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Basicity Measurements in Aqueous–Organic Solvents. 1. The 20% Ethanol–Aqueous Sulfuric Acid System

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The acidity functions H_0, H_{azo}, H_{dip}, H_{GF}, and H_A have been compared in the solvent 20% ethanol–aqueous sulfuric acid. They are all linearly related according to the $(H_X + \log c_{H^+}) = (1 - \phi_e)(H_0 + \log c_{H^+})$ relationship. The thermodynamic pK_{XH^+} values can be estimated for every base, even for those whose acidity function is unknown, by applying also in this solvent the Bunnett–Olsen equation. The protonation data of dimethyl ether and dimethyl sulfide show that the pK_{XH^+} value is not sufficient to define the protonation equilibrium of weak bases. In fact, the inversion of basicity order that occurs in going from dilute ($Me_2O > Me_2S$) to more concentrated ($Me_2S > Me_2O$) acid solutions can be accounted for only through the solvation parameter ϕ_e. Comparison of the ϕ_e values shows that the differentiation among acidity functions occurs because of differences in onium ion solvation energies, the number of hydrogen bonding sites making only a second-order contribution. For the same compound, the protonation parameters are in the mixed solvent only slightly different (pK_{XH^+} more negative, ϕ_e more positive) from those evaluated in aqueous acid solutions.

Acids in ethanol–water or dioxane–water have often been used to evaluate the basic properties of organic substrates sparingly soluble in purely aqueous media.[1] The practical importance of these systems notwithstanding, very limited attempts have been made to apply to mixed solvents the same unifying theories[2,3] that have considerably simplified the interpretation of acid–base equilibria in water. There is a general agreement[2-6] that, in water, the activity coefficients of the species involved in the protonation equilibrium of two bases X and B are linked through the following linear free-energy relationship:

$$\log (f_X f_{H^+}/f_{XH^+}) = (1 - \phi_e) \log (f_B f_{H^+}/f_{BH^+}) \qquad (1)$$

Equation 1 is easily rearranged in a form amenable to direct experimental verification by combining it with the equilibrium constant for the protonation of the base X ($XH^+ \rightleftharpoons X + H^+$)

(eq 2) and with the analogous relation for the base B.

$$pK_{XH^+} = \log (c_{XH^+}/c_X c_{H^+}) + \log (f_{XH^+}/f_X f_{H^+}) \quad (2)$$

$$\log (c_X c_{H^+}/c_{XH^+}) = (1 - \phi_e) \log (c_B c_{H^+}/c_{BH^+})$$
$$+ (1 - \phi_e)pK_{BH^+} - pK_{XH^+} \quad (3)$$

The resulting linear relationship (eq 3) between the logarithms of the experimentally available protonation quotients for the two bases has been verified in a number of cases by Bunnett and Olsen[2] and others.[5] Equation 3 may also be used to evaluate the pK_{XH^+}'s of any base on the same reference scale. If, as proposed by Bunnett and Olsen,[2] we take as base B a nitroaniline whose protonation behavior is described by the H_0 acidity function $[H_0 = -\log(a_{H^+} f_B/f_{BH^+})]$ and with $pK_{BH^+} = 0.0$, eq 3 may be rearranged into eq 4 which, upon addition of $H_0 + \log c_{H^+}$ to both sides, gives the Bunnett and Olsen equation[2] now commonly used[2,3,6] to evaluate pK_{XH^+}'s in water:

$$\log (c_{XH^+}/c_X) - \log c_{H^+} =$$
$$(\phi_e - 1)(H_0 + \log c_{H^+}) + pK_{XH^+} \quad (4)$$

$$\log (c_{XH^+}/c_X) + H_0 = \phi_e(H_0 + \log c_{H^+}) + pK_{XH^+} \quad (5)$$

Equation 1 may also be verified in a different way, as suggested by Hammett.[3] It follows in fact from eq 1 that the acidity functions defined by the base $X[H_X = -\log (a_{H^+} f_X/f_{XH^+})]$ and by the Hammett bases B (H_0) are linearly related according to

$$H_X + \log c_{H^+} = (1 - \phi_e)(H_0 + \log c_{H^+}) \quad (6)$$

By combining eq 2 and 6 and rearranging, the same general eq 5 may be easily derived.[3] It is now well known that each weak base defines its own acidity function,[6] and that only in limited cases is it possible to define an average acidity function which represents the behavior of a family of structurally related bases in all the acidity range. These limitations notwithstanding, we believe that eq 6 is more useful than eq 3 because it allows the verification of the relationship of eq 1 over a wide range of acidity. It is a common experience that log–log plots are prone to be linear, especially when examined over a short range as, by necessity, must be done by applying eq 3.

With these results in mind and with the aim to provide the simplest possible way to define the behavior of weak organic bases also in acid solutions containing an organic solvent, we have started an investigation covering several aqueous–organic solvents. The results obtained in the 20% ethanol–80% aqueous sulfuric acid solutions are discussed in this paper.

Results

The 20% ethanolic aqueous sulfuric acid has been prepared by diluting, as suggested by Kresge and Chen,[7] 10 mL of 95% aqueous ethanol with enough aqueous sulfuric acid to give a final 50 mL volume. The problems connected with the esterification of ethanol by concentrated sulfuric acid[8] have been dealt with following the suggestion reported in detail in the Kresge and Chen's paper.[7]

Four acidity functions have so far been defined in this solvent: H_0 (based on nitroanilines),[7] H_{azo} (based on azobenzenes),[7,9] H_{dip} (based on diphenylamines),[10] and H_{GF} (based on ferrocene).[11] To compare the four sets of data we must refer them to the same reference state, which will be defined in this work as the infinitely dilute solution in 20% ethanol–80% water. The same reference state has been used by Kresge and Chen[7] for the H_0 and H_{azo} acidity functions and their data need not be changed. The H_{dip} and H_{GF} acidity functions have been instead referred to water as the reference state. According to Kresge and Chen[7] the change to the 20% ethanolic standard state can be made for the H_{dip} acidity function by

adding −0.15 (the difference in pK_{XH^+} values of the reference base, diphenylamine, in water and 20% ethanol) to the published data.[10] More complex operations are required to change the reference state for the H_{GF} acidity function. This is based[11] upon the difference between the ferrocene half-wave potential, $E_{1/2}$, and the glass electrode potential, E_g. These potentials are defined as:

$$E_{1/2} = E^0 + (2.303RT/2F) \log (D_{Fec^+}/D_{Fec})$$
$$- (2.303RT/F) \log (f_{Fec}/f_{Fec^+}) \quad (7)$$

$$E_g = E_g^0 + (2.303RT/F) \log a_{H^+} \quad (8)$$

where f are the molar activity coefficients, D are the diffusion coefficients of ferrocene (Fec) and ferricenium ion (Fec$^+$), and a_{H^+} is the proton activity. By subtracting eq 8 from eq 7 we obtain:

$$E = E_{1/2} - E_g = K + (2.303RT/F)H_{GF} \quad (9)$$

where $H_{GF} = -\log (a_{H^+} f_{Fec}/f_{Fec^+})$ is, according to the definition of the acidity function, the acidity function based on the single indicator ferrocene, and $K = E^0 - E_g^0 - (2.303RT/2F) \log (D_{Fec^+}/D_{Fec})$ is constant at a given temperature.[12] To define the H_{GF} function one must evaluate at several acid concentrations the E potential and, in a solution of known proton activity, the K constant. We have measured the E potential in 20% ethanol–aqueous sulfuric acid solutions in the range 0.04–5.9 M as follows. Cyclic voltammetric curves relative to the Fec/Fec$^+$ system were recorded at a stationary mercury microelectrode. In this way one avoids the noise, arising in the measuring circuit from switching in the circuit controlling an electrode with periodical renewal of the diffusion layer, and the distance between anodic and catodic peaks (60 mV) gives immediately an indication of the measurement reliability. The cyclic voltammetry offers, in this way, a distinct advantage over the polarographic method used by Janata and Jansen,[11] especially at low acidities where the oxidation wave of ferrocene is relatively close to the current background,[11] thus making the polarographic values less reliable. The definition of the K constant is not directly feasible since, to the best of our knowledge, no buffer solution has been defined for the system 20% ethanol–aqueous sulfuric acid. We may, however, arrive at a reliable value by two independent methods. By definition,[3] all acidity functions must converge to the same point as the solution becomes more dilute and, hence, approaches ideality. In fact, H_0, H_{azo}, and H_{dip} all give the same 1.03 value at 0.082 M. If this is also true for the H_{GF} function, as it should be, one may evaluate from eq 9, and with the aid of the experimental E value (−0.259) in the 0.082 M acid solution, a K constant of −0.320. The second approach used implies that, as for the H_{azo} and H_{dip} acidity functions, H_{GF} also is related to H_0 according to eq 6. By substituting the H_{GF} value derived from this relationship into eq 9 and rearranging, one obtains eq 10:

$$E + (2.303RT/F) \log c_{H^+} = K + \alpha(H_0 + \log c_{H^+}) \quad (10)$$

where α is $2.303RT(1 - \phi_e)/F$. The plot $E + 0.059 \log c_{H^+}$ vs. $H_0 + \log c_{H^+}$ gives a straight line ($r = 0.9933$) with intercept −0.3215. The two K values are within the experimental error and we have computed the H_{GF} function by using $K = -0.321$. In Table I we have collected the E and H_{GF} values determined for several 20% ethanol–aqueous sulfuric acid solutions.

A smoothed H_{GF} function is obtained by plotting the values of Table I against the acid concentration. This function differs from the one reported by Janata and Jansen,[11] apart from minor differences in the more dilute acid solutions (see above), by a constant value, our data being 1.75 units more negative than the ones obtained[11] by anchoring the acidity function to the water solution. To extend the H_{GF} scale up to $c_{H^+} = 10$ M,

Table I. The H_{GF} Acidity Function Evaluation in 20% Ethanol–Aqueous Sulfuric Acid [a]

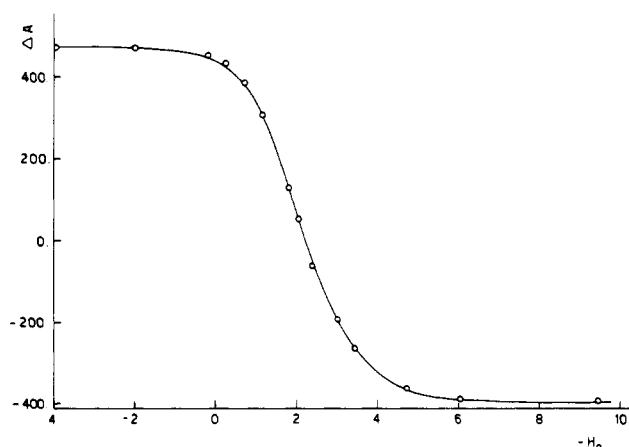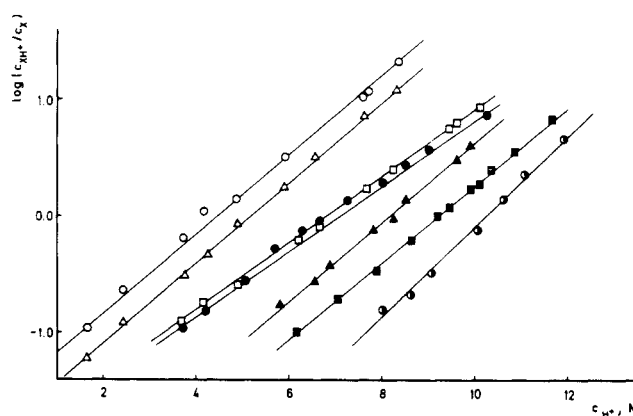| c_{H^+}, M	E^{b}	H_{GF}^{c}
0.04	−0.209	+1.898
0.082	−0.259	+1.051
0.150	−0.269	+0.881
0.240	−0.294	+0.458
0.390	−0.304	+0.288
0.500	−0.319	+0.034
0.530	−0.334	−0.220
0.590	−0.339	−0.305
0.845	−0.359	−0.644
1.020	−0.349	−0.475
1.460	−0.379	−0.983
2.000	−0.404	−1.407
2.505	−0.439	−2.000
3.100	−0.464	−2.424
3.600	−0.479	−2.678
4.150	−0.504	−3.102
4.590	−0.539	−3.695
5.050	−0.554	−3.949
5.900	−0.599	−4.711

[a] At 25 °C. [b] This is the difference between the ferrocene half-wave potential and the glass electrode potential. [c] Evaluated by using a K value of −0.321 (see text) and therefore referred to the infinitely dilute solution in 20% ethanol–water as reference state.

Figure 1. The protonation curve for p-methoxybenzamide in 20% ethanol–aqueous sulfuric acid.

Figure 2. The ionization ratios for substituted benzamides in 20% ethanol–aqueous sulfuric acid: 4-methoxy- (O); 3,4,5-trimethoxy- (△); 3-nitro- (□); 3-trifluoromethyl- (●); 3,5-dinitro-4-methyl- (▲); 2,3,6-trichloro- (■); 2,3,4,5,6-pentafluorobenzamide (◐).

we have added −1.75 to the values reported by Janata and Jansen[11] for solutions more concentrated than 6 M.

To complete the acidity functions set, we have defined the H_A acidity function, which should be more positive than H_0. To this end, guided by the work of Yates et al.[15] in aqueous solutions, we have selected seven substituted benzamides whose measurable ionization ratios overlap as much as possible. They are: 4-methoxy- (1); 3,4,5-trimethoxy- (2); 3-nitro- (3); 3-trifluoromethyl- (4); 3,5-dinitro-4-methyl- (5); 2,3,6-trichloro- (6); and 2,3,4,5,6-pentafluorobenzamide (7). The λ and ϵ values characteristic of the free amides and their conjugate acids, obtained respectively from the spectra registered in 20% ethanol–aqueous or dilute acid solutions and 20% ethanol–concentrated acid solutions (ca. 13.8 M), are listed in Table II; see paragraph at end of paper regarding supplementary material. The absorption maxima of the free base (λ_X) and of the conjugate acid (λ_{XH^+}) are conveniently separated, but for the 3-nitro- and the 2,3,6-trichlorobenzamide, to allow the use of the Davis and Geissman[16] method to obtain ionization ratios. According to this method,[16] we have evaluated, for each amide, the difference in absorbance at the two listed wavelengths for several acid solutions [$\Delta A = A(\lambda_X) - A(\lambda_{XH^+})$] and plotted the ΔA values against $-H_0$ to obtain titration curves as the one reported in Figure 1 for the p-methoxybenzamide.

The ΔA values for the free base (ΔA_X) and conjugate acid (ΔA_{XH^+}) were obtained from the sigmoids, as the value of the curve parallel to the x axis at low and high acidity, respectively. In the case of the 3-nitro- and 2,3,6-trichlorobenzamide the sigmoid curve was obtained by using the absorbance values at a single wavelength (233 and 261 nm, respectively). The logarithms of the ionization ratios [$I = c_{XH^+}/c_X = (\Delta A_X - \Delta A)/(\Delta A - \Delta A_{XH^+})$] are reported as a function of the acid concentration in Table III (see paragraph at end of paper regarding supplementary material) and plotted in Figure 2.

The data of Table III may be used to construct the H_A acidity function following the overlap method described by Hammett and Deyrup.[17] This involves the assumption that the difference in log I values (Δ log I) at constant c_{H^+} is equal to the difference in pK_{XH^+} values of the two overlapping in-

dicators. This assumption is strictly valid only if the Δ log I values remain constant over the measurable interval. Inspection of Figure 2 shows that this does not happen for some of the amides studied here. As a consequence, the pK values that can be determined from the Δ log I values are no more than approximate estimates of true values. From Figure 2 one can estimate that the pK_{XH^+} values of the substituted benzamides here studied must be more negative than that of the 4-methoxybenzamide by the following amounts: **2**, 0.26; **3**, 0.78; **4**, 0.81; **5**, 1.20; **6**, 1.58; **7**, 1.96.

We must now define the thermodynamic pK_{XH^+} value for the most basic indicator studied, p-methoxybenzamide, in order to refer the acidity function we are going to build to the 20% ethanolic reference standard state. Unfortunately, the benzamides are protonated only outside the dilute acid solution range and, therefore, the usual extrapolation of log (I/c_{H^+}) to zero acid concentration[7] cannot be employed. The same problem was faced in the definition of the H_A acidity function in water.[15] The proposal,[15] to use 2-pyrrolecarboxamide and p-nitroaniline to anchor the H_A acidity function to the aqueous reference state, has been criticized by Bunnett and Olsen[2] who have shown, by applying their equation to amides, that the acidity function anchored in this way is more negative than it should be by about 0.3 units. We have reached the same conclusion by studying the protonation behavior of sulfoxides,[18] which also appear to obey the same H_A acidity function. More recently, Edward and Wong[19] have confirmed that the published H_A scale is indeed incorrectly anchored in the dilute acid region. The most convenient method to define the ther-

Table IV. Acidity Function Values for 20% Ethanol–Aqueous Sulfuric Acid at 25 °C

c_{H^+}, M	$H_{GF}{}^a$	$H_{azo}{}^b$	$H_{dip}{}^c$	$H_0{}^b$	H_A	$H_0 + \log c_{H^+}$
0.25	+0.48	+0.47	+0.50	+0.46		−0.14
0.50	−0.10	+0.02	+0.15	+0.09	+0.28	−0.21
1.00	−0.65	−0.47	−0.32	−0.32	−0.04	−0.32
1.50	−1.05	−0.85	−0.65	−0.61	−0.30	−0.43
2.00	−1.46	−1.14	−0.95	−0.89	−0.52	−0.59
2.50	−1.86	−1.42	−1.24	−1.16	−0.71	−0.76
3.00	−2.27	−1.77	−1.49	−1.47	−0.89	−0.99
3.50	−2.67	−2.10	−1.78	−1.70	−1.07	−1.16
4.00	−3.06	−2.49	−2.05	−1.97	−1.23	−1.37
4.50	−3.50	−2.92	−2.37	−2.23	−1.40	−1.58
5.00	−3.94	−3.30	−2.70	−2.50	−1.55	−1.80
5.50	−4.37	−3.72	−3.00	−2.80	−1.70	−2.06
6.00	−4.85	−4.18	−3.37	−3.11	−1.85	−2.33
6.50	−5.44	−4.61	−3.70	−3.42	−2.01	−2.61
7.00	−6.03	−5.07	−4.05	−3.75	−2.17	−2.90
7.50	−6.67	−5.51	−4.38	−4.14	−2.32	−3.26
8.00	−7.35	−6.02	−4.74	−4.53	−2.49	−3.63
8.50	−8.05	−6.48	−5.10	−4.87	−2.65	−3.94
9.00	−8.73	−6.97	−5.46	−5.21	−2.78	−4.26
9.50	−9.41		−5.85	−5.62	−2.95	−4.64
10.00	−10.15		−6.20	−6.04	−3.15	−5.04
10.50			−6.60	−6.45	−3.34	−5.43
11.00			−6.96	−6.87	−3.55	−5.83
11.50				−7.30	−3.79	−6.24
12.00				−7.72	−4.06	−6.64
12.50				−8.15		−7.05
13.00				−8.62		−7.51
13.50				−9.15		−8.02

^{a} This scale was obtained beyond c_{H^+} = 6 M by adding −1.75 to the values reported in ref 11. ^{b} Taken from ref 7. ^{c} Obtained by adding −0.15 to the values reported in ref 10.

modynamic pK_{XH^+} value for p-methoxybenzamide would be through eq 5. However, we cannot be sure, at this point, that this equation could be applied to amides in the 20% ethanol–aqueous sulfuric acid solutions. We have therefore used the following procedure: (i) we have estimated a rough pK_{XH^+} value for the p-methoxybenzamide as the intercept of the log (I/c_{H^+}) vs. c_{H^+} plot (−1.66); (ii) we have derived, from the log I (see Table III) and ΔpK_{XH^+} (see above) values and through the relationship $H_A = pK_{XH^+} - \log I$, an H_A acidity function which will differ from the real one by as much as the approximate pK_{XH^+} value of p-methoxybenzamide differs from the thermodynamic one; and (iii) we have then checked that eq 6 is obeyed also by the H_A acidity function defined as above. A plot of $(H_A + \log c_{H^+})$ vs. $(H_0 + \log c_{H^+})$ gives a straight line, thus ensuring that the Bunnett–Olsen relationship can also be applied to amides in the 20% ethanolic solvent.

We have hence defined the thermodynamic pK_{XH^+} value of p-methoxybenzamide by applying eq 5 to its ionization data: The value obtained is −1.33. This has been used to build, as described above, the correctly anchored H_A acidity function, which is plotted in Figure 3 as a function of the acid concentration.

Inspection of Figure 3 shows that the H_A acidity function may be mediated, at the same acid concentration, among several different indicators. This is a consequence of the fact that the protonation of individual benzamides is complete in more than seven acid concentration units, and greatly reduces the inconvenience of the lack of parallelism between indicators. We have collected in the following Table IV all the acidity functions so far determined in the 20% ethanol–aqueous sulfuric acid system, together with the $H_0 + \log c_{H^+}$ values which will be subsequently used and proposed as the single scale to be used for the protonation behavior evaluation of any base in this solvent system.
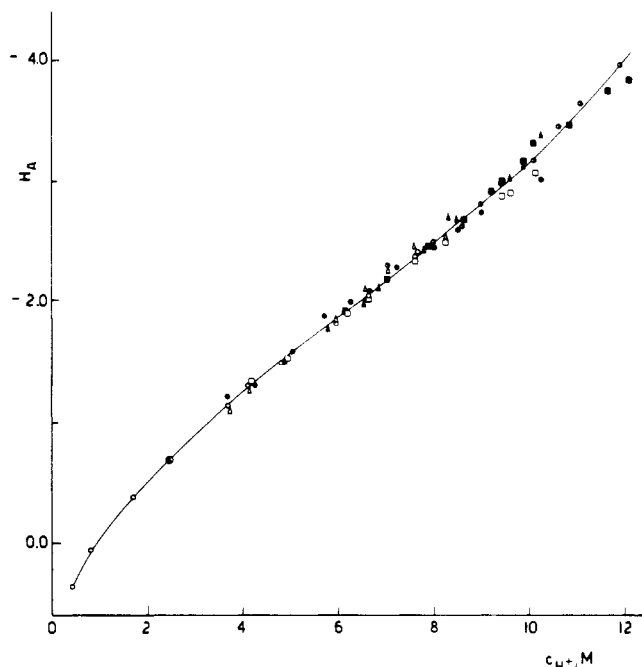

Figure 3. The H_A acidity function in 20% ethanol–aqueous sulfuric acid. The same symbols as in Figure 2 have been used to identify individual amides.
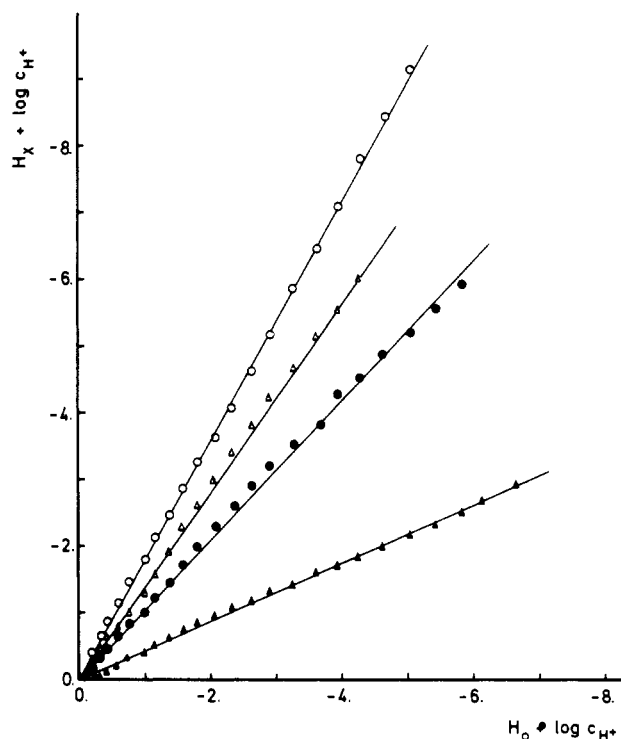

Figure 4. Correlation between acidity functions in 20% ethanol–aqueous sulfuric acid: H_{GF} (O); H_{azo} (△); H_{dip} (●); H_A (▲).

Figure 4, in which the $H_X + \log c_{H^+}$ data are plotted as a function of $H_0 + \log c_{H^+}$, shows the validity of the Bunnett–Olsen relationship also in the 20% ethanol–aqueous sulfuric acid solvent. The following values of slope $(1 - \phi_e)$ and intercept have been obtained from the least-squares analysis of the data plotted: H_{GF} 1.80, 0.004; H_{azo} 1.43, −0.018; H_{dip} 1.04, 0.052; H_a 0.43, −0.004.

We have applied the Bunnett–Olsen equation to study the protonation equilibria of triphenylcarbinol, dimethyl ether, and dimethyl sulfide. The protonation of the carbinol has been

Table VI. Protonation Equilibria of Substituted Benzamides, Triphenylcarbinol, Dimethyl Ether, and Dimethyl Sulfide in 20% Ethanol–Aqueous Sulfuric Acid [a]

compd	registry no.	pK_{XH^+} [b]	ϕ_e [b]	$(H_0)_{1/2}$ [c]	m [c]
substituted benzamides					
4-methoxy	3424-93-9	-1.33 ± 0.05	0.55 ± 0.02	-2.27	0.54
3,4,5-trimethoxy	3086-62-2	-1.66 ± 0.03	0.50 ± 0.01	-2.67	0.57
3-trifluoromethyl	1801-10-1	-1.85 ± 0.07	0.65 ± 0.02	-3.80	0.42
3-nitro	645-09-0	-1.89 ± 0.03	0.64 ± 0.01	-3.78	0.42
3,5-dinitro-4-methyl	4551-76-2	-2.53 ± 0.06	0.56 ± 0.01	-4.61	0.48
2,3,6-trichloro	4551-77-3	-2.69 ± 0.03	0.61 ± 0.01	-5.46	0.43
2,3,4,5,6-pentafluoro	652-31-3	-3.26 ± 0.09	0.57 ± 0.03	-6.28	0.50
triphenylcarbinol	76-84-6	-6.80 ± 0.12	-0.98 ± 0.13	-3.87	1.91
dimethyl ether	115-10-6	-2.66 ± 0.05	0.80 ± 0.01	-8.74	0.24
dimethyl sulfide	75-18-3	-6.88 ± 0.08	-0.12 ± 0.05	-6.27	1.11

[a] At 25 °C. [b] Obtained as slope (ϕ_e) and intercept (pK_{XH^+}) of the log I + H_0 vs. H_0 + log c_H + plots. [c] These are the H_0 values at half protonation and the slopes from the log I vs. $-H_0$ plots.
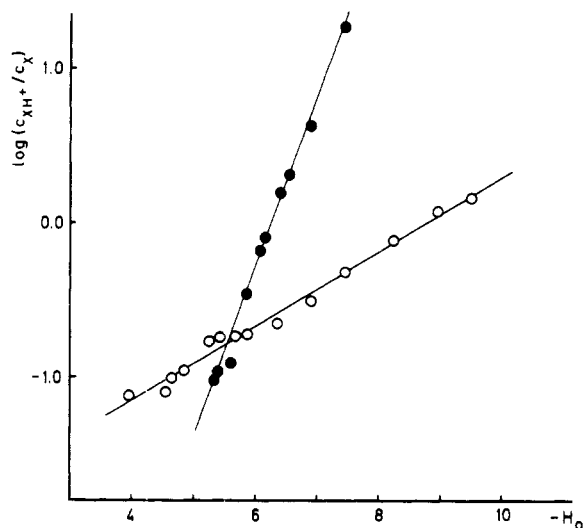
Figure 5. The ionization ratios for dimethyl ether (O) and dimethyl sulfide (●) in 20% ethanol–aqueous sulfuric acid solutions.

monitored by following the increase in absorbance at 410 nm. Being, however, that this compound is not stable in the acid solutions, the absorbance values have been extrapolated at zero time from at least three readings at different times after solution. A plot of $A(410)$ vs. $-H_0$ gives the usual sigmoid curve from which the A_X and A_{XH^+} values are easily determined and the log I data evaluated as before. The protonation of dimethyl ether and sulfide has been monitored with the same NMR technique used for the pK_{XH^+} evaluation in water,[20] which involves the measurement of the methyl protons chemical shift as a function of the medium acidity, taking the trimethylammonium ion as internal reference ($\Delta \nu = \nu - \nu_{ref}$). The methyl resonance of the substrates and of the reference is easily differentiated from that of the ethanolic solvent. The ionization ratios were obtained as usual[20] from the relationship $I = (\Delta \nu - \Delta \nu_X)/(\Delta \nu_{XH^+} - \Delta \nu)$, where $\Delta \nu_X$ and $\Delta \nu_{XH^+}$ are the differences in chemical shift for the free base and its conjugate acid, respectively. The ether protonation is incomplete also in the more concentrated acid solutions and the $\Delta \nu_{XH^+}$ value has been computed using the same method applied in aqueous solutions to the study of the protonation of the same[20] and other[21] compounds. The log I values for triphenylcarbinol, dimethyl ether, and dimethyl sulfide are collected in Table V (see paragraph at end of paper regarding supplementary material). In Table VI we report the pK_{XH^+} and ϕ_e values obtained by applying eq 5 to the log I data of Tables III and V, together with the H_0 data at half protonation, $(H_0)_{1/2}$, and the slopes m of the log I vs. $-H_0$ plots.

Discussion

Our finding that a different acidity function can be established for each family of bases in the 20% ethanol–aqueous sulfuric acid solvent system confirms the suggestion made several years ago by Gutbezahl and Grunwald[22] that it would be impossible to define a single acidity function in alcohol–aqueous acids mixtures. The differences among acidity functions are by no means trivial as illustrated by the fact that, for a solution of 10 M total acid concentration, we may evaluate proton donating abilities which differ by as much as 10^7, depending on the indicator used (ferrocene or substituted benzamide). As for the aqueous solutions,[6,18,23] we may actually infer that, at the precision limit, each base defines its own acidity function. It is, however, very convenient, from the practical point of view, to define average acidity functions which represent the behavior, over the whole acidity range, of a family of structurally related bases. Moreover, because of the roundings involved in the overlapping procedure (see above), the evaluated acidity functions, though still maintaining the necessary chemical relation to a defined class of bases, do not rigorously describe the behavior of any single base used to build it but only that of the hypothetical "average" aniline, benzamide, etc.

The fact that several acidity functions can be defined in a given acid solution has been termed "acidity function failure".[24] This must be intended as the failure of a single acidity function to describe the behavior of all types of bases and not of the acidity function concept. As a matter of fact, thanks to the existence of linear correlations among acidity functions, the very possibility of measuring several of them in a single acidic solvent generates much more information, for example as far as ions solvation and solvent effects are concerned, than the study in dilute acids where it is possible to define only the pH function (see infra).

Inspection of Figure 5 clearly shows that a very good correlation exists among the H_X + log c_{H^+} values (see eq 6) in the 20% ethanolic solvent used in this work. Moreover, as required by the acidity function definition, the values obtained for each family of indicators nicely converge to zero at low acidities. We must also remember that the H_{GF} acidity function, among those reported in Figure 4, has been defined by using a single indicator to cover the acid concentration range from 0.04 to 10 M, and, as such, it presents none of the problems discussed in connection with the overlapping indicators procedure. The fact that all the other acidity functions, and in particular H_0, are nicely linearly correlated with H_{GF} is proof of the reliability of the acidity function values reported in Table IV.

The existence of relationships such as those of Figure 4 and eq 6 is of very important practical consequence, since it makes possible the evaluation of the pK_{XH^+} values of every base,

even of those whose acidity function has not been defined, using a single reference scale (see eq 5). We propose that, as for the aqueous acid systems,[2,6] also for the 20% ethanol-aqueous sulfuric acid solvent, the $H_0 + \log c_{H^+}$ scale be taken as reference. In fact, the H_0 function has been defined for the 20% ethanolic sulfuric acid solutions by Kresge and Chen[7] with the greatest possible care both in the data collection (individual I values often result from *nine* experimental measurements) and in their treatment, made as objective as possible by the use of analytical interpolation of the experimental data. Moreover, as pointed out in a recent review,[6] changes in basicity in nitroanilines are accompanied by the least possible changes in onium ion solvation, since resonance interactions of the aryl group with the cationic center are absent, making substituted anilines the very class of bases in which the Hammett activity coefficient postulate is more likely to be obeyed. The convenience of having data in water and 20% ethanol evaluated on a reference scale based on the same type of bases is also obvious. Finally, the only sensible alternative to H_0 as reference scale could be the H_{GF} acidity function, which, however, suffers limitations that do not recommend its use as a general reference scale. In fact, H_{GF} can be neither evaluated in solutions containing halide ions, because their anodic waves at DME obstruct the oxidation wave of ferrocene, nor in solutions more acidic than 70% aqueous sulfuric acid, because of ferrocene protonation, nor in solutions containing compounds that could complex with the ferrocene indicator, as for instance carboxylic acids.[11]

If H_0 is chosen as reference, the general Bunnett and Olsen equation (eq 5) may be used also in 20% ethanol solutions to evaluate the pK_{XH^+} values of any base. These values, being obtained through the extrathermodynamic linear free-energy relationship of eq 1, should be rigorously considered as pK_{XH^+} estimates. However, we attribute to them the same thermodynamic meaning as the pK_{XH^+} values estimated through the Hammett's $\rho\sigma$ equation, the most familiar among linear free-energy relationships. However, the pK_{XH^+} values cannot be sufficient, both for practical and theoretical reasons, to describe the protonation of weak bases, because of the different solvent effects on the protonation equilibria, as evidenced by the acidity functions differentiation. This point is clearly illustrated by the comparison of the protonation data for the dimethyl ether and sulfide. The ionization data obtained in 20% ethanol-aqueous sulfuric acid for the two compounds are plotted in Figure 5 as a function of the medium acidity, expressed by the H_0 values.

It is very clear, as observed in water,[21] that the protonation equilibria of the two compounds are affected in a different way by changes in the solvent composition. As a consequence, the ether is more basic in dilute acid solutions and the sulfide in more concentrated acid solutions. The pK_{XH^+} values (-2.66 and -6.88 for the ether and the sulfide, respectively), which by definition indicate the position of the protonation equilibria in the reference standard state, do not tell us much of what is happening in the concentrated solutions, in which protonation really occurs. Without the aid of the ϕ_e solvation parameter, which is easily obtained as a slope of the ($\log I + H_0$) vs. ($H_0 + \log c_{H^+}$) plot, we would not have any way to know of the basicity order inversion that occurs at ca. $c_{H^+} = 9.5$ M, nor to evaluate the substrate protonation fraction. To obtain a greater insight into the meaning of the ϕ_e parameter, we may rearrange eq 1 as in the following

$$\log f_{H^+} - \log (f_{XH^+}/f_X) = (1 - \phi_e)[\log f_{H^+} - \log (f_{BH^+}/f_B)] \tag{11}$$

Equation 11 has been discussed in detail for aqueous solutions[6,20,21] and we will only briefly recall the conclusions

reached. Since the activity coefficients vary in the order $f_{H^+} > f_{XH^+} > f_X$,[6,25] the ϕ_e parameter will assume positive values when the f_{XH^+}/f_X ratio is greater than the ratio for the activity coefficients of the reference Hammett base B. The more positive the ϕ_e parameter is, the larger is the difference in free energy of transfer, from the standard state to the acid solution, between the XH^+ ion and its precursor X. Therefore, the ϕ_e parameter offers an estimate of the relative onium ions solvation. In the case of the dimethyl sulfide and dimethyl ether, the ϕ_e parameter indicates that the ion derived from the smaller and less polarizable oxygen base requires much more stabilization through solvation ($\phi_e = 0.80$) than that derived from the sulfur base ($\phi = -0.12$). The different behavior of two simple ions as Me_2SH^+ and Me_2OH^+ clearly illustrates that the differentiation among acidity functions occurs essentially because of the difference in the hydrogen bond strength between the onium ions and water, the number of hydrogen bonding sites coming into play only when other things are equal. In fact, if we compare the ϕ_e values obtained from the plots of Figure 4, we see that the more negative ϕ_e is obtained for the H_{GF} acidity function (-0.80), followed by H_{azo} (-0.43) and H_{dip} (-0.04), whereas H_A gives a positive value ($+0.57$), the ϕ_e for anilines being by definition zero. The trend is similar to the one found in water,[6,21] and it is rationalizable as for the aqueous solutions. We have in fact three types of onium ions: carbonium (ferrocene), ammonium (azobenzenes, diphenylamines, anilines), and oxonium ions (benzamides). It is known from aqueous solution studies that the solvation requirements of the three onium ion types increase in the above order[6,25] and therefore we expect the changes in ϕ_e parameters found. Only when the onium ion is of the same type (e.g., ammonium) does the number of the hydrogen bonding sites make a further, if smaller and not additive, differentiation into the acidity function values.[6,25] The pK_{XH^+} and ϕ_e values obtained in 20% ethanol-aqueous sulfuric acid (see Table VI) may be compared with the values reported for the same compounds[2,20,21] in aqueous sulfuric acid. The pK_{XH^+} are more negative and the ϕ_e more positive in the alcoholic solvent; the differences are, however, small and often within the experimental errors.[2,20,21] Since the free base is certainly more "salted in" in the aqueous organic solvent than in the purely aqueous one, one does expect some change in the ϕ_e parameter. However, one should not attempt a rationalization of the small, if real, effects so far observed before direct activity coefficient measurements become available. Moreover, a careful consideration of the 20% ethanol-aqueous sulfuric acid solvent composition does not suggest large differences with the purely aqueous solvent, as far as the protonation and solvation behavior is concerned. In fact, we must remember that ethanol is esterified by concentrated sulfuric acid.[8] According to the data reported by Kresge and Chen,[7] this reaction becomes important enough above 8 M total sulfate concentration to change drastically the amount of ethanol really present. As a consequence, the ratio [H_2O]/[EtOH] is lowered from ca. 15 in 20% ethanol-water to only ca. 10 in the more concentrated acid solution available (total sulfate concentration 14.9 M).[7] This, coupled with the greater basicity of water than ethanol,[26] indicates that the H_3O^+ ion will be the predominant acidic species also in the 20% ethanolic solvent. Moreover, we know from gas-phase studies[27] that the proton solvation in mixed methanol/water systems is mainly achieved through coordination by water molecules when the cluster reaches a total molecule number greater than 9. The two systems generated by aqueous sulfuric acid and 20% ethanol-aqueous sulfuric acid have therefore essentially the same acid (H_3O^+) and the same solvating agent (H_2O). As such, we do not expect to observe large differences in the protonation parameters measured for the same weak base in the two solvents.

Conclusion

As many acidity functions as bases can be defined in the solvent generated by adding aqueous sulfuric acid to 95% ethanol (20% by vol). We have shown that the linear free energy relationship found by Bunnett and Olsen[2] for aqueous solutions can be extended also to the partially organic solvent, as illustrated by Figure 5. Consequently, to define the protonation of a weak base, one needs to known in this system only a single reference acidity function. We propose that the definition of the weak bases protonation in 20% ethanol aqueous sulfuric acid be achieved through the Bunnett–Olsen equation (eq 5) with the aid of the carefully defined H_0 values reported by Kresge and Chen.[7] The comparison of the protonation data for dimethyl ether and dimethyl sulfide shows that the pK_{XH^+} evaluation must be accompanied by the determination of the ϕ_e solvation parameter. This is needed to evaluate the fraction of protonated substrate in the acid solutions. It also offers information on the importance of solvation in the onium ion stabilization and, as such, a way to rationalize differences among acidity functions, which occur mainly because of differences in the hydrogen bonding strength between onium ions and solvent molecules.

Experimental Section

Materials and Solvents. The indicators 3,5-dinitro-4-methyl- (**5**), 2,3,6-trichloro- (**6**), and 2,3,4,5,6-pentafluorobenzamide (**7**) were synthesized by bubbling gaseous NH_3 through the cooled (ice) ether solution of the corresponding acid chloride. After several recrystallizations they melted at: **5**, 189–191 °C, from 95% ethanol (lit.[28] mp 186–8 °C); **6**, 173–4 °C, from 95% ethanol (lit.[15] mp 170–1 °C); **7**, 150–2 °C (lit.[29] mp 150 °C). All the other compounds used in this work were commercial products, purified until their physical data agreed with accepted literature values.

Reagent grade commercial 95% ethanol was purified by distillation. Sulfuric acid solutions were made by diluting the commercial reagent grade 96% acid with deionized water. The 20% ethanol–aqueous sulfuric acid solutions were prepared and standardized following the procedure described in detail by Kresge and Chen.[7] The c_{H^+} values reported throughout this work correspond to the total acid concentration as obtained by titration.[7]

Indicator Measurements. Stock solutions of the indicators were prepared in CH_2Cl_2 at concentrations selected to give a final absorbance of ca. 0.500. Aliquots (5 mL) were then transferred into a 25-mL volumetric flask, the solvent distilled at reduced pressure, and the organic base dissolved with 25 mL of prethermostated (25 °C) 20% ethanolic–acqueous sulfuric acid solutions of the appropriate acid concentration. This procedure was preferred over the one described by Kresge and Chen[7] (stock solutions of the indicators in 95% ethanol and dilution with aqueous sulfuric acid) to avoid the amide hydrolysis which could become important as the temperature of the solution rises due to the considerable heat evolved during the dilution. After a preliminary scan with a Perkin-Elmer 402 spectrophotometer to select the appropriate wavelengths (see Table II), the spectra in the region of the chosen wavelengths were recorded using a Zeiss PMQ II spectrophotometer with the cell compartment thermostated at 25.0 ± 0.1 °C. The ionization ratios were then computed as described in the Results Section.

A similar procedure was used for the definition of triphenylcarbinol protonation except for the fact that, since the solutions were not stable with time, the absorbance values at each acid concentration were obtained by extrapolating at zero time the log A vs. t plots.

The dimethyl ether and dimethyl sulfide protonation has been monitored by using the same NMR technique described elsewhere[20,21,30] for the same measurements in aqueous acid solutions.

Cyclic Voltammetric Measurements. Cyclic voltammetric curves relative to the process ferrocene $\rightleftarrows$ ferricenium were recorded in several 20% ethanol–aqueous sulfuric acid solutions of ferrocene, using a mercury covered gold sphere as electrode and a scanning rate of 66 mV/s. The voltammetric unit was a three-electrode system assembled with the MP-system 1000 equipment previously described,[31] with the relevant feature of employing as voltage follower an MP 1032 electrometric operational amplifier suited to a glass reference electrode. The procedure adopted gives the peak potentials for the anodic, $(E_p)_a$, and cathodic, $(E_p)_c$, processes which are related to $E_{1/2}$ for a reversible process by the equation[32] $E_p = E_{1/2} \pm 0.029/n$.

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