Solvent Effects in Organic Chemistry. VIII. Acidity Function Failure in Different Aqueous Acids

Edward M. Arnett and George W. Mach[1]

Contribution No. 1309 from the Department of Chemistry of the University of Pittsburgh, Pittsburgh, Pennsylvania 15213, and Mellon Institute, Pittsburgh, Pennsylvania. Received September 25, 1965

Abstract: Acidity functions (H_0', H_0''', and H_R) are given for primary and tertiary aromatic amines and triarylcarbinols in aqueous hydrochloric, phosphoric, and *p*-toluenesulfonic acids. In all of these media, and sulfuric acid, the order in which the acidity functions change with acid concentration is $H_R > H_R' > H_0''' > H_0'$. Using such functions as $H_0''' - H_0'$ (*i.e.*, $\log f_{B'}f_{B'''H^+}/f_{B'H^+}f_{B'''}$) as a criterion of acidity function failure, it is found that these terms have a roughly linear relationship to the acid molarity in these media and in perchloric acid, but give variously shaped curves if plotted against $\log a_{H_2O}$. The slopes of the linear Setschenow-like plots for ($H_R' - H_0'$) in these acids fall in the order perchloric > sulfuric > phosphoric > hydrochloric, suggesting that sulfuric and perchloric acids are the worst media of the four as far as acidity function failure is concerned. The importance of factors (such as size) other than ion hydration in determining activity coefficients and, hence, acidity functions is noted. It is suggested that the failure of rates of acid-catalyzed reactions to give linear plots of $\log k_1$ *vs.* H_0 of unit slope be treated in a similar way. Plots of ($\log k_1 + H_0$) *vs.* molarity of acid are linear over a fair range of acidity in conformity with the Setschenow-like equation $\log f_S f_{BH^+}/f^* f_B$ = constant × molarity. Aqueous solutions of *p*-toluenesulfonic acid give a medium in which H_0' and H_0''' are very close together and might be a useful one for acidity function work. However, the solutions are only weakly acidic compared to the mineral acids and present a very limited range of acidities.

In our previous paper on this subject,[2] the following points were established. (a) Despite their close structural similarity to the primary nitrated anilines usually employed as Hammett indicators, tertiary nitrated anilines do not follow the traditional H_0 acidity function.[3] (b) A reasonable account of the behavior of the tertiary anilines could be given in terms of activity coefficients for model primary and tertiary anilinium ions. (c) The failure of the H_0 acidity function invalidates a number of interesting calculations which attempted to derive it in terms of ion hydration numbers and the activity of water. Since the acidity function depends upon the series of Brønsted bases used to derive it, there is no single acidity scale of this type that is fundamentally preferable to any other. (d) The difference between the tertiary amine acidity function (H_0''')[2] and that for primary anilines (H_0')[4] cannot be accounted for adequately in terms of a constant simple difference in hydration numbers.

This adds up to a rather negative picture and, in view of the fact that acid-catalyzed reactions are probably the largest single class of organic reaction mechanisms, the ground that has been lost with the erosion of a unifying theory of strong acids has been considerable. There are several approaches to repairing the damage. One would be to find acidic systems, if such exist, in which Hammett's activity coefficient postulate *will hold* and thus allow a good single acidity function which would be applicable to a variety of Brønsted bases. That is the path followed in the research described here, and we have used the degree of failure of the acidity function expressed by such terms as ($H_0''' - H_0'$) to find what factors will minimize the failure. The exploration has been limited to aqueous acids in which the activity of water is known so that the relationship between the acidity functions and this factor could also be examined. Furthermore, by measuring Deno's H_R acidity function[5] for triarylcarbinol–carbonium ion equilibria in the same media, it is possible to relate the five acidity functions H_0', H_0''', H_R, H_R', and $\log a_{H_2O}$ for the media we have studied (hydrochloric acid, phosphoric acid, and *p*-toluenesulfonic acid) and to compare them with previous results in aqueous sulfuric and perchloric acids, the best explored aqueous acid systems.

Experimental Section

The nitrated primary anilines were part of a set of Hammett indicators purchased from the Aldrich Chemical Co. References for the synthesis of the tertiary amine indicators are presented[2] and further details are given in the thesis of G. W. Mach,[1] from which this work is taken. The triarylcarbinols were generously presented to us by Professor Norman Deno of Pennsylvania State University. All compounds were examined carefully for purity by melting point and ultraviolet and infrared spectra before use. They had been shown previously to be stable in acid media of the strength used.

Phosphoric acid solutions were prepared from either Baker and Adamson Reagent, ACS grade phosphoric acid, or NF phosphoric acid diluted with distilled water. The compositions of the more concentrated solutions were determined routinely by measuring the density at 25° with a 25-ml pycnometer and estimating the weight per cent phosphoric acid from density tables in the "International Critical Tables."

The composition of the more dilute phosphoric acid solutions was determined titrimetrically with standard 0.1 *N* sodium hydroxide solution using brom cresol green indicator.

Hydrochloric acid solutions were prepared from Baker and Adamson reagent, ACS grade hydrochloric acid.

---

(1) National Science Foundation Cooperative Fellow, 1963–1965. This work was supported in part by National Science Foundation Grant G-14583 and is taken from the Ph.D. thesis of George Mach, University of Pittsburgh, 1964.

(2) E. M. Arnett and G. W. Mach, *J. Am. Chem. Soc.*, **86**, 2671 (1964).

(3) Reference 2 reviews many of the important references in this area up to the date of submission of that paper, and they will not be repeated here.

(4) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963). In this paper H_0' will be used interchangeably with the traditional H_0 function.

(5) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, **77**, 3044 (1955).

Table I. Dissociation Constants and Spectral Shifts for Compounds in Sulfuric, Phosphoric, Hydrochloric, and *p*-Toluenesulfonic Acids

Indicators	pK_a values				λ_{max},[d] mμ
	H_2SO_4[a]	H_3PO_4	HCl	HOTs	
N,N-Dimethyl-4-nitroaniline	0.66	0.66	0.66	0.66	423
N-(2,4-Dinitrophenyl)piperidine	−0.38	−0.44	−0.46	−0.34	395–397
N,N-Dimethyl-2,6-dinitro-4-methylaniline	−1.66	−1.73	−1.81	...	445–452
N,N-Dimethyl-2,4-dinitro-1-naphthylamine	−2.59	−2.72	−2.74	...	430
N-Methyl-4-nitrodiphenylamine	−3.42	−3.42	−3.31	...	417–427
N-Methyl-4′-bromo-4-nitrodiphenylamine	−4.21	−4.11	−4.16	...	413–424
N,N-Diethyl-2,4,6-trinitroaniline	−5.71	−5.81	−6.02	...	395–402
p-Nitroaniline	0.99^b	0.99	0.99^b	0.99	382
o-Nitroaniline	-0.25^b	−0.25, -0.22^b	−0.31, -0.29^b	−0.36	412
4-Chloro-2-nitroaniline	-0.97^b	−0.97, -1.01^b	−1.09, -1.03^b	...	425
2,5-Dichloro-4-nitroaniline	-1.78^b	−1.66	−1.82	...	371–372
2,4-Dichloro-6-nitroaniline	-3.34^b	−2.78, -3.10^b	−3.27	...	422–425
4,4′,4′′-Trimethoxytriphenylcarbinol	0.82^c	0.82^a	0.82^a	0.82	483
4,4′-Dimethoxytriphenylcarbinol	-1.24^c	−1.23	−1.06	−0.83	495–497
4-Methoxytriphenylcarbinol	-3.40^c	−3.42	−3.08	...	472–475
4-Methyltriphenylcarbinol	-5.24^c	−5.34	−4.93	...	450–452
Triphenylcarbinol	-6.63^c	−6.50	−6.12	...	432

[a] Reference 2. [b] References 4 and 6. [c] Reference 5. [d] Maximum absorption as a function of wavelength for increasing strength of hydrochloric acid solutions used in the respective indicator study. Reference 1.

Spectrophotometric measurements were made and treated in the usual way.[2] There was little trouble from solvent shifts of the wavelength maxima either from one acid system to another or within any given aqueous acid system. Detailed tabulation of the wavelengths and optical densities in different solutions may be found in the thesis of G. W. M.[1] The H_0''' scale was anchored to a standard state in water by means of a plot of log $(BH^+)/(B)$ − log (H^+) *vs.* molarity in aqueous hydrochloric acid for the most basic member of the series, N,N-dimethyl-4-nitroaniline, as recommended by Paul and Long.[6] Each of the three acidity scales measured directly here is based on a value found in this way.[5,6] The pK_a of this indicator is then used as a starting point for generating each of the scales in each of the acid series.

Table II. Acidity Functions in Hydrochloric Acid

% HCl	H_0'	H_0'''	H_R	H_R'[a]
0.10	1.55	1.57	1.70	1.70
0.20	1.23	1.27	1.36	1.36
0.30	1.05	1.09	1.16	1.16
0.40	0.94	0.91	1.08	1.08
0.60	0.78	0.70	0.83	0.83
1.00	0.52	0.49	0.56	0.56
2.00	0.16	0.09	0.11	0.12
4.00	−0.25	−0.46	−0.51	−0.49
6.00	−0.55	−0.83	−0.97	−0.94
8.00	−0.79	−1.16	−1.38	−1.33
10.00	−1.01	−1.51	−1.74	−1.67
12.00	−1.24	−1.84	−2.10	−2.01
14.00	−1.46	−2.12	−2.50	−2.39
16.00	−1.68	−2.40	−2.96	−2.82
18.00	−1.90	−2.68	−3.38	−3.20
20.00	−2.12	−2.96	−3.80	−3.58
22.00	−2.34	−3.27	−4.27	−4.01
24.00	−2.56	−3.59	−4.77	−4.46
26.00	−2.81	−3.94	−5.26	−4.90
28.00	−3.07	−4.29	−5.74	−5.32
30.00	−3.33	−4.63	−6.23	−5.75
32.00	−3.59	−4.96	−6.73	−6.18
34.00	−3.85	−5.30	−7.21	−6.58
36.00	−4.11	−5.63	−7.69	−6.97
38.00	−4.37	−5.96		

[a] $H_R' = H_R - \log a_{H_2O}$. See M. Randall and L. E. Young, *J. Am. Chem. Soc.*, **50**, 989 (1928), for the activity of water in hydrochloric acid.

Table III. Acidity Functions in Phosphoric Acid

% H_3PO_4	H_0'	H_0'''	H_R	H_R'[a]
0.54	1.71	1.73	1.82	1.82
1.02	1.52	1.56	1.60	1.60
2.06	1.28	1.30	1.41	1.41
4.00	1.06	1.02	1.14	1.14
8.00	0.75	0.66	0.77	0.77
12.00	0.52	0.42	0.41	0.42
16.00	0.33	0.17	0.06	0.08
20.00	0.15	−0.09	−0.30	−0.28
24.00	−0.01	−0.35	−0.66	−0.63
28.00	−0.17	−0.61	−1.03	−0.99
32.00	−0.34	−0.88	−1.39	−1.34
36.00	−0.53	−1.17	−1.75	−1.68
40.00	−0.72	−1.47	−2.12	−2.03
44.00	−0.89	−1.78	−2.55	−2.44
48.00	−1.07	−2.10	−3.05	−2.92
52.00	−1.27	−2.40	−3.56	−3.39
56.00	−1.47	−2.72	−4.06	−3.85
60.00	−1.66	−3.03	−4.65	−4.38
64.00	−1.91	−3.39	−5.34	−5.00
68.00	−2.16	−3.76	−6.04	−5.63
72.00	−2.42	−4.15	−6.76	−6.26
76.00	−2.71	−4.58	−7.49	−6.86
80.00	−3.05	−5.03	−8.20	−7.42
85.00	−3.48	−5.89		

[a] $H_R' = H_R - \log a_{H_2O}$. See K. E. Elmore, C. M. Mason, and J. H. Christensen, *J. Am. Chem. Soc.*, **68**, 2528 (1946), for the activity of water in phosphoric acid.

Results

The indicator measurements that we have made generate seven new acidity scales directly, that for tertiary amines in aqueous phosphoric, hydrochloric, and *p*-toluenesulfonic acids, that for the triarylcarbinols in these same media, and that for primary anilines in *p*-toluenesulfonic acid. Although H_0 has been known for many years in phosphoric and hydrochloric acids, we have repeated many of these measurements and generally agree with the older work. The data also yield the pK_a values of the conjugate acids of the amines or of the carbonium ions at a standard state of high dilution in water.[6,7] Since they are all referred to the same standard state, they should agree within 0.05

---

(6) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(7) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

Table IV. Acidity Functions in *p*-Toluenesulfonic Acid

% Acid	H_0'	H_0'''	H_R	$H_R'^a$
0.50	1.59	1.62	1.60	1.60
1.00	1.26	1.26	1.20	1.20
2.00	0.92	0.91	0.82	0.82
5.00	0.50	0.52	0.26	0.26
10.00	0.15	0.24	−0.20	−0.20
15.00	−0.04	0.05	−0.52	−0.51
20.00	−0.14	−0.08	−0.72	−0.70
25.00	−0.21	−0.15	−0.92	−0.90
30.00	−0.27	−0.21	−1.12	−1.09
35.00	−0.34	−0.28	−1.31	−1.27
40.00	−0.42	−0.46	−1.50	−1.45
45.00	−0.60	−0.66	−1.69	−1.62
50.00	−0.85	−0.86	−1.88	−1.79
55.00	−1.05	−1.14	−2.16	−2.04

[a] $H_R' = H_R - \log a_{H_2O}$. See O. D. Bonner and J. R. Overton, *J. Phys. Chem.*, 67, 1035 (1963), for the activity of water in aqueous solutions of *p*-toluenesulfonic acid.

pK_a unit if the experimental results are good and the overlap method is valid in each medium.[6,7] This kind of self-consistency is mostly found in Table I, where our results are compared with each other and with those of previous workers. The disparities will be considered in the Discussion. A complete tabulation of the new acidity functions is given in Tables II, III, and IV, and those for sulfuric acid may be found in our previous paper[2] or the references cited therein. The three measured acidity functions H_0', H_0''', and H_R, as well as the derived function H_R', in phosphoric and hydrochloric acids are compared graphically in Figures 1 and 2 with the equivalent plot for sulfuric acid in Figure 3, and later with that for *p*-toluenesulfonic acid in Figure 6. It will be noted that several kinds of concentration units are laid off along the abscissa.

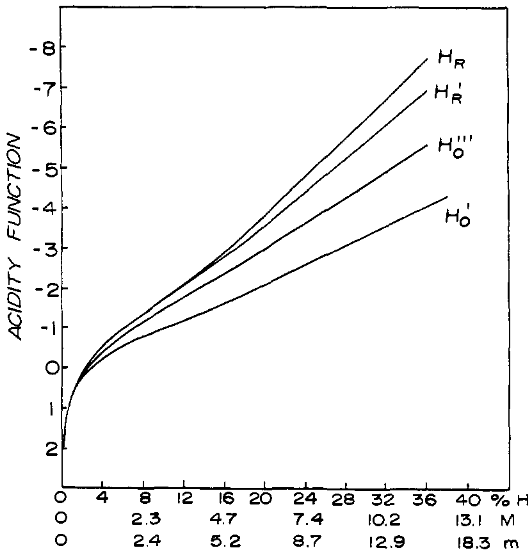

Figure 1. Acidity functions *vs.* concentration of hydrochloric acid in terms of weight per cent, molarity, and molality.

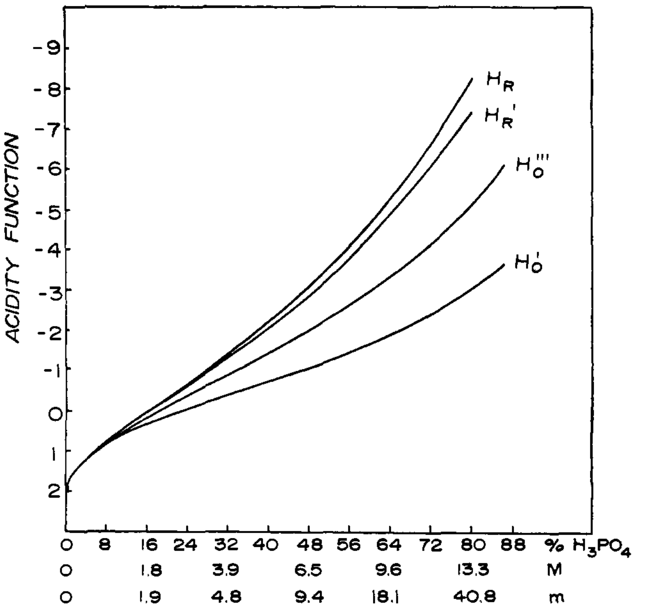

Figure 2. Acidity functions, *vs.* concentration of phosphoric acid in terms of weight per cent, molarity, and molality.

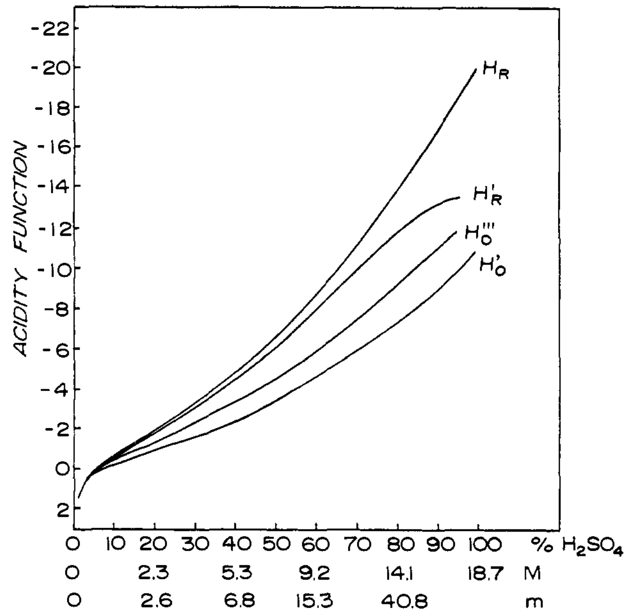

Figure 3. Acidity functions *vs.* concentration of sulfuric acid in terms of weight per cent, molarity, and molality.

Discussion

The experiments that we present here represent the perturbation of indicator acidity functions in terms of two variables: the structure of the indicator and the nature of the medium. We shall consider these below separately and then see how they may interact with each other.

1. Effect of Indicator Structure. Figures 1, 2, and 3 show that the difference in behavior between primary anilines, tertiary anilines, and triarylcarbinol indicators, which is observed in the aqueous sulfuric acid system, is also found in aqueous hydrochloric and phosphoric acids. The relatively good agreement of pK_a values for each series of compounds in the different media indicates that although a different acidity function is required for each series of bases (B_1, B_2 . . . B_i) within that series, Hammett's activity coefficient postulate[2,6,7]

$$\left(\frac{f_{B_1}f_{B_2H^+}}{f_{B_1H^+}f_{B_2}}\right) = 1$$

holds rather well. Therefore, structurally similar bases do seem to generate consistent acidity functions. The worst disagreement between pK_a values is naturally found for the least basic indicators since the values for them are obtained in media farthest removed from the standard state (pure water) to which pK_a values in all these media are referred. This is due to the cumulative effects of imperfect overlap. The triarylcarbinols seem to be slightly more sensitive to the nature of the medium than are the anilines.

We note that the order of acidity functions is the same in all three acids H_2SO_4, HCl, and H_3PO_4 (*p*-toluenesulfonic acid will be considered later), namely $H_R > H_R' > H_0''' > H_0'$ corresponding to the indicator order triarylcarbinols > tertiary amines > primary amines.

The equilibria involved are expressed by the following formal definitions.[2]

For primary anilines

$$B'H^+ \rightleftharpoons B' + H^+ \tag{1}$$

$$H_0' = -\log a_{H^+} - \log f_{B'} + \log f_{B'H^+} \tag{1a}$$

For tertiary anilines

$$B'''H^+ \rightleftharpoons B''' + H^+ \tag{2}$$

$$H_0''' = -\log a_{H^+} - \log f_{B'''} + \log f_{B'''H^+} \tag{2a}$$

For arylcarbinols

$$Ar_3C^+ + H_2O \rightleftharpoons Ar_3COH + H^+ \tag{3}$$

$$H_R = -\log a_{H^+} + \log a_{H_2O} - \log f_{Ar_3COH} + \log f_{Ar_3C^+} \tag{3a}$$

H_R' is defined as

$$H_R' = H_R - \log a_{H_2O} = -\log a_{H^+} - \log f_{Ar_3COH} + \log f_{Ar_3C^+} \tag{4}$$

so that it refers to the hypothetical reaction

$$Ar_3C^+ \rightleftharpoons Ar_3COH + H^+$$

e.g., that between a neutral base and a carbonium ion.[8] The comparison of acidity functions is now reduced to considering how and why the activity coefficients for the three types of bases (f_{B}', f_{B}''', and f_{Ar_3COH}) and their ions ($f_{B'H^+}$, $f_{B'''H^+}$, and $f_{Ar_3C^+}$) respond to increasing acidity relative to a standard state (all f values = 1) in pure water. The problem of how $\log a_{H^+}$ is affected by medium change vanishes if we compare the acidity functions with each other.[2,10,11] For instance, in the same series of media[7]

$$H_R' - H_0' = (\log f_{B'} - \log f_{ROH}) + (\log f_{R^+} - \log f_{B'H^+}) \tag{5}$$

or

$$H_0''' - H_0' = (\log f_{B'} - \log f_{B'''}) + (\log f_{B'''H^+} - \log f_{B'H^+}) \tag{6}$$

if we use as a standard of reference the primary aniline scale of Jorgenson and Hartter[4] which we have referred to previously as H_0' (ref 2). The difference $H_0''' - H_0'$ is then directly equated to

$$\log \left(\frac{f_{B'} f_{B'''H^+}}{f_{B'''} f_{B'H^+}} \right) \tag{7}$$

i.e., to the degree of failure of Hammett's activity coefficient postulate. We shall refer to terms of this form hereafter as "failure ratios."

Thanks to Deno[12] and Boyd[11] a good deal is known about the behavior of the six kinds of activity coefficients we are dealing with here in aqueous sulfuric acid, but we have no information about them in the other three acids.

What is found in sulfuric acid is that unprotonated nonelectrolytes are salted out in weak acid, then maintain nearly constant solubility in intermediate acid, but undergo a sharp increase in solubility in strong acid. Anilinium and carbonium ions are increasingly soluble as the acid strength increases. The rate of solubility increase for the three kinds of ions follows the order carbonium > tertiary anilinium > primary anilinium, the same in which the corresponding acidity functions increase.

Any quantitative interpretation is badly compromised from the start by the fact that almost all of the various classes of Brønsted bases used to set up acidity functions carry nitro groups to reduce their basicities, and these have large and specific effects on activity coefficients of ions and molecules.[2] However, the order triarylcarbinol > tertiary aniline > primary aniline can be qualitatively explained in at least two different ways.

The most obvious and naive one (and this appears to have been underemphasized in previous discussions) is that this order corresponds *very roughly* to that of the sizes of the molecules and ions of the three classes of indicators. A child looking at the structure of the three classes of indicators in Table I would notice at once that the H_0''' compounds are on the average about half again the size of the H_0' ones, and the H_R carbinols are two or three times as large.[13]

The second way of looking at the order of acidity functions is in terms of substitution at the acidic site in the ion and the degree of hydration that may be written for it. We have considered this previously[2] in the aqueous sulfuric acid system and will examine it further.

2. Effect of Acid Variation on the Acidity Functions. Figures 1, 2, 3, and 6 show that although the general order of the four acidity functions H_R, H_R', H_0''', and H_0' is maintained in the four acids H_2SO_4, H_3PO_4, HCl, and HOTs, each system has its own peculiarities. The four acids differ in a number of ways. Due to different molecular weights and densities, none of the concentration units shown on the plots is really comparable from one acid to another, although those for phosphoric and sulfuric acid are nearly so. In order to make the best analysis of factors that cause the variation of acidity function with acid in terms of relevant activity coefficients, we will use H_0' as our standard of reference and consider how the other functions depart from it in the four acids.

Since all activity coefficients are referred to the same standard state in pure water, we are free to do this. However, when we wish to compare the degree of acidity function failure, as manifested in ($H_0''' - H_0'$) or ($H_R' - H_0'$), from one acid to another, we face a serious problem since it is by no means clear

---

(8) Long[9] has criticized this definition of such a function on the grounds that triarylcarbinols are not good models as Brønsted base carbonium ion precursors.

(9) F. A. Long and J. Schulze, *J. Am. Chem. Soc.*, **86**, 327 (1964).

(10) R. W. Taft, Jr., *ibid.*, **82**, 2965 (1960).

(11) R. H. Boyd, *ibid.*, **85**, 1555 (1963).

(12) N. C. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

(13) We realize that relating acidity functions to the sizes of the base molecules is a gross oversimplification to which there are many well-known exceptions. We introduce the matter here because it seems to have dropped out of perspective recently.

what concentration units provide a common basis for comparison.

An attractive solution would be to plot these differences against log a_{H_2O}. Wyatt[14] discovered that it was possible to put the traditional H_0[4] values for a number of mineral acids on a nearly linear basis in terms of this function, and quite recently Yates and Wai[15] have found that very carefully determined values of H_0' in H_2SO_4 and $HClO_4$ may be fitted beautifully to a common curve.[16] One might expect that the H_0''' would also be a singular function of log a_{H_2O} and might even hope that the difference ($H_0''' - H_0'$) would be. Figure 4 demolishes this possibility.

One of the factors that is classically supposed to govern the behavior of ionic activity coefficients is hydration. In our previous paper, we rejected the idea that the difference between H_R' or H_0''' and H_0' could be entirely ascribed to constant differences in hydration between carbonium, tertiary, and primary ammonium ions across a wide range of aqueous sulfuric acid solutions. However, it might still be possible for the hydration difference to be a singular function of "free water" going from one acid to another. Clearly this is not the case; and *although all of the activity coefficient behavior can always be formally ascribed to different degrees of hydration,* this approach does not seem to explain the behavior of these acidity functions in any simple terms.

Other factors than hydration are also believed to affect activity coefficients in solutions of strong electrolytes. Long and his colleagues[6,17–19] have considered them as they bear on acidity functions by examining the effects of added salts on H_0 (*i.e.*, H_0'). Paul's[19] careful study of salt effects on *p*-nitroaniline in aqueous hydrochloric acid indicates that the H_0 values for this indicator are very sensitive to the quantity and nature of added salt and that much of the behavior of H_0 can be laid directly to salt effects on the f_B term. Salts that salt out most nonelectrolytes (*i.e.*, sodium chloride) sharply increase the apparent acidity of the medium as measured by H_0 through increasing the escaping tendency of the free base to its cation. The presence of tetralkylammonium salts, which salt-in free bases, sharply reduces the (indicator) acidity. Furthermore, Paul[19] found that the salt effect was related to the size of the indicator molecule, so that the salt effects on both H_0' and f_B were considerably greater for diphenylamine than for *p*-nitroaniline.[20]

Quite recently, two other groups of workers[21,22] have reported that the H_R function responds in the same way to added salt as does the H_0 function, but is considerably more sensitive. Again it appears that the salt effects on f_B are more important than on f_{BH^+} and that sensitivity to medium effects is correlated with the size of the indicator molecules. The general drift of these results suggests that although salt effects on nonelectrolytes (especially those with nitro groups) are quite specific, there is a crude general relation between the salting parameters for a base in a series of media and its acidity function behavior. The bigger the molecule, the more sensitive its solubility and its acidity function will be to added salts. However, not all salts have as big an influence on the acidity function as they have on the salting parameter. Sodium *p*-toluenesulfonate has a very large salting-in effect on *p*-nitroaniline but decreases its H_0 in HCl only slightly.

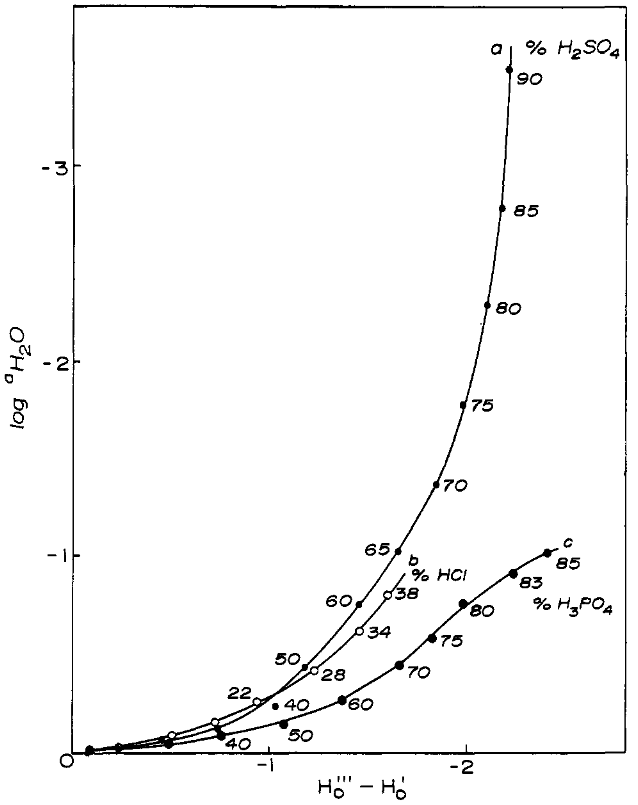

Figure 4. $H_0''' - H_0'$ *vs.* log a_{H_2O} for sulfuric, hydrochloric, and phosphoric acids.

If we may generalize again, it is intuitively attractive to consider that nonelectrolytes are more sensitive to salt effects than are electrolytes of the same molar volume. It is also reasonable that work terms, such as the activity coefficient, will be quite sensitive to the volumes occupied by solute molecules because of $P\Delta V$ work that must be expended against the internal pressure of the solvent.[23]

Aqueous acids such as sulfuric, hydrochloric, and perchloric acids are strong electrolytes, and aqueous phosphoric is less so. Therefore, at least some of their influence on activity coefficients and hence, on acidity functions, must be due to salt effects of their anions. Paul[19] indeed found that up to 3 M the indicator acidity of hydrochloric acid solutions could be explained in terms of its having the same general salt effect on itself as sodium chloride would have had if total electrolyte concentration were considered.

In view of these relationships between salting terms and acidity functions, we have tried to use the acid molarity as a suitable function for comparing the in-

---

(14) P. A. H. Wyatt, *Discussions Faraday Soc.*, **24**, 162 (1957).

(15) K. Yates and H. Wai, *J. Am. Chem. Soc.*, **86**, 5408, (1964).

(16) Professor Yates' group is now examining H_0''' in perchloric acid.

(17) F. A. Long and W. F. McDevit, *Chem. Rev.*, **51**, 119 (1952).

(18) F. A. Long and D. McIntyre, *J. Am. Chem. Soc.*, **76**, 3243 (1954).

(19) M. A. Paul, *ibid.*, **76**, 3236 (1954).

(20) We note from our present vantage point that a hydration argument could also be introduced here.

(21) B. J. Huckings and M. D. Johnson, *J. Chem. Soc.*, 5371 (1964).

(22) C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2773 (1963).

(23) N. C. Deno and C. H. Spink, *J. Phys. Chem.*, **67**, 1347 (1963).

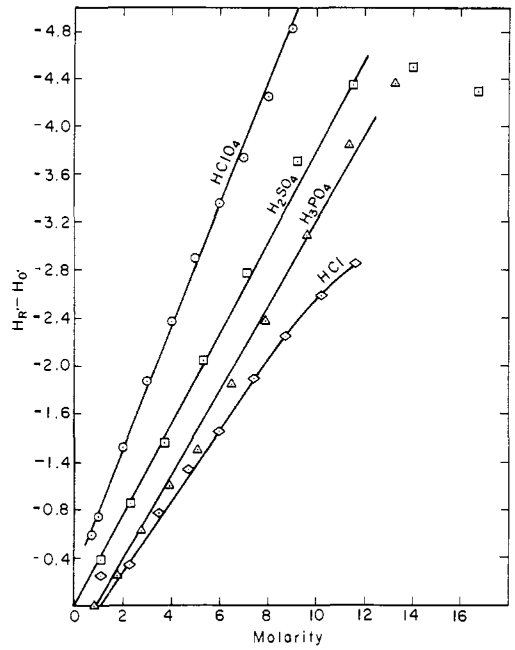

Figure 5. Correlation of the acidity function failure term ($H_R' - H_0'$) with acid molarity in H_2SO_4 (□), HCl (◇), H_3PO_4 (△), $HClO_4$ (○). The data for H_R in $HClO_4$ were taken from N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *J. Am. Chem. Soc.*, **81**, 2344 (1959).

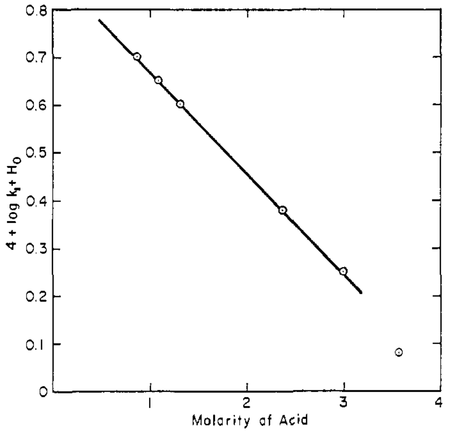

Figure 6. Kinetic plot of data for enolization of acetophenone in perchloric acid: L. Zucker and L. Hammett, *J. Am. Chem. Soc.*, **61**, 2791 (1939).

fluence of hydrochloric, sulfuric, and phosphoric acids on the logarithmic failure ratios (see eq 7) ($H_0''' - H_0'$), ($H_R' - H_0'$), and ($H_R' - H_0'''$). In contrast to the variously shaped curves shown in Figure 4, fairly good linear behavior is noted out to quite strong acid in Figure 5, which is an example of such a plot.

On all three plots of this type, the slopes of the failure functions run in the order $H_2SO_4 > H_3PO_4 > HCl$, and phosphoric acid shows no abnormalities relative to the other two.[14] These plots demonstrate that the activity coefficient terms for acidity function failure follow the same form as the Setschenow equation[9] for salt effects on activity coefficients of nonelectrolytes out to fairly high acidities. Using the data in Figure 5 as a criterion, acidity function failure is most serious in perchloric and sulfuric acids (the most popular media for acid catalysis work) and is somewhat less so in hydrochloric acid.

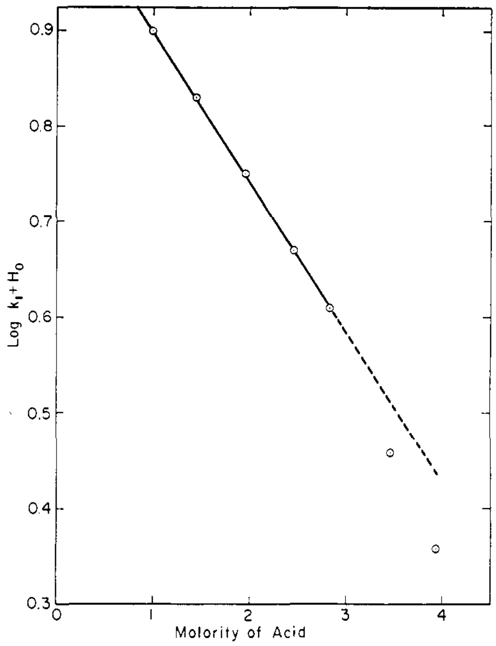

Figure 7. Kinetic data for hydrolysis of γ-butyrolactone in hydrochloric acid: F. Long, F. B. Dunkle, and W. F. McDevitt, *J. Phys. Chem.*, **55**, 829 (1951).

The only relevant datum on the salting behavior of nonelectrolytes or salts that we know of is the fact that salting parameters[9] for both oxygen and nitrous oxide also are considerably larger in sulfuric acid than in hydrochloric acid.

The failure of pseudo-first-order rate constants of acid-catalyzed reactions to follow the H_0 type of acidity function has received much attention through the years.[24] Here the degree of failure of the log k term to correlate with H_0 can be written in terms of an activity coefficient ratio

$$\log k = -H_0 + \log \frac{f_S f_{BH^+}}{f^* f_B} + \text{constant}$$

where S applies to the substrate undergoing acid-catalyzed reaction, B is the Hammett indicator for that part of the acidity range where k was measured, and f^* is the activity coefficient of the activated complex in the transition state.

In view of the rather good linearity which we have found for the plots of acidity function failure terms *vs.* molarity, it is attractive to try a test of eq 8

$$\log k + H_0 = AM_{\text{acid}} \tag{8}$$

which, if it were linear, would correspond to a complex Setschenow-type of function

$$\log \frac{f_S f_{BH^+}}{f^* f_B} = AM_{\text{acid}} = \log f_S + \log f_{BH^+} - \log f^* - \log f_B \tag{9}$$

Here A is a combined Setschenow product for the medium effect of the four activity coefficients and M is the molarity of the acid.

Figures 6 and 7 show the result of applying this approach to two classical cases, and it is seen that rather

---

[24] For good reviews see: K. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 430; F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957); and J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4935 (1961).

good linearity is found over a range of acidity comparable to the acidity function plots. If there is much generality to such plots, they may be of use for analyzing the causes of acidity function failure in kinetics and hence to a better understanding of acid catalysis. We believe that this method of presentation has the virtue of expressing the failure in terms of activity coefficients which are actually measurable rather than in terms of hydration numbers[24] which are very hard to establish. Such an analysis can lead directly to the activity coefficient behavior of the activated complex f^* which may then be compared with suitable model ions.

3. *p*-Toluenesulfonic Acid. The results of Long and McIntyre[18] make it clear that *p*-toluenesulfonate ion has a very large salting-in effect on nonelectrolytes of the Hammett indicator type, although it does not affect H_0' nearly as much. Since we were not able to cause large changes in the relative positions of H_0' and H_0''' through the series H_2SO_4, HCl, H_3PO_4, we decided to try *p*-toluenesulfonic acid. It was reasoned that the change to a potent salting-in anion might seriously disrupt the balance of factors affecting the acidity functions and give a clue to what ingredients should go into a medium in which a variety of Brønsted bases would indeed follow a common acidity function. In Figure 8 and Table IV, it is seen that in this medium a large change indeed has occurred and that H_0''' and H_0' have been brought close together. Whether this means that the acidity functions for other Brønsted bases would also behave in this way is a moot point; clearly H_R' is still separated.

Unfortunately, even if all Brønsted bases did follow a common acidity function in these media, it is plain from Figure 8 that they are too weakly acidic toward indicators to permit a broad range of acidities. Arenesulfonic acids are generally believed to be nearly as strong as sulfuric acid. Dinius and Choppin[25] have, in fact, shown that in terms of hydronium proton deshielding, *p*-toluenesulfonic acid is as strong as hydrochloric or nitric acid in moderately concentrated solutions. We conclude that its weak indicator acidity is a direct outcome of a strong salting-in of the free base by the toluenesulfonate ions. This reduces $\log f_{\mathrm{B}}$ relative to $\log f_{\mathrm{BH^+}}$ so greatly that these strongly acidic solutions (in terms of proton level) are effectively rather weak toward these Brønsted bases.

Log $a_{\mathrm{H_2O}}$ changes so little with increasing HOTs concentration that we could not include data for this acid on Figure 4. By this criterion also, it is a weak acid. The poor agreement for the $\mathrm{p}K_{\mathrm{a}}$ of 4,4′-dimethoxytriphenylcarbinol in this medium with that in the other three acids shown in Table I suggests that it is probably a poor system for acidity function work.

An attempt to reduce the salting-in factor and thus strike a happy compromise by using aqueous methanesulfonic acid soon led us to the conclusion that this acid behaves as a strong mineral acid, giving indeed a wide acidity range,[26] but again a large difference between H_0' and H_0'''. Thus, although *p*-toluenesulfonic acid is the first medium we have encountered in which the protonation behavior of primary and tertiary nitrated anilines is reasonably close together, it gives only a very short range of acidities (down to -1 H_0 unit), and there is no guarantee that other classes of Brønsted bases will behave as the nitrated anilines do in it. However, it may perhaps suggest a direction toward a better medium in which a single acidity function for many classes of Brønsted bases will be found.

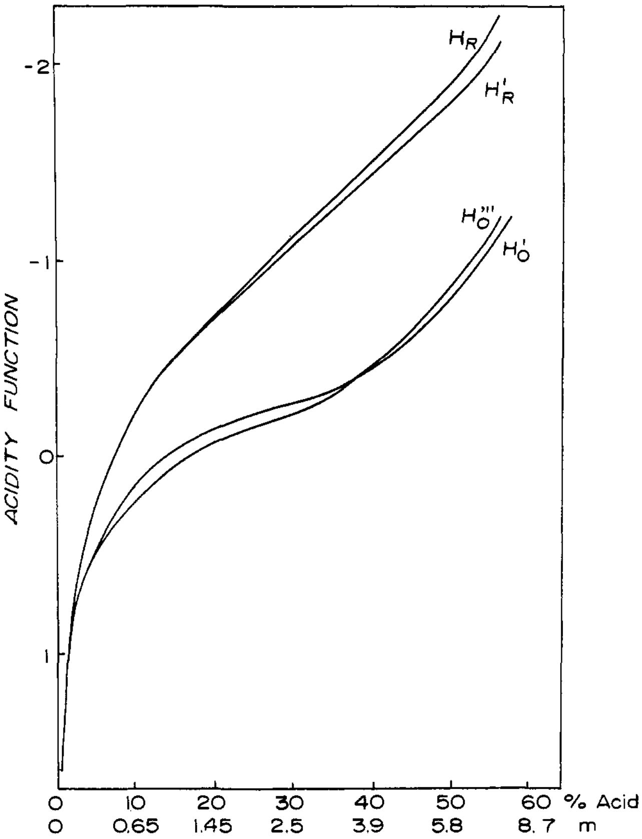

Figure 8. Acidity functions *vs.* concentration of *p*-toluenesulfonic acid in terms of weight per cent and molality.

We note in conclusion that the indiscriminant use of acidity functions for mechanistic interpretation[24] is now more hazardous than ever. Not only do different Brønsted bases follow different acidity functions, but the differences between them vary from one strong acid to another. Perhaps if more is learned about activity coefficients of organic molecules and ions in different acidic media, the situation may be simplified. For the present, we believe that careful mechanistic studies should include measurement of the actual acidity function for the series of bases under kinetic examination and that both rates and equilibria should be measured in the same media.[27,28]

---

(25) R. H. Dinius and G. R. Choppin, *J. Phys. Chem.*, **66**, 268 (1962); **68**, 425 (1964).

(26) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(27) See, for example, K. Yates, and J. B. Stevens, *Can. J. Chem.* **43**, 529 (1965).

(28) W. M. Schubert, H. Burkett, and A. L. Schy, *J. Am. Chem. Soc.*, **86**, 2520 (1964).