The problem of acidity in concentrated aqueous solutions of sulfuric acid

Nunziata C. Marziano,* Alberto Tomasin, Claudio Tortato and Paolo Isandelli

Dipartimento di Chimica, Università di Venezia, Dorso Duro 2137, 30123 Venice, Italy

Received (in Cambridge) 13th June 1997, Revised 24th April 1998, Accepted 5th August 1998

Concentrated aqueous sulfuric acid mixtures, which ionize according to the equilibria (a) and (b) [(a) $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$; (b) $H_2SO_4 \rightleftharpoons HSO_4^- + H^+$], have been analysed and the corresponding activity coefficient functions [Mc(s)] of the solvent [$Mc(HSO_4^-) = -\log (f_{SO_4^{2-}} f_{H^+}/f_{HSO_4^-})$; $Mc(H_2SO_4) = -\log (f_{HSO_4^-} f_{H^+}/f_{H_2SO_4})$] have been determined by using the concentrations of the species SO_4^{2-}, HSO_4^-, H_2SO_4. The Mc(s) have been compared with the Mc(i) function [$Mc(i) = -\log (f_B f_{H^+}/f_{BH^+})$], the latter one being determined by the protonation equilibria of weak bases (B) ($B + H^+ \rightleftharpoons BH^+$). The results show that the interactions of solute and solvent can be linearly related [*i.e.* $Mc(i) = n_{is}Mc^*(s)$ and $Mc^*(s) = Mc(HSO_4^-) + Mc(H_2SO_4)$] in the range 0.1–100 wt% H_2SO_4 provided that both equilibria of sulfuric acid, correctly normalized, are taken into account.

Slopes and pK_{BH^+} values of nitroanilines whose protonation equilibria have been studied in different monoprotic acids have also been analysed. The trend observed shows a progressive increase in the slope values for increasingly weaker bases and in sulfuric acid two different linear dependences between slopes and pK_{BH^+} of the various members of the series, related to the different equilibria of the solvent, have been recognized.

The differences between ‘activity coefficient function’ and ‘acidity function’ determined by solutes and solvents is discussed, as well as the parameter related to the ‘protonating ability’ of the solvent.

Introduction

Concentrated aqueous solutions of sulfuric acid are catalytically active mixtures which are used in a considerable number of chemical reactions. A necessary requirement in the study of an acid-catalysed process is the knowledge of the ‘acidic properties’ of the medium and in the present paper new results in this field, related to protonating ability of H_2SO_4–H_2O mixtures, are reported.

In the elucidation of the problems of acidity, the protonating ability of a given acid in aqueous systems has mainly been explored[1–5] using the protonation process of weak bases (B) whose equilibria [equilibrium (1)] are described by thermodynamic eqn. (2).

$$B + H^+ \rightleftharpoons BH^+ \qquad (1)$$

$$pK_{BH^+} = \log [BH^+]/[B] - \log [H^+] - \log (f_B f_{H^+}/f_{BH^+}) \qquad (2)$$

In addition, useful procedures have been devised, which are able to satisfactorily correlate the protonation process of B and the acidic properties of the solvent.[6–16] For instance, by using a set of indicators which protonate in concentrated acid solutions, two overlapping (B_1, B_2) bases have been compared by eqn. (3).[6–8]

$$\log [B_1H^+]/[B_1] - \log [H^+] = n_{b_1b_2} (\log [B_2H^+]/[B_2] - \log [H^+]) + \text{constant} \qquad (3)$$

This relationship, tested for a large number of B in different acids,[9–16] permits us to relate the activity coefficient ratio of two compounds by eqn. (4), and to derive eqn. (5) from eqn. (2) and eqn. (4), where $Mc(B^*)$ or ‘activity coefficient function’ (a.c.)[6] is defined by eqn. (6) or in the general form by eqn. (6′).

$$\log (f_{B_1} f_{H^+}/f_{B_1H^+}) = n_{b_1b_2} \log (f_{B_2} f_{H^+}/f_{B_2H^+}) \qquad (4)$$

$$pK_{BH^+} = \log [BH^+]/[B] - \log [H^+] + n_{bb^*}Mc(B^*) \qquad (5)$$

$$Mc(B^*) = -\log (f_{B^*} f_{H^+}/f_{B^*H^+}) \qquad (6)$$

$$Mc(B^*) = \log (\text{product of reactants' a.c.}) - \log (\text{product of products' a.c.}) \qquad (6')$$

In this procedure, the protonation of a weak base [equilibrium (1)] is described by two independent parameters (n_{bb^*}) and (pK_{BH^+}), related respectively to the slope (n_{bb^*}) and intercept (pK_{BH^+}) of the plots of ($\log [BH^+]/[B] - \log [H^+]$) *vs.* the $Mc(B^*)$ activity coefficient function. The $Mc(B^*)$ function is a measure of the deviations from the ideality of the acidic medium under investigation, with reference to that of a weak base (B^*) protonated at low acid concentrations and chosen as standard state.[6–8]

Further studies of non ideal aqueous solutions of monoprotic acids (HA)[15,16] whose dissociations [see equilibrium (7)]

$$HA\ (aq) \rightleftharpoons A^-\ (aq) + H^+\ (aq) \qquad (7)$$

are described by eqn. (8) have shown that new parameters

$$pK_{HA} = \log [HA]/[A^-] - \log [H^+] - \log (f_{A^-} f_{H^+}/f_{HA}) \qquad (8)$$

related to some specific properties of the solvents can be obtained. They are as follows: (i) an ‘activity coefficient function of the solvent’ [Mc(s)], defined by eqn. (9) and determined for HA with known [thermodynamic (pK_{HA}) or apparent (pK_a)] ionization constants and degree of dissociation (α),

$$pK_a - (\log [HA]/[A^-] - \log [H^+]) = n_sMc(s) \qquad (9)$$

where

$$\log [HA]/[A^-] - \log [H^+] = \log [(1 - \alpha)/\alpha^2c] = \log Q_a;$$
$$Mc(s) = -\log (f_{A^-} f_{H^+}/f_{HA}) \quad \text{and} \quad n_s = 1$$

(ii) an ‘acidity function of the solvent’ Ac(s), defined by eqn. (10).

$$pK_a - \log [HA]/[A^-] = -\log [H^+] - \log (f_{A^-} f_{H^+}/f_{HA}) = -\log [H^+] + Mc(s) = Ac(s) \qquad (10)$$

The Ac(s) function, obtained from the parameters of the solvents, is the ‘extension of the pH scale’ in concentrated aqueous acid solutions.

By comparing solutes (i) and solvents(s)[15,16] the following relationships have been observed: (iii) the *Mc*(B*) [or *Mc*(i)] and the *Mc*(s) functions are linearly related by eqn. (11) and (iv)

$$Mc(\mathrm{i}) = n_{\mathrm{is}}\,(Mc(\mathrm{s}) \qquad (11)$$

the *Ac*(i) and the *Ac*(s) functions are also found to be linearly related by eqn. (12). The observed n_{is} values are: 3.3 for CH_3-

$$Ac(\mathrm{i}) = \{-n_{\mathrm{is}} \log\,[\mathrm{H}^+] + Mc(\mathrm{i})\} \qquad (12)$$

SO_3H; 2.80 for HBr; 2.35 for $HClO_4$; 2.10 for CF_3SO_3H; 1.55 for HNO_3 when the protonation of nitroanilines is analysed and 2-nitroaniline is used as standard indicator of *Mc*(i).

Thus, according to eqns. (4) and (11), the protonation of a weak base in concentrated aqueous acid systems with known *Mc*(B*) and *Mc*(s) functions can be described by eqns. (5) and (5′) or alternately by one of them. It has been suggested that the

$$\mathrm{p}K_{\mathrm{BH}^+} = \log\,[\mathrm{BH}^+]/[\mathrm{B}] - \log\,[\mathrm{H}^+] + n_{\mathrm{is}}\,Mc(\mathrm{s}) \qquad (5')$$

n_{is} (or the $n_{\mathrm{bb*}}$) values are parameters related to ‘protonating ability’ of a solvent.[15,16]

Our concern in the present work is to report the results of the studies carried out in sulfuric acid where the distribution of $[SO_4^{2-}]$, $[HSO_4^-]$, $[H_2SO_4]$ species, involved in different dissociation equilibria,[3] has been taken into account and the separate contribution of the species to activity coefficient terms has been estimated.

Results and discussion

The *Mc* activity coefficient function of indicators: [*Mc*(i)]

The *Mc*(i) [or *Mc*(B*)] function in sulfuric acid has been determined by using different mathematical procedures[7,8,17,18] producing a significant improvement over the stepwise method applied earlier in this field.[6]

A complication revealed by these studies is the discrepancy observed, especially at high acid concentrations, when a comparison among the estimated functions is made. A possible explanation of these discrepancies could be due to factors limiting the accuracy of the results, in the range above 80 wt% H_2SO_4, which are not present when studying other acids.

For instance, the results of 4-nitro-*m*-xylene, obtained by following the protonation equilibrium of $-NO_2$ group in CF_3SO_3H and in H_2SO_4, show that a titration curve can be easily determined in CF_3SO_3H (see Table 1) but not in H_2SO_4. Further analyses by ^{13}C NMR and GCMS of aqueous acid mixtures and of the products isolated by extraction, show that 4-nitro-*m*-xylene and 2,4-dimethyl-5-nitrobenzenesulfonic acid are obtained in the protonation studies of 4-nitro-*m*-xylene in H_2SO_4. The results suggest that the appearance of new species[3] in very concentrated solutions of H_2SO_4 (as $H_3SO_4^+$, $H_2S_2O_7$, SO_3, *etc.*) can lead to undesirable by-products for indicators suitable to be sulfonated. Uncertainties in the values of the *Mc* function are to be expected when this type of indicator is used.

Complications in H_2SO_4 are also observed in the protonation process of 2,4,6-trinitroaniline. For instance, a discrepancy has been found in the order of half-protonation when the equilibria of unsubstituted- and 3-substitued-2,4,6-trinitroanilines in H_2SO_4[19–24] and in CF_3SO_3H (see Table 1) are compared. The experimental behaviour observed is as follows: 3-Me > 3-Br > H in H_2SO_4; 3-Me > H > 3-Br in CF_3SO_3H.

In order to assign unambigous numerical values to *Mc* function at high acid concentrations, weak bases with experimentally reliable data and with well known equilibrium constants have been used. The indicators chosen are essentially compounds which have been studied by different authors in different strong acids. This offers the advantage of comparing the results in different acid systems and obtaining, by the procedure already suggested,[16] $\mathrm{p}K_{\mathrm{BH}^+}$ values whose uncertainties for random errors are minimised. In the present study the number and the accuracy of experimental data available have been increased by new measurements in CF_3SO_3H (see Table 1), where complications of side reactions affecting the results are avoided. The numerical values of the *Mc*(i) estimated in H_2SO_4 are reported in Table 2.

Table 1 Protonation equilibria of indicators in aqueous CF_3SO_3H by UV spectroscopy at 25 °C

Compound	CF_3SO_3H (wt%)	log I^a	CF_3SO_3H (wt%)	log I^a
3-Me-2,4,6-NO_2-Aniline^b	86.77	−1.10	89.49	−0.14
	87.26	−0.88	90.40	0.18
	87.59	−0.66	90.84	0.31
	88.10	−0.49	91.50	0.46
	88.39	−0.42	92.58	0.80
	88.81	−0.30	94.92	1.57
2,4,6-NO_2-Aniline^c	86.85	−1.50	91.84	0.20
	87.58	−1.19	92.68	0.43
	88.68	−0.76	93.49	0.61
	89.47	−0.51	94.36	0.80
	90.25	−0.22	96.59	1.49
	91.03	−0.03		
3-Br-2,4,6-NO_2-Aniline^d	90.13	−1.05	92.41	0.24
	90.88	−0.59	92.77	0.39
	91.13	−0.45	93.20	0.56
	91.63	−0.14	93.90	0.78
	91.95	0.03	94.80	1.19
4-NO_2-*m*-Xylene^e	90.03	−1.35	94.87	0.26
	90.69	−1.11	95.60	0.51
	91.36	−0.86	96.35	0.82
	92.04	−0.64	97.11	1.24
	92.73	−0.41	97.87	1.55
	93.43	−0.20	98.66	1.80
	94.15	0.022		

^{a} log I = log $[BH^+]/[B]$ ionization ratios. Values determined by experimental procedure analogous to that described in the refs. 11, 12, 15. Wavelength employed (nm) and wt% CF_3SO_3H at half-protonation: ^{b} 350, 89.9. ^{c} 420, 91.3. ^{d} 350, 92. ^{e} 354, 94.1 (protonation of NO_2 group).

The variation of the *Mc*(i) functions with acid concentration in H_2SO_4 and in CF_3SO_3H—the latter used as an example of monoprotic acid—is shown in Fig. 1. The comparison reveals different trends of the functions with increasing acid concentration, in contrast with the consistent behaviour observed when different monoprotic acids are compared.[15,16]

This experimental observation suggested a detailed analysis of the dissociation equilibria of the aqueous solutions of sulfuric acid, where the concentration and also the nature of molecular and ionic species depend on the stoichiometric composition of the H_2SO_4–H_2O mixtures.

The *Mc* activity coefficient function of the solvent: [*Mc*(s)]

The dissociation of sulfuric acid in water over the entire concentration range has been studied by different authors[3] and the distribution of the main species available by Raman measurements[25–34] is reported in Fig. 2. The results show that HSO_4^- is observed, both in concentrated and in dilute acid, but it is involved in two different equilibria below and above 75–80 wt% H_2SO_4.

In concentrated acid (>80 wt%), the equilibrium (13) is

$$H_2SO_4(\mathrm{aq}) \rightleftharpoons HSO_4^-(\mathrm{aq}) + H^+(\mathrm{aq}) \qquad (13)$$

observed, whose parameters, described by thermodynamic eqn. (14), can be determined by eqn. (15).

$$\mathrm{p}K_{H_2SO_4} = \log\,[H_2SO_4]/[HSO_4^-] - \log\,[H^+] - \log\,(f_{HSO_4^-}f_{H^+}/f_{H_2SO_4}) \qquad (14)$$

$$\mathrm{p}K_{H_2SO_4} = \log\,[H_2SO_4]/[HSO_4^-] - \log\,[H^+] + n_{H_2SO_4}Mc(\mathrm{i}) \qquad (15)$$

Table 2 *Mc*(i) and *Mc*(s) values in H_2SO_4–H_2O mixtures at 25 °C

H_2SO_4 (wt%)	*Mc*(i)[a] (ind.)	*Mc*(s)[b] (sper.)	*Mc*(s)[c] (calc.)	*Mc*(s)[d] (norm.)
0.0	0.000	0.00	0.000	0.000
1	0.034	0.59	0.010	0.030
2	0.068	0.61	0.020	0.060
3	0.102	0.63	0.032	0.096
4	0.135	0.64	0.045	0.135
5	0.168	0.64	0.055	0.165
6	0.201	0.65	0.067	0.201
7	0.234	0.65	0.078	0.234
8	0.266	0.65	0.090	0.270
9	0.299	0.65	0.100	0.300
10	0.331	0.65	0.110	0.330
12	0.397	0.65	0.130	0.390
14	0.464	0.65	0.150	0.450
16	0.533	0.65	0.175	0.525
18	0.605	0.65	0.200	0.601
20	0.680	0.65	0.220	0.661
22	0.759	0.65	0.250	0.751
24	0.843	0.65	0.280	0.841
26	0.932	0.66	0.310	0.931
28	1.026	0.67	0.340	1.021
30	1.127	0.68	0.372	1.117
32	1.233	0.69	0.410	1.231
34	1.347	0.70	0.447	1.342
36	1.466	0.71	0.485	1.456
38	1.591	0.73	0.530	1.591
40	1.723	0.74	0.570	1.712
42	1.859	0.76	0.620	1.862
44	2.000	0.79	0.670	2.012
46	2.146	0.81	0.710	2.132
48	2.295	0.84	0.760	2.282
50	2.448	0.88	0.815	2.447
52	2.605	0.91	0.870	2.613
54	2.765	0.95	0.925	2.780
56	2.930	0.99	0.980	2.943
58	3.102	1.04	1.040	3.123
60	3.281	1.10	1.100	3.303
62	3.472	1.17	1.170	3.513
64	3.677	1.24	1.240	3.724
66	3.900	1.32	1.320	3.964
68	4.144	1.41	1.410	4.234
70	4.412	1.52	1.520	4.564
72	4.705			
74	5.021			
76	5.356	5.25		
78	5.701	5.70		
80	6.045	6.10		
82	6.373	6.40		
84	6.676	6.68		
86	6.947	6.90		
88	7.192	7.15		
90	7.431	7.40		
91	7.559	7.55		
92	7.698	7.70		
93	7.856	7.85		
94	8.037	8.05		
95	8.248	8.25		
96	8.494	8.50		
97	8.777	8.80		
98	9.102	9.15		
98.5	9.280			
99.0	9.468			
99.5	9.668			

[a] *Mc*(i) values determined by eqn. (3); mathematical treatment from refs. 7, 8, 15. [b] *Mc*(s) values determined by Raman data [see eqns. (19) (19′)]. [c] *Mc*(s) values determined by eqn. (18). [d] *Mc*(s) normalized values [see eqn. (20)] {The following normalized *Mc**(s) functions and n_{is} values of 2-nitroaniline used as standard indicator have been derived: $Mc^*(s) = [Mc/0.33(HSO_4^-) + Mc(H_2SO_4)]$ ($n_{is} = 1$); $Mc^*(s) = [Mc(HSO_4^-) + 0.33Mc(H_2SO_4)]$ ($n_{is} = 3$)}.

The constant ($pK_{H_2SO_4}$) and the slope ($n_{H_2SO_4}$) values were found to be −8.50 and 1, respectively, using $[H_2SO_4]$ and $[HSO_4^-]$ experimental data, together with the *Mc*(i) function, referred to 2-nitroaniline (see Fig. 3).

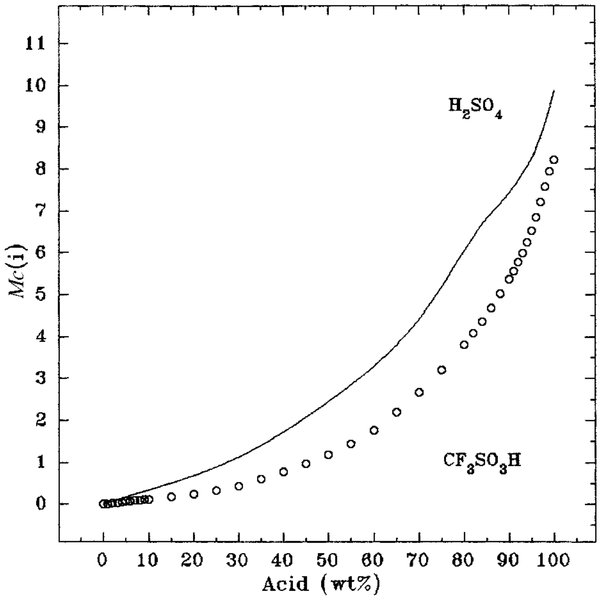

Fig. 1 Plot of *Mc*(i) *vs.* wt% H_2SO_4 and CF_3SO_3H at 25 °C. [*Mc*(i) values in H_2SO_4 from this work; in CF_3SO_3H from ref. 15.]

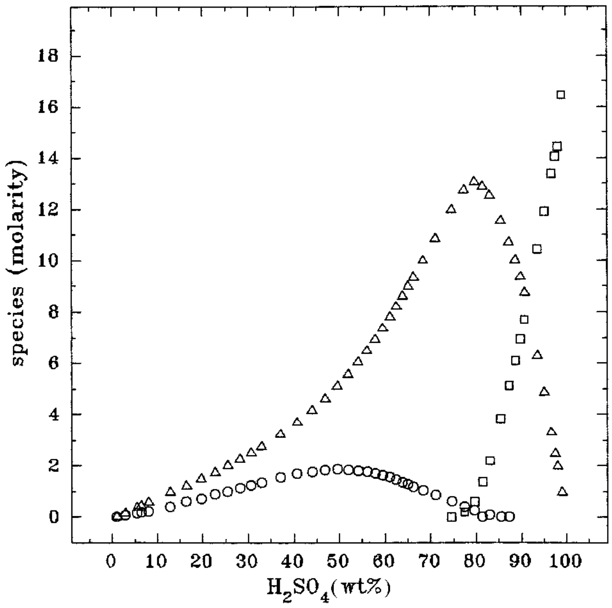

Fig. 2 Equilibrium composition of H_2SO_4–H_2O mixtures at 25 °C. Concentrations of: (□) $[H_2SO_4]$; (△) $[HSO_4^-]$; (○) $[SO_4^{2-}]$. (Experimental data from ref. 26.)

In the range <75–80 wt% H_2SO_4, the equilibrium (16) is

$$HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H^+(aq) \qquad (16)$$

observed (see Fig. 2). Also in this case the parameters described by thermodynamic eqn. (17) can be determined by eqn. (18).

$$pK_{HSO_4^-} = \log [HSO_4^-]/[SO_4^{2-}] - \log [H^+] - \log (f_{SO_4^{2-}} f_{H^+}/f_{HSO_4^-}) \qquad (17)$$

$$pK_{HSO_4^-} = \log [HSO_4^-]/[SO_4^{2-}] - \log [H^+] + n_{HSO_4^-} Mc(i) \qquad (18)$$

The results, obtained by following the variations of $[HSO_4^-]$, show a linear relationship in the range where $[HSO_4^-] \approx [SO_4^{2-}]$ and $[HSO_4^-] > [SO_4^{2-}]$ (see also Fig. 3). The intercept ($pK_{HSO_4^-}$) and the slope ($n_{HSO_4^-}$) were found to be −2.0 and 0.33, respectively. At lower acid concentrations, the $[HSO_4^-]/[SO_4^{2-}]$ ratio is

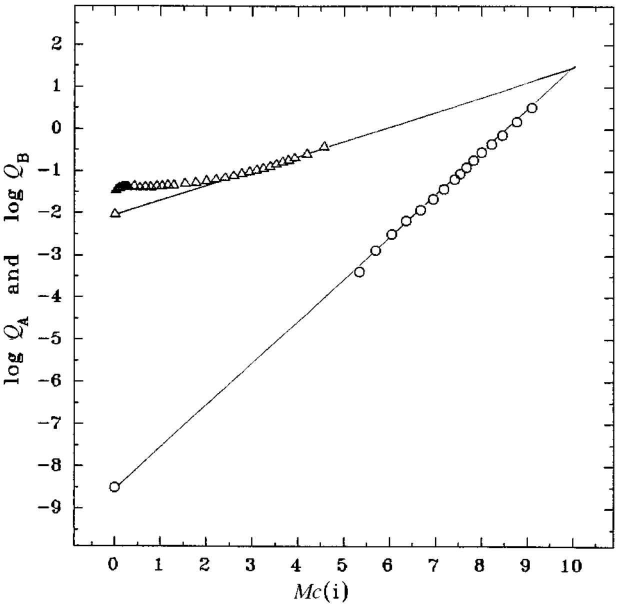

Fig. 3 Dissociation equilibria of H_2SO_4–H_2O mixtures at 25 °C. Plot of $\log Q_A$ (△) and $\log Q_B$ (○) *vs.* Mc(i): $\log Q_A = \log [HSO_4^-]/[SO_4^{2-}] - \log [H^+]$; $\log Q_B = \log [H_2SO_4]/[HSO_4^-] - \log [H^+]$. (Experimental data from refs. 25–34.)

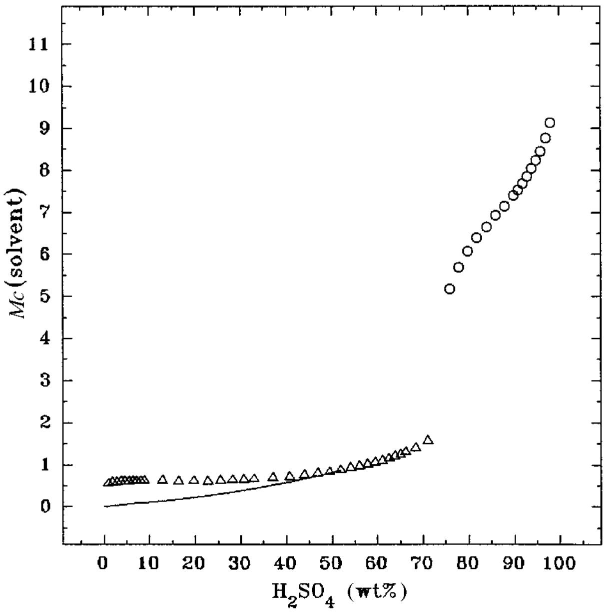

Fig. 4 Plot of Mc (solvent) *vs.* wt% of H_2SO_4 at 25 °C. (△) $Mc(HSO_4^-)$; (○) $Mc(H_2SO_4)$ [see text eqn. (19′)]; (——) Mc(s) values estimated by eqn. (18). (Experimental data from refs. 25–34.)

constant and deviations from linearity are found. This is related to the properties of the system in this range, characterized by the complicated dissociation of bisulfate to sulfate.[27,34–36]

The experimental data of equilibria (13) and (16) and the values of equilibrium constants, which are found to agree closely with previous independent estimates,[26,29,34–38] allow one to obtain the 'activity coefficient function of the solvent, Mc(s)'. This function, determined for H_2SO_4 by eqn. (19) and rewritten as eqn. (19′), is reported in Fig. 4.

$$Mc(s) = \{pK_{HSO_4^-} - (\log [HSO_4^-]/[SO_4^{2-}] - \log [H^+])\} + \{pK_{H_2SO_4} - (\log [H_2SO_4]/[HSO_4^-] - \log [H^+])\} \quad (19)$$

$$Mc(s) = [-\log (f_{SO_4^{2-}} f_{H^+}/f_{HSO_4^-})] + [-\log (f_{HSO_4^-} f_{H^+}/f_{H_2SO_4})]$$
$$Mc(s) = Mc(HSO_4^-) + Mc(H_2SO_4) \quad (19')$$

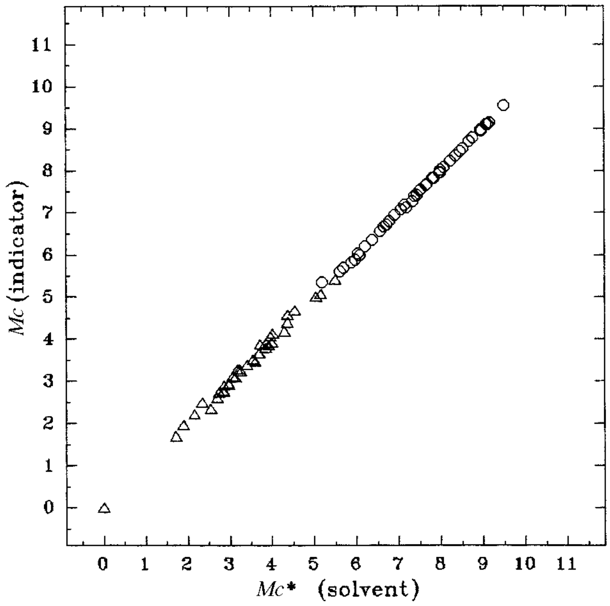

Fig. 5 Plot of Mc(indicators) *vs.* Mc*(solvent) in H_2SO_4 at 25 °C. Mc*(solvent) = [(△) $Mc°(HSO_4^-)$ + (○) $Mc(H_2SO_4)$] [see text eqn. (20)].

In the range 0.1–40 wt%, where deviations from linearity are observed, the profiles of the functions estimated by the experimental $[HSO_4^-]/[SO_4^{2-}]$ values and by eqn. (18) are also shown.

In Fig. 5 the functions determined by the equilibrium of the solvent and by the equilibria of indicators are compared. It can be seen that the Mc(i) can be linearly related to the corresponding Mc(s) provided that: (i) the equilibria (13) and (16) are taken into account, (ii) a normalization factor connecting between them the activity coefficient terms of the equilibria is used.

In Table 2 the experimental, estimated and normalized Mc(s) functions of the solvent are reported. The results suggest that the protonation of an indicator, at low and at high concentrations of sulfuric acid, is related to the corresponding equilibrium of the solvent, *i.e.* to two different equilibria when the process in the whole range of sulfuric acid concentrations is examined. Likewise, the $\log (f_{B*} f_{H^+}/f_{B*H^+})$ term of an indicator is related by eqn. (20) to the corresponding standard states of the solvent, that can be normalized between them by an appropriate factor.

$$Mc(i) = n_{is} Mc^*(s) \quad (20)$$

where $Mc^*(s) = [Mc°(HSO_4^-) + Mc(H_2SO_4)]$

or $Mc^*(s) = [Mc(HSO_4^-) + Mc°(H_2SO_4)]$

Further experimental observations obtained in very concentrated sulfuric acid show the following. (i) A plot of Mc(i) against $\sqrt{c}$ is linear, with a slope = 1, for solutions containing 91–99.4% H_2SO_4. Deviations are observed above this range. The concentration *c*, following the approximations already suggested,[21,37] has been determined from the known stoichiometric concentrations of H_2SO_4 and H_2O and has been taken as half of the total concentration of ions in the solutions. The linearity and slope suggest that the ionic activity coefficients are consistent with the Debye–Huckel Limiting Law, except in the range where the self-ionizations of sulfuric acid are expected to be, progressively, the predominant equilibria of the solvent. (ii) The best estimate of the Mc value in the pure solvent can be determined at the crossing of the plots of the equilibria (13) and (16) (see Fig. 3). Using this procedure the value of −9.8 is obtained, compatible with the value −10.5, as estimated by the Debye–Huckel Limiting Law. Analogous estimates are obtained using

Table 3 Slopes (n_{is}, n_{bb*})[a] and intercept (pK_{BH^+})[b] of indicators in CF_3SO_3H and H_2SO_4

	CF_3SO_3H		H_2SO_4	
	n_{is}	n_{bb*}	n_{bb*}	pK_{BH^+}
Nitroanilines[c]				
1) 4-NO_2	2.00	0.95	0.85	1.00
2) 2-NO_2	2.12	1.00	1.00	−0.27
3) 2-Cl-4-NO_2	2.23	1.04	0.98	−0.90
4) 4-Cl-2-NO_2	2.28	1.07	1.02	−1.05
5) 5-Cl-2-NO_2			1.02	−1.50
6) 2,5-di-Cl-4-NO_2			1.00	−1.80
7) 2-Cl-6-NO_2			1.07	−2.60
8) 2,6-di-Cl-4-NO_2			1.10	−3.45
9) 2,4-di-Cl-6-NO_2	2.62	1.25	1.16	−3.50
10) 2,4-di-NO_2	2.95	1.40	1.30	−5.25
11) 2,6-di-NO_2	3.00	1.45	1.15	−5.90
12) 4-Cl-2,6-di-NO_2[d]			(1.15)	(−6.50)
13) 2-Br-4,6-di-NO_2[e]	3.28	1.60	1.19	−7.80
14) 3-Me-2,4,6-tri-NO_2	3.73	1.75	1.37	−10.40
15) 2,4,6-tri-NO_2	3.78	1.79	1.20	−10.70
16) 3-Br-2,4,6-tri-NO_2	4.16	1.96	1.47	−12.25
17) 3-Cl-2,4,6-tri-NO_2			1.47	−12.50
Nitrobenzenes[c]				
18) 4-NO_2-*m*-Xylene	3.11	1.46		−10.00
19) 4-NO_2-Toluene	3.20	1.50		−11.50
20) Nitrobenzene	3.90	1.84		−15.00
21) 4-Cl-Nitrobenzene	4.16	1.96		−16.50

[a] n_{is} Values calc. by a plot of log $[BH^+]/[B]$ − log $[H^+]$ *vs.* *Mc*(s) [see eqn. (5′)]; n_{bb*} values calc. by a plot of log $[BH^+]/[B]$ − log $[H^+]$ *vs.* *Mc*(B*) [see eqn. (5)]. [b] Intercept of the plot log $[BH^+]/[B]$ − log $[H^+]$ *vs.* *Mc* functions [*Mc*(s) and *Mc*(B*) in CF_3SO_3H from ref. 15; in H_2SO_4 this work]. [c] Experimental data at 25 °C in CF_3SO_3H from ref. 15 and this work; in H_2SO_4 from refs. 19–24 and 39–46. [d] pK_{BH^+} Value in $HClO_4 = -7.30$ (ref. 15). [e] The protonation of 2-Br-4,6-di-NO_2 in H_2SO_4 shows two sets of values: $pK_{BH^+} = -6.60$, $n_{bb*} = 1.04$ (range 65–80 wt%, exp. data from refs. 20, 22, 23) $pK_{BH^+} = -7.80$, $n_{bb*} = 1.19$ (range 75–94 wt%, exp. data from refs. 19, 41).

different indicators with the exception of nitrobenzenes, whose protonation occurs in the range above 99% where the additional self-ionization equilibria of sulfuric acid cannot be neglected.

The behaviour of indicators in sulfuric acid

Slopes (n_{is} or n_{bb*}) and intercepts (pK_{BH^+}) of some nitroanilines with different basic strength, protonating in H_2SO_4, are reported in Table 3 and the values are compared with the results available in CF_3SO_3H.

In CF_3SO_3H a linear dependence between slopes and equilibrium constants is observed, as well as a progressive increase in the slope values for increasingly weaker bases (see Fig. 6a). An analogous trend has been found in $HClO_4$, HCl, HBr, CH_3SO_3H, HNO_3.[15,16]

In H_2SO_4, two different linear dependences can be recognized, relating respectively to the nitroanilines whose protonation process occurs below and above 80 wt% H_2SO_4 (see Fig. 6b).

The slopes of n_{bb*} *versus* pK_{BH^+} (N_{bb*} values), referred to pK_w of water, are 0.066 and 0.056, or 0.022 and 0.056 when the normalization factor relating the *Mc*(s) functions of sulfuric acid, at low and high acid concentrations, is taken into account.

It follows that the two equilibria of the solvent lead to distinct behaviours of indicators. Also, it follows that concentrated aqueous solutions of sulfuric acid exhibit a high protonating ability towards weak bases as expected from the catalytic effectiveness of a strong acid.

The *Ac*(s) and the *Ac*(i) acidity functions

The results previously reported allow one to estimate by eqn.

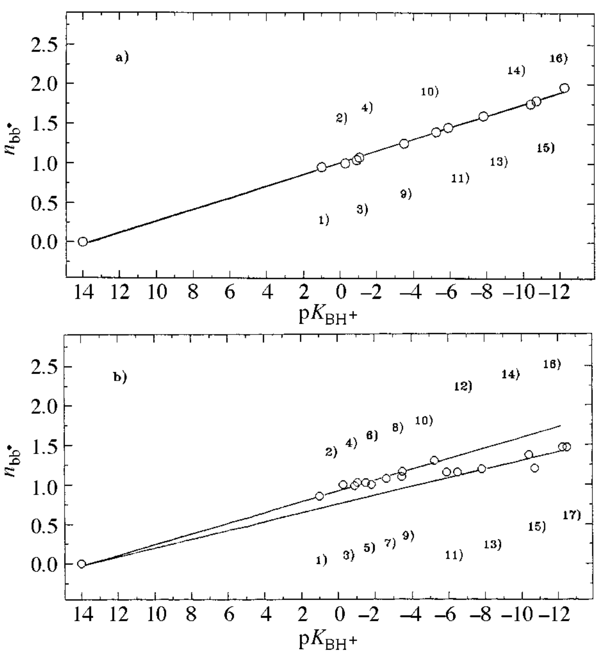

Fig. 6 (a) Nitroanilines in CF_3SO_3H at 25 °C. Plot of n_{bb*} *vs.* pK_{BH^+} (slope $N = 0.073$) (n_{bb*} and pK_{BH^+} values of indicators see Table 3). (b) Nitroanilines in H_2SO_4 at 25 °C. Plot of n_{bb*} *vs.* pK_{BH^+} (slopes $N = 0.066$ and 0.056) (n_{bb*} and pK_{BH^+} values of indicators see Table 3).

(21) the *Ac*(s) function related to equilibria of the solvent in sulfuric acid.

$$Ac(s) = \{-\log[H^+] + Mc(HSO_4^-)\} + \{-\log[H^+] + Mc(H_2SO_4)\} \quad (21)$$

The comparison of solutes and solvent by using *Ac*(i) and *Ac*(s) functions shows that the following parameters can be linearly related between them:

$$(-\log[H^+] + Mc(i) = \{-\log[H^+] + Mc^{o}(HSO_4^-)\} + \{-\log[H^+] + Mc(H_2SO_4)\}$$

or

$$-3\log[H^+] + Mc(i) = 3(\{-\log[H^+] + Mc(HSO_4^-)\} + \{-\log[H^+] + Mc^{o}(H_2SO_4)\}$$

The relationships have been derived, taking into account the normalization factors of the *Mc*(s) function and the n_{is} values of 2-nitroaniline.

In contrast, the behaviour of solutes determined by the Hammett procedure[1–5] shows unsatisfactory results. For instance, the comparison between the Hammett acidity function, *Ho*, and the *Ac*(s) normalized function with the slope of 1 for the standard indicator, reveals appreciable deviations from the linearity. Analogous deviations have been observed by comparing *Ho* and *Ac*(s) functions determined in HBr, HNO_3, $HClO_4$, CH_3SO_3H, CF_3SO_3H.[15]

In the light of these results, the ‘Hammett acidity functions’[1–5] cannot be accepted as parameters related to ‘acidity’ of concentrated aqueous acid solutions or to ‘acidity’ of non ideal acid systems.

Conclusions

It can be concluded that the new results may yield an improved understanding of the phenomena governing the protonation process of indicators in concentrated acid solutions. Indeed, from the available observations the following deductions can be made.

i) A reasonable description of the acidic properties of a solvent can be obtained by eqn. (22) where the proton transfer process from the solvent to the solute is taken into account.

$$-\log (f_{B} f_{H^+}/f_{BH^+}) = -n_{is} \log (f_{A^-} f_{H^+}/f_{HA}) \qquad (22)$$

One should remark that an analogous relationship holds in the description of the acidic properties of a solid acid catalyst. For instance in the protonation process on nitroanilines carried out in $HClO_4/SiO_2$, CF_3SO_3H/SiO_2 and H_2SO_4/SiO_2[47–49] the n values of indicators, compared to those observed for analogous compounds in aqueous acid solutions, differ by a factor of *ca.* 10^4 but the pK_{BH^+} values in both systems are found to be the same.

ii) The linear relationship (4) between two overlapping (B_1,B_2) bases and the effectiveness of this equation in describing a large number of equilibria in concentrated solutions of different acids are due to the validity of eqn. (22).

iii) According to eqn. (22) it seems reasonable to suppose, as a crude explanation of the results, that the n_{is} values can be interpreted as a measure of the specific interactions between solutes and solvents in the proton transfer process from $(H^+)_{aq}A^-$ to BH^+A^-.

iv) According to eqn. (4), the parameter related to the energetic proton transfer process from $(H^+)_{aq}A^-$ to $B^*H^+A^-$ is taken as unity for (B^*) chosen as reference (*i.e.* $n_{is} = 1 = n_{bb*}$) and the n_{bb*} values, determined for weaker bases, are referred to the latter standard state ($B^*H^+A^-$).

v) In water, taken as standard state of *Mc* scale,[50] the difference between n_{is} and n_{bb*} values disappears being $n_{is} = n_{bb*} = 0$ for H_2O.

References

1 L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill-Kogakusha, Tokyo, 1970.
2 C. H. Rochester, *Acidity Functions*, Academic Press, London, 1970.
3 M. Liler, *Reaction Mechanisms in Sulphuric Acid*, Academic Press, London, 1971.
4 R. Stewart, *The proton in Chemistry*, Academic Press, London, 1985.
5 G. A. Olah, G. K. Surya Prakash and J. Sommer, *Superacids*, J. Wiley, N. Y., 1985.
6 N. C. Marziano, G. Cimino and R. Passerini, *J. Chem. Soc.*, *Perkin Trans. 2*, 1973, 1915.
7 N. C. Marziano, P. Traverso, A. Tomasin and R. Passerini, *J. Chem. Soc.*, *Perkin Trans. 2*, 1977, 309.
8 N. C. Marziano, A. Tomasin and P. Traverso, *J. Chem. Soc.*, *Perkin Trans. 2*, 1981, 1070.
9 M. Sampoli, A. De Santis and N. C. Marziano, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 110.
10 M. Sampoli, A. De Santis, N. C. Marziano, F. Pinna and A. Zingales, *J. Phys. Chem.*, 1985, **89**, 2864.
11 N. C. Marziano, M. Sampoli and M. Gonizzi, *J. Phys. Chem.*, 1986, **90**, 4347.
12 N. C. Marziano, A. Tomasin and C. Tortato, *J. Chem. Soc.*, *Perkin Trans. 2*, 1991, 1575.
13 N. C. Marziano, A. Tomasin and M. Sampoli, *J. Chem. Soc.*, *Perkin Trans. 2*, 1991, 1995.
14 N. C. Marziano, C. Tortato and R. Bertani, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 955.
15 N. C. Marziano, A. Tomasin and C. Tortato, *Org. React.* (*USSR*), 1996, **30**, 29.
16 N. C. Marziano, A. Tomasin and C. Tortato, *Org. React.* (*USSR*), 1996, **30**, 39.
17 R. A. Cox and K. Yates, *J. Am. Chem. Soc.*, 1978, **100**, 3861.
18 A. Bagno, G. Scorrano and R. A. More O'Ferrall, *Rev. Chem. Intermed.*, 1987, **7**, 313.
19 L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, 1932, **54**, 2721.
20 M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, 1963, **85**, 878.
21 M. I. Vinnik and R. S. Ryabova, *Russ. J. Phys. Chem.*, 1964, **38**, 320.
22 C. D. Johnson, A. R. Katritzky and S. A. Shapiro, *J. Am. Chem. Soc.*, 1969, **91**, 6654.
23 P. Tikle, A. G. Briggs and J. M. Wilson, *J. Chem. Soc.* (*B*), 1970, 65.
24 R. J. Gillespie, J. E. Peel and E. A. Robinson, *J. Am. Chem. Soc.*, 1971, **93**, 5083.
25 F. Young, L. F. Maranville and H. M. Smith, *Structure of Electrolytic Solutions*, ed. W. J. Hamer, Wiley N. Y., 1959.
26 E. B. Robertson and H. B. Dunford, *J. Am. Chem. Soc.*, 1964, **86**, 5080.
27 H. Chen and D. E. Irish, *J. Phys. Chem.*, 1971, **75**, 2672.
28 B. S. W. Dawson, D. E. Irish and G. E. Toogood, *J. Phys. Chem.*, 1986, **90**, 334.
29 D. J. Turner, *J. Chem. Soc.*, *Faraday Trans.*, 1974, **70**, 1346.
30 N. G. Zarakahani and M. I. Vinnik, *Zh. Fiz. Khim.*, 1963, **37**, 503.
31 N. G. Zarakahani, N. B. Librovich and M. I. Vinnik, *Zh. Fiz. Khim.*, 1971, **45**, 1733.
32 V. D. Maiorov and N. B. Librovich, *Zh. Fiz. Khim.*, 1973, **47**, 2298.
33 N. B. Librovich and V. D. Maiorov, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1977, 684.
34 J. Balej, F. Hanousek, M. Pisarcik and K. Sarka, *J. Chem. Soc.*, *Faraday Trans.*, 1984, **80**, 521.
35 C. F. Baes, Jr., *J. Am. Chem. Soc.*, 1957, **79**, 5611.
36 K. S. Pitzer, R. N. Roy and L. F. Silvester, *J. Am. Chem. Soc.*, 1977, **99**, 4930.
37 J. C. D. Brand, *J. Chem. Soc.*, 1950, 997.
38 N. C. Deno and R. W. Taft, Jr., *J. Am. Chem. Soc.*, 1954, **76**, 244.
39 K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1959, 1096.
40 R. H. Boyd, *J. Am. Chem. Soc.*, 1963, **85**, 1555.
41 R. H. Boyd and C. H. Wang, *J. Am. Chem. Soc.*, 1965, **87**, 430.
42 R. S. Ryabova, I. M. Medvetskaya and M. I. Vinnik, *Russ. J. Phys. Chem.*, (*Engl. Trans.*), 1966, **40**, 182.
43 M. I. Vinnik and N. B. Librovich, *Tetrahedron*, 1966, **22**, 2945.
44 A. Jussiaume, M. Godel and F. Coussemant, *Bull. Soc. Chim. Fr.*, 1976, 1625.
45 Y. Marcus, E. Pross and N. Soffer, *J. Phys. Chem.*, 1980, **84**, 1725.
46 A. J. Kresge, H. J. Chen, G. L. Capen and M. F. Powell, *Can. J. Chem.*, 1983, **61**, 249.
47 N. C. Marziano, C. Tortato, Abdiqafar A. Sheikh-Osman, J. Riego and J. M. Zaldivar, *Org. React.* (*USSR*), 1996, **30**, 49.
48 N. C. Marziano, C. Tortato, Abdiqafar A. Sheikh-Osman, J. Riego and J. M. Zaldivar, *Org. React.* (*USSR*), 1997, **31**, 87.
49 N. C. Marziano, C. Tortato, L. Ronchin and C. L. Bianchi, *Catal. Lett.*, 1998, submitted for publication.
50 Personal suggestion of referee.

Paper 8/03473G