acid is in sufficient excess over sarin so that its concentration remains substantially constant during the course of reaction. Under these conditions, the reaction rate, k_{obs}, can be calculated from equation 7 which is derived from equations 5 and 6.[16]

$$k_{obs} = \frac{G_B[HA_{Tot}]\ K_A}{[H^+] + K_A}\left(\frac{K_w}{K_A}\right)^{\beta} \text{sec.}^{-1} \qquad (7)$$

Substituting numerical values for G_B and β established above, we obtain

$$k_{obs} = \frac{3.5 \times 10^{-9}\ [HA_{Tot}]\ K_A^{0.20}}{[H^+] + K_A}\ \text{sec.}^{-1} \qquad (7a)$$

As an example, we have plotted in Fig. 4 the quantitative relationship between reaction half-time ($t_{1/2} = 0.693/k_{obs}$) and hydroxamic acid pK_A at $[HA_{Tot}] = 10^{-3}$ M, and at pH 7.6, under the stipulated conditions.

The general relationship between pK_A and pH for *maximum reaction rate at fixed* pH, equation 8, can be derived from equation 7 by integration of the expression $dk_{obs}/dK_A = 0$. For the reaction

$$pK_A - pH = \log \frac{\beta}{1 - \beta} \qquad (8)$$

under consideration in the present study, where the value of $\beta = 0.80$, maximum rate will be obtained with the hydroxamic acid of $pK_A = pH + 0.60$.

Acknowledgments.—We would like to express our appreciation to Mr. Omer O. Owens and Dr. Brennie E. Hackley, Jr., for their assistance, and Dr. Gerard Endres and Dr. David Rosenblatt for having provided us with unpublished data.

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(16) For derivation and discussion of these relationships, see J. Epstein, D. E. Rosenblatt and M. Demek, THIS JOURNAL, **78**, 341 (1956), and G. M. Steinberg, R. Swidler and S. Seltzer, *Science*, **125**, 336 (1957). Similar relationships have been developed independently by A. L. Green, G. L. Sainsbury and M. Stansfield, private communication.

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

An Acidity Function for the Solvent System Consisting of 20 Vol. % Ethanol and 80 Vol. % Sulfuric Acid–Water Mixtures[1]

BY SI-JUNG YEH AND H. H. JAFFÉ

RECEIVED DECEMBER 20, 1958

A series of 32 mono- and disubstituted derivatives of azobenzene was used to establish an H_0 scale in the solvent system 20% ethanol–80% sulfuric acid–water mixture. *o*- and *p*-nitroaniline were used to connect this scale to potentiometrically measured pH's. The scale extends from dilute solution to 19 N acid. The scale is of particular interest since the indicators used are structurally closely related, and the B/BH^+ *vs.* acid concentration curves for the various indicators are almost exactly parallel in the overlap regions. The scale is compared with the H_0 scale in aqueous sulfuric acid.

The H_0 function originally introduced by Hammet and co-workers[2] is a tremendously useful acidity scale for the measurement of base strengths of weak, uncharged bases in aqueous acids, because it provides a quantitative measure of the ability of the aqueous solution under consideration to transfer a proton to the uncharged base. The H_0 functions for aqueous solutions of various strong acids have been established by the use of series of different indicators such as the derivatives of aromatic amines.[3] A basic requirement for the validity of an acidity function is that the plot of log (B/BH^+) *vs.* acid concentration be parallel for all indicators used in the regions of overlapping acid concentrations in which measurement of log (B/BH^+) is experimentally possible.[3] This condition has rarely been met in the past. It has been suggested that the use of structurally closely related indicators would greatly aid in achieving this ideal.[2,3]

Many weak organic bases are insufficiently soluble in dilute aqueous acid for convenient measurements of the pK by a spectrophotometric method, but addition of a small amount of an organic solvent, *e.g.*, ethanol, permits such measurements. Although the concept of the H_0 function can be extended to mixed solvent systems, the addition of a solvent with low dielectric constant to the aqueous acid also raises a problem as to the validity of the H_0 function in such mixed solvent systems.

The H_0 function for solutions of hydrochloric acid in ethanol has been studied by Braude[4] up to 1 M acid concentration using a single indicator, *p*-nitroaniline. Braude and Stern[5] have extended this study to a mixed solvent system containing varying proportions of ethanol at fixed hydrochloric acid concentrations of 0.1 M and 1 M, and have reported that, with increasing ethanol concentration, H_0 goes through a minimum at equimolar proportion of the two solvent. Grunwald and co-workers[6] have measured the pK's of various uncharged bases in ethanol and water mixtures by a potentiometric method, and found that the pK's in the mixed solvents are significantly different from the values in pure water; *e.g.*, the pK of aniline goes from 4.64 in pure water to 4.16 in 35 wt. % ethanol, passes through a minimum of 3.75 at 80 wt. % ethanol and increases to 5.70 in pure ethanol. These data demonstrate that the pK values are dependent on the solvent system and that for the measurement of the pK of a weak un-

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(1) This work was supported by a Bonita Geho Memorial Grant for Cancer Research from the American Cancer Society. This support is gratefully acknowledged.

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(3) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

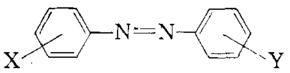
(4) E. A. Braude, *J. Chem. Soc.*, 1971 (1948).

(5) E. A. Braude and E. S. Stern, *ibid.*, 1976 (1948); E. A. Braude and E. S. Stern, *Nature*, **161**, 169 (1948).

(6) E. Grunwald and B. J. Berkowitz, THIS JOURNAL, **73**, 4939 (1951); E. Gutbezahl and B. Grunwald, *ibid.*, **75**, 559 (1953); **75**, 565 (1953).

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF AZO COMPOUNDS



X	M.p.,[a] °C.	Analyses,[b] %						Crude yield, %	λ_1[p]			λ_2[p]		
		C		H		N								
		Calcd.	Found	Calcd.	Found	Calcd.	Found		λ, mμ	ϵ_B	ϵ_{BH^+}	λ, mμ	ϵ_B	ϵ_{BH^+}
(a) Y = *m*-NO$_2$														
p-OC$_2$H$_5$	101–102[c]	61.98	62.36	4.82	4.75	15.55	15.33	89	352	1.99	0.220	464	0.305	4.82
p-OCH$_3$	113–114	60.70	60.95	4.31	4.31	16.33	16.49	90	354	2.27	.228	468	.193	4.64
p-CH$_3$	117–118	64.72	64.85	4.54	4.40	17.42	17.51	70	330	2.14	.363	430	.118	3.21
m-CH$_3$	73–74	64.72	64.68	4.54	4.37	17.42	17.49	80	318	1.84	.280	418	.020	2.63
p-Br[d]	118–119	47.08	47.23	2.63	2.47	13.73	13.58	81	328	2.32	.405	440	.100	3.48
m-Br[e]	107–108	47.08	47.45	2.63	2.53	13.73	13.81	91	312	1.99	.457	412	.061	2.46
p-COCH$_3$	114–115	62.45	62.47	4.12	4.25	15.61	15.77	85	320	2.60	.507	416	.048	3.03
m-COCH$_3$	105–106	62.45	62.17	4.12	4.21	15.61	15.87	85	316	1.92	.552	410	.034	2.56
p-CN	134–135	61.90	62.07	3.20	3.23	22.21	22.06	90	318	2.50	.600	410	.043	2.94
m-NO$_2$[f]	151–152								268	2.34	1.46	400	.035	2.58
(b) Y = *p*-OH														
p-OCH$_3$	143–144[g]					12.28	12.22	92	360	2.50	0.250	490	0.045	4.09
p-CH$_3$	153–153.5[h]					13.33	13.20	90	350	2.48	.270	470	.140	4.10
H[i]	155–156[i]							91	346	2.21	.250	460	.110	3.99
p-Br	160–161[j]					10.11	10.21	89	356	2.61	.275	480	.085	4.44
m-Br	142–143[k]					10.11	9.91	76	356	2.29	.280	460	.135	4.15
p-COCH$_3$	198–199	69.98	70.33	5.04	5.08	11.66	11.47	90	360	2.58	.310	480	.210	4.75
(c) Y = *p*-OCH$_3$														
p-OCH$_3$	165–166[l]					11.66	11.57	70	360	2.57	0.250	490	0.230	4.45
p-CH$_3$	111–112[m]					12.18	12.30	72	350	2.46	.320	470	.240	4.21
p-Br[n]	148–149	53.62	53.85	3.81	3.75	9.62	9.74	75	350	2.63	.490	480	.110	4.72
m-Br[o]	62–63	53.62	53.74	3.81	3.79	9.62	9.49	60	250	2.20	.290	470	.200	4.48

[a] Uncorrected. [b] Microanalyses were performed by A. Bernhardt, Mühlheim (Ruhr), Germany. [c] M.p. 96°; E. Baly, W. Tuck and E. Marsden, *J. Chem. Soc.*, **97**, 1501 (1910). [d] Br calcd. 25.79, found 25.88. [e] Br calcd. 25.79, found 25.88. [f] This compound was kindly provided by Prof. E. Malmberg, Ohio State University. [g] M.p. 142°; K. Kraus, *Ber.*, **32**, 124 (1899). [h] M.p. 151°; E. Grandmonugin and H. Freimann, *J. prakt. Chem.*, [2] **78**, 392 (1909). [i] Since this is a well known compound, no analysis was performed; m.p. 156°; K. H. Engel, THIS JOURNAL, **51**, 2989 (1929). [j] M.p. 162°; J. J. Fox and J. T. Hewitt, *J. Chem. Soc.*, **93**, 340 (1908). [k] M.p. 139–140°; P. Jacobson, G. Franz and K. Zaar, *Ber.*, **36**, 3867 (1903). [l] M.p. 165°; D. Vorländer, *ibid.*, **40**, 1422 (1907). [m] M.p. 110–111°; H. Wieland, *ibid.*, **48**, 1107 (1915). [n] Br calcd. 27.45, found 27.67. [o] Br calcd. 27.45, found 27.83. [p] The wave lengths given are not necessarily absorption maxima although they are usually quite close to them.

charged base in mixed solvent systems the original H_0 function cannot be used.

In connection with the study of the effect of substituents on the basicities of monosubstituted azobenzenes, Jaffé and Gardner[7] have established, based on *p*-nitroazobenzene as an arbitrary standard, an acidity scale for the solvent system consisting of 20 vol. % EtOH and 80 vol. % H_2SO_4–H_2O mixtures. Their acidity scale covered acidity ranges from 20 to 55 wt. % H_2SO_4. It appeared desirable to connect their acidity function to the *p*H scale and to extend it to higher acidity ranges. For this purpose we have prepared three series of disubstituted azobenzenes and measured the concentration ratios, c_B/c_{BH^+} in this particular solvent system by the spectrophotometric method.[8] Here c_B and c_{BH^+} are, respectively, the concentrations of the free base and of the conjugate acid of the substituted azobenzenes. Hammett's method was used to establish the H_0 scale.

Experimental

Compounds: Substituted Anilines.—Commercially available *p*-nitroaniline and *o*-nitroaniline were recrystallized twice from water and 95% ethanol, respectively; *p*-nitroaniline (m.p. 148–148.5°; *o*-nitroaniline, m.p. 72–73°; reported[9] in the literature are 147.5 and 71.5°, respectively).

Disubstituted Azobenzenes.—The *m*-(arylazo)-nitrobenzenes were prepared by condensation of appropriately substituted anilines with *m*-nitrosonitrobenzene in glacial acetic acid.[10] *m*-Nitrosonitrobenzene was obtained by the oxidation of *m*-nitroaniline with Caro acid.[11]

The *p*-(arylazo)-phenols were prepared by coupling phenol in alkaline solution with diazonium chlorides obtained by diazotization of the appropriately substituted anilines.[12]

The *p*-(arylazo)-phenols were methylated with dimethyl sulfate in alkaline solution to give **p-(arylazo)-anisoles.**[13]

All azo-compounds were recrystallized repeatedly from ethanol until constant melting points were obtained. Elemental analysis confirmed the purities of these compounds. The physical properties and analyses of all azo-compounds are summarized in Table I.

Determination of the Concentration Ratios c_B/c_{BH^+} by the Spectrophotometric Method: (a) Preparation of Solutions.—A stock solution of azo-compound (1 × 10^{-4} *M*) was prepared in 95% ethanol. Aliquots (10 ml.) of the stock solution were pipetted into a series of 50 ml. volumetric flasks, placed in a thermostat at 25.0 ± 0.1°, and then diluted to the mark with aqueous sulfuric acid solutions of appropriate concentration. In this way a series of solutions was obtained in which the concentration of azo compound and the content of ethanol were identical but which had varying acid concentration.

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(7) H. H. Jaffé and R. W. Gardner, THIS JOURNAL, **80**, 319 (1958).

(8) L. A. Flexser, L. P. Hammett and A. Dingwall, *ibid.*, **57**, 2103 (1935).

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(10) A. Bayer, *Ber.*, **7**, 1638 (1874).

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(13) G. Hiers and F. Hager, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 50.

(b) **Determination of Acidity of the Solutions.**—When the sulfuric acid concentration was low enough to permit *p*H measurements, the acidity of the solution under investigation was determined by a Beckman model G *p*H meter. The *p*H scale of the instrument was calibrated with standard buffer solution before use. For the solutions of higher acid concentration, the acidity was determined by a calibration chart of density *vs.* sulfuric acid content.[7]

(c) **Measurements of Concentration Ratios c_B/c_{BH^+}.**—The concentration ratios c_B/c_{BH^+} of the azo-compounds were measured by use of a Beckman DU quartz spectrophotometer using 1-cm. silica cells. The cell compartment was regulated at 25.00 ± 0.02° by a thermospacer assembly. When the solubility of the azo-compound is so low that 10-cm. cells must be used to obtain suitable absorbance, the measurement was carried out at room temperature of 25.0 ± 0.5°. The concentration ratios c_B/c_{BH^+} were calculated by the method described elsewhere.[7]

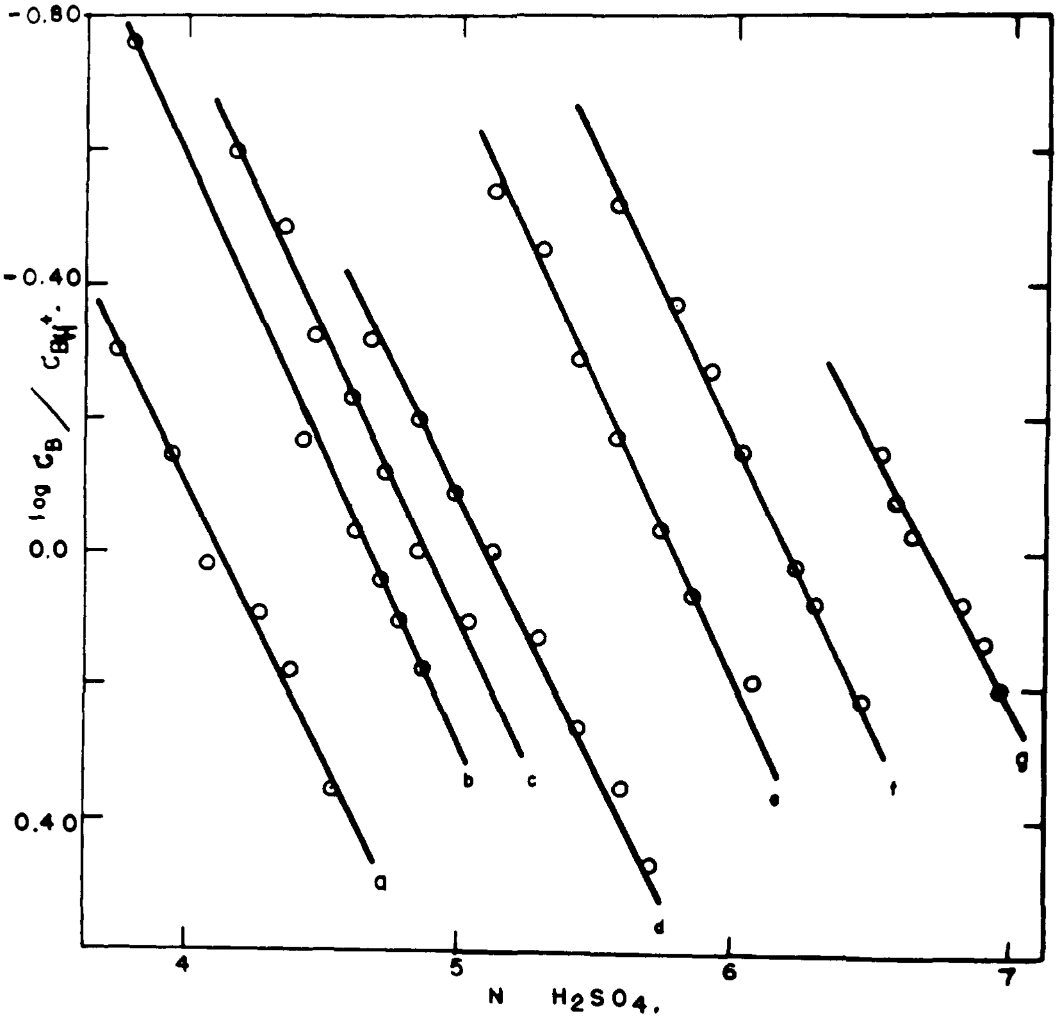

Fig. 1.—Plot of log (c_B/c_{BH^+}) *vs.* H_2SO_4 concentration for some of the indicators used: a, *p*-(*m*-bromophenylazo)-anisole; b, *p*-(*p*-nitrophenylazo)-anisole; c, *m*-phenylazotoluene; d, azobenzene; e, *p*-bromoazobenzene; f, *m*-bromoazobenzene; g, *m*-(*m*-nitrophenylazo)-toluene.

Procedure for Establishing H_0 Function for the Solvent System Consisting of 20 Vol. % EtOH and 80 Vol. % H_2SO_4–H_2O Mixtures.—In order to connect Jaffé and Gardner's H_0' scale to the *p*H scale, it is necessary to use the concentration ratios c_B/c_{BH^+} data for the monosubstituted compounds were taken from the work of Gardner.[14]

The *pK* of a weak base, B, in the solvent system consisting of 20 vol. % ethanol and 80 vol. % H_2SO_4–H_2O mixture is given by

$$pK = -\log \frac{c_{BH}}{c_{BH^+}} - \log \frac{a_{H^+}f_B}{f_{BH^+}} \qquad (1)$$

When the H_2SO_4 content is low enough for measurement of the *p*H of the solution, the *pK* of the base in this particular system can be obtained directly from eq. 1. This technique was used to set the standard of the H_0 function for this mixed solvent system. Since it was not possible to obtain disubstituted azobenzenes of strong enough basicity to permit the measurement of c_B/c_{BH^+} at sufficiently low acidity, *p*- and *o*-nitroaniline were used for this purpose.

As the H_2SO_4 content increases, one can no longer measure the *p*H of the solution and has to adopt the method of Hammett and Deyrup[2] to extend the H_0.

$$pK = -\log \frac{c_B}{c_{BH^+}} + H_0$$

where

$$H_0 \equiv -\log \frac{a_{H^+}f_B}{f_{BH^+}}$$

For the mono- and disubstituted azobenzenes there is sufficient overlap of experimentally measurable concentration ratios c_B/c_{BH^+} (only concentration ratios in the range

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[14] R. W. Gardner, M.S. Thesis, University of Cincinnati, 1957.

TABLE II

THE PROCEDURE OF THE EXTENSION OF THE H_0 FUNCTION

N H_2SO_4[a]	$-H_0$[b]	λ_1 log (c_B/c_{BH^+})	λ_1 $-pK_t$[c]	λ_1 $-H_0$[d]	λ_1 $-pK_t$[e]	λ_2 log (c_B/c_{BH^+})	λ_2 $-pK_t$[c]	λ_2 $-H_0$[d]	λ_2 $-pK_t$[e]
(a) Indicator: *m*-bromoazobenzene, λ_1 324 mμ, λ_2 4.6 mμ									
11.12	3.28	0.509	3.79	..	3.79	0.531	3.81	..	3.81
11.51	3.45	.345	3.81	..	3.81	.407	3.86	..	3.86
11.82	3.59	.267	3.86	..	3.86	.272	3.86	..	3.86
12.03	3.65	.165	3.82	..	3.82	.134	3.78	..	3.78
12.44	..	.031	(3.83)[f]	3.80	3.86	.017	(3.83)[f]	3.81	3.85
12.57	..	− .065	(3.83)[f]	3.90	3.82	− .106	(3.83)[f]	3.94	3.78
12.97	..	− .211	(3.83)[f]	4.04	3.86	− .219	(3.83)[f]	4.05	3.85
(b) Indicator: *m*-nitro-*p*'-methylazobenzene,[g] λ_1 330 mμ, λ_2 430 mμ									
11.83	3.58	0.253	3.83	..	3.83	0.238	3.82	..	3.82
12.00	3.64	.207	3.85	..	3.85	.164	3.80	..	3.80
12.15	3.70	.127	3.83	..	3.83	.079	3.78	..	3.78
12.26	..	.090	(3.82)[f]	3.73	3.85	.049	(3.82)[f]	3.78	3.81
12.41	..	.021	(3.82)[f]	3.80	3.84	− .025	(3.82)[f]	3.84	3.79
12.52	..	− .056	(3.82)[f]	3.88	3.81	− .101	(3.82)[f]	3.92	3.76
12.85	..	− .117	(3.82)[f]	3.94	3.89	− .155	(3.82)[f]	3.97	3.85
(c) Indicator: *p*-phenylazoacetophenone, λ_1 330 mμ, λ_2 420 mμ									
11.32	3.37	0.547	3.92	..	3.92	0.576	3.95	..	3.95
12.04	3.60	.322	3.92	..	3.92	.346	3.95	..	3.95
12.27	3.76	.208	3.97	..	3.97	.235	4.00	..	4.00
12.58	3.89	.097	3.99	..	3.99	.121	4.01	..	4.01
12.86	4.01	.013	4.02	..	4.02	.040	4.05	..	4.05
13.17	..	− .138	(3.99)[f]	4.13	3.99	− .106	(3.99)[f]	4.10	4.02
13.34	..	− .224	(3.99)[f]	4.21	3.98	− .204	(3.99)[f]	4.19	4.00

[a] Determined from the density. [b] As obtained from earlier compounds in the series. [c] The "temporary" pK. (*cf.* text). [d] Calculated from this compound. [e] The final value obtained from the smoothed H_0 function. [f] Average of the "temporary" pK's of this compound. [g] Since the pK for this compound is essentially the same as for the previous one, these data give a duplicate of the extension of H_0.

0.2 to 5 were used) to apply this method. A typical example of such overlap is shown in Fig. 1 in which log [c_B/c_{BH^+}] is plotted against the normality of H_2SO_4. A similar trend of overlap was observed in both lower acidity and higher acidity regions (1.5 N to 18 N H_2SO_4). The concentration ratios of *p*-(*p*-methoxyphenylazo)-phenol, the strongest base in the series of disubstituted azobenzenes, overlap adequately with those of *o*-nitroaniline which served as the indicator to connect the H_0 function to the *p*H scale. The general procedure of stepwise extension of the H_0 function is illustrated by Table II. The pK of *o*-nitroaniline was determined to be −0.336 in 20 vol. % ethanolic H_2SO_4 solution, and was used in conjunction with equation 2 to calculate the H_0 values for higher acid concentrations. H_0 values obtained here were used to calculate several values of a "temporary pK" of *p*-(*p*-methoxyphenylazo)-phenol; these values were averaged and then used to extend the H_0 scale to higher H_2SO_4 concentration. This procedure was repeated for all substituted azobenzenes. All measurements of concentration ratios c_B/c_{BH^+} were carried out at two wave lengths (one each near the absorption maxima of free base and of the conjugate acid, respectively), so that duplicate values of c_B/c_{BH^+} were available for each acid concentration. In addition, at least 3 or 4 independent pairs of the "temporary pK values" were obtained for each compound and were found to be consistent with each other. After the H_0 function was extended to 19 N H_2SO_4, the curve was smoothed and the pK of each compound was re-calculated using the H_0 values read from the smoothed curve. The pK's thus obtained did not differ from the "temporary pK" by more than three hundredths of a pK unit, and are summarized in Table IV.

Results and Discussions

The H_0 values for the solvent system consisting of 20 vol. % ethanol and 80 vol. % H_2SO_4–H_2O mixtures are listed in Table III. A plot of H_0 *vs.* normality of H_2SO_4 is shown in Fig. 2 together with Hammett's H_0 function in aqueous sulfuric acid solution.

TABLE III

THE H_0 FUNCTION IN 20% ETHANOL–80% AQUEOUS SULFURIC ACID, AND IN WATER

N H_2SO_4	$-H_0$ (20% EtOH)[a]	$-H_0$ (H_2O)[b]	N H_2SO_4	$-H_0$ (20% EtOH)[a]	$-H_0$ (H_2O)[b]
0.20	−1.30	−0.83	9.0	2.39	2.06
0.50	−0.72	− .44	10.0	2.82	2.28
1.00	− .41	− .13	11.0	3.24	2.51
1.50	− .18	+ .07	12.0	3.65	2.76
2.00	+ .02	.26	13.0	4.08	3.03
3.0	.35	.56	14.0	4.54	3.32
4.0	.61	.84	15.0	4.98	3.60
5.0	.89	1.12	16.0	5.49	3.87
6.0	1.24	1.38	17.0	5.97	4.14
7.0	1.57	1.62	18.0	6.44	4.40
8.0	1.96	1.85	19.0	6.91	4.65

[a] Interpolated from the smoothed curve. [b] Ref. 3.

Some similarities and differences between the H_0 function in the two solvent systems are apparent from Fig. 2. In the range of low H_2SO_4 concentration H_0 values for 20% ethanolic H_2SO_4 are only slightly more positive than H_0 values for aqueous H_2SO_4. This is reasonable because, according to the definition, for dilute H_2SO_4 solutions, H_0 values in both solvents must be identical with the *p*H and it is known that the addition of ethanol to dilute H_2SO_4 solution at fixed H_2SO_4 content decreases the activity of hydrogen ion. A similar observation has been reported by Braude.[4] Further, the H_0 function in both solvent systems increases almost linearly with the normality of the acid at higher acid concentrations (> 5 N H_2SO_4).

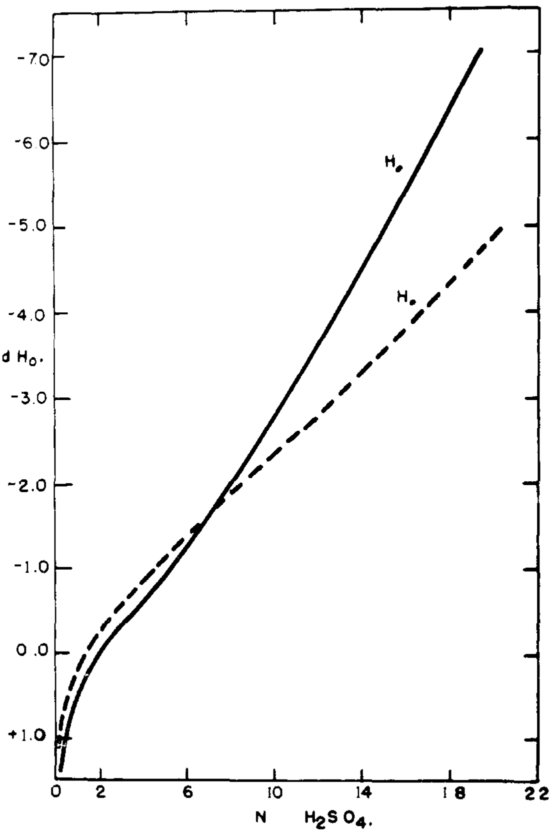


Fig. 2.—The H_0 function in H_2O and in 20% ethanol *vs.* sulfuric acid normality.

The most striking difference between the two solvent systems is that in 20 vol. % ethanolic H_2SO_4 H_0 increases much more rapidly than in aqueous solution at H_2SO_4 concentrations above 5 *N*.[15,16] The apparently greater acidity of the ethanolic H_2SO_4 solutions compared with the aqueous solutions at a fixed H_2SO_4 concentration above 5 *N* can be explained by a consideration of the relative basicities of water and ethanol. It has been shown that water is a stronger base than ethanol, *i.e.*, the conjugate acid of ethanol is a stronger acid than the conjugate acid of H_2O, and the equilibrium constant for the reaction

$$EtOH_2^+ + H_2O \rightleftarrows H_3O^+ + EtOH$$

has been estimated to be the order of 15. Thus, when we compare solutions of H_2SO_4 in water and in 20% ethanol at fixed H_2SO_4 content, we expect that the latter solution has higher apparent acidity due to the presence of $EtOH_2^+$ which is absent from the former. In other words, ethanol has a "leveling effect" to exhibit higher acidity. This phenomenon is also observed in the study of the H_0 function of a non-aqueous solvent system, *e.g.*, acetic acid.[17]

Part of the steeper increase of H_0 for 20% ethanolic H_2SO_4 compared to aqueous H_2SO_4 may be attributed to the more rapid increase in the molar concentration of ethanol in the mixed solvent system at higher H_2SO_4 concentrations. The increment in mole per cent. ethanol per unit increase of H_2SO_4 concentration expressed in normality is 0.1 at 3 *N* to 6 *N* H_2SO_4, 0.3 at 8 *N* H_2SO_4, 0.38 at 12 *N* H_2SO_4, 0.5 at 16 *N* H_2SO_4 and 0.65 at 19 *N* H_2SO_4, respectively.

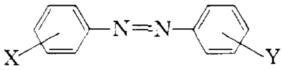
It is interesting to note that, at the higher acid concentrations, the more rapid increase of H_0 in 20% ethanol compared with the aqueous solutions persist even when the acid concentration is plotted as mole fraction.

The H_0 function presented here offers several advantages. It is based on a series of very closely related indicators, all of which, with the exception of *o*- and *p*-nitroaniline, are derivatives of azobenzene. They differ only in the nature of the substituents, which are reasonably far removed from the basic center. Hence it appeared reasonable that the activity coefficient ratio would remain reasonably constant throughout the series. That this expectation actually was realized appears to be borne out by an examination of Fig. 1, where it is seen that overlapping portions of the log (B/BH^+) *vs.* acid concentration plots are quite close to being parallel. Comparison with previous curves (*cf.*, *e.g.*, the plot given in Fig. 1 of ref. 3) indicates that in this respect the choice of the structurally closely related indicators had the desired effect.

These same results do, of course, raise the question again whether a truly general acidity function exists. Until indicators of different structure will have been investigated by this acidity function this question must remain unanswered.

A further advantage of the present H_0 function in 20% ethanolic H_2SO_4 lies in its usefulness for the measurements of *pK*'s of weak, uncharged bases which are not very soluble in dilute aqueous acid. The particular solvent system chosen has the advantage that it facilitates the preparation of a series of solutions of different H_2SO_4 concentrations but identical concentration of base and ethanol, and hence makes convenient the measurement of the concentration ratios by the spectrophotometric method.

Table IV

pK's of

in 20% EtOH

X	Y = *m*-NO_2 −*pK*	Y = H −*pK*	Y = *p*-OCH_3 −*pK*	Y = *p*-OH −*pK*
4-OEt	2.48 ± 0.03	1.28 ± 0.02	....	....
4-OMe	2.54 ± .03	1.36 ± .03	0.75 ± 0.03	0.56 ± 0.03
4-Me	3.83 ± .02	2.35 ± .02	1.03 ± .02	0.84 ± .03
3-Me	4.32 ± .02	2.70 ± .03	....	....
H	4.63 ± .02	2.90 ± .02	1.36 ± .03	1.02 ± .01
4-Br	5.04 ± .01	3.47 ± .02	1.74 ± .03	1.42 ± .01
3-Br	5.52 ± .02	3.83 ± .03	2.06 ± .02	1.67 ± .01
3-$COCH_3$	5.69 ± .02	....	....	....
4-$COCH_3$	5.96 ± .02	3.98 ± .04	2.23 ± .02	....
4-CN	6.50 ± .04	4.52 ± .02	....	....
3-NO_2	6.57 ± .07	4.63 ± .02	2.54 ± .03	....
4-NO_2	....	4.70 ± .02	....	....

o-Nitroaniline, *pK* = −0.34; *p*-nitroaniline, *pK* = 0.93

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(15) H. Goldschmidt, *Z. physik. Chem.*, **89**, 129 (1914); E. A. Braude, *J. Chem. Soc.*, 443 (1944).

(16) This observation is consistent with the findings of P. D. Bartlett and J. D. McCollum, This Journal, **78**, 1441 (1956).

(17) N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).