjerrum theory of ion pairing may be regarded as an approximation method for calculating the thermodynamic properties of the restricted primitive model (essentially charged hard spheres in a dielectric medium) for an electrolyte solution. For this model, with parameters appropriate to a 2-2 electrolyte in water or a 1-1 electrolyte in ethanol, the structural implications of Bjerrum's theory are compared with the structural information in the ion-ion pair correlation functions $g_{+-}(r)$ and $g_{++}(r)$ obtained in a new series of hypernetted chain equation (HNC) calculations for the same model.

The degree of ion pairing implied by Bjerrum's theory is rather similar to the comparable functional of $g_{+-}(r)$, although there are percentage differences even at concentrations as low as 1mM. The $g_{++}(r)$ results are interpreted as showing that triple ions make a strong contribution to the solution properties even at concentrations as low as 10mM.

The implications of these results for the interpretation of data for the electrical conductivity of electrolyte solutions and of data for the concentration dependence of electron exchange reactions such as $Fe^{2+} + Fe^{3+} =$ exchange are briefly discussed.

INTRODUCTION

In 1926 N. Bjerrum showed that the Debye-Hückel theory could be extended by blending it in a certain way with the law of mass action for the assumed chemical equilibrium between ion pairs, which are electrically neutral, and the ions of the Debye-Hückel ion atmosphere (1). Bjerrum's theory has a much greater range of applicability than most other extended forms of the Debye Hückel theory. It is widely used in the molecular interpretation of data for the electrical conductivity for ionic solutions (2) and it is applicable to other aspects of ionic systems as well (3).

The Bjerrum theory can be thought of as an approximation method for evaluating the properties of a certain model for ionic systems, namely the restricted primitive model. In this model the particles are governed by classical mechanics with a potential function U_N that is pairwise additive

$$U_N(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{1 \leq i < j \leq N} u_{ij}(\mathbf{r}_i, \mathbf{r}_j) \quad (1)$$

with the following very simple form for the pair potential (written for $r \equiv |\mathbf{r}_i - \mathbf{r}_j|$)

$$\begin{aligned} u_{ij} &= \infty & \text{if } r < R_{ij} \\ &= e_i e_j / \epsilon r & \text{if } r > R_{ij} \end{aligned} \quad (2)$$

These are the equations for the primitive model (4), roughly for charged hard spheres in a medium of dielectric constant ϵ . The relation of this model to real solutions has recently been elucidated by Høye and Stell (5). In the restricted primitive model we also assume that there are just two species of ions of the same size (i.e. all $R_{ij} = R$) and they have the same magnitude of charge.

The states of the restricted primitive model may be represented in terms of the reduced temperature (6)

$$T_r = R/b \quad (3)$$

where b , the so-called Bjerrum length or Landau length, is given by

$$b \equiv |z_+ z_-| e_{el}^2 / \epsilon k_B T, \quad (4)$$

where $-z_i e_l$ is the charge on a particle of species i , and the reduced density

$$\rho_r \equiv \frac{\pi}{6} \frac{N_+ + N_-}{V} R^3, \quad (5)$$

where N_i is the number of particles of species i in a system of volume V . The correspondence with real systems is made by assigning realistic parameters z_i , ϵ , and R to the latter (6). Figure 1 shows the "Bjerrum line", the locus of states in which, according to Bjerrum's theory, half of the ions are paired and half contribute to the ion atmosphere. Figure 1 also shows the locus of states with minimum electrical equivalent conductivity according to the theory of Fuoss and Kraus (7), and the coexistence curve that characterizes ionic systems, all calculated for the primitive model. The coexistence curve for this model is as yet poorly known; the curve in Figure 1 is based upon a combination of theory for the primitive model together with experimental data for real ionic systems (6).

The Bjerrum theory fails to give the coexistence curve shown in Figure 1 (6). Since the 2-2 aq. isotherm lies near the coexistence curve in Figure 1, one may doubt whether Bjerrum's theory is reliable on the 2-2 isotherm at densities $\rho_r > 10^{-2}$, where the two lines are close to each other. To test this point results from Bjerrum's theory are compared with those from the HNC integral equation (6) applied to the same model, all for states along the isotherm for 2-2 aqueous electrolytes in Figure 1. A similar study was recently made by Rasaiah (8), and some time before that, using a numerical solution to the full Poisson-Boltzmann equation for the primitive model, by Guggenheim (3).

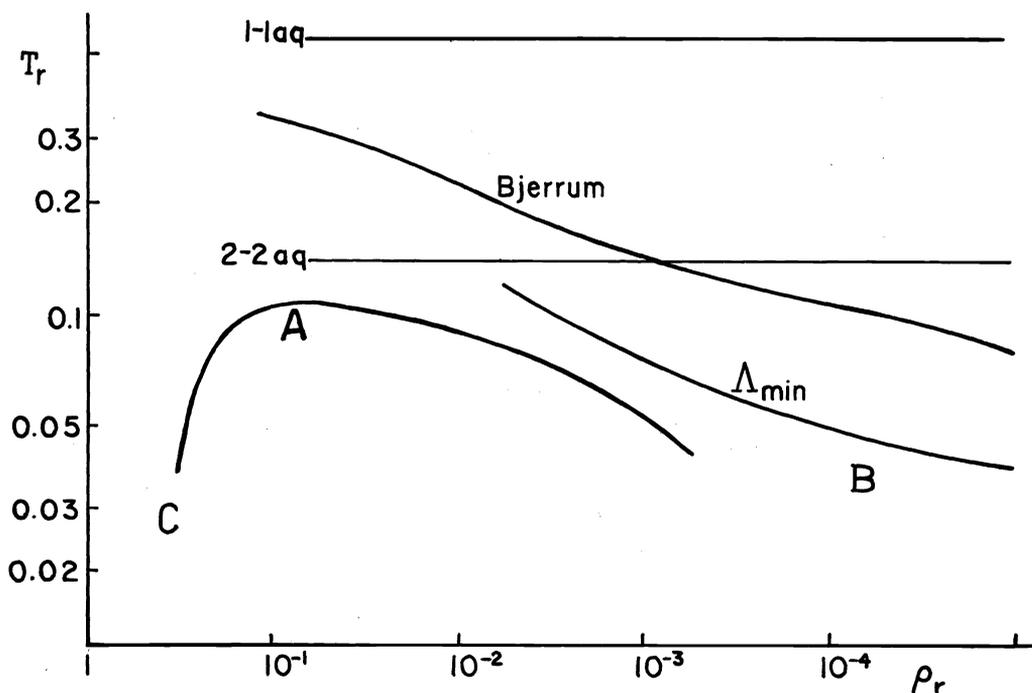


Fig. 1. The corresponding states diagram for an ionic fluid (6). Curve A is the estimated coexistence line for the restricted primitive model. Region B is typical of electrolyte solutions in weakly polar solvents while region C is typical of fused salts. The line 1-1 aq (2-2 aq) is the locus of states of a 1-1 (2-2) electrolyte in water at 25°C, assuming that $R=4\bar{R}$.

Bjerrum (1) assumed that the ionic solution had a certain structure, namely a mixture of ions and ion pairs. On the other hand, in either the full Poisson-Boltzmann equation or the HNC approximation method the structural features as well as the measurable properties are deduced from the model's Hamiltonian. It seems possible and useful to go somewhat beyond Guggenheim and Rasaiah to compare the actual structural features of the primitive model with those assumed by Bjerrum. It is especially interesting to do so along the isotherm for 2-2 aqueous electrolytes because, as noted above, this passes close to the coexistence curve (Fig. 1) where we already know (6,9,10) that there is a dominant structural effect, namely phase separation, that is missed by Bjerrum's theory.

The states on this isotherm also are close to those for solutions of 1-1 electrolytes in solvents with dielectric constant 20.

of r at zero concentration is used by Bjerrum to classify ion pairs; namely a cation and an anion whose separation is smaller than r_{\min} is an ion pair. Since r_{\min} , the value of r at which $r^2 g_{+-}(r)$ is a minimum, is a rather strong function of concentration (Fig. 2) we see that Bjerrum's classification becomes concentration dependent, a feature that is not accounted for by Bjerrum's theory. In fact $r_{\min} = b/2$ only at zero ion concentration.

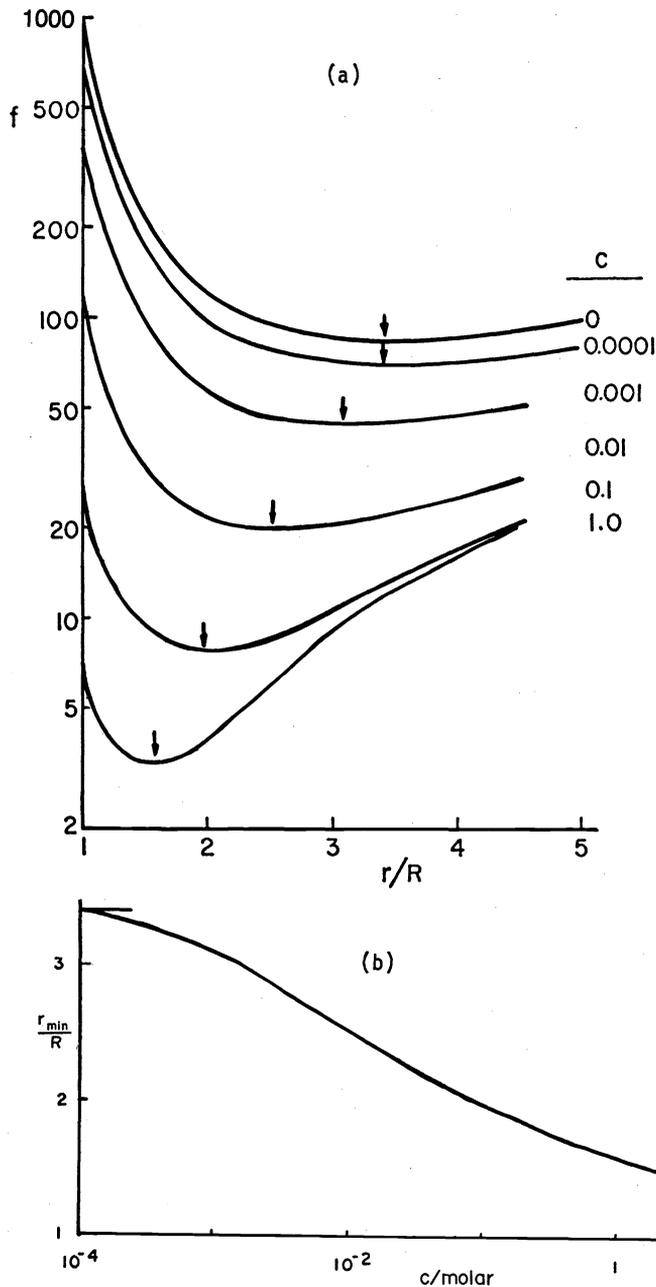


Fig. 2. a. The function $f = (r/R)^2 g_{+-}(r)$ at various concentrations (6). The arrows indicate the minima.
 b. The resulting r_{\min} , the value of r at the minimum, as a function of concentration.

To pursue this structural aspect we notice that, for a given choice of r_p , the Bjerrum theory α is related to the pair correlation function $g_{+-}(r)$ by the equations

$$\alpha = n_{+-}(r_p) \tag{11}$$

where, for any distance r' and any pair of species i and j , the running coordination number is defined as

For the rest we deal with the restricted primitive model. For real ionic systems, solutions as well as pure salts and plasmas, the primitive model is merely a caricature of the Hamiltonian. To elucidate the differences between the real Hamiltonian and the primitive model Hamiltonian one may compare measurable properties calculated from the latter with experimental properties. Recently Justice and Justice (2) and Barthel, Wachter, and Gores (2) have reported interesting results obtained in this way by the use of Bjerrum's theory or certain generalizations of it, so it is especially interesting to ask how faithfully the Bjerrum theory represents the primitive model.

In Section II the Bjerrum theory equations are summarized. Comparison with the results for some new HNC calculations for the same model are presented in Section III. In Section IV we present new results for the "pairing" of like-charged ions, deduced from the same calculations. These results are completely outside the scope of the Bjerrum theory and are relevant to certain experimental measurements on systems related to, but more complicated than aqueous 2-2 electrolytes.

SECTION II - BJERRUM THEORY

Writing C for cations and A for anions, with the charges suppressed, we define K as the equilibrium constant for the reaction of the ions to form pairs,

$$A + C = AC \quad (6)$$

If the primitive model is assumed then the equilibrium constant is given by

$$K = F \int_R^{r_p} e^{b/r} 4\pi r^2 dr \quad (7)$$

where r_p is the longest possible distance between A and C in a pair, F is a proportionality constant depending upon the units of the concentration c, and b is given by Eq.(4). The equilibrium constant also obeys the equation

$$K = \alpha/c(1-\alpha)^2 \gamma_{\pm}^2 \quad (8)$$

where α is the fraction of the free ions that are paired and γ_{\pm} is the mean activity coefficient of the free ions, assumed to be given by the equation

$$\ln \gamma_{\pm} = - \frac{1}{2} \kappa / (1 + \kappa) \quad (9)$$

where κ , the Debye kappa for the unpaired ions, is given by

$$\kappa = (8\pi b c (1-\alpha))^{1/2} \quad (10)$$

Bjerrum's choice for r_p , namely $r_p=b/2$, has been very widely discussed; a new aspect is presented in Section III. The most consistent choice for the length a seems to be $a=r_p$ (2), but other choices are often made (3,8,9). In this paper, references to the Bjerrum theory assume $a=r_p=b/2$ unless other values are specified.

SECTION III - COMPARISON OF BJERRUM AND HNC RESULTS

Like Rasaiah and Guggenheim we find that the Bjerrum theory gives reasonably accurate osmotic coefficients for the primitive model for aqueous 2-2 electrolytes. In fact ϕ from the Bjerrum theory agrees with ϕ calculated by the virial equation from the correlation functions yielded by the HNC approximation better than the results of the virial equation agree with the compressibility equation (6). In other words, the disagreement between the Bjerrum and HNC osmotic coefficients is within the uncertainty of the latter. Rather similar results are obtained using the modification of Bjerrum's theory in which one uses the expression for K assumed by Fuoss (11). Another version of the Bjerrum theory, in which $r_p=b/2$ and $a=R$ gives osmotic coefficients that are substantially too high, although this version does give a critical point near that in Fig. 1 (6,12). The osmotic coefficients ϕ are related to the activity coefficients by the Gibbs-Duhem equation, so the results for the latter will also be nearly the same for the Bjerrum theory as for the HNC equation.

The pair correlation function $g_{+-}(r)$ calculated from the HNC equation (13a) is shown in Fig.2 (The local concentration of a particle of species i in the solution at a distance r from a particle of species j is $c_i g_{ij}(r)$, where c_i is the overall or stoichiometric concentrations of species i. The pair correlation functions are structural quantities that may be calculated, at least approximately, for a given model system and they are closely related to the results of suitable diffraction experiments upon real systems (13a). Given the correlation functions and the Hamiltonian for a model system one can calculate most other equilibrium properties without further approximation if Eq. (1) applies (13a).) What is actually plotted in Fig. 2 is the function $r^2 g_{+-}(r)$ because the minimum in this particular function

$$n_{ij}(r') = (N_i/V) \int_0^{r'} g_{ij}(r) 4\pi r^2 dr, \quad (12)$$

the average number of particles of species i within distance r' of a particle of species j . In Fig. 3 we see that, at low concentration, α calculated from the Bjerrum theory and $n_{+-}(b/2)$ agree quite well but that at higher concentrations they become quite different and $n_{+-}(b/2)$ even exceeds unity, an indication of the formation of larger than two-ion clusters in the model system. Such clusters are not allowed for in Bjerrum's theory.

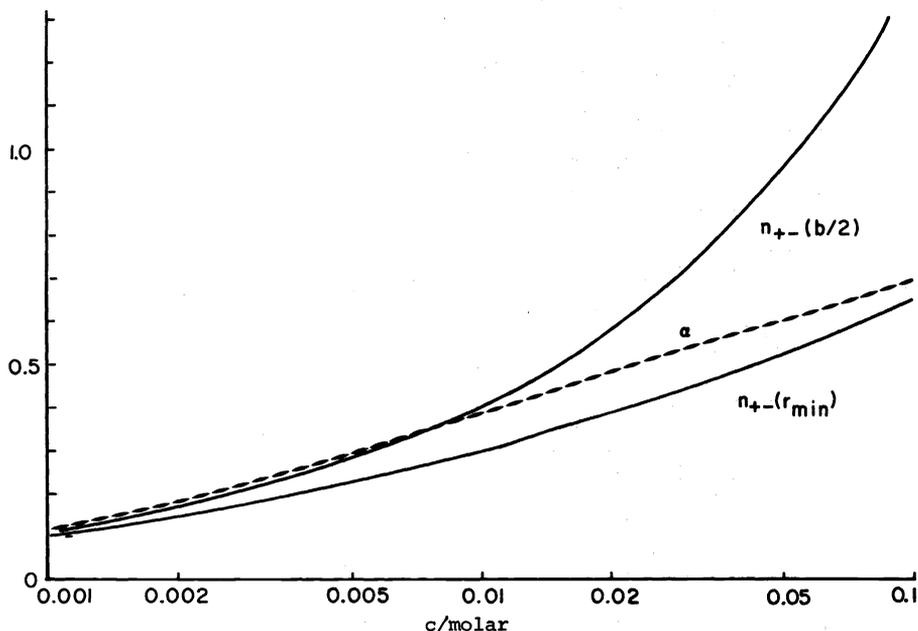


Fig. 3. The fraction of ions paired (α , Bjerrum) and the running coordination numbers $n_{+-}(b/2)$ and $n_{+-}(r_{\min})$, both calculated by HNC, as functions of concentration.

In Fig. 3 we also show $n_{+-}(r_{\min})$, where r_{\min} is defined above in terms of the minimum in $r^2 g_{+-}(r)$ as a function of r . A version of Bjerrum's theory in which an AC pair was defined in terms of a maximum separation $r_p = r_{\min}$ would yield values of α that should be compared with $n_{+-}(r_{\min})$. However such a version would not be a complete theory since the determination of the $g_{+-}(r)$ functions needed to find r_{\min} requires the use of some other theory, such as the HNC equation used here.

To bring out the significance of these results we consider one of the widely used conductivity equations that gives the equivalent conductance as a function of the free ion concentration $(1-\alpha)c$. The discussion above leads to the suggestion that an improvement might be the replacement of $(1-\alpha)c$ by $(1-n_{+-}(r_p))c$, which has the same sense as the former but which liberates us from dependence upon Bjerrum's theory. How should r_p be chosen? Figure 3 shows that whether one uses α or $n_{+-}(b/2)$ or $n_{+-}(r_{\min})$ changes the concentration of "free" ions by as much as 10% even at a concentration as low as 1mM and may have even much greater effects at higher concentration. Errors of the same order are expected to appear in the equilibrium constants derived from any of the usual combinations of a conductivity equation with the Bjerrum theory, even if there are no other sources of error in the conductivity equations themselves. (Still another definition of ion pairs, in terms of the "partners correlation function", is considered in reference 6.)

It may be inferred that further advances in the molecular interpretation of experimental data for systems in which ion pairs are important depend upon methods which allow for the contribution of all ionic configurations to the property measured. While this already is possible for the calculation of thermodynamic properties, at least within the accuracy of the HNC equation or the Monte Carlo simulation method, for transport coefficients such powerful methods are not yet available, except possibly Brownian Dynamics (13b).

On the other hand, for the calculation of the effects of composition changes upon the rate constants of chemical reactions the ionic interaction part of the theory is somewhat easier (14,15). The overlap of the electronic wave functions of the reacting particles, say i and j , is only important at small separation so that the rate of an activation-controlled reaction tends to vary with composition in the same way as $g_{ij}(r)$ at a value of r corresponding to a collision of the two particles; in the present context $g_{ij}(R)$ may be a useful guide. The discussion above shows that Bjerrum's theory is a qualitative guide to the structural features related to $g_{+-}(r)$ so one may expect that for an activation-controlled reaction of a cation with an anion a calculation via Bjerrum's theory of the change in a rate constant due to variations in the solution composition (i.e., assume that the rate of reaction is proportional to the concentration c of ion pairs) will be qualitatively in agreement with the calculation of the same effect using the HNC-derived $g_{+-}(R)$ in Figure 4.

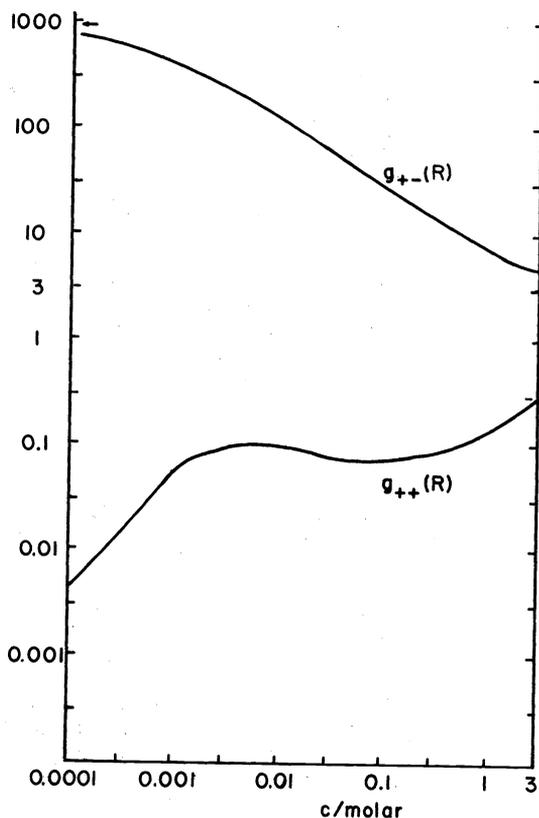


Fig. 4. Correlation functions at "contact" $g_{+-}(R)$ and $g_{++}(R)$ as functions of concentration. The arrows on the left-hand scale show the limiting values at vanishing concentration of the electrolyte.

Using the same reasoning as in the application of Bjerrum's theory to the reaction of an anion with a cation, one would conclude that if i and j were both cations then the rate of a chemical reaction between them would increase uniformly with increasing ionic strength, in contrast to the actual behavior of $g_{++}(R)$ which also is shown in Fig. 4. This observation motivated the study of the cation-cation interaction in the primitive model for aqueous 2-2 electrolytes as described in the following section.

SECTION IV - INTERACTION OF LIKE CHARGED IONS

Because of symmetry in the restricted primitive model one has $g_{++}(r) = g_{--}(r)$ so the following discussion, which is couched in terms of cation-cation interactions for simplicity, has a counterpart in terms of anion-anion interactions.

The concentration dependence of $g_{++}(R)$, shown in Fig. 4, is quite remarkable, especially in comparison with the much simpler $g_{+-}(R)$. Especially interesting is the fact that in the experimentally important range from 0.001M to 1M one finds that $g_{++}(R)$ is constant within a factor of two at a value two orders of magnitude larger than its limiting value at zero ion concentration. The essential features of $g_{++}(R)$ may be found in the work of Rasaiah (8),

although the new HNC computations reported here differ from the earlier ones in respect to $g_{++}(R)$ more than in the other coefficients reported.

A useful insight into the behavior of $g_{++}(r)$ in Fig. 4 comes from the graph of $g_{++}(r)$ as a function of r at several concentrations (Fig. 5). In the range from 0.0004M and up there is a well defined maximum in g_{++} at $r_{\max} \approx 2R$. The presence of this maximum implies that there is an important contribution to $g_{++}(r)$ for $r < 2R$ from triple ions $+++$. The most stable configuration of such a triple ion would be the linear one with a $2R$ separation between the cations; for bent configurations one would have $R < r < 2R$ and smaller $g_{++}(r)$ owing to the electrical work of bringing the two cations closer together, just as shown in Fig. 5. At very low concentrations there is no maximum in $g_{++}(r)$, hence no contribution from triple ions, presumably because there are so few ion pairs.

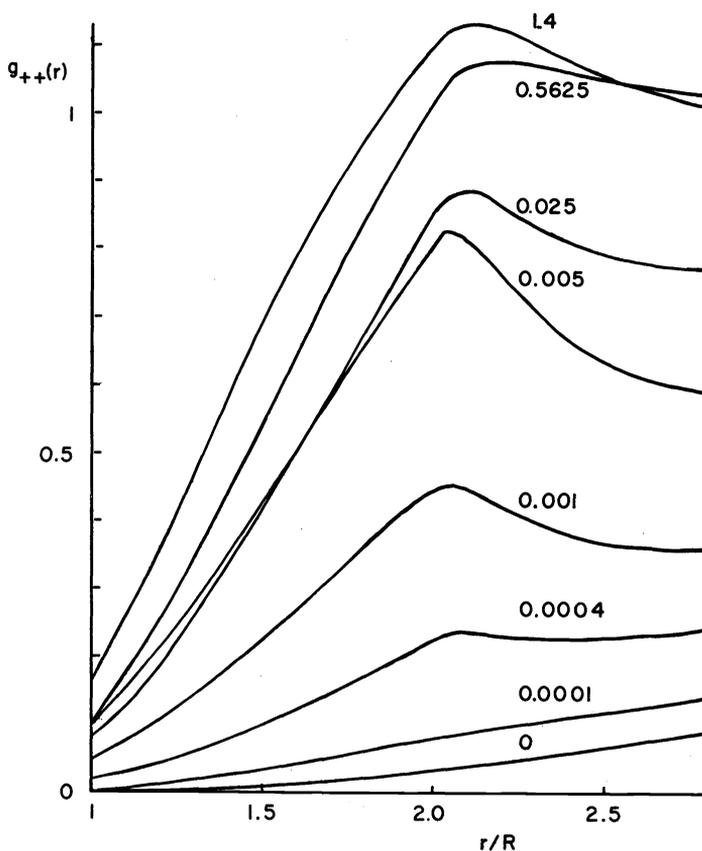


Fig. 5. Examples of $g_{++}(r)$ for various molarities.

The concentration dependence of r_{\max} is shown in Fig. 6. Part of its complexity may be attributed to the fact that the structure of the solution changes markedly near $c=0.03M$, judging from the behavior of functions related to g_{+-} (6).

Another aspect of these results is shown in Fig. 7 where the concentration dependence of $g_{++}(r)$ in the range $R \leq r \leq 2R$ is shown. From 0.001 to 0.01M the relative concentration dependence $\partial \ln g_{++}(r) / \partial c$ is rather precisely independent of r while even above this range the dependence is still rather weak. As also shown in the figure, the ratio of $n_{++}(2R)$ to the molarity is quite constant at a value near 0.7 in this concentration range. Thus at 5mM about 0.3% of the cations have a cation neighbor within a distance $2R$ while at 100mM 7% of the cations have such neighbors. These close cation pairs are, following the conclusion reached above, members of a triple ion. Such a triple ion contributes to the conductivity but is not allowed for in any of the contemporary conductivity theories, an omission that perhaps leads to percentage errors in the calculated conductivity for models with parameters close to those for 2-2 aqueous electrolytes.

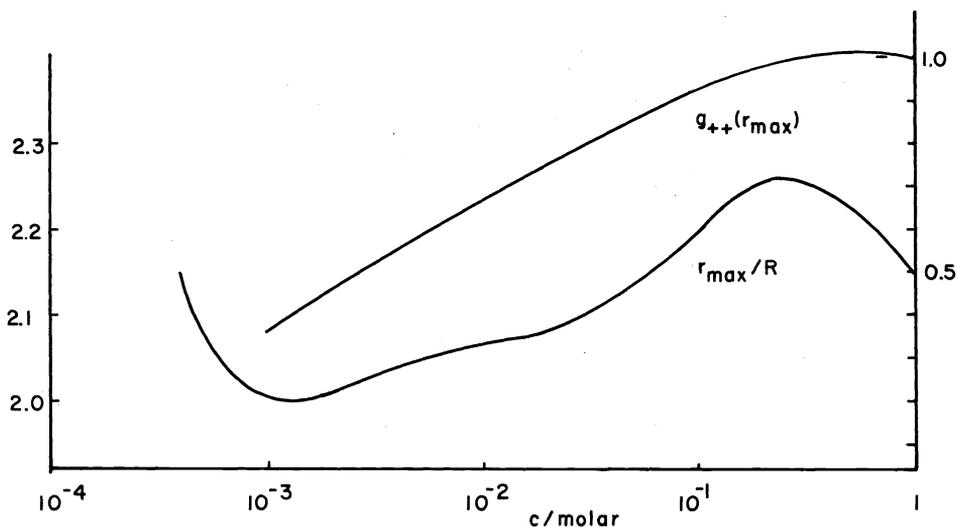


Fig. 6. The concentration dependence of r_{\max} , left scale, and $g_{++}(r_{\max})$; right scale.

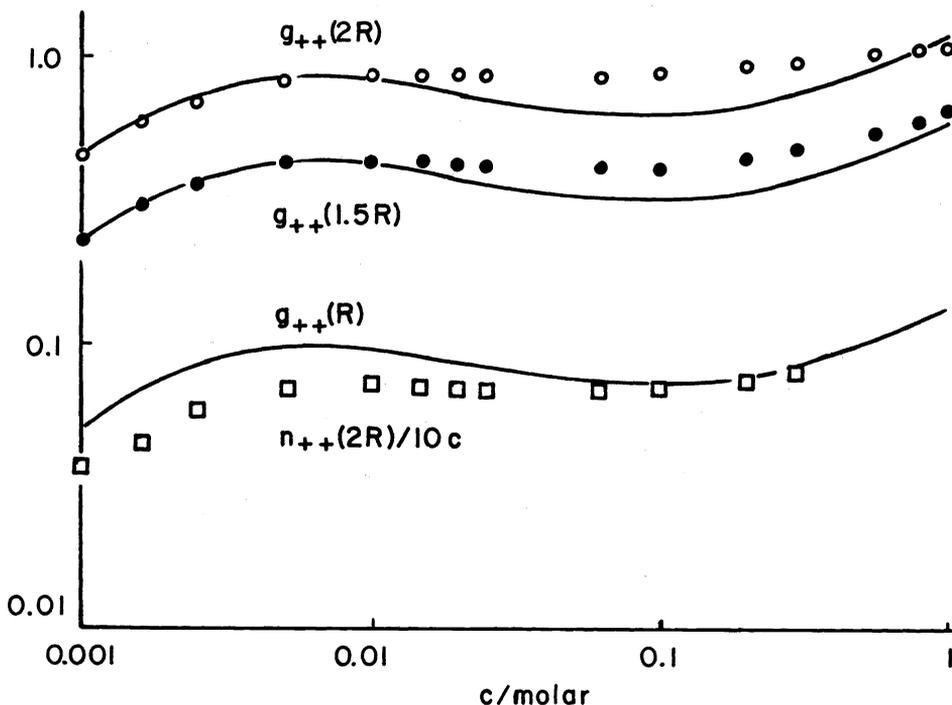


Fig. 7. The concentration dependence of $g_{++}(r)$ and $n_{++}(r)$ for r -values in the triple-ion range. The results for $g_{++}(R)$ are represented by the curve so labeled, the other results by data points. The other curves are obtained by shifting the $g_{++}(R)$ curve upwards to facilitate the intercomparison of these results.

The present results for $g_{++}(r)$ also may be relevant to certain observations in experimental chemical kinetics, for which we choose as an example the exchange of an electron between Fe^{2+} and Fe^{3+} in dimethyl sulfoxide (DMSO, $\epsilon = 46.4$ at 25°C). The experiments show (16) that the rate of the electron exchange is independent of ionic strength in the range from 0.01 to 0.2M, where the ionic strength is varied by addition of NaClO_4 . Letting $g_{23}(r)$ be the pair correlation functions of species Fe^{2+} , Fe^{3+} we see that the rate constant for this activation-con-

trolled reaction will be proportional to $g_{23}(R_{23})$, where R_{23} is the distance of closest approach of the two ions. If we may use the average Bjerrum length $b = 31\text{\AA}$ for the Fe^{2+} , ClO_4^- and Fe^{3+} , ClO_4^- interactions in DMSO, and an effective diameter of $R=5\text{\AA}$ for these interactions then we have $T_r=R/b=0.16$ compared to 0.1468 for the restricted primitive model for aqueous 2-2 electrolytes. On this basis we expect that a primitive model calculation for $g_{23}(r)$ would yield results that are qualitatively similar to $g_{++}(r)$ shown in Figs. 4 and 5. In particular we expect that over a wide range of ionic strength $g_{23}(R_{23})$ will be nearly constant and much larger than its value at zero ionic strength; and that this behavior is associated with the formation of an ion triple, Fe^{2+} , ClO_4^- , Fe^{3+} . On the other hand Menashi, Reynolds, and Van Auken (16) concluded from the lack of dependence of the rate constant upon ionic strength that ClO_4^- was not present in the transition state. It seems that this conclusion can not be firmly held in view of the fact that the primitive model calculations would predict this lack of dependence upon ionic strength even though a triple ion is involved.

It may be concluded that Bjerrum's theory is remarkably accurate for calculation of the osmotic coefficient but is less satisfactory for structural implications related to +- ion pairs. For ++ or -- pairs the HNC approximation method leads to remarkable conclusions that are altogether missed by Bjerrum's theory.

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