simplest interpretation is in terms of the ionic mechanism of the solvolytic reaction[15]

$$C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2^+ + Cl^-$$
$$C_6H_5CH_2^+ + H_2O \longrightarrow C_6H_5CH_2OH + H^+$$

The decrease in rate produced by the chloride and acetate ions is then attributed to an attack of these ions on the carbonium ion

$$C_6H_5CH_2^+ + Cl^- \longrightarrow C_6H_5CH_2Cl$$
$$C_6H_5CH_2^+ + CH_3COO^- \longrightarrow C_6H_5CH_2OOCCH_3$$

which either returns to the form of benzyl chloride or diverts to that of benzyl acetate some of the carbonium ion which would otherwise be converted to benzyl alcohol. The fact that the effects of chloride and acetate ions are so nearly the same is not a difficulty in view of the ample evidence that no parallelism exists between rate of reaction with carbon and the affinity for protons in the case of reactants so dissimilar in structure as are these ions.[16]

Because of the existence of two relatively improbable alternatives this mechanism cannot be taken to be unambiguously proven by the present data, but is merely given powerful support. The first alternative is that perchlorate reacts with benzyl chloride by a displacement reaction, and that the benzyl perchlorate is very rapidly hydrolyzed. Such a process would increase the total rate of formation of benzyl alcohol, and one might then conclude that chloride and acetate ions exert a salt effect, which, contrary to expectation, is negative, and which is masked in the case of perchlorate by the additional reaction. Certainly there is no measurable accumulation of benzyl perchlorate in the system, because the extent of reaction in the presence of perchlorate determined by acidimetric titration agrees exactly with that obtained by the titration of the chloride ion (Table III). The arguments against the hypothesis that benzyl perchlorate might be instantaneously hydrolyzed have been presented elsewhere.[17] The second alternative is that the salt effect in the solvolysis is a specific one, with perchlorate accelerating, while chloride and acetate retard, the reaction. This also is improbable.

Summary

The rates of the solvolytic or first-order reaction of benzyl chloride and of its second-order displacement reactions with hydroxyl and acetate ions have been measured in a 60.72% dioxane–39.28% water medium at 50°. The reactions exhibit pronounced salt and medium effects with relatively small changes in the nature of the medium, and the specific rates consequently vary with the initial concentrations of the reactants. Both chloride and acetate ions retard the solvolytic reaction, an effect which lends strong support to the hypothesis of an ionic intermediate in this reaction.

NEW YORK, N. Y.

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[15] (a) Ward, *J. Chem. Soc.*, 445 (1927); (b) Gleave, Hughes, and Ingold, *ibid.*, 236 (1935); (c) Hughes and Ingold, *ibid.*, 244 (1935).

[16] Hammett, *op. cit.*, pp. 137, 302, 307.

[17] Roberts and Hammett, THIS JOURNAL, **59**, 1063 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Acidity Scale in Glacial Acetic Acid. I. Sulfuric Acid Solutions. $-6 < H_0 < 0$[1,2]

BY NORRIS F. HALL AND WILLARD F. SPENGEMAN[3]

The ready availability of acetic acid and its properties as a solvent medium make desirable a quantitative survey of the acidity of its solutions. The successful application of colorimetric methods by Hammett and his associates[4-7] to acidity measurements in mixed solvents and in formic acid suggested an extension to this solvent. It was also thought that such a study would provide a desirable re-interpretation of the earlier work of Conant, Hall, and their co-workers[8,9] carried out largely by potentiometric methods.

This paper presents a survey of the values of

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[1] Reported at the Kansas City meeting of the American Chemical Society, April, 1936.

[2] This work was supported in part by a grant from the Wisconsin Alumni Research Foundation.

[3] Present address: care E. I. du Pont de Nemours & Co., 256 Vanderpool St., Newark, N. J.

[4] (a) Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932); (b) **54**, 4239 (1932).

[5] (a) Hammett and Paul, *ibid.*, **56**, 827 (1934); (b) **56**, 830, (1934); (c) **58**, 2182 (1936).

[6] (a) Hammett, Dingwall and Flexser, *ibid.*, **56**, 2010 (1934); (b) **57**, 2103 (1935); (c) Flexser and Hammett, *ibid.*, **60**, 885 (1938).

[7] (a) Hammett, *Chem. Rev.*, **13**, 61 (1933); (b) **16**, 67 (1937); (c) "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 265 ff.

[8] (a) Hall, *Chem. Rev.*, **8**, 191-212 (1931); (b) THIS JOURNAL, **52**, 5115 (1930); (c) Hall and Voge, *ibid.*, **55**, 239 (1933).

[9] (a) Conant, "Equilibria and Rates of Some Organic Reactions," Columbia University Press, New York, N. Y., 1932; (b) Conant and Bramann, THIS JOURNAL, **50**, 2305 (1928); (c) Conant and Werner, *ibid.*, **52**, 4436-50 (1930); (d) Conant and Chow, *ibid.*, **55**, 3745, 3752 (1933).

the acidity function H_0 in solutions of sulfuric acid in acetic acid, ranging in composition from 0.02 to 50% and in H_0 from 0 to −6. The visual colorimetric method employed was essentially that of Hammett[4] and five indicators of the simple basic type were used. However, since Paul and Hammett[5c] have published independent data on acetic acid solutions using two of these indicators, and since our results are in substantial agreement with theirs, our data for *o*-nitraniline are not reported, and the value $pK = -0.91$ for *p*-chloro-*o*-nitroaniline determined by them is used in this paper as the reference point for the stepwise comparison of the other indicators.

Experimental

Materials.—Glacial acetic acid from the Niacet Chemical Company was fractionally distilled in an all-glass still. Acid melting at 16.3° or higher was used. Standard sulfuric acid solutions were prepared by directly weighing out 100% sulfuric acid and acetic acid into volumetric flasks. The composition and density of these stock solutions are listed in Table I. The solutions being measured were made up by mixing definite volumes of the stock solution with definite volumes of acetic acid, assuming no change in volume on mixing. For solutions 3 M or less, the stock solutions could be measured from a micro-buret. For more concentrated solutions, however, it was necessary to weigh out the stock solution because of its viscosity. The acetic acid was measured from a micro-buret.

TABLE I

DENSITY OF SULFURIC ACID–ACETIC ACID MIXTURES AT 25°

$C(H_2SO_4)$ molarity	% H_2SO_4	d^{25}_4	$C(H_2SO_4)$ molarity	% H_2SO_4	d^{25}_4
0.1240	1.157	1.051	6.117	43.42	1.382
0.2472	2.288	1.059	7.712	52.05	1.453
1.362	11.90	1.123	8.283	55.00	1.477
3.587	28.04	1.255	9.087	58.97	1.511
4.539	34.11	1.305	13.39	78.55	1.672
5.098	37.53	1.332			

Clear 100% sulfuric acid was made by mixing 95% acid with fuming acid until a maximum freezing point was obtained (10.2–10.5°). The fuming sulfuric acid was made by distilling sulfur trioxide from 30% fuming sulfuric acid into 95% acid in an all-glass still. This procedure was necessary because the fuming acid as purchased always gave brown solutions.

Benzene-azodiphenylamine (E. K. Co.) was recrystallized from a water–alcohol mixture, m. p. 86°. *o*-Nitraniline (E. K. Co.) recrystallized from alcohol, m. p. 74°. *p*-Chloro-*o*-nitroaniline was prepared from its hydrochloride (E. K. Co.) and recrystallized from water, m. p. 116°. 2,4-Dichloro-6-nitroaniline was prepared by the chlorination of 4-chloro-2-nitroaniline by the method of Witt.[10] The product was recrystallized from alcohol, from water, and then from a 1-liter alcohol water mixture, m. p. 102°. 2,6-Dinitro-4-methylaniline was prepared by the nitration of aceto-*p*-toluidide according to the method of Jackson and Ittner,[11] and was recrystallized from an acetone–water mixture, m. p. 168°. N,N-Dimethyl-2,4,6-trinitroaniline was prepared from picryl chloride and dimethylamine according to the method of Von Romburgh[12] and recrystallized from glacial acetic acid, m. p. 141–142°. All the indicators were used as 0.01 M solutions in acetic acid.

Procedure.—The indicator solution was added to the sulfuric acid solution from a micro-buret and the acid concentration of the solution corrected for the volume of indicator added. A comparison standard was made by adding a definite volume of indicator to a definite volume of pure acetic acid. It had been determined previously that all the bases used in the sulfuric acid mixtures were entirely in the non-ionized or colored form in the pure solvent.

For solutions less concentrated than 2 M, colorimetric comparisons were made in a 100-mm. Bausch and Lomb colorimeter. For solutions more concentrated than 2 M, it was found necessary to compensate for the color of the sulfuric acid solutions. Many attempts were made to prepare colorless sulfuric acid–acetic acid mixtures, but even with the greatest of care the mixtures had a slight tinge of brown which made comparison with pure acetic acid impossible or uncertain. This difficulty was overcome by the use of a compensating solution, using a Bausch and Lomb hydrogen-ion colorimeter. Measurements were made at room temperature, about 23°, since it had been previously determined that the temperature variations that occurred did not affect the comparisons within the precision of visual matching.

Results and Discussion

Table II contains the results obtained covering a range of concentration up to 8 M sulfuric acid in acetic acid. The results obtained for *o*-nitraniline, which are not shown, and for *p*-chloro-*o*-nitroaniline are in good agreement with those obtained by Hammett and Paul.[5c] The strength in per cent. was computed from the molarity, M, and the density obtained from a smooth plot of the density data, given in Table I, against the molarity. The ionization ratio, $(BH^+)/(B)$, for each colorimetric comparison was computed from the equation derived by Hammett and Deyrup[4a]

$$\frac{(BH^+)}{(B)} = \frac{S}{I} - 1 \qquad (1)$$

For the case of an indicator which is non-ionized and colored in the pure solvent, I, the "stoichiometric color intensity relative to the solvent," is defined by the equation

$$I = \frac{C_s L_s}{C_a L_a} \qquad (2)$$

where C_a and C_s are the total concentrations of the indicator in solution A and in the pure solvent,

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(10) Witt. *Ber.*, **8**, 820 (1875).

(11) Jackson and Ittner, *Am. Chem. J.*, **19**, 6 (1897).

(12) Von Romburgh, *Rec. trav. chim.*, **2**, 105 (1883).

TABLE II

IONIZATION OF INDICATORS IN SULFURIC–ACETIC ACID MIXTURES AT 23°

% H_2SO_4	Molarity $C(H_2SO_4)$	I	$\log \frac{(BH^+)}{(B)}$	H_0
No. 1, *p*-chloro-*o*-nitroaniline, S = 1.00, pK = −0.91				
0.031	0.00326	0.91	−1.00	+0.09
.050	.0053	.86	−0.77	− .14
.097	.0103	.72	− .42	− .49
.193	.0205	.59	− .15	− .76
.385	.0411	.40	.18	−1.09
		.38	.21	−1.12
756	.0808	.198	.61	−1.52
1.50	.161	.109	.91	−1.82
2.23	.241	.087	1.02	−1.93
2.52	.272	.053	1.26	−2.17
3.35	.363	.042	1.36	−2.27
3.91	.426	.034	1.45	−2.36
4.00	.437	.0278	1.54	−2.45
5.89	.651	.0177	1.74	−2.65
7.07	.786	.023	1.63	−2.54
7.77	.868	.0155	1.80	−2.71
9.14	1.029	.0097	2.01	−2.92
13.96	1.621	.0056	2.25	−3.16
No. 2, 2,4-Dichloro-6-nitroaniline, S = 1.00, pK = −3.67				
2.38	0.245	0.99	−2.00	
10.90	1.240	.93	−1.10	
11.64	1.332	1.06		
12.56	1.445	0.97	−1.44	
12.84	1.479	.95	−1.28	
14.68	1.712	.79	−0.56	
14.71	1.716	.81	− .64	
15.30	1.794	.74	− .46	−3.21
17.98	2.145	.59	− .16	−3.51
20.19	2.441	.52	− .03	−3.64
21.74	2.589	.45	.09	−3.76
24.68	3.077	.337	.30	−3.97
26.12	3.291	.275	.42	−4.09
26.31	3.321	.307	.35	−4.02
27.60	3.517	.264	.45	−4.12
27.63	3.521	.273	.43	−4.10
31.34	4.093	.155	.74	−4.42
32.70	4.318	.096	.97	−4.64
36.64	4.961	.061	1.19	−4.86
40.06	5.551	.034	1.45	−5.13
43.45	6.145	.016	1.79	−5.46
No. 3, 2,6-Dinitro-4-methylaniline, S = 1.16, pK = −4.45				
8.71	0.978	1.04	−0.94	
11.22	1.28	1.19		
12.85	1.48	1.20		
13.00	1.50	1.20		
15.74	1.85	1.31		
17.05	2.02	1.05	− .98	
17.46	2.07	1.27		
18.85	2.26	1.03	− .90	
20.39	2.47	1.17		
20.69	2.51	1.14	−1.74	
21.05	2.56	1.06	−1.02	
21.82	2.67	1.04	−0.94	
23.37	2.89	0.95	− .66	−3.79
24.20	3.01	0.92	−0.59	−3.86
24.40	3.04	1.02	− .86	
25.08	3.14	0.93	− .60	−3.85
25.97	3.27	.76	− .28	−4.17
26.36	3.33	.88	− .50	−3.95
26.58	3.36	.83	− .40	−4.05
28.13	3.60	.69	− .17	−4.28
31.75	4.16	.53	.08	−4.53
32.49	4.28	.50	.12	−4.57
35.24	4.60	.41	.26	−4.71
36.08	4.87	.39	.30	−4.75
38.52	5.29	.26	.54	−4.99
40.68	5.66	.226	.62	−5.07
43.23	6.10	.129	.90	−5.35
46.04	6.61	.070	1.19	−5.64
48.94	7.14	.039	1.46	−5.91
52.45	7.81	.030	1.58	−6.03
No. 4, N,N-Dimethyl-2,4,6-trinitroaniline, S = 1.50, pK = −4.73				
2.78	0.301	1.04	−0.36	
4.65	.510	1.17	− .55	
7.85	.877	1.30	− .81	
11.38	1.16	1.34	− .92	
16.90	2.00	1.42	−1.25	
19.28	2.32	1.49	−2.16	
21.26	2.59	1.58		
21.47	2.62	1.41	−1.19	
21.74	2.66	1.52		
23.49	2.91	1.48	−1.89	
28.21	3.61	1.34	−0.92	
30.93	4.03	1.27	− .74	
32.36	4.26	1.12	− .47	
33.80	4.49	1.00	− .30	
34.96	4.68	0.86	− .12	
35.18	4.72	.94	− .22	
35.76	4.82	.86	− .13	
35.96	4.85	.82	− .08	−4.65
36.32	4.91	.77	− .03	−4.70
36.44	4.93	.68	.09	−4.82
37.01	5.03	.65	.11	−4.84
38.00	5.20	.53	.26	−4.95
38.82	5.34	.49	.32	−5.05
39.67	5.48	.44	.38	−5.11
39.90	5.52	.41	.42	−5.15
40.90	5.70	.32	.57	−5.30
41.45	5.79	.30	.60	−5.33
43.71	6.19	.189	.84	−5.57
45.05	6.43	.144	.97	
46.22	6.64	.094	1.17	
48.11	6.98	.066	1.33	
50.84	7.50	.036	1.62	
53.35	7.98	.016	1.96	
o-Nitraniline, S = 1.00, pK = −0.17				
0.030	0.00315	0.63	−0.22	0.05
.055	.00590	.43	+ .13	− .30
.090	.00954	.271	+ .43	− .60

and L_a and L_s are the lengths of a column of solution A and of the pure solvent containing these concentrations of the indicator at colorimetric

TABLE III

INDICATOR CONSTANTS AT 25°

Name	*pK* from HOAc–H_2SO_4	*pK* from H_2O–H_2SO_4	*pK* from H_2O–$HClO_4$	*pK* from H_2CO_2
o-Nitraniline[a]	−0.17	−0.13	−0.19	(−0.17)
(1) *p*-Chloro-*o*-nitroaniline[b]	(− .91)	− .85	− .94	−0.91
(2) 2,4-Dichloro-6-nitroaniline	−3.67	−3.22	−3.31	−3.18
(3) 2,6-Dinitro-4-methylaniline	−4.45	−4.32		
(4) N,N-Dimethyl-2,4,6-trinitroaniline	−4.73	−4.69		

[a] *pK* of −0.17 in hydrochloric acid–water mixtures, and −0.20 in nitric acid–water mixtures. [b] *pK* of −0.91 in hydrochloric acid–water mixtures, and −0.97 in nitric acid–water mixtures.

balance. *S*, the "specific color intensity of the colored form relative to the solvent," is defined by the equation

$$S = (B)_S L_S/(B)_a L_a \qquad (3)$$

where $(B)_S$ is the concentration of the colored base in the solvent, and $(B)_a$ its concentration in the solution A.

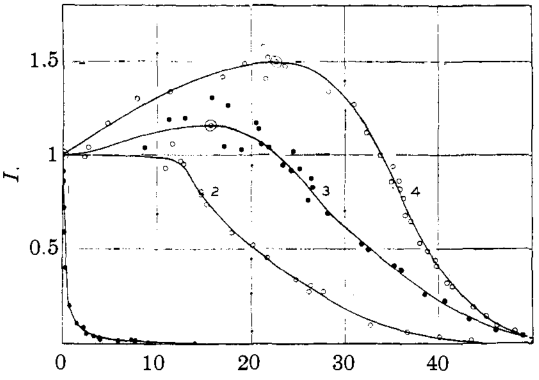

Fig. 1.—The numbers on the curves refer to the indicators listed in Table II, and the concentric circles, to the value of *S* taken for each indicator.

The values of *I* are plotted in Fig. 1, and the value of *S* for each indicator is taken at the point on these curves marked by the large open circles. Figure 2 is a plot of log $(BH^+)/(B)$, for each indicator, against the concentration of the sulfuric acid solutions in per cent. Since

$$\log\frac{(B_1H^+)}{(B_1)} - \log\frac{(B_2H^+)}{(B_2)} = pK_1 - pK_2 + \log\frac{f_{B_1}f_{B_2H^+}}{f_{B_1H^+}f_{B_2}} \qquad (4)$$

where

$$pK = -\log\frac{a_B a_{H^+}}{a_{BH^+}} \qquad (5)$$

and the subscripts refer to the indicator bases 1 and 2, the curves of log $(BH^+)/(B)$ should be as nearly parallel as the fundamental assumption upon which the H_0 scale of acidity is based is correct, namely, that the activity coefficient ratio of two bases of the same charge type is the same regardless of the nature of the medium in which they are compared, or that

$$\log\frac{f_{B_1}}{f_{B_1H^+}} \times \frac{f_{B_2H^+}}{f_{B_2}} = \eta \cong 0 \qquad (6)$$

The difference in ordinates of these curves for two indicators should then be constant and equal to the difference in the *pK* values of the two indicators. As can be seen, the curves are nearly parallel except in the more concentrated region, for indicator 4, where the medium effect is the greatest. Such a lack of parallelism was also found in the more concentrated sulfuric acid–water mixtures by Hammett and Deyrup.[4a] However, in this particular case, such a deviation may also be due in part to specific differences in ionic structure, and therefore to inapplicability of the fundamental assumption.

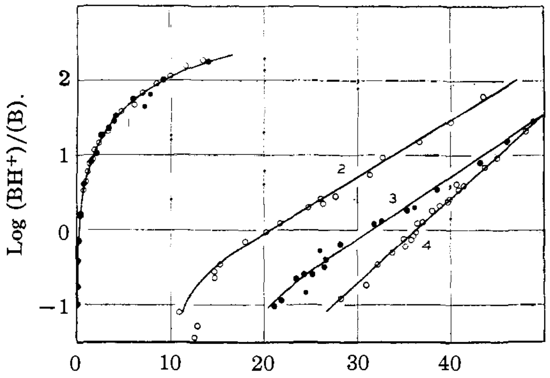

Fig. 2.—The numbers on the curves refer to the indicators listed in Table II. The open circles in Curve 1 refer to the data given by Hammett and Paul.[3c]

Using the value −0.91 found for *p*-chloro-*o*-nitroaniline by Hammett and Paul,[5c] the *pK* values of all the indicators used were obtained from the log $(BH^+)/(B)$ curves by a stepwise comparison. When two curves are not exactly parallel, the difference in ordinates between them is not constant, and the value obtained for the ΔpK of the indicators varies from point to point. The "best" single value would be obtained if one of the indicators were shown to conform to the fundamental assumption at the point where the second indicator was half-ionized. The "average" value obtained for the ΔpK of any two such indicators depends to some extent upon the position of the comparison range with respect to the point of half-ionization, the length of that range, and the scale of concentration used. The magnitude of these variations is determined by the extent that the curves deviate from parallelism, vanishing entirely as the curves become more nearly parallel. In determining the pK's of the indicators used, the largest possible range of overlap was taken in which the curves were most parallel. Except for the indicators 1 and 2 the range of the overlap is large (and the resulting uncertainty small). Attempts to use an indicator (p-nitrodiphenylamine) intermediate in strength between 1 and 2 were unsuccessful because the indicator underwent an irreversible color change, turning brown, in mixtures of sulfuric acid and acetic acid.

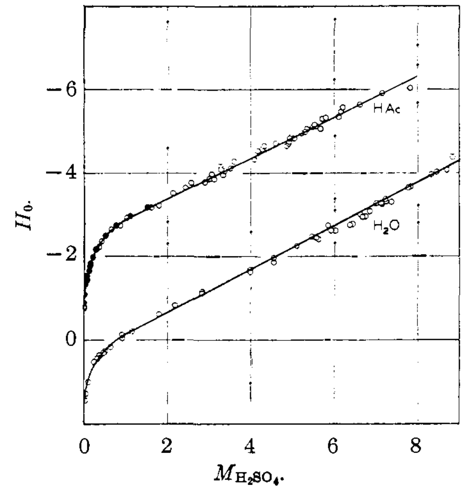

Fig. 3.—The data of Hammett and Paul for acetic acid are shown by closed circles.

The final values of pK obtained are listed in Table III, and are compared with the corrected values reported by Hammett and Paul.[5a]

The H_0 values are calculated from the definition: $H_0 = pK - \log (BH^+)/(B)$ for each solution. These values and those of Paul and Hammett,[5c] converted to a molarity basis, are shown in Fig. 3 along with the H_0 values in water taken from Hammett and Deyrup's work.[4a] Their data up to 9 M sulfuric acid have been recalculated in terms of molarity, using the density data in the "International Critical Tables" at 25°, and have been corrected 0.29 unit in accordance with the later work.[5a]

Figure 3 shows that H_0 is a linear function of the molarity from about 1 M to 8 M both in water and in acetic acid.[13] The two curves are parallel, have a slope of one-half within experimental error, and are separated by about 2.65 units. This indicates that the sulfuric acid solutions in acetic acid are $10^{2.65}$ or over four hundred times more acidic than solutions of the same concentration in water. For example, a 7.5 M solution in water has roughly the same acidity as a 2.3 M solution in acetic acid.

For dilute solutions, both in water and acetic acid, we find from Fig. 4 that H_0 is a linear function of log c (molarity). The slopes of the lines, -0.99 and -1.07, respectively, are the same within the limit of experimental error, as that obtained by plotting pH for a strong acid against log c in the water system.

Theoretically H_0 should equal the $pH^{(HAc)}$ of Conant and Hall[5a] but the two functions differ by an approximately constant amount as shown by the plot of some unpublished data of Hall for dilute sulfuric acid solutions in Fig. 4. For these dilute solutions, the relation, $H_0 = pH^{(HAc)} + 2$, is approximately true.

The Acidity Function and the Mean Ionic Activity.—In Fig. 4 a comparison is made of the mean ionic activity, $a_\pm$, of sulfuric acid both in water and in acetic acid with the acidity function, H_1. The activities for sulfuric acid in water were

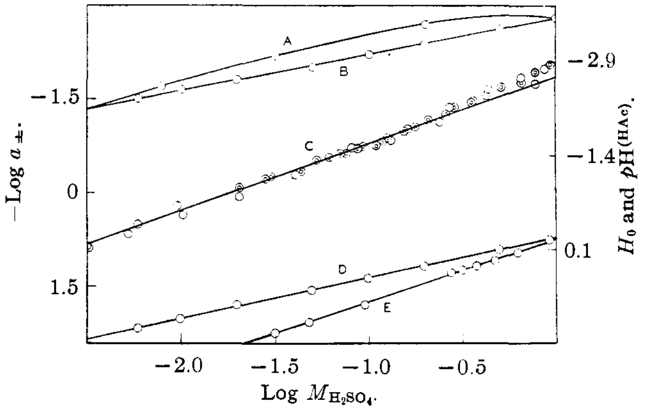

Fig. 4.—Curve A, $pH^{(HAc)}$; Curve B, $a_\pm$ in acetic acid; Curve C, H_0 in acetic acid (the data of Hammett and Paul are shown by concentric circles); Curve D, $a_\pm$ in water; Curve E, H_0 in water.

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(13) Further recalculation of Hammett's data by Mr. F. Meyer in this Laboratory has shown that H_0 is a linear function of molarity for sulfuric acid solutions in water from 1–18 M or from 9 to 96% H_2SO_4, with a slope of nealry one-half. The other acids, $HClO_4$, HCl and HNO_3, also show striking linear relationships between H_0 and *molarity*.

calculated from the data of Harned and Hamer,[14] from the equation

$$\log a_{\text{w}} = \frac{E_{0\text{w}} - E_0}{0.02958} \tag{7}$$

where a_{w} is the activity of the sulfuric acid in water, $E_{0\text{w}}$ is the E_0 for the cell $H_2|H_2SO_4(m)|$-$Hg_2SO_4|Hg$ in water and E_{w} is the e. m. f. at various molarities of sulfuric acid taken from a straight line plot of Harned and Hamer's data. $E_{0\text{w}}$ was taken as 0.615 volt. The mean ionic activity of sulfuric acid in water, $a_{\text{w}\pm}$, was calculated from

$$a_{\text{w}\pm} = a_{\text{w}}^{1/3} \tag{8}$$

The data as calculated are listed in Table IV.

The activity of sulfuric acid in acetic acid has been studied by Hutchison and Chandlee.[15] To make their data, which are referred to an infinitely dilute solution of sulfuric acid in acetic acid, comparable with activity measurements in water, it is necessary to calculate over to the standard state for the water system, namely, an infinitely dilute aqueous solution of sulfuric acid.

This can be done by considering the cells measured in each system as making up a double concentration cell without transference, as illustrated by the scheme

$$\underset{\text{in water}}{H_2|H_2SO_4(m)|Hg_2SO_4|}Hg\underset{\text{in acetic acid}}{|Hg_2SO_4|H_2SO_4(m)|H_2}$$

Then

$$E_{\text{w}} - E_{\text{A}} = \frac{RT}{2F}\ln a_{\text{A}} - \frac{RT}{2F}\ln a_{\text{w}} \tag{9}$$

where E_{A} is the e. m. f. at various molarities of sulfuric acid taken from a straight line plot of Hutchison and Chandlee's data in acetic acid and E_{w} and a_{w} have the significance given previously. Therefore, a_{A} will be the activity of sulfuric acid in acetic acid referred to an infinitely dilute *aqueous* solution of sulfuric acid as the standard. The mean ionic activity was calculated from the relation

$$a_{\text{A}\pm} = a_{\text{A}}^{1/2} \tag{10}$$

considering sulfuric acid to be a 1:1 electrolyte in acetic acid, as it probably is. The data are listed in Table IV.

TABLE IV

ACTIVITY OF SULFURIC ACID IN WATER AND ACETIC ACID

$c(H_2SO_4)$ molarity	log c	E_{w}	E_{A}	$-\log a_{\text{w}}^{1/3}$	$-\log a_{\text{A}}^{1/2}$
0.006	−2.222	0.808	0.526	2.176	−1.502
.01	−2.000	.795	.518	2.029	−1.640
.02	−1.699	.778	.508	1.837	−1.809
.05	−1.301	.754	.494	1.567	−2.014
.10	−1.000	.737	.484	1.375	−2.214
.20	−0.699	.719	.474	1.172	−2.384
.50	− .301	.696	.460	0.913	−2.620
1.00	.000	.679	.450	.721	−2.789

In Fig. 4 the logarithm of the mean ionic activity is shown to be a linear function of log c for these dilute solutions, 0.006 − 1 M, in both water and acetic acid. Thus for a 1 M solution in water $a_{\pm}$ is 0.2, while in acetic acid it is 615. This great difference is also shown by hydrogen chloride in the two solvents.[16]

Summary

The acidity of sulfuric acid solutions in glacial acetic acid up to a concentration of 8 M was studied with five simple monoprotic indicators according to the method and technique developed by Hammett and Deyrup.[4]

1. Using the value $pK = -0.91$ for *p*-chloro-*o*-nitroaniline, the pK's of three other indicators were determined and compared with values previously reported for other media.
2. The acidity function, H_0, for these solutions was determined and compared with sulfuric acid solutions in water for the same concentration range.
3. The various measures of acidity, H_0, $a_{\pm}$, and $p\text{H}^{(\text{HAc})}$, were compared for sulfuric acid solutions in both solvents.

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[14] Harned and Hamer, *ibid.*, **57**, 27 (1935).

[15] Hutchison and Chandlee, *ibid.*, **53**, 2881 (1931).

[16] Heston and Hall, *ibid.*, **56**, 1462 (1934).