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THEORY FOR STRONG ELECTROLYTES  
IN NOT TOO DILUTE SOLUTIONS

by

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THEORY FOR STRONG ELECTROLYTES  
IN NOT TOO DILUTE SOLUTIONS\*

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Summary. The theory describes a model where the space around a positive ion of an electrolytic solution is considered, taking explicitly into account interaction among first neighbors, and in addition the possibility that a given cell will be not occupied by ions. It is thus deduced an expression for  $\kappa$  which coincides - at the limit of extremely dilute solution - with the reciprocal of Debye's characteristic length, saving a normalization factor.

Following standard outlines, a formula for  $\ln f$  ( $f$ , activity coefficient) as a function of  $\underline{a}$  is obtained, being  $\underline{a}$  the mean distance of closest approach between two ions. The parameter  $\underline{a}$  is fitted for different electrolytes, varying concentration and temperature.

It is found that  $\underline{a}$  is not constant. In order to obtain agreement between theory and experiment,  $\underline{a}$  must increase with concentration, within the theory's range. An explanation of this result is given. The effect of temperature is discussed.

For the chlorides, there is good agreement between the ordination given by the values of the parameter  $\underline{a}$  and the ordering capacity of ions in aqueous solution.

Reasonable values of  $\underline{a}$  can be obtained for  $\text{IO}_3\text{K}$  and  $\text{NO}_3\text{K}$ , for which Debye-Huckel's theory fails.

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Introduction

The application of a statistical theory for strong electrolytes in not too dilute solutions (1) is studied in this paper.

With a method similar to that used by Bethe (2) in his work on binary alloys, interaction among first neighbors is considered explicitly, and in addition the possibility that a given cell may be not occupied by ions (empty shell). This introduces a convenient model for describing the problem's physical reality.

An expression for  $\ln f$ 's dependence on  $\underline{a}$  - the only adjustable parameter in the theory - is obtained.  $\underline{a}$  is the mean distance of closest approach between two ions. It represents, really, an average of mean distances of closest approach between two positive, negative or of different sign ions, distances which can be respectively labeled as  $\underline{a}(++)$ ,  $\underline{a}(--)$  and  $\underline{a}(+-)$ . With these definitions the model studied is regarded as a dynamical deformable lattice, due to the distinct partial ordinations that the ionic groups can take.

The parameter  $\underline{a}$  is calculated for different electrolytes, varying concentration and temperature; some of its properties, over which discrepancies exist, are discussed qualitatively. Doubts have been thrown-for example - over its constancy with respect to concentration (3). In that sense, it is attempted an interpretation of the influence of coulombian interactions and other variables related with that parameter.

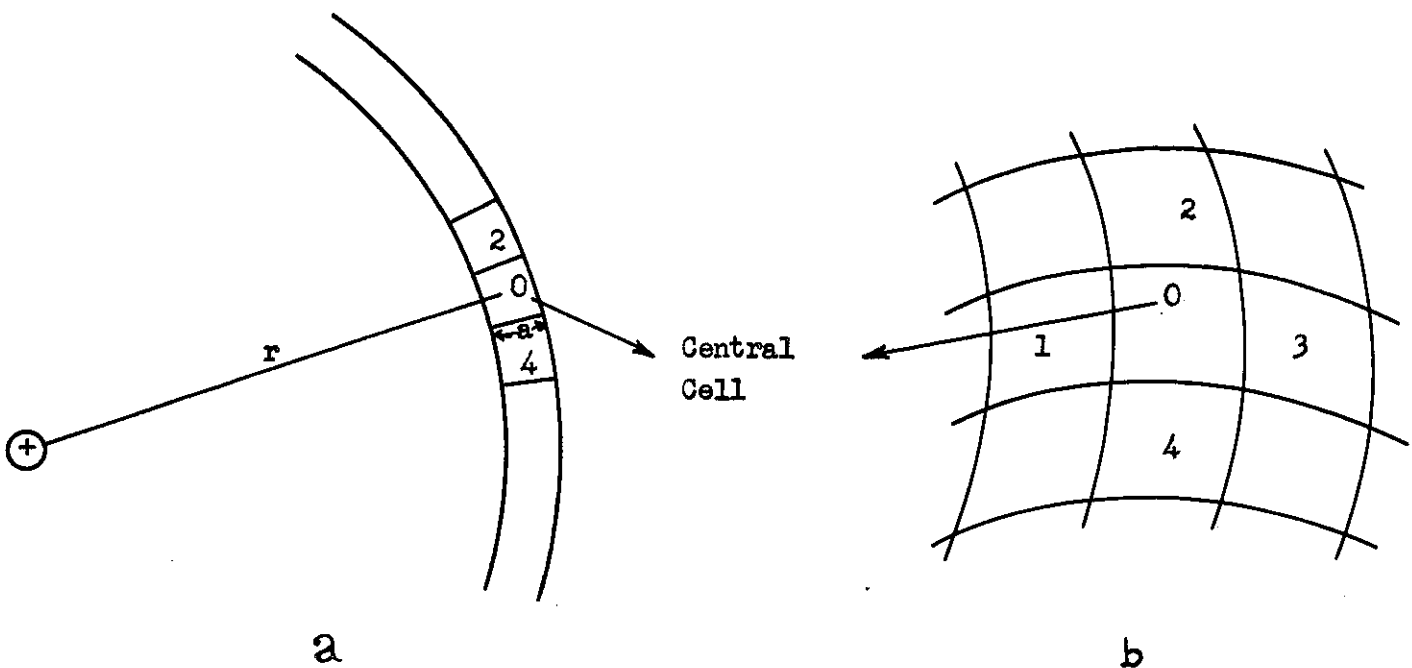
It is of interest estimating  $\underline{a}$  in particular cases such as  $\text{IO}_{\frac{1}{3}}\text{K}$  and  $\text{NO}_{\frac{1}{3}}\text{K}$ ; in fact, some values found in literature imply a

contradiction with the physical meaning assigned to the parameter.

The results obtained allow to fix the method's range of validity; that is, when a solution begins to be concentrated in terms of the theory.

### Review and application of Cernuschi's theory

Spherical concentric shells of thickness  $a$  around a positive ion are considered (Fig. 1-a). Each one is divided in cells of volume  $a^3$ , in such a way that any one has four neighboring cells in the same shell (Fig. 1-b).



On calculating the electric density  $\rho(r)$ , the following factors are taken into account:

- a)  $\Psi(r)$ , the potencial at the distance  $r$  from a positive ion, produced by the solution's whole charge distribution, excluding that of the spherical shell.
- b) The interaction between an ion and its first neighbors from the same spherical shell. One only ring of our neighboring cells is considered-approximation sufficient in phenomena ruled by short-range order.
- c) A potential  $\mathcal{V}$  representing the mean potential produced by the remaining ions from the spherical shell, on each of the neighboring cells.

The following functions are defined:

$$\begin{aligned} \xi(r) &= \exp(-z \epsilon \Psi(r)/kT) ; & \eta &= \exp(-z^2 \epsilon^2 / D a kT) \\ \zeta &= \exp(-z \epsilon \mathcal{V}/kT) & \delta &= \xi \zeta \end{aligned} \quad (1)$$

where, according to what precedes,  $\eta$  is the Boltzmann factor representing interaction between two ions with the same sign which are at a distance  $a$ ;  $\xi(r)$  is the Boltzmann factor corresponding to the potential at a distance  $r$  from a positive ion, over another positive ion; and  $\zeta$  the Boltzmann factor of the mean interaction between

the ions outside the first ring and one of the cells of the ring.

Calling  $f_+$ ,  $f_-$  and  $f_0$  the probabilities, saving a proportionality factor, that the central cell (Fig. 1) be occupied by a positive or negative ion, or empty,  $\rho(r)$  is expressed as:

$$\rho(r) = \frac{z\varepsilon}{a^3} \frac{N}{V/a^3} \frac{f_+ - f_-}{f_+ + f_- + f_0} = z\varepsilon n \frac{f_+ - f_-}{f_+ + f_- + f_0} \quad (2)$$

And writing explicitly  $f_+$ ,  $f_-$  and  $f_0$ :

$$\rho(r) = z\varepsilon n \left[ \xi(1 + \delta\eta + \delta^{-1}\eta^{-1})^4 - \xi^{-1}(1 + \delta\eta^{-1} + \delta^{-1}\eta)^4 \right] / \left[ \xi(1 + \delta\eta + \delta^{-1}\eta^{-1})^4 + \xi^{-1}(1 + \delta\eta^{-1} + \delta^{-1}\eta)^4 + (1 + \delta + \delta^{-1})^4 \right] \quad (3)$$

If interaction among neighboring ions is neglected, that is  $\eta = 1$ :

$$\rho(r) = z\varepsilon n(\xi - \xi^{-1})/3 \quad (4)$$

The density expression used by Debye and other authors, is relation (4), without the divisor 3. This difference is due to not considering the possibility of empty cells and to the use of Boltzmann factors without normalizing.

Any one of the cells of the spherical shell can be taken as central (1). With this basis it is possible to obtain other expressions for  $f_+$ ,  $f_-$  and  $f_0$ , which equalized to the former lead to:

$$\xi = \delta(1 + \delta + \delta^{-1})^3 / (1 + \eta^{-1}\delta^{-1} + \eta\delta)^3 \quad (5)$$

Removing  $\delta$  from (5), and replacing in (3), a Poisson equation is reached (valid also for concentrated electrolytes), depending on the parameter  $\eta$ .

In the limiting case of infinitely dilute solutions,  $\eta = 1$ ; therefore, on dealing with not too dilute solutions,  $\delta$  can be developed around  $\eta = 1$ :

$$\delta = \xi + (\partial\delta/\partial\eta)_{\eta=1}(\eta-1) + \frac{1}{2} (\partial^2\delta/\partial\eta^2)_{\eta=1} (\eta-1)^2 + \dots \quad (6)$$

because, by (5),  $\delta = \xi$  for  $\eta = 1$ .

With this approximation, and developing  $\xi$  in series

$$\xi \cong 1 - z\epsilon\psi/kT = 1 - x \quad (7)$$

an expression of the electrical density for not too dilute solutions is obtained in (3) and replaced in Poisson's equation. This allows to define a certain quantity  $\kappa$ , which plays in the theory the same part that Debye's  $\kappa$  (that is, the reciprocal of the characteristic length); it coincides with Debye's in the limiting case, saving the normalization factor.

$$\kappa^2 = 8\pi z^2 \epsilon^2 n(8\eta - 5)/9DkT \quad (8)$$

The values  $\eta$  can take in (8) appear limited in a not satisfactory manner. Therefore, it is tried to extend the range of the original development so as to avoid that limitation.

The expression for  $\kappa$  has been obtained from (6) considering only the first order term. With the second order one:

$$\delta = (1-x) + (-2x)(\eta-1) + \frac{1}{2}(2-8x)(\eta-1)^2 \quad (9)$$

Since, from (5):

$$(\partial\delta/\partial\eta)_{\eta=1} = \xi^2 - 1 ; \quad (\partial^2\delta/\partial\eta^2)_{\eta=1} = 2 - 8x$$

It is convenient to write (9) like this:

$$\delta \cong (\eta^2 - 2\eta + 2) - x(4\eta^2 - 6\eta + 3) \quad (10)$$

Similarly:

$$\delta^{-1} \cong (\eta^2 - 2\eta + 2) + x(4\eta^2 - 6\eta + 3) \quad (11)$$

Replacing (10) and (11) in (3), taking into account (5), and neglecting the terms in  $x^2$ :

$$\rho = \frac{z\epsilon n \left\{ A^{4/3} [1 - (4Bx/3) + x/3] - A^{-4/3} [1 + (4Bx/3) - x/3] \right\}}{1 + A^{4/3} [1 - (4Bx/3) + x/3] + A^{-4/3} [1 + (4Bx/3) - x/3]} \quad (12)$$

where

$$A = \eta^2 - 2\eta + 2 ; \quad B = (4\eta^2 - 6\eta + 3)/A \quad (13)$$

Developing  $\rho$  in Taylor's series, and replacing in Poisson's equation:

$$\Delta\Psi = - \frac{4\pi z\epsilon n(A^{4/3} - A^{-4/3})}{D(1 + A^{4/3} + A^{-4/3})} + \frac{4\pi z^2\epsilon^2 n(4B-1)(4 + A^{4/3} + A^{-4/3})}{3DkT(1 + A^{4/3} + A^{-4/3})^2} \Psi \quad (14)$$

which on changing variable reduces to

$$\Delta\Psi = \kappa^2\Psi$$

where

$$\kappa^2 = \frac{4\pi z^2\epsilon^2 n(4B-1)(4 + A^{4/3} + A^{-4/3})}{3DkT(1 + A^{4/3} + A^{-4/3})^2} \quad (15)$$



In the limiting case,  $A = 1$ ,  $B = 1$ , so that  $\kappa^2$  coincides again with Debye's expression (saving normalization). But now  $\kappa$  is real for any value of  $\eta$ .

Following usual approximations (4),  $\kappa$  is related with the experimental values for activity coefficients. In this formula that permits adjustment of parameter  $a$  is attained.

The work necessary to charge an ion is calculated, considering the potential over a sphere of radius  $a$  ( $\psi_b$ ), and an instantaneous charge  $\lambda z \epsilon$  ( $0 \leq \lambda \leq 1$ ). Repeating the procedure for each ion, the solution's potential energy is given by:

$$W = 2N \int_0^1 z \epsilon \psi_b (\lambda z \epsilon) d\lambda$$

Taking into account (15) it becomes:

$$W = - \frac{4z^3 \epsilon^3 N}{D} \sqrt{\frac{n\pi}{3DkT}} \int_0^1 \frac{\lambda^2 \sqrt{(4B-1)(4+A^{4/3}+A^{-4/3})} d\lambda}{1+A^{4/3}+A^{-4/3}+2z\epsilon a \sqrt{\frac{n\pi}{3DkT}} \lambda \sqrt{(4B-1)(4+A^{4/3}+A^{-4/3})}} \quad (16)$$

where  $A$  and  $B$  are given by (13), replacing  $z \epsilon$  by the instantaneous charge  $\lambda z \epsilon$ .

As  $\ln f = (1/kT) (\partial W / \partial N)$ , it is finally obtained:

$$\ln f = - \frac{6z^3 \epsilon^3}{DkT} \sqrt{\frac{n\pi}{3DkT}} \int_0^1 \frac{\lambda^2 \sqrt{(4B-1)(4+A^{4/3}+A^{-4/3})}}{1+A^{4/3}+A^{-4/3}+2z\epsilon a \sqrt{\frac{n\pi}{3DkT}} \lambda \sqrt{(4B-1)(4+A^{4/3}+A^{-4/3})}} d\lambda +$$

$$+ \frac{4z^4 \epsilon^4 a}{DkT} \frac{n\pi}{3DkT} \int_0^1 \frac{\lambda^3 (4B-1)(4+A^{4/3}+A^{-4/3})}{\left\{ 1+A^{4/3}+A^{-4/3}+2z\epsilon a \sqrt{\frac{n\pi}{3DkT}} \lambda \sqrt{(4B-1)(4+A^{4/3}+A^{-4/3})} \right\}^2} d\lambda$$

(17)

These integrals were calculated numerically by Simpson's formula.  $a$  is obtained by a four-point interpolation following Lagrange's method.

An electronic computer is used.

### Results; discussion

As is briefly indicated in the introduction,  $a$  is determined for several substances at different temperatures and concentrations.

The solution's dielectric constant at 25°C is adjusted

taking as a basis the data of Hasted Ritson and Collie (5), coherent with further theoretical estimations (6). Due to experimental error, formulae are extended to the other temperature considered.

The activity coefficients are picked from the tables of reference (7), saving those of  $\text{IO}_3\text{K}$  (8).

To control the theory's validity range, it is necessary to consider the conditions imposed by the value  $\underline{a} = 1/\kappa$ , and compatibility between distance  $\underline{a}$  and the number of ions in the solution.

Fig. 2 (Table 1) represents results for chlorides and  $\text{SO}_4\text{Mg}$  at 25°C. For chlorides, the mean distance of closest approach between two ions decreases - at a given concentration - for growing molecular weights; this ordination is the one suggested by electro-negativity scale (9). For  $\text{SO}_4\text{Mg}$ , the only bivalent salt considered, electrostatic attraction between ions seems to play now a more significant part.

Fig. 2 shows that  $\underline{a}$  increases with concentration, within the theory's range. This result is so interpreted: remembering the definition for  $\underline{a}$ , it is seen that  $\underline{a}(+-)$  is less than  $\underline{a}(++)$  and  $\underline{a}(--)$ ; in very dilute solutions, an ion tends to round itself with ions of opposite sign, and  $\underline{a}(+-)$  predominates. As concentration increases, interaction among first neighbors is no more almost only between ions of opposite sign;  $\underline{a}(++)$  and  $\underline{a}(--)$  concur more appreciably, through  $\eta$ , to the mean value of  $\underline{a}$ .

The curves are coherent with the hypothesis-made by some authors - that hydration is minimum at infinite dilution. When there are few ions in solution, the typical tetrahedral structure of water

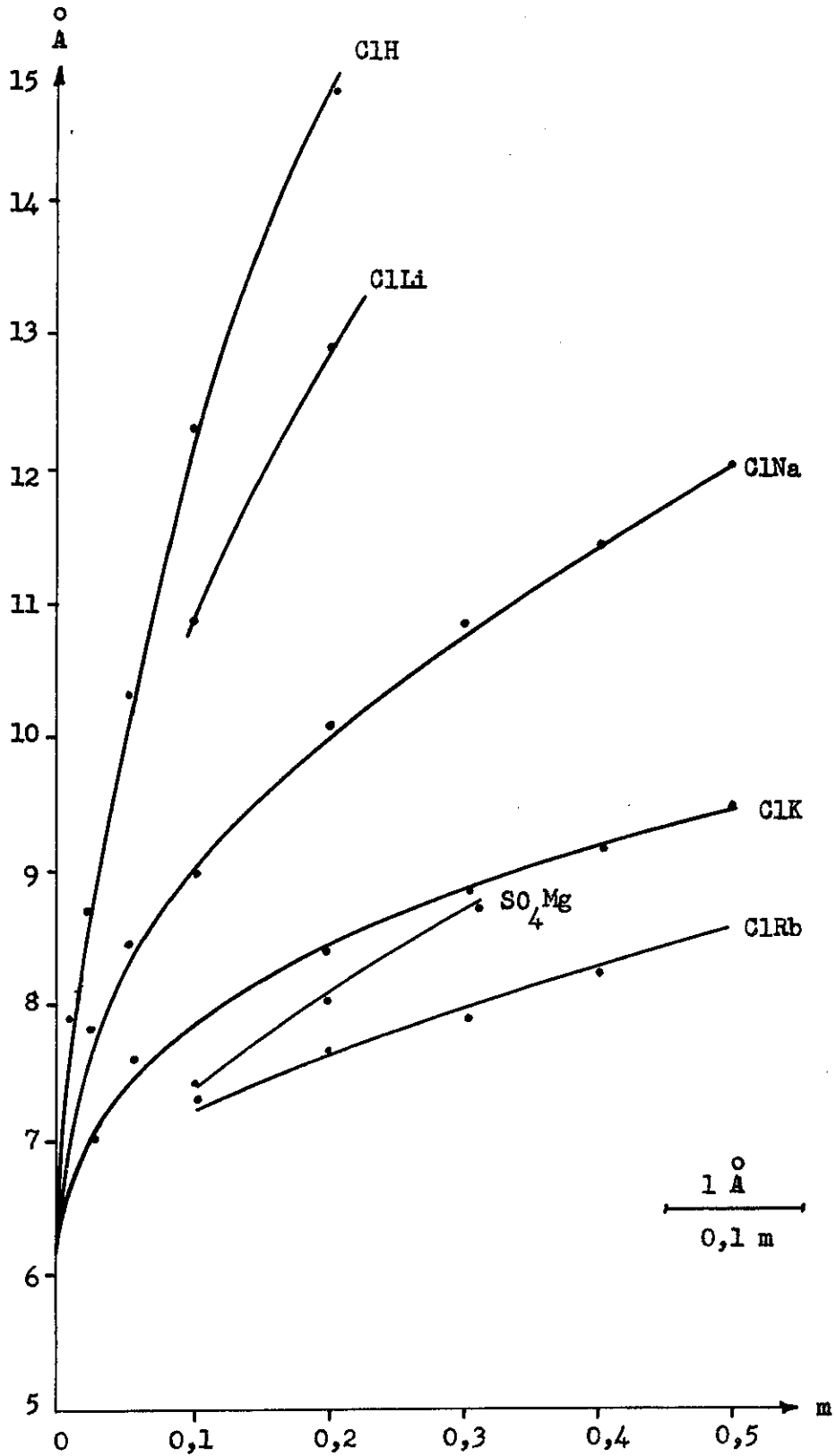


Fig. 2:  $\underline{a}$  as a function of concentration.

molecules is not affected. But when some ions can break such structure (owing to the fact that the interaction ion-dipole is stronger than that dipole-dipole (10)), for the next ions added to the solution it is easier to capture water molecules that do not belong any more to a stable structure. It follows, by hydration,  $\underline{a}$ 's increase with concentration. This picture gives also account of the ordination obtained for the chlorides: the ions' ordering capacity, calculated from entropy measurements (11), gives an order inverse to their size, following a column of the periodic table. Therefore small ions, as  $\text{Li}^+$  and  $\text{H}^+$ , the so-called "order-producers" round them, have greater effective radii.

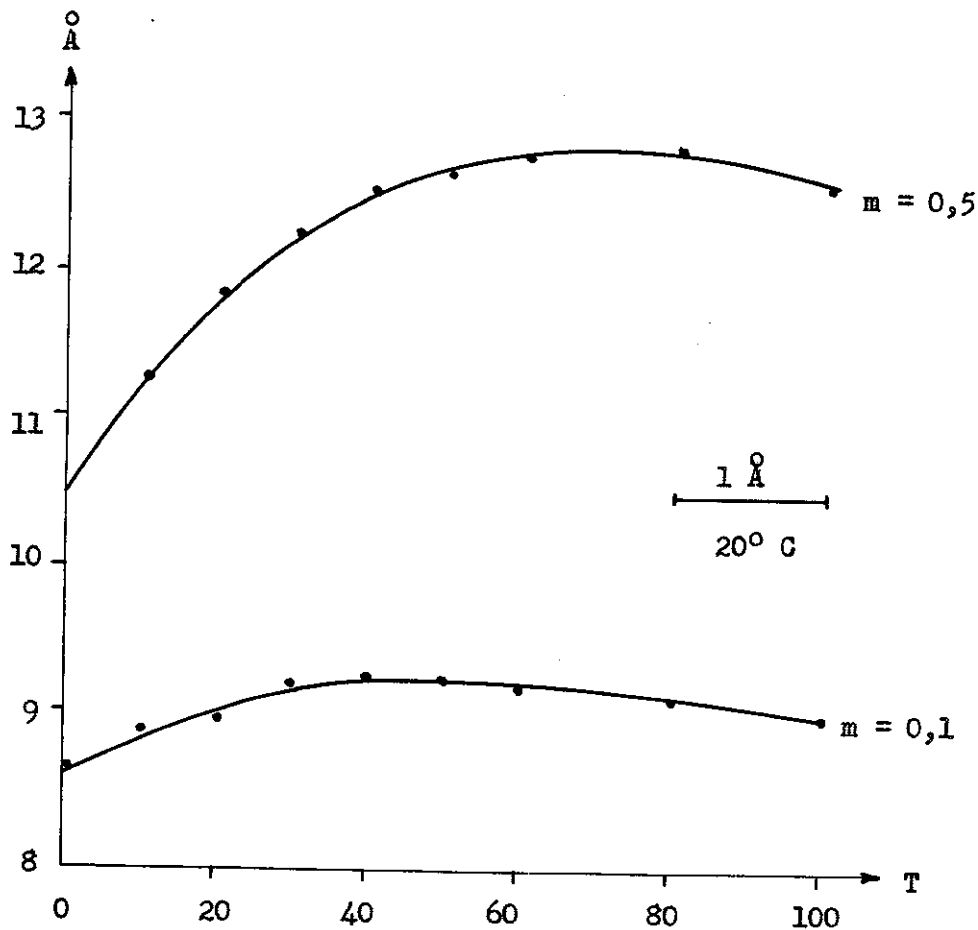


Fig. 3:  $\underline{a}$  (for ClNa) as a function of temperature at two different concentrations.

Variation of  $\underline{a}$  with temperature for ClNa at two different concentrations is shown in Fig. 3 (Table II). The following explanation of the observed behaviour is proposed. Rising temperature, the bombardment of water molecules draw the ions apart one from another, as it intensifies the particles' random motion. At the same time, the greater kinetic energy favours breaking the water tetrahedra, and thus ionic hydration. But when the greatest part of the ions is saturated, the opposite effect takes place with further increasing temperature; for water molecules will loose from the hydrated ions. With dilution, this last effect will be seen at lower temperatures because, being less the number of ions, they become saturated sooner. As interaction between an ion and the first layer of water round it seems too great for thermal effects to compete with it (10)(12), the described processes take place probably beyond the first layer, in the transition region (13). It must indeed be remarked the flatness of the curves, that is the weakness of the pictured effects. Statistical arguments assign to  $T \rightarrow \infty$  the same physical consequence that  $m \rightarrow 0$ . Results of Fig. 3, and the explanation just outlined - taking into account the method's inherent limitations, and temperatures with physical meaning - are conveniently related with those arguments.

In Fig. 4 (Tables I and II) values of parameter  $\underline{a}$  for ClNa depending on concentration, are compared for different temperatures.

Values of  $\underline{a}$ , close together for the lowest concentration calculated (Figs. 3 and 4) leave open the following question: Which would be the shape of the curves for  $\underline{a}(T)$ , on dealing with extremely dilute solutions.

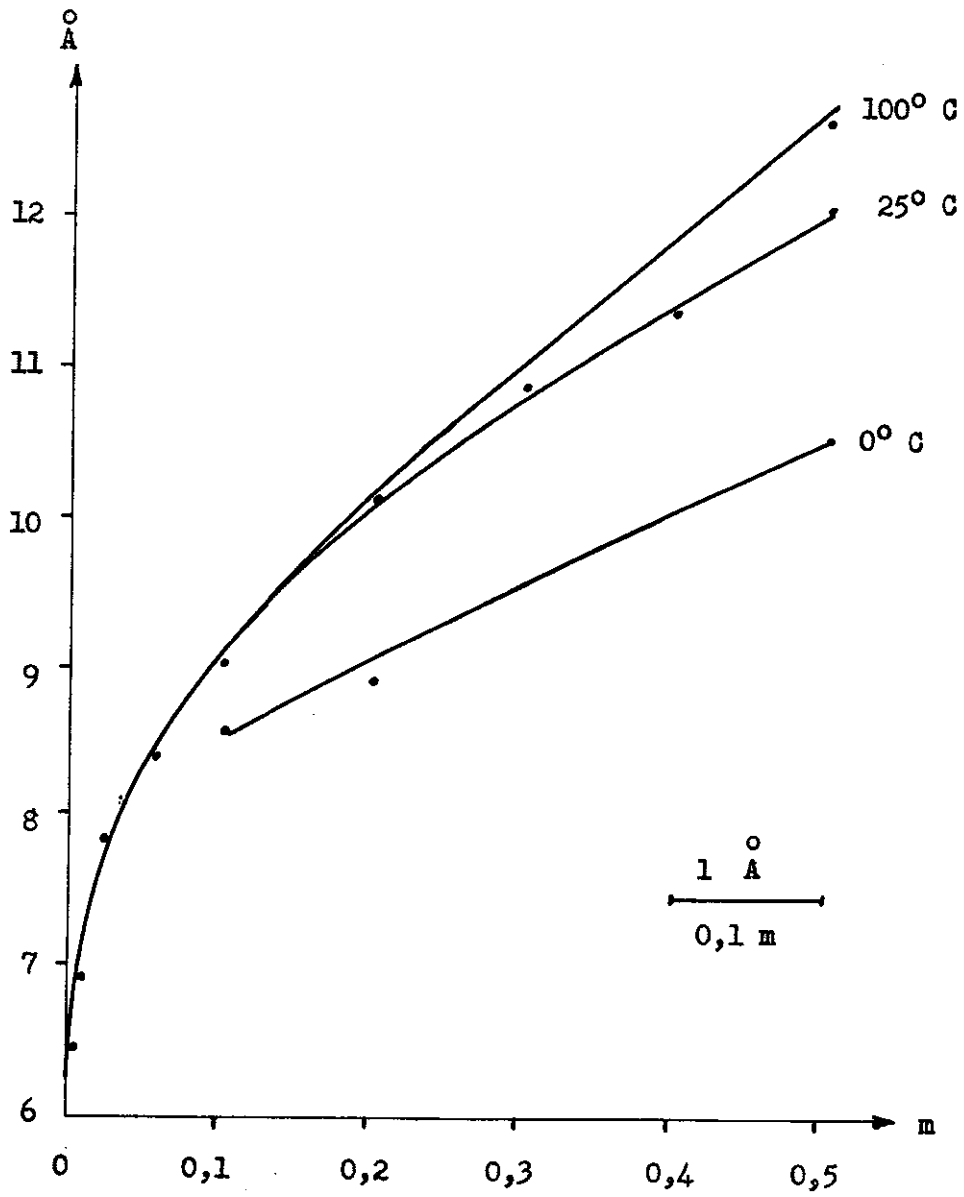


Fig. 4:  $\underline{a}$  (for  $\text{ClNa}$ ) as a function of concentration at three different temperatures.

Estimation of parameter  $\underline{a}$  in the calculation corresponding to  $\text{IO}_3\text{K}$  is only accomplished for  $m = 0,0001$ , since for higher concentrations activity coefficients data do not seem reliable. It is obtained a value of  $6,8\text{\AA}$ ; Debye-Huckel's theory, with the same data, give  $\underline{a} = -14\text{\AA}$ .

In the case of  $\text{NO}_3\text{K}$  there are no data for the dielectric constant's variation with concentration. For  $m = 0,1$ ; the other studied solutions have practically the same dielectric constant; at that concentration the calculated value for  $\underline{a}$  is  $5,4\text{\AA}$ . Results obtained for greater concentrations, and the general behaviour of the curves corresponding to the rest of the substances, suggest that the dielectric constant's decrease - supposed equal to that of  $\text{ClK}$  - is greater than this one and, in a general way, than that of alkaline halides. The values of  $\underline{a}$ , lower than the others at the same concentration, is also explained by the strong disordering character of the  $\text{NO}_3^-$  ion (13).

The order of magnitude resulting for  $\text{IO}_3\text{K}$  and  $\text{NO}_3\text{K}$  shows that the adopted model allows to surpass the objection mentioned in the introduction to Debye-Huckel's theory.

### Conclusions

- 1)  $\underline{a}$  is not constant regarding concentration and temperature.



- 2) For the cases considered,  $\underline{a}$  increases with concentration within the theory's range (more or less 0,4 molal).
- 3) For chlorides there is good agreement between the ordination given by the values of parameter  $\underline{a}$  and the ordering capacity of ions in aqueous solution.
- 4) It is possible to assign reasonable values of  $\underline{a}$  to  $\text{IO}_3\text{K}$  and  $\text{NO}_3\text{K}$ .

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#### Notation

k Boltzmann constant  
T absolute temperature  
 $ze$  charge of a positive ion  
D dielectric constant

f rational activity coefficient  
 N number of positive or negative ions in the solution  
 V volume of the solution  
 n number of positive or negative ions per unit volume  
 m molality

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Table I

m	ClH	ClLi	ClNa	ClK	ClRb	SO <sub>4</sub> Mg
0,0016			6,44	6,30		
0,0020	6,43					
0,0050	7,15					
0,0064			6,94	6,69		
0,0100	7,87					
0,0200	8,70					
0,0256			7,83	7,04		
0,0500	10,32					
0,0576			8,47	7,58		
0,1000	12,32	10,90	8,98	7,93	7,31	7,43
0,2000	14,92	12,94	10,07	8,44	7,64	8,10
0,3000			10,88	8,83	7,91	8,65
0,4000			11,47	9,23	8,25	
0,5000			12,06	9,53	8,60	

\* \* \* \*

Table II

T\m	0,1	0,2	0,5
273	8,54	8,93	10,55
283	8,89		11,31
293	9,02		11,80
303	9,18		12,17
313	9,24		12,47
323	9,20		12,64
333	9,20		12,76
353	9,18		12,83
373	9,08	10,12	12,64