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THE ACTIVITY OF STRONG ELECTROLYTES. IV. THE APPLICATION OF THE DEBYE-HÜCKEL EQUATION TO ALCOHOLIC SOLUTIONS

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Recently Hückel[1] has published an extension of the Debye theory of the activity of strong electrolytes which, by taking into account not only the magnitudes of the electric charges and the diameters of the ions but also the changing dielectric constant with changing electrolyte concentration, yields an equation that is applicable even in concentrated solutions and goes far toward solving the problems of the activity of strong electrolytes. One very practical advantage of such an equation is that it can be used to extrapolate to zero concentration independently of measurements on very dilute solutions and, therefore, can be applied where such measurements are inaccurate or entirely lacking.

Hückel has tested the equation with electromotive-force measurements on hydrogen, lithium and sodium chlorides in aqueous solution and found agreement with the experimental measurements within a few per cent., even up to 5 *M* concentrations. So valuable an equation warrants testing in every possible manner. The present paper applies the equation to solutions of hydrogen chloride in alcohol and in alcohol-water mixtures. It comprises the most exacting test yet made of the Debye theory, for the change in the activity coefficient is much greater in alcoholic than in aqueous solutions. In each solvent the agreement with the experimental measurements is within the error of the latter and much better than should be expected from the approximations involved in the derivation of the equation. The extended application also gives evidence bearing on the question of the nature of the action between the ions and the solvent.

The Debye-Hückel Equation

Hückel develops the general equation for any number of ions of any charge, but for simplicity the formulas of this paper are limited to the special case of a single uni-univalent electrolyte. The constants are given for 25° but the variation with temperature is indicated by inserting the proper power of $T/298.1$. The numerical values of the constants used in this paper, which differ slightly from those of Debye and Hückel, are based on the values of the universal constants used in the "International Critical Tables."

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[1] Hückel, *Physik. Z.*, **26**, 93 (1925).

The equation is[2]

$$-\log f = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c \qquad (1)$$

in which f is the ratio of the mean activity of the ions to the mole fraction of either ion ($a_{\pm}/N_{\pm}$) with the convention that the activity approaches the mole fraction at zero concentration, or 0.01 $a_{\pm}/N_{\pm}$ with the convention that the activity approaches the mole percentage at zero concentration, and c is the concentration of the salt in moles per liter, so that $2c$ is the sum of the concentrations of the ions.

For many practical purposes it is more convenient to work with γ or $a_{\pm}/m$. Since $\log N_{\pm} = \log m - \log (1 + 0.002\ mw_1) + \log 0.001\ w_1$, then

$$-\log \gamma = -\log f + \log (1 + 0.002\ mw_1) = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c + \log (1 + 0.002\ mw_1) \qquad (2)$$

in which w_1 is the molecular weight, or average molecular weight, of the solvent. The term $\log 0.001\ w_1$ is eliminated through the conventions that both f and γ approach unity at zero concentration.

$$A = \frac{249.4}{D_0^{3/2}} \times (298.1/T)^{3/2} \qquad (3)$$

$$\alpha = \frac{2.060 \times 10^8\ a}{D_0^{1/2}} \times (298.1/T)^{1/2} \qquad (4)$$

in which D_0 is the dielectric constant of the solvent, and a is the average diameter of the ions (distance of nearest approach of two ion centers) measured in centimeters.

To derive B, Hückel assumes that the dielectric constant of the solution is given by the equation $D = D_0 - \delta 2c$, in which δ is a constant. With this assumption B is not truly a constant, but a rather complicated function of the concentration, whose change, however, is small except when c itself is so small that the effect of the term $B2c$ on the activity coefficient is negligible. For example, calculating δ from B for 1 M hydrochloric acid, the variation in f or γ due to the change in B is never more than 1% up to 1.5 M. For most salts the variation is much smaller. For the purposes of the present paper, it is sufficient to know that B varies with δ/aD_0^2.

Aqueous Hydrochloric Acid

Since Hückel determined the constants for hydrochloric acid from the not very accurate measurements of Ellis, it seems worth while to recalculate them from the more accurate measurements with silver chloride electrodes, and to determine how accurately the formula may be made to fit the experimental data if its application is limited to concentrations not greater than 1 M. The values of the constants were determined from the values of

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[2] The constants A and α equal the corresponding constants of my earlier paper [THIS JOURNAL, **47**, 684 (1925)] multiplied by $1/\sqrt{2}$; B has an entirely different significance.

log f'/f'' for the solution pairs 0.05–0.5 and 0.1–1.0 M, these values being taken from the smooth curve of my previous paper.[3] The dielectric constant of water at 25° was taken as 78.8 from the equation of Drude, and the concentrations in moles per liter were determined from the densities to be published in the "International Critical Tables."

The use of Equation 1 or 2 implies the assumption that there is no chemical action between the ions and the water. Constants were also computed on the assumption that the hydrogen ion reacts with one molecule of water in a reaction so nearly complete that the concentration of the unhydrated ion is negligibly small compared to that of the hydrated ion. There does appear to be more direct evidence for the hydration of the hydrogen ion than for that of other ions, and some that only one molecule of water reacts.[4] This computation also serves to illustrate the magnitude of the effect of hydration on the activity coefficient. Such a reaction reduces the total number of moles. Moreover, Equation 1 applies to the activity coefficient of the hydrated ions, while γ as determined from the electromotive force is the ratio of the activity of the anhydrous ions to the molality of the sum of anhydrous and hydrated. The equation is

$$-\log \gamma = \frac{A\sqrt{2c}}{1 + \alpha\sqrt{2c}} - B2c + \log\,(1 + 0.001\,mw_1) + 0.5 \log a_w \qquad (5)$$

The activity of the water (a_w) was determined by graphic integration from that of the acid.

The values found for the constants are given in Table I. Table II contains the values of γ calculated by Equation 2 and Equation 5, as well as those derived in the previous paper. It also contains the values of E_0 determined by each of the first two series of γ values and the smoothed values of the electromotive force by use of the equation

$$E_0 = E + 0.1183 \log \gamma m = E_0' + 0.1183 \log \gamma \qquad (6)$$

Equation 2 gives values of γ which up to 1 M differ from those previously derived by a nearly constant amount of 0.4%, or 0.2 mv. If E_0 be given the value 0.2224 volt instead of 0.2226, the agreement of the actual experimental measurements with the theoretical equation is about the same as with the earlier smooth curve between 0.01 and 1 M. The average deviation of Linhart's measurements at lower concentrations is 0.1 mv. instead of zero, and the average deviation of γ calculated from the freezing-point measurements of Randall and Vanselow becomes +0.2% instead of —0.1%. Equation 5 also fits the experimental results between 0.01 and 1.0 M almost exactly if E_0 be changed to 0.2223 volt. This increases the average deviation of Linhart's measurements on dilute solutions to 0.2 mv., and the average deviation of the γ values from freezing points to 0.3%.

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[3] Scatchard, THIS JOURNAL, **47**, 641 (1925).

[4] For example, see Goldschmidt, *Z. physik. Chem.*, **60**, 728 (1907); Fajans, *Naturwissenschaften*, **9**, 734 (1921); Fajans and Joost, *Z. Physik*, **23**, 1 (1924).

TABLE I

CONSTANTS FOR HYDROCHLORIC ACID

Solvent	A	α	$a \times 10^8$	B	2δ
Water (Eq. 2)	0.357	0.940	4.05	0.0713	26.26
Water (Eq. 5)	.357	.950	4.09	.0627	23.10
50 mole % alc.	1.105	1.374	4.06	.129	13.16
Alcohol	1.973	1.830	4.46	.023	1.73

TABLE II

MEAN ACTIVITY COEFFICIENTS OF AQUEOUS HYDROCHLORIC ACID

Molality	γ Eq. 2	γ Eq. 5	γ Smooth curve	E_0 Eq. 2	E_0 Eq. 5
0.001	0.966	0.966	0.966	0.22258	0.22257
.002	.953	.953	.954	55	53
.005	.930	.929	.932	49	46
.01	.906	.905	.910	37	33
.02	.877	.876	.881	36	31
.05	.832	.831	.836	37	30
.1	.797	.795	.801	36	27
.2	.768	.766	.774	19	07
.3	.758	.756	.763	26	12
.4	.756	.754	.760	37	22
.5	.760	.757	.763	38	21
.6	.767	.764	.770	39	21
.75	.781	.778	.783	50	31
1.0	.814	.811	.817	37	17
1.5	.897	.896	.905	11	07

Since the theoretical equation involves approximations such that an agreement better than a few tenths of a per cent. is not to be expected, and since neither equation holds so exactly at 1.5 M, it seems to me preferable to retain the values of E_0 and γ previously derived and to attribute the error of 0.4–0.6% to the theory, at least until further work on other substances may indicate a greater precision of the theoretical equations.

It will be noted that the assumption of ionic hydration involves a change of 12% in B and only 1% in α. It would be possible to follow Bjerrum[5] and account for all of the second term by assuming that the ions of hydrochloric acid combine with about 8 molecules of water. Measurements on aqueous hydrochloric acid alone appear to offer no evidence as to whether this term should be attributed to change of dielectric constant or to hydration. Evidence will be presented in a later section that one, but only one, molecule of water enters into the reaction.

Alcoholic Solutions with Varying Acid Concentration

To test the equation with the measurements on alcoholic solutions, E_0' computed from the measurements of Harned and Fleysher[6] at 25° on the

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[5] Bjerrum, *Z. anorg. Chem.*, **109**, 275 (1920).

[6] Harned and Fleysher, THIS JOURNAL, **47**, 82 (1925).

cell Pt, H_2 | HCl, AgCl | Ag by the equation

$$E_0' = E + 0.1183 \log m \tag{7}$$

was plotted against $\sqrt{2c}$ and a smooth curve drawn through the points. From this curve $\log f'/f''$ was determined for the solution pairs $\sqrt{2c} = 0.4$ and 1.2, 1.2 and 2.2 in alcohol; and 0.4 and 1.0, 1.0 and 2.0 for 50 mole % of alcohol. Since there are no density determinations available on alcoholic hydrochloric acid solutions, the concentrations in moles per liter were calculated by the approximate equation

$$c = \frac{m}{v_0 + km} \tag{8}$$

in which v_0 is the specific volume of the solvent, with $k = 0.02$. For aqueous hydrochloric acid, k varies from 0.0182 to 0.0191 between 0.5 and 1.5 *M*. The error in concentration is probably never greater than a few tenths of a per cent. and diminishes rapidly with decreasing concentration.

The dielectric constants of alcohol and of alcohol-water mixtures have been measured by Nernst[7] at about 20°. The values at 25° were calculated by assuming that through this small temperature range the dielectric constant is a linear function of the temperature, and that the fractional change per degree, which is 0.002 for water and 0.004 for alcohol, is a linear function of the mole fraction. The dielectric constants at 25° were plotted against the mole fraction and a smooth curve was drawn through them for interpolation.

The values of the constants for the Debye-Hückel equation are given in Table I. In 50 mole % alcohol the average deviation of the experimental points from the theoretical equation is 0.3 mv. between 0.01 and 2.5 *M*. Below 0.01 *M* there is a deviation increasing from 1 to 9.5 mv., probably to be ascribed to the difficulties of e.m.f. measurements in very dilute solutions. Since Harned and Fleysher found the average deviation of their points from a smooth curve to be "less than ±0.4 mv." the equation obviously fits the experimental data within the error of the latter. It is impossible to calculate the constants assuming a hydrated hydrogen ion, for there are no means of calculating the activity of the water in these solutions.

In pure alcohol the average deviation is 0.5 mv. between 0.01 and 1.5 *M*. Harned and Fleysher write, "At concentrations up to 0.2 *M* . . . . the mean variation is less than ±0.5 mv., but for solutions higher than this the consistency is not so great." The point at 3.6 *M* lies 6.4 mv. off the curve, and the deviations below 0.01 *M* are about the same as in 50 mole % alcohol.

Danner[8] has measured the electromotive force at 25° of the cell Pt, H_2 | HCl, HgCl | Hg in alcohol. Harned and Fleysher note that his results

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[7] Nernst, *Z. physik. Chem.*, **14**, 622 (1894).

[8] Danner, This Journal, **44**, 2832 (1922).

in the range 0.01–0.1 M agree with theirs if the difference between the silver chloride and calomel electrodes be taken as 0.0350 volt, but that his two more concentrated solutions appear to contain small amounts of water. The measurements of Harned and Fleysher in aqueous solution agree with those of Linhart, Noyes and Ellis and Scatchard. Therefore the difference between their silver chloride electrodes and the calomel electrode should be 0.0466 volt, which should be independent of the solvent, since the reaction of the cell Ag | AgCl, HCl, HgCl | Hg is Ag + HgCl(sol.) = Hg + AgCl (sol.). This leaves a discrepancy between the two series of measurements of 11.6 mv., decreasing above 0.1 M. From a careful plot of the E_0 values of a later section against the mole fraction of water, or better against its square root, it was found that in nearly pure alcohol 0.1 mole % of water corresponds to a change in E_0 of 11 or 12 mv. instead of 3 mv. as estimated by Harned and Fleysher. Danner used the most anhydrous alcohol he could prepare; Harned and Fleysher believed that theirs contained less than 0.1 mole % of water. The discrepancies may be fully accounted for if Danner's alcohol be considered 100%,[8a] except above 0.1 M where some water was formed by the action of the acid and alcohol, and Harned and Fleysher's be assumed to be about 99.9 mole %. It is possible that the deviations of their experimental points from the theory below 0.01 M are due to a slightly lower water content.

To extrapolate to zero concentration Danner assumed that in dilute solutions γ approaches the conductance ratio, Λ/Λ_0; Harned and Fleysher assumed, by analogy to aqueous solutions, that $1 - \gamma = 3(1 - \Lambda/\Lambda_0)/2$. The values of E_0 for the cell Pt, H_2 | HCl, AgCl | Ag may be calculated from the data given by the authors. Danner's results give —0.0558 volt, or —0.0442 volt corrected for the difference between the two series. Harned and Fleysher's give —0.0552 volt. The Debye-Hückel theory gives —0.0490 volt, which is very near the mean of the other two. In 50 mole % alcohol Harned and Fleysher, through an erroneous interpretation of the Debye theory, extrapolated by assuming that log γ is a linear function of $1/D_0$ and found for E_0 0.1479 volt, compared with 0.1530 from the theory.

The values for a, the mean diameter of the ions, in water, in 50 mole % alcohol, and in alcohol are found to be 4.05, 4.06 and 4.46 $\times 10^{-8}$. The almost exact agreement of the first two should be regarded as a coincidence, and the 10% difference of the third is as small as could be expected. This difference could have been eliminated, however, without greatly changing the agreement with experiment, by subtracting 2 mv. from the value of E_0.

The values for 2δ, or the change in dielectric constant on the addition of one mole of acid to a liter of solution, are 26.3, 13.2 and 2.7, neglecting the influence of hydration on B. But hydration should decrease the first

[8a] Probably it contained a few hundredths of a per cent. of water. The values given apply to this solution rather than to 100.00% alcohol.

two by about 3.0. Moreover, δ is too complicated a function for its behavior to be predicted by theory more than approximately. For one-component solvents it should decrease more rapidly than the dielectric constant itself. In mixtures it should be larger than the value calculated from the quantity of water and alcohol in a liter, because the water is attracted to the vicinity of the ions where the effect is largest. Both of these qualitative predictions are fulfilled in this case.

Solutions of Various Concentrations of Alcohol

Harned and Fleysher also measured cells containing 0.1 M hydrochloric acid in 25, 75, 85, 90 and 95 mole % of alcohol, and cells containing 0.01 M acid in the first two. It is possible to calculate E_0 from the single measurements by interpolating the values for the constants. Those of A follow from those of D_0 alone. Those of α were calculated assuming that a is equal to 4.05×10^{-8} throughout. For the interpolation of B, B/D_0^2 was plotted against the mole fraction, which gave a curve concave upwards, and against weight fraction, which gave one convex upwards. The value used was the mean of the readings from the two curves, which never differed greatly from each other.[9]

TABLE III

HYDROCHLORIC ACID IN ALCOHOL-WATER MIXTURES

N_a	%	w_1	v_0	D_0	A	α	B	E_0	E_N
0.00	0.0	18.02	1.0016	78.8	0.357	0.940	0.0713	0.2226	0.2528
.25	46.0	21.25	1.0886	49.6	.715	1.185	.12	.1882	.2269
.50	71.9	25.90	1.1643	37.1	1.105	1.374	.129	.1530	.2019
.75	88.5	33.15	1.2231	30.2	1.505	1.518	.09	.1004	.1614
.85	93.5	37.33	1.2439	27.9	1.695	1.580	.07	.0687	.1364
.90	95.8	39.85	1.2540	26.9	1.790	1.609	.06	.0485	.1195
.95	98.0	42.72	1.2641	26.0	1.884	1.636	.04	.0198	.0944
.999	99.94	46.04	1.2738	25.2	1.973	1.830	.023	− .0490	.0295

N_a	γ_0	f_0	γ 0.01 M	γ 0.01 M	γ 1.0 M
0.00	1.00	1.00	0.906	0.797	0.814
.25.	1.95	1.66	.829	.656	.670
.50	3.88	2.69	.760	.535	.479
.75	10.8	5.92	.692	.432	.295
.85	20.0	9.64	.663	.391	.234
.90	29.6	13.4	.650	.372	.205
.95	51.8	21.8	.636	.353	.177
.999	198	93.8	.629	.351	.177

Table III contains the values of the constants used, the resulting values of E_0, and the values of γ for 0.01, 0.1 and 1.0 M solutions to illustrate the change of this quantity with changing composition of the solvent.

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[9] This double-graph method lessens the mechanical error of interpolating from three points which do not lie on a straight line and so makes the results easier to duplicate, but it does not, of course, ensure that they are the real values of the function represented.

The values for 99.9% alcohol are those of Table I in which $a \times 10^8 = 4.46$. The E_0 values fall on a smooth curve from which E_0 may be interpolated for any other concentration. In the 25 and 75 mole % solutions, where E_0 was calculated from two different measurements, the difference is 0.5 mv. in each case, or within the error to be expected in the experimental measurements. The averages are given in the table.

The preceding computations have been based on the convention that in each solvent the activity coefficient approaches unity at zero concentration. For the comparison of solutions in different solvents this convention must be dropped. A simple substitute is the retention of the convention for water solutions and the calculation of the activity in an ideally dilute solution in any other solvent relative to that in a solution of the same molality in water. This quantity, which we will call γ_0, may be defined by the equation

$$0.1183 \log \gamma_0 = E_{0 \text{ in water}} - E_0 \qquad (9)$$

To compare two solutions of finite concentration in different solvents the product $\gamma_0 \times \gamma$ should be used. The two are kept separate because γ may be determined more accurately than γ_0.

By the use of the equations and methods of interpolation given above and of the values given in Table III, it is possible to compute the mean activity of the ions of hydrochloric acid, and therefore other thermodynamic properties, in any mixture of water, alcohol and hydrogen chloride. For solutions less than 1 M in acid the accuracy of these calculated values should be about as great as that of the measurements in alcoholic solutions. Up to 2 M they should serve as useful approximations.

For theoretical purposes interest attaches to quantities relative to unit number of moles rather than to unit weight. We have used f as the ratio of the activity to the mole percentage with the convention that f approaches unity at zero concentration, and we will define f_0 as the activity coefficient of an ideally dilute solution with the convention that f_0 is unity for aqueous solutions. Similarly, we will let E_N correspond to E_0. These quantities are more precisely defined by the equations

$$E_N = E + 0.1183 \log 0.01\, N_{\pm} f = E_0 + 0.1183 \log 0.1\, w_1 \qquad (10)$$

$$0.1183 \log f_0 = E_{N \text{ in water}} - E_N \qquad (11)$$

Variation of Activity with Changing Composition of Solvent

Before attempting the important problem of explaining theoretically the variation of f_0 with changing composition of the solvent, it will be well to consider the assumptions already made and the further ones necessary for this treatment.

The Debye theory assumes that, in solutions in any given solvent, the activity of an ion is proportional to its mole fraction, except for the effect of the electric charges, through the concentration range in which the theory is applied (Henry's law). For changes from one solvent to another we will assume that for all the solvents considered the factor of proportionality is the same. A generalization of this to all solvents and concentrations leads to the factor unity (Raoult's law). It is highly improbable that this assumption is true generally; it is not for any neutral molecule. The case in which it might be expected to hold best is that of small ions in solvents of high dielectric constant, for there the solvent molecules are attracted so strongly to the ions that the particles may be considered as aggregates of solvent molecules with the ion as core. This is exactly the case of monatomic ions in water or alcohol.

The Debye theory assumes that the energy of the electric charge may be considered to be distributed on the surface of a sphere of radius b and, further, that b is equal to a, the mean diameter effective in collisions. If the molecules of the solvent are polarized, the energy of the charge must be distributed over a shell of considerable thickness. The sphere whose surface best represents this distribution must be larger than that influencing collisions but of the same order of magnitude. In the case treated by Debye and Hückel, in which the size of the sphere has only a small effect, it is permissible to make the simplifying assumption that b equals a. In the present case the whole effect is due to the size of the ion, and we must discard this much of the assumption. We will make the tentative assumption that b has the same magnitude in all the solvents.

It is assumed that, at least for the alkali and chloride ions, there is no chemical reaction with the solvent—that there is no hydration in the generally accepted sense. For the moment we will make the same assumption regarding the hydrogen ion. It is also assumed that the electrolytes to which the equation applies are completely ionized.

In counting the total number of molecules to compute the mole fraction, it is assumed that the solvent exists entirely as single molecules, or that there is no association in the chemical sense. If there is association but to the same extent in all the solvents there will be no effect on the activity of the ions. Even if the water exists entirely as dihydrol and the alcohol entirely as single molecules, the difference in the E_N values, which is 0.234 volt, will be increased only 0.036 volt. So association cannot change the order of magnitude of the effect, although it may prevent exact agreement of our calculations.

With these assumptions the work, in volt-faradays, of transferring a mole of uni-univalent electrolyte from an ideally dilute solution in a solvent of dielectric constant D_0' to one of the same mole fraction in a solvent of dielectric constant D_0'' is

$$E_N' - E_N'' = \frac{14.322 \times 10^{-8} (D_0' - D_0'')}{bD_0' D_0''} \qquad (12)$$

In Fig. 1 the circles are the values of E_N from Table III plotted against the mole fraction of alcohol (N_a). The full line AB is the smooth curve through them. The broken line AB is the curve of Equation 12 with $b = 1.65 \times 10^{-8}$ to fit the end-points. Evidently the shape of the two curves is entirely different, and the assumptions given will not account for the phenomenon.

The shape of the curve might be accounted for by assuming that $10^8 \times b$ is equal to about 4 in solutions less than 50 mole % alcohol and then decreases more and more rapidly to 2 in alcohol. It would then be necessary to explain why the size of the ion varies, and no ready explanation offers. Although this does not eliminate variation in b as the true explanation, it does prevent its being a helpful one.

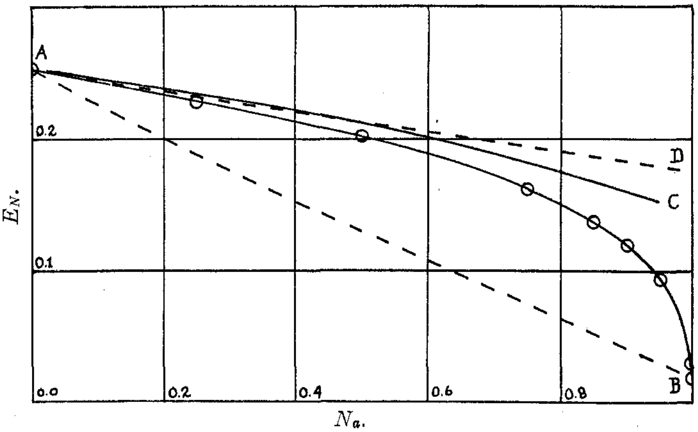

Fig. 1.—Hydrochloric acid in alcohol-water mixtures.

If the hydrogen ion exists in solution not as H^+ but as H_3O^+, the activity of the water must be taken into account. When the reaction is practically complete, the equation of f_0 for H_3O^+ and Cl^- is

$$0.1183 \log f_0 = E_{N\text{ for water}} - E_N + 0.05915 \log a_w \qquad (13)$$

To calculate a_w, the smoothed values of Lewis[10] from the data of Wrewsky[11] were extrapolated to 25°. The values so obtained are only approximate, particularly in solutions rich in alcohol, where the relative error in vapor pressure (which becomes absolute in the logarithm) is large. The full line AC is the curve through the values of $E_N - 0.05915 \log a_w$. Since the assumption of complete hydration is absurd in 100% alcohol, and the curve would there go to infinity, it is not carried beyond 95 mole % alcohol.

The broken line AD is the curve of Equation 12 with $10^8 \times b \doteq 5$, to coincide with AC at 0 and 50 mole % alcohol. At 95 mole % the difference between the two curves is about 30 mv. This difference is somewhat larger than the apparent experimental error in the determination of the curve AC,

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[10] Lewis, *J. Ind. Eng. Chem.*, **12**, 496 (1920).

[11] Wrewsky, *Z. physik. Chem.*, **81**, 14 (1912).

but it is small considering the very simple assumptions made in calculating the theoretical values. For example, it might be accounted for if, in addition to the electrical effects, the activity coefficient of the H_3O^+ ion varies as does that of water, or if $b \times 10^8$ varies from 5 to 4 between 50 and 95 mole % alcohol.

The evidence against the formation of a still higher hydrate is much stronger. A reaction with two molecules of water would require a very large value of b, one with more than two would require negative values. It appears safest to hold merely that the assumption of the existence of the ion H_3O^+ fits the experimental data to a better approximation than the assumption of no chemical action, and much better than the assumption of a higher hydrate.

Alcoholic Solutions of Salts

If the shape of the E_N curve for hydrochloric acid is due to the formation of H_3O^+ the effect should be absent from salt solutions. This can be tested by two sets of measurements—the electromotive force of lithium chloride concentration cells, and the solubility of sodium chloride.

Pearce and Hart[12] have measured the electromotive force at 25° of the cell Ag | AgCl, LiCl (0.1 M, in water) | Li, Hg | LiCl (m, in alcohol), AgCl | Ag through the range 0.006–0.6 M in methyl and ethyl alcohols. The concentrations in moles per liter were calculated by Equation 8 with $k = 0.02$. For aqueous lithium chloride k varies from 0.0180 to 0.0189 from 0.5 to 3.0 M. The constants calculated for the Debye-Hückel equation are given in Table IV. Excluding the points of 0.006 and 0.06 M in each series, since they do not lie on a smooth curve through the other points, the average difference between the observed and calculated values of E is 0.6 mv. in ethyl alcohol and 0.9 mv. in methyl alcohol, both probably within the experimental error. Table IV also contains the constants for aqueous lithium chloride determined by Hückel from the data of MacInnes and Beattie.

TABLE IV

CONSTANTS FOR LITHIUM CHLORIDE

Solvent	D_0	A	α	B	$a \times 10^8$	$b \times 10^8$	E_0	E_N
Water	78.8	0.357	0.84	0.0698	3.62	..	−0.1305	−0.1003
Methyl alcohol	30.2	1.505	1.62	.09	4.32	3.66	− .2388	− .1803
Ethyl alcohol	25.2	1.973	2.36	.023	5.73	4.56	− .2636	− .1851

The values of $a \times 10^8$ are 3.62 in water, 4.32 in methyl alcohol and 5.73 in ethyl alcohol; those of $b \times 10^8$ are 3.66 from the difference in E for water and methyl alcohol, and 4.56 for water and ethyl alcohol. In each case the b value is intermediate between the a values for the two solutions, and all the a and b values may be considered equal within the error of their de-

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[12] Pearce and Hart, THIS JOURNAL, 44, 2411 (1922).

termination, so that the change in E_N for lithium chloride is accounted for within the experimental error by the electrical work. Although lithium chloride is generally considered highly hydrated in solution, the reaction with even one molecule of water would require very large values of b, and with more than one would require negative values.

Danner[8] has measured the electromotive force at 25° of the cell Na, Hg (2-phase amalg.) | NaCl (satd. in water), HgCl | Hg, which must be independent of the solvent for saturated solutions. Hückel has calculated the constants for aqueous sodium chloride from the measurements of Allmand and Polack on concentrated solutions, and found $\alpha = 0.545$, $B = 0.0445$, $a = 2.35 \times 10^{-8}$. The average difference between the values of γ calculated with these constants and those which I computed from freezing-point and thermal data[2] is 1%; the maximum difference is 3.6% at 0.5 M.

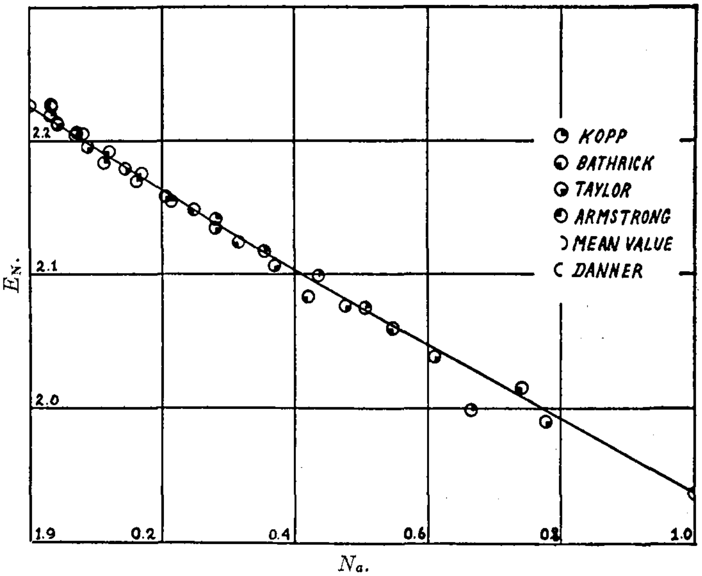

Fig. 2.—Sodium chloride in alcohol-water mixtures.

If it is assumed that a is the same in alcohol and in alcohol-water mixtures as in water, and that the ratio of B for sodium chloride to B for hydrochloric acid is the same in all mixtures of alcohol and water, it is possible to calculate E_N from the solubility of sodium chloride in various mixtures. Again the concentrations in moles per liter were computed by Equation 8 with $k = 0.02$. For aqueous sodium chloride k varies from 0.018 in 0.5 M to 0.021 in 5.0 M. The effect of errors in the constants or in the density is very small in solutions rich in alcohol, where the concentration is low. It is doubtful whether these errors are ever larger than those of the solubility measurements. In Fig. 2 are plotted the values of E_N calculated from the solubility measurements of Danner in absolute alcohol, and of Kopp, Bathrick, Taylor and Armstrong in alcohol-water mixtures.[13] For the data of Bathrick and of Taylor, the solubility at 25° was computed by straight-line extrapolation from measurements at 30° and 40°. The curve is that of Equation 12 with $b \times 10^8 = 1.31$; this value was chosen to fit the end-points. The agreement is so very good that it seems advisable to point out that the curve is entirely independent of the measurements on mixtures, but is determined by the measurements in water and alcohol and the dielectric constants of the mixtures.

The change in E_N for sodium chloride is explained quantitatively by the electrical work and there is no possibility of hydration having an important effect. The difference between E_N in water and alcohol is much larger for sodium chloride than for lithium chloride. The reverse should hold if lithium chloride is more hydrated. It will be noted that b for sodium chloride is not much larger than half a, for lithium chloride the two are nearly equal, and for hydrochloric acid, assuming the monohydrate, b is equal to or slightly greater than a. Variation in this direction is in agreement with the picture of polarization of the solvent molecules by the ions.

From the data, equations and interpolation methods given above, it is possible to compute the activity of the ions of sodium chloride in a solution of any concentration in any mixture of alcohol and water. By successive approximations one could calculate the solubility in any solvent of known dielectric constant. The minimum amount of data necessary for the calculation of the solubility of a salt and the activity of its ions by this method is sufficient activity measurements in one solvent to determine the constants of the Debye-Hückel equation and one measurement of the solubility in another solution of quite different dielectric constant. Great care should be taken, however, regarding both solutes and solvents to which the assumptions underlying Equation 12 are applied. It has already been remarked that monatomic ions in aqueous and alcoholic solutions present the most favorable case. The solubility measurements of Walden[14] show that, in general, solubility is not a function of the dielectric constant alone. In any case, however, Equation 12 should give the norm, the deviation from which is the measure of specific effects.

For potassium chloride the vapor-pressure measurements of Lovelace, Frazer and Sease[15] yield the constants $\alpha = 0.570$, $a = 2.47 \times 10^{-8}$, $B = 0.0235$. These, combined with the solubility measurements,[16] give 1.35 ×

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[13] Kopp, *Ann.*, **40**, 206 (1841). Bathrick, *J. Phys. Chem.*, **1**, 160 (1896). Taylor, *ibid.*, **1**, 724 (1897). Armstrong, *Proc. Roy. Soc.*, **79A**, 568 (1907).

[14] Walden, *Z. physik. Chem.*, **55**, 683 (1906).

[15] Lovelace, Frazer and Sease, THIS JOURNAL, **43**, 102 (1921).

[16] Berkeley, *Phil. Trans.*, **203A**, 207 (1904). Armstrong, *Proc. Roy. Soc.*, **73A**, 568 (1907). de Bruyn, *Rec. trav. chim.*, **11**, 156 (1892). Bathrick, *J. Phys. Chem.*, **1**, 160 (1896). Bodländer, *Z. physik. Chem.*, **7**, 316 (1891).

10^{-8} as the value of b. Debye and Mac Aulay[17] found 1.23×10^{-8} from freezing-point measurements on mixed aqueous solutions of sucrose and potassium chloride. The agreement is well within the error of their computation.

The E_N curve for potassium chloride is practically identical with that of sodium chloride. It will be noted that in solution dilute in alcohol where hydration is unimportant, the change in E_N, and therefore in activity, is much more than twice as great for potassium chloride as for hydrochloric acid. Then the increase in activity of the chloride ion cannot equal that of the potassium ion unless there is an actual decrease in the activity of the hydrogen ion. Such a decrease is extremely improbable; in terms of the theory it represents a negative value for b. This also throws some doubt on the validity of the assumption of equal changes in activities for these two ions with changing salt concentration in a single solvent, but there seems to be no direct experimental evidence for or against the assumption in this case.

I take this opportunity to express my gratitude to Professor P. Debye for helpful suggestions and criticism, and to Professor J. A. Beattie for the use of density data before their publication.

Summary

The Debye-Hückel equation for the activity of the ions of strong electrolytes has been tested by comparison with measurements of the e.m.f. of the cell Pt, H_2 | HCl, AgCl | Ag in water, alcohol and 50 mole % alcohol, and is found to fit the data accurately up to at least 1 *M* in each of these solvents. The relative values of the constants for the different solvents also confirm the theory in a striking manner.

Confirmation of the theory is also found in the e.m.f. measurements on lithium chloride solutions in ethyl and methyl alcohols and water, and in the measurements of the solubility of sodium chloride in mixtures of ethyl alcohol and water.

The variation in the activity of the ions in ideally dilute solutions in different solvents is explained in entirety for sodium and lithium chlorides by the difference in electrical energy. For hydrochloric acid this variation indicates the formation of the ion H_3O^+.

It is shown that it is extremely improbable that the change in activity with changing solvent is the same for potassium ion and for chloride ion. It is suggested that the change with changing salt concentration in a single solvent may not be the same for these two ions.

Equations, interpolation methods and data are given which permit the computation of the activity of the ions and other related quantities for hydrochloric acid and sodium chloride in any mixture of alcohol and water.

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[17] Debye and Mac Aulay, *Physik. Z.*, **26**, 22 (1925).