[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA-FISICA, UNIVERSITÀ DEGLI STUDI DI ROMA]

# Ionic Association. III. The Equilibrium between Ion Pairs and Free Ions

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Application of a method devised by Boltzmann to the equilibrium between ion pairs and free ions leads directly to the mass action equation $(1 - \gamma) = K_A c\gamma^2 f^2$ where $c$ is concentration, $f$ is the Debye–Hückel activity coefficient, $\gamma$ is the fraction of 1–1 electrolyte present as free ions and $K_A$ is the association constant. For the latter, the explicit value $K_A = 4\pi Na^3e^b/3000$ is found; $N$ = Avogadro's number, $a$ = ionic diameter, $b = e^2/aDkT$, $D$ = dielectric constant, $k$ = Boltzmann's constant and $T$ = absolute temperature. The functional form of $K_A$ is the same as that derived by Denison and Ramsey by a thermodynamic approach. The model used for the solvent was a continuum; therefore no factor appears which allows for solvent–solute interaction.

For many years, the Bjerrum theory of ion pairs has been used to interpret conductance data of associated ionophores despite its recognized defects, simply because no other theoretical tool was available. These defects are partly mathematical and partly physical. First, the Bjerrum probability function diverges; this difficulty was surmounted by arbitrarily cutting the integral off at the point where the integrand has a minimum. Second, the theory counts as associated pairs ions which are not in physical contact. Third, the cutoff leads to the prediction that association should cease abruptly at a critical value of dielectric constant $D$ and/or temperature $T$ for a given electrolyte. Recently, Denison and Ramsey[2] used a Born cycle to show that the association constant $K_A$ should be a continuous function of $DT$; their result for 1-1 electrolytes is

$$K_A = e^b \tag{1}$$

where

$$b = e^2/aDkT \tag{2}$$

In (2), $e$ is the electron charge, $a$ is the center-to-center distance of the ions in a pair and $k$ is Boltzmann's constant. Later, Gilkerson[3] applied Kirkwood's[4] partition function to the problem and obtained a result which can be stated in the form

$$K_A = K^0_A e^b \tag{3}$$

where $K^0_A$ is a factor which includes the effect of interaction between solvent and solute, and the free volume of the solute. Data of high precision by Kraus[5–7] and co-workers, when analyzed by the new method of Fuoss,[8] give association constants which are of the form (3), *i.e.*, simply proportional to $e^b$. The purpose of this note is to present an alternative derivation of the relation between dielectric constant and association constant, by applying a method used by Boltzmann[9] to a simple model.

First, let us consider in some detail what is meant by ionic association. When an anion and a cation collide, the resulting configuration presents a dipole field to an external observer; in an electrical field, the pair will experience a torque and tend to rotate, but neither ion will be free to contribute to transport of charge for the duration of the contact. Furthermore, neither ion can be counted as members of the atmospheres of other ions. Suppose we observe a reference cation for a time $t$ which is very long compared to the time between contacts with other ions. Let $t_2$ be the sum of the intervals during which the cation is in contact with an anion. Then, if $N$ is the total number of anions (or cations) in the volume $V$, we define as the concentration of ion pairs

$$N_2/V = (t_2/t)(N/V) \tag{4}$$

*i.e.*, we assume that the fraction of its existence which a reference ion spends in contact with an ion of opposite charge equals the fraction of ions which are associated. Alternatively, instead of a time average, we can compute $N_2/V$ as a number average, by making many instantaneous counts of the number of pairs present and then averaging over these counts. In general, when the dielectric constant is low, we would expect the duration of contact after collision to be long compared to the duration in media of high dielectric constant, but we would never expect $N_2$ to be zero; even uncharged particles, once in contact in liquids, tend to remain caged together for a while. In other words, by an ion pair, we shall mean a pair of ions in physical contact, regardless of the mechanism which stabilizes the contact. If they are not in immediate contact, we shall count them as free ions. In this way, we avoid the Bjerrum predicament of counting as pairs those ions not in actual contact. What both Bjerrum in his original derivation and Fuoss[10] in his convergent distribution function overlooked was the effect of the discontinuous structure of the solvent. Their distribution functions applied to a model in which distances would change continuously. Fuoss did, in fact, suggest cutting the integral off at a distance $(a + d)$ where $d$ is a distance of the order of the diameter of a solvent molecule but failed to make the now obvious step of requiring an all-or-nothing condition. Two ions of opposite charge at a short distance from each other represent a much more improbable configuration than continuum theory predicts; they will either move to contact or will diffuse further apart.

In order to allow for this tendency of ions to trap partners of the opposite charge, we shall represent the cations by charged conducting spheres of radius $a$ and the anions by charged point masses which can

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[1] On sabbatical leave from Yale University. Grateful acknowledgment is made for the award of a Fulbright Grant.

[2] J. T. Denison and J. B. Ramsey, THIS JOURNAL, **77**, 2615 (1955).

[3] W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956).

[4] J. G. Kirkwood, *ibid.*, **18**, 380 (1950).

[5] R. W. Martel and C. A. Kraus, *Proc. Nat. Acad. Sci.*, **41**, 9 (1955).

[6] P. L. Mercier and C. A. Kraus, *ibid.*, **41**, 1033 (1955).

[7] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **79**, 3304 (1957).

[8] R. M. Fuoss, *ibid.*, **79**, 3301 (1957).

[9] L. Boltzmann, "Gastheorie," Vol. II, Barth, Leipzig, 1898, p. 177.

[10] R. M. Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

penetrate the cationic spheres. (Or in order to avoid a quibble about a short circuit catastrophe, the anions may be represented as point charges in the centers of spheres of perfect insulator, whose radius is extremely small compared to $a$.) Electrostatically, contact between such anions and cations is equivalent to contact between oppositely charged spheres of radii $a/2$ or between spheres with center to center distance $a$. Let $\psi(r)$ be the potential at a distance $r$ from a cation, and assume the solution sufficiently dilute that the simplified Poisson–Boltzmann equation

$$\Delta\psi = \kappa^2\psi \tag{5}$$

may be used; here, $\kappa^2$ is the familiar Debye–Hückel parameter. The solution is, of course

$$\psi = Ae^{-\kappa r}/r;\ r \geqslant a \tag{6}$$

The field strength at the surface of the cation is

$$-(\mathrm{d}\psi/\mathrm{d}r) = Ae^{-\kappa a}(1 + \kappa a)/a^2 \tag{7}$$

and must equal $e/Da^2$, the field strength at the surface of a charged sphere. This condition evaluates the constant of integration and (6) becomes

$$\psi(r) = ee^{-\kappa r}\,e^{\kappa a}/rD(1 + \kappa a);\ r \geqslant a \tag{8}$$

By hypothesis, the sphere is conducting, and since a conductor cannot support a difference in potential, inside the sphere we must have

$$\psi = \text{const.};\ r < a$$

Alternatively, by Gauss's law, the charge on a conductor resides on the surface; hence the Poisson equation reduces to Laplace's for $r < a$. Hence

$$\Delta\psi = 0;\ r < a \tag{9}$$

The solution of (9) is

$$\psi = \alpha + (\beta/r) \tag{10}$$

and $\beta$ must vanish to avoid a singularity at the origin. Since the potential must be a continuous function of distance

$$\psi(a - 0) = \psi(a + 0) \tag{11}$$

By (8)

$$\psi(a + 0) = e/aD(1 + \kappa a) \tag{12}$$

and from (10), (11) and (12) we find

$$\psi(r) = e/aD(1 + \kappa a);\ r < a \tag{13}$$

The potential energy of an anion at the surface of the cation or anywhere in the volume occupied by the cation is therefore

$$u(r) = -e^2/aD(1 + \kappa a) \tag{14}$$

Our model thus allows for the fact that a pair of ions in contact has the energy specified by (14) and still permits use of the method of excluded volume. We shall consider a solution so dilute that the potential energy of an ion is negligible compared to $kT$ unless it is associated with an ion of opposite charge, when the energy is given by (14); that is, a given ion is considered to be either free or associated. Since ions in transition between free and associated are represented by a minimum in the distribution function,[10] their effects will be neglected. Our goal is to evaluate the association constant; it is sufficient to succeed for the limiting case of very dilute solutions because the value of a constant is naturally independent of the method used to evaluate it.

Now let us make the following experiment. Assume that there are $Z$ anions and $Z$ cations in the volume $V$. Let $Z_1$ be the number of free ions of a given species and $Z_2$ be the number of pairs. Then we add $\delta Z$ anions and naturally $\delta Z$ cations to maintain electroneutrality. Consider the anions: $\delta Z_1$ will remain free, *i.e.*, find locations not occupied by cations, and $\delta' Z_2$ will find sites inside cationic spheres, to form pairs. The probability that an added anion will not form a pair is proportional to $\delta Z$, the number of anions added, and to $(V - Z_1v)$, where $v = (4\pi a^3/3)$ is the volume of a cation. The probability that an added anion will form a pair is proportional to $Z_1\, v\delta Z$, and to the Boltzmann factor $e^{-u/kT}$, which is the weighting factor which favors sites inside cationic spheres above their simple geometric probability. The $\delta Z$ added cations will likewise distribute themselves through the solution; some will remain unpaired and others will trap anions. By the condition of neutrality, the number of pairs $\delta' Z_2$ formed by added cations equals the number formed by added anions; hence the total number $\delta Z_2$ of pairs formed is $2\delta' Z_2$. Therefore

$$\frac{\delta Z_2}{\delta Z_1} = \frac{2Z_1ve^{-u/kT}\delta Z}{(V - Z_1v)\delta Z} \tag{15}$$

We now continue to add electrolyte until a total of $N$ ions of each species is present in the volume $V$; this corresponds to integrating over $\delta Z$, whence

$$N_2 = N_1{}^2e^{-u/kT}v/V \tag{16}$$

if we neglect $Z_1v$, the volume of the cations with respect to $V$, the total volume of the system. The concentration of free ions, $N_1/V$, in practical units is given by

$$N_1/V = c\gamma L/1000 \tag{17}$$

where $c$ is stoichiometric concentration and $L$ is Avogadro's number. Dividing both sides of (16) by $V$ and substituting (17) and the analogous expression for $N_2/V$, we find

$$1 - \gamma = c\gamma^2(vLe^{-u/kT}/1000) \tag{18}$$

The energy $u$ is given by (14), which may be separated into a constant term and a concentration dependent term; dividing by $kT$, we have

$$-u/kT = b - b\kappa a/(1 + \kappa a) \tag{19}$$

The second term of (19) is immediately recognized as the logarithm of the square of the Debye–Hückel activity coefficient

$$b\kappa a/(1 + \kappa a) = e^2\kappa/DkT(1 + \kappa a) = -\ln f^2 \tag{20}$$

Substituting in (18), we find

$$1 - \gamma = c\gamma^2 f^2\,(4\pi La^3e^b/3000) \tag{21}$$

and thus identify the association constant

$$K_{\mathrm{A}} = 4\pi La^3e^b/3000 = 2.524 \times 10^{-3}\mathring{a}^3e^b \tag{22}$$

As stated in the introduction, the continuum model for the solvent automatically excludes any factors in $K_{\mathrm{A}}$ arising from solvent–solute interaction. But (22) can easily be generalized by multiplying by such factors as needed, corresponding to appropriate additional Boltzmann factors in the numerator and denominator of (15). The entropy term in

$$K_{\mathrm{A}} = K^0{}_{\mathrm{A}} \exp[(-\Delta F + T\Delta S)/RT]$$

for ion pair formation is unity; two free ions have each three degrees of translational freedom and the pair they form has three degrees each of translational and rotational freedom. By insisting on contact in pairs, vibrational freedom is excluded.

It is of interest to compare (22) with the value $K^{-1}$ derived from the Bjerrum–Fuoss function. The latter has been used mostly in the range of large $b$ values, where the asymptotic expansion[11] may be used

$$K^{-1} = (4\pi La^3/1000)(e^b/b) \qquad (23)$$

When $b$ is substantially larger than two, the exponential function $e^b$ almost completely masks the $b$ in the denominator, and over a considerable range $e^b$ and $(e^b/b)$ can approximate each other, with slightly different $a$-values. There is a slight systematic trend visible in the $a$-values reported by Fuoss and Kraus[11] for tetra-isoamylammonium nitrate in dioxane–water mixtures, but the average value of 6.40 Å. so well reproduced the data over a range of $10^{15}$ in $K$-values that the trend was ignored. Now, of course, we feel that it is real and is a consequence of the unnecessary $b$ in the denominator of the function (23). Denison and Ramsey[2] in fact showed that the early data conform well to the simpler function which they proposed. When $b$ is less than 4 or 5, the difference between $e^b$ and $e^b/b$ is, of course, easy to see, but data in this range of dielectric constants failed to reveal the inadequacy of the Bjerrum function, because the $K$-values calculated by conventional means from the data were forced to absorb the then unknown linear and $c$ log $c$ terms from electrophoresis and relaxation. Consequently, when $\mathring{a}$-values were calculated from the experimental $K$-values by means of the Bjerrum function for the systems in nitrobenzene mixtures, for example, and were found to vary systematically with dielectric constant, the discrepancy was ascribed to the missing higher terms rather than to the function itself.[12] In other words, when the $K$-values were reliable, the presence or absence of $b$ in the denominator was not detectable, while in the range where the two functions are visibly different, the $K$-values were not considered suitable for comparison with theory. Based on information now available, an equation of the form of (22) rather than that of (23) should be used in future treatment of ion pairs. Incidentally, a similar revision of the theory of association to ion triples[13,14] and quadrupoles[15] will also have to be made.

[11] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 1019 (1933); equation 7.

[12] H. Sadek and R. M. Fuoss, *ibid.*, **72**, 301 (1950); **76**, 5897, 5902, 5905 (1954).

[13] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

[14] R. M. Fuoss, *ibid.*, **56**, 1857 (1934).

[15] R. M. Fuoss and C. A. Kraus, *ibid.*, **57**, 1 (1935).

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# Acid-Base Reactions in Fused Salts. I. The Dichromate-Nitrate Reaction

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The reaction $2Cr_2O_7^{=} + 4NO_3^{-} \rightarrow 4NO_2 + O_2 + 4CrO_4^{=}$ proceeds at a measurable rate in fused $KNO_3$-$NaNO_3$ eutectic at 250°. A kinetic study of the reaction demonstates that the mechanism consists of two steps: the equilibrium $Cr_2O_7^{=} + 2NO_3^{-} \rightleftarrows N_2O_5 + 2CrO_4^{=}$ followed by the slow step $N_2O_5 \rightarrow$ decomposition products. The presence of the equilibrium is demonstrated by adding metal ions which precipitate the chromate and noting the effect on the reaction rate. Also, one of the metal ions, $Pb^{++}$, is known to form complex ions with $Cl^-$; the effect on the rate of adding $Pb^{++}$ and $Cl^-$ simultaneously also shows the presence of the equilibrium reaction.

Equilibrium studies have been made of a number of Lewis acid–base systems in fused salts.[1] However, no acid–base systems have been studied in which the equilibrium constant is very small; one technique for detecting an equilibrium which lies very much to the left is to study kinetically a reaction of one of the equilibrium products. The reaction between dichromate and nitrate in fused $KNO_3$–$NaNO_3$ eutectic produces very little of the equilibrium acidic product and chromate: $Cr_2O_7^{=} + 2\ NO_3^{-} \rightleftarrows N_2O_5 + 2CrO_4^{=}$. The decomposition of the acidic product is susceptible to kinetic study, however, and the presence of the equilibrium may be shown by studying the effect of variation in concentration of the stable equilibrium product, chromate; this is accomplished by adding various metal nitrates in varying concentration which precipitate the chromate ion.

## Experimental

**Materials and Apparatus.**—ACS reagent grade chemicals were used. All of the rate determinations were carried out in test-tube-shaped Pyrex reaction vessels immersed in a constant temperature bath consisting of a fused mixture of alkali nitrates. The temperature was maintained to within ±1° with a chromel–alumel indicating thermocouple controlling a Brown Potentiometer Pyrometer.

The reaction vessel used for most of the experiments was made from 31 mm. i.d. Pyrex tubing. A 40/50 standard taper glass joint at the top was used to give easy access to the solution and was fitted with a gas inlet tube which reached to within one-half inch of the bottom of the reaction vessel, and an outlet tube extending from the cap. This arrangement allowed one to agitate the reacting solution and to sweep any gaseous products out and into the absorbing solutions with a sweep gas.

The sweep gas (from cylinders) was first dried by passing it through a U tube containing anhydrous $Mg(ClO_4)_2$ and then preheated in coiled glass tubing immersed in the fused salt bath. The flow rate of the gas through the solution was determined with a gas flowmeter.

**Procedure.**—A solution of the precipitant ion in the fused eutectic was added to a dichromate solution in the same solvent. A total of 100 g. of solvent was used in each run. The solutions were maintained at the bath temperature.

[1] H. Flood and T. Forland, *Acta Chem. Scand.*, **1**, 592, 781 (1947); H. Flood, T. Forland and B. Roald, *ibid.*, **1**, 790 (1947); H. Flood and A. Muan, *ibid.*, **4**, 364 (1950).