electrode surface vary from one experiment to another, fluctuations in the peak current are observed and consequently the method is not to be recommended for analytical applications. On the other hand, the present method offers the possibility of studying indirectly the factors which might affect the uniformity of an electrolytic deposit having, say, ten atomic radii.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF FLORIDA STATE UNIVERSITY]

The Effect of Solvent on Equilibrium and Rate Constants. II. The Measurement and Correlation of Acid Dissociation Constants of Anilinium and Ammonium Salts in the System Ethanol–Water[1,2a]

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An extrathermodynamic relationship, the activity postulate, has been valuable in predicting the solvent dependence of equilibrium and rate constants in hydroxylic solvents. It is now tested further by means of the acid dissociation constants of anilinium and ammonium salts in the system ethanol–water. The acid dissociation constants of anilinium, *p*-toluidinium and N-methylanilinium chlorides are measured at 25.0° in ethanol–water mixtures containing 0, 20, 35, 50, 65, 80 and 95% wt.% ethanol. Published ratios of dissociation constants are recalculated on the basis of the new data to give acid dissociation constants, accurate to 0.05 pK unit, for eleven ammonium and anilinium salts. The solvent dependence of the acid dissociation constants is described quantitatively—as required by the activity postulate—by means of an activity function Y_0 and a set of parameters m_{BH} characteristic of the ammonium or anilinium salts. Values of Y_0 and relative values of m_{BH} are tabulated. The reaction constant ρ in the Hammett equation for the acid dissociation constants of *m*- and *p*-substituted anilines is solvent dependent, and a linear relationship between ρ and Y_0 is predicted and observed. In polar hydroxylic solvents, the substituent constant σ for polar substituents is also solvent dependent whenever the electron distribution is affected by solvation of the polar substituent. Criteria are given for detecting this effect. The general conditions for the existence of acidity functions are developed, and it is shown that the acidity functions H_0 and H_- do not exist in the system ethanol–water.

Many equilibria in solution are of the type

$$BZ + CZ' = BZ' + CZ \qquad (1)$$

where B and C are organic radicals, and Z and Z′ are functional groups. The mathematical analysis of the effect of a change in structure or solvent on this equilibrium involves four independent variables, corresponding to B, Z, Z′ and the solvent; the variable corresponding to C is not independent, for the equilibrium constant is unity when B = C.

The analysis is often carried out with so-called degenerate activity coefficients.[1] The equilibrium constant at infinite dilution, K, is written as

$$K = K^{w} \frac{f_{BZ} f_{CZ'}}{f_{BZ'} f_{CZ}} \qquad (2)$$

where K^w is the equilibrium constant in water at infinite dilution, and the f's are the degenerate activity coefficients in the infinitely dilute nonaqueous solution referred to the infinitely dilute aqueous state. The formulation (2) is advantageous for the study of equilibria, particularly in hydroxylic solvents. In the special case where Z and Z′ are constant, *i.e.*, where the analysis is limited to just one type of equilibrium, the solvent dependence of the ratios $f_{BZ}/f_{BZ'}$ is often simple and predictable. For example, we have noted on two previous occasions[1,3,4] that values of $\log f_{BZ}/f_{BZ'}$ for any two radicals B_1 and B_2 of the same electrical character remained proportional as the hydroxylic solvent is varied. These observations have led us to propose the *activity postulate*

$$\log f_{BZ}/f_{BZ'} = m_B Y_{Z,Z'} \qquad (3)$$

where the quantity m_B is independent of solvent and characteristic of B; and where $Y_{Z,Z'}$—the *activity function* for the two functional groups Z and Z′—depends only on the solvent.[1,3] The activity postulate thus separates $\log f_{BZ}/f_{BZ'}$ into two factors, m_B and $Y_{Z,Z'}$, which each depend on just one variable—a great simplification of the functional relationships.

According to equations (2) and (3), the dependence on solvent and structure of equilibrium constants for reactions like (1) is given by

$$\log K - \log K^{w} = \log f_{BZ}/f_{BZ'} - \log f_{CZ}/f_{CZ'} = (m_B - m_C) Y_{Z,Z'} \qquad (4)$$

which implies the existence of linear free energy relationships.[5]

The use of the degenerate activity coefficients is also advantageous in the analysis of equilibria like (5) and (5′).

$$BZ \overset{K_B}{=} BZ' + Q;\ CZ \overset{K_C}{=} CZ' + Q;\ \ldots \qquad (5)$$

$$BZ + P \overset{K_B'}{=} BZ' + Q;\ CZ + P \overset{K_C'}{=} CZ' + Q\ \ldots \qquad (5')$$

Equations analogous to (2) giving K_B, K_C, ..., as functions of degenerate activity coefficients contain the ratios $f_{BZ}/f_{BZ'}$ to which the activity postulate (3) may apply, especially in hydroxylic solvents. In particular, if only *relative* equilibrium constants $K_R = K_B/K_C$ or $K_{B'}/K_{C'}$ are of interest, equation (2) applies directly with $K = K_R$, and

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[1] Part I of this series: E. Grunwald and B. J. Berkowitz, THIS JOURNAL, **73**, 4939 (1951).

[2] (a) This work has been supported by a grant-in-aid from the Research Corporation; (b) Atomic Energy Commission Predoctoral Fellow at Florida State University, 1951–1952. This article is based on the Ph.D. Dissertation of Boris Gutbezahl, deposited in the Library of Florida State University, Tallahassee, Fla., 1952.

[3] E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948).

[4] S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951).

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

probably equation (4) will correlate the K_R values.

An important equilibrium of the type (5′) is the dissociation of various acids, Q being the lyonium ion. The dissociation constants at infinite dilution of carboxylic acids in the system ethanol–water have recently been measured, and the data are described accurately by equation (4).[1] In the present article we report acid dissociation constants in the system ethanol–water for a large number of anilinium and ammonium salts. These dissociation constants are, in part, the results of our own measurements; in part they are based on values proportional to our own constants and measured by other workers; and in part they are based on conductometric hydrolysis constants of anilinium salts of carboxylic acids. In all cases where comparisons are possible, the dissociation constants based on any two of these methods are in satisfactory agreement.

Equation (4) was again made the basis for the correlation of the dissociation constants, and again the correlation was successful. Thus again we have a case where values of $f_{BZ}/f_{BZ'}$ are approximated satisfactorily by the activity postulate, with $\mathrm{Z} = \geqslant\mathrm{N}{:}$, and $\mathrm{Z}' = \geqslant\mathrm{N\text{-}H}^+$.

Experimental Part

Measurement of Acid Dissociation Constants.—The acid dissociation constants of anilinium, N-methylanilinium and *p*-toluidinium chlorides were measured in ethanol–water mixtures containing 0.0, 20.0, 35.0, 50.0, 65.0, 80.0 and 95.0 wt. % ethanol. The procedures for solvents containing up to 80.0% ethanol were similar to those reported previously,[1,6] with certain modifications to improve the precision of the results. Glass and silver–silver chloride electrodes were used in all cells. The use of silver–silver chloride electrodes is permissible because the silver complexes of the anilines are sufficiently unstable.[7]

It was convenient to use a thermostat of conventional design, 8″ × 12″, containing water up to a height of about 3″ and maintaining the temperature at 25.00 ± 0.05°, and to mount the thermostat above a Mag-Mix stirring assembly. 7/8″ black plastic-coated magnetic stirring rods served to stir the cell contents. The plastic coating was insoluble in the solvents, for the stirring rods could be kept overnight in ethanol at reflux without the appearance of any color in the ethanol. It was unnecessary to pass solvent-saturated air over the cell solutions.

During the course of this work, the behavior of different types of Beckmann glass electrodes[8] in ethanol–water mixtures was observed, and the precision of the dissociation constants was greatly improved by selection of the best type. Glass electrodes were never used in partly ethanolic solutions unless they first satisfied the following two criteria in aqueous solutions: (i) after equilibration with water for 24 hours, electrodes had to give a constant reading within 15 minutes after immersion in 5×10^{-3} *N* aqueous hydrochloric acid, and this reading had to remain constant to better than 0.02 unit for the next hour. (ii) The differences in *p*H meter readings in two hydrochloric acid solutions, (1 and 5) $\times 10^{-3}$ *N*, had to be consistent within 0.02 unit with the known[9] hydrochloric acid activities of these solutions. A total of six #1190–42 electrodes[1] were tested and five were acceptable. Of five "high temperature" electrodes, #1190-90, only two were satisfactory. The #1190-42 electrodes were superior also for other reasons. They gave constant and reproducible readings to better than 0.01 unit within at most five minutes after magnetic stirring in all solvents up to 80% ethanol. The readings remained constant within this limit for several hours, but eventually began to drift. This happened at about the time when the cell solutions also turned yellow, presumably due to the photodecomposition of the anilinium salts. This yellow color seemed to appear sooner in solutions of high ethanol content. Measurements of dissociation constants were made only on freshly prepared, colorless solutions.

One "high *p*H" glass electrode,[8] #1190-75, was tested in 65% ethanol. It was rejected because the precision of the readings was only of the order of 0.05 *p*H unit. "High temperature" glass electrodes, #1190–90, were used in solvents containing up to 80% ethanol. The reproducibility of the readings was comparable to that for #1190–42, but the electrodes were not convenient because one had to wait for about 10 minutes after magnetic stirring until electrode equilibrium was attained. In spite of this inconvenience, a "high temperature" electrode was used to measure at least one dissociation constant in water, 50, 65 and 80% ethanol, and the results so obtained were always within the experimental error of those using the #1190-42 electrodes. This consistent agreement between the two different types of glass electrode, as well as the experiment in 95.0% ethanol described below, leads us to conclude that our results are as accurate as they are precise.

The experiments in the ethanol–water solvents did not change or damage the glass electrodes. After conclusion of the experiments in each organic solvent, electrodes were re-equilibrated with water for 24 hours and checked against three dilute aqueous hydrochloric acid solutions ranging from (1 to 5) $\times 10^{-3}$ *N*. The readings for the aqueous hydrochloric acid solutions at the conclusion of the experiments in a given solvent did not differ from those for the same solutions at the beginning by more than 0.02 unit, and usually by much less. Moreover, the differences in readings for all solvents were randomly distributed. Only one of the "high temperature" type electrodes was exceptional. After use in 50% ethanol, the drift was 0.10 unit, and the electrode was subsequently rejected.

In 95.0% ethanol, the procedure for the measurements had to be modified because none of the glass electrodes tested was perfectly stable in this solvent. For example, in a series of experiments using a #1190-42 glass electrode[8] the apparent *p*H readings drifted upward at the rates of 0.03, 0.01 and 0.005 unit/hr. in perchloric acid solutions (3.6, 1.6 and 0.9) $\times 10^{-3}$ *N*, respectively. Despite these drifts, it was still possible to obtain accurate *changes* in e.m.f. upon addition of titrating agent. The procedure was to measure the rate of drift over a period of 1 hour in the initial solution, add the titrating agent, and to measure the rate of drift again in the final solution. The observed change in e.m.f. due to the addition of the titrating agent could then be corrected for the drift (usually 0.005–0.01 unit) that had oc-

TABLE I

TITRATION OF PERCHLORIC ACID WITH 0.08 *N* SODIUM LYATE IN 95.0 WEIGHT PER CENT. ETHANOL AT 25.0°

	Titration 1 Total change in *p*H meter reading[a]			Titration 2 Total change in *p*H meter reading[a]	
Concn. $HClO_4$ $\times 10^3$	Obsd.	Calcd.[b]	Concn. $HClO_4$ $\times 10^3$	Obsd.	Calcd.[b]
0.9016	0.000	0.000	3.575	0.000	0.000
.5471	.235	.221	2.311	.190	.171
.3676	.385	.395	1.862	.280	.277
.2794	.545	.515	1.572	.370	.356
.1921	.680	.679	1.253	.470	.461
.1225	.890	.875	0.956	.570	.585
.0944	1.270	1.244	0.602	.785	.773

[a] *p*H changes have been corrected for drifts in e.m.f. due to the effect of solvent on the glass electrode. [b] The Debye–Hückel limiting law was used to estimate molar activity coefficients.

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[6] E. Grunwald, THIS JOURNAL, **73**, 4934 (1951). I wish to apologize for an error in my reference (5) in this previous article to the differential potentiometric method of measurement as used by S. Kilpi. The method which S. Kilpi has been pioneering and which he first reported almost twenty years ago employs the derivative d*p*H/d*e* measured at the inflection point, rather than at the equivalence point as has been our practice in this Laboratory.—E. Grunwald.

[7] E. W. Washburn, Ed., "International Critical Tables," Vol. VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 271.

[8] Manufactured by the National Technical Laboratories, Pasadena, Calif. The identification numbers mentioned in the text are those of this manufacturer.

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 547.

curred while the titrating agent was added. In order to prove that accurate pH changes were obtained in this way, increments of 0.08 N base were added to solutions containing $(1\text{–}3) \times 10^{-3}$ N perchloric acid and 1×10^{-3} N potassium chloride in 95.0% ethanol. As seen from the results in Table I, the agreement between the observed values and those calculated on the basis of the Debye–Hückel limiting law is very satisfactory.

If the dissociation constants in 95.0% ethanol had been measured by the usual procedure involving addition of six increments of base, the time required would have been very long due to the need of measuring electrode drifts, and significant photodecomposition of the anilinium salts could have occurred. The following procedure was therefore adopted. A precalculated amount of perchloric acid was added as described previously,[1,6] and the rate of drift was measured. One single aliquot of base, equivalent to twice the perchloric acid, was then added, a reading was taken, and the rate of drift was measured again. The dissociation constants obtained by this method, after correction for electrode drift, were almost as precise as those obtained in the other solvents. Because of the rapidity and good precision of this two-point method, we now recommend its use quite generally, even in solvents where the electrodes are quite stable.

Calculation of Acid Dissociation Constants.—For solvents up to 80% ethanol, the method of calculation was the same as described previously.[1,6] It was necessary to have the values of the functions $D(\tau)$ and f_0 for $0.40 \leq \tau \leq 0.60$. These were calculated and are made available elsewhere.[10] In 95.0% ethanol, the calculations were analogous, except that f_0 values calculated for *two*, instead of *seven*, experimental points had to be used. A complete table of these f_0 values is also made available.[10]

Reagents and Solvents.—The ethanol–water mixtures were prepared and standardized as described previously.[1]

Bureau of Standards benzoic acid, Baker and Adams C.P. potassium chloride, and Mallinckrodt analytical reagent 70–72% perchloric acid were used without further purification.

Eastman Kodak Co. "white label" p-toluidinium chloride was twice recrystallized from methanol containing a few drops of concentrated hydrochloric acid, and dried to constant weight *in vacuo* over paraffin; m.p. 245.9–246.1°; acid equivalent weight obsd. 143.3 ± 0.4, calcd. 143.6.

Eastman Kodak "white label" N-methylanilinium chloride was twice recrystallized from dry benzene–dry chloroform, and dried *in vacuo;* m.p. 123.0–123.1°; acid equivalent weight obsd. 143.7 ± 0.3, calcd. 143.6.

Baker and Adamson C.P. anilinium chloride was recrystallized four times from methanol–Skellysolve B with a few drops of concentrated hydrochloric acid, and dried to constant weight *in vacuo* over paraffin; m.p. 199.0–199.1°; acid equivalent weight obsd. 129.6 ± 0.3, calcd. 129.6.

p-Anisidinium chloride was prepared from Eastman Kodak "white label" p-anisidine and excess C.P. concentrated hydrochloric acid at 110°. The excess acid was evaporated, the salt was recrystallized four times from concentrated hydrochloric acid, and dried to constant weight *in vacuo* over calcium chloride; acid equivalent weight obsd. 159.7 ± 0.3, calcd. 159.6.

Analytical Procedures.—The primary acidimetric standard was Bureau of Standards potassium acid phthalate. Acid–base titrations were done with calibrated Koch microburets. It was found that in the more viscous ethanol–water mixtures, particularly around 65% ethanol, drainage was very slow. A drainage time of as much as four hours was sometimes necessary! When sufficient drainage time was allowed, results were precise to 0.2% or better.

Solutions of perchloric acid and sodium lyate in the mixed solvents were prepared as previously described.[1,6] The base solutions were not accepted for use unless titers to brom thymol blue and either methyl red or brom phenol blue were the same within experimental error. In 95.0% ethanol fresh base solution had to be prepared for every measurement since a white solid precipitated within a few hours even when the solution was kept under nitrogen.

Since such a long drainage time was necessary during the titrations, it was assumed that automatic pipets were incapable of delivering exact aliquots. The cells for the e.m.f. measurements were therefore prepared gravimetrically. In calculating the volume of the cell contents the densities of the pure solvents were used. The titers calculated from the gravimetric data were often checked by acid–base titration. The results from the two methods always agreed within the combined experimental error of 0.5%.

Acid Dissociation Constants and their Correlation

Experimental Results.—Our results are summarized in Tables II and III. The symbols used in these tables and in the remainder of this article

TABLE II

THE ACID DISSOCIATION CONSTANTS OF p-TOLUIDINIUM CHLORIDE AT 25.0° IN THE SYSTEM ETHANOL–WATER

Wt.% ethanol	$c_0 \times 10^3$	$\mu \times 10^3$	$K_A' \times 10^5$
0.0	2.032	2.160	0.791
	4.479	4.679	.815
	6.110	6.354	.789
			0.798 ± 0.011
20.0	3.414	3.616	1.16
	6.081	6.579	1.14
	15.21	15.69	1.18
	15.26	15.65	1.19
			1.17 ± 0.02
35.0	1.512	1.738	2.23
	6.365	6.820	2.28
	6.381	6.891	2.31
	11.09	11.74	2.28
			2.28 ± 0.02
50.0	2.431	2.806	3.64
	4.820	5.216	3.66
	15.91	16.43	3.74
	23.39	24.26	3.78
			3.70 ± 0.05
65.0	1.950	2.280	4.86
	3.685	4.203	4.90
			4.88 ± 0.02
80.0	3.281	3.909	5.11
	5.922	6.636	4.92
	18.57	19.72	4.67
	18.67	19.64	4.62
			4.83 ± 0.18
95.0	2.576	2.750	1.57
	3.863	4.200	1.93
	3.976	4.382	1.82
	4.165	4.477	1.86
	6.518	7.162	1.57
	10.40	10.92	1.75
	23.38	24.62	1.68
	24.19	24.91	1.56
			1.75 ± 0.11
95.0[a]	3.299	3.574	2.15
	6.161	6.449	2.42
	15.73	16.24	2.31
	30.35	30.86	2.06
			2.24 ± 0.17

[a] At 35.0 ± 0.1°.

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[10] (a) B. Gutbezahl, Ph.D. dissertation, Florida State University, 1952, pp. 52, 53, 59; (b) Order Document 3679 from American Documentation Institute, % Library of Congress, Washington 25, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

are defined in the same way as before.[1,6] Table II presents the complete set of results for *p*-toluidinium chloride. These illustrate the ranges of concentration and ionic strength used, the precision obtained, and the lack of dependence of the K_A' values on c_0 and ionic strength. The latter is predicted by the Debye–Hückel limiting law. It is interesting that this prediction is borne out for ionic strengths ranging from (1.7 to 32.4) $\times 10^{-3}$ and even in solvents containing 95% ethanol. In accordance with these observations we have taken K_A as equal to the mean of the experimental K_A' values. The data also illustrate the considerable improvement of the precision of the K_A' values, primarily due to the refinement of analytical procedures and careful testing of the glass electrodes. The mean probable error of a single K_A' value has been reduced from the previous value of 4%[1,6] to 1.6%.

Table III summarizes the remainder of our results. The columns list the compounds used, the solvent compositions, the number of determinations, the c_0 ranges, the ionic strength ranges, and the mean $K_{A'}$ values with their mean deviations. The data prove again that the relative strengths of two acids may vary considerably with solvent. For example, anilinium ion is a stronger acid than N-methylanilinium ion in water and solvents up to 50% ethanol but is weaker in solvents containing more than 50% ethanol.

TABLE III

SUMMARY OF EXPERIMENTAL RESULTS: ACID DISSOCIATION CONSTANTS AT 25.0° IN THE SYSTEM ETHANOL–WATER

Compound	Wt. % ethanol	No. of detn.	c_0 range ($\times 10^3$)	μ range ($\times 10^3$)	Mean K_A' ($\times 10^5$)
Benzoic acid	0.0	5	1.833–9.209	1.093–3.599	6.34 ± 0.13[a]
p-Anisidinium chloride	0.0	5	2.664–16.28	2.818–16.57	0.494 ± 0.013
Anilinium chloride	0.0	3	1.705–7.390	1.941–7.844	2.31 ± .04
	20.0	5	2.399–25.76	2.702–26.76	3.81 ± .07
	35.0	3	1.988–12.71	2.512–13.86	6.91 ± .02
	50.0	3	2.996–15.97	3.631–16.56	12.0 ± .1
	65.0	6	2.572–25.85	3.389–27.82	15.9 ± .6
	80.0	3	4.211–27.62	5.189–32.37	17.8 ± .8
	95.0	6	4.538–28.91	5.057–30.44	6.52 ± .21
N-Methylanilinium chloride	0.0	4	3.645–12.12	3.985–12.67	1.44 ± .01
	35.0	3	2.700–13.03	3.142–14.00	5.30 ± .02
	50.0	5	2.017–18.85	2.548–24.39	12.5 ± .5
	65.0	3	2.535–15.39	3.173–17.70	23.1 ± .4
	80.0	3	7.751–19.32	9.158–21.55	38.3 ± 1.1
	95.0	3	6.122–28.45	7.404–31.45	29.7 ± 0.5

[a] Mean K_A value calculated with the Debye–Hückel limiting law approximation for activity coefficients.

A number of comparisons are possible to determine the accuracy of our results. In water our value for the dissociation constant of benzoic acid is within 1% of the currently accepted conductometric value,[11] well within the combined experimental and computative errors due to the use of the Debye–Hückel limiting law for the molar activity coefficients. The agreement between our results for anilinium, *p*-toluidinium, N-methylanilinium and *p*-anisidinium chlorides in water and those of N. F. Hall and M. R. Sprinkle is also well within the mutual experimental errors; the mean deviation between the two sets is 0.025 unit, with random deviations.[12] The agreement between our values for the acid dissociation constants of anilinium and *p*-toluidinium chlorides in water and the conductometric values obtained by James and Knox[13] is even more striking; the average difference is only 0.01 *pK* unit. In 95.0% ethanol our pK_A values for anilinium and N-methylanilinium chlorides are 0.10 unit higher than those obtained by interpolation from published data in solvents of comparable water content.[14] This discrepancy, which is within the experimental error of the other data, sets an extreme upper limit for the accuracy of our results.

Summary of Acid Dissociation Constants for Anilinium and Ammonium Salts in the System Ethanol–Water.—Our new results have been used to calculate acid dissociation constants from the apparent *pK* values measured by Mizutani[15] at 18–22°. The apparent *pK* values were first corrected to 25° with the same temperature coefficients that have been used in water.[12] To justify the implicit assumption that the small temperature corrections are indeed independent of solvent composition, we have measured the temperature coefficient for *p*-toluidinium chloride in 95.0% ethanol (Table II) and found it to be the same, within experimental error, as the value in water. Since Mizutani's solvents differed in composition from ours, we then obtained the apparent *pK* values for our solvent compositions by interpolation on large scale plots. The interpolations were done only for solvents containing up to 65 wt. % ethanol since the plots have too much curvature for accurate interpolation in solvents containing more than 80 vol. %. Finally, we calculated the pK_A values from the apparent *pK* values by the following procedure: anilinium and N-methylanilinium chlorides were studied by both Mizutani and ourselves. The difference between the mean pK_A values of these compounds, as measured by us, and the mean apparent *pK* values of Mizutani was added to the apparent *pK* values for other anilinium and ammonium salts, and this gave pK_A values for the other salts. The accuracy of these pK_A values is about 0.05 unit, estimated by comparison of the data in water with those of Hall and Sprinkle[12] and of ourselves. However, the internal consistency of the pK_A values for any one acid is better than 0.05 unit because the data may be correlated as described below with a probable error of fit of only 0.02 unit. Thus we infer that part of the disagreement of Mizutani's pK_A values in water is due to systematic error caused perhaps by trace impurities in the reagents.

Table IV is a summary of pK_A values of anilinium and ammonium salts in the system ethanol–water. The table contains our own values, those based on the work of Mizutani, and, for 100% ethanol, those of Goldschmidt and Mathieson.[14] The latter are accurate to better than 0.2 unit and internally consistent to 0.04 unit.

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[11] B. Saxton and H. F. Meier, THIS JOURNAL, **56**, 1918 (1934); F. G. Brockman and M. Kilpatrick, *ibid.*, **56**, 1483 (1934).

[12] N. F. Hall and M. R. Sprinkle, *ibid.*, **54**, 3469 (1932).

[13] J. C. James and J. G. Knox, *Trans. Faraday Soc.*, **46**, 254 (1950).

[14] H. Goldschmidt, *Z. physik. Chem.*, **99**, 116 (1921); H. Goldschmidt and E. Mathieson, *ibid.*, **119**, 439 (1926).

[15] M. Mizutani, *ibid.*, **116**, 350 (1925).

TABLE IV

pK_A VALUES FOR AMMONIUM AND ANILINIUM IONS AND VALUES OF Y_0 IN THE SYSTEM ETHANOL–WATER AT 25.0°

Acid	Ethanol by weight, % 0.0	20.0	35.0	50.0	65.0	80.0	95.0	100.0
Anilinium	4.636	4.416	4.161	3.921	3.799	3.750	4.186	5.70
p-Toluidinium	5.098	4.928	4.642	4.430	4.312	4.316	4.762	6.24
N-Methylanilinium	4.839	4.62[a]	4.276	3.903	3.636	3.417	3.527	4.86
Monoethylammonium	10.71	10.47	10.20	9.87	9.71	.....	.....	.....
Monomethylammonium	10.70	10.41	10.11	9.80	9.58	.....	.....	.....
Dimethylammonium	10.58	10.26	9.95	9.61	9.36	.....	.....	.....
Trimethylammonium	9.79	9.45	9.13	8.69	8.36	.....	.....	.....
Ammonium	9.26	9.00	8.78	8.57	8.45	.....	.....	.....
N-Dimethylanilinium	5.01	4.75	4.30	3.81	3.50	.....	.....	4.37
m-Toluidinium	4.77	4.54	4.28	3.99	3.87	.....	.....	5.78
o-Toluidinium	4.46	4.25	3.96	3.68	3.56	.....	.....	5.55
Methyl yellow[b]	3.25	3.03	2.28	1.87	.....	.....	.....	.....
α-Naphthyl red[c]	....	4.10	3.72	3.41	3.30	3.38	.....	.....
Y_0	0.000	−0.057	−0.136	−0.266	−0.379	−0.570	−0.882	−1.000

[a] Interpolated value. [b] *p*-Dimethylaminoazobenzene. [c] *p*-α-Naphthylaminoazobenzene.

Correlation of Acid Dissociation Constants for Anilinium and Ammonium Salts.—The acid dissociation of anilinium and ammonium salts is a reaction of the type (5), and dissociation constants may be correlated according to equation (4). We define $\Delta pK_A(\text{BH}) \equiv pK_A(\text{BH}) - pK_A{}^{\text{w}}(\text{BH})$, where BH is the acid. From equation (4) we predict the relationship

$$\Delta pK_A(\text{BH}) - \Delta pK_A(\text{C}_6\text{H}_5\text{NH}_3) = (m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3})\mathbf{Y}_0 \quad (6)$$

The symbol $\mathbf{Y}_0$ is used to denote the activity function in analogy with the symbol $\mathbf{H}_0$ for the acidity function of neutral bases.[16]

Values of $\mathbf{Y}_0$ for ethanol–water mixtures have been calculated by statistical methods entirely analogous to those described previously for the carboxylic acid correlation.[1] $\mathbf{Y}_0$ was taken as 0.000 in water and as −1.000 in absolute ethanol. The $\mathbf{Y}_0$ values so obtained are given in Table IV.

The parameters $m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3}$ in equation (6) have been calculated in a manner similar to that used before.[1] Since the acid dissociation constants in water are no more accurate than in the nonaqueous solvents, a slope–intercept method of calculation had to be used, *i.e.*

$$\Delta pK_A(\text{BH}) - \Delta pK_A(\text{C}_6\text{H}_5\text{NH}_3) = (m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3})\mathbf{Y}_0 + \beta(\text{BH}) \quad (7)$$

where the intercepts β(BH) are due to the error of the fit in water. Values of β(BH) are equal to $b_{\text{BH}} - b_{\text{C}_6\text{H}_5\text{NH}_3}$, the b's being the errors of the fit for the individual acids. In order to calculate these b values, we use the fact that the mean value of $\beta = -b_{\text{C}_6\text{H}_5\text{NH}_3}$; the mean value of b_{BH} is zero because the sample is of reasonably large size.

TABLE V

CORRELATION OF pK_A VALUES FOR AMMONIUM AND ANILINIUM SALTS IN THE SYSTEM ETHANOL–WATER AT 25.0°

Acid	$m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3}$	b_{BH}	$p\mathbf{K}_A{}^{\text{w}}$	r
Anilinium	0.000	0.009	4.627	...
p-Toluidinium	−0.109	− .016	5.114	0.014
N-Methylanilinium	1.025	− .036	4.875	.021
Monoethylammonium	0.454	− .007	10.72	.020
Monomethylammonium	.697	.014	10.69	.014
Dimethylammonium	.942	.021	10.56	.017
Trimethylammonium	1.507	.005	9.78	.027
Ammonium	−0.134	.021	9.24	.018
N-Dimethylanilinium	1.873	− .025	5.03	.023
m-Toluidinium	0.189	− .001	4.77	.017
o-Toluidinium	0.209	− .006	4.47	.014

Table V contains a summary of the correlation on this basis. The new symbols used in the Table are $p\mathbf{K}_A{}^{\text{w}} = pK_A{}^{\text{w}} - b$, and r, the probable error of the fit of equation (7). The fit of the correlation is excellent. The mean value of r is only 0.018, and the mean value of $|b|$ is 0.015. Thus equation (6) describes most of the pK_A values accurately within the limits of their experimental error, although the error of the fit is somewhat greater than the experimental error for the most accurate data. Equation (6) is therefore not an *exact* relationship. Yet it is valuable, for it permits the prediction of approximately accurate ΔpK_A(BH) values with only one adjustable parameter, $(m_{\text{BH}} - m_{\text{C}_6\text{H}_5\text{NH}_3})$. When the physical basis of equation (6) or—more fundamentally—of equation (3) is understood, it will perhaps be possible to predict the m_{BH} values from other constitutive properties.

The variation with structure of the m_{BH} values for the anilinium and ammonium salts is greater than for the carboxylic acids.[1] N-Alkyl substitution generally increases m, and the members of the anilinium series appear to be more sensitive in this respect than the members of the ammonium series.

Additional Correlations for *m*- and *p*-Substituted Anilinium Salts.—One case where it is already possible to predict m_{BH} values from other constitutive properties is the acid dissociation of *m*- and *p*-substituted anilinium salts. Let $K_A{}^0$, m^0, $K_A(\sigma)$ and $m(\sigma)$ represent the K_A and m values of the unsubstituted and *m*- or *p*-substituted anilinium salts, respectively. According to the Hammett equation[5]

$$\log K_A(\sigma) - \log K_A^0 = \rho\sigma \quad (8)$$

where σ is a substituent constant and ρ is a solvent-

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[16] L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932).

dependent reaction constant. Whenever equation (8) is valid, it follows from (8) and (6) that

$$\frac{\rho - \rho^{w}}{\mathbf{Y}_0} = \frac{m(\sigma) - m^{\circ}}{\sigma} = \beta_0 \qquad (9)$$

where β_0 is a parameter characteristic of the equilibrium being studied, and of the temperature. Equation (9) has been tested in the system ethanol–water. The relevant data and literature sources are summarized in Table VI. The fit of equation (9) is adequate. The probable error of the fit of

$$\rho = 3.18 - 0.573\ \mathbf{Y}_0$$

is 0.14, and the probable error of the ρ values is also 0.14. It is probably a coincidence that the magnitude of β_0 for anilinium salts, −0.57, is very nearly equal to the value, 0.628, of β_- obtained for the benzoic acids.[1]

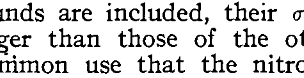
TABLE VI

CORRELATION OF ρ-VALUES FOR ACID DISSOCIATION CONSTANTS OF ANILINIUM SALTS, 25.0°

Solvent (wt. % ethanol)	ρ	$\mathbf{Y}_0$	ρ (calcd.)[a]	References
0.0	3.03 ± 0.14	0.000	3.18	[c], 12
24.7	3.43 ± .14	− .083[b]	3.23	[c]
93.3	3.45 ± .13	− .841[b]	3.66	14
97.7	3.74 ± .16	− .945[b]	3.72	14
100.0	3.90 ± .13	−1.000	3.75	14

[a] $\rho = 3.18 - 0.573\ \mathbf{Y}_0$. [b] Obtained by interpolation. [c] G. M. Bennett, G. C. Brooks and S. Glasstone, *J. Chem. Soc.*, 1821 (1935).

The ρ-values listed in Table VI are uniformly calculated from the pK_A values of the halo- and alkyl-substituted anilines only. pK_A values for the nitroanilines are also available for some solvents,[17] but are not used because we suspect that equations (8) and (6) are not strictly applicable to them. The $\rho\sigma$ term in (8) is proportional to the change in potential energy of reaction due to the substituent.[5] When the substituent and the solvent are both highly polar, the electron distribution is altered due to solvation of the substituent, and consequently σ is not independent of solvent. The effect ought to be particularly pronounced for *p*-nitroaniline where the energy of the valence bond structure



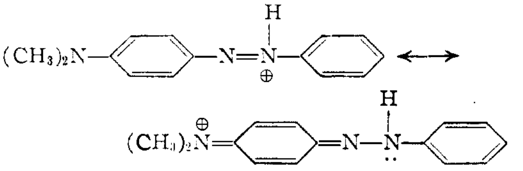
(10)

and hence the electron distribution in the resonance hybrid, varies greatly with the solvent. We have by now several examples attesting to the reality of this effect, and we are presenting part of our evidence below.

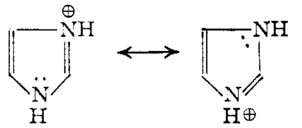
The success of equation (8) in a number of solvents with only one set of σ values may be apparent rather than real. For example, if *m*- and *p*-nitro compounds are included, their σ values are so much larger than those of the other substituents in common use that the nitrocompounds largely determine the value of ρ. Thus the plots of log K *vs.* σ may be linear in each solvent within a reasonable error of fit—say, 0.06 unit—but the solvent dependence of the apparent ρ values is not given by equation (9). The success or failure of equation (6) for all substituents is a much more sensitive criterion for the validity of equation (8) than the approximate linearity of log K with σ. For equation (8) with just one solvent-independent value of σ must fail for all those substituents for which equation (6) fails.

Some Structural Limitations.—The acid dissociation constants of methyl yellow and α-naphthyl red have been calculated from apparent pK values[18] by a method similar in principle to the one employed here, and which is described in detail elsewhere.[19] The pK_A values for these compounds are included in Table IV. The fit of equation (6) is poor; the probable errors for the two compounds are 0.10 and 0.07 unit, respectively, and the deviations are not random. The probable error of fit of equation (6) to the data for *p*-nitroaniline[17] is also large, about 0.07 unit, but it is not certain that this is outside the limit of experimental error.

We ascribe these large deviations to a failure of the activity function $\mathbf{Y}_0$ whenever there is considerable charge distribution in the conjugate acid or base. In compounds such as the conjugate acid of methyl yellow (11), or of imidazole[14,20] (12), and such as *p*-nitroaniline (10), the charge is spread by resonance, and we no longer deal with a simple proton addition as in the case of the amines.



(11)



(12)

The fact that the pK_A values for anilines and amines are correlated with the same activity function indicates, however, that there is some latitude in the possible degree of charge distribution.

Conditions for the Existence of Acidity Functions.—An acidity function exists whenever the quantity $a_{\mathrm{H}}f_{\mathrm{B}}/f_{\mathrm{BH}}$ is independent of the structure of the base B.[21] According to equation (6) this means either that the value of the activity function $\mathbf{Y}$ is zero, or that the acids studied have equal m values. We know that m values differ greatly for amines and anilines, at least in the systems water–ethanol, water–methanol[15] and water–dioxane.[13] Therefore $\mathbf{H}_0$ exists probably only if $\mathbf{Y}_0$ values are zero or very nearly so.

It has been shown that $\mathbf{H}_0$ exists in sulfuric acid–water and perchloric acid–water mixtures.[16,22] This fact is not inconsistent with the behavior of the $\mathbf{Y}_0$ function in the system ethanol–water. If

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(17) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1971, 1976 (1948).

(18) H. Baggesgaard and F. Reimers, *Dansk. Tidsskr. Farm.*, **7**, 164 (1933).

(19) B. Gutbezahl and E. Grunwald, THIS JOURNAL, **75**, 565 (1953), equation 16.

(20) A. H. M. Kirby and A. Neuberger, *Biochem. J.*, **32**, 1146 (1938).

(21) Reference (5) chap. IX.

(22) L. P. Hammett and M. A. Paul, THIS JOURNAL, **56**, 827 (1934).

we suppose that in largely aqueous media $\mathbf{Y}_0$ depends mainly on solvent polarity (as measured, for example, by the dielectric constant), we can extrapolate $\mathbf{Y}_0$ from ethanol–water into the still more polar systems sulfuric acid–water and perchloric acid–water. On the plot of $\mathbf{Y}_0$ *vs.* wt. % ethanol, $\mathbf{Y}_0$ approaches the origin with nearly zero slope. Therefore upon extrapolation into the systems mineral acid–water, $\mathbf{Y}_0$ remains constant at zero. Of course as the mineral acid concentration is increased and the medium becomes largely mineral acid, $\mathbf{Y}_0$ may depart noticeably from zero, and values of f_B/f_{BH} may be quite different for different structures. The actual acid–base ratios measured in solvents of around 85% sulfuric acid are correlated by one single acidity function with only moderate accuracy.[23] This would seem to confirm our preceding analysis.

To evaluate acidity functions for new solvents or charge types, one must first prove that f_B/f_{BH} is independent of acid structure. For this purpose it is necessary to study several acids of widely different m values, and our tabulations for amines and carboxylic acids can serve as a guide in designing significant experiments. Recently an attempt was made to define an acidity function $\mathbf{H}_0$ for the system ethanol–water on the basis of data for only two acids.[17] On the basis of such limited data it was not possible to decide even whether there is an acidity function,[24] and our work now shows conclusively that there is not. For the same reasons it is not possible to define[16] a function $\mathbf{H}_-$ for the carboxylic acids in the system ethanol–water. In fact, it is unlikely that $\mathbf{H}_-$ would exist even in sulfuric acid–water mixtures, for in the system ethanol–water, $\mathbf{Y}_-$ changes very rapidly with solvent composition and polarity near the origin, as the ethanol concentration approaches zero. It is interesting to note that the function $\mathbf{H}_-$ has never been reported for sulfuric acid–water mixtures even though the function $\mathbf{H}_0$ has been used for 20 years.

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(23) See, for example: V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 2109 (1951).

(24) Reference 17, pp. 1972, 1983; see also ref. 13 for relevant data in the system dioxane–water.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE FLORIDA STATE UNIVERSITY]

The Acidity and Basicity Scale in the System Ethanol–Water. The Evaluation of Degenerate Activity Coefficients for Single Ions[1a]

BY BORIS GUTBEZAHL[1b] AND ERNEST GRUNWALD

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Acid dissociation constants in the system ethanol–water are given for carboxylic acids by (i) $pK_A - pK_A^w = \log f_H + m(\text{HA})\ \mathbf{Y}_-$, and for anilinium and ammonium salts by (ii) $pK_A - pK_A^w = \log f_H + m(\text{BH}^+)\ \mathbf{Y}_0$. In (i) and (ii), $m(\text{HA})$ and $m(\text{BH}^+)$ are empirical parameters characteristic of the acid, $\mathbf{Y}_-$ and $\mathbf{Y}_0$ are the corresponding activity functions,[8,9] and $\log f_H$ is a function of solvent and temperature. Values of m at 25.00° are 1.035 for acetic acid, 3.614 for aniline; and values for other acids may be calculated from these and previous correlations.[8,9] Values of $\log f_H$ for the system ethanol–water are tabulated. The empirical equations (i) and (ii) are consistent with theoretical equations involving degenerate activity coefficients only if the quantities *antilog* $(m\mathbf{Y})$ are equal to the degenerate activity coefficient ratios f_b/f_a of the bases and their conjugate acids. When either the base or the acid is a neutral molecule, the value of f for it may be measured directly, and the value of f for its ionic conjugate may then be calculated. When f has been evaluated for any one ion, values of f for other ions may be calculated by standard methods.[15] Thus there is now a method for evaluating degenerate activity coefficients for single ions. This implies, from a logical point of view, that the concept *single ion degenerate activity coefficient* is a valid one and has physical significance.

It is shown that f_H is equal to the ratio of the basicity constant (as defined by Bronsted[18]) of water to that of the ethanol–water solvent, S. As such, f_H is the equilibrium constant for the reaction SH^+ (extremely dilute, in S) + $\text{HOH}(l) = \text{H}_3\text{O}^+$ (extremely dilute, in water) + S(l), and may well be called the lyonium ion degenerate activity coefficient. With single ion degenerate activity coefficients evaluated, one can measure liquid potentials at the junction of salt solutions in two different ethanol–water solvents of different composition. As an example, the liquid potentials at the junctions: dilute solution X in ethanol–water solvent/KCl(satd., aq.) are tabulated for a number of dilute solutes X and are virtually independent of the nature of the solute.

Concordant values for the autoprotolysis constants of the ethanol–water solvents are derived from three independent potentiometric methods. Consequently values of the function $f_{OH} = K_W/K_S f_H$ are calculated. f_{OH} is equal to the ratio of the acidity constant (as defined by Brönsted[18]) of water to that of the ethanol–water solvent, and is the equilibrium constant for the reaction lyate^- (extremely dilute, in S) + $\text{HOH}(l) = \text{OH}^-$ (extremely dilute, in water) + S(l). The solvent dependences of f_H and f_{OH} are consistent with predictions based on the known relative acidity and basicity of ethanol and water.

The functions f_H and f_{OH} and equations (i) and (ii) are powerful tools for the elucidation of the detailed mechanism of acid- and base-catalyzed reactions from relative reaction rates in different solvents. The methods for inferring reaction mechanism are illustrated by use of the data for the lyonium ion-catalyzed rearrangement of phenylpropenylcarbinol to its allylic isomer in the system ethanol–water. The function f_H generates an acidity scale $p\text{A}$, and f_{OH} generates a basicity scale $p\text{B}$, with the properties (i) that solutions in different solvents of equal proton activities have equal values of $p\text{A}$ and $p\text{B}$, and (ii) that $p\text{A}$ and $p\text{B}$ reduce to $p\text{H}$ and $p\text{OH}$ in water. A number of good practical approximations to $p\text{A}$ and $p\text{B}$ are discussed. The simplest of these are $p_c\text{A} = -\log f_H - \log c_{\text{SH}^+}$, and $p_c\text{B} = -\log f_{OH} - \log c_{\text{lyate}}$.

Acidity is a chemical concept. An acidity scale must be so defined as to have chemical significance: It must measure the tendency of a solution to donate a proton to a base in a chemical equilibrium or acid-catalyzed reaction. The $p\text{A}$ function,

(1) (a) This work has been supported by a grant-in-aid from the Research Corporation; (b) Atomic Energy Commission Predoctoral Fellow at Florida State University, 1951–1952.