

ASSOCIATION OF IONS IN A BI-UNIVALENT ELECTROLYTE.

By A. R. MILLER.

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The question of ion association in a uni-univalent electrolyte has been considered by Fuoss.¹ Fuoss regarded the ions of opposite kind as paired and showed that two types of pairs predominated: (*a*) short-range pairs of zero nett electric charge, and (*b*) free ions or long-range pairs. In this paper the analysis of Fuoss is extended to a bi-univalent electrolyte in which a greater number of possibilities than these two have to be considered.

The configurations that occur can be divided into the following three main types:

- (i) an electrically neutral ion-triple formed by three associated ions—the two negative ions are situated at small distances from the positive ion;
- (ii) an associated ion-pair together with one free ion—one negative ion is at a small distance from the positive ion and the other negative ion is at a large distance from this pair;
- (iii) a group of three free ions—the two negative ions are at large distances from the positive ion.

At moderate dilutions it is shown that of these (ii) is by far the most probable and (iii) is more probable than (i).

Derivation of the Distribution Function.

Consider a bi-univalent electrolyte consisting of N positive ions, each of charge $+2e$, and $2N$ negative ions, each of charge $-e$. Each positive

¹ R. M. Fuoss, *Trans. Faraday Soc.*, 1934, **30**, 967; and *Chem. Rev.*, 1935, **17**, 27.

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ion is regarded as "mated" with two negative ions to form an ion-triple. Following the definition given by Fuoss of an ion-pair in a uni-univalent electrolyte such an ion-triple is defined as follows: "A positive ion and two negative ions whose centres are at distances from the positive ion of measures lying between the limits $r_1, r_1 + dr_1$ and $r_2, r_2 + dr_2$, respectively are said to form an ion-triple provided no other unmated negative ion lies within a sphere of radius r about the positive ion, r being the greater of r_1, r_2 . In this way the ions are completely counted as triples, and no ion is counted more than once."

To set up a distribution function for the trio of ions we take the centre of the positive ion as origin, O. Let r_1 cm. be the distance from O of the nearer negative ion at a point P_1 and r_2 cm. that of the more distant negative ion at a point P_2 . Let G_1 be the distribution function referring to the negative ion at P_1 and G_2 that referring to the negative ion at P_2 .

If $g \cdot dr$ is the probability that there is a negative ion lying within the limits $r, r + dr$, then following the usual argument,² and remembering that there are $2N$ negative ions, we have

$$g = \frac{8\pi N}{V} r^2 \exp(\epsilon\psi/kT),$$

where ψ is the electrostatic potential due to all the ions other than the negative ion under consideration, and V and T are the volume and absolute temperature of the system respectively.

Now $G_1 dr_1$ is the probability that the positive ion at O is mated with a negative ion which lies within the spherical shell of volume $4\pi r_1^2 dr_1$ and that no other negative ion, not mated with a positive ion other than that at O, lies within the spherical volume $\frac{4}{3}\pi r_1^3$. Then

$$G_1 = g f_1,$$

$$\text{where} \quad f_1 = 1 - \frac{2N-1}{2N} \int_a^{r_1} G_1 dx = 1 - \int_a^{r_1} G_1 dx,$$

a cm. being the nearest distance of approach of a positive and a negative ion.

$G_2 dr_2$ is the probability that the positive ion at O is mated with a negative ion which lies within the spherical shell of volume $4\pi r_2^2 dr_2$, and that the only other negative ion within the spherical volume $\frac{4}{3}\pi r_2^3$ about O, and not mated with a positive ion other than that at O is the negative ion at P_1 . Then

$$G_2 = g f_2,$$

$$\text{where} \quad f_2 = 1 - \frac{2N-2}{2N-1} \int_a^{r_2} G_2 dx = 1 - \int_a^{r_2} G_2 dx.$$

Thus, in each case there is obtained an integral equation of the form

$$G_k = 2Ar_k^2 \exp(\epsilon\psi_k/kT) \cdot \left(1 - \int_a^{r_k} G_k dx\right) \quad (k = 1; 2) \quad (1).$$

where ψ_k has to be determined at the position of each negative ion of the trio, and $A = 4\pi N/V$. An approximate value for ψ_k is obtained by

² R. H. Fowler, *Statistical Mechanics*, second edition, Cambridge University Press, 1936, page 553.

neglecting the contributions to the potential of all ions other than the three mated ions under consideration.

Our information about P_2 is that it is distant r_2 cm. from O, that is, it may be anywhere on the surface of a sphere of radius r_2 about O. For the contribution to the potential at P_1 due to the negative ion at P_2 , we take the average potential at P_1 due to a charge $-\epsilon$ as it moves about the surface of a sphere of radius r_2 about O. Thus, since with respect to this sphere P_1 is an internal point, we have

$$\psi_1 = \frac{2\epsilon}{Dr_1} - \frac{\epsilon}{Dr_2},$$

and

$$\frac{\epsilon\psi_1}{kT} = \frac{4q}{r_1} - \frac{2q}{r_2},$$

where

$$q = \epsilon^2/2DkT.$$

Likewise, for the contribution of the negative ion at P_1 to the potential at P_2 we take the average potential at P_2 due to a charge $-\epsilon$ as it moves about the surface of a sphere of radius r_1 about O. Thus, since with respect to this sphere P_2 is an external point, we have

$$\psi_2 = \epsilon/Dr_2,$$

from which it follows that

$$\epsilon\psi_2/kT = 2q/r_2.$$

Thus, for G_1, G_2 we have the integral equations:

$$G_1 = 2A \exp(-2q/r_2) \cdot r_1^2 \exp(4q/r_1) \cdot \left(1 - \int_a^{r_1} G_1 dx\right) \quad (2)$$

$$G_2 = 2Ar_2^2 \exp(2q/r_2) \cdot \left(1 - \int_a^{r_2} G_2 dx\right) \quad (3)$$

By differentiating both members of these equations with respect to r_1, r_2 respectively, expressions can be obtained for G_1, G_2 involving arbitrary functions of r_2, r_1 respectively, viz.,

$$G_1 = \phi(r_2) \cdot r_1^2 \exp\left\{\frac{4q}{r_1} - 2Ae^{-2q/r_2} \int_a^{r_1} t^2 e^{4q/t} dt\right\}.$$

$$G_2 = \theta(r_1) \cdot r_2^2 \exp\left\{\frac{2q}{r_2} - 2A \int_a^{r_2} t^2 e^{2q/t} dt\right\}.$$

By substituting these expressions in (2) and (3) respectively it is found that

$$\phi(r_2) = 2Ae^{-2q/r_2}, \quad \theta(r_1) = 2A,$$

giving finally

$$G_1 \equiv G_1(r_1, r_2) = 2Ae^{-2q/r_2} r_1^2 \exp\left\{\frac{4q}{r_1} - 2Ae^{-2q/r_2} \int_a^{r_1} t^2 e^{4q/t} dt\right\} \quad (4)$$

$$G_2 \equiv G_2(r_2) = 2Ar_2^2 \exp\left\{\frac{2q}{r_2} - 2A \int_a^{r_2} t^2 e^{2q/t} dt\right\} \quad (5)$$

$G_1(r_1, r_2)$ is the distribution function for the presence of a negative ion at $P_1(r_1)$ and $G_2(r_2)$ that for the presence of a negative ion at $P_2(r_2)$. We assume that the distribution function for the three-ion configuration,

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that is, for the presence of a negative ion at $P_1(r_1)$ and of another negative ion at $P_2(r_2)$ is given by the product

$$G(r_1, r_2) \equiv G_1(r_1, r_2) \cdot G_2(r_2) \quad (6)$$

Contour Map for the Distribution Function.

Since G_2 is independent of r_1 , then

$$\frac{\partial G}{\partial r_1} = G_2 \frac{\partial G_1}{\partial r_1}.$$

and it is easily shown that $\frac{\partial G}{\partial r_1}$ is zero at approximately

$$r_1 = 2q, \quad r_1 = \{\exp(2q/r_2)/2A\}^{\frac{1}{2}} = \rho(r_2).$$

Since we are concerned only with values of r_1 less than r_2 the contour map for $G(r_1, r_2)$ is necessarily bound by the lines $r_1 = a$, $r_1 = r_2$: that is, it lies within the shaded portion of Fig. 1. A section of the surface (such as that through AB in Fig. 1) formed by the intersection of the surface by a plane $r_2 = \alpha$, where α is a constant, is a curve C having turning values at approximately

$$r_1 = 2q, \quad r_1 = \{\exp(2q/\alpha)/2A\}^{\frac{1}{2}} = \rho(\alpha),$$

provided these are at accessible distances. It can be easily shown that the former is a minimum and the latter a maximum. For the minimum

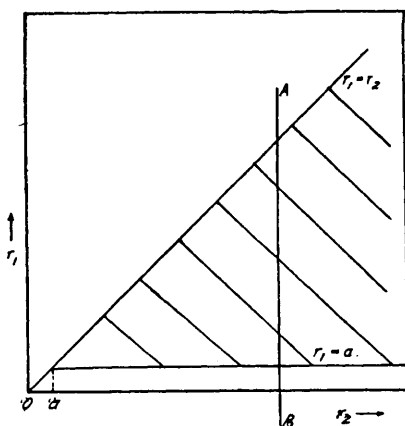


FIG. 1.—Physically accessible region of the contour map.

$r_1 \leq r_2$, then for values of α less than (roughly) 25 the curve C cannot attain its maximum. In general a section of the surface by a plane $r_2 = \alpha$ (α a constant) has the shape shown in Fig. 2. For values of α such that

$$\{\exp(2q/\alpha)/\alpha^3\} > 2A$$

the curve is cut off to the left of the maximum.

Thus a topographer would describe the surface $G(r_1, r_2)$ in the following terms. There is a mountain ridge along $r_1 = a$, a valley along $r_1 = 2q$,

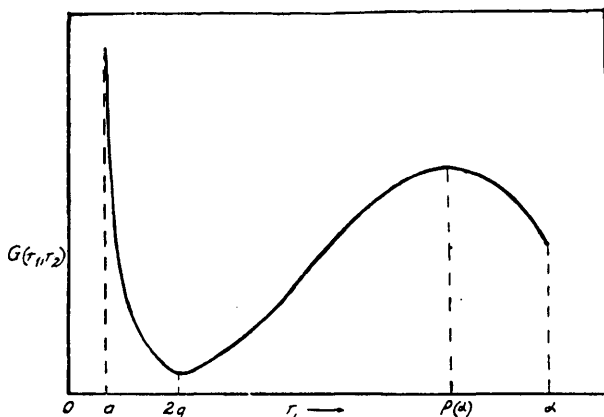
to be at an accessible distance it is necessary that a should be less than $2q$: for the discussion of the general case we take this to be so. The value of ρ which is of the order of magnitude of the mean ionic separation depends on α , that is on r_2 . Taking the dielectric constant of the medium to be 80, and the temperature as 293°K , then $q = 3.58 \times 10^{-8}$ and for a concentration of 10^{-2} equivalent per litre the constant A has the value 3.788×10^{19} . With these values, ρ increases from 24.8 for $\alpha = 50$ to 25.7 for $\alpha = 30$. For values of α less than 25, ρ is greater than 25. Since we are concerned only with values of

and, for values of r_1, r_2 for which it is a physically accessible region of the contour map, there is a mountain range along the curve

$$r_1 = \{\exp(2q/r_2)/2A\}^{\frac{1}{2}}.$$

In Fig. 3 a contour map showing the variation of G with r_1, r_2 has been constructed for a concentration of 10^{-2} equivalent per litre.

FIG. 2.—Section of the surface $G(r_1, r_2) = G_1(r_1, r_2), G_2(r_2)$ by a plane $r_2 = \alpha$ (α a constant).



The point C of the contour map represents those configurations in which each of the negative ions is at a distance from the positive ion of the same order of magnitude as the mean ionic separation. The ions

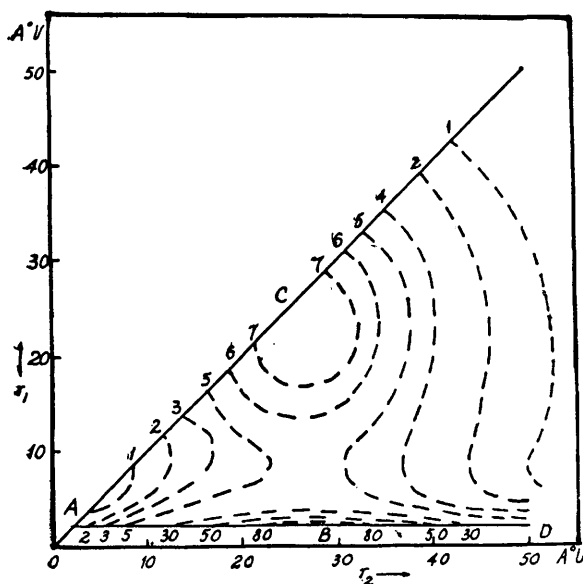


FIG. 3.—Contour map of $G(r_1, r_2)$ for a concentration 10^{-2} equivalent per litre.

in such a group must be treated as free (unassociated) ions. Along ABD there is a mountain ridge having a peak at B. A mountain ridge such as ABD corresponds to a configuration in which one negative ion is at a small distance from the positive ion (r_1 small); the point B of

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this ridge represents that configuration in which the other negative ion is separated from the positive ion and the former negative ion by a distance of the order of magnitude of the mean ionic separation. That is, one negative ion is associated with the positive ion to form a group with a nett positive charge. The point A corresponds to those configurations in which the two negative ions are associated with the positive ion to form an electrically neutral associated ion-triple.

Effect of Changes in Concentration.

At $r_1 = a = r_2$ we have

$$G \approx 4\lambda^2 a^4 e^{4q/a} c^2,$$

where λ is a constant and c equivalent per litre is the concentration. Thus, for small values of r_1, r_2 , G varies directly as c^2 .

At $r_1 = (2A)^{-\frac{1}{2}} = r_2$ we have

$$G \approx (4\lambda^2/e^2)^{\frac{1}{2}} c^{\frac{1}{2}}.$$

Thus, when both r_1, r_2 are of the order of magnitude of the mean ionic separation G varies directly as $c^{\frac{1}{2}}$.

Again, at $r_1 = a, r_2 = (2A)^{-\frac{1}{2}}$, we have

$$G \approx (2\lambda)^{\frac{1}{2}} e^{4q/a} e^{-\frac{1}{2}a^2} \cdot c^{\frac{1}{2}},$$

so that in this case G varies directly as $c^{\frac{1}{2}}$.

It follows that as the concentration increases the value of G at the points A and B of the contour map will increase *relatively* to the value at the point C, that at A increasing more rapidly than that at B. Thus at very high concentrations the point A of the ridge may be higher than the peak at B. Hence with increasing concentration, the associated ion-triple and associated ion-pair (with one free ion) configurations are of greatly increased relative occurrence. On the other hand, the relative number of free ions decreases with increasing concentration. In the contrary case, with decreasing concentration, the relative number of free ions will increase while the associated ion-triple and associated ion-pair configurations are of relatively less frequent occurrence.

These effects accord with what would be expected. As the concentration increases the ions are packed more closely together; the inter-ionic forces are of greater importance, so that the fraction of associated groups will be greater and the fraction of free ions less. As the concentration decreases the separate ions have more space available in which to move, so that the interionic forces have less effect. It follows that groups of associated ions will be of relatively less frequent occurrence while free (unassociated) ions will be present in relatively greater abundance.

Summary.

In this paper the association of ions in a bi-univalent electrolyte is considered. The new feature introduced, compared with the simple case of a uni-univalent electrolyte considered by other investigators, is that in addition to free ions and associated groups of zero nett electric charge we have to consider also the possibility of configurations representing various

intermediate stages of association and are led to conclude that such configurations are highly probable. This is in agreement with what has been surmised from conductivity measurements.

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*Mathematics Department,
University of Melbourne.*
