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THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. III. TESTING OF THE THEORY IN ALCOHOLIC SOLVENTS

BY ARTHUR A. NOYES AND WARREN P. BAXTER

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Introduction

Recently there have become available accurate electromotive-force data for concentration cells in which alcohols are used as solvents, and from which the activity coefficients of certain largely ionized solutes in alcoholic solutions can be calculated. This makes it possible to test the inter-ionic attraction theory developed by Milner[1] and by Debye and Hückel,[2] from the new view-point of the effect of the variation of the dielectric constant of the medium. It is the purpose of this article to show to what extent this aspect of the theory is confirmed by the existing data.

In the first article of this series, in which a critical review of the theory was given by A. A. Noyes,[3] the following expression for the activity coefficient or activation[4] of an ion was derived:

$$-ln\ \alpha_A = \frac{Az_A^2\sqrt{\Sigma(cz^2)}}{R\cdot(\kappa T)^{1.5}} \qquad (1)$$

In this expression α_A denotes the activation of any ion A of valence z_A (taken algebraically), R the gas constant, κ the dielectric constant of the solution, and A a product of universal constants whose value is 7.77×10^{15} c.g.s. units when the concentration c is expressed in moles per cc. The quantity cz^2 following the summation sign is to be summed for all the kinds of ions in the solution. Owing to certain simplifying assumptions made in its derivation this form of the equation may be expected to be reasonably accurate only when applied to dilute solutions, certainly not more concentrated than 0.05 N.

Experimental testings of this equation were presented[5] in the early part of 1924 by means of the data then available for fairly dilute aqueous solutions. These tests showed that the equation holds true, at any rate as a first approximation, not only with respect to the predicted functional relations to valence and concentration, but also as to the numerical value of

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[1] Milner, *Phil. Mag.*, **23**, 551 (1912); **25**, 742 (1913).

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Debye, *ibid.*, **24**, 334 (1923). Also *Rec. trav. chim.*, **42**, 597 (1923).

[3] Noyes, THIS JOURNAL, **46**, 1080 (1924).

[4] The term activation will be here used in place of activity coefficient, as was recently proposed by A. A. Noyes.

[5] Debye and Hückel, Ref. 2. Noyes, Ref. 3, p. 1098. See also Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

the coefficient A. Unusually accurate freezing-point determinations in highly dilute aqueous solutions have since been published by Randall and Vanselow,[6] which have made possible the testing of the equation at lower concentrations, where it may be expected to be more nearly exact; and, correspondingly, their data do in fact show an even closer conformity with the theory than those earlier available. Thus Scatchard[7] has recently shown that this is true of their data with hydrochloric acid; and it can readily be shown that the statement applies also to their results with the other two substances, thallous chloride and lead nitrate.[8]

The Electromotive-Force Data Available for Alcoholic Solutions

Danner[9] recently made measurements of the electromotive force of the cells, H_2, HCl (in C_2H_5OH), Hg_2Cl_2 + Hg, and Na (two-phase amalgam), $NaOC_2H_5$ (in C_2H_5OH), H_2, the concentrations being varied from about 0.3 to 0.005 N. Harned and Fleysher[10] have published results on the cell, H_2, HCl (in C_2H_5OH or in $C_2H_5OH.H_2O$), AgCl + Ag, carrying the concentration as low as 0.001 N. Their results in the dilute solutions in pure ethyl alcohol are found to be in excellent agreement with those of Danner when calculated to the same units of concentrations and when allowance is made for the difference in potential of the mercurous and silver chloride electrodes. Pearce and Hart[11] measured cells of the type Ag + AgCl, LiCl (at c in C_2H_5OH or CH_3OH), $LiHg_x$, LiCl (at 0.1 N in H_2O), AgCl + Ag. Previously, Pearce and Mortimer[12] had measured similar cells with water, methyl, ethyl, *n*-propyl, *n*-butyl and *iso*-amyl alcohols; but their results seem to be considerably in error.

None of these cells involves liquid junctions, so that relative activation values can be calculated without complications due to transference phenomena. The electromotive force E of the above cells can, in fact, be simply expressed in terms of the activations α_A and α_B of the two ions by the equation

$$\mathrm{E} = \mathrm{E}^0 - \frac{RT}{\mathrm{F}} \ln (c^2 \alpha_A \alpha_B) \qquad (2)$$

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[6] Randall and Vanselow, This Journal, **46**, 2418 (1924).

[7] Scatchard, *ibid.*, **47**, 641 (1925).

[8] Thus, using the final activation values given by Randall and Vanselow and plotting the corresponding values of the activation function used by Noyes[5] against the square-root of the formal concentration of the salt, the graphs are found to be almost exactly straight lines up to 0.02 N; and the coefficients corresponding to their slopes are 0.268 for hydrochloric acid, 0.291 for thallous chloride, and 0.323 for lead nitrate, while the theoretical one for water at 0° is 0.346. (For such a plot of their data for hydrochloric acid see Fig. 1 of this article.) This is mentioned since the authors themselves considered their results to be unfavorable to the inter-ionic attraction theory.

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

[10] Harned and Fleysher, *ibid.*, **47**, 82 (1925).

[11] Pearce and Hart, *ibid.*, **44**, 2411 (1922).

[12] Pearce and Mortimer, *ibid.*, **40**, 509 (1918).

Substituting the values of $ln()/\log()$ and of R, F and T (taken as 298.1) and writing for $-E^0/0.1183$ a single constant G, this becomes

$$G + \log \sqrt{\alpha_A\ \alpha_B} = \frac{-E}{0.1183} - \log c \qquad (3)$$

The constant is usually determined for a given type of cell by extrapolation to infinite dilution or by making an arbitrary assumption as to the value of $\sqrt{\alpha_A\ \alpha_B}$ at some small concentration; but it will here be treated for the present as an unknown constant.

In Table I are given the values of $G + \log \sqrt{\alpha_A\ \alpha_B}$ calculated by Equation 3 for each of the above-mentioned cells. Since in developing the interionic attraction theory the number of ions per unit volume was considered, the concentrations were first recomputed on the basis of moles per liter of solution. No values have been included for concentrations greater than 0.2 N.

TABLE I

ELECTROMOTIVE FORCES OF CELLS WITH ALCOHOLIC SOLVENTS

Harned and Fleysher. Cell: H_2, HCl at c, AgCl + Ag at 25°

Solvent, C_2H_5OH			Solvent, $C_2H_5OH.H_2O$		
10^3c	E	$G + \log\sqrt{\alpha_A\ \alpha_B}$	10^3c	E	$G + \log\sqrt{\alpha_A\ \alpha_B}$
0.785	+0.3053	+0.524	1.72	0.4765	−1.263
1.570	.2770	.463	4.29	.4346	−1.307
3.926	.2392	.384	8.59	.4028	−1.339
7.85	.2109	.322	17.18	.3730	−1.388
15.70	.1830	.257	42.94	.3333	−1.450
19.55	.1746	.233	85.9	.3037	−1.501
33.21	.1548	.170	171.8	.2733	−1.545
39.26	.1484	.151			
97.6	.1153	.036			
139.9	.1011	.000			
157.0	.0977	− .022			

Danner. Solvent, C_2H_5OH at 25°

Cell: H_2, HCl at c, Hg_2Cl_2 + Hg			Cell: Na in Hg, $NaOC_2H_5$ at c, H_2		
8.86	+0.2406	+0.019	3.02	+1.0543	−6.392
13.9	.2232	− .019	19.30	0.9767	−6.541
27.4	.1957	− .092	42.85	.9459	−6.633
87.7	.1538	− .243	51.6	.9395	−6.654
170.3	.1326	− .352	81.7	.9220	−6.708
			112.0	.9135	−6.771

Pearce and Hart. Cell: Ag + AgCl, LiCl (in CH_3OH or C_2H_5OH), $LiHg_x$, LiCl (0.1 N in H_2O), AgCl + Ag

Solvent, CH_3OH at 25°			Solvent, C_2H_5OH at 25°		
4.96	−0.0439	+1.933	5.00	−0.0224	+2.112
10.68	− .0034	1.942	10.47	+ .0163	2.118
29.73	+ .0396	1.862	30.03	.0593	2.024
49.57	+ .0526	1.750	49.95	.0722	1.911
99.4	+ .0893	1.757	103.1	.1085	1.904

Comparison of the Experimental Activation Values with the Theory

The best way of testing the theory with these data is to plot $G + \log \sqrt{\alpha_A \alpha_B}$ against $\sqrt{c}$, the square root of the concentration, and to compare the curves so obtained, especially their approach to straight lines and their slopes, with those predicted by the theory.

Equation 1 may be written for a uni-univalent solute (for which $z_A = -z_B = 1$ and $\Sigma cz^2 = 2c$), for $T = 298.1°$, and for the concentration of the solute in moles per liter as follows.

$$-\log \sqrt{\alpha_A \alpha_B} = \frac{353 \sqrt{c}}{\kappa^{1.5}} \qquad (4)$$

Using the volumes of the dielectric constant κ derived from plots made of the data in the literature,[13] the special values of the coefficient $353/\kappa^{1.5}$ in Equation 4 are found to be those given in Table II.

TABLE II

THEORETICAL VALUES OF THE NUMERICAL COEFFICIENT FOR UNI-UNIVALENT SOLUTES IN VARIOUS SOLVENTS AT 25°

Solvent	H_2O	$C_2H_5OH.H_2O$	CH_3OH	C_2H_5OH
Dielectric constant κ	78.7	36.5	31.7	24.6
$353/\kappa^{1.5}$	0.505	1.60	1.98	2.90

The large variation in the numerical coefficient is particularly striking; thus it is seen that the value for ethyl alcohol is nearly six times greater than that for water. This difference is due entirely to the dielectric constant of the solvent, and a comparison of the values calculated for the coefficient with the facts therefore affords a good means of testing this aspect of the inter-ionic attraction theory.

In Fig. 1 have been plotted the values of $G + \log \sqrt{\alpha_A \alpha_B}$ given in Table I against those of $\sqrt{c}$ for hydrochloric acid in ethyl alcohol and in the equimolal mixture of ethyl alcohol and water (that is, in $C_2H_5OH.H_2O$, which may be considered a pure solvent), except that from each set of data in the table there has been first subtracted such a numerical constant as would bring $G + \log \sqrt{\alpha_A \alpha_B}$ within the scale of the plot. These constants were, in fact, so chosen that for the more dilute solutions the remainder after the subtraction coincided approximately with the theoretical value of $-\log \sqrt{\alpha_A \alpha_B}$.

In the figure Danner's values are represented by squares and Harned and Fleysher's data by circles. It will be seen that they agree very closely. It is seen also from the curves that, although the extrapolation to zero concentration is a rather long one, the values are consistent with $\log \sqrt{\alpha_A \alpha_B}$ becoming equal to zero at infinite dilution, particularly in the

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[13] The data used were those of Drude [*Ann. Physik*, **59**, 61 (1896)] and Coolidge [*ibid.*, **69**, 134 (1899)] for water; of Drude [*Z. physik. Chem.*, **23**, 267 (1897)] for CH_3OH; of Abegg and Seitz [*ibid.*, **29**, 24 (1899)] and Walden [*ibid.*, **70**, 569 (1910)] for C_2H_5OH; and of Nernst [*ibid.*, **14**, 622 (1894); *Ann. Physik*, **60**, 600 (1897)] for $C_2H_5OH.H_2O$.

case of hydrochloric acid in $C_2H_5OH.H_2O$. It is true, to be sure, that in ethyl alcohol there is a marked curvature upwards in the very dilute solutions; but this is probably due to the difficulty of obtaining accurate electromotive-force measurements at such dilutions (about 0.001 *N*) especially in alcohol. For this reason the last point of Harned and Fleysher's was omitted from the plot. It should be emphasized that, no matter what assumption is made concerning the constant to be subtracted, the form and slope of the curves must remain unchanged.

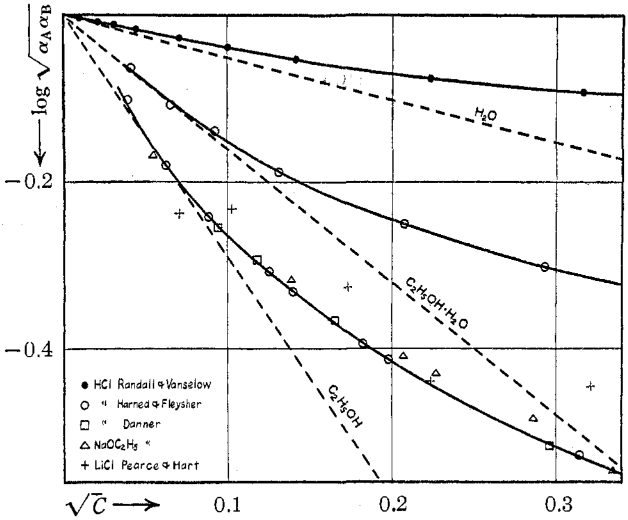

Fig. 1.

For comparison, the accurate activation values for hydrochloric acid in water given by Randall and Vanselow[14] have been included in the figure. This figure is therefore a plot of $\log \sqrt{\alpha_A\ \alpha_B}$ against $\sqrt{c}$ for this acid in three solvents (H_2O, $C_2H_5OH.H_2O$ and C_2H_5OH). The theoretical curves for these solvents are shown by dotted lines. On the same plot are shown Danner's data for sodium ethylate (represented by triangles) and Pearce and Hart's data for lithium chloride in ethyl alcohol (represented by crosses).[15]

Discussion of the Results

It is seen from the figure that the requirement of Equation 1 that different salts of the same valence type have the same values for their activation is well fulfilled for the two very different chemical substances, hydrochloric acid and sodium ethylate in ethyl alcohol solution, a fact already pointed out by Danner.

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[14] Ref. 6, p. 2433.

[15] The values of the constants subtracted from the term $G + \log \sqrt{\alpha_A\ \alpha_B}$ in constructing the curves were, in the order in which the sets of data are given in Table I, as follows: +0.564; —1.200; +0.274; —6.224; +2.350.

A second requirement of Equation 1 to the effect that a plot of log $\sqrt{\alpha_A \alpha_B}$ against $\sqrt{c}$ should show straight-line graphs is fairly well conformed to only in the dilute solutions. This simple expression of the theory is, however, only a limiting equation for infinite dilution, and it can be expected to hold with approximate accuracy only up to small concentrations. In fact, for hydrochloric acid in water the values of Randall and Vanselow show a perfectly straight line up to 0.02 *N*, and similarly for this acid in $C_2H_5OH.H_2O$ the points for the four most dilute solutions lie on a nearly straight line. The graph in pure ethyl alcohol seems to be affected by experimental error at the extreme dilution, as mentioned above.

The extent to which the further requirement of Equation 1, that the numerical coefficients have the values given in the last column of Table II, is shown in Fig. 1 by the degree of correspondence of the slopes of the experimental graphs with the dotted straight lines representing the theoretical slopes, and in Table III by the tabulation side by side of the theoretical coefficients and of those corresponding to the slopes of the experimental graphs of Fig. 1 in the more dilute region (0.005 – 0.02 *N*).

It will be seen from Fig. 1 that the graphs for the organic solvents are similar in form to that for water, that all the graphs deviate from the theoretical slopes for the respective solvents in the direction of larger activation values and by roughly the same fractional angle, and that these deviations become less as the concentration decreases. Table III shows, moreover, that even in the more dilute solutions, the coefficients are only

TABLE III

COMPARISON OF THE THEORETICAL AND EXPERIMENTAL COEFFICIENTS OF THE ACTIVATION-CONCENTRATION FUNCTION

Solvent	Solute	Theoretical coefficients	Experimental coefficients[a]	Ratio of experimental to theoretical coefficients
H_2O	LiCl	0.505	0.35	0.69
	HCl		.38	.75
	KIO_3[b]		.54	1.06
$C_2H_5OH.H_2O$	HCl	1.60	1.26	0.79
CH_3OH	LiCl[c]	1.98	1.3	.66
C_2H_5OH	HCl	2.90	1.88	.65
	LiCl		1.4	.48
	$NaOC_2H_5$		1.77	.61

[a] The experimental coefficients were obtained from the smooth graphs by the slopes of the straight lines drawn between the points on the curves corresponding to 0.005 and 0.02 *N*.

[b] Values for other uni-univalent electrolytes lie between the limits 0.35 and 0.54. See Noyes, Ref. 3, p. 1103.

[c] The data for lithium chloride in methyl alcohol have not been included in Fig. 1. The experimental points, however, coincide roughly with those of lithium chloride in ethyl alcohol, each pair of data showing approximately the same deviation from a smooth curve.

60 to 75% of the theoretical values, but that this percentage is not far from the same for the four solvents.

These results are especially significant in the respect that they prove that the activation function is inversely proportional, at least approximately, to the three-halves power of the dielectric constant as Equation 1 requires, thus substantiating one of the basic features of the inter-ionic attraction theory as to the electrical origin of the effect. They again show, however, as in the case of aqueous solutions, that the actual numerical coefficients have values one-third to one-fourth less than the theoretical values even at concentrations as low as 0.01 *N*, but that through the whole range of concentration the slopes are changing towards the value required by the theory.

Thus far any attempt to estimate absolute activation values in these alcoholic solvents, such as was made by Danner and by Harned and Fleysher, has been deliberately avoided, so as not to introduce any uncertain hypothetical element into the comparison between the experimental values and those required by the theory. It is, however, of some interest to estimate approximately the activation values which prevail in the different solvents. As stated above, the graphs in Fig. 1 were arbitrarily located on the plot in such a way as to make the points for the most dilute solutions approach the theoretical linear graph. The fact that this (theoretical) straight line passing through the origin forms a natural, unbroken continuation of the experimental graphs at higher concentrations affords some reason for thinking that this arbitrary location was not far from the true one. Assuming this to be the case, absolute activation values can be obtained from the experimental graphs in Fig. 1. Values so derived are given in Table IV.

TABLE IV

ESTIMATED ACTIVATION VALUES IN ALCOHOLIC SOLVENTS

Solvent	Solute	0.001	0.002	0.005	0.01	0.02	0.05	0.10
H_2O	Perfect	0.964	0.949	0.921	0.890	0.848	0.771	0.692
	HCl	.973	.962	.940	.916	.884	.840	.809
$C_2H_5OH.H_2O$	Perfect	.890	.848	.771	.692	.594	.439	.312
	HCl	..	.851	.777	.706	.633	.549	.486
CH_3OH	Perfect	.866	.815	.725	.634	.525	.361	.237
	LiCl	..	..	.73	.66	.59	.49	.43
C_2H_5OH	Perfect	.810	.742	.624	.513	.389	.225	.121
	HCl	..	.747	.628	.545	.465	.361	.294
	LiCl	..	..	.62	.55	.49	.40	.34
	$NaOC_2H_5$	..	..	.636	.564	.478	.373	.298

Summary

The accurate electromotive-force data existing in the literature that are suitable for calculating the activations of ionized solutes in alcoholic solvents have been summarized and utilized for this purpose. Activation values so derived for hydrochloric acid in ethyl alcohol and in an equimolal mixture of alcohol and water, for lithium chloride in methyl and ethyl alcohols, and for sodium ethylate in ethyl alcohol have been used to test the inter-ionic attraction theory, assuming that the deviation resulted wholly from this source and not at all from incomplete ionization. The results are shown to be in general agreement with that theory as in the case of aqueous solutions; and especially it is proved (what it was the main object of this research to test) that the logarithm of the activation is, at least approximately, inversely proportional to the three-halves power of the dielectric constant, thus demonstrating the electrical origin of the effect. The actual numerical coefficients in the equation expressing the relation between activation and its parameters are, however, again found to be one-third to one-fourth less than the theoretical ones at 0.01 − 0.02 *N*, but they are changing with decreasing concentration in the direction of the theoretical limiting value.

PASADENA, CALIFORNIA

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THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. IV. THE INFLUENCE OF VARIATION OF DIELECTRIC CONSTANT ON THE LIMITING LAW FOR SMALL CONCENTRATIONS

BY P. DEBYE AND LINUS PAULING

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Introduction

There has recently been derived[1] with the aid of Poisson's equation and the Boltzmann principle an equation representing the mutual electrical effect of ions in solution and expressing the activities of ions and various properties of ionized solutes. The effect arises from the tendency of every ion to attract towards itself ions of unlike sign and repel those of like sign; as a consequence every ion is, owing to its ion-atmosphere, at an average potential P_0, of sign opposite to that of its charge.

It has been shown that for ions of any finite size in a solution of uniform dielectric constant K, the expression for this quantity P_0 reduces for very dilute solutions to the limiting value

$$\mathrm{P}_0 = -\frac{z\,e\,B}{\mathrm{K}} \tag{1}$$

where

$$B^2 = \frac{4\pi\, e^2\, \Sigma(n_i z_i{}^2)}{\mathrm{K}\, kT} \tag{1a}$$

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[1] (a) Debye, "Hand. v. h. XIX Nederlansch Natuur en Geneeskundig Congres," April, **1923.** (b) Debye and Hückel, *Physik. Z.*, **24,** 185 (1923). (c) Debye, *ibid.*, **25,** 97 (1924). For a re-presentation of this theory in somewhat different form see also Noyes, THIS JOURNAL, **46,** 1080 (1924).