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THE POTENTIOMETRIC MEASUREMENT OF ACID DISSOCIATION CONSTANTS AND pH IN THE SYSTEM METHANOL-WATER. pK$_A$ VALUES FOR CARBOXYLIC ACIDS AND ANILINIUM IONS

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In recent years, acid dissociation constants have become increasingly important as tools in determining molecular structure and in solving questions of organic theory (1, 2). Many measurements have been made using a commercial pH meter and the cell

$$\text{glass electrode/solution X/KCl (sat., aq.)/}Hg_2Cl_2\text{-Hg} \qquad [1]\cdot$$

In this method of measurement it is convenient, by use of a buffer of known pH (3) and of the zero adjustment knob of the meter, to make the potentiometer scale direct-reading in pH units. However, the choice of a standard buffer solution requires some care since the method requires that the junction e.m.f. at the solution X/KCl (sat., aq.) boundary be equal for standard and unknown. For example, if solution X is dissolved in one of the popular, partly organic, solvents such as 50% methanol, the standard buffer should also be made up in 50% methanol and should resemble solution X as nearly as possible with respect to solute concentration and structure. Unfortunately, the requisite thermodynamic data are scarce in solvents other than pure water.

In the present paper, we report measurements of thermodynamic pK$_A$ values for a series of carboxylic acids and anilinium ions in methanol-water mixtures containing up to 95% (vol.) methanol. The new data enable us to re-examine pH measurements with cell 1 or its variants, and to propose standard buffer solutions and procedures.

MEASUREMENT OF K$_A$ VALUES

Principle of the method. The acid dissociation constants were measured potentiometrically, using a Beckman model G or model GS pH meter and the cell,

$$\text{glass electrode/}H^+(c_H),\ Cl^-(c_{Cl}),\ \text{other solutes, methanol-water/AgCl-Ag} \qquad [2].$$

The method of measurement employs the principle of the differential method (4, 5) but is simpler than the latter. The method has proved so satisfactory that we wish to describe it more fully.

A known amount of strong acid (in our case, HCl) is added to a solution of the weak acid HA, and the e.m.f. is measured. Sufficient NaOH then is added to neutralize all of the strong acid and some of the HA, and the e.m.f. is again measured. In the first solution, c_H depends chiefly on the amount of strong acid added since it represses the ionization of HA, whereas in the second solution c_H depends on the $HA = H^+ + B$ equilibrium and hence on K$_A$. If we define a quantity ϵ by the equation

$$\epsilon = [Eq(HA) + Eq(HCl) - Eq(NaOH)]/Eq(HA) \qquad [3].$$

(Eq = equivalents added to the cell), the fundamental expression for K_A is

$$\frac{c_H[c_H - (\epsilon - 1)c]}{[\epsilon c - c_H]} = K_A \frac{y_{HA}}{y_H y_B} \equiv k_A \qquad [4].$$

where $c = c_{HA} + c_B$, and the y's are molar activity coefficients (5). Experimentally we measure the ratio c_H'/c_H'' of the hydrogen ion concentrations in the two solutions. Upon solving [4] for c_H we find

$$c_H'/c_H'' = Z'/Z'', \qquad [5].$$

where

$$Z = (\epsilon - 1)c - k_A + [(\epsilon - 1)^2c^2 + 2k_Ac(1 + \epsilon) + k_A^2]^{\frac{1}{2}} \qquad [6].$$

Z' and Z'' are the values of Z at the two experimental points. Since Z'/Z'' is a function of k_A', k_A'', and hence of K_A, the latter may be evaluated.

Nature of the cell. We used cell [2] rather than the more conventional cell [1] chiefly because it has no liquid junctions (except at the glass membrane of the glass electrode). The glass electrode gave stable, reproducible readings in all solvents, including 95% methanol, even with solutions as dilute as 0.0001 *M*.* In contrast to cells employing the Pt-H_2(g) or quinhydrone electrodes (7–9), cell [2] is relatively free from irreversible side reactions.

The preparation of the silver-silver chloride electrode required special care. In solvents containing up to 80% methanol, we obtained satisfactory results with the thermal-electrolytic (Harned's type II) electrode (10), as determined by the following criteria: K_A values in water were in good agreement with previous results; for all acids, K_A values were constant in a given medium within the precision of the potentiometric data over wide ranges of all independent variables (c', ϵ', c'', ϵ''). By these criteria, the results obtained in 95% methanol were not satisfactory, as shown by some data for acetic acid in Table I. Further experiments showed that the e.m.f. for a given solution in the cell depended on the length of time the electrode was kept in the solution (11). The problem was finally solved by preparation of a silver mirror-electrolytic silver chloride electrode. With this electrode, the cell e.m.f. proved to be completely reversible, and K_A values were constant over wide ranges of ϵ'', as shown in Table I.

Molar activity coefficients. Since cell [2] enables measurements to be made at very low ionic strengths, activity coefficients y may be predicted with good accuracy from the interionic attraction theory. In solvents where ion-pair formation may be neglected (12), y is given for 1–1 electrolytes by

$$-\log y = S\sqrt{\mu}/(1 + As\sqrt{\mu}) \qquad [7].$$

In equation [7], $S = 1.825 \times 10^6/(DT)^{3/2}$, $A = 50.30 \times 10^8/(DT)^{1/2}$, s is the "distance of closest approach" of the ions and μ is the ionic strength; D is the solvent dielectric constant and T the absolute temperature. In principle, s is a function of solvent and electrolyte, but in practice, s is usually found to be *ca.*

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* In one previous case (6), 95% ethanol, we noted that the e.m.f. of cell [2] drifted slowly but significantly with time.

TABLE I

DATA FOR CELL [2] WITH VARIOUS Ag-AgCl ELECTRODES: COMPUTED pK_A VALUES FOR ACETIC ACID IN 95% (VOL.) METHANOL, 25.0°

Thermal Silver-Electrolytic Silver Chloride		Silver Mirror-Electrolytic Silver Chloride	
$1 - \epsilon''$	pK_A (calc'd)[a]	$1 - \epsilon''$	pK_A (calc'd)[a]
0.0015	7.90	0.163	7.853
.0058	7.84	.331	7.853
.010	7.83	.415	7.856
.032	7.81	.500	7.858
.054	7.80	.584	7.854
.076	7.79	.673	7.876

[a] y-values calulated from equation [7].

5.0 Å (9, 12). Moreover, As $\sqrt{\mu}$ is only a small correction term in dilute solution, and we have therefore used s = 5.0 Å as an adequate approximation in all calculations. Numerical values of D, S, and 5.0 A $\times 10^{-8}$ for various methanol-water mixtures at 25.0° are given in Table II.

In cases where ion-pair formation is not negligible, the total activity of a given ionic species is equal to the activity of the dissociated fraction of the species (12, 13). Thus, if αc is the concentration and y' is the activity coefficient of the free ions (α being the degree of dissociation), the activity is given by

$$a = \alpha c y' \tag{8}$$

In the treatment of ion pair formation, it is useful to distinguish between "loose" or solvent-separated ion pairs, and "intimate" or "touching" ion pairs (14–16). Solvent-separated ion pairs exist by virtue of the Coulomb attraction between solvated ions. The order of magnitude of this phenomenon in a given solvent may be estimated from Bjerrum's theory when D and s are known (17, 18). On this basis, taking s = 5.0 Å, α is predicted to be 0.950 and 0.982, respectively, in 95% and 80% methanol for 1–1 electrolytes at 0.01 *M* concentration. At higher dielectric constant or lower concentration, α is even closer to unity. Since most

TABLE II

PHYSICAL CONSTANTS OF METHANOL-WATER SOLVENTS, 25.0°

% Methanol by		D[a]	S	(5.0 A) × 10^{-8}
(vol.)	(wt.)			
20	16.47	71.47	0.5866	1.722
40	34.47	63.49	.7005	1.828
50	44.10	59.03	.7815	1.896
60	54.20	54.34	.885	1.976
80	75.94	44.43	1.197	2.185
95	93.74	36.04	1.638	2.426

[a] Albright and Gosting, *J. Am. Chem. Soc.*, **68**, 1061 (1946).

of our data were obtained at ionic strengths well below 0.01 *M*, the formation of solvent-separated ion pairs has been neglected.

The prediction of the order of magnitude of intimate ion pair formation in our systems is not possible at the present time. However, we may infer from the constancy of the computed K_A values that it, too, may be neglected. (See Tables I, VI) Thus we have used equation [7], with $s = 5.0$ Å, in all calculations of y.

Accuracy of cell [2]. We speak of cell [2] as being accurate if the cell e.m.f. measures the activity product $a_H a_{Cl}$: according to the e.m.f. relation

$$E = E^* - (RT/F) \ln a_H a_{Cl} \qquad [9].$$

E is the measured e.m.f. (in volts), R the gas constant per mole, F the coulombs per faraday, and E* the reference e.m.f. of the silver-silver chloride electrode with respect to the glass electrode. We use E* rather than the more conventional symbol E° in order to emphasize that E* for a given solvent and temperature is constant only for a given glass electrode. In fact, E* values vary somewhat for different commercial glass electrodes, as shown by the data for two glass electrodes in Table III.

The question of accuracy is important even if we suppose that our criteria for silver-silver chloride electrodes are reliable. It is well known that glass electrodes become inaccurate in aqueous solution at both ends of the *p*H range. Due to the lower basicity of solvents of high alcohol content (19), it is plausible that the *absolute* acidity or *proton activity* is high even at rather low lyonium ion concentrations, and the glass electrode may conceivably give inaccurate, though stable, readings.

In order to test cell [2], we have measured the e.m.f. of solutions of known $a_H a_{Cl}$ in 95% methanol. Rearranging equation 9 and using numerical values at 25.0° and equation [7] we obtain for E*,

$$E^* = E + 0.05915 \log c_H c_{Cl} - 0.11831\ S \sqrt{\mu}/(1 + As\sqrt{\mu}) \qquad [10].$$

As is shown in Table III, the computed values of E* are satisfactorily constant, the variations being within the precision of the potentiometer. This is shown with good sensitivity by the data obtained with the Beckman Model GS *p*H meter whose precision is *ca.* 0.1 mv. Thus cell [2] is accurate over the *p*H range tested.

In the pK_A determinations of the weaker acids, equation [10] was used at *p*H values higher than those of the test range. Here we infer from the constancy of the calculated pK_A values that this extrapolation is permissible. If there were error, the error would increase progressively with *p*H, and the pK_A values would drift.

Calculation of K_A *values.* The calculation is based on equations [5] and [6]: c_H'/c_H'' is obtained from the experimental values of E', E'', c_{Cl}', c_{Cl}'', μ' and μ'' *via* equation [10]. Next, a plausible first estimate is made for K_A, and k_A', k_A'', Z' and Z'' are computed from equations [4] and [6]. If the ratio Z'/Z'' is greater than c_H'/c_H'', the assumed value of K_A is too small, and the calculation is repeated using a greater value. The process is continued until c_H'/c_H'' lies between two computed values Z'/Z''. To obtain the correct value of K_A, Z'/Z''

TABLE III

DATA FOR CELL [2] IN 95% (VOL.) METHANOL, 25.0°

Solute	10^3c_H	10^3c_{Cl}	$-E^{*a}$
Glass Electrode A			
HCl	0.975	0.975	0.6182[b]
	1.950	1.950	.6181[b]
	2.925	2.925	.6181[b]
	4.875	4.875	.6181[b]
	24.38	24.38	.6181[b]
Glass Electrode B			
HCl	0.10 to 0.69		.5692[c]
			±.0004
Aniline•HCl, HCl	0.765	4.195	.5691[c]
	1.182	3.005	.5690[c]
N-Methylaniline•HCl, HCl	0.932	4.544	.5689[c]
	0.868	2.824	.5690[c]
N-Dimethylaniline•HCl, HCl	1.120	7.122	.5684[c]

[a] Calculated from equation 10. [b] Measured with Model GS *p*H meter. [c] Measured with Model G *p*H meter.

is plotted *vs.* the assumed K_A. K_A is correct when $Z'/Z'' = c_H'/c_H''$. To illustrate the procedure, we are showing some sample data in Table IV, and the graphical evaluation of K_A from these data in Figure 1. In Figure 1, the solid vertical line intersects the correct value of K_A, and the dotted lines show the limits of error, based on the known error in c_H'/c_H''. By the procedure just described, the calculation of K_A from the experimental data takes about 30 minutes. The finding of the correct value of K_A from a first estimate is greatly facilitated by the approximate relationship,

$$K_A/K_A(\text{assumed}) = [(Z'/Z'')/(c_H'/c_H'')]^2 \qquad [11].$$

K_A VALUES IN METHANOL-WATER

We have measured K_A values for formic, acetic, propionic, butyric, and benzoic acid and for anilinium, N-methylanilinium, and N-dimethylanilinium ion in methanol-water solvents contaning up to 95 vol.-% methanol. The results are shown in Table V, together with the available (20, 21) pK_A values in 100% methanol. Each K_A value is the average of 2–5 determinations covering wide

TABLE IV

SAMPLE DATA FOR PROPIONIC ACID, 60 VOL.-% METHANOL, 25.0°

$10^4c'$, c'': 78.02, 77.46; y', y'': 0.9655, 0.9590;
$10^4\mu'$, μ'': 3.188, 4.599; ϵ', ϵ'': 1.0409, 0.9815;
$E' - E''$: −0.946 c_H'/c_H'': 8.64 ± .12
10^7K_A(assumed), Z'/Z'': 9.00, 8.47; 8.50, 8.84; 8.00, 9.26

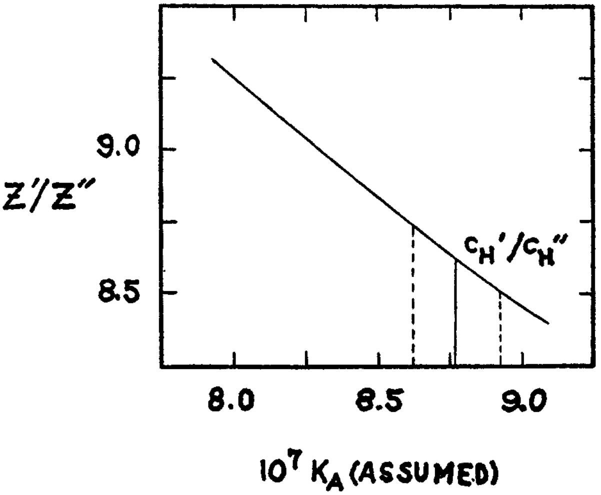

FIG. 1. GRAPHICAL EVALUATION OF K_A

ranges of all the independent variables, as is illustrated by some typical data in Table VI. The average precision of the K_A values is within 3 %, and careful consideration of all known sources of error indicates that the accuracy should be within 5 %.

Excepting the data for benzoic acid, there is good agreement with previously reported K_A values in all cases where legitimate comparisons can be made. All our data in water are in excellent agreement with previous values (6, 17, 22). Our data for acetic and propionic acid fall on a single smooth curve with those reported for 10 and 20 weight-% methanol (23, 24). Our (interpolated) pK_A value for anilinium ion in 50 vol.-% methanol, 4.24, agrees adequately with the value, 4.25, calculated from the data of Kuhn and Wasserman (25) at 18°. How-

TABLE V

pK_A VALUES IN THE SYSTEM METHANOL-WATER, 25.0°

Acid	Methanol, % by volume						
	0	20	40	60	80	95	100
Formic	3.745	3.919	4.159	4.597	5.282[d]	6.542	—
Acetic	4.756	5.011	5.334	5.808	6.500	7.858	9.720[b]
Propionic	4.869	5.150	5.572	6.053	6.813	—	—
Butyric	4.809	5.123	5.597	6.081	6.816	—	—
Benzoic	4.201	4.514	4.967	5.536	6.286	7.473[d]	9.380[a]
Anilinium	4.620	4.463	4.322	4.168	4.068	4.613	5.804[a]
N-Methylanilinium	4.848	4.698	4.476	4.177	3.900	4.149	5.27[c]
N-Dimethylanilinium	5.150	4.964	4.726	4.306	3.821	3.953	5.02[c]

[a] Ref. 20a. [b] Calculated from relative pK_A values of ref. 20b and pK_A for benzoic acid. [c] Calculated from relative pK_A values of ref. 21 and pK_A for anilinium ion. [d] Measured with cell [18].

TABLE VI

DATA FOR ANILINE•HCl IN 80 VOL.-% METHANOL, 25.0°

$10^3c'$	$10^3\mu'$	$\epsilon' - \epsilon''$	c'_H/c''_H	10^5K_A
2.78	3.83	.379	3.44	8.68
3.93	5.03	.280	2.95	8.30
4.17	4.63	.226	2.47	8.45
7.58	8.45	.230	3.20	8.76

ever, our pK_A values for benzoic acid in 20 and 50 vol.-% methanol are 0.1–0.2 unit below those reported previously (25, 26). The reason for this discrepancy is not clear. The previous workers have used Pt-H_2(g) or quinhydrone electrodes, and these electrodes are known sometimes to behave abnormally in benzoate solutions (7, 8). Our own values have been independently verified by two of the present authors.

*p*H MEASUREMENTS IN CELLS WITH A LIQUID JUNCTION

Theory of the junction e.m.f. The present discussion is limited to cells like cell [1] or its variants which contain a liquid junction between a dilute solution of variable solute composition and a concentrated solution (*e.g.*, sat. KCl) of fixed composition. In modern practice, the junction is usually made *via* a porous plug of high mechanical impedance, such as an asbestos fibre sealed into a glass capillary, or a ground glass joint. The junction e.m.f. may be computed to a first approximation if the nature of the boundary region is known. In Planck's model, the two solutions are brought in contact through a porous plug which prevents bulk mixing of the two surface layers but permits diffusion of the ions. In Henderson's model, the contact is established by rapid mixing of the surface layers during which time diffusion is negligible (27, 28). The physical nature of the actual junction is almost certainly intermediate between these two extremes.

If the two solutions are in the same solvent, the e.m.f. at the junction

solution 1 (dilute)/solution 2 (concentrated)

is given, assuming $c_1 \ll c_2$, by the expression (27):

$$\text{Diffusion boundary: } E_L = \left(\frac{U_2 - V_2}{U_2 + V_2}\right)\frac{RT}{F}\ln\frac{c_1}{c_2} \qquad [12].$$

$$\text{Mixture boundary: } E_L = \left(\frac{U_2 - V_2}{U_2 + V_2}\right)\frac{RT}{F}\ln\frac{U_1 + V_1}{U_2 + V_2} \qquad [13].$$

where

$c_1(c_2)$ = total concentration (in equivalents per liter) of electrolyte in solution 1 (2)

$U_1(U_2)$ = $\Sigma c_i\lambda_i$ over all cations in solution 1 (2)

$V_1(V_2)$ = $\Sigma c_i\lambda_i$ over all anions in solution 1 (2)

c_i = normal concentration of i-th ionic species

λ_i = equivalent conductance of i-th ionic species

If we write $U_1 + V_1 = \Lambda_1 c_1$ and $U_2 + V_2 = \Lambda_2 c_2$ (where the Λ's are the equivalent conductances of solutions 1 and 2), the arguments of the logarithms in expressions [12] and [13] differ by the term Λ_1/Λ_2. As the electrolyte in solution 1 is varied, the range of c_1 amounts to several powers of 10, whereas the variation of Λ_1 is well within a factor of 3 for all electrolytes except in certain cases such as HCl or NaOH in water. Therefore in equation [13], the major variable entering the logarithmic term is c_1. Since this is the sole variable in equation [12], and since the actual liquid junction is intermediate between the models leading to [12] and [13], we propose to use equation [12] as a basis for further discussion.

The important feature of equation [12] is that the junction e.m.f. is a constitutive property of the electrolyte in solution 2 (through U_2 and V_2), but is a *colligative function* of normal concentration in solution 1. By choosing an electrolyte in solution 2 for which $U_2 \doteq V_2$, E_L can also be made small. Consequently cell [1] is a suitable basis for *p*H-measurement.

When solution 2 contains saturated potassium chloride, equation [12] reduces to, at 25.0°:

$$E_L = 0.05915 \frac{\lambda_K - \lambda_{Cl}}{\lambda_K + \lambda_{Cl}} \log \frac{c_1}{s_{KCl}} \qquad [14].$$

where s_{KCl} is the solubility of potassium chloride in the given solvent. The e.m.f. of cells of the type.

Hydrogen electrode or glass electrode/solution X (c_1 solvent Y)/

KCl (s_{KCL}, solvent Y)/Hg_2Cl_2–Hg or Ag Cl–Ag [15].

is then given by the expression

$$E = A^* - 0.05915 \log a_H + 0.05915 \frac{\lambda_K - \lambda_{Cl}}{\lambda_K + \lambda_{Cl}} \log c_1 \qquad [16].$$

where A^* is the sum of several constant terms characteristic of the electrode pair and solvent.

Application to data in aqueous solution. In water at 25.0°, $\lambda_K = 73.52$, $\lambda_{Cl} = 76.34$ (29), and hence the coefficient of $\log c_1$ in equation [16] is 1.04×10^{-3}V. In order to test equation [16], we make use of the e.m.f. data for the cell

H_2/solution X (aq.)/KCl (sat., aq.)/KCl (0.1N, aq.)/Hg_2Cl_2-Hg [15a].

Bates has summarized the available data for a number of buffer solutions whose a_H values can be computed independently on the basis of known K_A values and

TABLE VII

E.M.F. DATA FOR CELL [15a] CONTAINING CHLOROACETIC ACID-SODIUM CHLOROACETATE BUFFER, 25.0°

c_1	E (v)	$-\log a_H$	$E + .05915 \log a_H$	A^* (v)
0.0019	0.5176	3.077	0.3356	0.3328
.0114	.5075	2.924	.3345	.3325
.0184	.5056	2.900	.3341	.3323

TABLE VIII

VALUES OF B AND A* FOR VARIOUS BUFFER SYSTEMS IN CELL [15a], 25.0°

Buffer System	Range of c_1	B (mv)	A* (v)
Acetic acid-Sodium acetate	0.001-0.01	−0.8	0.3329
Chloroacetic acid-Sodium chloroacetate	.002- .02	−1.5	.3325
Glycolic acid-Lithium glycolate-Li Cl	.01 - .02	−2.7	.3328
KH_2PO_4-Na_2HPO_4	.015- .075	−0.9	.3338
Borax	.01 - .05	−1.4	.3333
HCl	.02 - .04	0.0	.3335
HCl-KCl	.02 - .04	−2.0	.3332
HCl-NaCl	.02 - .04	−3.0	.3326
		Ave. −1.5 ± 0.8	

the interionic attraction theory (3). Some typical data for chloroacetic acid-sodium chloroacetate buffers are shown in Table VII. It is seen that the quantity $E + 0.05915 \log a_H$ decreases significantly with increasing c_1, and that the predicted correction term $0.00104 \log c_1$ considerably reduces this drift, as shown by the better constancy of A*. In order to further test the theory, we have written equation [16] in the form

$$E = A - 0.05915 \log a_H + B \log c_1 \qquad [17].$$

where A and B are treated as empirical constants.† Values of A* and B have been computed from Bates' data (3) for a number of buffer systems and are shown in Table VIII. It is seen that B values are generally near the predicted value of −1.04 mv., the deviations being greatest for the less accurate values which are obtained from data covering only a narrow range of c_1. The average value of B is −1.5 ± 0.8 mv., in adequate agreement with theory.

In the determination of the *p*H of aqueous solutions with cell [1], it is fairly general practice to compute *p*H from equation [17] with B = 0. A is evaluated by means of a standard buffer. Since the actual magnitude of B is small, this procedure results in considerable error only in the rare cases when c_1 is very different for buffer and unknown. However, the use of the term $-0.00104 \log c_1$ does improve the accuracy of the measured value, and we recommend its use.

Application to methanol-water solutions. We have used equation [17] in the calculation of $\log a_H$ from e.m.f. values of the cell

glass electrode/solution X (in 80% or 95% methanol)/KCl (sat., in 80% or 95% methanol)/AgCl-Ag [18].

The constants A and B were evaluated from data for hydrochloric acid. This acid is suitable for this purpose since a_H can be estimated directly from the stoichiometric concentration and equation [7] for y, and since its equivalent conductance is not unusual compared to that of other electrolytes in 80% or 95% methanol (21, 30). Plots of $E + 0.05915 \log a_H$ *vs.* $\log c_1$ are shown in

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† The symbol A* is used when the coefficient of $\log c_1$ is obtained from conductivity data, and the symbol A is used for the intercept of the plot of $E + 0.05915 \log a_H$ *vs.* $\log c_1$.

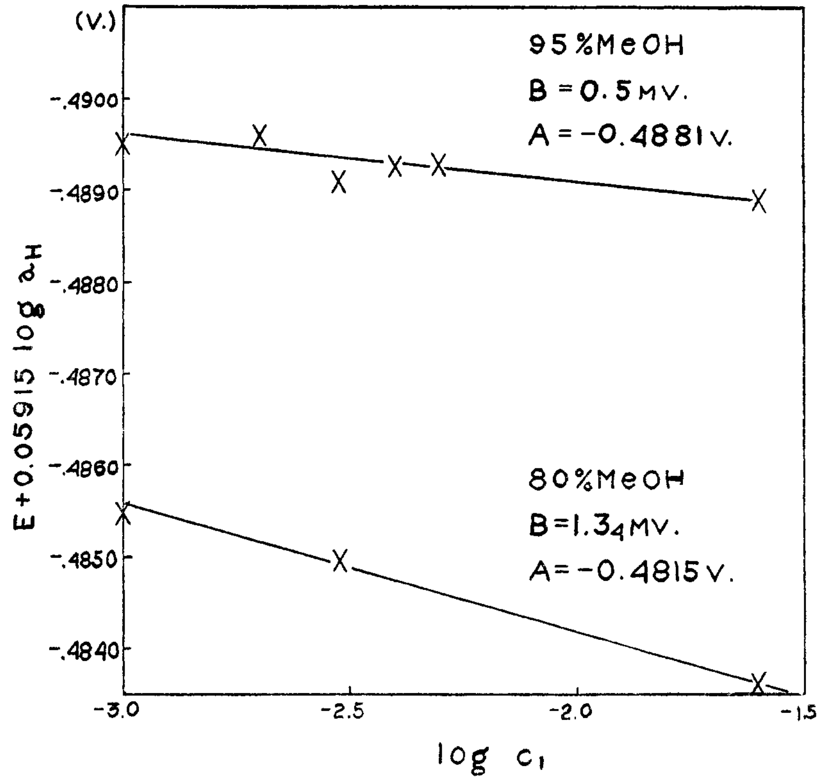

FIG. 2. TEST OF EQUATION 17. DATA FOR HYDROCHLORIC ACID, 25.00°

Figure 2. Within experimental error, the trends of the data are linear, as required by equation [17], and the computed values of A and B are listed in Figure 2. In order to test whether this method gives accurate a_H values also for other solutes, we measured the e.m.f. of several buffer solutions containing a carboxylic acid and its sodium salt in cell [18]. From these data and from the known values of the concentrations, we calculated a_H *via* equation [17] and K_A *via* equations [4] and [7]. The results are compared with K_A values obtained by means of cell [2] in Table IX. The agreement of the two sets of data is excellent, thus confirming the validity of equation [17].

In order to show the sensitivity of the K_A values to the method of calculation of a_H from the e.m.f. data, we have calculated K_A also without allowing for the variation of E_L with c_1. The presumed relationship between e.m.f. and a_H was

$$E = C - 0.05915 \log a_H. \qquad [19].$$

The constant term C was the average of all the values obtained from the HCl data, and this value was then used to calculate a_H and hence K_A for the buffer solutions. As is shown in Table IX, the difference between pK_A values based on equation [19] and those based on [17] is inappreciable in 95% methanol where B is small, but amounts to several times the limit of precision for our data in

TABLE IX

Comparison of pK_A Values, 25.0°

Acid	Cell [2]	Cell [18] Equation [17]	Cell [18] Equation [19]
80% Methanol			
Benzoic	6.286 ± .011	6.280 ± .002	6.329 ± .008
Acetic	6.500 ± .020	6.517 ± .013	6.540 ± .017
95% Methanol			
Formic	6.542	6.547 ± .006	6.548 ± .008
Acetic	7.858 ± .009	7.862 ± .007	7.863 ± .009

80% methanol. It is clear that calculation of a_H on the basis of equation [19] results in unnecessary loss of accuracy.

In spite of the evident advantage of equation [17], it must be stressed that this equation is still not exact. For example, in 95% methanol where B is taken as 0.5 mv., A = −0.4881 v. for HCl solutions, but −0.4891 v. for $HClO_4$-$NaClO_4$ solutions. Other examples are shown in Table VIII. The variations of A with solute structure are usually within 1 mv., so that log a_H values for unknowns should be accurate to better than 0.02 unit when obtained by this method.

pH Measurement. In solvents other than water, it is useful to distinguish between two acidity-measuring functions, *pA* and *pH*, defined as follows:

$$pA = -\log a_{\oplus} \qquad [20].$$

$$pH = -\log a_H \qquad [21].$$

The pA function measures the actual proton activity $a_{\oplus}$ of the given solution (19, 31), whereas pH measures the molar lyonium ion activity referred to the extremely dilute solution in the given solvent. The pA scale of methanol-water solutions will be discussed more fully in a subsequent paper (32). In the present discussion of pH, we accept the basic equation [21], but avoid the problems arising from the impossibility of measuring the molar activity of single ions (33, 34) by using the operational definition

$$pH = -\log c_H + S\sqrt{\mu}/(1 + As\sqrt{\mu}) \qquad [22].$$

Equation [22] has been the basis for discussion in the preceding sections.

In the measurement of pH with commercial pH meters and cell [15], it is customary to use a buffer of known pH, set the meter scale to the known pH value, and adjust the zero adjustment knob until the meter is in balance. The scale is then presumed to read directly the pH of unknowns. This procedure neglects the variation of E_L with the nature of solution X and therefore is accurate to the same degree as equation [19]. Errors of the order of 0.1 unit are entirely possible.

The error may be reduced to less than 0.02 unit if equation [17] is made the basis of *p*H measurement. In this case, it is natural to make the *p*H-meter scale direct reading in the quantity

$$pH + B' \log c_1 = L \qquad [23].$$

where $B' = BF/RT$ and L the *p*H-meter scale reading. Thus one would use a buffer of known *p*H and c_1, set the meter scale to the known value of $pH + B' \log c_1$, and adjust the zero adjustment knob until the meter is in balance. The scale will then read directly the values of $pH + B' \log c_1$ for unknowns. The constant B′ may be evaluated in a given solvent by using two buffers whose known *p*H and c_1 values are pH′, c_1', pH″, and c_1''. If the scale readings are, respectively, L′ and L″,

$$B' = \frac{L' - L'' - (pH' - pH'')}{\log(c_1'/c_1'')} \qquad [24].$$

Since equation [24] contains only the difference of two meter readings, $L' - L''$, zero-adjustment of the meter is not required in the measurement of B′.

Some commercial *p*H meters, *e.g.* the Beckman Model GS meter, are precise to much better than 0.02 unit. For example, the precision of the Beckman Model GS meter is 0.002 unit. In order to measure *p*H with accuracy even approaching this figure, it is necessary not only to make the $B' \log c_1$ correction of equation [23], but also to choose the standard buffers so as to resemble the unknowns as nearly as possible with respect to structure and concentration of solutes.

EXPERIMENTAL PART

Materials. Commercial synthetic methanol was dried by the magnesium method and fractionated through a two-foot column. The middle fraction was analyzed for traces of residual water by Karl Fischer titration and then used to prepare the mixed solvents. Water was redistilled from alkaline permanganate.

The aniline hydrochlorides were prepared from the purified anilines and hydrogen chloride in anhydrous ether as described previously (22) and were stored *in vacuo* prior to use. Benzoic acid was a standard sample obtained from the National Bureau of Standards. Formic acid was reagent grade material in concentrated aqueous solution. It was redistilled at reduced pressure and assayed before use. Acetic, propionic, and butyric acid were reagent grade materials and were purified by distillation at reduced pressure, followed by several cycles of freezing, partial thawing, and rejection of the molten portion. For criteria of purity of the acids, we used the K_A values in water which were in good agreement with reported values (Table V), and the equivalent weights, based on benzoic acid primary standard, which were determined for all acids except formic acid and which were within 0.3% of theory.

Preparation of solutions. The mixed solvents were prepared from the purified components on a 2-kg. analytical balance so as to have the desired volume composition at 25.0°. The solvent compositions were accurate to 0.02%. Standard hydrochloric acid solutions were prepared from constant-boiling hydrochloric acid (35), the mixed solvent, and the calculated amount of pure methanol to allow for the water in the constant-boiling acid. Standard sodium hydroxide solutions were prepared gravimetrically from standard carbonate-free aqueous base and pure methanol. The gravimetric normalities were checked by direct titration and were generally within 0.5%. Solutions of the aniline hydrochlorides and of the carboxylic acids were prepared freshly before use so as to minimize errors due to de-

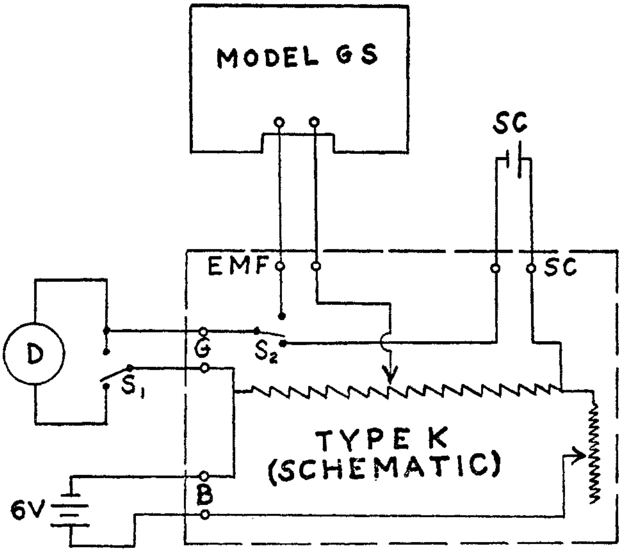

FIG. 3. SCHEMATIC DIAGRAM OF MEASURING APPARATUS

composition and esterification. The aniline hydrochloride solutions remained colorless over periods of time much longer than required for an experiment. N-dimethylaniline hydrochloride was hygroscopic and was handled with special precautions. The esterification of the carboxylic acids was followed by titration and amounted to less than 1% during the period of measurement for all acids except formic acid. Here the rate amounted to several per cent, and the formic acid concentration was determined titrimetrically at the conclusion of each experiment. The outer limit of error of the K_A values due to this cause was estimated as 3%.

Potentiometric procedure I. All pK_A determinations for anilinium salts and all determinations for carboxylic acids in 0–80% methanol by means of the differential method were done with a Beckman Model G *p*H meter. The cell consisted of a 180 ml. electrolytic beaker equipped with two glass electrodes (Beckman #1190-42) and a silver-silver chloride electrode of the Harned type II (10). The volumes of the test solutions ranged from 50 to 100 ml. Details of the thermostating, stirring of the solutions, selection and testing of the glass electrodes, and meter calibration have been previously described (6, 22).

Potentiometric procedure II. The remaining experiments were done with a Beckman Model GS *p*H meter in conjunction with a Rubicon Type K potentiometer. The Model GS *p*H meter differs from the Model G in that the sensitivity of the null detector has been greatly increased and a direct-reading "helipot" has been substituted for the zero-adjustment knob. The circuitry of the Model GS meter is such that the e.m.f. across the input leads is given by

$$E = V_p - V_H \qquad [25].$$

where V_p is the voltage drop across the slide wire of the meter, between the "balance point" of the slide wire* and the given range setting, and V_H is the voltage drop over the engaged portion of the helipot. V_H is directly proportional to the helipot scale setting. For our instrument, 1 scale division corresponded to 0.2000 mv. V_p is measured with the type K potentiometer, as follows.

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* When the input terminals of the meter are shorted and the helipot set at zero, the slide wire (*p*H-dial) can be set so that a null reading is obtained. This setting is called the "balance point" of the slide wire and is found near the middle of the scale.

The helipot is set to zero so that E = V_p, and the e.m.f. output of the type K potentiometer is connected across the input terminals of the Model GS meter. By varying the e.m.f. output of the type K, the e.m.f. value is found at which the galvanometer *of the Model GS meter* is in balance. At this point, the output e.m.f. of the type K is equal to V_p. A schematic diagram of the measuring circuit is shown in Figure 3. The measuring procedure is similar to the standard procedure for the type K potentiometer (36), except that a switch S_1 is provided which shorts the galvanometer terminals G during the measurement of V_p, but connects a detecting device D across G during the slide wire calibration with the standard cell SC. For the detecting device D we used an Industrial Control Co. model 200 DC millivoltmeter (which converts the DC signal to amplified AC), the output of which was read on a Hewlett-Packard model 400C vacuum tube voltmeter. With this device, zero voltage across D is recorded instantly as a sharp minimum on the voltmeter scale. SC was an Eppley standard cell and was calibrated by the National Bureau of Standards. The accuracy of the V_p values was limited by the sensitivity of the detecting device of the model GS *p*H meter and was estimated to be ±0.02 mv.

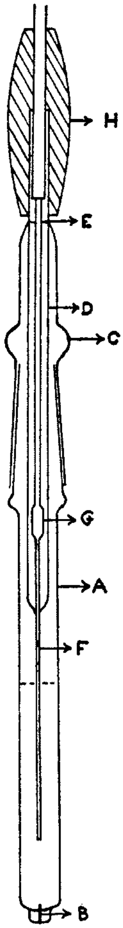

FIG. 4. DIAGRAM OF THE HALF-CELL: KCl(sat.)/AgCl-Ag

Cell e.m.f. measurements were made as follows: First, the slide wire (*p*H dial) of the

Model GS meter was set to a position where $E - V_p$ will fall within the range of V_H, 0–200.0 mv. Next, V_p was measured. Then, with V_p remaining fixed, V_H was varied until the meter was in balance. The measurement of V_H was repeated at suitable intervals until the attainment of electrode equilibrium in the cell had been ascertained. Finally, V_p was measured again to check that the slide wire setting had not been disturbed. The accuracy of the e.m.f. values was within 0.1 mv.

The cell was similar to that used in procedure I. Volumes of solutions ranged from 25–50 ml., and agitation of the cell contents was manual. Temperature control was within 0.02°.

The silver mirror-electrolytic silver chloride electrode. Construction, testing, and performance of this electrode have been reported elsewhere (11).

The half-cell: KCl(sat.)/AgCl-Ag. A diagram of this half-cell is shown in Figure 4. The container, A, consisted of 10 mm. x 100 mm. Pyrex tubing with a 14/35 standard-taper innerjoint at the top. Liquid junction contact with the cell solution was made through an asbestos fibre, B, (*ca.* 0.5 mm. x 5.0 mm.) sealed into the bottom of the container. The electrode cover, C, was a 14/35 standard-taper outer joint with a throughtube, D, (6 mm. Pyrex tubing) attached *via* a ring seal at E. The electrode consisted of a c.p. silver wire, F, (*ca.* 1 mm. diam.) coated with silver chloride. The silver wire was silver soldered to the copper lead at G. A Plaster of Paris cast, H, served to seal the cover and to strengthen the assembly.

The silver wire was cleaned with concentrated nitric acid and aqueous concentrated ammonia, then rinsed with distilled water. A thin coating of silver chloride was then deposited by anodization in 0.1 *M* hydrochloric acid for five minutes with a current of 5 ma. Heavier coatings of silver chloride produced by longer periods of anodization were less satisfactory.

When not in use, the half-cell was kept filled with solvent saturated with potassium chloride. Prior to any series of measurements with a particular solute, the compartment, A, was cleaned and a fresh solution of saturated potassium chloride was added. The asbestos fibre was purged of foreign solutions by attaching the lower tip of compartment A to a water aspirator. Reproducibility was obtained only when these techniques were employed.

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SUMMARY

Thermodynamic pK_A values were measured for formic, acetic, propionic, butyric, and benzoic acid and for anilinium, N-methylanilinium, and N-dimethylanilinium ion in methanol-water solvents containing 0, 20, 40, 60, 80, and 95 volume-percent methanol. The pK_A values were measured by means of the cell: glass electrode/H^+, Cl^-, other solutes/AgCl-Ag, using a Beckman Model G or Model GS *p*H meter and a simple adaptation of the differential potentiometric procedure which is of very general applicability. The glass electrode was found to give accurate e.m.f.'s in these solvents. The preparation of the silver-silver chloride electrode required special care. Measurements were made at ionic strengths below 0.01 *M*, and activity coefficients were obtained accurately from the interionic attraction theory. The data indicated that, at these ionic strengths, the formation of ion pairs can be neglected.

The measurement of *p*H by means of the cell: hydrogen or glass electrode/solution X/KCl(sat.)/Hg_2Cl_2-Hg or AgCl-Ag was reinvestigated. The theories

of Planck and of Henderson lead to nearly equivalent expressions for the junction e.m.f. at the boundary: solution X/KCl(sat.). The expression: $p\mathrm{H} = (\mathrm{F}/\mathrm{RT})\ (\mathrm{E} - \mathrm{A} - \mathrm{B} \log c_1)$, derived on this basis, differs from the usual expression for *p*H by a term proportional to $\log c_1$, c_1 being the equivalent concentration of electrolyte in solution X. According to the theory, A and B are independent of the nature of the solute in solution X. The use of this new expression greatly improves the accuracy of the measured *p*H values.

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