

A THEORY OF STRONG ELECTROLYTES IN SOLUTION BASED ON A NEW STATISTICS. II.

EQUILIBRIUM PHENOMENA : ACTIVITY COEFFICIENTS

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(Communicated by S. N. Bose, F.N.I.)

(Received January 19, 1954; read October 7, 1955)

INTRODUCTION

In support of the use of an intuitively obtained distribution formula different from that of Boltzmann in Bagchi's modification (1950) of the Debye-Hückel theory (1923) of strong electrolytes in solution, a distribution formula has been deduced theoretically (Dutta and Bagchi, 1950) as

$$n_{\pm, r} = \frac{1}{\bar{b}_{\pm} \left(e^{\nu_{\pm} + \frac{z_{\pm} \epsilon \psi_r}{kT}} + 1 \right)} \quad \dots \quad (1)$$

where

- (i) $n_{\pm, r}$ = number-density of positive or negative ions in solution, at a point where the electrostatic potential is ψ_r ;
- (ii) \bar{b}_{\pm} = volumes of covering-spheres (Deckungssphären) of positive or negative ions due to close approach among like ions only;
- (iii) ν_{\pm} = parameters of distribution;
- (iv) z_{\pm} = valency of positive or negative ions;
- (v) ϵ, k and T have their usual significance.

The deduction of the above formula (1), which is similar in form only to that used by Bagchi, is based on a general formalism developed by Dutta (1947, 1948, 1951) for the theoretical treatment of real gases, and rests on the simple assumption that ions, having a characteristic volume of their own, are under the influence of the mutual electrostatic field in solution. Subsequently, Eigen and Wicke (1951) have also utilised in their theory of strong electrolytes in solution, a distribution formula which they have claimed to be new, but which, as shown by Dutta (1952), is practically the same as formula (1) written in a different form with new symbols and with slightly different explanations for the parameters involved.

The application of the above formula (1) to the theory of strong electrolytes in solution was initiated in the first paper of the present series (Dutta and Sengupta, 1954). Among the many satisfactory consequences of the application of the present statistics as pointed out there, the more important are:

- (i) In the earlier theories the charge density ρ becomes unbounded for $\psi \sim \infty$, thus contradicting the basic physical picture assumed there. But in the present theory, as also in that of Bagchi (1950), ρ tends to

a finite value (which is plausible also, according to the quasi-lattice model proposed by Dutta, 1953), as $\psi \rightarrow \infty$.

- (ii) Sengupta (1954) has shown that the value of the potential at the surface of the ion, which only is of actual significance in the subsequent thermodynamic calculations, is generally large and does not satisfy the basic assumption of the Debye-Hückel theory (namely that,

$$\psi \sim 0 \text{ or } \lambda = \frac{\epsilon \psi}{kT} \ll 1). \text{ This necessitates some evaluation of the}$$

Poisson equation for large values of ψ . As in the present theory ρ tends to a finite value when $\psi \rightarrow \infty$, this can easily be done by the method of approximate evaluation used in the calculations of Bagchi.

In the first paper (Dutta and Sengupta, 1954), as also in the paper of Bagchi (1950), in order to obtain a good approximation to the integral of the Poisson equation, the original equation was replaced there by two separate equations, one for $\lambda \sim 0$ and the other for $\lambda \sim \infty$, and their solutions were fitted together on the surface $\lambda = m_+$. Further, it was proposed that λ would be taken to be represented by λ_1 when $\lambda < m_+$, and by λ_2 when $\lambda > m_+$. Now, from the expressions for λ_1 and λ_2 as obtained in the first paper, λ is seen to increase monotonically as the distance to the ion-surface decreases from infinity. Therefore, when λ at the ion-surface (i.e. $\lambda(a_+)$) is less than m_+ , the entire field outside the ion is represented by λ_1 ; the other solution λ_2 is non-significant in this case, as the Poisson equation cannot be expected to be valid for the field in the interior of the ion. In dilute solutions m_+ is a large quantity and hence is expected to be greater than $\lambda(a_+)$; consequently λ is given by λ_1 alone, and the present treatment reduces to that of Debye and Hückel in dilute solutions. When m_+ is not large, as in concentrated solutions, $\lambda(a_+)$ is expected to be greater than m_+ ; consequently, in this case, the potential in the neighbourhood of the ion-surface is given by λ_2 , while that at large distances from the ion is given by λ_1 . From such considerations as these, $\lambda(a_{\pm})$ were taken to be represented by λ_2 in the first paper, as there only concentrations above (or equal to) 1 molar were considered. But closer scrutiny shows that even at such high concentrations, the conditions necessary for λ at the surface of both positive and negative ions of an electrolyte to be represented by λ_2 (viz., $\lambda(a_{\pm}) > m_{\pm}$) are not always satisfied simultaneously; and that at concentrations below 1 molar, the conditions are violated more markedly, as expected. This has been shown below for CsCl.

TABLE I

(i) $\lambda(a_{\pm})$ for Cs⁺ and Cl⁻ ions and (ii) m_{\pm} , calculated by equations (31) and (17) respectively of the first paper

$$(a_{\text{Cs}^+} = 1.67 \text{ \AA} \text{ and } a_{\text{Cl}^-} = 1.81 \text{ \AA})$$

	·1m	·2m	·5m	1m	2m	4m
$\lambda(a_{\text{Cs}^+})$	4.095	3.792	3.272	2.861	2.531	2.347
m_+	42.21	21.33	8.82	4.675	2.656	1.824
$\lambda(a_{\text{Cl}^-})$	4.032	3.703	3.117	2.680	2.297	2.075
m_-	53.75	27.17	11.24	5.954	3.382	2.322

The above findings demand that in order to maintain consistency of the theory, both solutions of the Poisson equation be utilised in a composite manner for the calculation of activity coefficients. This has been done in the present paper.

Further, it was found in the first paper that it is not possible to carry out the calculations above a certain concentration, particularly in the case of electrolytes with large ionic radii, unless the consideration of the overlapping of exclusion-spheres is introduced. It is proposed, therefore, to incorporate second-order overlapping correction into the scheme of calculations of the present paper.

Finally, the theory has been subjected to a more exhaustive verification by extending it to the case of unsymmetrical electrolytes.

EVALUATION OF λ AND CALCULATION OF AVAILABLE ELECTRIC ENERGY

As before, the law of distribution of ions will be taken to be given by (1), so that the charge density ρ at any point in the solution where the electrostatic potential is ψ_r , is given by

$$\rho = \epsilon (n_{+,r} z_+ - n_{-,r} z_-).$$

The scheme of subsequent calculations is essentially similar to that in the first paper, with the important modification that the exclusion volumes b_{\pm} are no longer constant because of overlapping. For a system of n similar particles per c.c. the average exclusion volume \bar{b} of each particle after introducing second-order overlapping correction, has been shown (Dutta, 1952) to be given by:

$$b = b^{\circ} \left(1 - \frac{17}{96} n b^{\circ} \right) \quad \dots \quad \dots \quad \dots \quad (2)$$

where b° = exclusion volume after neglecting overlapping. Since, close approach among like ions only is taken into consideration in deducing the distribution formula (1), therefore equation (2) reduces in our case to

$$b_{\pm} = b_{\pm}^{\circ} \left(1 - \frac{17}{96} n_{\pm} b_{\pm}^{\circ} \right) \quad \dots \quad \dots \quad \dots \quad (2a)$$

Due to this dependence of b_{\pm} on the concentration n_{\pm} , the scheme of calculations is modified only when differentiation with respect to n_{+} or n_{-} is encountered. The two solutions of the Poisson equation are therefore given as before by

$$(\lambda_{\pm})_1 = \frac{z_{\pm} \epsilon^2 \kappa e^{\xi a_{\pm}}}{DkT (1 + \xi a_{\pm})} \frac{e^{-\xi}}{\xi} \quad \dots \quad \dots \quad \dots \quad (3)$$

and

$$(\lambda_{\pm})_2 = m_{\pm} \left[\frac{\xi^2}{6} + \frac{1}{2} \left\{ 1 - (1 + g_{\pm})^{\frac{2}{3}} \right\} + \frac{g_{\pm}/3}{\xi} \right] \quad \dots \quad (4)$$

where

- (i) $\lambda = \frac{\epsilon}{kT} \psi$ and $\xi = \kappa r$
- (ii) $\kappa^2 = \frac{4\pi \epsilon^2}{DkT} \left[\sum n_i z_i^2 - \sum n_i^2 z_i^2 b_i \right]$
- (iii) $m_{\pm} = \frac{z_{\mp}}{b_{\mp}} \frac{1}{\sum n_i z_i^2 - \sum n_i^2 z_i^2 b_i} \quad \dots \quad \dots \quad \dots \quad (5)$

$$(iv) \quad g_{\pm} = \frac{3z_{\pm} \epsilon^2 \kappa}{m_{\pm} D k T} + (\kappa a_{\pm})^3 \equiv \kappa^3 \left[a_{\pm}^3 + \frac{z_{\pm}}{z_{\mp}} (2a_{\mp})^3 \frac{b_{\mp}}{b_{\pm}} \right]$$

$$(v) \quad b_{\pm}^{\circ} = \frac{4}{3} \pi (2a_{\pm})^3, \quad a_{\pm} \text{ being the radii of positive or negative ions.}$$

For the available electric work w_{\pm} , we have

$$w_{\pm} = z_{\pm} \epsilon \int_0^1 [\psi^*(a_{\pm})]_x dx,$$

where $\psi^*(a_{\pm})$ = potential at the ion-surface due to the ion-atmosphere. Thus we have, for the work required in charging a single ion whose surface-potential is given by λ_1 , the usual Debye expression, viz.

$$(w_{\pm})_1 = -\frac{(z_{\pm} \epsilon)^2}{D} \left[\frac{1}{\kappa^2 a_{\pm}^3} \left\{ \ln(1 + \kappa a_{\pm}) - \kappa a_{\pm} + \frac{1}{2} (\kappa a_{\pm})^2 \right\} \right] \quad \dots \quad (6)$$

$$= -\frac{(z_{\pm} \epsilon)^2 \kappa}{D} \theta_{\pm} \text{ (say)}$$

and that for charging an ion whose surface-potential is given by λ_2 , the same expression as obtained in the first paper, viz.

$$(w_{\pm})_2 = \frac{z_{\pm} k T m_{\pm}}{2} \left[\frac{1}{2} (\kappa a_{\pm})^2 + P + \phi_{\pm}(g_{\pm}) \right] \quad \dots \quad (7)$$

where

$$P = \frac{1}{2} + \frac{1}{\sqrt{3}} \tan^{-1} \sqrt{3} - \frac{1}{2} \ln 3 \equiv .5551$$

and

$$\phi_{\pm}(g_{\pm}) = \frac{1}{2} \ln \left[(1 + g_{\pm})^{\frac{3}{2}} + (1 + g_{\pm})^{\frac{1}{2}} + 1 \right] - \frac{1}{2} (1 + g_{\pm})^{\frac{3}{2}} - \frac{1}{\sqrt{3}} \tan^{-1} \frac{2(1 + g_{\pm})^{\frac{1}{2}} + 1}{\sqrt{3}}$$

ACTIVITY COEFFICIENTS

In deducing the expression for the mean ionic activity coefficient of an electrolyte, three distinct cases may arise, thus:

- (i) The surface-potential of both positive and negative ions is given by λ_1 .
- (ii) The surface-potential of both positive and negative ions is given by λ_2 .
- (iii) The surface-potential of the positive ion is given by λ_1 and that of the negative ion by λ_2 , or *vice versa*.

In the first case, the total work required in charging all the ions is given by

$$W = n_+(w_+) + n_-(w_-)$$

Then, the activity coefficient of the positive ions is given by

$$\ln f_+ = \frac{1}{k T} \frac{\partial W}{\partial n_+}$$

$$= -\frac{\epsilon^2 \kappa}{D k T} \left[z_+^2 \theta_+ + D_+ \left\{ \frac{n_+ z_+^2}{2(1 + \kappa a_+)} - n_+ z_+^2 \theta_+ \right\} + D_+ \left\{ \frac{n_- z_-^2}{2(1 + \kappa a_-)} - n_- z_-^2 \theta_- \right\} \right]$$

where

$$D_{\pm} = \frac{z_{\pm}^2 - 2n_{\pm} z_{\pm}^2 b_{\pm} + \frac{1}{6} n_{\pm}^2 z_{\pm}^2 b_{\pm}^2}{\sum n_i z_i^2 - \sum n_i^2 z_i^2 b_i}$$

A similar expression holds for $\ln f_{-}$. For the mean ionic activity coefficient of the electrolyte we have

$$\begin{aligned} \ln f_{\pm} &= \frac{z_- \ln f_+ + z_+ \ln f_-}{z_+ + z_-} \\ &= - \frac{z_+ z_-}{(z_+ + z_-)} \frac{\epsilon^2 \kappa}{DkT} \left[(z_+ \theta_+ + z_- \theta_-) (1-S) + S \frac{1}{2} \left(\frac{z_+}{1 + \kappa a_+} + \frac{z_-}{1 + \kappa a_-} \right) \right] \end{aligned} \quad (8)$$

where

$$S = n_+ D_+ + n_- D_- = 1 - \frac{\sum n_i^2 z_i^2 b_i - \frac{1}{6} \sum n_i^3 z_i^2 b_i^2}{\sum n_i z_i^2 - \sum n_i^2 z_i^2 b_i}$$

The above formula (8) reduces to the usual Debye-Hückel formula, viz.

$$\ln f_{\pm} = - \frac{z_+ z_- \epsilon^2}{2DkT} \frac{\kappa}{1 + \kappa a} \quad \text{with} \quad \kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum n_i z_i^2,$$

if the separate ionic radii be replaced by a single 'mean distance of closest approach between the ions' (i.e., $a_+ = a_- = a$, say) and also, the finite volumes of exclusion be neglected (i.e., $b_{\pm} = 0$). This shows that in the Debye-Hückel theory, the effect of the finite ionic dimensions is taken into account in only an incomplete manner.

In the second case, when the surface-potential of both type of ions is given by λ_2 , we have

$$W = n_+(w_+)_2 + n_-(w_-)_2$$

and

$$\begin{aligned} \ln f_+ &= \frac{m_+ z_+}{2} \left[\frac{1}{2} (\kappa a_+)^2 + (P + \phi_+) (1 - n_+ D_+) + E_+ n_+ D_+ \right] + \\ &+ \frac{m_- z_-}{2} \left[\frac{1}{2} (\kappa a_-)^2 \left(\frac{b_+^{\circ}}{b_+} - 1 \right) + (P + \phi_-) \left(\frac{b_+^{\circ}}{b_+} - 1 - n_+ D_+ \right) + E_- \left(n_+ D_+ - \frac{2b_+^{\circ} - b_+}{z_- \frac{b_+^{\circ}}{8} + b_+} \right) \right] \end{aligned}$$

where

$$\begin{aligned} E_{\pm}(g_{\pm}) &= \frac{1}{2} \frac{\frac{g_{\pm}}{(1+g_{\pm})^{\frac{1}{2}}} + \frac{g_{\pm}}{2(1+g_{\pm})^{\frac{3}{2}}}}{(1+g_{\pm})^{\frac{3}{2}} + (1+g_{\pm})^{\frac{1}{2}} + 1} - \frac{g_{\pm}}{2(1+g_{\pm})^{\frac{1}{2}}} \\ &- \frac{g_{\pm}}{3(1+g_{\pm})^{\frac{1}{2}} \left[1 + \frac{1}{3} \{ 2(1+g_{\pm})^{\frac{1}{2}} + 1 \}^2 \right]} \\ &= - \frac{1}{2} \left\{ (1+g_{\pm})^{\frac{1}{2}} - 1 \right\}. \end{aligned}$$

A similar expression holds for $\ln f_-$, and we have

$$\ln f_{\pm} = \frac{z_+ z_-}{z_+ + z_-} \left[\frac{m_+}{2} \left\{ \frac{1}{2} (\kappa a_+)^2 \frac{b_-^\circ}{b_-} + (P + \phi_+) \left(\frac{b_-^\circ}{b_-} - S \right) + E_+ \left(S - \frac{2}{3} \frac{b_-^\circ - b_-}{z_- \frac{b_-^\circ}{b_+} + b_-} \right) \right\} + \right. \\ \left. + \frac{m_-}{2} \left\{ \frac{1}{2} (\kappa a_-)^2 \frac{b_+^\circ}{b_+} + (P + \phi_-) \left(\frac{b_+^\circ}{b_+} - S \right) + E_- \left(S - \frac{2}{3} \frac{b_+^\circ - b_+}{z_+ \frac{b_+^\circ}{b_-} + b_+} \right) \right\} \right] \dots (10)$$

The above formula (10) reduces in the case of uniunivalent electrolytes, on neglecting the overlapping correction (i.e. $b_{\pm} = b_{\pm}^\circ$), to the expression for $\ln f_{\pm}$ obtained in the first paper.

In the last case, when the surface-potential of one type of ions (say, positive ions) is given by λ_1 and that of the other type by λ_2 , we have

$$W = n_+(w_+) + n_-(w_-)_2.$$

Then,

$$\ln f_+ = - \frac{(z_+ \epsilon)^2 \kappa}{DkT} \left\{ \theta_+ (1 - n_+ D_+) + n_+ D_+ \frac{1}{2(1 + \kappa a_+)} \right\} + \\ + \frac{m_- z_+}{2} \left\{ \frac{1}{2} (\kappa a_-)^2 \left(\frac{b_+^\circ}{b_+} - 1 \right) + (P + \phi_-) \left(\frac{b_+^\circ}{b_+} - 1 - n_+ D_+ \right) + \right. \\ \left. + E_- \left(n_+ D_+ - \frac{2}{3} \frac{b_+^\circ - b_+}{z_+ \frac{b_+^\circ}{b_-} + b_+} \right) \right\}$$

and

$$\ln f_- = - \frac{z_+ z_- \epsilon^2 \kappa}{DkT} \left\{ -\theta_+ n_- D_- + n_- D_- \frac{1}{2(1 + \kappa a_+)} \right\} + \frac{m_- z_-}{2} \left\{ \frac{1}{2} (\kappa a_-)^2 + \right. \\ \left. + (P + \phi_-) (1 - n_- D_-) + E_- n_- D_- \right\}$$

so that

$$\ln f_{\pm} = \frac{z_+ z_-}{z_+ + z_-} \left[- \frac{z_+ \epsilon^2 \kappa}{DkT} \left\{ \theta_+ (1 - S) + S \frac{1}{2(1 + \kappa a_+)} \right\} + \right. \\ \left. + \frac{m_-}{2} \left\{ \frac{1}{2} (\kappa a_-)^2 \frac{b_+^\circ}{b_+} + (P + \phi_-) \left(\frac{b_+^\circ}{b_+} - S \right) + E_- \left(S - \frac{2}{3} \frac{b_+^\circ - b_+}{z_+ \frac{b_+^\circ}{b_-} + b_+} \right) \right\} \right] \dots (11)$$

An expression similar to (11) holds if, reversely, the potential of the positive ions is given by λ_2 and that of the negative ions by λ_1 .

COMPARISON WITH EXPERIMENTAL RESULTS

For the actual calculation of activity coefficients, it is at first necessary to know which of the above three formulae (8), (10) and (11) to use at any particular concentration. For this, the value of λ on the surface of both positive and negative ions, and the quantities m_{\pm} must first be calculated by means of equations (3) or (4), and (5) respectively. Then, equation (8), (10) or (11) is to be used according as (i) $\lambda(a_{\pm}) < m_{\pm}$ or (ii) $\lambda(a_{\pm}) > m_{\pm}$ or (iii) $\lambda(a_{+}) < m_{+}$ and $\lambda(a_{-}) > m_{-}$ respectively.

In the following tables are given the calculated (molar) and the observed (molal) values of activity coefficients of the three uniunivalent electrolytes CsCl, RbCl and KCl, and that of the unsymmetrical electrolyte BaCl₂.

TABLE II

Activity coefficients of uniunivalent electrolytes

$$(a_{\text{Cl}^-} = 1.81 \text{ \AA})$$

		.1m	.3m	.5m	.7m	1m
CsCl ($a_{\text{Cs}^+} = 2.35 \text{ \AA}$)	Obs.	.755	.653	.604	.573	.543
	Cal.	.740	.638	.588	.563	.542*
RbCl ($a_{\text{Rb}^+} = 2.85 \text{ \AA}$)	Obs.	.764	.675	.634	.607	.583
	Cal.	.746	.651	.622*	.592*	.579*
KCl ($a_{\text{K}^+} = 3.35 \text{ \AA}$)	Obs.	.769	.687	.650	.626	.605
	Cal.	.752	.668	.638*	.627*	.625*

TABLE III

Activity coefficients of BaCl₂

$$(a_{\text{Ba}^{++}} = 4.0 \text{ \AA} \text{ and } a_{\text{Cl}^-} = 1.81 \text{ \AA})$$

	.1m	.2m	.3m	.4m	.5m	.7m	1m
Obs.	.492	.436	.411	.398	.390	.384	.392
Cal.	.462*	.407*	.386*	.387*	.393*	.427*	.577*

*Calculated by (11).

CONCLUSION

It is seen that by utilising both solutions of the Poisson equation for the calculation of activity coefficients, as was proposed in the first paper (Dutta and Sen Gupta, 1954), agreement between the calculated and observed values can be obtained throughout the entire range of concentrations within which calculations are possible. However, the calculations here have not been extended to the region of very high concentrations, because, for this, overlapping correction of order higher than the second which has been neglected in the present treatment, must be taken into account.

It will be noted that somewhat larger values of ionic radii have been necessary here, as compared to those in the first paper, to give the best fit between the calculated and observed values of activity coefficients. This may possibly be due to the fact that the calculations here have been carried out for more dilute solutions, where the hydration of ions which is an important factor controlling the ionic size, is likely to be greater. Incidentally, hydration may therefore become more significant than the Coulombian field in determining the average distance of closest approach between the ions, consequently, the assumption made hitherto, viz. $b_{+} \ll b_{\pm}$, may not be justified any more. It becomes necessary therefore to utilise the complete distribution formula, without the above approximation. This will form the subject of the next communication.

ACKNOWLEDGEMENTS

The author's best thanks are due to Prof. S. N. Bose for his kind interest in this work and especially to Dr. M. Dutta for his helpful guidance.

SUMMARY

The activity coefficients of three univalent electrolytes KCl, RbCl and CsCl and of the unsymmetrical electrolyte BaCl₂ have been calculated by a method, developed in the first paper of this series (Dutta and Sengupta, 1954), which utilises a new distribution formula in place of the Boltzmann statistics. The main modification introduced here over the method as developed there lies in utilising both solutions of the Poisson equation compositely and taking into account the correction for the overlapping of the covering spheres of ions, up to the second order. The latter helps to extend the range of concentration within which calculations are possible. The agreement obtained between the calculated and observed values is found to be good.

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