[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Transition Cases in the Distribution of Ions

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Introduction

In a recent paper,[1] it was stated that "the conductance of incompletely dissociated binary electrolytes as a function of concentration obeys the equation

$$\Lambda = \gamma(\Lambda_0 - \alpha\sqrt{c\gamma}) \qquad (1)$$

exactly up to concentrations at which specific ionic interactions of higher order than pairwise become appreciable." Equation (1) is derived on the assumption that free ions and ion pairs are the only molecular species present. Using a distribution function for ion pairs, derived by the author,[2] it is possible to show that a critical concentration

$$c_0 = \frac{1000}{4\pi N}\left(\frac{DkT}{\epsilon^2}\right)^3 e^{-x}\, x^3(2 - x) \qquad (2)$$

where

$$x = 3 - \sqrt{3} \qquad (3)$$

exists, above which interactions of higher order than pairwise become significant. This concentration agrees with the concentration found experimentally above which deviations between observed conductances and values calculated from (1) exceed the experimental error.

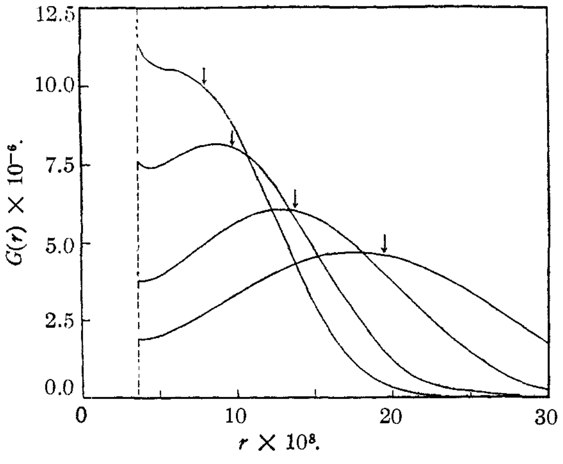

Fig. 1.—Distribution curve for $D = 78.6$; $a = 3.67 \times 10^{-8}$; $c = 0.025, 0.05, 0.10, 0.15$; arrow marks $1/\kappa$.

Derivation and Discussion

The distribution function mentioned above gives the probability that a given positive ion will have a negative ion in dr at r such that the negative ion is the nearest otherwise unpaired ion to the central positive ion. The mathematical form of the function is

$$G(r) = \frac{4\pi N}{V} r^2 \exp.\left(\frac{\beta}{r} - \frac{4\pi N}{V}\int_a^r e^{\beta/x}\, x^2\, dx\right) \qquad (4)$$

where N = total number of positive ions of charge ϵ in a total volume V, r = center to center distance between ions, $\beta = \epsilon^2/DkT$, D = dielectric constant, k = Boltzmann constant, T = absolute temperature and a = ion size.

Examples of the distribution function are given in Figs. 1 and 2. For Fig. 1, $D = 78.57$, $t = 25°$ and $a = 3.67 \times 10^{-8}$ cm.; the example thus refers to aqueous solutions. The lowest curve corresponds to $c = 0.025$. Here $G(r)$ has a maximum at 18×10^{-8} cm. and the distribution to both sides of the maximum is fairly symmetrical. Pairs for which $r = 18 \times 10^{-8}$ are better than twice as probable as pairs in contact, so that association is negligible. The next two higher curves correspond to $c = 0.05$ and $c = 0.10$, respectively; with increasing concentration the maximum moves to smaller pairwise distances and at $c = 0.15$ the maximum has practically vanished. At higher concentrations, the shorter the pairwise distances, the greater the probability for the configuration. This effect is not to be con-

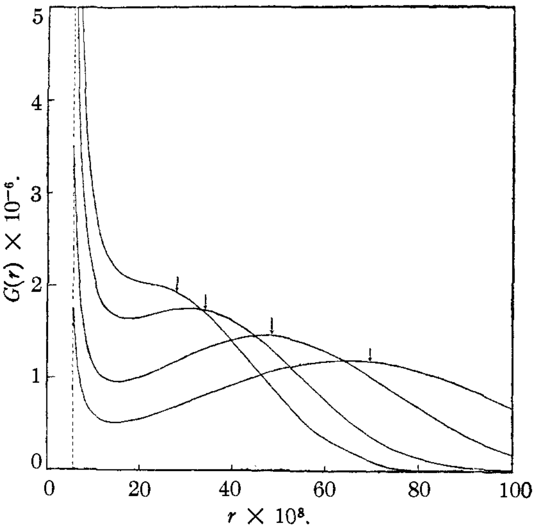

Fig. 2.—Distribution curve for $D = 20$; $a = 5.57 \times 10^{-8}$; $c = 0.5, 1, 2, 3 \times 10^{-3}$.

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[1] Fuoss, THIS JOURNAL, **57**, 488 (1935).

[2] Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934); *Chem. Rev.*, **17**, 27 (1935).

sidered an association due to Coulomb forces; it is simply a space crowding. In Fig. 2, we have an example of true association. Here $D = 20$, $t = 25°$, $\beta = 27.8 \times 10^{-8}$, $a = 5.57 \times 10^{-8}$ cm. The lowest curve is for $c = 5 \times 10^{-4}$; it has a long range maximum corresponding to high probability for free ions and also an exponential peak at $r = a$ corresponding to a high probability for associated short range pairs. As concentration is increased, the long range maximum moves to shorter distances, and the peak at $r = a$ climbs rapidly, so that the long range maximum eventually vanishes. Above $c = 3 \times 10^{-3}$, the pair probability is greater, the shorter the distance. Here we have both Coulomb attraction and space crowding responsible for the disappearance of the free ion maximum.

The general behavior of these curves reminds one somewhat of the isotherms for a van der Waals gas near the critical point. At low concentrations there are, in general, two well-defined peaks, one corresponding to free ions and one to associated. As concentration is increased, a concentration is finally reached at which the maximum, the minimum and the included inflection point coincide. Above this concentration, free and associated ions, as defined on the basis of $G(r)$, become indistinguishable, and we should expect that equations based on the classification of ions by means of $G(r)$ relating properties and concentration would fail at concentrations of this critical order of magnitude, no matter how closely they reproduced experimental data at lower concentrations.

The critical concentration can be found very easily. We have, on differentiating (4)

$$\frac{dG}{dr} = G(r)\left(\frac{2}{r} - \frac{\beta}{r^2} - \alpha r^2 e^{\beta/r}\right) \qquad (5)$$

$$\frac{d^2G}{dr^2} = G(r)\left(\frac{2}{r^2} - \frac{2\beta}{r^3} + \frac{\beta^2}{r^4} - 6\alpha r e^{\beta/r} + 3\alpha\beta e^{\beta/r} + \alpha^2 r^4 e^{2\beta/r}\right) \qquad (6)$$

where

$$\alpha = 4\pi N/V \qquad (7)$$

Setting $dG/dr = 0$, we obtain

$$\alpha e^{\beta/r} = 2/r^3 - \beta/r^4 \qquad (8)$$

and setting $d^2G/dr^2 = 0$ and substituting (8) to eliminate the transcendental, we obtain the equation

$$x^2 - 6x + 6 = 0 \qquad (9)$$

where

$$x = \beta/r \qquad (10)$$

as the condition which must be fulfilled at the critical point. The root of (9) which has physical meaning is

$$x = 3 - \sqrt{3} \qquad (11)$$

Substituting in (8) we finally obtain, after rearrangement

$$c_0 = \frac{1000}{4\pi N}\left(\frac{DkT}{\epsilon^2}\right)^3 e^{-x}\, x^3(2 - x) \qquad (2)$$

which is the result announced in the introduction. At 25°

$$c_0 = 3.2 \times 10^{-7}\, D^3 \qquad (12)$$

for 1-1 electrolytes.

Another derivation of (2) can be obtained by requiring that the two roots of (5) coincide; by writing (5) in the form

$$r = \beta/2 + \alpha r^4 e^{\beta/r}/2 = f(r) \qquad (13)$$

it is obvious that this condition will be fulfilled when $df/dr = 1$. Combining this requirement with the vanishing of (6), a fourth degree equation is obtained, which, of course, has $(3 - \sqrt{3})$ as one of its roots.

The value, r_0, of r at $c = c_0$ is given by

$$r_0 = 0.789\beta = (440/D) \times 10^{-8} \text{ cm. at } 25°$$

In water, this corresponds to 5.6×10^{-8} cm. and the critical concentration is 0.155 N, with $1/\kappa = 7.7 \times 10^{-8}$ cm. Here $1/\kappa$ is the characteristic distance of the Debye–Hückel theory

$$\kappa^2 = 8\pi N\epsilon^2/VDkT$$

If we assume that ordinary ions have diameters about equal to 3×10^{-8} cm. in water, then at 0.155 N, the maximum charge in the ionic atmosphere would be roughly two diameters away from a given ion. It seems dangerous, therefore, to extrapolate the concept of ionic atmosphere or equations based on it into concentrations greater than the critical; the ions are too close together to permit a time average treatment of their interaction.

Incidentally, $1/\kappa$ agrees in order of magnitude with ρ, the distance at which $G(r)$ has its long range maximum. At $r = r_0$

$$\kappa r_0 = 2/\sqrt{e^x(4/x - 1)} = 0.7228$$

which, as a numerical constant, is the same for all 1-1 electrolytes in all solvents. With decreasing concentration, both $1/\kappa$ and ρ increase; the ratio of these distances, $\kappa\rho$, is approximately 18.7 $c^{1/6}D^{-1/2}$ for $\rho > 2\, r_0$. Since $c^{1/6}$ changes only very slowly with concentration, we see that over quite a wide range of concentration, $\kappa\rho$ remains in order of magnitude unity. At very low concentrations, $1/\kappa >> \rho$, but when such concentrations are reached, the interionic effects become negligible practically in that they become unobservable experimentally. The ionic atmosphere thus appears as an approximation device for the average effects of free ions on free ions, where the average distances are of the order of $(V/2\pi N)^{1/3}$.

Let us now consider a typical example of the application of our result. The conductance of potassium chloride in liquid ammonia ($D = 22.38$ at $-33.35°$)[3] obeys equation (1) at low concentrations[4] but deviations larger than experimental error begin to appear at several thousandths normal. For liquid ammonia at $-34°$

$$c_0 = 1.8 \times 10^{-3} \tag{14}$$

In Table I are given the conductance data, together with the deviation between Λ observed and Λ calculated from (1) using $\Lambda_0 = 347.85$ and $K = 8.73 \times 10^{-4}$. At 1.8×10^{-3} N, the deviation is well beyond the experimental error, but as concentration decreases, exact agreement is found.

TABLE I

$c \times 10^5$	Λ (obsd.)	% deviation
2.471	334.27	−0.12
3.957	328.27	− .04
5.766	322.00	+ .02
9.320	311.77	+ .02
12.030	305.08	+ .03
15.619	297.48	− .04
24.021	282.42	+ .01
33.413	268.63	+ .03
50.79	250.93	+ .02
80.52	229.28	− .03
104.20	216.62	+ .05
137.60	202.81	+ .30
209.91	182.23	+ .69
313.94	163.74	+1.16
453.25	147.42	+1.99
702.29	130.21	+2.86
973.98	118.45	+4.14

In ethylene chloride ($D = 10.2$), the deviations between calculated and observed values become significant at several ten thousandths normal;[5,6] in anisole ($D = 4.29$) at several hundred thousandths;[5,7] and in benzene ($D = 2.27$), divergence from simple binary properties appears at several millionths normal.[8] In every case, equation (2) predicts the concentration above which conductance data cannot be computed by means of (1).

It is of interest to consider the physical interpretation of the result. Using the distribution function $G(r)$, we have divided the ions into several groups: free ions, which have no unpaired ion in the immediate neighborhood, associated ions, which have a single partner of opposite charge at a distance of molecular dimensions, and transition ions, which are those for which the pair distance is of the order of that corresponding to the probability barrier at $r = \beta/2$, the Bjerrum radius. Assuming that the equilibrium betweeen free and associated ions may be treated by the law of mass action, if allowance is made for the long range interaction of free ions on free ions, a conductance equation (1) is derived which is in exact agreement with data at low concentrations. In other words, as long as free ions have a relative maximum probability in terms of $G(r)$, we find properties which can be ascribed to an association equilibrium of the following type

$$A^+ + B' \rightleftharpoons AB$$

When, according to (3), free ions are no longer definable, a new set of properties appears; in the conductance curves, for example, Λ becomes larger with increasing concentration than (1) allows, and eventually a minimum in the Λ-c curve appears, after which conductance *increases* with increasing concentration. This effect has been explained in terms of higher association to triple ions;[9] the same hypothesis can be arrived at if we consider the approximations made in the derivation of $G(r)$. Long range interaction of short range pairs with free ions was neglected as a $1/r^2$ energy, compared to the $1/r$ energy of free ion-free ion interaction, but when a large fraction of the solute is present as short range pairs, it is clear that this interaction must be taken into account. If we redefine free ions to be those which are relatively far from either another free ion or from an ion pair, then we can again predict properties, but now five (+, −, +−, +−+, −+−) rather than only three molecular species are assumed to be present. Counting part of the solute present as triple ions is in effect removing some area (ions) from the $G(r)$ curve near $r = \beta/2$, and the maximum is thus restored.

Summary

Using the ion pair distribution function previously derived by the author, a critical concentration is shown to exist, above which free and pairwise associated ions become indistinguishable. This concentration, $3.2 \times 10^{-7}D^3$ at 25° for 1-1

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[3] Hooper and Kraus, THIS JOURNAL, **56**, 2265 (1934).

[4] Vincent F. Hnizda, Thesis, Brown University, 1935.

[5] Cox, Kraus and Fuoss, *Trans. Faraday Soc.*, **31**, 750 (1935).

[6] Donald L. Fowler, Thesis, Brown University, 1935.

[7] Bien, Kraus and Fuoss, THIS JOURNAL, **56**, 1860 (1934).

[8] Fuoss and Kraus, *ibid.*, **55**, 3614 (1933).

[9] Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).

electrolytes, is experimentally the concentration above which the simple laws of dilute solutions of electrolytes are no longer obeyed, so that a numerical significance is attached to the phrase "at low concentrations." At higher concentrations, higher types of association must be considered for the case of non-aqueous solutions.

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[Contribution from the Department of Chemistry of the University of California at Los Angeles]

The Potentiometric Determination of Quadrivalent Osmium with Chromous Sulfate

By William R. Crowell and Harlan L. Baumbach

In previous papers we have presented a direct[1] and an indirect[2] method of determining quadrivalent osmium. The former method is highly inaccurate, and the latter has the disadvantages of having two volatile constituents involved and of being applicable only to dilute acid solutions. The work of Thornton and Sadusk[3] suggested to us the possibility of using chromous sulfate as the reducing agent and the present work deals with the use of solutions of this salt. As in the case of titration with titanous salts the osmium is reduced from the quadrivalent to the trivalent state.

Because of the rapid reaction between chromous sulfate and oxygen we found it most satisfactory to have the apparatus all of glass as far as possible, to have all rubber connections of best quality heavy rubber, and all joints sealed with a suitable material such as lacquer cement. Of lesser importance is the tendency for chromous sulfate to react with hydrogen ion. Asmanoff[4] states that solutions may be as high as 10 N in sulfuric acid or 3 N in hydrochloric acid before any appreciable evolution of hydrogen takes place. Thornton and Sadusk state that they prepared 0.07 N solutions 0.18 N in sulfuric acid which remained unchanged in titer for two months. The solutions used by us were not greater than 0.03 N in sulfuric acid.

Reagents

The chromous sulfate solution was prepared by a method developed by Messrs. Stone and Beeson of the Chemistry Department at the University of California at Los Angeles. A solution of 0.01 M chrome alum 0.01 N in sulfuric acid was reduced by passage over amalgamated zinc. The yield of chromous ion was nearly 100% and the acid concentration was practically unchanged by the process.

The potassium bromoosmate and the potassium chloroosmate were prepared from osmium tetroxide in much the same manner that Gilchrist[5] prepared the ammonium bromo and chloro compounds in his determination of the atomic weight of osmium. A potassium hydroxide solution of osmium tetroxide was prepared as previously described.[6] The solution was acidified with sulfuric acid, the osmium tetroxide distilled into hydrobromic or hydrochloric acid, and the procedure carried out according to the method of Gilchrist except that potassium instead of ammonium salts were used.

The hydrobromic acid was prepared from red phosphorus and bromine. The middle fraction of the distillation of the products of the reaction was redistilled several times until a water-white liquid was obtained.

The constant boiling hydrochloric acid was obtained by twice distilling a mixture of equal volumes of concentrated hydrochloric acid and distilled water and retaining the middle fraction of the second distillation.

The potassium ferricyanide and potassium iodate used in standardizing the chromous sulfate and the sodium thiosulfate were recrystallized from the chemically pure salts.

Apparatus, Experimental Procedure and Results

The titration beaker consisted of a heavy-walled Pyrex beaker of about 125-cc. capacity. The cover consisted of a large rubber stopper which was cemented in place. In this stopper were openings for a mercury-sealed stirrer calomel and platinum electrodes, carbon dioxide inlet and outlet, burets, apparatus for introducing solids, and apparatus for treating and transferring solutions. In the bottom of the beaker was sealed a heavy stopcock to allow solutions to be withdrawn and the beaker to be rinsed without admitting air.

Figure 1 shows a diagram of the apparatus used for storing and handling the chromous sulfate solution. The system was flushed with nitrogen and the standard solution forced into the 5-liter flask A and stored under a total pressure of about 1.5 atm. of nitrogen. The nitrogen was purified by passing it through a strong solution of chromous sulfate. The capacity of the flask was about two liters of solution. E, F and G are heavy stopcocks. The solution was allowed to flow into the buret C and fill the bulb B. I was sealed off and after standing long enough to remove all adsorbed oxygen from the walls of the buret and bulb, the solution was displaced by nitrogen at

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(1) Crowell and Kirschman, This Journal, **51**, 1695 (1929).

(2) Crowell, *ibid.*, **54**, 1324 (1932).

(3) Thornton and Sadusk, *Ind. Eng. Chem.*, *Anal. Ed.*, **4**, 240 (1932).

(4) Asmanoff, *Z. anorg. allgem. Chem.*, **160**, 209 (1927).

(5) Gilchrist, *Bur. Standards J. Research*, **9**, 279 (1932).

(6) Crowell and Kirschman, This Journal, **51**, 175 (1929).