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DIRECT MEASUREMENT OF THE PRIMARY, SECONDARY AND TOTAL MEDIUM EFFECTS OF ACETIC ACID

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Introduction

In calculating the "universal constant" in their equation for the activity coefficient of an electrolyte, Debye and Hückel¹ employ $D^{3/2}$, the $3/2$ power of the dielectric constant of the solvent. This satisfactorily describes the variation of activity coefficients with composition of the solvent so long as all activity coefficients are referred to unity at infinite dilution in their respective solvents. It is well known, however, that variation in solvent is also attended by an *absolute* change in the values of the activity coefficients (referring them all to one particular solvent), and that this absolute change is sometimes 10 to 100 times greater than the relative change accounted for by the term $D^{3/2}$ in the Debye-Hückel equation. In this paper these absolute and relative changes in activity coefficients, hereafter referred to as *primary and secondary medium effects*, will be given careful definition, and a number of fundamentally important equations concerning them will be derived. The direct calculation of the primary and total medium effects from e. m. f. data will be illustrated by the interesting case in which the medium itself, being a weak electrolyte in various concentrations, contributes to the ionic strength and complicates the calculations. The data were derived from cells containing hydrochloric acid, water, and acetic acid in various proportions, and from them a new empirical relation between medium effect and concentration of acetic acid will be derived, and compared with the relation discovered by Harned and Owen.²

Theoretical

The full generality and scope of the term medium effect was not apparent from the definition of Harned and Owen. They were concerned with the primary effect only, and, having found it proportional to the molality of acetic acid, referred to the proportionality constant as "the" medium effect. To secure the greatest generality, the emphasis must be removed from the proportionality constant and directed upon the influence of the medium on the activity coefficients, so that the definition may be free from any dependence upon empirical relationships.³

In a solution of an electrolyte in the presence of neutral (non-aqueous)

¹ Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

² Harned and Owen, *THIS JOURNAL*, **52**, 5079 (1930).

³ It will be shown later that the proportionality found by Harned and Owen is probably approximate, even in dilute solution, and it was never considered valid for high concentrations.

molecules, the total medium effect is defined as the logarithm of the ratio of the activity coefficient of the electrolyte in the presence of the neutral molecules and in pure water at the same concentration of electrolyte. The primary medium effect is the limit to which the total effect converges as the electrolyte concentration approaches zero. The secondary medium effect is always given by the difference between the total and primary effects.

Throughout this paper all activity coefficients in any medium are referred to unity at infinite dilution in water, unless written with an asterisk (γ^* , y^* , etc.), in which case they are referred to infinite dilution in the medium itself. Subscripts indicate the electrolyte concentration, but will usually be omitted except in the important case where this is zero. When the medium is pure water, a superscript zero will be used; thus, $\gamma^0 = \gamma_m^0, \gamma_0^0 = 1$, etc. For all concentrations we may write

$$\log \gamma = \log \gamma_0 + \log \gamma^* \quad (1)$$

and, by combining it with the identity

$$\log \gamma^0 \equiv \log \gamma_0^0 + \log \gamma^0 \quad (2)$$

obtain a fundamental relation between total, primary and secondary medium effects, thus

$$\log \gamma/\gamma^0 = \log \gamma_0/\gamma_0^0 + \log \gamma^*/\gamma^0 \quad (3)$$

For convenience the primary effect can be written simply $\log \gamma_0$ because $\gamma_0^0 \equiv 1$. $\log \gamma^*/\gamma^0$ is the secondary effect and in dilute solutions is calculable by

$$\log \gamma^*/\gamma^0 = -\alpha\sqrt{c} + \beta c \quad (4)^4$$

where

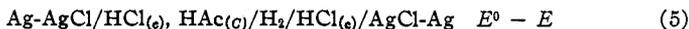
$$\alpha = 352.6 [(1/D)^{3/2} - (1/D^0)^{3/2}] \quad (4a)^5$$

From the definition of total medium effect, it is obvious that its value may depend upon some or all of the following conditions: (1) nature and (2) concentration of the neutral molecules, (3) nature and (4) concentration of the electrolyte, and (5) the concentration units involved in the definitions of activity coefficient. The effect of varying all of these conditions (except the first) will be considered in this paper. Because Harned and Owen² have already discussed the primary medium effect of acetic acid in terms of "water-molality" units, it was decided to study conditions (2) and (5) simultaneously by making measurements and calculations in different units, and comparing the final results by suitable transformation formulas. Harned and Owen used "molality" for moles per kilo of water, but in the present paper, dealing with mixed solvents, the term "water-molality" is coined for this unit so that "molality" can retain its usual meaning—moles per kilo of solvent.

⁴ It will be shown in a later section that equation 4 is quite accurate for concentrations as high as 0.2 normal; cf. Fig. 3.

⁵ Using 0.357 for the universal constant at 25°, and $D^0 = 78.8$; Noyes, THIS JOURNAL, 46, 1098 (1924); Drude, *Ann. Physik*, 59, 61 (1896).

Thus, for the double cell



the concentrations of hydrochloric acid and acetic acid are in moles per liter of solution. Using the letter "y" to represent activity coefficients when the concentrations are expressed in molarities, the e. m. f. is given at 25° by

$$E^0 - E = 0.05915 \log \frac{y_{\text{H}} y_{\text{Cl}} c_{\text{H}} c}{y_{\text{H}}^0 y_{\text{Cl}}^0 c^0 c^0} \quad (6)$$

Making $c = c^0$ to comply with the definition of medium effect, and writing y^2 for $y_{\text{H}} y_{\text{Cl}}$ and y^{02} for $y_{\text{H}}^0 y_{\text{Cl}}^0$, this equation becomes

$$(E^0 - E)/0.05915 - \log c_{\text{H}}/c = 2 \log y/y^0 \quad (7)$$

The term $\log c_{\text{H}}/c$ would, of course, be zero if the acetic acid were replaced by a non-electrolyte, but it will be shown that the ionization of acetic acid is sufficient to make this term amount to 3 to 10% of the total medium effect for the cells in which c is as low as 0.0296. Such values are, fortunately, still small enough to permit certain simplifying approximations in their calculation without introducing appreciable error into the corresponding medium effects. Their calculation will be taken up in some detail.

The ionization constant of acetic acid may be expressed in several concentration units. Thus, if \bar{M} and C are (total) water-molality and molarity of acetic acid, and \bar{m} and c are water-molality and molarity of hydrochloric acid, or the ions indicated by subscripts

$$K = \bar{\gamma}_{\text{A}}^2 \frac{\bar{m}_{\text{H}} \bar{m}_{\text{Ac}}}{\bar{M} - \bar{m}_{\text{Ac}}} = y_{\text{A}}^2 \frac{c_{\text{H}} c_{\text{Ac}}}{C - c_{\text{Ac}}} \quad (8)$$

and

$$C = \frac{\bar{M}(d - wc)}{1 + W\bar{M}}, \quad c = \frac{\bar{m}(d - wc)}{1 + W\bar{M}} \quad (9)$$

where d is the density of the solution, and w and W are the molecular weights in kilograms of hydrochloric and acetic acids, respectively. Writing the total acetic acid concentration for the concentration of un-ionized acetic acid, equation 8 may be combined with equation 9 to give

$$y_{\text{A}}^2 = \bar{\gamma}_{\text{A}}^2 (1 + W\bar{M})/(d - wc) \quad (10)$$

and

$$c_{\text{H}} = c + KC/(c_{\text{H}} y_{\text{A}}^2) \quad (11)$$

Equation 11 yields c_{H} if y_{A}^2 is known; but y_{A}^2 depends upon the medium effect being sought. Fortunately, if the assumption⁶ be made that $\bar{\gamma}_{\text{A}}$ is approximately the same in HCl-HAc and NaCl-HAc solutions of equal ionic strength and HAc concentration, $\bar{\gamma}_{\text{A}}$ (and hence y_{A}) may be estimated

⁶ This assumption can reasonably be expected to give values of $\bar{\gamma}_{\text{A}}$ less than 10 to 15% in error when c is as low as 0.0296, and such an accuracy is more than is required for this lowest concentration studied. For higher concentrations the error that can be tolerated in $\bar{\gamma}_{\text{A}}$ increases very rapidly with the concentration, as a glance at equations 7 and 11 will show.

from the curves and data published by Harned and Owen. Thus, the empirical equation⁷

$$\log \bar{\gamma}_A^2 = -\sqrt{\mu} + (0.75 + 0.055 \bar{M}) \mu \quad (12)$$

allows the calculation of values of $\log \bar{\gamma}_A^2$ differing from the observed experimental values by less than 5% so long as \bar{M} does not exceed 10, or μ exceed 0.3.

Experimental

The acids used were of the highest purity obtainable commercially. The freezing point of the acetic acid indicated 0.1% water by comparison with the tables of Rudorff.⁸ All solutions were made up by weight (corrected for displaced air) in accurately gaged 500-cc. flasks, and every effort was made to have all concentrations known to better than 0.1%. Fresh electrodes were prepared for each cell from silver oxide⁹ and pure chloroplatinic acid.¹⁰ The cells were the simple H-type. Vacuum technique was not employed in filling them because the acetic acid cells and reference cells were prepared and measured identically, and only the *difference* in their e. m. f.'s enters into medium effect calculations. The hydrogen was electrolytic from sodium hydroxide solution. The cells attained equilibrium in two to four hours, after which their potentials were constant within a few hundredths of a millivolt. The recorded potential is the average of readings taken over two or three hours at equilibrium, and corrected to a partial pressure of one atmosphere of hydrogen. To make these corrections, the excess of each solution not required for filling cells was used for vapor pressure measurements in a 200-cc. isoteniscope. Contrary to the results of earlier investigators,¹¹ who found vapor pressures of the order of 30 mm. for 20 to 75% acetic acid solutions, the results of these measurements were in rough agreement with Raoult's law. The general form of the vapor pressure-composition curves can be represented by the data in Table I to better than the nearest mm. of mercury.

Table II records the experimental data and various calculated functions. To express the concentration of acetic acid, its mole fraction in the solvent

⁷ The family of curves A to F in Fig. 1 of Harned and Owen's paper may be represented by straight lines

$$(\log k' - \sqrt{\mu'}) = \log k^0 - 0.75 + (0.055 \bar{M}) \mu'$$

for small ionic strengths. Their slopes were read from a large plot and found to be a complicated function of \bar{M} , which could, however, be simplified to $0.75 + 0.055 \bar{M}$ as a first approximation. Equation 12 is derived by combining this equation with $\log k^0/K = \log k'/k$ (equation 17, Harned and Owen) and $\log K = \log \bar{\gamma}_A^2 + \log k$ (definitional), and remembering that μ' is not very different from μ in HCl-HAc solutions.

⁸ Rudorff, *Ber.*, **3**, 390 (1870).

⁹ Electrode Type 2, Harned, *THIS JOURNAL*, **51**, 416 (1929).

¹⁰ Harned, *ibid.*, **48**, 326 (1926).

¹¹ Kahlbaum, *Z. physik. Chem.*, **13**, 51 (1894); Konowalow, *Wied. Ann.*, **14**, 34 (1881).

TABLE I
VAPOR PRESSURES OF HCl-HAc-H₂O SOLUTIONS AT 25°

Solvent, % HAc.....	Vapor pressures in mm.		
	15%	35%	60%
Molarity of HCl = 1.116	21.5	21.0	19.5
Molarity of HCl = 0.03 to 0.56	22.0	22.0	21.0

(*N*, Column 1) was selected because of the straight line relation exhibited in Fig. 1. In Column 3 are recorded the e. m. f. data for the half-cells comprising equation 5. The first e. m. f. in each section of the table is for a

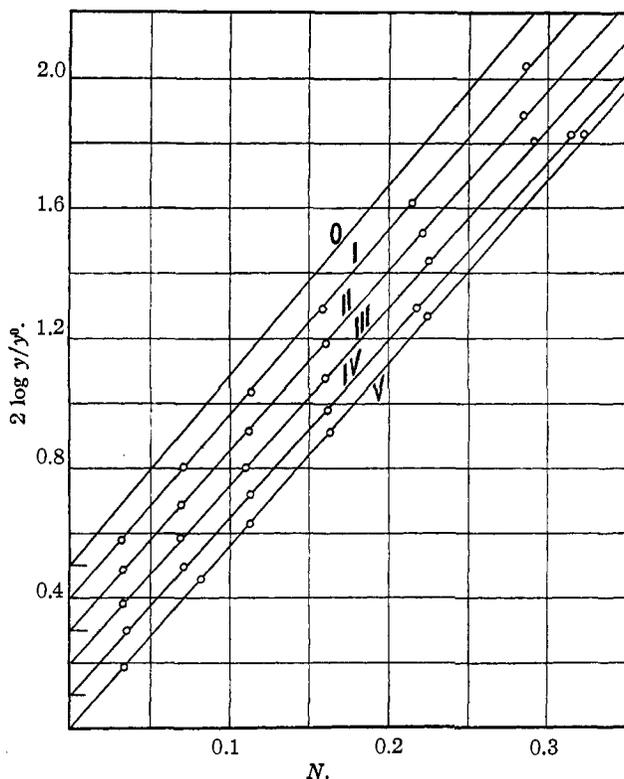


Fig. 1.—Variation of total medium effect with mole fraction of acetic acid. The origins of the five uppermost curves have been shifted. Normality of hydrochloric acid—0; I = 0.0296; II = 0.1112; III = 0.2255; IV = 0.5655; V = 1.1160.

cell containing *c*-molar hydrochloric acid, but no acetic acid. It is therefore E^0 , the e. m. f. of the reference cell, for that particular section. Of course, *c* is constant throughout each section and is identical to c_H for the reference cell heading the section. Each e. m. f. is the average for two similar cells, except the reference values, which are each the average for

four cells. The difference between any two e. m. f.'s averaged is given as δE in millivolts. When four e. m. f.'s are averaged, δE is the greatest difference between any two. The values of $\bar{\gamma}_A^2$ were calculated by equation 12, c_H by equation 11, and $2 \log y/y^0$ by equation 7. The densities, d , are included to make possible the transformation of N and c into other concentration units. The quantities NJ in the last column are given to demonstrate the extent of the validity of the empirical equation 13, the values of J being given in parentheses at the top of each section.

TABLE II
DATA ON CELLS CONTAINING HYDROCHLORIC ACID IN ACETIC ACID-WATER SOLUTIONS
AT 25°

N	d	$\frac{E}{0.05915}$	δE	$\bar{\gamma}_A^2$	c_H	$\text{Log } (c_H/c)$	$2 \text{Log } y/y^0$	NJ
0.0	0.9975	6.9478	0.04	..	0.02960	0.0	0.0	(5.669)
.0319	1.0110	6.7526	.01	0.709	.03081	.0174	.1778	.1808
.0705	1.0244	6.5158	.09	.712	.03177	.0307	.4013	.3997
.1124	1.0354	6.2773	.0	.719	.03239	.0391	.6314	.6372
.1583	1.0445	6.0154	.01	.728	.03275	.0439	.8885	.8974
.2147	1.0523	5.6856	.19	.744	.03288	.0456	1.2166	1.2171
.2861	1.0589	5.2651	.09	.764	.03278	.0443	1.6384	1.6221
0.0	0.9990	5.8681	.04	..	.11120	0.0	0.0	(5.542)
.0329	1.0129	5.6831	.15	.577	.11162	.0016	.1834	.1823
.0692	1.0252	5.4810	.0	.595	.11193	.0029	.3842	.3835
.1115	1.0364	5.2517	.05	.604	.11216	.0037	.6127	.6179
.1604	1.0460	4.9798	.10	.653	.11223	.0040	.8843	.8889
.2210	1.0542	4.6429	.08	.702	.11222	.0040	1.2212	1.2248
.2843	1.0598	4.2770	.09	.768	.11212	.0036	1.5875	1.5756
0.0	1.0010	5.2822	.10	..	.22550	0.0	0.0	(5.486)
.0329	1.0145	5.1012	.01	.521	.22573	.0004	.1806	.1805
.0688	1.0270	4.9008	.16	.556	.22588	.0007	.3807	.3774
.1100	1.0378	4.6813	.02	.602	.22597	.0009	.6000	.6035
.1605	1.0477	4.4035	.10	.670	.22600	.0010	.8777	.8805
.2253	1.0564	4.0477786	.22595	.0009	1.2336	1.2360
.2914	1.0623	3.6773	.19	.951	.22587	.0007	1.6042	1.5986
0.0	1.0072	4.4784	.08	..	.56550	0.0	0.0	(5.483)
.0351	1.0215	4.2827	.04	.540	.56559	.0001	.1956	.1925
.0704	1.0330	4.0870	.10	.647	.56563	.0001	.3913	.3860
.1128	1.0440	3.8608	.13	.775	.56565	.0001	.6175	.6185
.1616	1.0535	3.5999	.07	1.01	.56563	.0001	.8784	.8861
.2178	1.0610	3.2872	.0	1.42	.56560	.0001	1.1911	1.1942
.3143	1.0690	2.7513	.06	2.90	.56555	.0001	1.7270	1.7233
0.0	1.0166	3.8015	.11	..	1.1160	0.0	0.0	(5.631)
.0331	1.0300	3.6173	.13	..	1.1160	.0	.1842	.1864
.0817	1.0447	3.3441	.01	..	1.1160	.0	.4574	.4601
.1127	1.0527	3.1722	.15	..	1.1160	.0	.6293	.6346
.1622	1.0620	2.8911	.32	..	1.1160	.0	.9104	.9140
.2244	1.0699	2.5367	.02	..	1.1160	.0	1.2648	1.2636
.3224	1.0773	1.9739	.11	..	1.1160	.0	1.8276	1.8155

Discussion of Results

The family of straight lines obtained by plotting the medium effect against the mole fraction of acetic acid in the solvent is illustrated in Fig. 1, and represented mathematically by

$$2 \log y/y^0 = NJ \quad (13)$$

J is independent of N , but varies with c after the manner of an activity coefficient. The important primary medium effect is equal to the total medium effect at infinite dilution of electrolyte, and can therefore be obtained by extrapolation of $2 \log y/y^0$, or its equivalent NJ . Since $y_0^0 \equiv 1$, equation 13 becomes

$$2 \log y_0 = NJ_0 \quad (14)$$

at infinite dilution, and $\log y_0$ is the primary medium effect. The form of the extrapolation function can be derived by combining equations 3 and 4, transposing, and rewriting in the proper concentration units, thus

$$(2 \log y/y^0 + 2\alpha \sqrt{c}) = 2 \log y_0 + 2\beta c \quad (15)$$

The parameter α varies with N and could be calculated by equation 4a if the dielectric constant of the medium were known. Unfortunately, this is

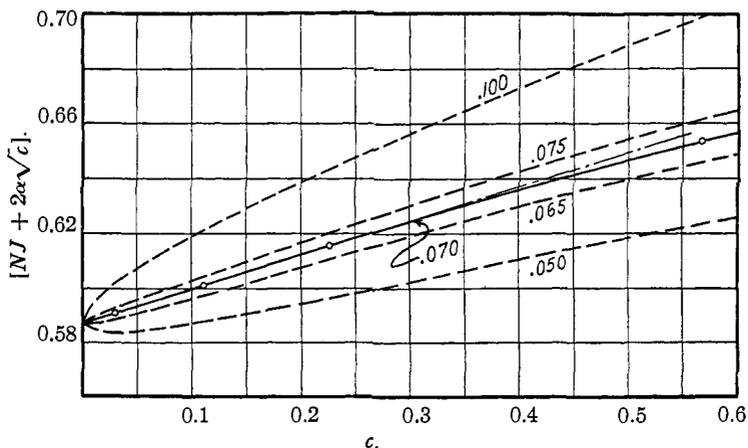


Fig. 2.—Extrapolation to J_0 for the various values of α as indicated, and $N = 0.1$.

not known, but the value of α , giving a straight line (in dilute solution, at least) when the terms in parenthesis are plotted against c , can be determined by trial. In Fig. 2, equation 15 has been plotted for $N = 0.1$ and the several values of α indicated. A straight line is obtained in dilute solution when $\alpha = 0.07$, and it extrapolates to $J_0 = 5.87$. Such a value of α would demand that the dielectric constant of 27% acetic acid solution (mole fraction 0.1) be about 72, which is not unreasonable, but as long as there is no experimental check on this value, α should be regarded as

purely empirical, for it is quite possible that the dielectric constant is much lower and the curvature of the uppermost curves is due to suppression of the "ionic radius" term of the Debye-Hückel formula used in deriving equation 4a.

The secondary medium effect has been defined as the difference between the total and primary medium effects. Since these latter have been shown to be proportional to N (Equations 13, 14), it follows that the *secondary medium effect*, $\log y^*/y^0$, must also be proportional to N ; thus, c being constant

$$\log y^*/y^0 = \frac{1}{2}N(J - J_0) \quad (16)$$

In dilute solutions, the variation of the secondary medium effect with the concentration of electrolyte, is given by equation 4 rewritten in the proper units, thus, N being constant

$$\log y^*/y^0 = -\alpha \sqrt{c} + \beta c \quad (17)$$

In Fig. 3 the experimental values of $\log \theta$, calculated for $N = 0.1$ by equation 16, are indicated by points on the continuous curve. The dashed

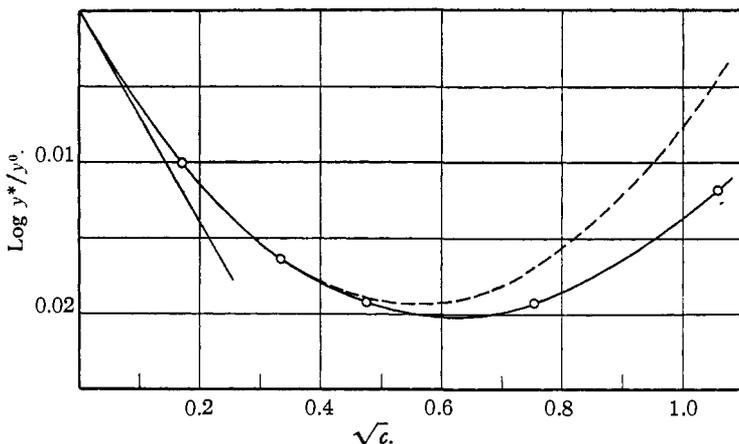


Fig. 3.—Variation of secondary medium effect, N being constant and equal to 0.1: —○—, $\frac{1}{2}N(J_0 - J)$; ---, $0.07 - \sqrt{c} + 0.063c$.

curve represents the values calculated by equation 17, using the values $\alpha = 0.07$ and $\beta = 0.063$ corresponding to the straight line (slope = 2β) in Fig. 2. These curves demonstrate that equations 4 and 17 fit the experimental data quite accurately up to $c = 0.2$.

Complete weight and density data were recorded in making up the cell solutions, so that a study could be made of the effect of different concentration units in plotting the medium effect, in the hope of discovering other relations similar to equations 13 and 14. No other simple relationship was found, although combinations of water-molality, molality and molarity were tried, but the relation of Harned and Owen (equation 17, their paper)

should be derivable from these data if differences in calculation and definition of medium effect be taken into consideration. This involved making the ionic strength (c_H) identical on both sides of the cell (equation 5), thus changing both the value of E^0 and the sign of $\log c_H/c$ in equation 7. The net result of these changes was a series of medium effects almost identical with those calculated by equation 7.¹² The transformation of all of these medium effects into water-molality units proved to be a very complicated proceeding and involved so many graphical interpolations that it was abandoned in view of the fact that transformation of units could not be expected to improve extrapolation by equation 15. The primary medium effect, however, may be studied much more directly.

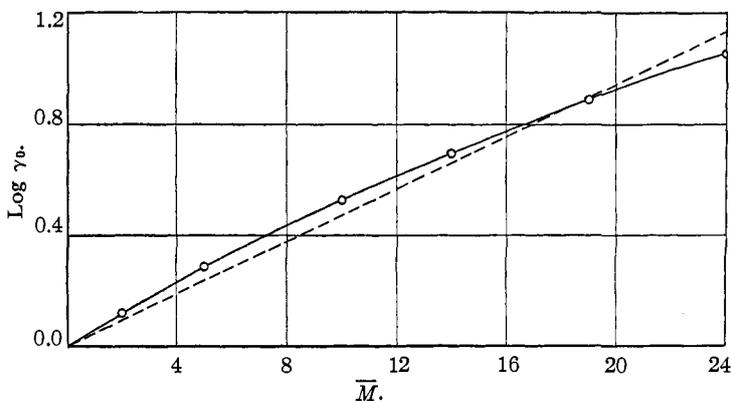


Fig. 4.—Variation of primary medium effect of acetic acid with molality. Broken line from calculations of Harned and Owen.

The primary medium effects in different concentration units are simply interrelated at zero ionic strength.

$$\log y_0 = \log \gamma_0 + \log d^0/d = \log \bar{\gamma}_0 + \log d^0/d + \log (1 + W\bar{M}) \quad (18)$$

γ_0 corresponds to m in moles per kilogram of solvent, \bar{M} is the water-molality of the non-aqueous component of the solvent, and W is its molecular weight in kilograms. The density of water, d^0 , appears because the standard state of y_0 is 1000 cc. of pure water, and not 1000 g., as for $\bar{\gamma}_0$ and γ_0 . This equation is general, being derivable from definitions only. Thus, at infinite dilution of electrolyte, $a_0 = m_0\gamma_0 = \bar{m}_0\bar{\gamma}_0 = c_0y_0(1/d^0)$ and $c_0 = m_0d = \bar{m}_0d/(1 + W\bar{M})$ (cf. equation 9), which give equation 18 by simple combination. Using $J_0 = 5.87$ in equation 14, and combining it with equation 18, $\log \gamma_0$ and $\log \bar{\gamma}_0$ may be calculated for any value of N for which equation 14 is valid (up to about $N = 0.25$). In Fig. 4, $\log \bar{\gamma}_0$ calculated in this way is plotted with the straight line obtained by Harned

¹² All values were identical with those in Column 8, Table II, except those for $c = 0.0296$ and 0.1112 , which were slightly higher, J being 5.695 and 5.545 , respectively.

and Owen.¹³ It will be observed that the numerical agreement is fair, considering the differences involved in the methods of calculation and their complexity, but the form of the two curves brings out the fact that $2 \log \gamma_0 = NJ_0$ and $2 \log \bar{\gamma}_0 = \bar{M}S$ are not compatible. This means that one, or perhaps both, of these relations is not strictly true, but this is not surprising because they are both empirical and deal with fairly concentrated solutions of acetic acid. Furthermore, Harned and Owen's relation could not be expected to hold for very concentrated solutions because it would lead to the absurd result that the activity coefficient of hydrochloric acid is infinite in pure acetic acid.

The results of Åkerlöf's¹⁴ study of hydrochloric acid and the alkali chlorides, in water-methyl alcohol solutions, not only permit the verification of two important equations interrelating the medium effects in terms of different electrolytes, but also can be used to demonstrate the general applicability of equation 15 in the calculation of primary medium effects. In his paper the electrolyte concentrations are expressed in moles per kilogram of solvent, and the composition of the solvent is expressed in per cent. of methyl alcohol by weight. In such units no simplifying relation corresponding to equation 13 is evident, so the determination of the primary medium effect, $\log \gamma_0$ (written $\log \gamma_\infty$ in his notation), necessitated an extrapolation for each concentration of methyl alcohol studied. Equation 15 is readily adapted to this purpose. If E' be the total e. m. f. of the amalgam double cells used by Åkerlöf, or the total e. m. f. ($E^0 - E$), of a hydrochloric acid double cell (similar to equation 5, if the acetic acid be replaced by methyl alcohol, and c by m), then the total medium effect is given by¹⁵

$$E' = (0.05915) 2 \log \gamma/\gamma^0 \quad (19)$$

Combining this equation with equation 15, expressed in appropriate units, and writing α' for 0.05915α and β' for 0.05915β , we obtain a very useful and simple extrapolation function,

$$(E' + 2\alpha'\sqrt{m}) = 0.1183 \log \gamma_0 + 2\beta'm \quad (20)$$

Extrapolation of Åkerlöf's data by this equation leads to two significant results. In the case of hydrochloric acid, the extrapolation is very nearly a straight line when α' is calculated from the known dielectric constants by equation 4a, and the extrapolated values of $\log \gamma_0$ agree closely with $\log \gamma_\infty$ calculated by Åkerlöf. In the case of the alkali chlorides, these theoretical values of α' appear to be too small, for the extrapolation function bends upward as the axis is approached, much after the manner of the

¹³ From their paper (equation 17), $S\bar{M} = 2 \log \bar{\gamma}_{\text{HCl}}/\bar{\gamma}_{\text{HCl}}^0$, which becomes $S\bar{M} = 2 \log \bar{\gamma}_0$ in the present nomenclature at zero ionic strength. Their value of S is 0.047.

¹⁴ Åkerlöf, THIS JOURNAL, 52, 2353 (1930).

¹⁵ Cf. equation 7. The ionization of methyl alcohol is negligible compared with that of the chlorides, or hydrochloric acid.

lowermost curves in Fig. 2. This behavior is in accord with Åkerlöf's findings, for he was unable to fit his data to the Debye-Hückel equation without arbitrarily assigning greater values to the "universal constant" than those calculable from the dielectric constants.

Medium Effect on Different Electrolytes.—Two approximate equations interrelating the primary medium effects of a given solvent upon two similar electrolytes may be derived immediately from equation 20, and applied to Åkerlöf's data¹⁴ to obtain an idea of the concentration range throughout which they may be safely used. Writing equation 20 for each of two electrolytes of the same concentration and medium and subtracting one equation from the other, we obtain an equation in which m appears only in the term $2m(\beta'_{(1)} - \beta'_{(2)})$, which may be neglected when m is small, and we may write

$$E'_{(1)} - E'_{(2)} = 0.1183 (\log \gamma_{0(1)} - \log \gamma_{0(2)}) \quad (21)$$

Åkerlöf's data show that the approximation involved in the use of this equation for concentrations as high as 0.05 in 50% alcohol correspond to an experimental error of 0.2 to 0.3 millivolt.

Rewriting equation 20 for two electrolytes of the same concentration and medium and dividing the two equations one by the other, we obtain two ratios, each containing terms in m . Fortunately, the m -terms appear only as additions to larger terms, and are therefore negligible by comparison when m is small, and the ratios may be simply written

$$\frac{E'_{(1)}}{E'_{(2)}} = \frac{\log \gamma_{0(1)}}{\log \gamma_{0(2)}} = R_{(1,2)} \quad (22)$$

This equation has been tested for all possible combinations of the three alkali chlorides and hydrochloric acid up to $m = 0.5$ and 50% alcohol, and found to describe the data with an average uncertainty of about plus or minus 6%, and individual deviations sometimes twice this figure. Such a high uncertainty¹⁶ is unfortunate, but does not prevent the equation from rendering very important service where complete data are lacking, for *within the same limits of accuracy $R_{(1,2)}$ is independent of both m and the alcohol concentration.* Thus, if complete medium effect data are available for electrolyte (1), only one additional measurement, $E'_{(2)}$, is required for the approximate calculation of complete medium effect data for a similar electrolyte (2) within the limits of concentration and accuracy just specified.

Summary

1. The primary, secondary and total medium effects have been clearly defined, and equations presented for their calculation from electromotive force data.

2. Electromotive force measurements have been made upon hydrochloric acid solutions containing acetic acid. From these data the total

¹⁶ Due in part to a mathematical magnification of experimental errors.

medium effect of acetic acid has been directly determined, and full details of the calculations are included.

3. A simple extrapolation function has been derived, and applied to a determination of the primary medium effect of acetic acid and to the data of Åkerlöf.¹⁴

4. It has been demonstrated experimentally that the primary, secondary, and total medium effects of acetic acid are closely proportional to the mole fraction of acetic acid in the solvent when the concentration of the electrolyte is expressed as molarity.

5. Equations relating the primary medium effects in different concentration units were derived and applied to a comparison of the primary medium effect obtained in this paper, with that calculated by Harned and Owen² from data on sodium chloride solutions containing acetic acid.

6. Two useful approximate equations were derived which interrelated the primary medium effects of a particular medium upon two similar electrolytes. The importance of these equations, in the calculation of approximate medium effects from very limited data, has been pointed out, and the magnitude of the approximations involved has been estimated from Åkerlöf's data.

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THE SPEED OF DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF HYDROCHLORIC ACID

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The decomposition of hydrogen peroxide into oxygen and water in the presence of hydrochloric acid has been studied recently by Livingston and Bray,¹ who measured the concentration of peroxide after various time intervals by titration with permanganate, and also by Maass and Hiebert,² who followed the reaction by measuring the rate of evolution of oxygen. Both pairs of investigators worked mainly at 25° and found the reaction to be unimolecular with respect to the hydrogen peroxide. Maass and Hiebert, however, obtained velocity coefficients which differed from those of Livingston and Bray for (presumably) identical conditions and they also found a well-marked period of acceleration for the more concentrated solutions. In Fig. 1 some of the values obtained by these workers are shown in the one graph, values of $\log k$ being plotted as ordinates and the concentration of hydrochloric acid (in g. moles per liter) as abscissas. Curve I shows some of Livingston and Bray's results and Curve II some

¹ R. S. Livingston and W. C. Bray, *THIS JOURNAL*, **47**, 2069 (1925).

² O. Maass and P. G. Hiebert, *ibid.*, **46**, 290 (1924).