

**AN ANALYTIC SOLUTION OF THE  
NON-LINEAR EQUATION  $\nabla^2\lambda(r) = f(\lambda)$  AND ITS APPLICATION TO  
THE ION-ATMOSPHERE THEORY OF STRONG ELECTROLYTES**

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**ABSTRACT.** For a long time the formulation of a mathematically consistent statistical mechanical theory for a system of charged particles had remained a formidable unsolved problem. Recently, the problem had been satisfactorily solved, (see Bagchi [1] [2]), by utilizing the concept of ion-atmosphere and generalized Poisson-Boltzmann (PB) equation. Although the original Debye-Hueckel (DH) theory of strong electrolytes [3] cannot be accepted as a consistent theory, neither mathematically nor physically, modified DH theory, in which the exclusion volumes of the ions enter directly into the distribution functions, had been proved to be mathematically consistent. It also yielded reliable physical results for both thermodynamic and transport properties of electrolytic solutions. Further, it has already been proved by the author from theoretical considerations (cf. Bagchi [4]) as well as from a posteriori verification (see refs. [1], [2]) that the concept of ion-atmosphere and the use of PB equation retain their validities generally. Now during the

past 30 years, for convenience of calculations, various simplified versions of the original Dutta-Bagchi distribution function (Dutta & Bagchi [5]) had been used successfully in modified DH theory of solutions of strong electrolytes. The primary object of this extensive study, (carried out by the author during 1968-73), was to decide a posteriori by using the exact analytic solution of the relevant PB equation about the most suitable, yet theoretically consistent, form of the distribution function. A critical analysis of these results eventually led to the formulation of a new approach to the statistical mechanics of classical systems, (see Bagchi [2]). In view of the uncertainties inherent in the nature of the system to be discussed below, it is believed that this voluminous work, (containing 35 tables and 120 graphs), in spite of its legitimate simplifying assumptions, would be of great assistance to those who are interested in studying the properties of ionic solutions from the standpoint of a physically and mathematically consistent theory.

KEY WORDS AND PHRASES. Statistical Mechanics of Solutions, Electrolytes, Plasmas, Non-linear Partial Differential Equation, Theoretical Physics.

SUBJECT CLASSIFICATION CODE: 0024, 0064, 1150, 1160.

## I. INTRODUCTION.

In a previous publication in this journal, (Bagchi [2]), a new approach to the statistical mechanics of classical systems based on the partition of the phase-space ( $\mu$  - space) into configuration space and momentum space and on the concept of ion-atmosphere had been proposed. This approach had been found to be mathematically consistent and led to physically reliable results for dense systems also. In particular, even in the linear approximation of the ion-atmosphere potential, this technique yielded satisfactory results for both thermodynamic and transport properties of fused alkali halides. These results verified conclusively the previous theoretical proof, (see Bagchi [4]), that the ion-atmosphere concept and the generalized Poisson-Boltzmann equation remain valid generally for any system of charged

particles interacting with Coulomb forces. It is to be noted in this connection that for such systems one cannot even formulate a mathematically consistent theory if one follows the traditional techniques. Consequently, it can safely be asserted that at the present stage of our knowledge, the techniques adopted in this new approach offer us the only feasible method to tackle any classical system at any density in a rigorous manner.

The concept of ion-atmosphere, which plays a central role in this new approach, was first introduced by Debye & Hueckel [3] in order to calculate the "excess" free energy of a system due to Coulomb interaction between the charged particles. The original DH theory, however, cannot be accepted even as a limiting theory for infinitely dilute solutions. It suffers from many mathematical and physical inconsistencies, mainly due to the fact that it cannot incorporate short range repulsive forces in the framework of the theory. Both the original DH theory and Gibbs' configuration integral become mathematically meaningless if one takes into account only the Coulomb forces. If, however, one incorporates polarisation forces and short range forces, one cannot use PB equation of the original DH theory. Also, in this case a direct evaluation of Gibbs' phase integral becomes almost impossible. Consequently, during the last fifty years many workers have tried to improve upon the original DH theory by using arbitrarily and in an ad hoc way various recipes. It is now generally believed, (albeit erroneously), that Mayer-McMillan theory offers a rigorous approach to the problem of ionic solutions. But a careful scrutiny of the foundation of this theory, (cf. Friedman [6], [7]; Anderson [8]), would reveal that this theory is also based on a convenient recipe, specifically invented to avoid divergence difficulties of the original DH theory, which has no theoretical foundation within the formalism of Mayer's cluster integral technique. The extensive literature on the subject of the ion-atmosphere theory of strong electrolytes contains many conclusions which cannot be justified if one insists on a theoretically consistent approach. Further, many of the fundamental objections raised

against the ion-atmosphere theory have already been proved to be either irrelevant or inapplicable for the DH model of the actual system. Various modifications of the original DH theory as well as objections raised against the ion-atmosphere concept itself and the DH technique for calculating the "excess" electrostatic free energy of the system had been critically discussed in the previous paper, (Bagchi [2]), and will not be repeated here. As had been mentioned there, the only feasible way in which the problem of a system of charged particles and, in particular, of ionic solutions can be tackled in a mathematically and physically consistent way is to utilize the DH technique for calculating the electrostatic free energy of the system by using a new distribution function, instead of the Boltzmann distribution used by Debye & Hueckel, which incorporates directly the exclusion volumes of the ions. This permits one to use modified Poisson-Boltzmann equation. The repulsive forces being taken into account in the exclusion volume, the theory becomes mathematically and physically consistent. The polarization forces are also indirectly taken into account by the macroscopic dielectric constant of the medium. Thus the problem becomes tractable as well as mathematically rigorous, though one might consider this modified DH theory still as a legitimate approximation due to the fact that the medium is treated as a continuum with a fixed dielectric constant. It is interesting to note here that if one uses the low value, ( suggested by the work of Hasted et al [9]), of the dielectric constant of aqueous solutions instead of the macroscopic value ( 78.3) of pure water, calculated results become physically unacceptable. This points out our lack of knowledge regarding the detailed structure of water molecules in the neighbourhood of ions. Consequently, in view of additional uncertainties inherent in the nature of the system to be discussed below, it would be a futile exercise to try to formulate a more exact theory. However, it may be noted that such an exact theory can be formulated with the help of this new approach by taking into consideration water molecules also as discrete particles and by incorporating all types of forces and a suitable partial differential equation in

the formalism of the theory.

During the last 30 years, the work of various authors on the modified DH theory have been proved to be not only mathematically consistent but also yielded reliable physical results both for thermodynamic and for transport properties of solutions of strong electrolytes even at high concentrations, (see references [10], [11], [12]). Now, in modified DH theory several parameters which enter into the theory cannot be unequivocally determined from theoretical considerations, although they are conceptually well defined. Consequently, in view of all these uncertainties and for convenience of calculation, in the literature several models were chosen for these parameters in order to obtain good agreement between calculated and experimental values.

The exact solution of the generalized Poisson-Boltzmann equation  $\nabla^2\lambda(r) = f(\lambda)$ , obtained first by Bagchi, Das and Chakravarti [13], gave excellent results for the nonlinear potential of the system for the case of the original DH theory, (see Bagchi & Plischke [14]), in complete agreement with those calculated by Guggenheim [15] with the help of an electronic computer. It was therefore decided to calculate the exact nonlinear potential  $\lambda(r)$  and activity coefficients for various models of the modified DH theory as well as for the original DH theory for fixed values of the various relevant parameters.

The principal aim of this extensive study was not to get the results to fit the experimental values, namely, the mean activity coefficients, but to decide a posteriori about the most suitable, yet theoretically consistent, form of the distribution function of the ions around a central ion. Further, it was expected that the voluminous results for different values of the relevant parameters would permit one to choose correctly the appropriate effective radius of the ion, the exclusion volumes as well as the nonlinear potential for the actual system of interest without undertaking too many laborious calculations. It might be noted that once these parameters are chosen properly for a system, its thermodynamic

properties are given uniquely throughout the concentration range without incorporating any further ad hoc assumptions.

For simplicity as well as due to the fact that most of the literature was confined to binary electrolytes, we shall also deal here with only such systems.

Comparison of the calculated and experimentally obtained activity coefficients indicates that the most satisfactory distribution function of ions around a central ion 'i' is given by

$$n_{\pm}(r) = \frac{1}{b} \frac{1}{[A_{\pm} \exp \left( \frac{e_i \psi_i}{kT} \right) + 1]} \quad (1.1)$$

where  $b = \gamma b_0$ ;  $b_0 = \frac{4}{3} \pi (r_+ + 2 r_{H_2O} + r_-)^3$ ;

$$A_{\pm} = \frac{1}{n_{\pm}^+ b} - 1 \quad (1.2)$$

$\gamma$  denotes the overlap - correction factor for the given system.

$r_{\pm}$  are the crystallographic radii of the ions and  $r_{H_2O}$  that of water.

(For the meaning of other symbols, see Sec. 3, p. 16)

In the literature the model A of (1.1) where  $r_+ = r_- = a$ , the effective average radius of the ions, and  $b = \frac{4}{3} \pi a^3$  had been used most widely. It is capable of reproducing satisfactorily equilibrium and nonequilibrium properties of solutions of electrolytes even at high concentrations, (see references [11] and [12]). Unfortunately, most often such overlap - uncorrected exclusion volume  $b$  becomes physically inconsistent, namely,  $(n_0^+ b + n_0^- b)$  becomes greater than unity. Further, in these calculations one used the linear approximation of the ion-atmosphere potential. Consequently, such agreement cannot be relied upon for quantitative verification of the theory, since the present investigation shows that there are significant differences between linear and nonlinear values. But for large values of  $a$  ( $>2\text{\AA}$ ) and for large concentrations ( $c > 2N$ ) the differences tend to become smaller, specially for 1-1 electrolyte.

For the sake of comparison we have used this model A as well as the model B

in which we have also set  $r_+ = r_- = a$ , but  $b = \frac{4}{3} \pi (a + r_{H_2O})^3$ . Obviously, this represents the average hydrated ionic volume and cannot give the correct exclusion volume.

As had been discussed before, (cf. [2]), it is almost impossible to calculate exactly the correct  $b$ . But if one uses (1.1), one can determine the only unknown parameter  $\gamma$  from a comparison of theoretical results with the experimental values by trial and error. But in this investigation we have not attempted to carry out this programme, since our aim was to determine the correct distribution function.

The distribution function (1.1) implies the partition of the configuration space into cells of equal size  $b$  for the distribution of two kinds of ions. As discussed before, (cf. [2]), this mode of distribution has considerable theoretical justification and does not suffer from physical inconsistencies encountered in other distribution functions.

It is interesting to note that this distribution can be obtained through a non-permissible approximation of the original Dutta-Bagchi distribution function (1.3):

$$n^\pm(r) \frac{1 - n^\pm(r) b_{\pm}}{b_{\pm} [A_{\pm} \exp(e_1 \psi_1 / kT) + 1]} \quad (1.3)$$

(For the meaning of the symbols see Section 3, p. 16)

The distribution function (1.1) was later derived by Wicke & Eigen [16] as well as by Falkenhagen [11]. None of these derivations appear to be satisfactory. All the distribution functions used in modified DH theory and their modes of derivation had been critically discussed and scrutinised in the previous paper (Bagchi [2]) and a new rigorous method of deriving the distribution function of the type given in eq. (1.1) had been proposed there. In this new method of derivation the two kinds of particles are distributed independently in the cells of the configuration space. One can therefore use different exclusion volumes

for different ions. But if one uses Boltzmann's concept of exclusion volume and takes this as the cell size of the configuration space, then it is much more justifiable to use the same cell size  $b$  for both the ions. Detailed investigations on simpler systems as fused alkali halides, where the situation is not complicated by the presence of water molecules, showed that for thermodynamic and transport properties much better results were obtained by using the same exclusion volume  $b$  and the actual crystallographic radii of the ions for calculating the ion-atmosphere potential on the surface of the ion where the boundary condition of the PB equation is applied. But in ionic solutions where the positive ions are usually permanently hydrated and where at least a layer of water molecules separates adjacent unlike ions, ' $a$ ' is to be taken as the hydrated ionic radius and not the crystallographic one. But one must also remember special cases. For example, large cations like  $\text{Cs}^+$  and anions are generally not hydrated. Also, small cations like  $\text{Li}^+$  can be embedded inside the tetrahedral structure of water molecules.

Finally, if we recall that the correct form of any physical statistics can be determined only a posteriori, it is found that the correct distribution function has the same form as the expression (1.1), but the relation between the exclusion volume  $b$  and the distance  $a_1$ , where the boundary condition of the PB equation is to be taken, has to be determined from the overlap-correction of Boltzmann's covering sphere and by taking into consideration that at least a layer of water molecules separates the adjacent unlike ions. In spite of the difficulty of calculating the exact value of  $b$ , it is reassuring to know that the expression (1.1) is theoretically consistent and reasonably approximate values of the parameters are adequate enough to predict satisfactorily the physical properties of the ionic solutions without any ad hoc assumption outside the formalism of the ion-atmosphere concept and the framework of the modified DH theory. But this valuable and extremely helpful insight was obtained



by detailed and rigorous comparative studies of all versions of the ion-atmosphere theory.

The starting points of this investigation are:

- (i) The calculation of the exact nonlinear potential  $\lambda(r)$  of the relevant Poisson-Boltzmann (PB) equation.
- (ii) The original Dutta-Bagchi distribution function, the expression (1.3), which leads to the distribution function (1.1) as well as to Boltzmann distribution function.

The insight that the distribution function (1.3) suffers from several practical difficulties and physical inconsistencies and that the correct distribution function has the form (1.1) which can be derived rigorously without any approximation came from this study and the problem had been discussed in the previous paper (Bagchi [2]) and will not be discussed here again.

## 2. AN ANALYTIC SOLUTION OF $\nabla^2\lambda(r) = f(\lambda)$ .

Our problem is to find a spherically symmetric solution of the above differential equation, i.e., of the equation

$$\frac{d^2\lambda}{dr^2} + \frac{2d\lambda}{rdr} = f(\lambda) \quad (2.1)$$

for  $r \geq a$  with the boundary conditions

$$\lambda \rightarrow 0 \text{ as } r \rightarrow \infty \text{ and } \left(\frac{d\lambda}{dr}\right)_{r=a} = C, \text{ (a constant),} \quad (2.2)$$

The existence and uniqueness of the solution of (2.1) with the boundary conditions (2.2) had been proved by Gronwall [17]. Mathematicians had studied the equation  $\nabla^2\lambda = f(\lambda)$  without boundary conditions but their concern was mainly to discuss the growth condition on  $f(\lambda)$  which would ensure the existence of an entire solution. Keller [18] generalized the previous work of mathematicians on this topic.

But physicists need an explicit series solution in order to test a theory and to apply it to specific problems. To my knowledge, no explicit analytic solution of the generalized equation (2.1) with the boundary conditions (2.2) was known before the work of Bagchi et al [13]. They obtained a solution in the form of an integral equation as well as in the form of a convenient explicit series solution needed in practice. The only assumption was that  $f(\lambda)$  should be monotonic and could be expanded in a power series about  $\lambda = 0$ . For our problem of electrolytes,  $f(0) = 0$ , (the condition of electro-neutrality).

These assumptions are consistent with those stipulated by Gronwall [17] and Keller [18]. Bagchi & Plischke [14] proved the absolute convergence of this series solution for  $r \geq a$  and, as mentioned before, obtained a very accurate solution for the particular case where  $f(\lambda)$  was chosen to be the function given by DH theory. Previously, Gronwall et al [19] also obtained an explicit series solution for this particular case. But they could not prove the overall convergence of their series solution. Moreover, the main drawback of their solution was the slow convergence of the series. On the contrary, the series solution proposed by Bagchi et al [13] proved to be very rapidly convergent and has many other practical advantages. These were discussed in the paper of Bagchi & Plischke [14].

(i) The Solution.

For convenience, a brief outline of the method of solution is given below.

Let the solution be given by a power series in  $\alpha$ , a parameter independent of  $r$ , such that

$$\lambda(r) = \sum_{s=1}^{\infty} \alpha^s b_s(r) \cdot r^{-1} \quad (2.3)$$

Since in our case

$$f(\lambda) = f'(0) + \frac{f''(0)}{2!} \lambda^2 + \frac{f^{(3)}(0)}{3!} \lambda^3 + \dots \quad (2.4)$$

we can express the differential equation (2.1) in the form

$$\frac{d^2(r\lambda)}{dr^2} - \chi^2 (r\lambda) = r[f(\lambda) - \chi^2 \lambda] \tag{2.5}$$

We have set here  $f'(0) \equiv \chi^2 \geq 0$ , (for its physical significance see Sec. 6 (ii)) (2.6)

Now substituting the expression for  $r\lambda$  from (2.3) and expanding the right hand side of (2.5) also in powers of  $\alpha^s$ , we get

$$\sum_{s=1}^{\infty} \alpha^s [ b_s'' (r) - \chi^2 b_s (r) ] = \sum_{s=1}^{\infty} \alpha^s G_s (r) \tag{2.7}$$

where  $G_s$  is given by (2.8). The expression (2.9) gives the explicit form of the general term  $G_s$ .

$$G_s = (r/s!) \partial^s / \partial \alpha^s \cdot [f(\lambda) - \chi^2 \lambda]_{\alpha=0} = (r/s!) \partial^s / \partial \alpha^s \cdot \left[ \frac{f''(0)}{2!} \lambda^2 + \frac{f^{(3)}(0)}{3!} \lambda^3 + \dots \right]_{\alpha=0} \tag{2.8}$$

The general term can be obtained from the multinomial expression

$$\begin{aligned} (r/s!) \partial^s / \partial \alpha^s \cdot [f^{(n)}(0) / (n!) \cdot (r^{-1} b_1 \alpha + r^{-1} b_2 \alpha^2 + r^{-1} b_3 \alpha^3 + \dots)^n]_{\alpha=0} \\ = (r/s!) \partial^s / \partial \alpha^s \cdot [f^{(n)}(0) / (n!) \cdot (n! / (a_1! a_2! \dots)) \cdot (b_1 b_2 \dots)^{a_1 + a_2 + \dots}]_{\alpha=0} , \end{aligned}$$

$$\alpha^{a_1 + 2a_2 + 3a_3 + \dots} ,$$

where  $a_1 + a_2 + \dots = n$ ;  $a_1 + 2a_2 + \dots = s$ , if we note that only the coefficient of  $\alpha^s$  contributes to  $G_s$ . Since  $n$  can vary from  $s$  to 2, we have

$$G_s(r) = r \sum \frac{f^{(n)}(0)}{n!} \cdot \frac{n!}{a_1! \dots a_{s-1}!} \left(\frac{b_{s-1}}{r}\right)^{a_{s-1}} \tag{2.9}$$

summed over all permissible values of  $a_1, a_2, \dots, a_{s-1}$ .

Hence equating the coefficients of  $\alpha^s$  on both sides of the eq (2.7) we obtain a system of differential equations

$$b_1' - \chi^2 b_1 = 0; \quad b_s'' - \chi^2 b_s = G_s(r), \text{ for } s \geq 2 \tag{2.10}$$

The solutions of (2.10), apart from integration constants, are

$$b_1 = \exp(-\chi r); \quad b_s = \frac{1}{\chi} \int_r^{\infty} G_s(x) \sinh \chi (x-r) dx; \quad (s \geq 2) \quad (2.11)$$

Of the two integration constants of the eq. (2.1), one vanishes due to the first boundary condition and the other can be determined from the given second boundary condition.

The solution is therefore given by the integral eq. (2.12)

$$\lambda(r) = r^{-1} \alpha \exp(-\chi r) + (\chi r)^{-1} \int_r^{\infty} g(x) \sinh \chi(x-r) dx \quad (2.12)$$

where

$$g(x) \equiv x[f(\lambda) - \chi^2 \lambda] \quad (2.13)$$

In this form  $\alpha$  is contained explicitly only in the linear term and we want to replace it by the constant  $C$  of the second boundary condition. For this we first note that  $\lambda(a)$  is given by

$$\lambda(a) = -\frac{Ca}{1+\chi a} - \frac{\exp(\chi a)}{1+\chi a} \int_a^{\infty} g(x) \exp(-\chi x) dx \quad (2.14)$$

The first term

$$\lambda_L(a) = -\frac{Ca}{1+\chi a} \quad (2.15)$$

is the value of the solution

$$\lambda_L(r) = -\frac{Ca^2}{1+\chi a} r^{-1} \exp -\chi (r-a) \quad (2.16)$$

of the linearized equation

$$\frac{d^2 \lambda}{dr^2} + \frac{2}{r} \frac{d\lambda}{dr} = \chi^2 \lambda \quad (2.17)$$

at  $r = a$  under the boundary conditions (2.2)

Now the value of  $\lambda(r)$  at any point  $r > a$  can be expressed in terms of  $\lambda(a)$  as

$$\lambda(r) = X_1(r) \lambda(a) + X_2(r) \lambda^2(a) + \dots \quad (2.18)$$

Since 
$$\lambda(r) = \alpha b_1(r) r^{-1} + \alpha^2 b_2(r) r^{-1} + \dots \quad (2.19)$$

and 
$$X_n \lambda^n(a) = X_n [\alpha b_1(a) \cdot a^{-1} + \alpha^2 b_2(a) \cdot a^{-1} + \dots]^n$$

one can, by equating the coefficients of equal powers of  $\alpha$  in (2.19) obtain  $X_n$  in terms of  $b_{j+1}$  and  $X_j$ , ( $j \leq n - 1$ ). Thus  $\lambda(r)$  can be expressed completely in terms of  $b_s(r) \cdot r^{-1}$  only.

As proved before, (cf. ref. [14]), the parameter  $\alpha$  can be chosen in such a way, (e.g.  $\alpha < a \exp(\chi a)$ ), that the series (2.3) converges uniformly for all values of  $r > 0$ . Further, in the final form of the solution, namely, eq. (2.18), the parameter  $\alpha$  does not appear explicitly. The solution  $\lambda$  can be expressed completely in terms of the function  $\exp(-\chi r) r^{-1}$  and consequently converges very rapidly. This particular method of expansion can therefore be used conveniently for investigating nonlinear nuclear or meson potentials, as will be shown in a later work.

(ii) Numerical Evaluation Of  $\lambda(r)$ .

To evaluate  $\lambda(r)$  one calculates first  $\lambda(a)$  from eq. (2.14) and then  $\lambda(r)$  with the help of equation (2.18). For this it is necessary to calculate the first few terms of the functions  $G_s(r)$ ,  $b_s(r)$ ,  $X_s(r)$ . Tables 1 - 3 give these terms up to  $s = 7$ . Higher terms, if necessary, can be easily obtained from the general expressions for these functions.

$\lambda(a)$  is calculated from eq. (2.14). For this the integrand is first expressed in terms of  $\lambda(a)$  by using eq. (2.18) in the expansion of  $f(\lambda)$  and terminating it at a suitable point. The integral is then evaluated by Simpson's rule:

$$\int_{x_0}^{x_{2n}} y dx = h/3 \cdot [y_0 + y_n + T_n + S_n] \quad (2.20)$$

where

$$T_n = 4 \sum_{i=1}^n y_{2i-1}; \quad S_n = 2 \sum_{i=1}^{n-1} y_{2i}$$

and  $h$  = distance between points on the abscissa.

This gives a relation

$$\lambda(a) = \lambda_L(a) + H(\lambda(a)), \quad (2.21)$$

where  $H(\lambda(a))$  is a known function of  $\lambda(a)$ . Finally,  $\lambda(a)$  is then determined from (2.21) by Horner's method. Once  $\lambda(a)$  is found, the value of  $\lambda$  at any point  $r$  is obtained from (2.18) by again terminating the series at a suitable point.

If one calculates  $\lambda(r)$  first for a central positive ion, then for a negative central ion, one can just substitute  $-\lambda$  in place of  $+\lambda$ .

There are two sources of error in the numerical calculation. One comes from the integration in steps of  $ma$  to the final value  $na$  (instead of up to  $\infty$  in infinitesimal steps) and the other from the termination of the series (2.18). In each case the error was practically eliminated by carrying out the calculation so far that no significant difference in the results up to fourth significant place could be obtained.

### 3. ION-ATMOSPHERE THEORY OF STRONG ELECTROLYTES.

The concept of ion-atmosphere and its usefulness had been critically discussed before, (see Bagchi [2]). It has been shown there that for a mathematically consistent theory one must use the modified Debye-Hueckel theory. For a comparative study of the different versions of the modified theory as well as the original DH theory, it is convenient to start from the distribution function (1.3), since this distribution leads to the distribution function (1.1) as well as to Boltzmann's distribution used in DH theory. The distribution function (1.3) is obtained by the approximation of an intractable expression by neglecting higher order terms. Its validity is restricted by the conditions, (for the derivation, see Dutta & Bagchi [5]), that the quantities  $n_0^+ b_{\pm}^+$ ,  $n_0^+ b_{+-}$  are much smaller than unity such that all of their higher powers except the first can be neglected. For actual ionic volumes these conditions are justifiable even at high concentrations.

But if we use Boltzmann's exclusion volumes, as we must, they are unacceptable, even at moderate concentrations.

It should however be emphasized again that this distribution function (1.3) and its mode of derivation suffer from several difficulties and the approximation used to obtain the distribution function (1.1) is not permissible. The correct distribution function of the modified theory, as noted before (see Bagchi [2]) and once again confirmed by the results obtained from this study, must be based on the distribution function (1.1) which can be derived rigorously without any approximation.

Nevertheless, as noted above, the starting point of this comparative study is the distribution function (1.3). The different versions of the ion-atmosphere theory are then given by

version I:

$$n^{\pm} = \frac{1 - n^{\mp} b_{\pm-}}{b_{\pm} [A_{\pm} \exp(z_{\pm} \lambda) + 1]} \quad (3.1)$$

$$\nabla^2 \lambda = f(\lambda) \quad (3.2)$$

$$f(\lambda) = - \frac{4 \pi \epsilon^2}{DkT} \left\{ \frac{z_+ b_- [A_- \exp(z_- \lambda) + 1] + z_- b_+ [A_+ \exp(z_+ \lambda) + 1] - b_{+-} (z_+ + z_-)}{b_+ b_- [A_+ \exp(z_+ \lambda) + 1] [A_- \exp(z_- \lambda) + 1] - b_{+-}^2} \right\} \quad (3.3)$$

Neglecting terms involving  $b_{+-}$ , we get the version II. Thus,

version II:

$$n^{\pm} = \frac{1}{b_{\pm} [A_{\pm} \exp(z_{\pm} \lambda) + 1]} \quad (3.4)$$

$$\nabla^2 \lambda = f(\lambda) \quad (3.5)$$

$$f(\lambda) = - \frac{4 \pi \epsilon^2}{DkT} \left\{ \frac{z_+}{b_+ [A_+ \exp(z_+ \lambda) + 1]} + \frac{z_-}{b_- [A_- \exp(z_- \lambda) + 1]} \right\} \quad (3.6)$$

Finally, for  $b \rightarrow 0$ , we get the original expressions of DH theory.

DH theory:

$$n^{\pm} = n_0^{\pm} \exp - (z_{\pm} \lambda) \quad (3.7)$$

$$\nabla^2 \lambda = f(\lambda) \quad (3.8)$$

$$f(\lambda) = - \frac{4\pi\epsilon^2}{DkT} \{z_+ n_0^+ \exp - (z_+ \lambda) + z_- n_0^- \exp - (z_- \lambda)\} \quad (3.9)$$

Here,

$n^{\pm}$  = number of positive (negative) ions at a distance  $r$  from the central ion

$b_{+-}$ ,  $b_{\pm}$  are the exclusion volumes of two unlike ions and two like ions respectively

$e_{\pm} = z_{\pm} e$  are the charges of two kinds of ions

$$\lambda = \frac{\epsilon\psi}{kT}$$

$\epsilon$  is the magnitude of the elementary (electronic) charge and  $z_{\pm}$  (positive/negative) are the valencies of the ions.

$\psi(r)$  is the potential at a distance  $r$  from the central ion

$k$  = Boltzmann's constant

$D$  = dielectric constant of the (continuous) medium

$$A_{\pm} = \frac{1 - n_0^{\pm} b_{\pm}}{n_0^{\pm} b_{\pm}} - 1, \text{ (for I)}$$

$$= \frac{1}{n_0^{\pm} b} - 1, \text{ (for II)}$$

$n_0^{\pm}$  = average number of ions per unit volume,

$$\nabla^2 \equiv \frac{\partial^2}{\partial r^2} - \frac{2}{r} \frac{\partial}{\partial r}$$

#### 4. EXPRESSIONS NEEDED TO CALCULATE THE RESULTS.

We first derive the required formulae for the three versions of the ion-atmosphere theory.

(i) The Charge Density.

To get the charge density



$$\rho(r) = z_+ \epsilon n^+(r) + z_- \epsilon n^-(r) \quad (4.1)$$

we must obtain  $n^+(r)$  and  $n^-(r)$  as functions of  $\lambda(r)$ . For a central positive ion, from eq. (1.3) we get for the excess positive charge, expressed as a fraction of the magnitude of the elementary charge, the expression

$$\frac{z_+ \epsilon (n^+ - n_0^+) dV}{\epsilon} = 4\pi r^2 dr z_+ \left\{ \frac{b_- [A_- \exp(z_- \lambda) + 1] - b_{+-}}{b_+ b_- [A_+ \exp(z_+ \lambda) + 1] [A_- \exp(z_- \lambda) + 1] - b_{+-}^2} n_0^+ \right\} \quad (4.2)$$

Similarly, the excess negative charge (for the positive central ion) is given by

$$\frac{z_- \epsilon (n_0^- - n^-) dV}{\epsilon} = 4\pi r^2 dr z_- \left\{ n_0^- - \frac{b_+ [A_+ \exp(z_+ \lambda) + 1] - b_{+-}}{b_+ b_- [A_+ \exp(z_+ \lambda) + 1] [A_- \exp(z_- \lambda) + 1] - b_{+-}^2} \right\} \quad (4.3)$$

The net charge, expressed as a fraction of  $\epsilon$ , is the difference between (2) and (3). That is,

$$(z_+ n^+ + z_- n^-) dV = 4\pi r^2 dr \left\{ \frac{z_+ b_- [A_- \exp(z_- \lambda) + 1] + z_- b_+ [A_+ \exp(z_+ \lambda) + 1] - b_{+-} (z_+ + z_-)}{b_+ b_- [A_+ \exp(z_+ \lambda) + 1] [A_- \exp(z_- \lambda) + 1] - b_{+-}^2} \right\} \quad (4.4)$$

The corresponding expressions for the version II are:

$$z_+ (n^+ - n_0^+) dV = 4\pi r^2 dr z_+ n_0^+ \left\{ \frac{1}{(1 - n_0^+ b_+) \exp(z_+ \lambda) + n_0^+ b_+} - 1 \right\} \quad (4.5)$$

$$z_- (n_0^- - n^-) dV = 4\pi r^2 dr z_- n_0^- \left\{ 1 - \frac{1}{(1 - n_0^- b_-) \exp(z_- \lambda) + n_0^- b_-} \right\} \quad (4.6)$$

$$\frac{\rho}{\epsilon} dV = 4\pi r^2 dr \left\{ \frac{z_+ n_0^+}{(1 - n_0^+ b_+) \exp(z_+ \lambda) + n_0^+ b_+} + \frac{z_- n_0^-}{(1 - n_0^- b_-) \exp(z_- \lambda) + n_0^- b_-} \right\} \quad (4.7)$$

For the Debye-Hueckel theory the corresponding expressions are:

$$\begin{aligned} & \frac{4\pi r^2 dr z_+ \varepsilon (n_+^+ - n_0^+)}{\varepsilon} \\ &= (\chi a)^2 \left(\frac{r}{a}\right)^2 \left(\frac{DkT a}{\varepsilon^2}\right) \frac{\exp-(z_+\lambda)-1}{z_+ - z_-} d(r/a) \end{aligned} \quad (4.8)$$

$$\begin{aligned} & \frac{4\pi r^2 dr z_- \varepsilon (n_0^- - n^-)}{\varepsilon} \\ &= (\chi a)^2 \left(\frac{r}{a}\right)^2 \left(\frac{DkT a}{\varepsilon^2}\right) \frac{\exp-(z_-\lambda)-1}{z_+ - z_-} d(r/a) \end{aligned} \quad (4.9)$$

$$\frac{\rho dV}{\varepsilon} = (\chi a)^2 \left(\frac{r}{a}\right)^2 \left(\frac{DkT a}{\varepsilon^2}\right) \frac{\exp-(z_+\lambda)-\exp-(z_-\lambda)}{z_+ - z_-} \left(\frac{r}{a}\right)^2 d(r/a) \quad (4.10)$$

(ii) Expressions for  $f(0)$ ,  $f'(0)$ ,  $f''(0)$ ,  $f^{(3)}(0)$ , etc.

In order to solve the differential equation we need the values of these quantities.

It is easily proved that in all the three cases  $f(0) = 0$ , (the condition of electro-neutrality).

For (I):

$$\begin{aligned} f'(\lambda) &= -\frac{4\pi\varepsilon^2}{DkT} \left\{ \frac{z_+ z_- b_- A_- \exp(z_- \lambda) + z_+ z_- b_+ A_+ \exp(z_+ \lambda)}{b_+ b_- [A_+ \exp(z_+ \lambda) + 1][A_- \exp(z_- \lambda) + 1] - b_{+-}^2} \right\} \\ &\quad - \frac{f(\lambda) \frac{d}{d\lambda} \{b_+ b_- [A_+ \exp(z_+ \lambda) + 1][A_- \exp(z_- \lambda) + 1] - b_{+-}^2\}}{b_+ b_- [A_+ \exp(z_+ \lambda) + 1][A_- \exp(z_- \lambda) + 1] - b_{+-}^2} \end{aligned} \quad (4.11)$$

Since  $f(0) = 0$ , the second term will vanish. Hence

$$\begin{aligned} f'(0) &\equiv \chi^2 \\ &= -\frac{4\pi\varepsilon^2}{DkT} z_+ z_- \left\{ \frac{n_0^+(1-n_0^+ b_{+-}) - n_0^-(1-n_0^- b_{+-})}{1 - n_0^+ b_{+-} - n_0^- b_{+-}} \right\} \end{aligned} \quad (4.12)$$

$$f''(0) = \chi^2 \frac{z_+ A_+ b_+ + z_- A_- b_-}{b_+ A_+ + b_- A_-} \quad (4.13)$$

$$-2\chi^2 \frac{b_+ b_- [z_+ A_+ (A_- + 1) + z_- A_- (A_+ + 1)]}{b_+ b_- (A_+ + 1)(A_- + 1) - b_{+-}^2}$$

and

$$f^{(3)}(0) = \chi^2 \frac{z_-^2 A_- b_- + z_+^2 A_+ b_+}{b_- A_- + b_+ A_+}$$

$$-2\chi^2 \frac{(z_- A_- b_- + z_+ A_+ b_+) b_+ b_- [z_+ A_+ (A_- + 1) + z_- A_- (A_+ + 1)]}{(b_- A_- + b_+ A_+) [b_+ b_- (A_+ + 1)(A_- + 1) - b_{+-}^2]}$$

$$+4\chi^2 \frac{(b_+ b_-)^2 [z_+ A_+ (A_- + 1) + z_- A_- (A_+ + 1)]^2}{[b_+ b_- (A_+ + 1)(A_- + 1) - b_{+-}^2]^2}$$

$$-3\chi^2 \frac{b_+ b_- \{z_+^2 A_+ (A_- + 1) + 2z_+ z_- A_+ A_- + z_-^2 A_- (A_+ + 1)\}}{b_+ b_- (A_+ + 1)(A_- + 1) - b_{+-}^2}$$

$$-f''(0) \frac{b_+ b_- [z_+ A_+ (A_- + 1) + z_- A_- (A_+ + 1)]}{b_+ b_- (A_+ + 1)(A_- + 1) - b_{+-}^2} \quad (4.14)$$

For (II):

$$f'(0) = \chi^2 \frac{4\pi e^2}{DkT} z_+ z_- \{n_0^+ (1 - n_0^- b_-) + n_0^- (1 - n_0^+ b_+)\} \quad (4.15)$$

$$f''(0) = \frac{\chi^2}{\frac{z_+^2 A_+}{b_+ (A_+ + 1)^2} + \frac{z_-^2 A_-}{b_- (A_- + 1)^2}} \left\{ \frac{z_+^3 A_+}{b_+ (A_+ + 1)^2} - \frac{2z_+^3 A_+^2}{b_+ (A_+ + 1)^3} \right. \\ \left. + \frac{z_-^3 A_-}{b_- (A_- + 1)^2} - \frac{2z_-^3 A_-^2}{b_- (A_- + 1)^3} \right\} \quad (4.16)$$

$$f^{(3)}(0) = \frac{\chi^2}{\frac{z_+^{A_+}}{b_+(A_++1)^2} + \frac{z_-^{A_-}}{b_-(A_-+1)^2}} \left\{ \frac{z_+^{4A_+}}{b_+} \left[ \frac{1}{(A_++1)^2} - \frac{6A_+}{(A_++1)^3} + \frac{6A_+^2}{(A_++1)^4} \right] \right. \\ \left. + \frac{z_-^{4A_-}}{b_-} \left[ \frac{1}{(A_-+1)^2} - \frac{6A_-}{(A_-+1)^3} + \frac{6A_-^2}{(A_-+1)^4} \right] \right\} \quad (4.17)$$

For D-H theory:

$$f'(0) = \chi^2 = \frac{4\pi\epsilon^2}{DkT} n_0 z_+ (z_+ - z_-) \quad (4.18)$$

$$f''(0) = \chi^2 \frac{z_-^2 - z_+^2}{z_+ - z_-} \quad (4.19)$$

$$f^{(3)}(0) = -\chi^2 \frac{z_-^3 - z_+^3}{z_+ - z_-} \quad (4.20)$$

(iii) Expressions for  $\frac{\partial\chi}{\partial N^+}$ ,  $\frac{\partial\chi}{\partial N^-}$ ,  $\frac{\partial\chi}{\partial V}$

In order to calculate activity coefficients we need these quantities.  $N^+$ ,  $N^-$  denote the total number of positive and negative ions in the solution of volume  $V$ .

In order to obtain these quantities we first rewrite  $\chi^2$  in the form (cf. eq. 4.12),

$$\chi^2 = - \frac{4\pi\epsilon^2}{DkT} z_+ z_- \left\{ \frac{\frac{N^+}{V} (1 - \frac{N^+ b_{+-}}{V} - \frac{N^- b_{-+}}{V}) + \frac{N^-}{V} (1 - \frac{N^- b_{+-}}{V} - \frac{N^+ b_{-+}}{V})}{1 - \frac{N^- b_{+-}}{V} - \frac{N^+ b_{-+}}{V}} \right\} \dots\dots\dots(4.21)$$

On differentiation we get

$$\begin{aligned} \frac{\partial \chi}{\partial N^+} = & - \frac{1}{2\chi} \frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{V} \left\{ \left[ \frac{1-2n_0^+ b_{+-} - n_0^- b_{-+} - n_0^- b_{-}}{1-n_0^- b_{+-} - n_0^+ b_{-+}} \right] \right. \\ & \left. + b_{+-} \left[ \frac{n_0^+(1-n_0^+ b_{+-} - n_0^- b_{-}) + n_0^-(1-n_0^- b_{+-} - n_0^+ b_{-+})}{(1-n_0^- b_{+-} - n_0^+ b_{-+})^2} \right] \right\} \end{aligned} \quad (4.22)$$

$$\begin{aligned} \frac{\partial \chi}{\partial N^-} = & - \frac{1}{2\chi} \frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{V} \left\{ \left[ \frac{1-2n_0^- b_{+-} - n_0^+ b_{-+} - n_0^+ b_{-+}}{1 - n_0^- b_{+-} - n_0^+ b_{-+}} \right] \right. \\ & \left. + b_{+-} \left[ \frac{n_0^+(1-n_0^+ b_{+-} - n_0^- b_{-}) + n_0^-(1-n_0^- b_{+-} - n_0^+ b_{-+})}{(1-n_0^- b_{+-} - n_0^+ b_{-+})^2} \right] \right\} \end{aligned} \quad (4.23)$$

$$\begin{aligned} \frac{\partial \chi}{\partial V} = & - \frac{\chi}{2V} - \frac{1}{2\chi} \frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{V} \left\{ \frac{n_0^+ + n_0^-}{1-n_0^- b_{+-} - n_0^+ b_{-+}} - \frac{n_0^+(1-n_0^+ b_{+-} - n_0^- b_{-}) + n_0^-(1-n_0^- b_{+-} - n_0^+ b_{-+})}{(1-n_0^- b_{+-} - n_0^+ b_{-+})^2} \right\} \\ & \dots\dots\dots(4.24) \end{aligned}$$

For (II):

$$\frac{\partial \chi}{\partial N^+} = \frac{1}{2\chi} \left\{ - \frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{V} [1-n_0^-(b_- + b_+)] \right\} \quad (4.25)$$

$$= \frac{1}{2\chi} \left\{ - \frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{V} (1-2n_0^- b) \right\}; \text{ (for } b_- = b_+ = b) \quad (4.26)$$

$$\frac{\partial \chi}{\partial N^-} = \frac{1}{2\chi} \left\{ -\frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{2V} [1 - n_0^+ (b_+ + b_-)] \right\} \quad (4.27)$$

$$= \frac{1}{2\chi} \left\{ -\frac{4\pi\epsilon^2}{DkT} \frac{z_+ z_-}{V} (1 - 2n_0^+ b) \right\}; \quad (\text{for } b_- = b_+ = b) \quad (4.28)$$

$$\frac{\partial \chi}{\partial V} = \frac{1}{2\chi} \left\{ \frac{4\pi\epsilon^2}{DkTV} (n_0^+ b_+ z_+^2 + n_0^- b_- z_-^2) \right\} - \frac{\chi}{2V} \quad (4.29)$$

For DH theory:

$$\frac{\partial \chi}{\partial N^+} = \frac{1}{2\chi} \left\{ \frac{4\pi\epsilon^2}{DkT} \cdot \frac{z_+^2}{V} \right\} \quad (4.30)$$

$$\frac{\partial \chi}{\partial N^-} = \frac{1}{2\chi} \left\{ \frac{4\pi\epsilon^2}{DkT} \cdot \frac{z_-^2}{V} \right\} \quad (4.31)$$

$$\frac{\partial \chi}{\partial V} = -\frac{\chi}{2V} \quad (4.32)$$

For all cases

$$\frac{\partial \chi}{\partial T} = -\frac{\chi}{2T} \quad (4.33)$$

$$\frac{\partial \Gamma(\chi a)}{\partial \chi} = \frac{1}{\chi} \left\{ \frac{1}{1+\chi a} - 2\Gamma(\chi a) \right\} \quad (4.34)$$

where

$$\Gamma(x) = \frac{1}{x^2} \{x - \ln(1+x)\} \quad (4.35)$$

## (iii) Free Energy And Mean Activity Coefficient

For the calculation of the free energy and mean activity coefficients we follow the original method of Debye and Hueckel, namely, simultaneous charging process. We need analytic expressions for  $\lambda(r)$  and  $\lambda(a)$ . For convenience of calculation, instead of using (2.18), (2.12) and (2.14), we represent  $\lambda(r)$  by the following series:

$$\lambda(r) = B_1 \lambda_L(r) + B_2 \lambda_L^2(r) + B_3 \lambda_L^3(r) + \dots \quad (4.36)$$

where  $\lambda_L(r)$  is the linearized solution given by (2.16)

In actual computation we have used only the first three terms and determined the constants  $B_1, B_2, B_3$  from the conditions

$$\left. \frac{d\lambda(r)}{dr} \right|_{r=a} = \sum_{n=1}^3 B_n \left. \frac{d\lambda_L^n(r)}{dr} \right|_{r=a} \quad (4.37)$$

$$\lambda(a) = \sum_{n=1}^3 B_n \lambda_L^n(a) \quad (4.38)$$

$$\lambda(R) = \lambda_L(R); \quad R \gg a \quad (4.39)$$

At the surface of the central ion of charge  $z_+ \epsilon$  and "effective" radius  $a_+$ , the potential due to the atmospheric ions is

$$\phi(a_+) = \psi(a_+) - \frac{z_+ \epsilon}{Da_+}$$

$$= B_1^+ \psi_L(a_+) + B_2^+ \left(\frac{\epsilon}{kT}\right) \psi_L^2(a_+) + B_3^+ \left(\frac{\epsilon}{kT}\right)^2 \psi_L^3(a_+) - \frac{z_+ \epsilon}{Da_+} \quad (4.40)$$

where

$$\psi_L(a_+) = \frac{z_+ \epsilon}{Da_+} \frac{1}{1 + \chi a_+} \quad (4.41)$$

If we decrease the elementary charge from  $\epsilon$  to  $\mu\epsilon$  ( $0 \leq \mu \leq 1$ ) simultaneously and at the same relative rate for all the  $N$  ions present in this particular subsystem in which the central ion is distinguished from other ions, while keeping the configuration fixed, the potential due to the atmospheric ions is given by

$$\begin{aligned} \phi(\mu\epsilon, a_+) &= B_1^+ \frac{z_+ \mu\epsilon}{Da_+} \frac{1}{1 + \mu\chi a_+} + B_2^+ \frac{\mu\epsilon}{kT} \left(\frac{z_+ \mu\epsilon}{Da_+} \frac{1}{1 + \mu\chi a_+}\right)^2 \\ &+ B_3^+ \left(\frac{\mu\epsilon}{kT}\right)^2 \left(\frac{z_+ \mu\epsilon}{Da_+} \frac{1}{1 + \mu\chi a_+}\right)^3 - \frac{z_+ \mu\epsilon}{Da_+} \end{aligned} \quad (4.42)$$

Suppose now we let the elementary charge  $\mu\epsilon$  increase from 0 to  $\epsilon$ . Then in any infinitesimal increase  $d(z_+ \mu\epsilon)$  of the charges, the corresponding change in the free energy  $df_+^{el}$  due to the central ion as well as all other atmospheric ions is given by

$$df_+^{el} = \phi(\mu\epsilon, a_+) d(z_+ \mu\epsilon) \quad (4.43)$$

In the entire process, the change is given by

$$f_+^{el} = \int_0^1 \phi(\mu\epsilon, a_+) z_+ \epsilon d\mu$$



$$\begin{aligned}
&= B_1^+ \frac{(z_+ \varepsilon)^2}{Da_+} \int_0^1 \frac{\mu}{1+\mu\chi a_+} d\mu + B_2^+ \frac{z_+^3 \varepsilon^4}{(Da_+)^2 kT} \int_0^1 \frac{\mu^3}{(1+\mu\chi a_+)^2} d\mu \\
&+ B_3^+ \frac{z_+^4 \varepsilon^6}{(Da_+)^3 (kT)^2} \int_0^1 \frac{\mu^5}{(1+\mu\chi a_+)^3} d\mu - \frac{z_+^2 \varepsilon^2}{Da_+} \int_0^1 \mu d\mu
\end{aligned} \tag{4.44}$$

Integrating we get,

$$\begin{aligned}
f_+^{el} &= B_1^+ \frac{z_+^2 \varepsilon^2}{Da_+} \Gamma(\chi a_+) + B_2^+ \frac{z_+^3 \varepsilon^4}{(Da_+)^2 kT} \eta(\chi a_+) \\
&+ B_3^+ \frac{z_+^4 \varepsilon^6}{(Da_+)^3 (kT)^2} \xi(\chi a_+) - \frac{z_+^2 \varepsilon^2}{2Da_+} ,
\end{aligned} \tag{4.45}$$

where

$$\Gamma(\chi a_+) = \frac{1}{(\chi a_+)^2} \{ \chi a_+ - \ln(1 + \chi a_+) \} \tag{4.46}$$

$$\begin{aligned}
\eta(\chi a_+) &= \frac{1}{(\chi a_+)^4} \left\{ \frac{(1 + \chi a_+)^2}{2} - 3(1 + \chi a_+) + 3 \ln(1 + \chi a_+) \right. \\
&\left. + \frac{1}{1 + \chi a_+} + \frac{3}{2} \right\}
\end{aligned} \tag{4.47}$$

$$\begin{aligned} \xi(\chi a_+) &= \frac{1}{(\chi a_+)^6} \left\{ \frac{(1 + \chi a_+)^3}{3} - \frac{5}{2} (1 + \chi a_+)^2 \right. \\ &\quad \left. + 10 (1 + \chi a_+) - 10 \ln (1 + \chi a_+) - \frac{5}{1 + \chi a_+} \right. \\ &\quad \left. + \frac{1}{2(1 + \chi a_+)^2} - \frac{10}{3} \right\} \end{aligned} \quad (4.48)$$

The quantity  $f_+^{el}$  is the electrostatic free energy of the particular subsystem in which a particular positive ion plays the role of the central ion. An identical derivation can be carried out for a negative central ion and will give a similar result. However, for convenience of calculations, we treat the negative central ion as if they were positive and replace  $+\lambda(r)$ ,  $+\lambda(a)$  by  $-\lambda(r)$ ,  $-\lambda(a)$  respectively. Hence in solving (4.36) with (37-39) we shall get as coefficients of the series (36) for the negative central ion,  $+B_1^-$ ,  $-B_2^-$ ,  $+B_3^-$ . Thus the corresponding expression for the free energy due to a negative central ion will be

$$\begin{aligned} f_-^{el} &= B_1^- \frac{z_-^2 \epsilon^2}{Da_-} \Gamma(\chi a_-) - B_2^- \frac{z_-^3 \epsilon^4}{(Da_-)^2 kT} \eta(\chi a_-) \\ &\quad + B_3^- \frac{z_-^4 \epsilon^6}{(Da_-)^3 (kT)^2} \xi(\chi a_-) - \frac{z_-^2 \epsilon^2}{2Da_-} \end{aligned} \quad (4.49)$$

Since the given system, in Debye's model (cf. ref. [2]), is composed of  $N^+$  independent identical subsystems and  $N^-$  identical subsystems, also mutually independent, the total electrostatic free energy of the given solution is thus given

by 
$$F^{el} = N^+ f_+^{el} + N^- f_-^{el} \quad (4.50)$$

and the activity coefficient of a positive ion ( $\gamma_+$ ) by

$$\begin{aligned} \ln \gamma_+ &= \frac{1}{kT} \frac{\partial F^{el}}{\partial N^+} \\ &= \frac{1}{kT} \left\{ f_+^{el} + N^+ \frac{\partial f_+^{el}}{\partial N^+} + N^- \frac{\partial f_-^{el}}{\partial N^+} \right\} \end{aligned} \quad (4.51)$$

where

$$\frac{\partial f_+^{el}}{\partial N^+} = \frac{\partial f_+^{el}}{\partial \chi} \left\{ \frac{\partial \chi}{\partial N^+} + \frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N^+} \right\} \quad (4.52)$$

$$\frac{\partial f_-^{el}}{\partial N^+} = \frac{\partial f_-^{el}}{\partial \chi} \left\{ \frac{\partial \chi}{\partial N^+} + \frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N^+} \right\} \quad (4.53)$$

To compute these expressions we need the quantities  $\frac{\partial \chi}{\partial N^+}$ ,  $\frac{\partial \chi}{\partial N^-}$ ,  $\frac{\partial \chi}{\partial V}$  given in

4. (iii). We also need the following formulae:

$$\frac{\partial}{\partial \chi} \Gamma(\chi a) = \zeta(\chi a) = \frac{1}{\chi} \left\{ \frac{1}{1+\chi a} - 2 \Gamma(\chi a) \right\} \quad (4.54)$$

$$\begin{aligned} \frac{\partial}{\partial \chi} \eta(\chi a) = \theta(\chi a) &= -\frac{4}{\chi} \eta(\chi a) \\ &+ \frac{a}{(\chi a)^2} \left\{ (1+\chi a) - \frac{3\chi a}{1+\chi a} - \frac{1}{(1+\chi a)^2} \right\} \end{aligned} \quad (4.55)$$

$$\begin{aligned} \frac{\partial}{\partial \chi} \xi(\chi a) = \Omega(\chi a) = & -\frac{6}{\chi} \xi(\chi a) + \frac{9}{(\chi a)^6} \{(1+\chi a)^2 \\ & - 5(1+\chi a) + \frac{10\chi a}{1+\chi a} + \frac{5}{(1+\chi a)^2} - \frac{1}{(1+\chi a)^3}\} \end{aligned} \quad (4.56)$$

Substituting these expressions in (4.51) we finally obtain

$$\begin{aligned} \ln \gamma_+ = & B_1^+ \frac{z_+^2 \epsilon^2}{Da_+ kT} \Gamma(\chi a_+) + B_2^+ \frac{z_+^3 \epsilon^4}{(Da_+)^2 (kT)^2} \eta(\chi a_+) \\ & + B_3^+ \frac{z_+^4 \epsilon^6}{(Da_+)^3 (kT)^3} \xi(\chi a_+) - \frac{z_+ \epsilon^2}{2Da_+ kT} \\ & + [N^+ B_1^+ \frac{z_+^2 \epsilon^2}{Da_+ kT} \zeta(\chi a_+) + N^+ B_2^+ \frac{z_+^3 \epsilon^4}{(Da_+)^2 (kT)^2} \theta(\chi a_+) \\ & + N^+ B_3^+ \frac{z_+^4 \epsilon^6}{(Da_+)^3 (kT)^3} \Omega(\chi a_+) + N^- B_1^- \frac{z_-^2 \epsilon^2}{Da_- kT} \zeta(\chi a_-) \\ & - N^- B_2^- \frac{z_-^3 \epsilon^4}{(Da_-)^2 (kT)^2} \theta(\chi a_-) + N^- B_3^- \frac{z_-^4 \epsilon^6}{(Da_-)^3 (kT)^3} \Omega(\chi a_-)] \cdot \\ & \cdot \left\{ \frac{\partial \chi}{\partial N^+} \frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N^+} \right\} \end{aligned} \quad (4.57)$$

Similarly, we have for  $\ln \gamma_-$  the equation:

$$\ln \gamma_- = B_1^- \frac{z_-^2 \epsilon^2}{Da_- kT} \Gamma(\chi a_-) - B_2^- \frac{z_-^3 \epsilon^4}{(Da_-)^2 (kT)^2} \eta(\chi a_-)$$

$$\begin{aligned}
 & + B_3^- \frac{z_-^4 \epsilon^6}{(Da_-)^3 (kT)^3} \xi (\chi_{a_-}) - \frac{z_-^2 \epsilon^2}{2Da_- kT} \\
 & + [N^+ B_1^+ \frac{z_+^2 \epsilon^2}{Da_+ kT} \zeta (\chi_{a_+}) + N^+ B_2^+ \frac{z_+^3 \epsilon^4}{(Da_+)^2 (kT)^2} \theta (\chi_{a_+}) \\
 & + N^+ B_3^+ \frac{z_+^4 \epsilon^6}{(Da_+)^3 (kT)^3} \Omega (\chi_{a_+}) + N^- B_1^- \frac{z_-^2 \epsilon^2}{Da_- kT} \zeta (\chi_{a_-}) \\
 & - N^- B_2^- \frac{z_-^3 \epsilon^4}{(Da_-)^2 (kT)^2} \theta (\chi_{a_-}) + N^- B_3^- \frac{z_-^4 \epsilon^6}{(Da_-)^3 (kT)^3} \Omega (\chi_{a_-})]. \\
 & \cdot \left\{ \frac{\partial \chi}{\partial N^+} + \frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N^+} \right\} \dots \dots \dots (4.58)
 \end{aligned}$$

Thus using the standard relation we get the following expression for the mean activity coefficient  $\gamma_{\pm}$ :

$$\ln \gamma_{\pm} = \frac{|z_-| \ln \gamma_+ + |z_+| \ln \gamma_-}{|z_+| + |z_-|} \tag{4.59}$$

This completes the number of expressions needed for the calculation of the mean activity coefficient. The formulae hold good for all three cases and for any type of binary electrolyte. The differences between the three cases arise from the different expressions for  $\chi$ ,  $\left\{ \frac{\partial \chi}{\partial N^+} + \frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N^+} \right\}$  and  $\left\{ \frac{\partial \chi}{\partial N^-} + \frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N^-} \right\}$ .

It is to be noted that by putting  $B_1^+ = B_1^- = 1$ ;  $B_2^+ = B_2^- = B_3^+ = B_3^- = 0$ , in (4.37-39) we obtain the corresponding expressions for the linear activity coefficient. From (4.36) it is obvious  $B_1^+ = B_1^- = 1$ .

Finally, a word of caution is necessary here. As shown previously (cf. Bagchi [2]), for the calculation of the correct electrostatic free energy of the

system one should use Debye-Hueckel's original method of simultaneous charging process and not the method proposed by Guentelberg.

#### 5. AN AD HOC SOLUTION OF $\nabla^2\lambda = f(\lambda)$ FOR THE CALCULATION OF ACTIVITY COEFFICIENTS.

As would be evident from the previous section, for the calculation of the excess free energy it is the value of the potential  $\lambda(a)$  on the surface of the ion which is of importance. Consequently, we need a convenient analytic expression for  $\lambda(a)$  in order to calculate thermodynamic properties. The eq. (2.14) is too cumbersome for this. But since we know the exact numerical values of  $\lambda(r)$  and  $\lambda(a)$ , in the section 4 we expressed  $\lambda(r)$  in terms of a power series of  $\lambda_L(r)$ . It was found that in most cases only three terms of the series gave excellent results. The mean activity coefficients  $\gamma_{\pm}$  reported in this paper had been calculated from the formulae given in section 4.

Previous to the work of Bagchi et al., (see refs. [13 & 14]), the nonlinear potential of the modified PB equation and the pertinent activity coefficients were calculated by the method devised previously by Bagchi [20]. He used the so-called "fit method" to obtain the nonlinear solution. Since it gave a simple closed expression, activity coefficients could be calculated easily by following DH method of obtaining the excess free energy. Later on, Dutta & Sengupta [10] and Sengupta [10] utilized this method for calculating activity coefficients for both the distribution functions (1.1) and (1.3) of the modified DH theory. They claim to have obtained good agreements between calculated and observed values for definite values of  $a$  and  $b$ . But it might be noted that the values of  $b$  chosen by them lead to physical inconsistencies for moderate concentrations, since  $(n_0^+b_+ + n_0^-b_-)$  becomes greater than unity. Further, as shown below (see Table 4), for given values of  $a$  and  $b$ , the values of  $\lambda(a)$  and  $\gamma_{\pm}$  obtained by the fit method in general differ significantly from their exact values obtained from the rigorous analytic solution of the PB equation. Nevertheless, the results calculated by the Calcutta

school (cf. refs. [10]) indicate that good agreement between calculated and observed values of activity coefficients may be obtained by ad hoc method by using suitable values of the parameters  $a$  and  $b$  which are also physically consistent. The German school (cf. refs. [11] , [12]) also obtained good agreement, but they always used the linear solution of the PB equation and a single value of the parameters, namely, the average radius  $a$  of the hydrated ion and  $b = \frac{4\pi}{3} a^3$ , i.e., the model A treated here. This study revealed that, in general, there are significant differences between linear and nonlinear values. Further, in attempting to obtain good agreement they had to use often unrealistic values of  $a$  and  $b$ , violating the criterion of physical consistency, namely  $(n_0^+b + n_0^-b)$  should always be less than unity. However, all these investigations indicated that the modified DH theory could lead to satisfactory results which would also be physically and mathematically consistent, contrary to the original DH theory, provided one chose judiciously the parameters.

Consequently, in view of the convenience and practical usefulness of the ad hoc method, it would be desirable to present here an outline of this method devised by Bagchi [20] before the analytic solution was obtained. We give the results for the case of 1-1 electrolyte for the distribution function (1.1). The formulae, however, are given for any binary electrolyte for the generalized distribution function of type (1.1). It should be noted that the formulae given by Dutta & Sengupta [10] and Sengupta [10] are not generally correct.

(1) The Non-linear Solution By The Ad Hoc Method.

We have to solve the equation

$$\nabla^2 \lambda(r) = - \frac{4\pi\epsilon}{DkT} \rho(r) \quad (5.1)$$

$\rho$  is the charge density around a given central ion. It should be noted here that for Boltzmann distribution of the original DH theory  $\rho$  becomes infinity for  $r \rightarrow 0$ , contrary to the known physical results. The modified theory does not suffer from this physical inconsistency.

The eq. (5.1) can be solved easily for the two limiting conditions:

$\lambda \rightarrow \infty$  and  $\lambda \rightarrow 0$ . The first gives

$$\nabla^2 \lambda_1 = \chi^2 m_{\pm} \quad (5.2)$$

$$\text{where } \chi^2 = -\frac{4\pi\epsilon^2}{DkT} z_+ z_- \{n_0^+(1 - n_0^- b_-) + n_0^-(1 - n_0^+ b_+)\} \quad (5.3)$$

and

$$m_{\pm} = \frac{1}{b_{\mp} z_{\pm} \{n_0^+(1 - n_0^- b_-) + n_0^-(1 - n_0^+ b_+)\}} \quad (5.4)$$

It should be noted that for (1.1)  $b_+ = b_- = b$ .

In terms of the dimensionless variable  $\xi = \chi r$ , the solution of (5.2) is

$$\lambda_1(\xi) = m_{\pm} \left( \frac{\xi^2}{6} + \frac{H}{\xi} + C \right) \quad (5.5)$$

where H and C are integration constants.

For  $\lambda \rightarrow 0$ , we have the equation

$$\nabla^2 \lambda_2(\xi) = \chi^2 \lambda_2(\xi) \quad (5.6)$$

Its solution is

$$\lambda_2(\xi) = A \exp(-\xi)/\xi + B \exp(+\xi)/\xi \quad (5.7)$$

Using the boundary conditions (2.2), we get

$$\lambda_2(\xi) = \frac{z_+ \epsilon^2 \chi}{DkT(1 + \xi_a)} \cdot \exp - (\xi - \xi_a)/\xi \quad (5.8)$$

In view of the fact that the potential on the surface of the ion even at a large radius  $a \approx 4 \text{ \AA}$  does not satisfy the linearity condition  $\epsilon\psi/kT \ll 1$  and becomes greater than unity if we use the solution  $\lambda_2$  given by (5.8) (cf. Sengupta [21]), it is obvious that the potential on the actual surface of the ion would be given by the eq. (5.5). Previously, Bagchi [20] also used  $\lambda_1$  for similar reasons.



The integration constant H is obtained from the second boundary condition of (2.2) and is given by

$$H = \frac{z_+ e^2 \chi}{m D k T} + \frac{\chi^3 a_+^3}{3} \equiv \frac{g_1}{3}, \quad (\text{say}). \quad (5.9)$$

The other constant C was evaluated by fitting  $\lambda_1, \lambda_2$  at a suitable point  $\xi_1$  where they would fit in smoothly. It was suggested by Bagchi [20] that the two solutions should have to be fitted at  $\xi = \xi_1$  where  $\lambda_1 = \lambda_2 = m_{\pm}$  and

$$\left. \frac{d\lambda_1}{d\xi} \right|_{\xi=\xi_1} = \left. \frac{d\lambda_2}{d\xi} \right|_{\xi=\xi_1} \quad \text{so that their second derivatives at this point also}$$

would become equal and consequently, the two curves would fit into each other smoothly at this point. Following this method we get

$$\xi_1 = (1 + 3H)^{1/3} - 1 \quad (5.10)$$

and

$$C = \frac{1}{2} \{1 - (1 + g_1)^{2/3}\} \quad (5.11)$$

Thus the potential  $\lambda_1$  is obtained concretely for any given system as a function of  $r$ . It should also be noted that the solution  $\lambda_1$  given by eq. (5.5) has a minimum value and consequently the potential  $\lambda_1$  is not a monotonic function for all values of  $r$ .

Now, following DH technique we get the excess free energy  $f_+^{el}$  of the subsystem in which the central ion is a positive ion the expression

$$f_+^{el} = \frac{kTm_+}{2} \left\{ \frac{1}{2} \chi^2 a_+^2 + P + Q_+ \right\} \quad (5.12)$$

where

$$P = \frac{1}{2} + \frac{1}{\sqrt{3}} \tan^{-1} \sqrt{3} - \frac{1}{2} \ln 3 = 0.5551 \quad (5.13)$$

and

$$Q_+(g_+) = \frac{1}{2} \ln [(1 + g_+)^{2/3} + (1 + g_+)^{1/3} + 1] - \frac{1}{2} (1 + g_+)^{2/3} - \frac{1}{\sqrt{3}} \tan^{-1} \frac{2(1 + g_+)^{1/3} + 1}{\sqrt{3}} \quad (5.14)$$

Similar expression is obtained for a subsystem in which the central ion is a negative one. The total electrostatic free energy of the given system is therefore

$$F^{el} = N f_+^{el} + N f_-^{el} \quad (5.15)$$

The mean activity coefficient  $\gamma_{\pm}$ , according to Dutta & Sengupta [10], for 1-1 electrolyte and  $a_+ = a_- = a$ ;  $b_+ = b_- = b$ , is given by

$$\ln \gamma_{\pm} = \frac{m}{2} \left\{ \frac{1}{2} \chi^2 a^2 + (P + Q)(1 - 2n_0 B) + 2n_0 B E \right\} \quad (5.16)$$

where,

$$B = \frac{1 - 2n_0 b}{2n_0(1 - n_0 b)} \quad (5.17)$$

$$E = \frac{1}{2} \{ (1 - (1 + g)^{2/3}) \}; Q_+ = Q_- = Q \quad (5.18)$$

Table 4 gives the values for  $\lambda(a)$  and  $\gamma_{\pm}$  calculated from this method (see columns 5 and 7) as well as those calculated from the exact analytic solution of the PB equation (columns 6 and 8) for a few specific cases both for models A and B of the distribution function (1.1). Columns 3 and 4 also show the values of  $m$  and  $r_1$  ( $= \xi_1/\chi$ ) where the two solutions  $\lambda_1$  and  $\lambda_2$  were fit. Note also the surprising values of  $r_1$ . Obviously, it has no physical significance and consequently this 'fit method' should be considered as a mathematical trick only. Further, the results show that the "fit method" does not give the potential and the activity coefficients correctly for a given model.

Consequently, the agreement claimed by Dutta & Sengupta [10] has little mathematical and physical justification, particularly in view of the facts that eq. (16) is not quite correct and their values of  $b$  lead to physical inconsistencies.

Since our principal interest is to calculate the potential on the surface of

the ion, the aim of the ad hoc method was to evaluate the constant C in  $\lambda_1$  (cf. eq. 5.5). This can also be achieved by setting  $\lambda_1 = \lambda_2$  at  $\xi_{\min} = (3H)^{1/3}$ , the minimum point of  $\lambda_1$  vs.  $\xi$  curve, instead of fitting the two curves at some value of  $\xi$ . Now, the values of  $r_m \equiv \xi_{\min}/\chi$ , as expected, always lie outside the surface of the central ion, (contrary to the case obtained by the "fit method"). Also the values of  $\lambda(a)$  for the model A become closer to the corresponding exact values. For the model B, however, the values are not so good. These values are also given in Table 4 in brackets.

In this case,

$$\xi_{\min} = (3H)^{1/3} \equiv g_i^{1/3} \quad (5.19)$$

and

$$C = \frac{1}{m_i} \cdot \frac{z_i \epsilon^2 \chi \exp(\chi a_i)}{DkT(1 + \chi a_i)} \cdot \frac{\exp - \xi_{\min}}{\xi_{\min}} - \frac{\xi_{\min}^2}{2} \quad (5.20)$$

The electrostatic free energy for the positive central ion is given by

$$f_+^{el} = \frac{kTm_+}{4} [\chi^2 a_+^2 - g_+^{2/3}] - \frac{z_+ \epsilon}{Da_+ g_+^{1/3}} [\exp - (g_+^{1/3} - \chi a_+)] - \frac{z_+ \epsilon}{Da_+ g_+^{1/3}} \int_0^1 dv \exp - (g_+^{1/3} - \chi a_+) / (1 + \chi a_+ v) \quad (5.21)$$

A similar expression is obtained for the negative central ion. The total excess free energy is thus given by

$$F^{el} = N_+ f_+^{el} + N_- f_-^{el} \quad (5.22)$$

The values of mean activity coefficients for these two ad hoc methods have not yet been calculated accurately. But it appears that the ad hoc method where  $\lambda_1$  is put equal to  $\lambda_2$  at  $\xi_{\min}$  seems more promising for calculating thermodynamic properties with adequate accuracy throughout the concentration range for both the models A and B, provided one chooses appropriate values of a and b, which however must be physically consistent. In a subsequent paper we shall examine carefully this question on the suitability of the ad hoc method for obtaining the nonlinear potential

on the surface of the ion and for calculating the properties of ionic solutions.

It must, however, be always kept in mind that the ad hoc method can be recommended only for convenience of calculation and in case of doubts, the results had to be checked with those obtained from the exact method presented in sections 2,3 and 4.

Finally, it should be emphasized again that for any method, either the ad hoc method or the exact method, one must choose the parameters (e.g.  $a_1$  and  $b$ ) in such a way that they satisfy the criteria of physical consistencies at all possible concentrations.

## 6. A CRITICAL DISCUSSION ON THE UNCERTAINTIES INVOLVED IN THE THEORY.

In spite of theoretical and practical justifications as well as a posteriori verification of the modified DH theory, several questions have to be answered satisfactorily before we can apply the theory of ion-atmosphere successfully to actual concrete cases.

First, how to select the various parameters entering into the theory, namely, exclusion volumes  $b_+$ ,  $b_-$ ,  $b_{+-}$  and the "effective" radii of the ions ( $a_+$ ,  $a_-$ ), where the boundary condition is to be applied?

This problem of the correct choice of parameters is intimately connected with the problem of hydration of ions. Consequently, we have to know how many water molecules shield the ions and what is the "effective" radius of the hydrated ion?

We shall discuss this difficult question of the proper choice of parameters below. But before that let us mention here two other related problems of theoretical nature which would help us to throw some light on the correct choice of these parameters.

One is connected with the surface at which the continuity condition of normal induction is to be applied. For a spherically symmetric potential  $\psi$ , (continuous everywhere), and in absence of charge at the boundary surface, one can show from classical electromagnetic theory

$$\left. \frac{\partial \psi}{\partial r} \right|_{a+\delta} = - \frac{Q}{Da^2}, \quad (6.1)$$

where  $D$  is the dielectric constant of the medium just outside, ( $\delta$  is an infinitesimal quantity), the neutral surface of the sphere of radius  $a$  and  $Q$ , the total charge inside the sphere of radius  $a$ . Consequently, it is the dielectric constant of water outside the "effective" radius of the central ion that matters. Further, it shows that we cannot take any arbitrary radius of the central ion. Either we

can take the surface as that of the "bare central ion" or of the completely "hydrated ion" so that the surface becomes neutral. One cannot go further out due to the presence of other atmospheric ions and there should not be net "polarization" charges inside the surface as long as one sticks to the usual boundary condition,

$$-D \left. \frac{\partial \psi}{\partial r} \right|_{r=a_1} = \frac{z_1 |e|}{a_1^2} \quad (6.2)$$

The problem of the value of the dielectric constant cannot be resolved theoretically unless we have a better knowledge of the structure of water molecules in the presence of ions. Consequently, at the present state of our knowledge we have to decide about the value of the dielectric constant empirically and note the fact that in this theory the medium is considered as a continuum with a fixed value of the dielectric constant. We have always used the static value (78.3) of the dielectric constant of pure water, though it is known [9] that the static dielectric constant of aqueous solution changes considerably from that of pure water and the dielectric constant of water surrounding the central ion may be as low as 5-15. We calculated a few cases with  $D=50$  and 5 reported by Hasted et al and found the results to be far worse and untenable than those calculated with  $D=78.3$ .

The other problem is connected with the effect of hydration of ions on thermodynamic properties. In the ion-atmosphere theory of solutions the effect of hydration is taken fully into account by the choice of the "effective" ionic radii and the exclusion volumes.

But it is worthwhile to mention here again, (see Bagchi [2]), that some authors, instead of using the modified DH theory, had attempted to get closer agreement with experimental values of activity coefficients by calculating the contributions from the free energy of the DH theory as well as that from hydration energy. But hydration energy can have no effect on the activity coefficients of

electrolyte solutions, since this is already present in the limiting case where DH theory is supposed to be strictly valid. In the change of activity coefficients with increasing concentrations, it is not the hydration energy which comes but the heat of dilution, a quantity whose magnitude cannot explain the differences between the actual activity coefficients and those calculated from DH theory.

(1) Discussions on the Choice of Parameters.

In the modified theory we have to choose the parameters  $r_+$ ,  $r_-$ ,  $a_+$ ,  $a_-$ ,  $b_+$ ,  $b_-$ ,  $b_{+-}$ . The values of bare ionic radii,  $r_+$ ,  $r_-$ , are quite well known. But in the solution, due to hydration and because of the fact that in the theory we are treating the medium as a dielectric continuum, we have to determine the effective ionic radii. Further, even if we could know the values of these effective ionic radii, the question remains: What would be the value of  $a_{\pm}$  where the second boundary condition is to be applied? From the discussions above, it would be evident that we cannot answer this last question unequivocally. For the moment, let us assume that these values are known exactly.

We have still to choose the exclusion volumes  $b_+$ ,  $b_-$  and  $b_{+-}$ . Due to electrostatic field, ions of like signs will, on the average, be further apart than ions of unlike signs. In order to determine interionic distances correctly, we have also to know the positions and number of water molecules in between the ions.

In principle, the distance of closest approach, (the average value), of the ions and the arrangement of water molecules in the solution could be obtained experimentally from careful quantitative x-ray diffraction studies of ionic solutions and the correct analysis of the radial distribution functions (RDF). Unfortunately, systematic and careful investigations of ionic solutions at various concentrations are not available. Accurate RDF curves have been given by Brady [22] but only for two concentrations of KOH solutions and one each for KCl and LiCl solutions. Further, the curves have been analysed by the conventional method which, as had been proved before [23], is neither correct theoretically nor adequate to

decipher quantitatively the details of interatomic distributions. Nevertheless, for lack of any satisfactory data, we shall discuss here Brady's results in order to get a fair idea what would be the reasonable values for the closest distance of approach of the ions in the solution.

For KOH there are two pronounced peaks, one at  $2.87\text{\AA}$  (or  $2.92\text{\AA}$ , depending on the concentration) and the other at  $4.75\text{\AA}$ . The latter one corresponds to the second nearest neighbour-distance in water. The ionic radii of both  $\text{K}^+$  and  $\text{OH}^-$  are  $1.33\text{\AA}$  and the radius  $r_{\text{H}_2\text{O}}$  of water molecule is  $1.38\text{\AA}$ . Consequently, we find that the first peak could very well be due to the distances  $\text{H}_2\text{O} - \text{H}_2\text{O}$ ;  $\text{K}^+ - \text{H}_2\text{O}$ ;  $\text{OH}^- - \text{H}_2\text{O}$ ;  $\text{K}^+ - \text{OH}^-$ .

In the case of KCl solution, there is a prominent peak at  $4.75\text{\AA}$  which obviously is due to the second neighbour - distance between water molecules, and another prominent peak (with a shoulder on the left) at  $3.16\text{\AA}$ . We have from the known radii,  $\text{H}_2\text{O} - \text{Cl}^- = 3.2\text{\AA}$ ;  $\text{K}^+ - \text{Cl}^- = 3.14\text{\AA}$ ,  $\text{K}^+ - \text{H}_2\text{O} = 2.71\text{\AA}$ . The shoulder at the left side of the first main peak presumably indicates the  $\text{K}^+ - \text{H}_2\text{O}$  distance.

In both cases, the available analysis of the curves do not eliminate the possibility that the closest distance between the oppositely charged ions is not the sum of their individual radii but corresponds to the distance between opposite ions separated by a water molecule. In a close-packing arrangement without water molecules, we would have the distance of separation between the oppositely charged ions  $r_{+-} = r_+ + r_-$ , and that between like ions  $\sqrt{2}r_{++}$ . In the presence of water molecules, the most likely values would be  $(r_+ + 2r_{\text{H}_2\text{O}} + r_-)$  between two unlike ions and  $2\sqrt{2} (r_+ + r_{\text{H}_2\text{O}})$  between two positive ions and  $2\sqrt{2} (r_- + r_{\text{H}_2\text{O}})$  between two negative ions.

Complications would arise if the sizes of the two unlike ions differ considerably, as in LiCl. In such cases, as is already known, the small  $\text{Li}^+$  ion can come into the interstices of tetrahedrally arranged water molecules and the large  $\text{Cl}^-$  ion can break the tetrahedral structure of water molecules.



Consequently, if the ions are distributed in sequence as envisaged in the derivation of the distribution functions (1.3), (cf. ref. [5]), one could determine the "effective" volume of an ion quite reasonably. The difficulty comes in when we want to calculate Boltzmann's exclusion volumes needed in the theory. As discussed previously (cf. Bagchi [2]), even for simple systems like hard spheres and fused alkali halides, the problem is not yet solved. For solutions, a picture of the possible motions of different kinds of ions would at once convince any one that it is almost impossible to estimate the numerical values of the exclusion volumes even if we had exact values of interionic distances. Further, as we have noted before (cf. [2]), the distribution function (1.3) suffers from several other difficulties and inconsistencies. Nevertheless, some results obtained from this distribution function with definite values of the parameters have been calculated to demonstrate that, apart from these theoretical difficulties, the calculated results cannot possibly agree with the experimental values, even if we had correct values of the three exclusion volumes,  $b_+$ ,  $b_-$  and  $b_{\pm}$ . Further, it is likely that any possible value of  $b_{\pm}$  would lead to physical inconsistencies because  $(n_0^+ b_+ + n_0^- b_-)$  would be greater than unity.

As noted before, (cf. [2]), the correct distribution function is given by the expression (1.1). Nevertheless, due to these uncertainties, for a satisfactory agreement between the calculated and experimental results we have to find empirically suitable values of these parameters. But the choice must be physically realistic and consistent. This does not mean that the ion-atmosphere theory used with the distribution function (1.1) is not theoretically rigorous but only indicates the difficulties as regards the choice of the exact values of these parameters, which are mathematically and physically well defined.

(ii) Physical Significance of  $\chi$ .

Mathematically, the parameter  $\chi$  is defined by  $f'(0) \equiv \chi^2$ , a positive quantity, (see eq. 2.6), and it appears in the solutions (2.12 - 2.16) of the differential equations (2.1 and 2.17). It is obvious from these solutions that the correct

physical significance of  $\chi$  lies in the fact that it determines the slope and range of the effective potential around the central ion due to the presence of other charges. Further, this effective potential has a much shorter range than the Coulomb potential mainly due to the shielding effect of opposite charges. The parameter  $\chi$  is mainly responsible for the fact that a system of charged particles interacting with Coulomb forces becomes physically and mathematically consistent. It should also be again emphasized that this parameter can come naturally only through the differential equation of PB type. The expressions for  $\chi^2$  in the three versions of the ion-atmosphere theory are given in eqs. (4.12), (4.15) and (4.18) respectively.

But the usual physical interpretation, namely,  $\chi^{-1}$  measures the radius for the ion-atmosphere outside the central ion, obviously cannot be true generally. In order to prove this, let us, for simplicity, consider (4.15) and (4.18) for 1-1 electrolyte. In this case, we have

$$\chi^2 = \chi_D^2 (1 - n_o^- b); \quad \chi_D^2 = \frac{4\pi\epsilon^2}{DkT} \sum_i n_i^+ z_i^2 = \frac{8\pi\epsilon^2}{DkT} n_o^+; \quad (n_o^+ = n_o^- = n_o) \quad (6.3)$$

For 1-1 electrolyte at  $c=10$  N,  $\chi_D^{-1}=0.96\text{\AA}$ , well inside the volume of alkali ions, except  $\text{Li}^+$ . For  $c=20$  N,  $\chi_D^{-1}$  would be also less than the radius of  $\text{Li}^+$ . The values become still less for 1-2, 1-3, 2-2 ions, e.g.  $\chi_D^{-1}=0.39$  for 1-3 salt at 10 N. In the case of fused alkali halides  $\chi^{-1}$  as well as  $\chi_D^{-1}$  always lie inside the volume of the central ion. For example, for KCl, we get  $\chi^{-1}=0.28\text{\AA}$ ,  $\chi_D^{-1}=0.24\text{\AA}$ , (cf. ref. [2]).

The usual attempt to prove the consistency of the obvious condition of electro-neutrality, namely, the total atmospheric charge should be equal and opposite to the charge of the central ion is also mathematically inconsistent since for the actual charge density one should use the complete nonlinear potential and not the linear potential. (For the conventional interpretation see Falkenhagen [11] and also Fowler & Guggenheim [24]). The condition of electro-neutrality is always satisfied since  $f(o)=o$  for all cases.

7. CALCULATIONS

## (1) Choice of Parameters

In this paper, only a few cases involving the distribution function (1.3) have been calculated for the corresponding values of 'a' with the definite models given by:

$$b_{+-} = \frac{4}{3}\pi \sigma_{+-}^3; \sigma_{+-} = a_+ + a_- = 2a \quad (7.1)$$

$$b_+ = b_- = \frac{4}{3}\pi \sigma_{\pm}^3 \{1 - n_0^{\pm} (17/96) \frac{4}{3}\pi \sigma_{\pm}^3\} \quad (7.2)$$

$$\sigma_+ = \sigma_- = 2(a + r_{H_2O}) \text{ or, } 2\sqrt{2} a \quad (7.3)$$

Obviously, for any concrete case these relations are not at all justified. For example, we know definitely that the radii of positive and negative ions, ( $r_{\pm}$ ), are different and, usually, only the cations are hydrated. Further, there is no a priori reason to assume  $r_+ = a_+$ ;  $r_- = a_-$ . The expressions  $b_{+-}$ ,  $b_{\pm}$  given in (7.1)-(7.3) have been proved to be physically unrealistic. For example, for 1-1 electrolyte even for a small 'a' ( $=1.5 \text{ \AA}$ ), the total exclusion volume becomes greater than unity for  $c=5N$ . This is obviously due to the fact that the overlap-correction factor  $\gamma \equiv (1 - \frac{17}{96} n_0^{\pm} b_{\pm})$ , (cf. 7.2), given by Dutta [25] cannot be correct for high concentrations. Further the correct  $b_{+-}$  should also be obtained by applying a proper overlap-factor to (7.1).

For the distribution function (1.1) we have also taken  $r_+ = a$ , the distance from the centre of the central ion where the second boundary condition is applied. In this case, we have used two models for exclusion volumes. Both will lead to satisfactory results provided "a" is suitably chosen and the exclusion volumes are corrected appropriately. But for convenience of calculations and comparison we have used throughout fixed values of the single exclusion volume b.

In model A, we have chosen

$$b = \frac{4}{3} \pi \sigma^3 \quad (7.4)$$

where

$$\sigma = \frac{r_+ + r_-}{2} = a \quad (7.5)$$

In this case the mean exclusion volume of the ion is taken to be the effective physical volume of the ion. This also leads to physical inconsistencies for  $a=4.0\text{\AA}$ . Remembering the fact that the volume within this surface should not contain any polarization charges, it is highly unlikely that both the ions could have such high values of 'a'. For example, in the case of  $\text{K}^+$ ,  $a_+$  may be equal to  $4.1\text{\AA}$ , but for  $\text{Cl}^-$  then  $a_-$  must be  $1.81\text{\AA}$ . Further, this shows that even the average volume of the hydrated ion is greater than the correct exclusion volume b.

In model B, we have used the relation

$$b = \frac{4}{3} \pi \sigma^3 \quad (7.6)$$

but now, 
$$\sigma = a + r_{\text{H}_2\text{O}} \quad (7.7)$$

In this model B, we have therefore implicitly assumed that there is always a water molecule between two unlike ions. X-ray data do not preclude this model. The fact that most of the cations are permanently hydrated suggests that this model might correspond to the actual situation in ionic solutions, provided one uses different values of  $a_{\pm}$  for the two ions, namely,  $a_+ = r_+ + 2 r_{\text{H}_2\text{O}}$  and  $a_- = r_-$ . Nevertheless,  $(n_+^+ b + n_-^- b)$  becomes greater than unity, (physically untenable), even for reasonable values of the effective radius of the ion, (e.g.  $a = 2.5\text{\AA}$ ,  $c = 4N$ ). This points out clearly that the total exclusion volume needs an overlap-correction, not considered here.

For the original DH theory, we have the only parameter  $a_{\pm}$ , the effective radii of the ions and so such discrepancies do not arise. But the calculated results are not even qualitatively correct, contrary to those obtained from eq. (1.1).

#### (ii) Procedures for Calculations.

The procedures for the calculations are the same for all three cases. The values of the physical constants have been taken as:

Number of each ion per cc of normal solution =  $6.02 \times 10^{20}$ ;

Boltzmann's constant  $k = 1.38047 \times 10^{-16}$  erg/K°;

Electronic charge  $e = 4.8029 \times 10^{-10}$  e.s.u.;

$\pi = 3.14159$ ;  $T = 298^\circ\text{K}$ ;  $D = 78.3$ .

All the results have been calculated for fixed values of 'a' at definite molar concentrations c. For example, we had taken

$$a = 0.5 \text{ \AA}^0; 1.0 \text{ \AA}^0; 1.5 \text{ \AA}^0; 2.0 \text{ \AA}^0; 2.5 \text{ \AA}^0; 3.0 \text{ \AA}^0; 4.0 \text{ \AA}^0; 5.0 \text{ \AA}^0$$

$$c = 0.01 \text{ N}; 0.1 \text{ N}; 1.0 \text{ N}; 2.0 \text{ N}; 3.0 \text{ N}; 4.0 \text{ N}; 5.0 \text{ N}$$

For each of the above radius and concentration the quantities  $\lambda(a)$ ,  $\lambda_L(a)$ ,  $(\gamma_\pm)_L$ ,  $\gamma_\pm$  have been calculated. We had also calculated  $\lambda(r)$  for various values of  $r/a$ . These results had also been shown in graphs, but for lack of space neither the tables nor the graphs are reproduced here. Only a few curves illustrating the typical nature of the function are given here.

The calculations proceed in the following manner. For a given radius and concentration, the quantities  $\chi^2$ ,  $f''(0)$ ,  $f^{(3)}(0)$ , .. are calculated. The only condition applied here is that  $\chi^2$  be positive. This is always the case for DH theory. In the modified theory, we sometimes get  $\chi^2 < 0$ , if the concentration and the exclusion volume are large enough. When this is the case, no further calculations are carried out as  $\chi^2 < 0$  is a physical impossibility for ionic solutions and this also indicates that the size of the exclusion volume used is physically unrealistic. We did not proceed further if  $(n_0^+ b_+ + n_0^- b_-)$  becomes greater than unity since such values are physically untenable.

Next we calculate the recursion coefficients  $X_1(r)$ ,  $X_2(r)$ ,  $X_3(r)$ , ... Whenever  $f''(0) = 0$ , we calculate  $X_1(r)$ ,  $X_3(r)$ , ... for  $r$  going from  $r = a$  to  $r = 7a$  in steps of  $0.1a$ . When  $f''(0) \neq 0$ , we calculate  $X_1(r)$ ,  $X_2(r)$ ,  $X_3(r)$ , ... for  $r$  varying from  $r = a$  to  $r = 9a$  in steps of  $0.1a$ .

We then perform the numerical integration of eq. (2.14) to obtain  $\lambda(a)$  and  $\lambda(r)$  is obtained from the recursion relation (2.18). This enables us also to compute

the charge densities as a function of the distance from the central ion. Our next task is to calculate the activity coefficient. For convenience, we use the perturbation series given by eq. (4.36) and determine only the first three coefficients  $B_1, B_2, B_3$  from eqns. (4.37- 4.39). This gives  $\gamma_{\pm}$  to a reasonable degree of accuracy, (cf. eqns. 4.45 -4.53).

(iii) Critical Assessment of Calculations

First, in the recursion relation

$$\lambda(r) = X_1(r) \lambda(a) + X_2(r) \lambda^2(a) + \dots \quad (2.18)$$

we take as many terms as necessary to obtain accurate results. In all our calculations we used only the first three recursion coefficients,  $X_1, X_2, X_3$ . In a few cases, we tested to see if the terms containing  $X_4, X_5, X_6, X_7$  would make a significant contribution and came to the conclusion that it was not worthwhile to include them. The difference, though noticeable, was only a small percentage of  $\lambda(a)$ . For  $a = 0.5A^0$  this difference was the largest but amounted to less than 1%. Consequently, in order to save computer time, we always took the first three terms.

Another source of error is involved in the use of perturbation series

$$\lambda(r) = \sum_{n=1}^{\infty} B_n \lambda_L^n(r) \quad (4.36)$$

needed for the convenient calculation of the activity coefficient.

We have always used the first three terms and the coefficients have been calculated from the conditions (4.37-4.39).

For values of 'a' less than  $1A^0$ , the first three terms of this series do not give a very good fit with the accurate  $\lambda(r)$  calculated from the recursion relation mentioned above. Better fit can be obtained if one takes two more terms and determines the coefficients  $B_4$  and  $B_5$  from the conditions

$$\lambda(r_1) = \sum_{n=1}^5 B_n \lambda_L^n(r_1)$$

$$\left. \frac{d\lambda}{dr} \right|_{r=r_1} = \sum_{n=1}^5 B_n \left. \frac{d}{dr} \lambda_L^n \right|_{r=r_1}$$

We tested these for a few values of  $r_1$ ,  $r_2$ , etc. not much greater than 'a' and found that  $\lambda(r)$  became sufficiently accurate. But we did not use these higher terms for calculating activity coefficients, since the relevant formulae became too cumbersome. For 'a' greater than  $1A^0$ , the series (4.36) with the first three terms gives good results for  $\lambda(r)$  over the entire range of  $r$ , generally within 1.5%. Near the surface of the ion the accuracy is even greater so that by taking the first three terms of this series we get sufficiently accurate values for the mean activity coefficient.

## 8. RESULTS

Due to lack of space, it is not possible to reproduce here the voluminous results contained in 35 Tables and 120 graphs for the three distribution functions. Further, since the results were calculated for fixed values of relevant parameters, not meant to be the actual parameters for concrete cases, it would also not be very useful for practical purposes to reproduce here all these results. It must be repeated here again that the values calculated in this study were not intended to show agreement between calculated and experimental results, but to choose a posteriori the most suitable and also theoretically and physically consistent distribution function. Consequently, we present here very briefly some results to illustrate the nature of the relevant values obtained from all the theories of ion-atmosphere used in the theory of strong electrolytes and note some of their striking properties not revealed before.

These results were calculated by my various part-time undergraduate students during the period 1968-1973. I would like to express my thanks to all of them, in particular to M. Plischke who initiated the computer programme for calculations which were followed by others. I would also wish to thank the directors of the computer departments of Concordia University, McGill University and Montreal University for providing the computer facilities.

## (1) The Distribution Function (1.3)

Calculations using this distribution function had not been done exactly before. Previously, Sengupta [10] calculated a few values of activity coefficients with this function, but with the approximation  $b_{\pm} \approx b_{+-}$ . This approximation is physically inconsistent with the derivation of this distribution function, (cf. ref. [5]). Moreover, he used the "fit method" to calculate the nonlinear potential which, as we have shown before, does not give reliable results. Further, the exclusion volume which he used leads to physical inconsistencies, namely, the total exclusion volume,  $(n_0^+ b_+ + n_0^- b_-)$  becomes greater than unity even with the overlap-correction factor introduced by Dutta [25] for moderate concentrations.

We have calculated the relevant values with the parameters noted before, (see section 7), for 1-1, 1-2, 2-1 and 2-2 electrolytes. The calculations prove that even for 1-1 electrolyte the total exclusion volume becomes greater than unity for the reasonable value of  $a = 1.5A^0$ ;  $c = 5.N$ ;  $a = 2.0A^0$ ;  $c = 3.0N$ . For  $a = 4.0A^0$  and  $5.0A^0$  it becomes greater than unity even for  $c = 1.0N$ . This proves convincingly that the overlap-correction factor given by Dutta [25] and also used here is not physically tenable. Further, for fused alkali halides, where the situation is not complicated by the presence of water molecules, the known shortest distances between positive-positive, (negative-negative), ions from the central ion would make the exclusion volumes  $b_{\pm}$  physically inconsistent, even if they could be calculated exactly.

A closer scrutiny of all the calculated results indicates that this distribution function can reproduce the qualitative nature of the expected experimental results but is unlikely to yield experimental values even if the exclusion volumes could be properly corrected for the overlapping effect. Further, due to other difficulties and inconsistencies inherent in this distribution function discussed before, it is believed that the correct distribution function should be the expression (1.1) rather than (1.3). Consequently, in order to save space we have not presented here results obtained from this distribution function (1.3).



(ii) The Distribution Function (1.1) And The Boltzmann Distribution of DH Theory.

(a) Nonlinear Potential  $\lambda(r)$

Except for a few physically unrealistic cases mentioned below, the nonlinear potential  $\lambda(r)$  vs  $r/a$  has the same functional nature for all three cases. Individual cases differ only in the magnitudes and slopes of the functions. A few typical cases for models A and B of the distribution function (1.1) are shown in figures 1 to 6. In most cases the corresponding curves for the DH theory resemble relatively more closely to the model A. In all cases both potentials and mean activity coefficients differ significantly from the corresponding linear values. For values of  $a \geq 2.0A^0$  they tend to differ less, particularly for 1-1 electrolyte. Potentials on the surface of the ion for some realistic cases are given in Table 5.

Exceptional cases are observed for very small values of 'a' and large values of c where  $\lambda(r)$  becomes negative at  $r/a > 1.0$  and, after reaching a minimum quickly, approaches the value zero. A typical case is shown in Fig. 7 for the model B.

Qualitatively similar features were obtained for the following cases.

Model B:

1-2 electrolyte for  $a = 0.5A^0$ ;  $c = 3.0N$ ;  $5.0N$

1-3 and 2-1 electrolyte for  $a = 0.5A^0$ ;  $c = 1.0N$ ,  $3.0N$ ,  $5.0N$

2-2 electrolyte for  $a = 0.5A^0$ ;  $c = 1.0N$ ,  $3.0N$ ,  $5.0N$ ,  
and  $a = 1.0A^0$ ;  $c = 1.0N$ ,  $3.0N$

2-3 electrolyte for  $a = 0.5A^0$ ;  $c = 3.0N$ ,  $5.0N$   
and  $a = 1.0A^0$ ;  $c = 1.0N$ ,  $3.0N$ ,  $5.0N$

3-1 electrolyte for  $a = 0.5$  &  $1.0A^0$ ;  $c = 3.0N$ ,  $5.0N$

$\lambda(r)$  vs  $r/a$  were not calculated for 3-2 and 3-3 electrolyte for small values of a.

Model A:

All the curves showed regular features except the case of 2-3 electrolyte at  $a = 0.5A^0$ ,  $c = 5.0N$  where a very slight relatively flat decrease was noticed.

Similar feature was also observed in the case of DH theory only for 3-1 electrolyte at  $a = 0.5A^{\circ}$ ,  $1.0A^{\circ}$  and  $c = 1.0N$ ,  $3.0N$ ,  $5.0N$ . (The values for  $2.0N$  and  $4.0N$  were not calculated). But here the potential becomes positive again before decreasing to zero, see figure 7.

These novel features of the potential are obviously caused by the strong field of the central ion and large excess of negative ions in the atmosphere so that the total potential due to the atmospheric ions exceeds that due to the central (positive) ion.

(b) Mean Activity Coefficients.

Nonlinear mean activity coefficients  $\gamma_{\pm}$  for various cases are shown in figures 8-22. It will be noticed that both models of the distribution function (1.1) can reproduce the qualitative features of the observed activity coefficients. The results also confirm the well known fact that the original DH theory cannot predict even the qualitative behaviour of the observed activity coefficients. It might however be noted that, contrary to the common opinion, it is found that activity coefficients increase very slightly for high concentrations and large  $a$ . This is presumably due to the full contribution of the nonlinear terms including the term  $\frac{\partial \chi}{\partial V} \frac{\partial V}{\partial N_{\pm}} = kT \ln \gamma_{\pm} = \frac{\partial F^{el}}{\partial N_{\pm}}$ .

For physical reasons, I think, the correct distribution function for binary electrolytic solutions is the expression (1.1) with a model similar to the model B discussed here. Scrutinising the extensive data quantitatively I have come to the conclusion that a close agreement between calculated and experimental values over the entire concentration range can be achieved only by this model provided appropriate values of  $a_{\pm}$  and overlap-corrected  $b$  are taken into consideration for each given system. It is important to note carefully that the value of  $b$  chosen should not lead to any physical inconsistency, namely, the total exclusion volume  $(n_o^+ b_+^+ + n_o^- b_-^-)$  should not exceed unity and that  $\chi^2$  should not be negative, contrary to the cases reported in the literature as well as encountered in this study for

some values of  $a$  and  $c$ . This was evidently caused by the large values of  $b$ .

Finally, some special features of the activity coefficients obtained from this study are noted below.

For 2-2, 2-3 and 3-3 electrolytes, the nonlinear activity coefficients become vanishingly small for small values of ' $a$ ' even for low concentrations. Table 6 gives a few values. This evidently means that the ions are effectively undissociated. Consequently, it proves directly the remark of Gronwall *et al* [19] that the ion-association effect is already included in the ion-atmosphere theory and there is no theoretical justification to treat this ion-association effect outside it and separately, (cf. also ref. [2]).

But the most striking feature appears in extremely high nonlinear activity coefficients of 1-3, (and consequently 3-1), electrolyte for  $a=0,5 A^0$  and  $c=0.01N$ , (see Table 7).

Although a high value as 500, (for  $HClO_4$  at 16m [26]), has been reported such a high value at this low concentration had never been observed, presumably because such a small average ionic radius is not physically possible.

It is difficult to offer any satisfactory explanation for such a high value for the hypothetical electrolyte with  $a=0.5A^0$ . The fact that water dipoles near the ions exert great repulsive forces cannot be relevant for our case, since we are dealing here with a continuous medium with  $D=78.3$ . Possibly, such a high value may be ascribed to the steep slope of  $\frac{\partial F^{eL}}{\partial N_{\pm}}$

## 9. CONCLUSION

A mathematically and physically consistent theory for solutions of strong electrolytes cannot be based on the original Debye-Hueckel theory using Boltzmann distribution. Even if one ignores theoretical inconsistencies of this theory, calculations of activity coefficients from the exact nonlinear potential of the ion-atmosphere clearly point out that it cannot predict experimental results even

qualitatively. Neither additional hypotheses, e.g., ion-association, hydration energy, nor ad hoc recipes mentioned before are permissible in a rigorous theory. A theoretically consistent theory had to be based on the modified DH theory in which the Boltzmann distribution is replaced by the distribution function (1.1). This distribution can provide a good agreement between theoretical and experimental results for the entire range of concentrations, if one chooses carefully the surface at a distance ' $a_1$ ' from the central ion where the continuity condition is applied and the correct Boltzmann's exclusion volume  $b$ .

The extensive results of this study suggest that for a good fit one should use

(i) the distribution function (1.1) with a fixed  $a_1$  and  $b$  for a given system;

(ii) the value of  $a_1$  should be taken as the radius of the permanently hydrated ion and the same for all concentrations;

(iii) the value of  $b$  is given by  $b = \gamma b_0$ ;  $b_0 = \frac{4\pi}{3}(r_+ + 2r_{H_2O} + r_-)^3$ ,

$\gamma$  is the overlap-correction factor, which may depend on the concentration.

It is extremely difficult to calculate  $\gamma$  exactly and as yet it had not been possible for the simplest possible condensed system. Once the correct  $b$  is found either by calculation or by trial and error, the modified theory can predict all thermodynamic and transport properties of ionic solutions, (as well as of fused salts, cf. ref. [2]), without any ad hoc assumption outside the ion-atmosphere theory. At the present state of our knowledge modified DH theory seems to offer us the only way to tackle a system of charged particles interacting with Coulomb force in a mathematically and physically consistent manner.

TABLE 1: Expressions for  $G_s(r)$  for  $s=1$  to 7.

$$G_1(r) = 0$$

$$G_2(r) = f''(0)/(2!) \cdot r^{-1} b_1^2(r)$$

$$G_3(r) = f^{(3)}(0)/(3!) \cdot r^{-2} b_1^3 + f''(0)/(1!) \cdot r^{-1} b_1 b_2$$

$$G_4(r) = f^{(4)}(0)/(4!) \cdot r^{-3} b_1^4 + f^{(3)}(0)/(2!) \cdot r^{-2} b_1^2 b_2 \\ + f''(0)/(2!) \cdot (r^{-1} b_2^2 + 2! r^{-1} b_1 b_3)$$

$$G_5(r) = f^{(5)}(0)/(5!) \cdot r^{-4} b_1^5 + f^{(4)}(0)/(3!) \cdot r^{-3} b_1^3 b_2 \\ + f^{(3)}(0)/(2!) \cdot (r^{-2} b_1 b_2^2 + r^{-2} b_1^2 b_3) \\ + f''(0)/(1!) \cdot (r^{-1} b_2 b_3 + r^{-1} b_1 b_4)$$

$$G_6(r) = f^{(6)}(0)/(6!) \cdot r^{-5} b_1^6 + f^{(5)}(0)/(4!) \cdot r^{-4} b_1^4 b_2 \\ + f^{(4)}(0) \cdot r^{-3} [b_1^2 b_2^2/(2!2!) + b_1^3 b_3/(3!)] \\ + f^{(3)}(0) \cdot r^{-2} [b_1 b_2 b_3 + b_1^2 b_4/(2!) + b_2^3/(3!)] \\ + f''(0) \cdot r^{-1} [b_1 b_5 + b_2 b_4 + b_3^2/(2!)]$$

$$G_7(r) = f^{(7)}(0)/(7!) \cdot r^{-6} b_1^7 + f^{(6)}(0)/(5!) \cdot r^{-5} b_1^5 b_2 \\ + f^{(5)}(0)/(4!) \cdot r^{-4} (2! b_1^3 b_2^2 + b_1^4 b_3) \\ + f^{(4)}(0) \cdot r^{-3} [b_1 b_2^3/(3!) + b_1^2 b_2 b_3/(2!) + b_1^3 b_4/(3!)] \\ + f^{(3)}(0)/(2!) \cdot r^{-2} (2! b_1 b_2 b_4 + b_1 b_3^2 + b_2^2 b_3 + b_1 b_5) \\ + f''(0) \cdot r^{-1} (b_1 b_6 + b_2 b_5 + b_3 b_4).$$

TABLE 2: Expressions for  $b_s(r)$  for  $s=1$  to 7.

$$\begin{aligned}
b_1(r) &= \exp(-\chi r) \\
b_2(r) &= f''(0)/(2!) \cdot \chi^{-1} \int_r^\infty x^{-1} \cdot b_1^2(x) \sinh \chi(x-r) dx \\
b_3(r) &= f^{(3)}(0)/(3!) \cdot \chi^{-1} \int_r^\infty x^{-2} \cdot b_1^3(x) \sinh \chi(x-r) dx \\
&\quad + f''(0)/(2!) \cdot \chi^{-1} \int_r^\infty x^{-1} b_1(x) b_2(x) \sinh \chi(x-r) dx \\
b_4(r) &= f^{(4)}(0)/(4!) \cdot \chi^{-1} \int_r^\infty x^{-3} b_1^4 \sinh \chi(x-r) dx \\
&\quad + f^{(3)}(0)/(2!) \cdot \chi^{-1} \int_r^\infty x^{-2} b_1^2 b_2 \sinh \chi(x-r) dx \\
&\quad + f''(0)/(2!) \cdot \chi^{-1} \int_r^\infty [x^{-1} b_2^2 + 2x^{-1} b_1 b_3] \sinh \chi(x-r) dx \\
b_5(r) &= f^{(5)}(0)/(5!) \cdot \chi^{-1} \int_r^\infty x^{-4} b_1^5 \sinh \chi(x-r) dx \\
&\quad + f^{(4)}(0)/(3!) \cdot \chi^{-1} \int_r^\infty x^{-3} b_1^3 b_2 \cdot \sinh \chi(x-r) dx \\
&\quad + f^{(3)}(0)/(2!) \cdot \chi^{-1} \int_r^\infty [x^{-2} b_1 b_2^2 + x^{-2} b_1^2 b_3] \sinh \chi(x-r) dx \\
&\quad + f''(0) \cdot \chi^{-1} \int_r^\infty [x^{-1} b_2 b_3 + x^{-1} b_1 b_4] \sinh \chi(x-r) dx \\
b_6(r) &= \chi^{-1} \int_r^\infty [f^{(6)}(0)/(6!) \cdot x^{-5} b_1^6 + f^{(5)}(0)/(4!) \cdot x^{-4} b_1^4 b_2 \\
&\quad + f^{(4)}(0) x^{-3} \{b_1^2 \cdot b_2^2/(2!2!) + b_1^3 b_3/\theta!\}] \\
&\quad + f^{(3)}(0) x^{-2} \{b_1 b_2 b_3 + b_1^2 b_4/(2!) + b_2^3/(3!)\} \\
&\quad + f''(0) x^{-1} \{b_1 b_5 + b_2 b_4 + b_3^2/(2!)\}] \cdot \sinh \chi(x-r) dx \\
b_7(r) &= \chi^{-1} \int_r^\infty [f^{(7)}(0)/(7!) \cdot x^{-6} b_1^7 + f^{(6)}(0)/(5!) \cdot x^{-5} b_1^5 b_2 \\
&\quad + f^{(5)}(0) \cdot x^{-4} \{2! b_1^3 b_2^2/(4!) + b_1^4 b_3/\theta!\}] \\
&\quad + f^{(4)}(0) \cdot x^{-3} \{b_1 b_2^3/(3!) + b_1^2 b_2 b_3/(2!) + b_1^3 b_4/(3!)\} \\
&\quad + f^{(3)}(0) \cdot x^{-2} \{b_1 b_2 b_4/(1!) + b_1 b_3^2/(2!) + b_1^2 b_5/(2!) + b_2^2 b_3/(2!)\} \\
&\quad + f''(0) x^{-1} \{b_1 b_6 + b_2 b_5 + b_3 b_4\}] \sinh \chi(x-r) dx
\end{aligned}$$

TABLE 3: Expressions for  $X_s(r)$  for  $s=1$  to 7.

$$X_1(r) = a \cdot r^{-1} \exp[-\chi(r-a)]$$

$$X_2(r) = a^2 \cdot \exp(2\chi a) \{r^{-1} b_2(r) - X_1(r) \cdot a^{-1} b_2(a)\}$$

$$X_3(r) = a^3 \cdot \exp(3\chi a) \{r^{-1} b_3(r) - X_1(r) \cdot a^{-1} b_3(a)\} - 2aX_2(r)b_2(a) \exp(2\chi a)$$

$$X_4(r) = a^4 \cdot \exp(4\chi a) \{r^{-1} b_4(r) - X_1(r) \cdot a^{-1} b_4(a)\}$$

$$-a^2 X_2(r) \exp(4\chi a) \{b_2^2(a) + 2b_1(a) b_3(a)\} - 3aX_3(r) b_2(a) \exp(2\chi a)$$

$$X_5(r) = a^5 \cdot \exp(5\chi a) \cdot \{r^{-1} b_5(r) - X_1(r) \cdot a^{-1} b_5(a)\} - 4a X_4(r) b_2(a) \exp(2\chi a)$$

$$- 3a^2 \cdot X_3(r) \{ \exp(4\chi a) \cdot b_2^2(a) + \exp(3\chi a) b_3(a) \}$$

$$- 2a^3 X_2(r) \{ \exp(4\chi a) b_4(a) + \exp(5\chi a) b_2(a) b_3(a) \}$$

$$X_6(r) = a^6 \cdot \exp(6\chi a) \cdot \{r^{-1} b_6(r) - X_1(r) a^{-1} b_6(a)\}$$

$$- a^4 \cdot X_2(r) \exp(6\chi a) \{b_3^2(a) + 2b_1(a) b_5(a) + 2b_2(a) \cdot b_4(a)\}$$

$$- a^3 \cdot X_3(r) \exp(6\chi a) \{b_2^3(a) + 3b_1^2(a)b_4(a) + 6b_1(a)b_2(a)b_3(a)\}$$

$$- a^2 X_4(r) \exp(6\chi a) \{6b_1^2(a)b_2^2(a) + 4b_1^3(a)b_3(a)\}$$

$$- 5a X_5(r) \exp(6\chi a) \cdot \{b_1^4(a) b_2(a)\}$$

$$X_7(r) = a^7 \cdot \exp(7\chi a) \{r^{-1} b_7(r) - X_1(r) a^{-1} b_7(a)\}$$

$$- 6a X_6(r) \exp(7\chi a) \cdot \{b_1^5(a) \cdot b_2(a)\}$$

$$- 5a^2 X_5(r) \exp(7\chi a) \cdot \{b_1^4(a) b_3(a) + 2b_1^3(a) b_2^2(a)\}$$

$$- 4a^3 X_4(r) \exp(7\chi a) \cdot \{b_1^3(a)b_4(a) + b_1(a)b_2^3(a) + 3b_1^2(a) b_2(a) b_3(a)\}$$

$$- 3a^4 X_3(r) \exp(7\chi a) \cdot \{b_1^2(a) b_5(a) + b_2^2(a) \cdot b_3(a)$$

$$+ b_3^2(a) b_1(a) + 2b_1(a) b_2(a) b_4(a)\}$$

$$- 2a^5 X_2(r) \exp(7\chi a) \cdot \{b_1(a)b_6(a) + b_2(a) b_5(a) + b_3(a) b_4(a)\}$$

TABLE 4: Potentials on the surface of the ion and the mean activity coefficients calculated by the Ad hoc method.

a(A <sup>0</sup> )	C(N)	m	r <sub>1</sub> (A <sup>0</sup> )	λ(a)		γ <sub>±</sub>	
				Ad hoc method	Exact	Ad hoc method	Exact
Model A: $b = \frac{4}{3} \pi a^3$							
1	5	40.163	0.291 (1.26)	8.463 (3.563)	3.604	1.952	0.203
2	5	5.513	1.233 (2.52)	2.167 (1.251)	1.470	0.537	0.479
3	5	2.227	2.213 (3.78)	1.073 (0.709)	0.859	1.678	0.303
4	3	2.002	2.781 (5.39)	0.896 (0.564)	0.681	0.891	0.409
5	1	2.316	3.018 (6.30)	0.722 (0.508)	0.607	0.878	0.784
Model B: $b = \frac{4}{3} (a + r_{H_2O})^3$							
1	5	3.544	1.119 (2.44)	4.295 (3.891)	4.311	0.261	0.260
2	5	2.001	1.869 (3.60)	1.746 (1.505)	1.778	0.537	0.495
3	2	2.048	2.282 (4.81)	1.218 (0.966)	1.168	0.728	0.607
4	1	2.097	2.635 (6.03)	0.997 (0.862)	0.887	0.780	0.688
5	0.1	8.170	1.158 (7.27)	1.458 (0.799)	0.948	1.025	0.788

The values within the bracket ( ) were calculated from the condition  $\lambda_1 = \lambda_2$  at  $\xi_{\min}$ . All the values of this table were calculated by N. Mukerji.



TABLE 5: Potentials calculated from the exact solution of the distribution (1.1) and for DH theory.

a(A <sup>0</sup> )	c(N)	$\lambda_L(a)$				$\lambda(a)$		
		models:		B	A	DH	B	A
<u>1-1 Electrolyte</u>								
1.5	1.0		3.23	3.20	3.20	3.11	2.98	2.96
1.5	5.0		2.48	2.29	2.27	2.54	2.18	2.11
2.0	1.0		2.20	2.17	2.16	2.16	2.08	2.06
2.0	5.0		1.74	1.49	1.45	1.78	1.47	1.40
4.0	1.0		0.88	0.81	0.77	0.89	0.81	0.76
<u>1-2 Electrolyte</u>								
1.5	1.0		3.00	2.98	2.98	2.48	2.22	2.16
1.5	5.0		2.16	2.05	2.03	2.01	1.62	1.54
2.0	1.0		2.01	1.99	1.98	1.75	1.64	1.60
2.0	5.0		1.44	1.31	1.28	1.39	1.14	1.07
4.0	1.0		0.75	0.71	0.69	0.72	0.67	0.63
<u>1-3 Electrolyte</u>								
1.5	1.0		2.83	2.81	2.81	2.08	1.61	1.66
1.5	5.0		1.96	1.88	1.86	1.57	1.16	1.21
2.0	1.0		1.88	1.86	1.85	1.34	1.16	1.28
2.0	5.0		1.27	1.18	1.16	0.76	0.74	0.87
4.0	1.0		0.67	0.64	0.63	0.21	0.29	0.54
<u>2-1 Electrolyte</u>								
1.5	1.0		5.99	5.95	5.95	6.03	5.30	4.97
1.5	5.0		4.32	4.09	4.06	5.22	4.02	3.61
2.0	1.0		4.02	3.97	3.97	4.19	3.82	3.66
2.0	5.0		2.88	2.61	2.56	3.56	2.79	2.51
4.0	1.0		1.50	1.42	1.37	1.66	1.53	1.43
<u>2-2 Electrolyte</u>								
1.5	1.0		5.65	5.62	5.62	5.01	3.46	3.00
1.5	5.0		3.91	3.75	3.73	4.12	2.80	2.28
2.0	1.0		3.75	3.71	3.71	3.35	2.70	2.42
2.0	5.0		2.55	2.36	2.32	2.79	2.04	1.72
4.0	1.0		1.34	1.28	1.25	1.35	1.22	1.12

Table 5 (continued)

a(A°)	c(N) models:	$\lambda_L$ (a)			$\lambda$ (a)		
		B	A	DH	B	A	DH
<u>2-3 Electrolyte</u>							
1.5	1.0	5.39	5.37	5.36	4.65	2.43	2.14
1.5	5.0	3.62	3.50	3.48	3.46	2.07	1.65
2.0	1.0	3.54	3.52	3.51	2.79	1.94	1.78
2.0	5.0	2.32	2.18	2.15	2.24	1.50	1.30
4.0	1.0	1.23	1.19	1.16	1.00	0.88	0.91
<u>3-1 Electrolyte</u>							
1.5	1.0	8.49	----	8.43	9.67	----	6.57
1.5	5.0	5.87	5.63	5.59	8.26	6.43	4.85
2.0	1.0	5.63	5.58	5.56	6.60	6.29	5.03
2.0	5.0	3.82	3.55	3.49	9.01	4.83	3.45
4.0	1.0	2.01	1.93	1.88	3.20	2.91	2.05
<u>3-2 Electrolyte</u>							
1.5	1.0	----	8.05	8.04	----	5.23	3.51
1.5	5.0	5.43	5.25	5.22	6.16	5.28	2.75
2.0	1.0	5.32	5.27	5.26	5.47	4.65	2.94
2.0	5.0	3.48	3.28	3.23	4.69	3.40	2.16
4.0	1.0	1.85	1.78	1.74	2.27	2.03	1.51
<u>3-3 Electrolyte</u>							
1.5	1.0	7.76	7.73	7.72	5.16	4.61	2.41
1.5	5.0	5.09	4.94	4.92	5.23	3.06	1.92
2.0	1.0	5.06	5.03	5.02	4.88	3.12	2.06
2.0	5.0	3.22	3.06	3.03	3.58	2.48	1.56
4.0	1.0	1.72	1.67	1.64	1.71	1.44	1.18

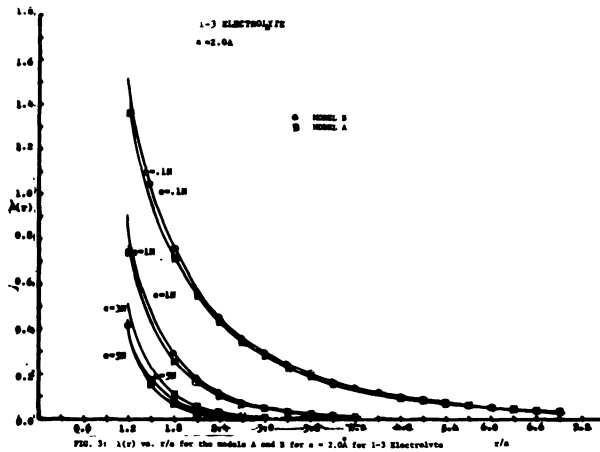
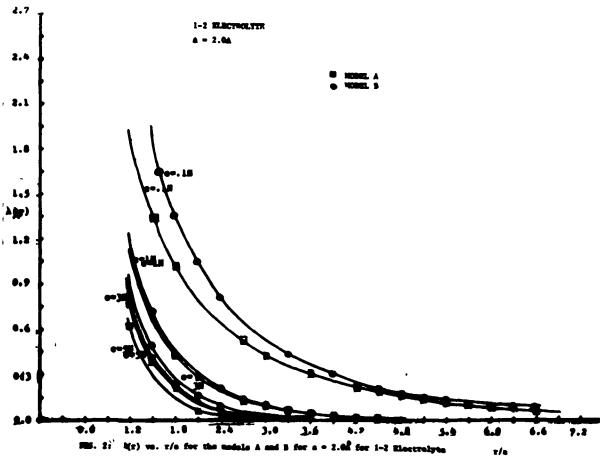
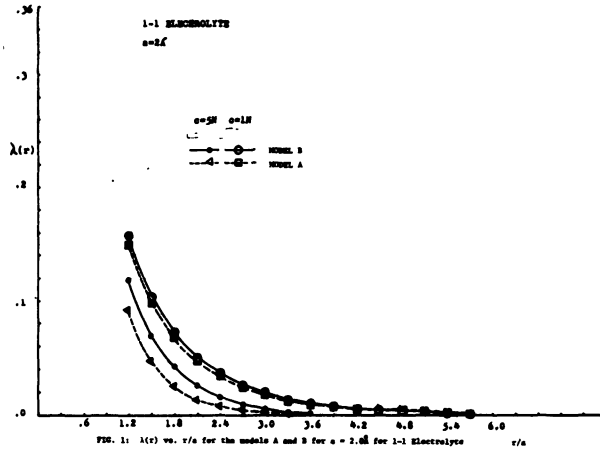
TABLE 6: Extremely Small Values of Mean Activity Coefficients.

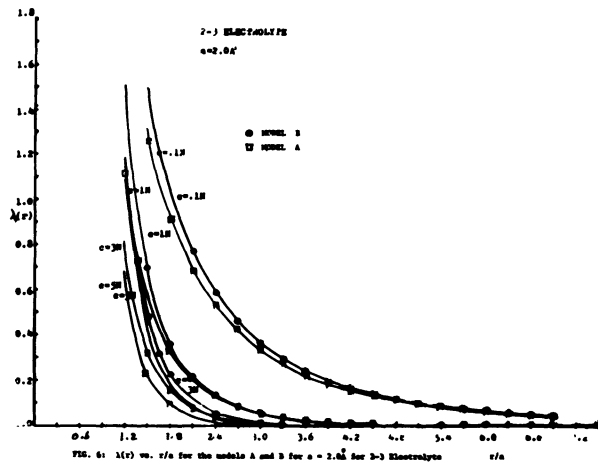
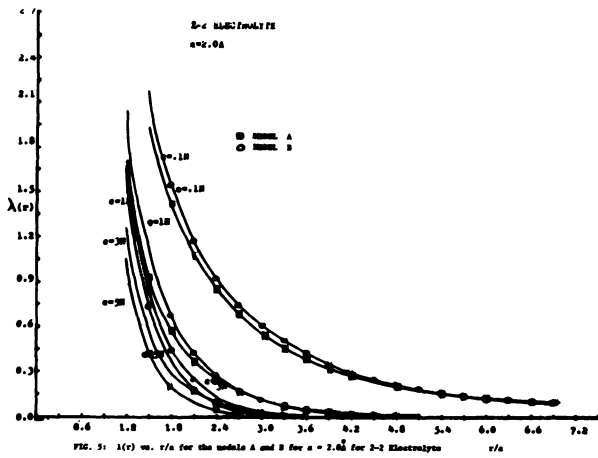
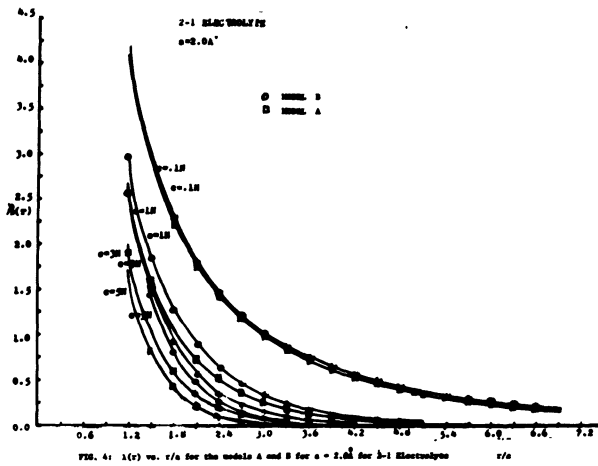
a(A°)	c(N)	$(\gamma_+)$			$\gamma_+$		
		model B	model A	DH	model B	model A	DH
<u>2-2 Electrolyte</u>							
0.5	0.01	0.521	0.521	0.521	1.17 E-03	5.83 E-07	3.55 E-07
1.0	0.01	0.529	0.529	0.529	2.10 E-02	2.98 E-03	2.24 E-03
2.0	0.01	0.543	0.543	0.543	0.168	0.127	0.115
<u>2-3 Electrolyte</u>							
0.5	0.01	0.336	0.336	0.336	8.76 E-05	9.87 E-10	5.47 E-10
1.0	0.01	0.346	0.346	0.346	1.81 E-03	8.05 E-05	5.27 E-05
2.0	0.01	0.363	0.363	0.363	3.42 E-02	1.80 E-02	1.43 E-02
<u>3-3 Electrolyte</u>							
0.5	0.01	-----	0.168	0.168	-----	1.11 E-17	5.58 E-18
1.0	0.01	0.176	0.176	0.176	2.51 E-06	1.03 E-08	6.03 E-09
2.0	0.01	0.192	0.192	0.192	9.66 E-04	2.61 E-04	1.81 E-04

TABLE 7: Extremely High Values of Mean Activity Coefficients.

<u>1-3 Electrolyte</u>							
0.5	0.01	0.613	0.613	0.613	6.02 E03	1.27 E08	1.67 E08
1.0	0.01	0.620	0.620	0.620	3.72 E01	2.57 E02	2.57 E02
2.0	0.01	0.633	0.633	0.633	2.01	2.33	2.05

(The symbol Eon means  $10^n$  and E-on means  $10^{-n}$ )





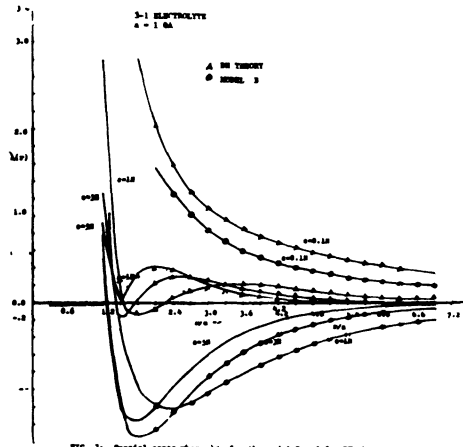


FIG. 7: Special case where  $\nu_+ = 1$  for the model 2 and for BH theory

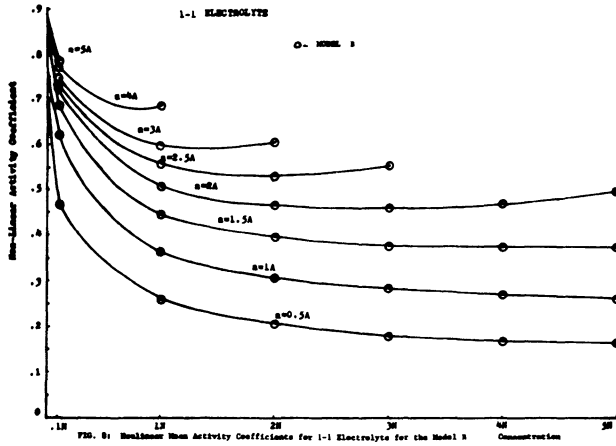


FIG. 8: Mean Activity Coefficients for 1-1 Electrolyte for the Model 2

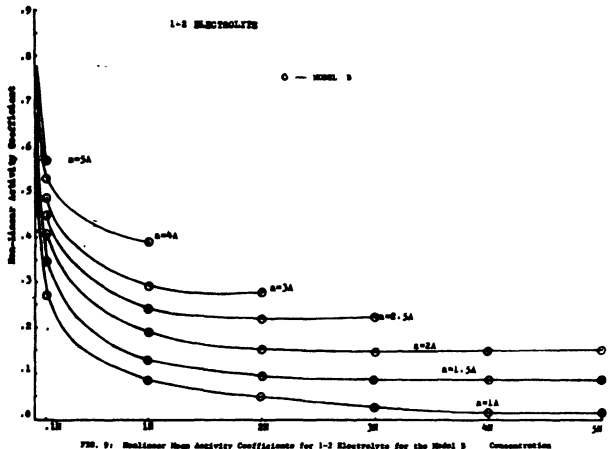
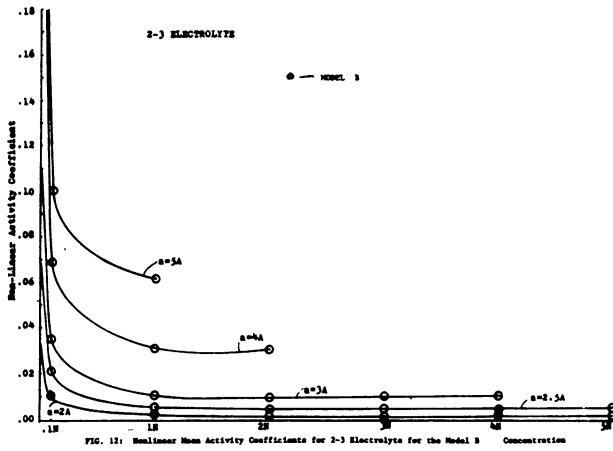
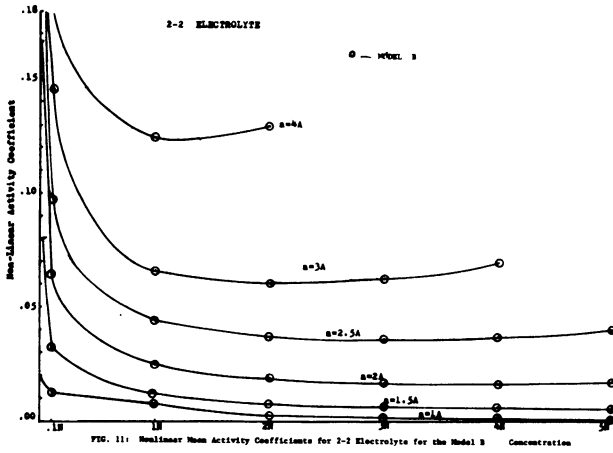
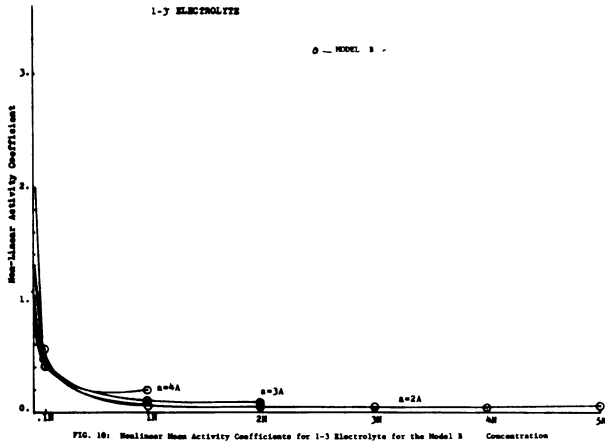
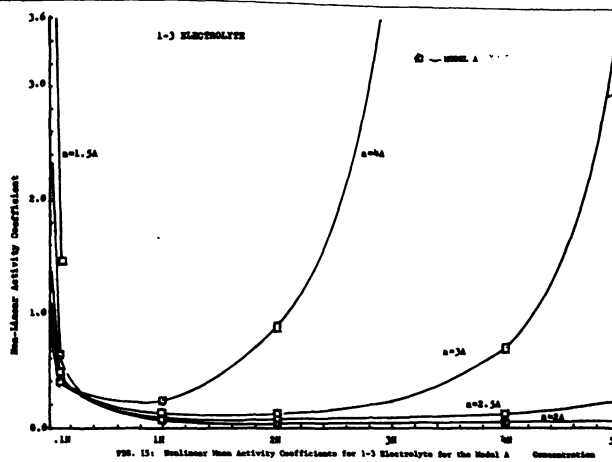
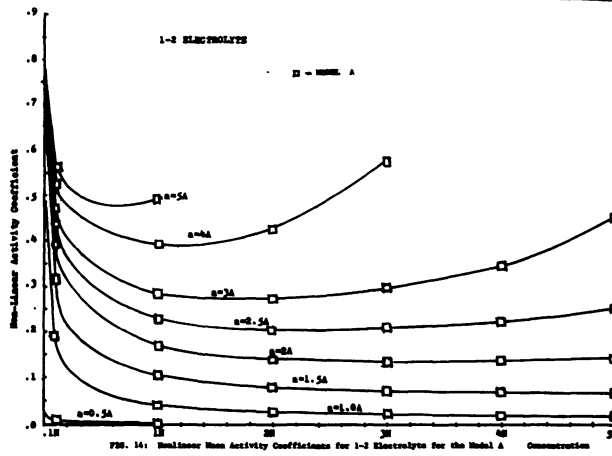
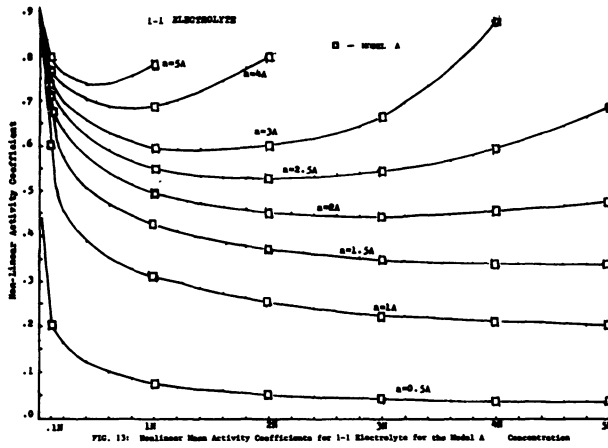


FIG. 9: Mean Activity Coefficients for 1-2 Electrolyte for the Model 2







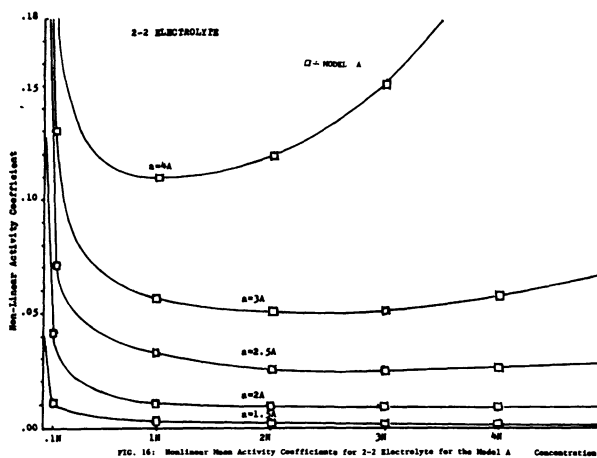


FIG. 16: Nonlinear Mean Activity Coefficients for 2-2 Electrolyte for the Model A

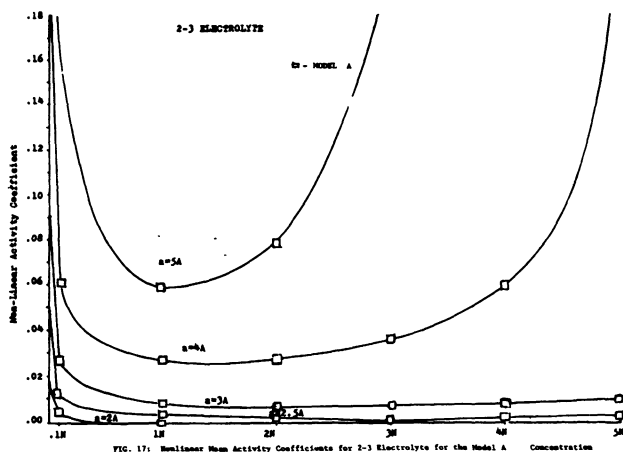


FIG. 17: Nonlinear Mean Activity Coefficients for 2-3 Electrolyte for the Model A

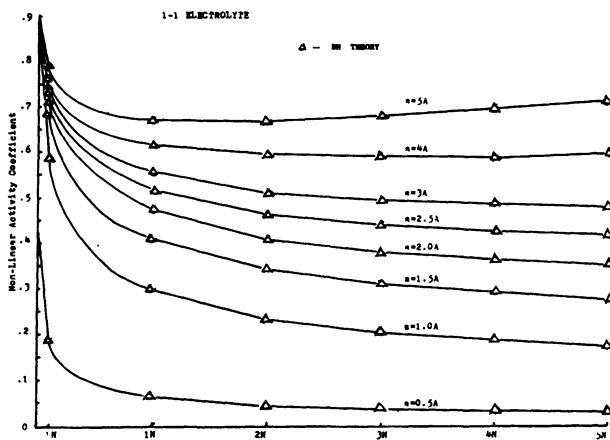
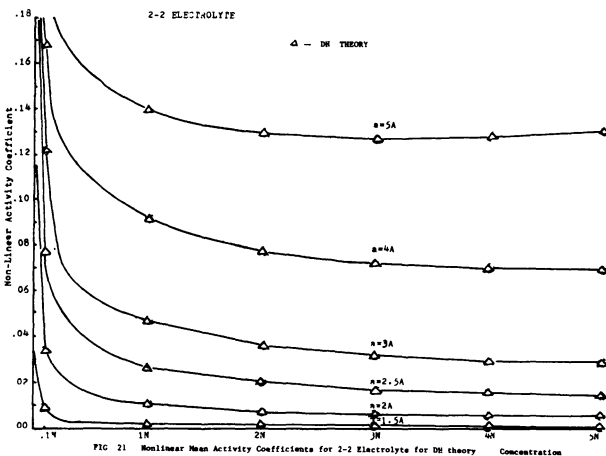
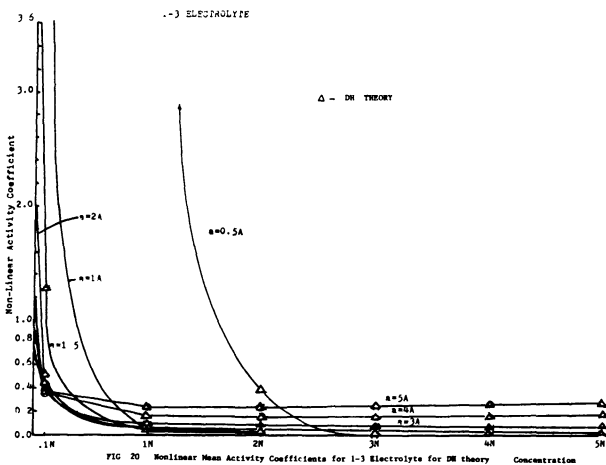
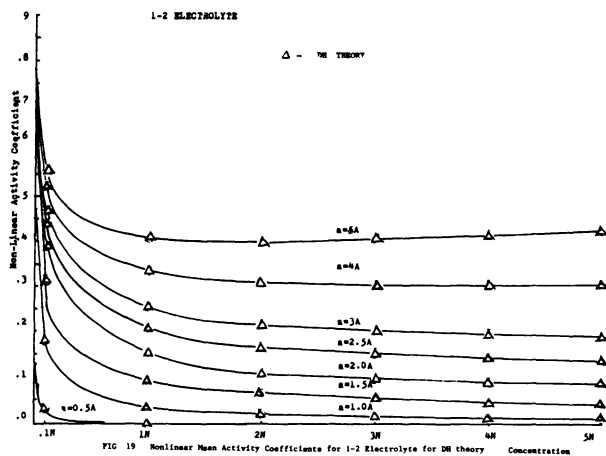


FIG. 18: Nonlinear Mean Activity Coefficients for 1-1 Electrolyte for DH theory



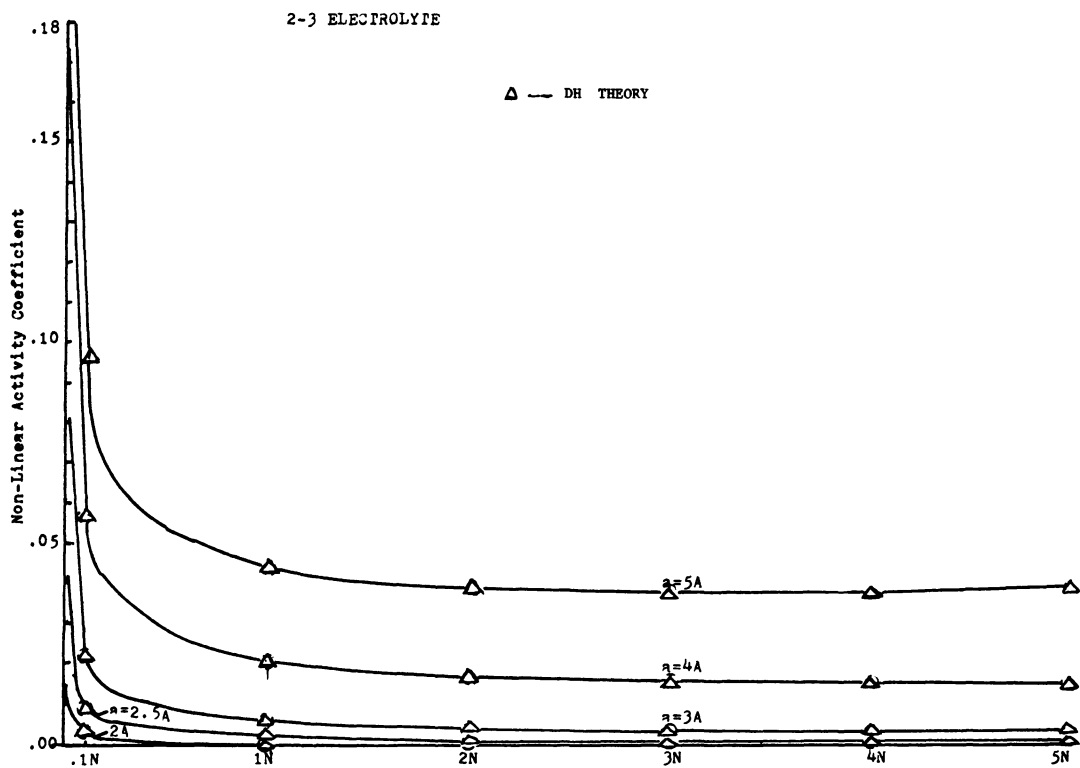


FIG. 22: Nonlinear Mean Activity Coefficients for 2-3 Electrolyte for DH theory Concentration

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