# Excess Acidities. A Generalized Method for the Determination of Basicities in Aqueous Acid Mixtures

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Abstract: Excess acidities, X, have been derived using ionization ratio data for 165 weak bases in 0–99.5% aqueous sulfuric acid, and for 76 weak bases in 0–78% aqueous perchloric acid, using a computerized version of the Marziano–Passerini method. These X functions, of the form log $(f_{B*}f_{H+}/f_{B*H+})$ for a hypothetical standard base B*, permit the determination of accurate pK_{BH+} values for any base in any acidity region. This includes protonation at N, C, O, and S atoms, and bases of any charge type: negative, positive, and dipositive as well as neutral. Use of X involves the assumption that for real bases the activity coefficient terms log $(f_B f_{H+}/f_{BH+})$ are linear in one another. This avoids the more drastic cancellation assumption, and the resulting plethora of Hammett-type acidity functions. There is only *one* X function per acid system. The functions, derived pK_{BH+} values, and the associated slope parameters $m*$, characteristic of each base's ionization behavior, are compared and discussed, with a view to defining the utility and limitations of this and other methods of basicity determination.

For a weak base B which only becomes significantly protonated in strongly acidic media, K_{BH+} can be defined as the acid dissociation constant of the protonated form, BH^+:

$$B + H^+ \xrightleftharpoons{K_{BH+}} BH^+$$
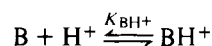
$$K_{BH+} = a_B a_{H+}/a_{BH+} = (C_B/C_{BH+})C_{H+}(f_B f_{H+}/f_{BH+})$$

where a = activity, C = molarity, and f = molarity activity coefficient. On taking logarithms, the equation

$$pK_{BH+} = \log(C_{BH+}/C_B) - \log C_{H+} - \log(f_B f_{H+}/f_{BH+}) \tag{1}$$

which is thermodynamically exact, results.

By definition the activity coefficient term in eq 1 is zero in the aqueous reference state. This reference state is the one used for pH measurements, a hypothetical ideal 1 M solution of the acid being used[1] (since C_{H+} in eq 1 is in molarity units); i.e., in water eq 1 reduces to the familiar

$$pK_{BH+} = \log I + pH \tag{2}$$

in which for brevity the ionization ratio C_{BH+}/C_B has been replaced by the symbol I.

If this equation is to be extended into nonideal, strongly acidic media, the activity coefficient term in eq 1 must be accounted for in some way. This was first attempted by Hammett and Deyrup 45 years ago.[2] They postulated that there exists an acidity function, H_0,[2,3] defined so as to be an extension of the pH scale:

$$pK_{BH+} - \log I = H_0 = -\log C_{H+} - \log (f_B f_{H+}/f_{BH+}) \tag{3}$$

A comparison of eq 3 and 1 reveals that the assumption regarding the activity coefficient term made here is that it is the same for all weak bases, i.e., that the acidity function H_0 is a unique function of acid concentration. H_0 was determined by measuring ionization ratios for progressively weaker bases;[2] writing eq 3 for two bases A and B and using this assumption shows that $pK_{AH+} - \log I_A = pK_{BH+} - \log I_B = H_0$, and log $(f_A f_{BH+}/f_B f_{AH+}) = 0$. This is the Hammett activity coefficient postulate, or the *cancellation assumption*. The acidity function H_0 was soon in general use, and proved to be a valuable tool in the study of the kinetics and mechanisms of organic reactions in strong acids.[3,4]

It became apparent, however, after a good deal of experimental work by Arnett[5] (who used the term "acidity function failure")[6] and others,[7-9] that H_0 was not a unique function but only one of many possible acidity functions. It was found that equations like eq 3 define acidity functions applicable only to

closely related compounds, H_A for amides,[7] H_1 for indoles,[8] H_0''' for tertiary amines,[5] and so on; the H_0 function was restricted to primary aromatic amines.[10] The cancellation assumption was assumed to apply within classes of compound, but not between different classes. Many different acidity functions are now available;[11] in the limit, *each* individual base B will define its own acidity function:

$$H_B = -\log I_B + pK_{BH+}$$

In 1966 Bunnett and Olsen showed that another assumption regarding the activity coefficient term in eq 1 leads to considerable simplification.[12] Their approach is to write, from eq 3 above,

$$H_0 + \log C_{H+} = -\log (f_{Am}f_{H+}/f_{AmH+}) \tag{4}$$

in which Am represents the amines used in defining the H_0 scale.[10] It is then assumed that the activity coefficient terms for individual bases are linear in eq 4, which is an "average" term for all the primary aromatic amine bases used in defining H_0:

$$\log (f_B f_{H+}/f_{BH+}) = (1 - \phi) \log (f_{Am}f_{H+}/f_{AmH+})$$

$$= (\phi - 1)(H_0 + \log C_{H+})$$

On substituting this into eq 1 and adding $(H_0 + \log C_{H+})$ to each side, the equation

$$\log I + H_0 = \phi(H_0 + \log C_{H+}) + pK_{BH+} \tag{5}$$

results.[12] By using this linear equation the number of different acidity functions needed to describe the protonation behavior of different bases has been reduced, in effect, to one. This approach works well;[12] it has been advocated by several authors,[13-15] and used extensively by Modena and Scorrano[14] and others.[16-17]

There is a drawback to this method, however; a Hammett-type acidity function is still needed, and, to derive it, the cancellation assumption must be made. Thus, two assumptions are involved, cancellation and linearity. The first of these is unnecessary; a better approach is simply to assume that all activity coefficient terms, log $(f_B f_{H+}/f_{BH+})$, are linear in one another. This is the method used by Marziano, Passerini, and their co-workers[18-21] for acid systems, and by Cox, Stewart, et al., for basic media;[22,23] the validity of the necessary assumption of linearity has been extensively tested by those groups.[20,23]

To use this approach we write

$$\log (f_B f_{H+}/f_{BH+}) = m* \log (f_{B*}f_{H+}/f_{B*H+})$$

$$= m*X \tag{6}$$

Table I. Polynomial Coefficients Giving X as a Function of wt % Acid for Aqueous Sulfuric and Perchloric Acid Mixtures

Polynomial coefficient[a]	Gives X for	
	H$_2$SO$_4$	HClO$_4$
a_1	−1.219241173460021D00	−7.450771759016141D-01
a_2	1.742125866157227D00	1.009146101776148D00
a_3	−6.297238507610308D-01	−3.059160129915656D-01
a_4	1.163763738683231D-01	4.973852154742056D-02
a_5	−1.045666178433201D-02	−4.051706497847973D-03
a_6	3.611802574524021D-04	1.285522691362373D-04

[a] Given as FORTRAN double precision values. To use these, wt % acid is expressed as z (eq 9), and X calculated using eq 10. For hand calculators, eight significant figures are sufficient to reproduce X at all acidities.

Table II. Values of Log C_{H^+} in Dilute Aqueous Sulfuric Acid[a]

% acid	Log C_{H^+}	% acid	Log C_{H^+}
0.002	−3.398	1.0	−0.898
0.005	−3.008	1.2	−0.823
0.010	−2.718	1.6	−0.702
0.015	−2.555	2.0	−0.607
0.02	−2.439	2.5	−0.511
0.03	−2.275	3.0	−0.432
0.04	−2.158	3.5	−0.364
0.06	−1.996	4.0	−0.305
0.08	−1.883	4.5	−0.252
0.10	−1.796	5.0	−0.205
0.15	−1.641	6.0	−0.122
0.2	−1.531	7.0	−0.051
0.3	−1.376	8.0	0.011
0.4	−1.264	9.0	0.067
0.6	−1.105	10.0	0.117
0.8	−0.989	12.5	0.225

[a] For more concentrated solutions, see Table III. Below 0.002% acid, bisulfate ion is fully ionized, and log C_{H^+} = log (2 × acid molarity). Obtained from ref 28.

The "excess acidity",[24] X, which is the difference between the observed acidity and that which the system would have if it were ideal, is defined as the activity coefficient ratio term for a hypothetical standard base B*. (In Marziano and Passerini's papers[18-21] X is referred to as M_c or as $M_c f(x)$, and the m^* values are the various n_{ij}; we prefer the simpler terminology used here.) On substituting eq 6 into eq 1 and rearranging we have the linear equation

$$\log I - \log C_{H^+} = m^* X + pK_{BH^+} \tag{7}$$

In order to use eq 7, we have as available data measurement of log I as a function of weight percent acid (or acid molarity) for a large number of weakly basic molecules, and values for log C_{H^+}; m^* and pK_{BH^+} are unknown constants characteristic of each base, and X is an unknown variable which applies to all bases. This situation is ideally suited to iterative solution techniques using a computer, and this is the approach herein adopted; in this paper we deal with the two commonest aqueous acid systems, 0–99.5% w/w sulfuric acid and 0–78% w/w perchloric acid. In a subsequent paper the X-function approach will be applied to kinetic studies;[25] strongly basic media have been discussed previously.[22,23]

Experimental Section

Computer Algorithm. In principle we can proceed as follows. Estimates of pK_{BH^+} and m^* for each base can be substituted into eq 7, and multiple estimates for X covering the entire acidity range obtained:

$$(\log I - \log C_{H^+} - pK_{BH^+})/m^* = X \tag{8}$$

Since most log I measurements are quoted in terms of wt % acid (w), X can be fitted to a polynomial in w:

$$X = a_0 + a_1 w + a_2 w^2 + a_3 w^3 + \ldots$$

The resulting coefficients a_i can then be used to calculate smoothed

values of X, and eq 7 used to give new estimates of pK_{BH^+} and m^*. These can give new X values, and the entire process can be repeated until no further change results.

After some experimentation it was found better not to use w itself, but z as defined in the equation

$$z = \text{antilog } (w/100) \text{ for H}_2\text{SO}_4$$

$$= \text{antilog } (w/80) \text{ for HClO}_4 \tag{9}$$

z varies between 1 and 10 as w varies between 0 and 100%, or 0 and 80%, and thus is more compatible with X, which varies between 0 and 12, approximately.[18] The range of possible z values was arbitrarily but conveniently divided into 225 equal segments of 0.04: 1–1.04 corresponds to 0–1.70% w/w, 5.48–5.52 to 73.88–74.19%, and 9.96–10 to 99.83–100% sulfuric acid. Thus the antilog form of z also counteracts the exponential increase in X,[18] which results because deviations from ideality are small in dilute solutions, and much larger in concentrated ones.

The estimates of X (eq 8) were weighted according to the corresponding log I (see below), and assigned to one of these 225 divisions, according to their wt % acid. The total in each division was then divided by the number of values assigned to it, and the resulting weighted average X fitted to a modified polynomial in z:

$$X = a_1(z - 1) + a_2(z^2 - 1) + a_3(z^3 - 1) + \ldots \tag{10}$$

This form was adopted to account for the fact that X must be zero when $Z = 1$ (0% acid), i.e., the deviation from ideality is zero in the standard state. The polynomial fitting subroutine used was a standard one, adapted from Bevington.[26a] The technique described resulted in 200–225 points being used in the fit for both sulfuric and perchloric acids, regardless of the number of individual measurements involved (1718 and 813, respectively). Thus adding more data increases the accuracy of each point rather than the total number of points to be fitted, in general. Also, no one acidity region is given priority over another; otherwise the fact that many more studies are available at low rather than high acidities would unduly emphasize this region in the fit.

Six polynomial coefficients to describe X were calculated, this being found to be the best compromise between minimizing random errors and generating random numbers; they are given in Table I. For the linear plots against X, to generate new pK_{BH^+} and m^* values, a standard weighted line-fitting subroutine from Bevington[26b] was used.

The final pK_{BH^+} and m^* values were found to be independent of the initial values chosen, as they should be. In theory, almost random numbers could be used initially; this was occasionally tested inadvertently, by keypunching errors. In practice, reasonable numbers were chosen, to minimize computer time: acidity function values and slopes[27] for perchloric acid, and the slopes and intercepts at $H_0 = 0$ of log I vs. −H_0 plots for sulfuric acid.

The program was written in the WATFIV version of FORTRAN IV; details can be obtained from the authors.

Data and Calculations. Values of log C_{H^+} in aqueous sulfuric acid are given, for convenience, in Tables II and III. These were obtained using a variety of literature data concerning the dissociation of bisulfate ion in these mixtures;[28] space considerations preclude detailed discussion here. Values of log C_{H^+} in perchloric acid were obtained directly from the acid molarity, using published 25 °C densities,[29] and assuming the acid to be fully dissociated.[30] These were provided for the computer as polynomial coefficients in a subroutine, to avoid possible graphical interpolation errors.

Table III. Values of Log C_{H+}[a] and X for 0-99.5% Aqueous Sulfuric Acid, and of X for 0-78% Aqueous Perchloric Acid

% acid	H₂SO₄ Log C_{H+}	H₂SO₄ X	HClO₄ X
5	−0.205	0.103	0.091
10	0.117	0.231	0.212
15	0.315	0.387	0.371
20	0.461	0.573	0.571
25	0.577	0.790	0.819
30	0.674	1.038	1.116
35	0.757	1.317	1.468
40	0.828	1.628	1.879
45	0.891	1.969	2.354
50	0.945	2.345	2.908
52.5	0.970	2.548	3.220
55	0.992	2.763	3.561
57.5	1.014	2.992	3.932
60	1.033	3.238	4.337
62.5	1.052	3.505	4.775
65	1.069	3.795	5.241
67.5	1.084	4.112	5.727
70	1.097	4.459	6.220
72	1.108	4.759	6.607
74	1.118	5.080	6.983
76	1.128	5.421	7.356
78	1.136	5.779	7.766
80	1.143	6.150	
82	1.143	6.528	
84	1.133	6.906	
86	1.109	7.277	
88	1.066	7.637	
90	0.996	7.985	
92	0.894	8.340	
94	0.749	8.743	
95	0.654	8.989	
96	0.539	9.285	
97	0.392	9.656	
98	0.187	10.132	
99	−0.153	10.754	
99.5	−0.504	11.136	

[a] See ref 28.

For the aqueous sulfuric acid system, we used available ionization ratio data for 15 primary amines,[10,32-37] diphenylamine,[33] and 4-nitrotoluene;[37] 14 amides[7] and related compounds;[38,39] 15 tertiary amines;[5,32] 7 hydroxy- and methoxybenzenes;[40] 12 indoles;[8] 5 positive and dipositive cobalt ethylenediamine complex ions;[41] 3 carboxylic acid anions[9,42] and 5 other negative ions;[9,34] 13 alkenes;[43] 16 carbonyl compounds (esters, acids, aldehydes, ketones, amides);[17,44] 6 α,β-unsaturated ketones and 3 steroidal ketones;[45] 13 benzophenones;[46] and 36 thio compounds;[47] 165 compounds in all. In perchloric acid, we used data for 14 primary amines;[27a,48-51] 11 amides;[27,38,52] 13 tertiary amines;[27] 15 hydroxy- and alkoxybenzenes;[40] 6 azulenes;[53] 11 azo compounds;[54] and 6 negative ions;[9] 76 compounds in all.

In many cases, measurements by different authors on the same compound have been reported. These data were amalgamated and treated simultaneously, except for that for benzophenone[17,46] and 3-hydroxycyclohex-2-en-1-one,[17,45] where the modern medium-effect-free results, obtained after the application of characteristic vector analysis,[17] are not strictly comparable with the older ones.[45,46] For instance, log I values for 4-nitroaniline in sulfuric acid have been reported by five different groups,[32-36] giving a total of 81 separate log I measurements. Only two data sets were not included, owing to incompatibility with other studies: Rochester's data for 4-nitroaniline[49] and Bonner's for 2,4-dinitroaniline,[50] both in perchloric acid. No distinction was made between measurements at 25 °C and those at "room temperature", since the probable difference between them[35,36,49] is much less than the observed experimental scatter.

Since the errors in log I measurements increase with increasing distance from 50% ionization,[55] the data were weighted to reflect this, using an error function given by Kresge and Chen[55] as a subroutine. This function was also used to calculate random errors in the original sigmoid graphs used in obtaining log I, which are linear (i.e., have the
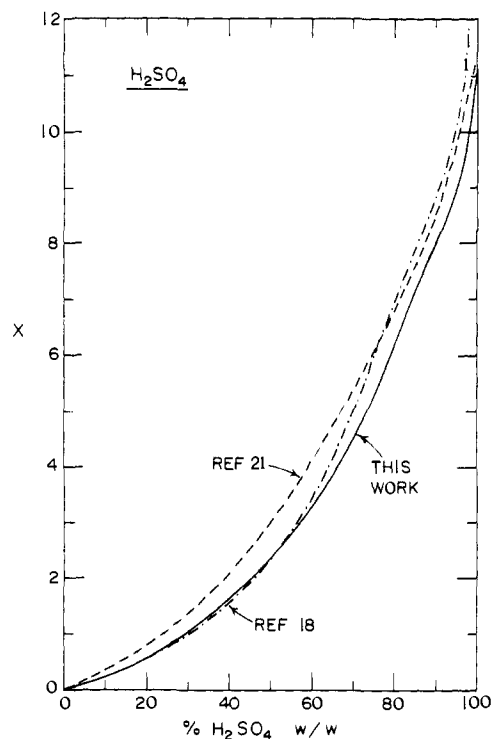
Figure 1. X as a function of wt % sulfuric acid. Solid line, this work; dashed lines, Marziano, Passerini, et al.[18,21]

same magnitude regardless of the value of log I, usually the error involved in reading optical density values from a UV spectrum), rather than random errors in the log I values themselves, which are not. These errors were used to reject points which, to a 95% confidence level, did not form part of the data set, using t statistics: in general not more than one or two points per base were rejected in this way, usually none for sets of fewer than 15 total points. They were also used as the test for convergence; the average error over all the bases was compared to the previously obtained one, for successive passes through the iterative routine; when no change was observed, convergence had occurred. This was found to be the best test; the average correlation coefficient could also be used. Comparing old and new pK_{BH+} values was less satisfactory, because for these the differences between successive passes are a function of the values themselves, being much larger at high acidities.

Results

The X functions for the sulfuric and perchloric acid systems, obtained as described in the Experimental Section, are given in Table III and illustrated, along with those determined by Marziano, Passerini, et al.,[18,21] in Figures 1 and 2. The agreement between our functions and the early ones given by Marziano, Cimino, and Passerini[18] is very good, considering that the latter were derived using the older procedure of plotting (log I − log C_{H+}) for adjacent overlapping indicators against one another.[18,22] Agreement with the more recent function given by Marziano et al.,[21] which we have multiplied by 10 and converted to wt % for comparison in Figure 1, is also reasonable, considering that a different algorithm[56] and a different data base[21] were used. In the present case, every precaution was taken to ensure the best possible fit (see Experimental Section), and considerably more experimental data were included. The overall shapes of all the functions are very similar.

Excellent linear plots according to eq 7 were obtained for all compounds studied. A correlation coefficient of 0.9917 was obtained on averaging over the 165 compounds studied in sulfuric acid, with an average 10.41 data points per base; averaging over the 76 compounds in perchloric acid gave a correlation coefficient of 0.9920 for 10.70 data points per base.

Table IV. pK_{BH^+} and m^* Values for Primary Amines and Related Compounds[a] in Sulfuric Acid

Compd[b]	pK_{BH^+} AF[a,c]	pK_{BH^+} MCP[d,e]	pK_{BH^+}[f]	m^*[f]	r[g]	N[h]	Error[i]
4-NO₂-An	1.00	1.00[j]	1.040 ± 0.002	0.97 ± 0.04	0.950	81 (3)	±0.002
Diphenylamine	0.71	—	0.765 ± 0.002	1.07 ± 0.03	0.992	31 (2)	±0.001
2-NO₂-An	−0.30	−0.34	−0.274 ± 0.005	1.00 ± 0.01	0.996	45 (3)	±0.002
4-Cl-2-NO₂-An	−1.02	−1.14	−1.01 ± 0.02	1.00 ± 0.03	0.991	23	±0.007
2,5-Di-Cl-4-NO₂-An	−1.76	−1.72	−1.72 ± 0.03	0.94 ± 0.02	0.994	25 (1)	±0.007
2-Cl-6-NO₂-An	−2.40	−2.49	−2.40 ± 0.04	0.98 ± 0.02	0.996	18 (1)	±0.007
2,4-Di-Cl-6-NO₂-An	−3.01	—	−3.30 ± 0.03	1.10 ± 0.01	0.9995	9	±0.003
2,6-Di-Cl-4-NO₂-An	−3.27	−2.98	−3.36 ± 0.05	1.05 ± 0.02	0.996	20 (1)	±0.007
2,4-Di-NO₂-An	−4.27	−4.09	−4.53 ± 0.06	1.11 ± 0.02	0.998	15	±0.005
2,6-Di-NO₂-An	−5.43	−4.97	−5.23 ± 0.16	0.99 ± 0.04	0.991	25 (2)	±0.014
4-Cl-2,6-di-NO₂-An	−6.14	—	−6.07 ± 0.11	1.04 ± 0.02	0.998	9	±0.005
2-Br-4,6-di-NO₂-An	−6.61	−6.20	−5.88 ± 0.08	0.89 ± 0.02	0.997	28 (2)	±0.007
3-Me-2,4,6-tri-NO₂-An	−8.21	−8.09	−7.64 ± 0.11	0.91 ± 0.02	0.997	29 (1)	±0.008
3-Br-2,4,6-tri-NO₂-An	−9.40	−9.18	−10.49 ± 0.31	1.14 ± 0.04	0.994	20 (2)	±0.016
3-Cl-2,4,6-tri-NO₂-An	−9.71	—	−10.70 ± 0.61	1.13 ± 0.07	0.995	5	±0.017
2,4,6-Tri-NO₂-An	−10.00	−8.15	−9.80 ± 0.13	0.99 ± 0.01	0.997	43 (2)	±0.013
4-NO₂-toluene	−11.35	—	−14.14 ± 0.69	1.28 ± 0.06	0.989	10	±0.011

[a] References 10, 32–37. [b] An = aniline. [c] Acidity function; averages if reported values differ. [d] Marziano–Cimino–Passerini, based on 4-nitroaniline, ref 18. [e] Bunnett–Olsen calculations on some of these compounds, reported in ref 16, are probably in error. [f] This work; given with standard deviation. [g] Correlation coefficient. [h] Number of points; any rejected are bracketed (see Experimental Section). [i] See text. [j] Assumed.
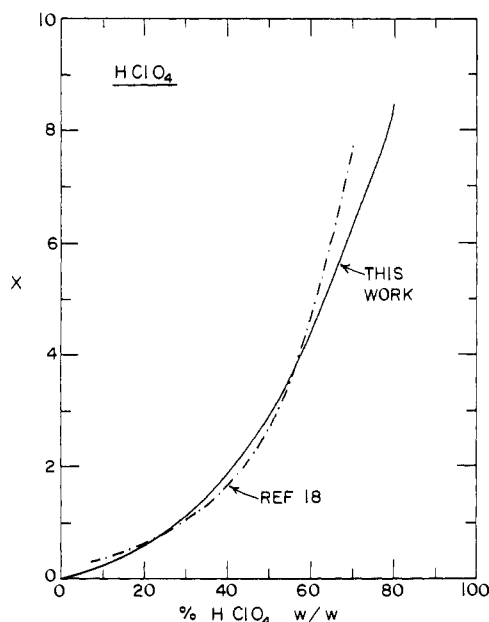
Figure 2. X as a function of wt % perchloric acid. Solid line, this work; dashed line, Marziano, Cimino, and Passerini.[18]

Standard formulas[26c] show that the probability of 10 data points with a correlation coefficient of 0.992 *not* being correlated is 1.78×10^{-8}, a negligibly small value. Thus the assumption we are using, that the activity coefficient ratios of different bases are linearly related, is amply justified.

In Table IV may be found the pK_{BH^+} values obtained in sulfuric acid for the primary amines and related compounds usually regarded as being H_0 indicators,[10,32–37] along with previous estimates;[18] also given are the m^* slope values, and relevant statistical information. Similar tables for all the other compounds investigated can be found as Tables VI–XXI in the microfilm edition of this journal. Representative plots according to eq 7 are in Figures 3 and 4. Dashed lines across these figures show log I values; the weighted line-fitting plot used fits values between −1 and +1 preferentially, weighting values outside this range much less.[55] Figure 3 illustrates the low acidity region in sulfuric acid with some of the amines of Table

IV. The data of Vinnik and Librovich[33] include log I's as high as +4 for diphenylamine and 2- and 4-nitroaniline; as can be seen, the plots remain linear even at these high values, despite their diminished accuracy.[33] Figure 4 shows the high acidity region for perchloric acid, and includes amides (O-protonation),[27] tertiary amines (N-protonation),[27] and alkoxybenzenes(C-protonation).[40,57]

The errors quoted in Tables IV and VI–XXI, when multiplied by $(A_B - A_{BH^+})/0.8686$, give the random errors in the UV absorbance (A) measurements originally used to determine the ionization ratios,[55] using $I = (A_B - A)/(A - A_{BH^+})$. The average error for the 165 compounds studied in sulfuric acid was ±0.0081, which amounts to overall agreement with experiment within 1%. This can only be described as excellent. For the 76 compounds in perchloric acid the even better number ±0.0065 was obtained.

In Table V we have quoted the average m^* values for compounds usually regarded as forming sets of acidity function indicators; the m^*'s for all compounds studied are illustrated in histogram form in Figure 5. A comparison of pK_{BH^+} values for 50 compounds which have been studied both in sulfuric and perchloric acid is in Figure 6.

Discussion

Firstly, it is necessary to consider what an X function actually is, in the acidity function context.[58] It was mentioned in the introduction that, in the limit, ionization ratio measurements for any base B define an acidity function applicable only to that base. If these ionization ratios were available over the entire acidity range a family of individual acidity function curves would result:

$$H_B = -\log I_B + pK_{BH^+}$$

The simplifying assumption used here, based on experimental observation,[12,20,22] is that all these possible curves are related; acidity functions have been shown to be linear in one another.[1,27] The differences between log C_{H^+} and each $-H_B$ (i.e., log $(f_B f_{H^+}/f_{BH^+})$) follow the same functional form (X) and differ from one another only by constant scaling factors (m^*). Thus the assumption we are using could be written

$$-H_B - \log C_{H^+} = m^*_B X$$

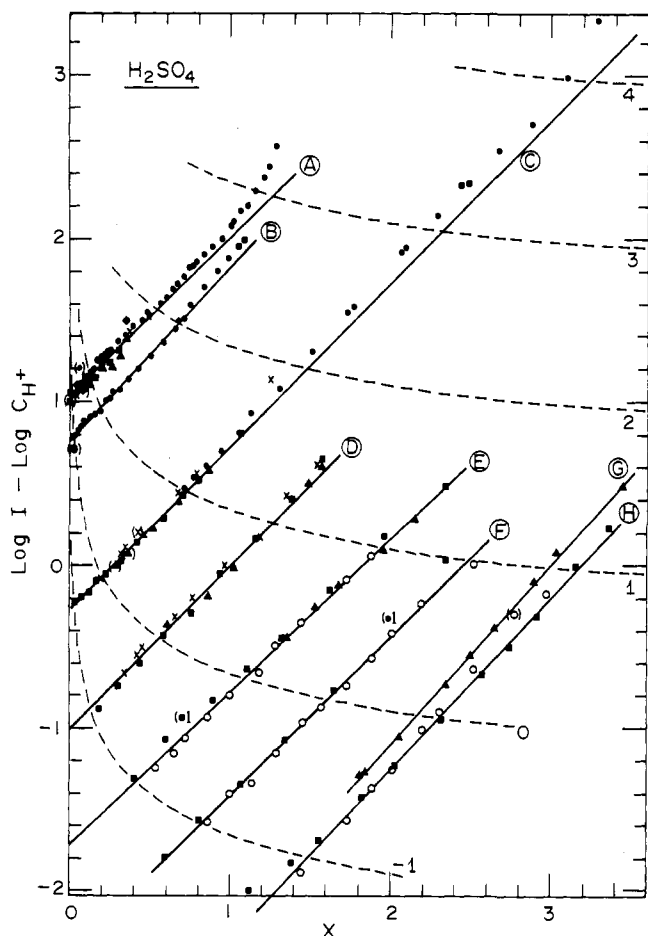and elimination of H_B between these two equations yields eq

Figure 3. Plots of (log I — log C_{H+}) vs. X, for 4-nitroaniline (A), diphenylamine (B), 2-nitroaniline (C), 4-chloro-2-nitroaniline (D), 2,5-dichloro-4-nitroaniline (E), 2-chloro-6-nitroaniline (F), 2,4-dichloro-6-nitroaniline (G), and 2,6-dichloro-4-nitroaniline (H), in aqueous sulfuric acid. Log I data from (X) ref 32, (●) ref 33, (◆) ref 34, (■) ref 35, (▲) ref 36, (O) ref 10. Numbers to the right of the dashed lines are log I values.

Figure 4. Plots of (log I — log C_{H+}) vs. X, for 2,4-dichloro-3,5-dinitrobenzamide (A), 2,4,6-trinitrobenzamide (B), N-methyl-X',4'-dibromo-2,4-dinitrodiphenylamine (C), N-methyl-2,2',4,4'-tetranitrodiphenylamine (D), 1,3-dimethoxybenzene (E), and 1-hydroxy-3,5-dimethylbenzene (F), in aqueous perchloric acid. Log I data for amides (●) and tertiary amines (■) from ref 27a; for the substituted benzenes (O) from ref 40. Numbers to the right of the dashed lines are log I values.

Table V. Average m^* Values for Acidity Function Sets

Compds	Acidity function	No.[a]	m^{*b}	Ref
		H_2SO_4		
Primary amines	H_0	16	1.02 ± 0.08	10, 32–37
Amides	H_A	14	0.60 ± 0.11	7, 38, 39
Tertiary amines	H_0'''	15	1.42 ± 0.23	5, 32
Indoles	H_1	9	1.55 ± 0.08	8
Anions	H_-	8	0.98 ± 0.31	9, 34, 42
Benzophenones	H_B	13	0.75 ± 0.24	46
Thio compounds	H_T	36	1.39 ± 0.14	47
		$HClO_4$		
Primary amines	H_0	14	1.09 ± 0.25	27a, 48–51
Amides	H_A	11	0.51 ± 0.07	27, 38, 52
Tertiary amines	H_0'''	13	1.65 ± 0.42	27
Azulenes	H_m	5	1.84 ± 0.22	53
Azo compounds	H_{Az}	11	1.26 ± 0.12	54
Anions	H_-	6	1.18 ± 0.25	9

[a] Number of indicator bases included. [b] Mean value with standard deviation.

7. We have thus generalized the acidity function concept by making use of the excess acidity, X.

This X function is a unique function of acid concentration, that is, the *shape* of the curves in Figures 1 and 2 is uniquely determined for a given acid system (given a sufficiently large family of bases). Hence our assertion that there is only *one X* function per acid system. However, in order to define a reasonable scale of multipliers (m^* values), it is necessary to define one m^* in some fashion, i.e., to have a reference compound. Bunnett and Olsen chose a hypothetical primary aromatic amine which follows H_0 exactly,[12] since their method is based on H_0. Marziano, Cimino, and Passerini chose a real primary amine as a reference,[18] as did Cox and Stewart.[22] In this work we have chosen a hypothetical compound B*, unspecified as to type, which has $m^* = 1.000$. This is an *arbitrary* choice.[59] Nevertheless it was thought that m^* values compatible with the large number of preexisting ϕ values would result if this choice was made, although this was not an essential requirement of the method. In fact this turned out to be the case. To a reasonable approximation $m^* \approx 1 - \phi$ and the two are interconvertible, at least in sulfuric acid; $H_0 + \log C_{H+} \approx - X$ (see eq 4). This agreement only arises because H_0 is a well-behaved acidity function in this medium, as discussed below.

Cox and Stewart[22] have suggested that a variation in m^* values within ±0.1 is required for a series of compounds to form a suitable acidity function set. It can be seen from Table V that
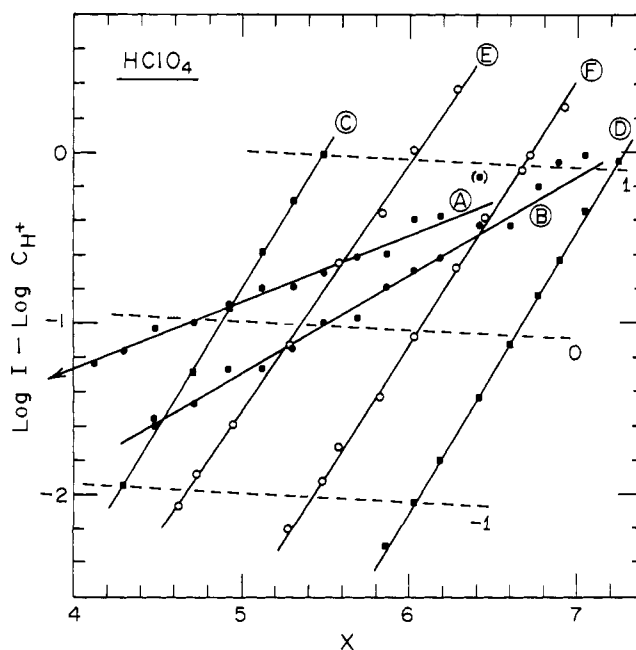
only three sets meet this criterion, the H_0 primary amines[10,32–37] and H_1 indoles[8] in sulfuric acid and the H_A amides[27,38,52] in perchloric acid. Stretching a point and increasing the allowable variation to ±0.15, only three more sets can be included, the H_A amides[7,38,39] and H_T thio compounds[47] in sulfuric and a series of azo compounds[54] in perchloric acids. Thus *more than half* of the acidity function sets in Table V do not meet this criterion. Comment seems superfluous. In particular, primary amines are not nearly so "well behaved" in perchloric as they are in sulfuric acid, as may also be seen from Passerini, Marziano, and Traverso's n_{ij} values.[19] This may explain why the Bunnett–Olsen technique seems to be much less satisfactory in the latter case.[12] It will be apparent that agreement between X-function pK_{BH+} values and acidity function ones will be good only if the latter were derived using a well-behaved indicator set.

A fair number of the compounds investigated in sulfuric acid
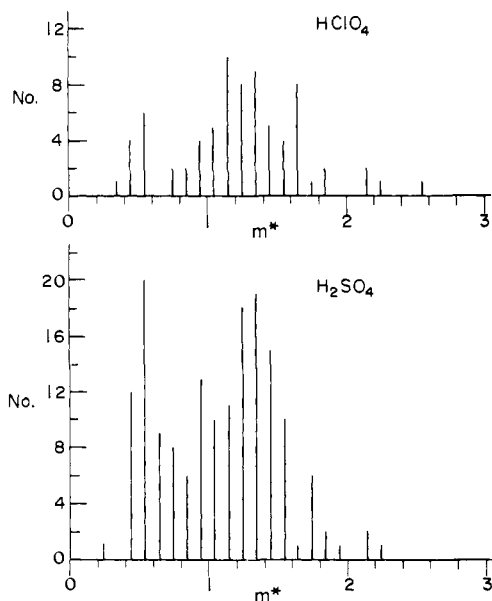
Figure 5. Histograms of $m*$ values in sulfuric and perchloric acids. Divisions are 0.1 units apart; the number of compounds with $m*$ within each division is plotted vertically.

Figure 6. A comparison of pK_{BH^+} values extrapolated from measurements in sulfuric (x axis) and perchloric (y axis) acids. Data from Tables IV and VI-XXI; the line drawn has unit slope.

have also been studied by the Bunnett–Olsen method[12] using H_0: some amides, tertiary amines and indoles,[12] carbonyl compounds,[17] benzophenones,[14] and thio compounds.[47] The values obtained using the two methods are generally in good agreement.[60] This is a reflection of the above observation that the H_0 amines form a well-behaved set in sulfuric acid, i.e., the cancellation assumption applies to them. It should be emphasized, however, that this may well only be a fortunate coincidence (see Table V), and the fact that pK_{BH^+} values obtained using the X-function method described here and the Bunnett–Olsen method are often very similar should not be allowed to overshadow the consideration that the X-function method involves fewer assumptions, as was shown in the introduction. Also, it uses a much larger data basis in its derivation, 165 compounds of all types, vs. 12 primary aromatic amines[35] (in sulfuric acid).

It has been suggested by Carpentier et al.[62] that any weak base should follow one of only five acidity functions. This should result in only five values for $m*$, but Figure 5 does not exhibit five peaks. With some imagination, trends can be discerned in the $m*$ values and Figure 5, however; certainly carbonyl group protonation seems to give $m*$'s of 0.4–0.6, and protonation at carbon values above 1.5 (with much scatter). Protonation at sulfur and tertiary nitrogen gives values of 1.4–1.6, generally. It is probable that these numbers can be rationalized in terms of hydration changes, etc., but further discussion seems unwarranted at present.

The pK_{BH^+} values obtained for 50 compounds which have been studied in both acids are compared in Figure 6. Agreement is fair until the strong acid region is reached, when the perchloric acid numbers become more negative than the sulfuric acid ones. One possible reason for this divergence may be the partial breakdown of the assumption that perchloric acid remains fully dissociated,[30] even in the 60–78% region. It may be possible to correct for this, but published data both for the degree of dissociation of perchloric acid[31] and its density in these regions[29] do not yet seem sufficiently accurate or reproducible[31] to justify this.

Throughout it has been assumed that proton transfer to the base under investigation occurs from protonated water, $H^+(H_2O)_n$. This is justifiable even in strong acid; since we are dealing with equilibria, we can postulate proton transfer from (say) undissociated H_2SO_4 to H_2O, and then from H_3O^+ to
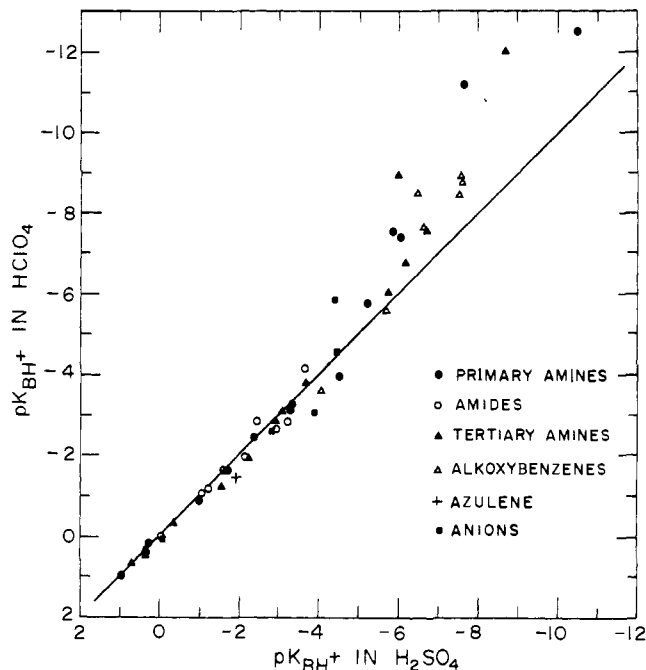
B. Still, undissociated H_2SO_4 predominates in sulfuric acid mixtures more concentrated than 85% w/w,[63] and this assumption begins to look somewhat artificial. An alternative formulation of the X-function method in very strong sulfuric acid is currently under study.

Conclusions

We conclude by considering the advantages which the X-function method has over more conventional ones for the determination of weak basicities.

Any amount of data can be accommodated. It is possible to obtain an X function using log I data for only *one* compound; this is a trivial case, though, since the initial and final pK_{BH^+} and $m*$ will be the same. Obviously the more data, the more accurate is X; the point of diminishing returns is probably 30–40 compounds. In this study X functions were also derived for the 50 compounds studied in both media; they are not included here, since they are practically identical with those in Table III. We would suggest that the best thermodynamic pK_{BH^+} estimates currently available for new compounds are those obtained via eq 7 using the X functions given in Table III.

It is not necessary for compounds to be of the same type; indeed, it is preferable to include compounds of many different types, for greater generality. The X function for sulfuric acid given in Table III includes protonation at N (amines of various types), O (ketones, other carbonyl compounds, amides), C (alkoxybenzenes, indoles, olefins), and S (thioureas, thiobenzamides, thionbenzoate esters); positively (cobalt complex ions, some pyrimidine heterocycles) and negatively (carboxylate anions, polycyano compounds) charged bases. Only simple protonation equilibria were included; for protonation-dehydration equilibria of the type

$$ROH + H^+ \rightleftharpoons R^+ + H_2O$$
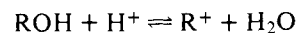
it is preferable to consider the water activity, and to plot (log I − log C_{H^+} + log a_{H_2O}) in eq 7, to obtain $-pK_{ROH}$ and $m*$.

This is an extrapolative method; the further away from the standard state, the longer the extrapolation and the higher the

errors in the intercept pK_{BH^+}'s, as can be seen from the standard deviations in Table IV. At higher acidities, increasing the number of measurements greatly increases the accuracy; see 2,4,6-trinitroaniline and the two compounds adjacent to it in Table IV, for example. Conversely, since the deviation from ideality is small at low acidity, the range of X values there is small, and the m^* slopes are more uncertain.

Overlap between adjacent indicators is not necessary when using this computerized technique to derive X functions, overcoming one drawback of the original Marziano–Cimino–Passerini method.[18,22] It is better, though, to have measurements over a wide acidity range in deriving a generally applicable X function.

Anchoring (always a problem in acidity function work)[4,51] is not necessary, since X functions automatically become zero in the standard state.

If needed, an acidity function applicable to any particular compound can be obtained from the equation

$$m^*X + \log C_{H^+} = \log I - pK_{BH^+} = -H$$

There is no longer any need to derive new Hammett-type acidity functions.

Values of log $(f_B f_{H^+}/f_{BH^+})$ for any specific compound at any acidity are readily obtainable from eq 6. This is of considerable advantage in kinetic studies, as will be demonstrated in subsequent papers.[25]

Supplementary Material Available: Calculated pK_{BH^+} values, m^* slopes, correlation coefficients, and errors for all bases (Tables VI–XXI) (17 pages). Ordering information is given on any current masthead page.

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