[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, COLUMBIA UNIVERSITY AND THE FLORIDA STATE UNIVERSITY]

The Measurement and Correlation of Acid Dissociation Constants for Carboxylic Acids in the System Ethanol–Water. Activity Coefficients and Empirical Activity Functions[1a]

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The acid dissociation constants of formic acid, acetic acid and benzoic acid are measured at 25.0° in ethanol–water mixtures containing 0, 20, 35, 50, 65 and 80 weight % ethanol. Published ratios of dissociation constants for carboxylic acids are recalculated on the basis of the new data to give acid dissociation constants, accurate to better than 10%, for fourteen carboxylic acids. The solvent dependence of the acid dissociation constants is given by $K_A = K_A^w f_{HA}/f_H \cdot f_A$, where K_A^w is the dissociation constant in water and the f's are degenerate activity coefficients referred to water. The data for carboxylic acids are described quantitatively on the basis of the *activity postulate* $\log(f_A/f_{HA}) = m_A Y$, where m_A is characteristic of the carboxylic acid, and Y depends on solvent only. Empirical values of the *activity function* Y, and relative values of the slope m_A are tabulated. Values of m_A vary greatly with acid structure and in general increase as the acid radical becomes less polar. The variation with solvent of the reaction constant ρ for the dissociation of *m*- and *p*-substituted benzoic acids is given quantitatively as a linear function of the *activity function* Y.

Definitions.—Since the value of the activity coefficient γ in a given state S is a function of the reference state J, activity coefficients are written in the form $\gamma(\underline{J}, S)$, where the first, underlined member in parenthesis is the reference state, the second the actual state under consideration. The reference state is defined by $\gamma(\underline{J}, J) = 1$.

In the present work it is useful to choose the infinitely dilute aqueous state W^* as the standard state. Let S^* and S be the infinitely dilute and actual states in the solvent under study. Then equations 1 define the *molar* activity coefficient y in the customary manner,[5] and the activity coefficient f. Since f is independent of concentration, we

$$y = \gamma(\underline{S}^*, S) \qquad f = \gamma(\underline{W}^*, S^*) \qquad (1)$$

term it the *degenerate* activity coefficient of the solvent–solute system although the name *distribution coefficient* has been used.[2a] Equation 2 is readily derived.

$$\gamma(\underline{W}^*, S) = fy \qquad (2)$$

The strength of weak acids[2b] is measured by the acid dissociation constant $K_A = c_H c_A/c_{HA} \cdot y_H y_A/y_{HA}$, and also by the acidity constant $K_{Acid} = f_H K_A$. The latter has no physical meaning in the Guggenheim sense[3] because it requires knowledge of the degenerate activity coefficient f_H of the lyonium ion.

The other symbols employed here have been defined in the preceding article[4] and conform as much as possible to the symbolism of Harned and Owen.[5]

Acid Strength in the System Ethanol–Water.—In spite of the great practical importance of the system ethanol–water, the number of accurate determinations of dissociation constants is limited. Most of the data for pure water have been summarized by Harned and Owen.[5] Some measurements in solvents containing up to 20% ethanol have been reported by Patterson and Felsing.[6] At the other extreme of composition, much information is available due to the pioneering work of Goldschmidt and co-workers[7] and of other investigators.[8–11] In the intermediate range of composition, the conductance data of Bradley and Lewis[12] are valuable.

The accurate determination of *relative* dissociation constants is easier experimentally than the determination of *absolute* constants. Potentiometric methods employing suitable cells with liquid junctions may be used since the junction potentials are demonstrably[13b] nearly equal for structurally related compounds such as the carboxylic acids.[14a,15,16] Spectrophotometric methods are free even from this limitation.[9b,17] There is available an extensive list of such relative constants for carboxylic acids in the system ethanol–water.[9b,13–18]

It is obvious that upon availability of accurate standards, the relative dissociation constants already available may be recalculated to give absolute dissociation constants.[9b] While there are standards of high accuracy for aqueous and nearly aqueous systems,[5] the results in solvents containing greater proportions of ethanol are less accurate. The dissociation constants based upon conductance data[7,12] were obtained prior to the recent improvements in experimental and computational techniques.[19–21] The potentiometric data[10] are based

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(1) (a) Most of the material in this article was presented at the Atlantic City Meeting of the American Chemical Society, September, 1949. (b) Frank B. Jewett Fellow, 1948–1949.

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upon reasonable but not exact estimates of liquid junction potentials. The dissociation constants based upon rates of specific lyonium-catalyzed reactions[11] are apparently free from criticism but differ sometimes by as much as 2.5 pK units from concordant results obtained by several other methods.

We have used the differential potentiometric method described in the preceding article[4] for the measurement of the dissociation constants of formic acid, acetic acid and benzoic acid in ethanol-water mixtures with a precision of about 3%. Our results harmonize with the available absolute and relative dissociation constants for these and other carboxylic acids obtained by entirely independent methods. Considering all the available data, we have been able to compute absolute dissociation constants for an extensive list of carboxylic acids and to obtain a set of values in whose accuracy there is considerable confidence.

Experimental

Solvents.—Distilled water was redistilled from alkaline permanganate in an all-glass still protected from carbon dioxide by an Ascarite tube. Commercial absolute ethanol was treated with sodium (*ca.* 6 g./l.) and allowed to stand for several days. It was then fractionated through a ten-plate bubble-cap column equipped with still-head and take-off and protected by Ascarite, the first and last quarter of each batch being rejected. The purified solvent still contained *ca.* 0.2% water by Karl Fischer titration.[22]

Ethanol-water mixtures were prepared gravimetrically in 1000-g. lots from calculated amounts of the purified solvents. The solvent compositions were checked by density determination on each lot of 25.00° with an accuracy of 0.01%.

Reagents.—Formic acid containing 12.0% water by Karl Fischer titration,[22] acetic acid containing 0.4% water, benzoic acid, and perchloric acid (60%) were the same as described previously.[4] Suitable weights of these reagents were dissolved in the ethanol-water mixtures, and absolute ethanol was added to the solutions when necessary to correct for the water introduced with the reagents.

Base solutions were prepared as follows. Commercial 95% ethanol was treated with sodium and fractionated in the same way as the absolute ethanol, yielding a distillate (presumably the azeotrope) containing 6.16% water by weight. Enough clean sodium was added to this to produce a solution about 1 N in alkali. Known weights of this fresh solution were diluted with the calculated amounts of water and mixed solvent to prepare about 150 ml. of 0.05 N sodium lyate. (A solution x N in sodium lyate is produced from the reaction of x equivalents of sodium with mixed solvent followed by dilution to 1 l.) The sodium lyate solutions were accepted as carbonate-free and used only when titers against perchloric acid were identical within experimental error to methyl red and brom thymol blue. All normalities used in this work were based on Bureau of Standards benzoic acid primary standard.

Apparatus, Procedure and Method of Calculation.—Throughout this work, the apparatus and procedures already described for cell II were used.[4] Dissociation constants were calculated as before[4] from empirical slopes based on data near the equivalence point.

There were only minor modifications of the reported procedure[4] in the partly organic solvents. The waiting period between stirring and potential measurement was extended to at least one minute. Electrodes were kept immersed in the solvents for at least one day before measurements. In this way empirical slopes were as reproducible in the ethanol-water mixtures as in water,[4] and there was no trouble due to erratic or drifting E′ readings. However there was evidence of a very slow drift in voltage due to changes in the glass electrode. The value of E′ for an hydrochloric acid standard increased gradually by 0.4 unit over a five-months working period. This drift was too slow to be noticeable during the 30 minutes normally required for the measurement of an empirical slope, or even during routine tests for constancy of E′ values for a given solution extending over several hours.

In order to prove that the solvent composition did not change during the course of a measurement under experimental conditions, 35% ethanol, $d^{25.0}$ 0.94102 ± 0.01%, was subjected to the identical treatment as the test solutions. The density at 25.0° after treatment was 0.94106 ± 0.01% and did not differ significantly from the original value.

The esterification rates of the carboxylic acids in the ethanol-water mixtures were investigated. There was no significant esterification for acetic and benzoic acid over a period of several days as evident from constancy in alkali titers. On the other hand alkali titers for formic acid solutions decreased, usually a few per cent. per day for 0.05 M stock solutions at 25°. Calculation showed that the errors due to esterification were never greater than the indeterminate error of the empirical slopes, and usually smaller.

Results

Results of the Present Investigation.—In Table I we present our data for formic acid, acetic acid and benzoic acid. Columns 1-5 contain the experimental data, and column 6 lists values of K_A', the concentration dissociation constant. Probable errors are estimated at 1-2% for $dp\mathrm{H}/d\epsilon$, and at about 3% for K_A'. Within this limit there is no discernible dependence of K_A' on c_0 which has been varied from 0.001 to 0.01. Therefore at these concentrations K_A' is a function chiefly of ionic strength, so that values of the activity coefficient y_{HA} for the un-ionized acids must be approximately equal to unity.

The thermodynamic dissociation constant K_A is given as a function of K_A' by equation 3. The activity coefficient $y_{\mathrm{HA}} \doteq 1$; values of the quantity

$$K_A = K_A' \, y_{\mathrm{H}} y_{\mathrm{A}} / y_{\mathrm{HA}} \tag{3}$$

$y_{\mathrm{H}} y_{\mathrm{A}}$ may be estimated to several approximations. The first approximation uses the Debye-Hückel limiting law[24a] and gives estimates of K_A^{I}. The second approximation is effected by means of Hückel's extended equation[23] which takes into account the apparent diameters of the ions and salting-out phenomena.[24b] This yields estimates of K_A^{II} which are greater than K_A^{I} because the correction terms increase the values of the activity coefficients. A third approximation accounts in addition for higher order terms of the Debye-Hückel equation[24c,25] and/or for ion association.[24d] This approximation predicts values K_A^{III} in closer agreement with K_A^{I} than K_A^{II} at low ionic strengths since introduction both of higher order terms and of ion association lowers the activity coefficients.

As a matter of fact, calculated[26] values of K_A^{I} show no significant trends with ionic strength and display the expected scatter of 3-4% (see column 7, Table I). This prompts the assumption that in aqueous ethanol at the ionic strengths used (0.0002-0.006) the limiting law is approximately correct, probably because the various deviation terms tend to compensate. Activity coefficients in absolute

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TABLE I

ACID DISSOCIATION CONSTANTS IN THE SYSTEM ETHANOL–WATER, 25.0°

Weight % ethanol[a]	$10^3 c_0$	$10^3 c_{\mathrm{KCl}}$	$10^3 \mu$	$\left(\frac{dpH}{d\epsilon}\right)_{\epsilon=1}$	$10^6 K_A'$	$10^6 K_A^{\mathrm{I}}$	$10^6 K_A$
Formic acid							
20.3	8.49	1.782	3.676	2.149	113.0	94.3	
	7.84	3.411	5.258	2.001	122.7	98.9	96.6 ± 2.3
34.9	1.738	0.751	1.425	1.307	72.2	63.7	
	3.748	0.745	1.814	1.891	65.3	56.7	
	1.285	2.150	2.747	1.205	65.2	54.7	
	3.482	2.134	3.182	1.918	64.8	53.6	
	1.228	3.428	4.005	1.183	65.3	52.9	
	3.385	4.337	5.398	1.673	78.3	61.7	
	4.301	4.316	5.456	1.911	73.3	57.3	57.2 ± 3.1
50.1	5.975	1.322	2.362	3.272	31.3	24.7	
	6.108	2.518	3.549	3.167	34.4	25.8	
	5.427	3.603	4.581	3.019	33.8	24.3	24.9 ± 0.6
65.1	3.015	0.655	1.063	3.619	12.63	10.28	
	2.378	1.560	1.913	3.267	12.37	9.39	
	4.942	2.700	3.281	4.394	13.83	9.63	9.77 ± 0.34
79.9	6.47	0.673	1.013	10.55	2.94	2.23	
	4.94	1.091	1.377	9.08	3.05	2.20	
	6.05	2.517	2.860	8.79	4.01	2.52	2.32 ± 0.13
Acetic acid							
20.3	3.578	0.940	1.329	4.708	8.44	7.57	
	3.416	2.693	3.062	4.581	8.54	7.24	
	7.221	4.745	5.297	6.425	8.93	7.19	7.33 ± 0.16
34.9	3.163	0.342	0.579	6.374	3.95	3.65	
	1.736	1.096	1.282	4.632	4.28	3.80	
	3.304	2.415	2.685	6.126	4.48	3.77	
	6.983	4.496	4.868	8.517	4.81	3.53	3.69 ± 0.10
50.1	6.96	1.362	1.601	13.71	1.82	1.50	
	13.90	1.359	1.699	19.31	1.82	1.49	
	6.62	2.589	2.818	13.50	1.79	1.38	
	6.31	3.701	3.925	12.89	1.87	1.38	1.44 ± 0.06
65.1	1.318	0.075	0.136	10.83	0.553	0.514	
	1.318	.225	.288	10.78	.559	.502	
	5.18	.224	.357	20.20	.616	.547	
	5.22	.672	.805	20.16	.623	.521	
	11.42	1.462	1.676	28.99	.656	.506	
	4.98	2.508	2.626	19.05	.667	.482[b]	
	5.42	6.23	6.38	18.47	.772	.466[b]	0.518 ± 0.013
79.9	5.11	0.692	0.755	38.5	.165	.130	
	11.16	1.512	1.610	52.4	.193	.136	
	4.77	2.585	2.645	32.4	.218	.140	0.135 ± 0.004
Benzoic acid							
20.3	2.588	0.847	1.309	2.778	18.9	17.0	
	2.480	2.436	2.900	2.671	19.7	16.8	
	4.746	3.885	4.537	3.505	21.0	17.2	17.0 ± 0.2
34.4	2.055	2.669	2.936	3.923	7.11	5.93	5.93
35.2	2.140	1.271	1.543	4.00	7.10	6.22	
	2.086	2.163	2.430	4.15	6.39	5.42	
	2.025	2.669	2.933	3.91	7.05	5.88	
	1.939	3.49	3.75	3.85	6.99	5.70	
	2.292	6.016	6.303	4.06	7.36	5.65	5.75 ± 0.21
50.1	2.886	1.221	1.394	8.17	2.16	1.80	
	6.11	2.587	2.837	12.02	2.09	1.61	
	5.96	3.156	3.408	10.94	2.47	1.86	
	5.82	3.697	3.943	11.18	2.30	1.70	1.74 ± 0.09

TABLE I (*Continued*)

Weight, % ethanol[a]	$10^3 c_0$	$10^3 c_{KCl}$	$10^3 \mu$	$\left(\frac{dpH}{d\epsilon}\right)_{\epsilon=1}$	$10^6 K_A'$	$10^6 K_A^I$	$10^6 K_A$
65.1	1.136	0.222	0.285	8.85	0.721	0.649	
	4.48	0.224	.358	16.82	.771	.684	
	4.48	0.672	.806	16.64	.787	.658	
	4.38	1.313	1.444	16.09	.825	.649	
	4.18	2.504	2.652	15.59	.839	.606	
	9.29	2.784	2.976	23.07	.847	.600	
	4.01	3.601	3.725	14.52	.929	.632	0.640 ± 0.023
79.9	5.30	0.691	0.761	35.17	.206	.162	
	5.17	1.350	1.422	31.48	.252	.181	
	4.94	2.580	2.645	33.35	.214	.137	
	10.46	4.09	4.20	41.14	.298	.170	0.163 ± 0.013

[a] Solvent densities: 0.9660 (20.3%); 0.9427 (34.4%); 0.9418 (34.9%); 0.9410 (35.2%); 0.9095 (50.1%); 0.8750 (65.1%); 0.8394 (79.9%). [b] Value was not used in the calculation of K_A.

TABLE II

pK_A VALUES[a] AND THEIR CORRELATION[b] IN THE SYSTEM ETHANOL–WATER, 25.0°

Acid	References	Ethanol by weight, % 0.0	20.3	35.0	50.1	65.1	79.9	100.0	$m_A - m_{HAc}$	r
Formic	7, 29a, 31a	3.75	4.02	4.24	4.60	5.01	5.64	9.15	−0.270	0.017
Acetic	8, 10, 14, 29b, 34a	4.76	5.13	5.43	5.84	6.29	6.87	10.32	.000	...
Propionic	14, 29c, 35	4.87	5.33	5.68	6.13	6.63	7.17	...	.225	.013
Butyric	14, 29d, 31a, 35	4.82	5.31	5.70	6.15	6.65	7.22	...	.317	.010
Isovaleric	14	4.78	5.29	5.75	6.22	6.76	7.35	...	.472	.014
Chloroacetic	14, 16, 30, 31b, 34b	2.86	3.26	3.57	3.95	4.41	4.98	...	.024	.013
Cyanoacetic	12, 31a	2.47	2.78	3.07	3.39	3.81	4.39	7.49	− .189	.015
Glycolic	14, 32a	3.83	4.21	4.51	4.86	5.27	5.77	...	− .095	.040
Lactic	14, 32b, 33	3.86	4.14	4.44	4.80	5.26	5.77	...	− .175	.018
Malonic	14, 36	2.75	3.14	3.38	3.65	3.94	4.41	...	− .312	.089
Succinic	14, 36	4.13	4.54	4.86	5.21	5.64	6.16	...	− .016	.036
Glutaric	14, 36	4.34	4.64	5.00	5.42	5.94	6.53	...	.038	.035
Benzoic	7, 8, 10, 13, 14, 31c, 37	4.20	4.77	5.24	5.76	6.19	6.79	10.25	.536	.028
Salicylic	7, 8, 12, 14	3.00	3.23	3.62	3.99	4.46	5.03	8.68	− .101	.036
Y-		0.000	0.349	0.596	0.816	0.924	0.964	1.000		

[a] pK_A values for formic, acetic, benzoic acid in the mixed solvents obtained in this research; other values based on the articles referred to; values for 100.0% ethanol are averages of the published results. In the calculation of the absolute pK_A values, the temperature dependence of relative pK_A values was neglected, as justified by the data in this and other partly aqueous systems.[5,12] [b] m_A-m_{HAc} and Y_- are defined by equations 6 and 7; r is the probable error of the fit[40] of equation 7.

ethanol are likewise represented to a fair approximation by the limiting law.[11,27,28] Therefore we list in column 8 of Table I the means of the K_A^I values as probably the best estimates of K_A derivable from the data. At the same time we make available the complete set of experimental data in the hope that future developments in methods of extrapolation will further enhance its usefulness.

Tabulation and Accuracy of Dissociation Constants for Carboxylic Acids in the System Ethanol–Water.—Table II list pK_A values for fourteen carboxylic acids in the system ethanol–water at 25.0°. The data for water are the results of careful investigations by accepted methods, and their accuracy is usually better than 0.01 pK unit. The data in ethanol, on the other hand, are neither highly precise nor readily reproducible by various investigators. Their probable accuracy is of the order of 0.1 unit.

The results of the present investigation are precise to about 0.02 unit, and the relative pK_A values to about 0.03 unit. The precision of reported[13,14,16] relative pK_A values based on cells with liquid junctions is estimated at about 0.03 unit from the scatter of duplicate determinations reported by various workers. Halford[13b] has shown that errors due to differences in junction potentials are within this limit for structurally related acids. Relative pK_A values based on solubility measurements[13b] are somewhat more precise.

Our measurements and the various quoted investigations afford a number of comparisons of relative pK_A values. The median deviations of relative pK_A values obtained by any two investigators range from 0.03 to 0.04 unit and are therefore consistent with the experimental precisions. Only one case—the relative pK_A values for benzoic acid and salicylic acid—has appeared where there is a marked discrepancy between two sets of results.[13b,14] In this case the thorough work of Halford[13b] has been given the greater weight.

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It remains to show that the *absolute* pK_A values are also accurate. Halford has used the conductometric results of Bradley and Lewis[12] together with his own careful measurements of relative pK_A values to tabulate absolute pK_A values for benzoic acid.[13b] The median deviation between these and our results for benzoic acid is 0.04 unit and constitutes an upper limit to the probable error of our results.

It is pertinent that preliminary experiments, not yet reported, on the dissociation constant of acetic acid in 65.1% ethanol using platinum–hydrogen and silver–silver chloride electrodes corroborate the present results.

Discussion

Correlation of pK_A Values with the Aid of the Activity Postulate.—The variation of pK_A with solvent is given by equation 4

$$\Delta pK_A \equiv pK_A - pK_A^w = \log f_H + \log(f_A/f_{HA}) \qquad (4)$$

where pK_A^w is the pK_A value for water and the f's are degenerate activity coefficients referred to the infinitely dilute aqueous state. Water is used as the reference solvent since the data for aqueous dissociation are the most accurate.

We have prepared plots of ΔpK_A for the carboxylic acids *vs.* solvent composition. In each case ΔpK_A increases with increasing ethanol content of the solvent, but the magnitudes of the increases are characteristic of the individual acid; *i.e.*, ΔpK_A is a function of both solvent and acid structure. Since $\log f_H$ is a function of solvent only, it follows from equation 4 that $\log(f_A/f_{HA})$ must at least be a function of acid structure and possibly of solvent. To this extent the present systems differ from the media of high dielectric constant investigated by Hammett and Deyrup[38] where to a good approximation f_A/f_{HA} (A is a neutral base) is independent of structure.

The solvent dependence of activity coefficient ratios of the type f_A/f_{HA} has been discussed previously in connection with specific solvolysis rates.[39] The latter data were successfully correlated with the aid of the following activity postulate:

For systems of the type AZ, BZ, . . ., AZ′, BZ′, . . ., consisting of the radicals A, B, . . ., and the functional groups Z and Z′, it is postulated that as the solvent is varied, relation 5 remains valid. In

$$(1/m_A)\log(f_{AZ}/f_{AZ'}) = (1/m_B)\log(f_{BZ}/f_{BZ'}) \equiv \mathbf{Y}_{Z,Z'} \qquad (5)$$

equation 5, m_A and m_B are specific parameters for the systems A and B. The equation defines a function $\mathbf{Y}_{Z,Z'}$ characteristic of the change Z → Z′ and to which numerical values for each solvent may be assigned by empirical methods. $\mathbf{Y}_{Z,Z'}$ is called an *activity function* and is in general not simply related to other physical properties of the solvents such as their dielectric constant or molar volume.

We have attempted to fit the data on acid dissociation on the basis of the activity postulate, equation 5. On this basis, ΔpK_A is given by equation 6 where the activity function $\mathbf{Y}_-$ is characteristic of carboxylate–carboxylic acid equilibria. The notation $\mathbf{Y}_-$ is consistent with Hammett and Deyrup's[38] usage of $\mathbf{H}_-$.

$$\Delta pK_A = \log f_H + m_A \mathbf{Y}_- \qquad (6)$$

Equation 7 defines a function $D_{A,B}$ for any two acid–base systems A and B. Equation 8 follows from equation 7 for any two solvents S and S' and acids A and B. This latter equation was used to calculate, by the method of least squares, ratios of $\mathbf{Y}_-(S)/\mathbf{Y}_-(S')$ from values of the function $D_{A,HAc}$

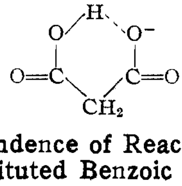
$$D_{A,B} = \Delta pK_A - \Delta pK_B = (m_A - m_B)\mathbf{Y}_- \qquad (7)$$

$$D_{A,B}(S) = \frac{\mathbf{Y}_-\ (S)}{\mathbf{Y}_-\ (S')} D_{A,B}(S') \qquad (8)$$

(HAc = acetic acid) based on the ΔpK_A values in Table II. Ratios of $\mathbf{Y}_-$ values were converted to absolute $\mathbf{Y}_-$ values by the arbitrary assignment $\mathbf{Y}_- = 1.000$ in 100% ethanol, as summarized in Table II. The $\mathbf{Y}_-$ values are accurate to 0.02 for the partly aqueous solvents and about 0.10 for 100% ethanol. Values of the quantity $m_A - m_{HAc}$ in equation 7 have also been computed by least methods and are summarized in Table II together with the probable errors of the fit,[40] r, of equation 7. With the possible exception of the data for malonic acid, the probable errors are in every case consistent with the experimental precision, their mean value being only 0.023.

It is noteworthy that the relative magnitudes of the m_A values vary with structure in a predictable manner. Almost without exception an increase in the polar character of the acid radical is attended by a decrease in m_A (see Table IV), as evident from the sequences: formic < acetic < propionic < butyric < isovaleric; malonic < succinic < glutaric; acetic ≈ chloroacetic > glycolic > cyanoacetic. At the same time there is no correlation between m_A and pK_A^w. This is not unexpected since the m_A values represent statements about activity coefficients and therefore may well vary with structure in a manner different from acid strength.

The probable error of the fit of equation 7 to the data for malonic acid is 0.089, considerably larger than the other values of the probable error. While this figure is probably still within the experimental error of the ΔpK_A values which are less accurate than the others because pK_A is low, it is more attractive to ascribe the effect to the proximity of the second carboxyl group. For example, if acid malonate ion has the cyclic hydrogen-bonded structure 9, we deal with an entirely different structural change of the type Z → Z′ than in the case of the other carboxylic acids, and equation 7 need not apply.



(9)

Solvent Dependence of Reaction Constants for *m*- and *p*-Substituted Benzoic Acids.—Hammett has shown[41] that the effect of *m*-*p*-substituents on side-chain reactions of benzene derivatives can be

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[38] L. P. Hammett and A. J. Deyrup, This Journal, **54**, 2721 (1932).

[39] E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948).

[40] Margenau and Murphy, "Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 502.

[41] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

represented by equation 10. In this equation, K and K_0 are equilibrium or rate constants for the substituted and unsubstituted materials, σ is the

$$\log K = \log K_0 + \rho\sigma \qquad (10)$$

substituent function for which Hammett has tabulated[42] empirical values, and ρ is the reaction constant. For the ionization of substituted benzoic acids, the reaction constant in water, ρ^w, is equal to unity, and ρ varies greatly with solvent (see Table III).

TABLE III

REACTION CONSTANTS FOR THE IONIZATION OF SUBSTITUTED BENZOIC ACIDS IN VARIOUS SOLVENTS, 22 ± 4°

Solvent	ρ	Y_-	Reference[d]
Water	1.000	0.000	41
50 Vol. % ethanol	1.464	0.737[a]	18
Ethanol	1.626	1.000	17
50 Vol. % methanol	1.241	0.384[b]	42
Methanol	1.374	0.595[b]	17
Butanol-1, 0.05 M LiCl	1.476	0.758[b,c]	15

[a] By interpolation from Table II. [b] Calculated from equation 11. [c] Using the data of Wooten and Hammett[15] for aliphatic acids and benzoic acid in butanol-1, and of Table II for the same acids in 50.1% ethanol, the ratio of Y_- values for the two solvents has been computed from equation 8. On this basis, $Y_- = 0.727$ for butanol-1. [d] In some cases, ρ values were computed by the present authors from the published data.

It follows from equations 6 and 10 that the variation of ρ with solvent is given by equation 11 where β is a parameter. On the basis of data for the

$$\rho = \rho^w + \beta Y_- \qquad (11)$$

system ethanol–water (Table III), equation 11 is valid to an excellent approximation, and for $\beta = 0.628$ the probable error of the fit is only 0.002. ρ values for the other solvents have been used to estimate $\mathbf{Y}_-$ with the aid of equation 11. These tentative estimates are listed in Table III. For the solvent butanol-1, $\mathbf{Y}_-$ was also computed from data for aliphatic acids using equation 8. The value obtained in this way is in satisfactory agreement with the one based on equation 11 (see Table III), so that the present correlations do not seem to be limited in scope to the system ethanol–water.

On the Determination of Degenerate Single Ion Activity Coefficients.—If equation 6 is accepted, the way is open for the determination of log f_H values and thus of other degenerate single ion activity coefficients. From the data reported in this article alone it is not possible to solve equations 6 for log f_H since there is one more unknown than there are equations. However when values of pK_A and of the activity function for other structural types become available, the number of independent equations increases more rapidly than the number of new unknowns, and solutions for m_A and log f_H become possible. This phase of the problem is being actively pursued.

Acknowledgments.—It is a pleasure to thank Professor L. P. Hammett in whose laboratory much of this work was done for his great hospitality, and to thank him and Professor D. Y. Curtin for many valuable discussions. One of us (E. G.) is grateful to the Frank B. Jewett Fellowship Committee for the award of a fellowship which has made this work possible.

TALLAHASSEE, FLA. RECEIVED MARCH 13, 1950

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(42) R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 1, 31, 44 (1928).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Theory of Polarographic Currents Controlled by Rate of Reaction and by Diffusion[1]

BY PAUL DELAHAY

An equation is derived for polarographic currents controlled by rate of reaction and by diffusion. The Ilkovic equation corresponds to a special case of the more general equation reported in the present paper. The average limiting current is calculated. Variations of the limiting current with the head of mercury are discussed quantitatively. A simple graphic method for the computation of rate constants from experimental data is reported. The theory is applied to the reduction of weak acids. Experimental data confirming the theoretical conclusions are presented for pyruvic acid.

Two quantitative treatments of polarographic currents controlled by rate of reaction and by diffusion have been reported in the recent years. The theory of Brdicka and Wiesner,[2] although interesting, is based on rather arbitrary hypotheses as pointed out by Lingane.[3] The more rigorous treatment of Koutecky and Brdicka[4] involves elaborate mathematical operations. A new treatment is discussed in the present paper and some of the difficulties of previous theories are eliminated. New features of diffusion-rate controlled currents are also reported.

Case of Linear Diffusion

Boundary Condition.—We consider the electrolytic reduction of two substances B and R which are transformed into one another according to the reaction B $\rightleftarrows$ R. We assume that R is reduced at less negative potentials than B, and that the concentration of R is negligible in comparison with that of B. Moreover, the potential of the electrode is adjusted in such a manner that only R is reduced. Under these conditions, B is transformed into R in the immediate neighborhood of the electrode as the reduction of R proceeds. If the transformation B $\rightleftarrows$ R is a first order reaction the number of moles B transformed into R at the surface of the electrode

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(1) Paper presented before the division of Physical and Inorganic Chemistry of the International Congress of Pure and Applied Chemistry held in New York in September, 1951.

(2) R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Commun.*, **12**, 138 (1947).

(3) J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

(4) J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 337 (1947).