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Properties of Electrolytic Solutions. XV. Thermodynamic Properties of Very Weak Electrolytes

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In the preceding paper of this series,¹ cryoscopic data for a series of electrolytes in benzene were presented. It is the purpose of this paper to extend a previous treatment² of the osmotic properties of dipole solutes and to apply the results to experimental data for dilute solutions of tri-*i*-amylammonium picrate in benzene.

I. The Limiting Law

Using an ellipsoid with axes a and λa , $\lambda < 2^{-1/2}$, containing a point dipole of strength μ at the center, as the model for the solute particles, the following expression³

$$\frac{p_i - p}{p_i} = \frac{N}{V} \left(\frac{\pi}{3}\right)^{3/2} \frac{\mu^2 z}{DkT} \frac{e^y}{2 y^{7/2}} \quad (1)$$

was derived for the osmotic pressure of a solution containing N such particles in a total volume V . If we use N to denote Avogadro's number and introduce the Lewis and Randall j -function for an undissociated solute, we have

$$j = \frac{Nd}{1000} \left(\frac{\pi}{3}\right)^{3/2} \frac{\mu^2 z}{DkT} \frac{e^y}{2 y^{7/2}} m \quad (2)$$

where d = density of the solution, $z = (-1 + 1/2\lambda^2)^{-1/2}$, $y = \mu^2/\lambda^3 a^3 DkT$ and m = molality.

According to (2), then, the deviation function j should be a linear function of the molality at low concentrations for solutes which satisfy the assumptions implied in the model. In solvents

(1) Batson and Kraus, *THIS JOURNAL*, **56**, 2017 (1934).

(2) Fuoss, *ibid.*, **56**, 1027 (1934).

(3) Ref. 2, equation (12). The left side of this equation should read $(p_i - p)/p_i$ where $p_i = NkT/V$.

of low dielectric constant, ordinary binary electrolytes appear to be highly associated to clusters, the simplest of which is the ion pair. The dissociation constants of the ion pairs are so small ($< 10^{-16}$) for the electrolytes so far investigated⁴ that the concentration of free ions is practically negligible in comparison with that of ion pairs. For total concentrations above say $10^{-6} N$, therefore, it is more convenient to refer molecular weight determinations to the formula weight, and to describe deviations from this value in terms of various interactions of ion pairs with each other (and, if necessary, with the free ions present). It has been shown⁵ that the ion pairs possess dipole moments of the order ϵa where $\epsilon = 4.774 \times 10^{-10}$ e. s. u. and a is at least several Ångström units. The ion pairs thus satisfy the condition that $\mu^2/\lambda^3 a^3 DkT \gg 1$, implied in (2), but they do not contain point dipoles. The ternary picrates $R_3HN^+ \cdot O^- C_6H_2N_3O_6$, however, approximate this structure when R represents a large carbon chain, because the distance between the charges on the oxygen and nitrogen atoms is small compared to the external dimensions of the molecule. In other words, the ternary picrates satisfy approximately the two requirements implied in the derivation of (1): that the dipole be a point dipole and that the mutual energy of two dipoles in contact be large compared to thermal

(4) Fuoss and Kraus, *THIS JOURNAL*, **55**, 3614 (1933).

(5) Kraus and Hooper, *Proc. Nat. Acad. Sci.*, **19**, 939 (1933).

energy. We therefore shall apply (2) to the cryoscopic data for tri-*i*-amylammonium picrate in benzene, which are given in Table I.

TABLE I
CRYOSCOPIC DATA FOR TRI-*i*-AMYLAMMONIUM PICRATE IN BENZENE

m	j	k_1	m	j	k_4
0.000903	0.0349	..	0.00347	0.0238	0.118
.001780	.0250	..	.00610	.0416	.107
.00383	.0317	0.095	.00851	.0545	.111
.00624	.0482	.095	.01126	.0675	.112
.00896	.0610	.101	.02547	.1220	.106
.01175	.0743	.099	.03348	.1448	.105
.01505	.0902	.100	.04805	.1927	.084
.000704	-.0149	..	.07798	.2747	.046
.00165	.0003	..	.09013	.3096	.038

Curve I of Fig. 1 is a plot of j against molality for this salt. A curve is obtained, but at low concentrations, we can draw a limiting tangent

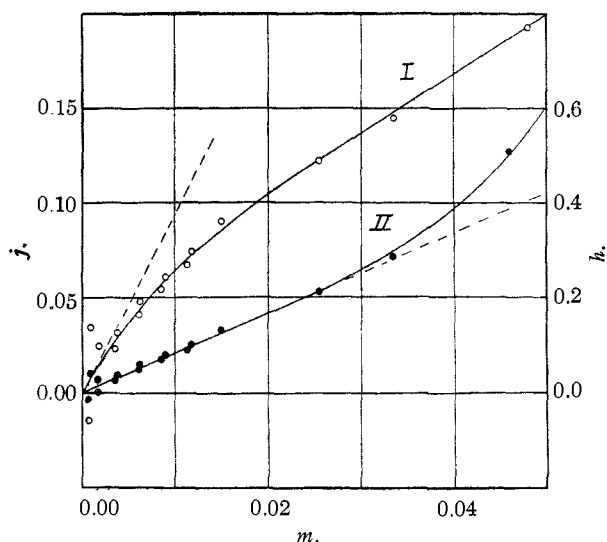


Fig. 1.—Tri-*i*-amylammonium picrate in benzene: Curve I, j -plot; Curve II, equation (13).

with slope 9.5. Substituting numerical⁶ values in (2), we have

$$(dj/dm)_{m=0} = 3.35 \times 10^{-3} \mu_D^2 e^v y^{-1/2} = 9.5 \quad (3)$$

where μ_D is the moment, measured in Debye units. Using Kraus and Hooper's value⁵ $\mu_D = 12.9$ and assuming that $\lambda = 1/2$ so that $z = 1$, we obtain

$$e^v y^{-1/2} = 17.05$$

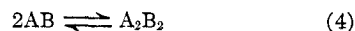
whence $y = 11.3$ and $\lambda a = 5.54 \times 10^{-8}$ cm. That is, assuming the ternary picrate ion pair to be an ellipsoid with axes in the ratio 2:1, we obtain a reasonable size for the diameter perpendicular to the dipole axis.

(6) $D = 2.27$, $d = 0.895$, $T = 278.6^\circ$; Meyer, *Ann. Physik*, **75**, 801 (1924).

II. Ion Pair Association to Quadrupoles

In the derivation of (2), all terms of power higher than the first in concentration were neglected. It would be extremely complicated to develop the higher terms of the series, in order to account for properties at finite concentrations, but the fact that the principal contributions to the corresponding phase integral arise from configurations of four ions in contact suggests a different method of attacking the problem. It has been shown that the short range ion-ion interaction can be described formally by the methods of dissociation theory⁷ by assuming an equilibrium between free ions and ion pairs. In solvents of very low dielectric constant, the ion pairs in turn interact with each other due to their (approximate) dipole fields, and this interaction may again be formally described as an association to quadrupoles, because the principal contribution to the phase integral arises from configurations containing two ion pairs in contact.

We therefore postulate the following equilibrium



in order to account for clusters containing two positive and two negative ions, and describe it by means of the equation

$$[AB]^2/[A_2B_2] = k_4 \quad (5)$$

Now let us consider the osmotic equation for a solution assumed to contain c equivalents per liter of an electrolyte which may exist as free ions and clusters containing up to four ions. (We shall neglect two, three and four ion groups containing ions all of the same charge, and unsymmetrical 4-ion groups; *i. e.*, we shall include the species +, -, +-, +-+, -+- and +-+-.) For the case of very weak electrolytes, for example, ternary ammonium picrates in benzene, the concentrations of single and triple ions are, however, negligible compared to the concentrations of either 2- or 4-ion groups, as is shown by an order of magnitude calculation based on conductance data.⁸ We therefore use the approximation

$$p/RT = c(\gamma_2 + \gamma_4) \quad (6)$$

where

$$\gamma_2 + 2\gamma_4 = 1$$

Substitution of the symbols for concentration in (5) gives

$$2c\gamma_2^2 = k_4(1 - \gamma_2) \quad (7)$$

(7) Fuoss, *Trans. Faraday Soc.*, **30**, 967 (1934).

(8) Kraus and Fuoss, *This Journal*, **55**, 21 (1933); Table X.

For low concentrations (*i. e.*, when $8c/k_4 \ll 1$)

$$\gamma_2 = 1 - 2c/k_4 + \dots$$

so that in this limiting case, (6) becomes

$$p = cRT(1 - c/k_4)$$

giving

$$j = c/k_4 \quad (8)$$

thus identifying k_4^{-1} with the coefficient of concentration in (2).

For finite concentrations, we shall test the more general equation (6). We have $(\gamma_2 + \gamma_4)$ equal to the ratio of the formula weight to the apparent molecular weight, so that

$$\gamma_4 = j \quad \gamma_2 = 1 - 2j \quad (9)$$

Substituting (9) in (7) and rearranging gives

$$c = k_4 j / (1 - 2j)^2 = k_4 h \quad (10)$$

According to (10), h , which can be calculated directly from the observed freezing points, should be a linear function of concentration. The constant k_4 is determined as the slope of the line. Curve II of Fig. 1 is a plot of h against m for the concentration range 0.001–0.05 N , using Batson and Kraus' cryoscopic data for the tri-*i*-amylammonium picrate solutions in benzene. The points lie, within the experimental error, on a straight line with a slope of 8.5 up to a concentration of about 0.03 N . Comparison with Curve I shows that the function (10) is linear over the range of concentration where the simpler j - m plot is curved. The deviations from linearity at higher concentrations presumably are due to ionic interaction of order higher than those so far considered.

For the equilibrium constant, we have $k_4 = 0.895/8.5 = 0.105$ as determined by the slope. (The factor 0.895, the density of benzene, is to convert molality to normality; volume concentrations are implied in (5).) In the third and sixth columns of Table I are given the values of this constant calculated from the data by means of (10) for the experimental points. Except for the most dilute points where the experimental error is relatively large (at 0.001 N , an error of 0.1% in the apparent molecular weight corresponds to a 5% error in k_4), the constancy is satisfactory up to about 0.03 N .

III. Calculation of k_4 from Coulomb's Law

We have shown in the preceding section that the association of ion pairs to quadrupoles provides a description of osmotic properties up to

moderate concentrations for the one case where data are available and which satisfies the assumptions made in the various derivations. The next step is a calculation of k_4 based on Coulomb's law; since we assume that only electrostatic forces (and a force of repulsion, taken into account by the assignment of a finite size to the solute particle) are acting, it should be possible to calculate a numerical value for k_4 .

If we define k_4 by the relation

$$e^{-u/kT} = 2 \times 1000/Nk_4 \quad (11)$$

which is similar to the definition of apparent mass action constants for other electrolytic equilibria, it is obvious that

$$1/k_4 = \frac{N}{2000} \left(\frac{\pi}{3} \right)^{3/2} \frac{u^2}{DkT} \frac{ze^u}{y^{1/2}} \quad (12)$$

if we compare (8) and (2) and recall the derivation underlying (1).

The above result applies to a molecule which may be represented as an ellipsoid, with axes a and λa , containing a point dipole of strength μ at the center (and with its axis parallel to the major axis of the ellipsoid). For the case of quaternary salts, the length of the dipole becomes comparable to the external dimensions of an ion pair; for this case, a more detailed model, which allows for the finite distance between the charges of the dipole, is necessary. Below is given the result for a model in which the ion pair is represented as two equal and oppositely charged spheres in contact. The details of the derivation are indicated by the following steps. We define k_4' for the association of two ion pairs to a quadrupole by the relation

$$2000/Nk_4' = (1/4\pi) \int \int \int e^{-u/kT} d\Omega d\Omega' r^2 dr$$

where

$$u = -\frac{e^2}{D} \left(\frac{1}{r_{13}} + \frac{1}{r_{24}} - \frac{1}{r_{23}} - \frac{1}{r_{14}} \right)$$

Here ions 1 and 2 are in the first ion pair and ions 3 and 4 in the second. For the case where $(-u/kT) \gg 1$, we obtain, after substituting for the r_{ij} 's their values in terms of r , θ' , ϕ' , θ'' and ϕ'' , by the method of asymptotic expansion, the leading term

$$(k_4')^{-1} = \frac{NA}{4000} \left(\frac{e^2}{DkT} \right)^3 \frac{\exp.(2 - \sqrt{2})b}{b^{11/2}} \quad (13)$$

where

$$A = \frac{32 \pi^{3/2}}{\sqrt{7} \sqrt{64 - 40\sqrt{2}} + 109/8} = 14.68$$

and

$$b = e^2/aDkT$$

Using (12) and the slope of the straight line of Fig. 1—II, we obtain the same result for the parameter λa as was obtained using the slope of the limiting tangent to curve I. The difference between (2) and (10) is two-fold: the former represents a limiting law, while the latter is valid at finite concentrations and the former involves primarily only mathematical approximations while the latter involves in addition the physical approximation implied in (5).

It is interesting to note that it is impossible to treat the data for tri-isoamylammonium picrate by means of the equation deduced using two spherical ions in contact. At 5.5°, (13) gives

$$\begin{aligned} -\log k'_1 &= 4.605 + 0.2544b - 5.5 \log b & (14a) \\ &= 4.605 + \log F(b) & (14b) \end{aligned}$$

The function $\log F(b)$ defined in (14) has a minimum value of -2.96 where $b = 9.4$. If we substitute 0.105 in (14a) for k'_1 , we obtain $\log F(b) = -4.584$, which lies below the minimum. It follows, therefore, that there is no value of b , and hence of a , which will simultaneously satisfy both the data and (14). (If we had an explicit formula for k'_1 instead of the asymptotic expansion, k'_1 as a function of b would have no minimum, but values of b less than 10 would correspond to absurdly large a values in benzene.) As we might have expected from our notions of the chemical structure of $(C_5H_{11})_3HN \cdot OC_6H_4N_3O_6$, the ellip-

soidal model ($\cdot \cdot + - \cdot \cdot$) is in much better agreement with experiment than the spherical $(-)(+)$.

In the case of salts with symmetrical ions of the type $R_4N \cdot X$, where the spherical model might be expected to apply, the osmotic deviations are large even at 0.001 N , and, consequently, in order to test the model, it would be necessary to have reliable data at lower concentrations. At present the only available data are at higher concentrations⁹ where the apparent molecular weight is so much larger than the formula weight that none of our present equations apply. Further work on strong salts at lower concentration and in other solvents is in progress.

Summary

1. The hypothesis is made that ion pairs may, under suitable conditions, associate to groups containing four ions.
2. The osmotic properties of a very weak electrolyte, tri-*i*-amylammonium picrate in benzene, are shown to be in agreement with the hypothesis.
3. The molecular diameter, calculated from the data by proper application of Coulomb's law, is of the correct order of magnitude.

(9) Tetra-*i*-amylammonium nitrate in dioxane, Kraus and Vin-gee, *THIS JOURNAL*, **56**, 511 (1934); silver perchlorate and tetra-*i*-amylammonium thiocyanate in benzene, Batson and Kraus, *loc. cit.* PROVIDENCE, R. I. RECEIVED JUNE 8, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Action of Acids upon Hydrous Alumina

BY ARTHUR W. THOMAS AND RICHARD D. VARTANIAN

Stiasny¹ has directed attention to the fact that the nature of the anions greatly influences the resistance of simple ol compounds of chromium to the action of acids. He has given the following order of anions with respect to their deolating tendency: nitrate < chloride < sulfate < formate < oxalate, which is the same as the order for their tendency to be coördinatively bound to the central atom.

In previous publications² from this Laboratory

(1) E. Stiasny, "Gerbereichemie (Chromgerbung)," Verlag von Theodor Steinkopff, Leipzig, 1931, p. 351.

(2) (a) A. W. Thomas and T. H. Whitehead, *J. Phys. Chem.*, **35**, 27 (1931); (b) A. W. Thomas and A. P. Tai, *THIS JOURNAL*, **54**, 841 (1932); (c) A. W. Thomas and F. C. von Wicklen, *ibid.*, **56**, 794 (1934); (d) A. W. Thomas "Colloid Chemistry," McGraw-Hill Book Co., New York, 1934, Chapter VII.

it has been postulated that the micelles in aluminum oxysalt and chromium oxysalt³ hydrosols are essentially polyolated structures. As a consequence of this viewpoint, acids producing anions which do not manifest a strong tendency to be coördinatively bound and therefore do not exert a deolating tendency should favor the formation of colloidal dispersions of the oxides. On the other hand, acids whose anions are strongly bound coördinatively to the central metallic atom should disrupt the ol linkages and as a consequence a colloidal dispersion should not be produced when such acids act upon a pure hydrous oxide which is not oxolated.

(3) Such sols are generally denoted in the colloid literature as "aluminum oxide" and "chromium oxide."