Since these quantities are very useful in numerous thermodynamic calculations, we have included them here. The equations which summarize our results for the two solutions are thus found to be

$$\begin{array}{rcl@{\qquad}rcl}
 & \text{LiOH} & & & \text{NaOH} & \\
\Phi & = & -19.98 + 12.53\, m^{1/2} & \Phi & = & -26.59 + 17.49\, m^{1/2} \\
\bar{C}_{p_2} & = & -19.98 + 18.80\, m^{1/2} & \bar{C}_{p_2} & = & -26.59 + 26.24\, m^{1/2} \\
\bar{C}_{p_1} - \bar{C}^{\circ}_{p_1} & = & -0.1129\, m^{3/2} & \bar{C}_{p_1} - \bar{C}^{\circ}_{p_1} & = & -0.1579\, m^{3/2}
\end{array}$$

Summary

We have used the adiabatic twin calorimeter method to determine the specific heats of aqueous solutions of lithium and sodium hydroxides at 25° from 0.04 *m* to over 2 *m*. From these data we have calculated the apparent molal heat capacity of the solutes. When plotted against $\sqrt{m}$ they both give straight lines over the whole range of concentration. Equations are included for the apparent and partial molal heat capacities of the solute and the relative partial molal heat capacity of the solvent. From these it is possible to calculate the heat capacity of these solutions with great precision at any concentration in the range studied.

EVANSTON, ILLINOIS RECEIVED SEPTEMBER 30, 1932
PUBLISHED MARCH 7, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. III. The Dissociation Constant

BY RAYMOND M. FUOSS AND CHARLES A. KRAUS

I. Introduction

Experimental data for weak electrolytes in water and for most electrolytes in solvents of lower dielectric constant indicate the existence of an equilibrium of the type

$$A^{+} + B' \rightleftharpoons AB \qquad (1)$$

In the preceding paper of this series,[1] we have shown that it is possible to describe conductance data (up to moderate concentrations) exactly by means of the mass action equation, provided the influence of interionic forces, in the usual sense of the term, on the thermodynamic properties and mobilities of the ions be taken into account.[2]

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(1) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(2) It should be pointed out that all terms in activity and migration velocity of higher order than $c^{1/2}$ in concentration are necessarily included in our dissociation constants derived from conductance data. Since the method of calculation is applied only to low (ion) concentrations, we believe that our K describes primarily the effect which we are naming mass action, *i. e.*, the formation of electrically neutral structures from ions. It is evident, both on experimental and theoretical [Kramers, *Proc. Amsterdam*, **30**, 145 (1927)] grounds that some *specific* interaction between ions of opposite charges must be considered in addition to the interionic effect described by Debye's time-average potential The specific interaction is most simply treated by means of arguments based on Equation (1).

The relative concentration of ions was defined as the fraction of the total solute free to carry the current in the conduction process, and the concentration of undissociated molecules was determined by difference. It was assumed that the undissociated molecules were normal in their thermodynamic behavior and that the dielectric constant of the solution was that of the pure solvent. These assumptions appeared to be justified by the results obtained in accounting for conductance data.

It is our present purpose to discuss the mechanism underlying (1) and to compare our results with experimental data. We assume that the ions in a solution may be treated as uniformly charged spheres which, on account of solvation, are presumably larger than the corresponding gaseous ions. The electrostatic forces between ions will cause ions of unlike charges to attract one another, and for any pair of ions the mutual potential energy as a function of distance is given by Coulomb's law. If two unlike ions "approach to contact," a definite amount of energy is required to separate them; if this energy is much less than the kinetic energy of the solvent molecules, thermal agitation will soon dissociate the ion pair, while if the energy is considerably greater, the ion pair has a good chance of existing for some time. These considerations permit us to express the energy and hence the dissociation constant of an electrolyte in terms of the size of the ions involved and the dielectric constant of the solvent.

A similar calculation has been made by Bjerrum,[3] and applied to electrolytes in solvents of fairly high dielectric constant. The ion sizes calculated from activity data seem somewhat small, and it is quite possible that ion sizes so determined include other effects than association. In view of Bjerrum's result that electrolytes with sum of radii greater than 3.5×10^{-8} cm. will not associate to any great extent in water, combined with ideas of ion sizes derived from other sources, it seems quite probable that most salts are completely dissociated in water. It is only in solvents of lower dielectric constant, where the Coulomb energy is correspondingly greater, that an ion pair has sufficient energy to be stable. Also, in solvents of lower dielectric constant, the fraction of solute associated is sufficiently great to permit its accurate determination by means of conductance experiments.

In this paper the dissociation constant, calculated on the hypothesis of Coulomb forces, will be derived as an explicit function of the dielectric constant of the solvent and of a parameter a, the "ion size." The results have been compared with experimental data covering a variety of salts and solvents. Particular attention has been given to the dependence of dissociation constant on dielectric constant; this has been investigated over a range of dielectric constant from 2.4 to 40. The calculated dissociation energies agree with experimental values very closely over the entire range.

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[3] Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, No. 9 (1926); Falkenhagen, "Electrolyte." Verlag von S. Hirzel, Leipzig, 1932, p. 257 ff.

II. The Dissociation Constant

We are given a binary electrolyte dissolved in a volume V of solution. Let there be N ions of each charge, so that the number of ions per cubic centimeter, n, equals N/V. Then, if a positive ion with charge $+e$ is in a volume element dv_1, the probability that a negative ion with charge $-e$ will be in a volume element dv_2 at a distance r_{12} from dv_1 is

$$P = n \exp\left(\frac{e^2}{r_{12}DkT}\right) dv_1 dv_2$$

where D is the dielectric constant, k is Boltzmann's constant, and T is the absolute temperature. In spherical coördinates, with the origin at the first ion, this is

$$P = n \exp\left(\frac{e^2}{rDkT}\right) r^2 \sin\theta \, d\theta \, d\varphi \, dr \, dv_1$$

If we keep the positive ion fixed, P has a minimum at a distance

$$r_{min} = q = e^2/2DkT \tag{2}$$

The energy required to separate the two ions at a distance q is $2kT$, four times the mean thermal energy per degree of freedom. This result was first obtained by Bjerrum.[3] Two ions at a distance $r < q$ are to be considered as an associated ion pair. We may then determine[4] the free energy ψ associated with the reaction

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

by evaluating the phase integral for the system

$$Ne^{-\psi/kT} = n \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta \, d\theta \int_a^q \exp\left(\frac{e^2}{rDkT}\right) r^2 \, dr \int_v dv_1$$

where the positive ion is allowed to be anywhere in the volume V, and the negative ion ranges over the sphere between $r = a$ (contact) and $r = q$ (dissociation). Substituting a new variable of integration

$$y = e^2/(DkTr)$$

and performing the integration, we obtain

$$e^{-\psi/kT} = 4\pi \left(\frac{e^2}{DkT}\right)^3 \int_2^b e^y y^{-4} \, dy \tag{3}$$

The definite integral

$$Q(b) = \int_2^b e^y y^{-4} \, dy \tag{4}$$

is a function of

$$b = e^2/aDkT \tag{5}$$

that is, depends on the ion size and the dielectric constant of the solvent. The conventional mass action constant K is expressed in terms of concentrations in equivalents per liter; if we consider one equivalent of each species of ions, $nV = N = 6.06 \times 10^{23}$, Avogadro's number, and we have the following relation between ψ and K

$$N\psi = RT \ln (1000 \, K/N)$$

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[4] Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, p. 307.

Substituting in (3), our final result is

$$K^{-1} = \frac{4\pi N}{1000}\left(\frac{e^2}{DkT}\right)^3 Q(b) \tag{6}$$

The values of the function $Q(b)$ have been tabulated by Bjerrum for $1 \leqslant b \leqslant 15$. (The function $Q(b)$ has no physical significance for $b < 2$ because $b = 2$ corresponds to the limiting case of complete dissociation when $a = q$). This range of b values was insufficient for our calculations; a further range of values is given in Table I.

TABLE I

$\text{LOG}\ Q(b) \approx 0.4343b - 4\ \text{LOG}\ b + \text{LOG}\ (1 + \delta)$

b	$\log Q(b)$	b	$\log Q(b)$
15	1.96	40	11.01
17	2.59	50	14.96
20	3.59	60	18.98
25	5.35	70	23.05
30	7.19	80	27.15

The values given in Table I are approximate. The expansion of $Q(b)$ is

$$Q(b) = \frac{1}{6}\left\{e^2 - Ei(2) + Ei(b) - \frac{e^b}{b}\left(1 + \frac{1}{b} + \frac{2}{b^2}\right)\right\}$$

and the available tables[5] for the integral exponential $Ei(x) = \int_{\infty}^{-x} e^{-u}u^{-1}\,du$ run only to $x = 15$. We therefore used the asymptotic expansion

$$Ei(x) \sim \frac{e^x}{x}\left(1 + \frac{1!}{x} + \frac{2!}{x^2} + \frac{3!}{x^3} + \dots\right)$$

in order to compute $Ei(b)$ for $b > 15$, and in taking the logarithm, $(^1/_6)\left\{e^2 - Ei\ (2)\right\} = 0.41$ was neglected in comparison with the other terms. This gives

$$\log Q(b) \approx 0.4343\, b - 4 \log b + \log (1 + \delta)$$

$$\delta = \frac{4}{b} + \frac{4.5}{b^2} + \frac{4.5.6}{b^3} + \dots$$

These approximations cause an error of several per cent. in $\log Q(b)$ for b equal to 15, but this error decreases rapidly as b increases.

If the dissociation constant of an electrolyte is known, $Q(b)$ is determined by (6). From a graph of $Q(b)$ against b, the corresponding value of b is obtained, and then a is evaluated from (5). Conversely, if a is known, K may be computed.

The functional relation (6) between the dissociation constant of an electrolyte and the dielectric constant of the solvent shows that K must decrease very rapidly as D decreases. If we retain only the first term of the asymptotic expansion, we have, approximately

$$1/K \approx \frac{4\pi N}{1000} a^3 \frac{aDkT}{e^2} \exp\left(\frac{1}{a}\frac{e^2}{DkT}\right) \tag{7}$$

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(5) Jahncke and Emde, "Funktionentafeln," Teubner, 1909.

so that $1/K$ increases very much like e^b/b. Since $(-kT \log K)$ measures the work done against the Coulomb forces on separating a pair of ions from contact $(r = a)$ to the distance $(r = q)$ at which their thermal motion has an even chance of carrying them further apart, we may interpret (6) as a relation between the dissociation energy of an ion pair and the dielectric constant of the medium. It should be noted that K is extremely sensitive to the value of a when D is small, as is shown in (7).

Equations (6) also contains the statement that, for a given salt, dissociation is complete in solvents having a dielectric constant above a definite value. When the distance at contact is equal to (or greater than) q, the Coulomb forces no longer suffice to render an ion pair stable and then the only interaction between ions is that described by the usual "ion atmosphere." The condition $a = q$ is equivalent to $b = 2$ and $Q(b) = 0$. For example, for a salt with $a = 6.40 \times 10^{-8}$, K increases with increasing dielectric constant until at $D = 41.4$, $K = 1$. Beyond this value of D, K increases very rapidly and the limit $K = \infty$ corresponds to $D = 43.6$ where $b = 2$. In other words, on a $(-\log K)$–D plot, the $(-\log K)$ curve crosses the axis at $D = 41.4$ and becomes asymptotic to a vertical line at $D = 43.6$. In solvents of higher dielectric constant, there can be no ion association. For a given solvent, there is likewise a maximum value of a above which electrolytes do not form ion pairs; for example, in water at 25°, this critical value of a is about 3.5×10^{-8} cm.

It is to be expected that a will depend on the atomic properties of the constituent ions of the electrolytes. But there is considerable evidence indicating that the ions are solvated, *i. e.*, that each ion is surrounded on the average by a certain number of solvent molecules which accompany the ion in question. (This average number need not, of course, be integral.) Consequently, the value of a may also depend on the atomic properties of the solvent. In general, we might except that the more intense the field around an ion, the greater will be the value of a. If two solvated ions approach within a distance $r < q$, they probably will approach to "contact" and will form an ion pair (which will eventually be dissociated by a high speed collision). As an approximate model of the solvated ion, we may picture the central ion as a small sphere carrying a charge $\pm e$, surrounded by several shells of solvent molecules, the inner shells firmly bound and the outer layers less and less firmly held (or, better, oriented with respect to the central ion), until at a moderate distance from the center a solvent molecule has a good chance of assuming a random orientation. On this basis, as two ions form an ion pair, it seems reasonable to suppose that the center to center distance a of the ion pair will be less than the sum $(r_1 + r_2)$ of the radii of the freely migrating ions, because the effective dielectric constant of the polarized solvate shell around each ion is certainly less than the macroscopic dielectric constant, and the Coulomb forces are correspondingly increased. The ions may indeed approach so closely that the assumed spherical symmetry of the charge of the central ion no longer obtains. The mechanism of the ion-pair formation as here pictured is undoubtedly over-simplified; nevertheless, it provides a tentative working scheme which appears to be in agreement with the facts available.

III. Comparison with Experiment

Influence of the Dielectric Constant.—We shall first consider the dissociation constant of tetraisoamylammonium nitrate. The conductance of this salt has been measured at 25° in dioxane, water, and in a series of mixtures of dioxane and water covering the dielectric constant range 2.2 to 80.[6]

In water, the salt is a strong electrolyte. The conductance in the dilute region is nearly linear against the square root of concentration, and extrapolation by Onsager's method gives $\Lambda_0 = 86.9$. This small value of Λ_0 indicates a rather large ion size, which, indeed, might be expected for a salt of this structure. Despite the fact that the observed conductance curve approaches its limiting tangent from below, we are inclined to consider the salt as completely dissociated in water and to ascribe the negative deviations to causes other than incomplete dissociation.[7]

In a mixture of dioxane and water containing 53% water, with a dielectric constant of 38.0, the $\Lambda-\sqrt{c}$ curve is nearly parabolic at concentrations below 0.002 N. The viscosity of dioxane–water mixtures has been determined[8] at 20 and 40° for several compositions. We have interpolated values for our mixtures at 25° in order to evaluate the coefficient of the square root term in the conductance equation. Using Onsager's approximate equation

$$\Lambda = \Lambda_0 - \alpha\sqrt{c} - (\Lambda_0/K)\,c$$

we obtain $\Lambda_0 = 42.8$ and $K = 0.28$. Using $\Lambda_0 = 42.8$ and $\alpha = 69.5$, and computing K for several higher concentrations by means of equations (2), (3) and (7) of our previous paper,[1] where $\beta = 1.51$ and $\delta = 1.0$, we obtain the following results: $c = 0.00748, 0.00441$; $\Lambda = 36.32, 37.72$; $\gamma = 0.9865, 0.9875$; $f = 0.759, 0.806$; $K = 0.31, 0.21$, av. 0.26.

The values of the constants Λ_0 and K for the mixtures containing 20.2 and 14.95% water were obtained by our intercept method. The specific and derived constants are as follows: water content = 20.2, 14.95; $D = 11.9, 8.5$; $\eta = 0.0174, 0.0161$; $\beta = 8.6, 13.5$; $\Lambda_0\delta = 79, 100$; $\Lambda_0 = 34, 31$; $K = 9.0 \times 10^{-4}, 1.00 \times 10^{-4}$.

For lower concentrations of water, we have no data at electrolyte concentrations sufficiently low to permit the application of the intercept

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[6] Kraus and Fuoss, THIS JOURNAL, **55**, 21 (1933).

[7] Onsager, *Physik. Z.*, **28**, 296 (1927).

[8] Herz and Lorentz, *Z. physik. Chem.*, **140**, 407 (1929).

method of determining Λ_0 and K. The ion concentrations are quite small on account of the low dissociation, so that the interionic terms may be estimated with fair accuracy; the difficulty is that the effect which eventually produces a minimum in the conductance curve causes deviations from our equations which prevent extrapolation for Λ_0. At concentrations well removed from the minimum, we may make a good estimate of K if we assume a reasonable value of Λ_0 (based on viscosity) and estimate the corrections due to interionic effects. For the present, the deviations due to the minimum will be neglected; in the concentration range used below to calculate K this is justified. In the next paper of this series, the situation at the minimum point will be considered.

The mixture containing 9.5% water has a dielectric constant of 5.84 and a viscosity of 0.0161. Assuming $\Lambda_0 = 30$, $\alpha = 473$, $\delta = 4.5$, $\beta = 25$, we obtain the following: $c \times 10^4 = 0.835, 1.378, 2.66, 4.01$; $\Lambda = 4.53, 3.74, 2.90, 2.48$; $\gamma = 0.1605, 0.1336, 0.1055, 0.0915$; $f = 0.815, 0.785, 0.743, 0.715$; $K \times 10^6 = 1.69, 1.74, 1.82, 1.89$. The increase of K with increasing concentration is due to the neglected influence of the minimum, which makes the conductance greater than it would otherwise be. Extrapolating the above values of K to zero concentration in order to eliminate this error, we obtain $K = 1.65 \times 10^{-6}$ for $D = 5.84$. Similar calculations for the other mixtures containing smaller amounts of water lead to the values of log K given in Table II.

TABLE II

CONSTANTS FOR TETRAISOAMYLAMMONIUM NITRATE IN DIOXANE-WATER MIXTURES

% Water	D	$-\log K$	K	E, cal.	$a \times 10^8$
0.60	2.38	15.7	2×10^{-16}	21,400	6.01
1.24	2.56	14.0	1×10^{-14}	19,100	6.23
2.35	2.90	12.0	1×10^{-12}	16,400	6.36
4.01	3.48	9.6	2.5×10^{-10}	13,100	6.57
6.37	4.42	7.53	3.0×10^{-8}	10,300	6.65
9.50	5.84	5.78	1.65×10^{-6}	7,900	6.45
14.95	8.5	4.00	1.00×10^{-4}	5,450	6.50
20.2	11.9	3.05	9.0×10^{-4}	4,150	6.70
53.0	38.0	0.60	0.25	820	6.15

In the fourth column are given the values of K and in the fifth column the corresponding energies, $E = -RT \ln K$, the dissociation energies per gram molecule. It will be noted that in solvents of low dielectric constant the dissociation energy reaches values comparable with those of ordinary reactions.

On substituting values for the constants in (6), we obtain for 25°

$$K^{-1} = 1.320 \times 10^6 D^{-3} Q(b)$$

whence

$$-\log K = 6.120 + \log Q(b) - 3 \log D \qquad (8)$$

By means of (8), log $Q(b)$ is determined, and from a graph of this function against b, values for b are obtained. These, substituted in (5), together with the appropriate dielectric constants, yield the values of a tabulated in the sixth column of Table II.

In the various dioxane–water mixtures considered above, the molar water concentration was always greatly in excess of the salt concentration. Furthermore, in view of the high polar moment of water, it seems reasonable to assume that the solvate molecules would be predominantly water, and that the relative hydration of the solute ions would be more or less independent of the absolute water concentration at the high water concentrations involved. In this event, we might expect that a would be the same for any mixture of dioxane and water. This is actually the case as is shown in Table II, the extreme variation being only 10%.

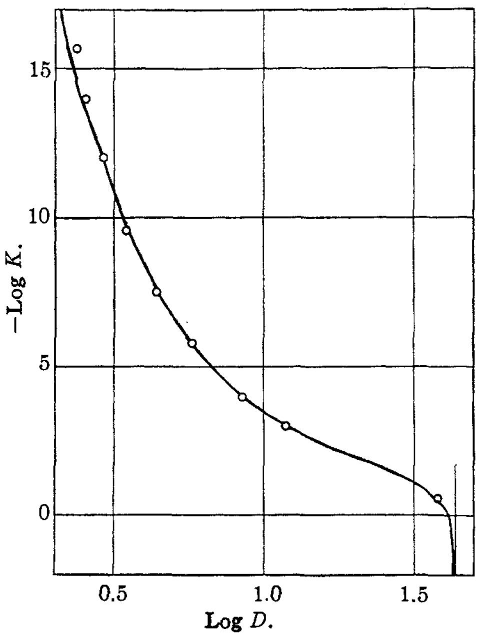

Fig. 1.—Dissociation constants for tetraisoamylammonium nitrate in dioxane–water mixtures. Solid curve calculated, circles observed.

Using the average value, $a = 6.40 \times 10^{-8}$ cm., we may compute the dissociation constant of tetraisoamylammonium nitrate in any mixture of dioxane and water by means of equations (4), (5) and (6). The result of this calculation is shown in the accompanying figure, where ($-\log K$) is plotted against $\log D$. The circles represent the experimental values. The agreement between the observed values and those calculated on the basis of a *single* value of a is satisfactory over a range of fifteen powers of ten in the constant K. It is interesting to note that no association of the type described by our equations is possible for tetraisoamylammonium nitrate in mixtures having a dielectric constant greater than 43.6, where the curve tends to $1/K = 0$ ($\log K = \infty$).

Influence of the Solvent Medium.—The same electrolyte in different solvents will have different values of a, if this parameter depends on the solvent as well as on the solute. We have applied the intercept method to the conductance data for solutions of silver nitrate in the following solvents: acetonitrile at 25°,[9] benzonitrile at 25°,[10] and ammonia at −33°.[11] The

[9] Walden and Birr, *Z. physik. Chem.*, **144**, 269 (1929).

[10] Martin, *J. Chem. Soc.*, 3270 (1928).

[11] Franklin and Kraus, *Am. Chem. J.*, **23**, 277 (1900); THIS JOURNAL, **27**, 191 (1905).

constants for these systems were obtained by extrapolation of the conductance data by the method previously described by us.[1]

The values of Λ_0 and $(-\log K)$ thus obtained are given in Table III in the first and second columns; the values of a calculated from the dissociation constant by means of (4), (5) and (6) are given in the third column; the dielectric constants and polar moments of the solvents[12] are given in the last two columns.

TABLE III

CONSTANTS FOR SILVER NITRATE IN DIFFERENT SOLVENTS

Solvent	Λ_0	$-\log K$	$a \times 10^8$	D	$\mu \times 10^{18}$
Benzonitrile	55.2	3.495	1.62	25.2	3.91
Acetonitrile	186	1.775	1.90	36	3.11
Ammonia	291	2.314	5.78	22	1.49

It will be noted that a varies from solvent to solvent, and that, while neither log K nor a changes in the same order as D, a decreases as the electrical moment of the solvent increases. Although the values of a for the nitriles seem somewhat small, the results are in accord with what might be expected of silver nitrate in these solvents. Ammonia forms a very stable complex with silver ion, even in water. Hence, in ammonia, the positive ion is relatively large, and solvation, in the sense of solvent dipoles oriented by the ionic field, further increases the effective radius. The result is that silver nitrate is a much stronger electrolyte in ammonia of dielectric constant 22 than in benzonitrile of dielectric constant 25

Influence of the Ions.—Finally we shall consider a series of different salts in the same solvent: the nitrates of the alkali metals in liquid ammonia at −40°.[13] The constants are given in Table IV. The single conductances are computed on the basis of Franklin and Cady's[14] transference data which give $\Lambda\ (NO_3)/\Lambda(K^+) = 1.006$ at −33°.

TABLE IV

CONSTANTS FOR THE ALKALI METAL NITRATES IN AMMONIA AT −40°

Salt	Λ_0	$K \times 10^4$	$a \times 10^8$	Ion	Λ_0 (ion)	$r^* \times 10^8$
$LiNO_3$	277	36.5	5.04	Li^+	112	0.28
$NaNO_3$	295.1	28.84	4.46	Na^+	130.1	0.41
KNO_3	329.0	14.71	3.57	K^+	164.0	0.82
$RbNO_3$	341.8	11.41	3.34	Rb^+	176.8	1.20
$CsNO_3$	333.5	9.66	3.21	Cs^+	168.5	1.48

For this series the variation of the dissociation constant is perfectly regular; the salts become weaker electrolytes (K and hence a decrease) as the atomic number of the cation increases. This indicates a decreasing solvation as the size of the external electron ring in the alkali metal ion

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(12) Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931.

(13) Monosson and Pleskow, *Z. physik. Chem.*, **A156**, 176 (1931).

(14) Franklin and Cady, THIS JOURNAL, **26**, 499 (1904).

increases, that is, as the external field due to the single excess charge in the nucleus of the ion becomes progressively weaker and consequently exerts less force on the solvent dipoles. This is also shown by the ion conductances, which increase regularly from lithium to rubidium. The reversal from rubidium to cesium does not appear surprising in view of the fact that the radius r^* of the external electron shell in the alkali ions, as calculated by Pauling,[15] changes but little in going from rubidium to cesium. The solvation is apparently about the same for the two ions, and the net sphere equivalent to the cesium ion plus solvate is a little larger than that for rubidium. No values for radii calculated from Λ_0 are given, because the equations of motion of a charged particle in a dipole liquid are not yet known with sufficient certainty.[16]

In the light of the foregoing discussion, it appears that the application of Coulomb's law to the (binary) ionic equilibrium in solvents of widely varying dielectric constant accounts for the change of dissociation constant with dielectric constant within the limit of experimental error. The function connecting K and D involves only a single disposable parameter a, of the nature of a distance. The value of this parameter depends on the constituent ions of the electrolyte, and, for a given electrolyte, on the properties of the solvent medium. For mixtures of dioxane and water a has a constant value. The results of the present investigation therefore lend support to the view that the so-called mass action effect is primarily controlled by Coulomb forces between the ions.

Summary

1. Bjerrum's ion-pair model for undissociated molecules of electrolytes in solution gives a physical picture which agrees well with observed conductance data.

2. The dissociation constant of a binary electrolyte is a function of the dielectric constant of the solvent, and can be evaluated numerically if the value of a parameter a is given.

3. The parameter a depends on the atomic properties of solute and solvent, and is roughly an additive function of the constituent ions.

PROVIDENCE, RHODE ISLAND

RECEIVED OCTOBER 1, 1932
PUBLISHED MARCH 7, 1933

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(15) Pauling, *Proc. Roy. Soc.* (London), **A114**, 181 (1927).

(16) M. Born, *Z. Physik*, **1**, 221 (1920)· H. Schmick, *ibid.*, **24**, 56 (1924).