

# On the acidity of liquid and solid acid catalysts: Part 1. A thermodynamic point of view

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The protonation equilibria of weak bases (B) in solid acids (HClO<sub>4</sub>/SiO<sub>2</sub>, CF<sub>3</sub>SO<sub>3</sub>H/SiO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub>) were studied by UV spectroscopy and the results were compared to those obtained for analogous compounds in concentrated aqueous solutions of strong acids (HClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H, H<sub>2</sub>SO<sub>4</sub>). The behaviour of B in liquid (L) and solid (S) phase was analysed by titration curves, log[BH<sup>+</sup>]/[B] ratios and thermodynamic p*K*<sub>BH<sup>+</sup></sub> values. It has been shown that the proton transfer process acid → base (i.e., from (H<sup>+</sup>A<sup>-</sup>)<sub>(L,S)</sub> to (BH<sup>+</sup>A<sup>-</sup>)<sub>(L,S)</sub>) can be described by the relationship observed between the activity coefficient terms that are to be taken into account for acid–base equilibria occurring in nonideal systems ( $-\log(f_B f_{H^+} / f_{BH^+})_{(L,S)} = -n_{BA} \log(f_{A^-} f_{H^+} / f_{HA})_{(L,S)}$ ) and can be estimated by the *n*<sub>BA</sub> values. Two “activity coefficient functions” (i.e., Mc(B) =  $-\log(f_B f_{H^+} / f_{BH^+})$  and Mc(s) =  $-\log(f_{A^-} f_{H^+} / f_{HA})$ ) were used to describe, respectively, the equilibria of B and the equilibria of the acids in concentrated aqueous solutions and the meaning of terms “activity coefficient function” and “protonating ability of an acid” were discussed. The difference between “acidity functions”, determined for solutes (Ac(i)) and solvents (Ac(s)) in aqueous acids, and the H<sub>x</sub> acidity functions, the latter developed for solutes in analogous media by the Hammett procedure, was also shown.

**Keywords:** liquid acid catalysts, surface acidity, activity coefficient functions, acidity functions, protonating ability of acids

## 1. Introduction

The conversion reagent–products over solid acids used as catalysts represents an advantageous alternative route to the conventional processes carried out in concentrated aqueous acid solutions. The main requirement of these materials is their catalytic performance that is related to the “acid strength” of their acid sites. Understanding the acidic properties of the sites is, thus, an important step for the potential application of solid acids in the acid-catalyzed reactions.

A large variety of methods dealing with the measurements of “acidity” have already been developed [1–5], of interest for the practical use of different materials in the field of acid catalysis. However, the problems concerning the “acidic properties” of acid sites also raised the question of how the inherent protonating power of strong acidic media can most realistically be evaluated.

In the present paper the results of some studies in concentrated aqueous acid solutions are reported and the thermodynamic parameters related to acid–base equilibria of solutes and solvents are discussed. Our interest in studying aqueous systems is concerned with some theoretical and practical topics to be taken into account as good starting points for a sound comparison of acidity in different media, and also as useful tools to gain more insight into the problems of surface acidity. Indeed, new results in concentrated aqueous solutions of HCl, CH<sub>3</sub>SO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H, HNO<sub>3</sub>, HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> [6–9] show that reliable descriptions of nonideal acid systems can be obtained when the proper-

ties of the medium under investigation are determined and the “parameters” related to these properties are used. For instance, “activity coefficient functions” (or Mc functions), “acidity functions” (or Ac functions) and “protonating ability of a solvent” have been estimated by studying the dissociation of some acids (HA) in the HA + H<sub>2</sub>O mixtures and the protonation of some bases (B) in the B + HA + H<sub>2</sub>O mixtures.

The results obtained by studying the protonation of B in the B + HA<sub>(solid)</sub> solid acid materials are also reported. Analogies and differences between liquid and solid systems have been tested by comparing titration curves, ionization ratios (log[BH<sup>+</sup>]/[B]) and equilibrium constants (p*K*<sub>BH<sup>+</sup></sub>) of analogous B in both systems.

A comparison between the new functions (Mc and Ac) and the well known H<sub>x</sub> functions, the latter ones originally developed by Hammett and Deyrup [10–14], is presented. The conclusions to be drawn lead one to view H<sub>x</sub> as a rather unrealistic measure of acidity [6–9,15–21], despite their large applications in different liquid and solid acid systems of practical interest.

## 2. The parameters of acidity in strong monoprotic acids

### 2.1. Equilibria of solvents (HA + H<sub>2</sub>O mixtures)

Studies in concentrated aqueous solutions of monoprotic acids (HA), with known ionization constants (thermodynamic (p*K*<sub>HA</sub>) or apparent (p*K*<sub>a</sub>) constants) and with known

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degrees of dissociation ( $\alpha$ ), have shown that the acid–base equilibria of the HA + H<sub>2</sub>O mixtures can be described by suitable thermodynamic parameters [6,7]. For instance:

- (i) for aqueous solutions of HBr, CH<sub>3</sub>SO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H, HNO<sub>3</sub>, HClO<sub>4</sub>, whose dissociation (equilibrium (1)) is described by equation (2):



$$\begin{aligned} \text{p}K_{\text{HA}} &= \log[\text{HA}]/[\text{A}^-] - \log[\text{H}^+] \\ &\quad - \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}), \end{aligned} \quad (2)$$

an “activity coefficient function of the solvent” (Mc(s)) has been defined by equation (3):

$$\text{p}K_{\text{a}} - [\log[\text{HA}]/[\text{A}^-] - \log[\text{H}^+]] = n_{\text{s}} \text{Mc}(s), \quad (3)$$

where

$$\log[\text{HA}]/[\text{A}^-] - \log[\text{H}^+] = \log[(1-\alpha)/\alpha^2 c] = \log Q_{\text{a}},$$

$$\text{Mc}(s) = -\log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}) \quad \text{and} \quad n_{\text{s}} = 1;$$

- (ii) furthermore, an “acidity function of the solvent” Ac(s), that is, an “extension of the pH scale in concentrated aqueous acid solutions” has been defined by equation (4):

$$\begin{aligned} \text{p}K_{\text{a}} - \log[\text{HA}]/[\text{A}^-] \\ &= -\log[\text{H}^+] - \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}) \\ &= -\log[\text{H}^+] + \text{Mc}(s) = \text{Ac}(s). \end{aligned} \quad (4)$$

The Mc(s) and Ac(s) functions were estimated from the degrees of dissociation of HA in water ( $\alpha$  values), the latter determined by Raman measurements of the ionizable anion groups (A<sup>−</sup>) in a set of differently concentrated HA + H<sub>2</sub>O acid solutions [6].

## 2.2. Equilibria of solutes (B + HA + H<sub>2</sub>O mixtures)

In the elucidation of the problems of acidity, the protonating ability of a given acid in aqueous systems has mainly been explored as a significant parameter of the interactions between solutes and solvents [10–14]. It requires measurements related to protonation process of weak bases (B) used as indicators (i), whose equilibria (equilibrium (5)) are described by thermodynamic equation (6):



$$\begin{aligned} \text{p}K_{\text{BH}^+} &= \log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+] \\ &\quad - \log(f_{\text{B}} f_{\text{H}^+} / f_{\text{BH}^+}). \end{aligned} \quad (6)$$

In the study of B undergoing protonation in concentrated acid solutions,  $\text{p}K_{\text{BH}^+}$  values with a thermodynamic significance are to be obtained. From a practical point of view, the knowledge of the activity coefficient term is of importance since, in these chemical systems, we are concerned with weak bases in acid solutions outside the range of pH. Accordingly, suitable procedures have been adopted:

- (i) Providing the acid concentration [ $C_{\text{A}}$ ] is not too high (<ca. 2 M), extrapolation to infinite dilution of the plots  $\log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+]$  vs. [ $C_{\text{A}}$ ] leads to a reliable value for  $\text{p}K_{\text{BH}^+}$  (see equation (7)). This is essentially due to the linear variation observed between the activity coefficient term of solutes (B) and [ $C_{\text{A}}$ ] (see equation (8)) [10,11,15]:

$$\text{p}K_{\text{BH}^+} = \log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+] + b[C_{\text{A}}], \quad (7)$$

$$-\log(f_{\text{B}} f_{\text{H}^+} / f_{\text{BH}^+}) = b[C_{\text{A}}]. \quad (8)$$

- (ii) As the acid concentration is increased, a set of bases of decreasing strength in a series of acid solutions can be analysed. Indeed, the comparison by equations (9) and (9') of any two overlapping (B<sub>1</sub>, B<sub>2</sub>) weak bases, of analogous or differing chemical type with or without the same functional basic site,

$$\begin{aligned} \text{p}K_{\text{B}_1\text{H}^+} &= \log[\text{B}_1\text{H}^+]/[\text{B}_1] \\ &\quad - \log[\text{H}^+] - \log(f_{\text{B}_1} f_{\text{H}^+} / f_{\text{B}_1\text{H}^+}), \end{aligned} \quad (9)$$

$$\begin{aligned} \text{p}K_{\text{B}_2\text{H}^+} &= \log[\text{B}_2\text{H}^+]/[\text{B}_2] \\ &\quad - \log[\text{H}^+] - \log(f_{\text{B}_2} f_{\text{H}^+} / f_{\text{B}_2\text{H}^+}), \end{aligned} \quad (9')$$

shows an empirical linear relationship between them (equation (10)) [6,7,15–17]:

$$\begin{aligned} \log[\text{B}_1\text{H}^+]/[\text{B}_1] - \log[\text{H}^+] \\ &= n_{\text{b}_1\text{b}_2} (\log[\text{B}_2\text{H}^+]/[\text{B}_2] - \log[\text{H}^+]). \end{aligned} \quad (10)$$

This has suggested the description of the activity coefficient term by equation (10'):

$$\log(f_{\text{B}_1} f_{\text{H}^+} / f_{\text{B}_1\text{H}^+}) = n_{\text{b}_1\text{b}_2} \log(f_{\text{B}_2} f_{\text{H}^+} / f_{\text{B}_2\text{H}^+}) \quad (10')$$

and the construction of an “activity coefficient function by indicators” or Mc(B\*) as expressed in equation (11), with the choice of an indicator B\* taken as reference [6,7,15–17]:

$$\text{Mc}(\text{B}^*) = -\log(f_{\text{B}^*} f_{\text{H}^+} / f_{\text{B}^*\text{H}^+}). \quad (11)$$

In the Mc treatment by indicators, equilibrium (5) is described by two independent parameters – intercept ( $\text{p}K_{\text{BH}^+}$ ) and slope ( $n_{\text{bb}^*}$ ), as shown in equation (12):

$$\begin{aligned} \text{p}K_{\text{BH}^+} &= \log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+] \\ &\quad + n_{\text{bb}^*} \text{Mc}(\text{B}^*). \end{aligned} \quad (12)$$

## 2.3. Relationships between the equilibria of solutes (i) and solvents (s)

The results of the studies obtained by comparing the equilibria of solutes (i) and solvents (s) in CH<sub>3</sub>SO<sub>3</sub>H, HBr, HClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H and HNO<sub>3</sub> [6,7] have shown that:

- (i) The Mc(B) (or Mc(i)) and the Mc(s) functions have been found to be linearly related between them (see equation (13) rewritten as (13') and figure 1(a)), with slopes values ( $n_{\text{is}}$ ) very different from unity.

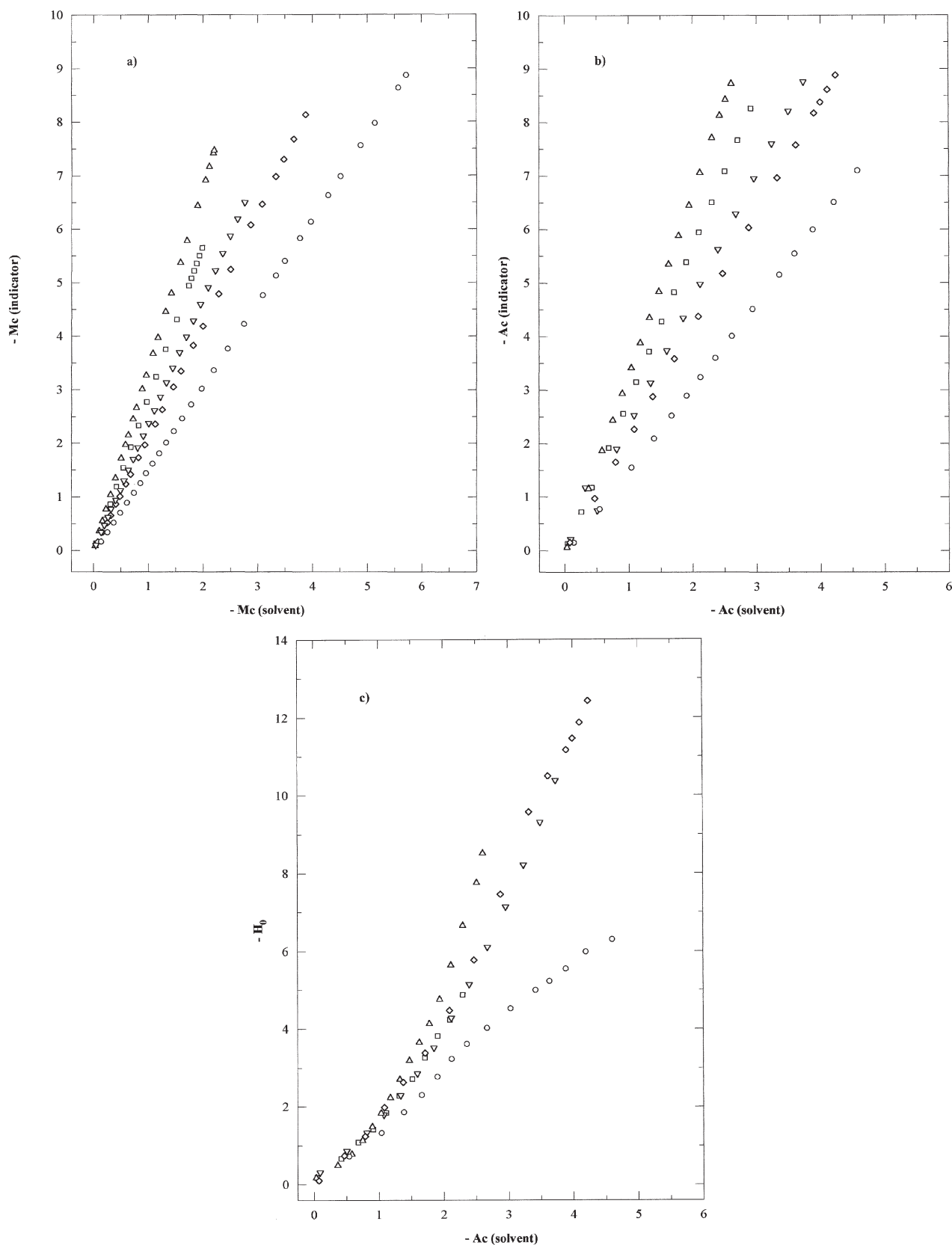


Figure 1. (a) Plot of  $Mc$  (indicator) vs.  $Mc$  (solvent) in: ( $\Delta$ ) MeSO<sub>3</sub>H, ( $\square$ ) HBr, ( $\nabla$ ) HClO<sub>4</sub>, ( $\diamond$ ) CF<sub>3</sub>SO<sub>3</sub>H, ( $\circ$ ) HNO<sub>3</sub>.  $Mc(i)$  and  $Mc(s)$  values from [6]. (b) Plot of  $Ac$  (indicator) vs.  $Ac$  (solvent) (range  $> 1$  M) in: ( $\Delta$ ) MeSO<sub>3</sub>H ( $n_{is} = 3.30$ ), ( $\square$ ) HBr ( $n_{is} = 2.80$ ), ( $\nabla$ ) HClO<sub>4</sub> ( $n_{is} = 2.35$ ), ( $\diamond$ ) CF<sub>3</sub>SO<sub>3</sub>H ( $n_{is} = 2.10$ ), ( $\circ$ ) HNO<sub>3</sub> ( $n_{is} = 1.55$ ).  $Ac$  (indicator) =  $-n_{is} \log[H^+] + Mc(i)$  (see equation (15));  $Ac(i)$ ,  $Ac(s)$ ,  $[H^+]$ ,  $Mc(i)$  values from [6]. (c) Plot of  $H_0$  vs.  $Ac$  (solvent) (range  $> 1$  M) in: ( $\Delta$ ) MeSO<sub>3</sub>H, ( $\square$ ) HBr, ( $\nabla$ ) HClO<sub>4</sub>, ( $\diamond$ ) CF<sub>3</sub>SO<sub>3</sub>H, ( $\circ$ ) HNO<sub>3</sub>.  $Ac(s)$  values from [6];  $H_0$  values from [6,10,11] and references therein.

The observed values are: 3.3 for  $\text{CH}_3\text{SO}_3\text{H}$ , 2.8 for  $\text{HBr}$ , 2.35 for  $\text{HClO}_4$ , 2.10 for  $\text{CF}_3\text{SO}_3\text{H}$ , 1.55 for  $\text{HNO}_3$  when the protonation of nitroanilines is analysed and 2-nitroaniline is used as standard indicator of  $\text{Mc}(i)$  scale [15–17]:

$$\text{Mc}(i) = n_{\text{is}} \text{Mc}(s), \quad (13)$$

$$-\log(f_{\text{B}^*} f_{\text{H}^+} / f_{\text{B}^* \text{H}^+}) = -n_{\text{is}} \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}). \quad (13')$$

It allows the equilibrium of any weak base (equation (5)) to be described by empirical equation (14) or by equation (12) for aqueous acid systems with unknown  $\text{Mc}(s)$  values:

$$\text{p}K_{\text{BH}^+} = \log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+] + n_{\text{is}} \text{Mc}(s). \quad (14)$$

- (ii) Linear relationships have also been observed by comparing the  $\text{Ac}(i)$  (*acidity function of indicators*) and the  $\text{Ac}(s)$  functions, defined, respectively, by equations (15) and (4) (see figure 1(b)):

$$\text{Ac}(i) = -n_{\text{is}} \log[\text{H}^+] + \text{Mc}(i). \quad (15)$$

These experimental observations suggest that the  $n_{\text{is}}$  (or the  $n_{\text{bb}^*}$ ) values are very important parameters related to the “*protonating ability of a solvent*”, that is, to the energetic process involved in the proton transfer from  $\text{H}^+\text{A}^-$  to  $\text{BH}^+\text{A}^-$  (using the  $\text{Mc}(s)$  functions), or from  $\text{B}^*\text{H}^+\text{A}^-$  to  $\text{B}'\text{H}^+\text{A}^-$  species (using the  $\text{Mc}(i)$  functions).

The new data also suggests that the  $\text{H}_x$  acidity functions [10–14] are parameters unrelated to acidity of strong acids in the range outside the pH. Two additional observations support an analogous conclusion:

- An “extension of the pH scale” in concentrated aqueous acid solutions can properly be determined by using the parameters of the solvent (i.e., by the corresponding  $\text{Ac}(s)$  functions (see equation (4)).
- The  $\text{H}_x$  are found to be unrelated to  $\text{Ac}(s)$  functions (see figure 1(c)). As appears from equations (15) and (16), the  $\text{Ac}(i)$  and  $\text{H}_x$  functions differ by the  $n_{\text{is}}$  values or by the parameters expressing the interactions between solutes and solvents:

$$\begin{aligned} \text{H}_x &= \text{p}K_{\text{BH}^+} - \log[\text{BH}^+]/[\text{B}] \\ &= -\log[\text{H}^+] - \log(f_{\text{B}} f_{\text{H}^+} / f_{\text{BH}^+}). \end{aligned} \quad (16)$$

Further experimental details of the behaviour of indicators with analogous basic site and with decreasing basic strength are of interest. For instance:

- a progressive increase in the  $n_{\text{bb}^*}$  and  $n_{\text{is}}$  values for successively weaker bases estimated, respectively, by the  $\text{Mc}(B)$  and  $\text{Mc}(s)$  functions according to equations (12), (14) has been observed (see table 1);
- a linear dependence between slopes  $n_{\text{bb}^*}$  or  $n_{\text{is}}$  and  $\text{p}K_{\text{BH}^+}$  values of indicators has also been found. As suggested in the earlier conclusions [6–9,15–21], the

Table 1  
Slopes<sup>a</sup> ( $n_{\text{is}}$ ,  $n_{\text{bb}^*}$ ) and intercepts<sup>b</sup> ( $\text{p}K_{\text{BH}^+}$ ) for the protonation equilibria of nitroanilines in concentrated aqueous solutions of  $\text{HClO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  at 25 °C.

Nitroanilines <sup>c</sup>	$\text{HClO}_4$		$\text{CF}_3\text{SO}_3\text{H}$		$\text{p}K_{\text{BH}^+}$
	$n_{\text{is}}$	$n_{\text{bb}^*}$	$n_{\text{is}}$	$n_{\text{bb}^*}$	
4-NO <sub>2</sub>	2.17	0.95	2.00	0.95	1.00
2-NO <sub>2</sub>	2.35	1.00	2.12	1.00	−0.27
2-Cl-4-NO <sub>2</sub>	2.45	1.04	2.23	1.04	−0.90
4-Cl-2-NO <sub>2</sub>	2.50	1.07	2.28	1.05	−1.05
5-Cl-2-NO <sub>2</sub>					−1.50
2,5-di-Cl-4-NO <sub>2</sub>	2.55	1.10			−1.80
2-Cl-6-NO <sub>2</sub>	2.75	1.23			−2.60
2,6-di-Cl-4-NO <sub>2</sub>	2.87	1.28			−3.45
2,4-di-Cl-6-NO <sub>2</sub>	2.90	1.27	2.62	1.25	−3.50
2,4-di-NO <sub>2</sub>	3.37	1.44	2.95	1.40	−5.25
2,6-di-NO <sub>2</sub>	3.32	1.45	3.00	1.45	−5.90
4-Cl-2,6-di-NO <sub>2</sub>	3.72	1.62			−7.30
2-Br-4,6-di-NO <sub>2</sub>	3.64	1.57	3.28	1.60	−7.80
3-Me-2,4,6-tri-NO <sub>2</sub>	4.05	1.73	3.73	1.75	−10.40
2,4,6-tri-NO <sub>2</sub>			3.78	1.79	−10.70
3-Br-2,4,6-tri-NO <sub>2</sub>	4.33	1.84	4.16	1.96	−12.25
3-Cl-2,4,6-tri-NO <sub>2</sub>					−12.50

<sup>a</sup> Slopes ( $n_{\text{is}}$ ) of the plots  $\log[\text{BH}^+]/[\text{B}][\text{H}^+]$  vs.  $\text{Mc}(s)$  (see equation (14)); slopes ( $n_{\text{bb}^*}$ ) of the plots  $\log[\text{BH}^+]/[\text{B}][\text{H}^+]$  vs.  $\text{Mc}(B^*)$  (see equation (12)).

<sup>b</sup> Intercepts of the plots  $\log[\text{BH}^+]/[\text{B}][\text{H}^+]$  vs.  $\text{Mc}$  functions;  $\text{Mc}(s)$  and  $\text{Mc}(B^*)$  in  $\text{HClO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  from [6].

<sup>c</sup> Experimental data and thermodynamic values in  $\text{HClO}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$  from [6,7] and references therein.

correlation strongly supports the validity of the  $\text{Mc}$  treatment. A further clear evidence, in this respect, comes from the experimental observation that the plots  $n_{\text{is}}$  or  $n_{\text{bb}^*}$  can be extrapolated to intercept at the  $\text{p}K_{\text{w}}$  of water. Indeed, in water taken as standard state of  $\text{Mc}$  scale, the difference between  $n_{\text{is}}$  and  $n_{\text{bb}^*}$  disappears being  $n_{\text{bb}^*} = n_{\text{is}} = 0$  for water.

### 3. The parameters of acidity in solid acids

An extension of the previous studies has also been attempted [22,23] by exploiting the protonation equilibria of weak bases (B) in solid acid materials (i.e., acid +  $\text{SiO}_2$ ). 2-chloro-4-nitroaniline ( $\text{B}_1$ ) and 2,4-dichloro-6-nitroaniline ( $\text{B}_2$ ) have been chosen as B and  $\text{HClO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ ,  $\text{H}_2\text{SO}_4$  as acids, the latter being one of the most commonly used acidic media in liquid and solid phase in spite of its complex dissociation equilibria [8,9]. A comparison of the results obtained in liquid and solid systems shows that:

- (i) Small amounts of acid in solids, compared with those occurring in liquids, were used on the protonation process of analogous nitroanilines. According to our estimates obtained by comparing the results at the same  $\log[\text{BH}^+]/[\text{B}]$ , it appears that the amount of acid differs by a factor  $10^5$ – $10^4$ .
- (ii) Titration curves with narrow acidity ranges are obtained (see figure 2), as well as an anionic dependence of the protonating ability of the solid acids.

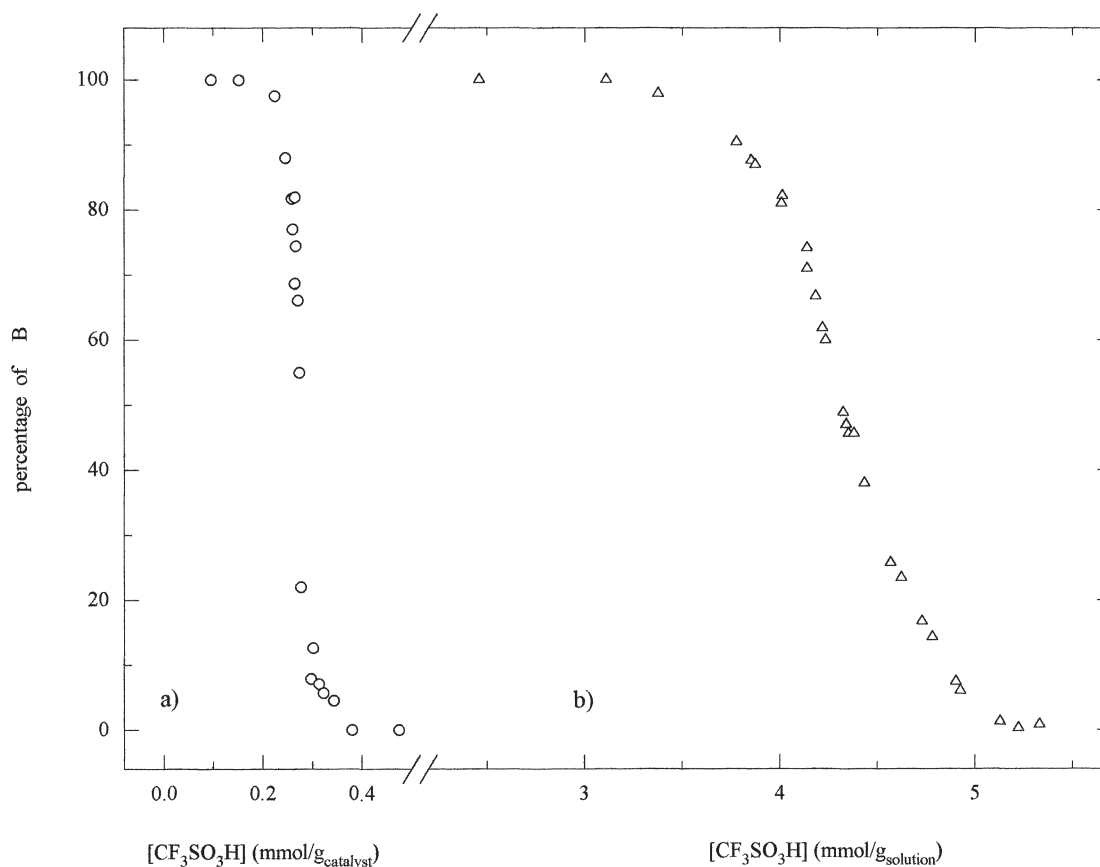


Figure 2. Protonation equilibrium of 2,4-dichloro-6-nitroaniline (B) by UV spectroscopy at 420 nm in: (a) solid phase: percentage of B vs. CF<sub>3</sub>SO<sub>3</sub>H/SiO<sub>2</sub> (mmol/g<sub>catalyst</sub>); (b) aqueous solution: percentage of B vs. CF<sub>3</sub>SO<sub>3</sub>H (mmol/g<sub>solution</sub>).

The experimental trend in the order of half-protonation (HClO<sub>4</sub> > H<sub>2</sub>SO<sub>4</sub> > CF<sub>3</sub>SO<sub>3</sub>H) is consistent with the behaviour of 2,4-dichloro-6-nitroaniline in aqueous acid solutions where the acid concentrations observed at half protonation are at 46.5% in HClO<sub>4</sub>, 47.5% in H<sub>2</sub>SO<sub>4</sub>, 66% in CF<sub>3</sub>SO<sub>3</sub>H [7].

- (iii) Owing to the small amount of acid used on the protonation process of the indicators in the solid phase, the dependence of  $\log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+]$  vs.  $[C_A]$  was tested (see equation (7)), using the experimental ionization ratios ( $\log[\text{BH}^+]/[\text{B}]$ ) measured by UV spectroscopy and the approximation  $[\text{H}^+] = [C_A]_{\text{st}}$  ( $[C_A]_{\text{st}} = \text{HClO}_4$  mmol/g SiO<sub>2</sub>, CF<sub>3</sub>SO<sub>3</sub>H mmol/g SiO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> mmol/g SiO<sub>2</sub>).

Values of  $pK_{\text{BH}^+}$  (−0.90 for B<sub>1</sub> and −3.50 for B<sub>2</sub>) analogous to the previous estimations in aqueous solutions were obtained, but slope values higher by a factor of ca. 10<sup>4</sup> were observed (see table 2).

The experimental trend suggests that the solid acid catalysts under investigation exhibit one type of acid site,  $pK_{\text{BH}^+}$  values that can be referred to water as standard state and strong interactions between acids and added weak bases.

It follows that a reasonable description of the acidic properties of a solid acid catalyst can be obtained by a relationship analogous to that used in liquid phase (see equa-

Table 2  
Slopes<sup>a</sup> ( $n_b$ ) and intercepts<sup>b</sup> ( $pK_{\text{BH}^+}$ ) for the protonation equilibria of nitroanilines in solid acids<sup>c</sup> at 25 °C.

Nitroanilines <sup>d</sup>	$n_b$			$pK_{\text{BH}^+}$
	HClO <sub>4</sub> /SiO <sub>2</sub>	CF <sub>3</sub> SO <sub>3</sub> H/SiO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> /SiO <sub>2</sub>	
2-Cl-4-NO <sub>2</sub>	$8 \times 10^4$	$5.2 \times 10^4$	$5.5 \times 10^4$ <sup>e</sup>	−0.90
2,4-di-Cl-6-NO <sub>2</sub>	$4.2 \times 10^4$	$2.6 \times 10^4$	$3.7 \times 10^4$ <sup>f</sup>	−3.50

<sup>a</sup> Slopes ( $n_b$ ) of the plot  $\log[\text{BH}^+]/[\text{B}][\text{H}^+]$  vs. HA/SiO<sub>2</sub> (mmol/g) (see equation (7)).

<sup>b</sup> Intercepts of the plot  $\log[\text{BH}^+]/[\text{B}][\text{H}^+]$  vs. HA/SiO<sub>2</sub> (mmol/g) (see equation (7)).

<sup>c</sup> Solid acid samples were prepared by the procedure in [22,23]; for details by UV measurements see also [22,23].

<sup>d</sup> Experimental data and thermodynamic values in HClO<sub>4</sub>/SiO<sub>2</sub> and CF<sub>3</sub>SO<sub>3</sub>H/SiO<sub>2</sub> from [22,23]; in H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> from [24,25].

<sup>e</sup> Slope ( $n_{bb^*}$ ) in aqueous H<sub>2</sub>SO<sub>4</sub> ≈ 1 (see equation (12)) from [8,9].

<sup>f</sup> Slope ( $n_{bb^*}$ ) in aqueous H<sub>2</sub>SO<sub>4</sub> = 1.16 (see equation (12)) from [8,9].

tion (13')), where the variation of activity coefficient term and the energetic process related to the proton transfer between an acid and a base are taken into account.

On the other hand, the slopes of indicators in the solids – as expected for practical catalysts – point out an high-protonating ability (or efficient catalytic properties) of the acid samples. Indeed, the materials prepared by adding suitable amounts of H<sub>2</sub>SO<sub>4</sub> to SiO<sub>2</sub> can satisfactorily be used as catalysts in the nitration process at 25 °C of activated and deactivated aromatic compounds (for instance, toluene

and nitrobenzenes) [24,26], as well as in the esterification between 25 and 70 °C of benzoic acid with methanol [24]. Good yields of products (>98%) in very short time are usually obtained in both cases.

Further experimental details concerning the catalytic performance of the materials and their acidic properties are in progress. For instance, in order to help in the understanding for the surface layer, the solid catalysts were characterized by XPS measurements using pyridine chemisorption [27] and investigation of the N<sub>1s</sub> XPS band. Samples of HA/SiO<sub>2</sub> with different acids and with different contents of acid have been tested. In all cases a single peak at 401.4 eV was found, highlighting only the presence of rather strong Brønsted acid sites.

#### 4. Conclusions

A number of studies of concentrated aqueous acid solution suggests that an improved understanding of the phenomena governing the “acidity” can be obtained when suitable properties of acidic medium are recognized and the energetic proton transfer process between an acid and a base is measured.

The intrinsic properties of an acidic medium, as we are going from dilute to progressively concentrated solutions, were characterized by an *Mc(s) activity coefficient function* as a unique scale, related to the deviations of activity coefficients of real solutions from dilute-solution approximations, and also by an *Ac(s) acidity function* as an extension of the concept of pH in nonideal acids.

In contrast, the *acidity of an acid* or its *protonating ability* towards a solute was characterized by the energetic proton transfer process acid → base of the specific acid–base pair. Experimental observations obtained in liquid (L) and solid (S) acids show that the *n<sub>BA</sub>* parameter of the general equation (17) can be used as a measure of the specific interactions between solutes (B) and acids (A):

$$\begin{aligned} & -\log(f_B f_{H^+} / f_{BH^+})_{(L,S)} \\ & = -n_{BA} \log(f_{A^-} f_{H^+} / f_{HA})_{(L,S)}. \end{aligned} \quad (17)$$

The acid–base interactions allow us to account for the different “*H<sub>x</sub> acidity functions*” that have been observed using the protonation equilibria of indicators with different basic site. This complex behaviour of solutes made in the past determination of the “acidity” very difficult, particularly when the Hammett procedure was used. The *Mc* approach get over the above difficulties since the “*Mc(B) activity coefficient functions*” determined for solutes are referred to an indicator B\* chosen as standard state (or as

reference indicator) and can be changed by a change of B\*. However, due to validity of equation (17), a linear relationship holds also between the *Mc(B)* functions referred to a different standard indicator.

#### References

- [1] P.A. Jacobs, in: *Characterization of Heterogeneous Catalysts*, Vol. 15, ed. F. Delannay (Chemical Industries, 1984) chapter 8, p. 367.
- [2] I.M. Campbell, *Catalysis at Surface* (Chapmann and Hall, London, 1988) chapters 2 and 5.
- [3] J. Kijenski and A. Baiker, *Catal. Today* (1989) 5.
- [4] K. Tanabe, H. Hattori, T. Yamaguchi and T. Tanaka, *Acid–Base Catalysis* (VCH, New York, 1989).
- [5] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [6] N.C. Marziano, A. Tomasin and C. Tortato, *Org. React. (Estonia)* 30 (1996) 29.
- [7] N.C. Marziano, A. Tomasin and C. Tortato, *Org. React. (Estonia)* 30 (1996) 39.
- [8] N.C. Marziano, A. Tomasin, C. Tortato and P. Isandelli, *J. Chem. Soc. Perkin Trans. 2* (1998) 2535.
- [9] N.C. Marziano, A. Tomasin, C. Tortato and J.M. Zaldivar, *J. Chem. Soc. Perkin Trans. 2* (1998) 1973.
- [10] L.P. Hammett, *Physical Organic Chemistry* (McGraw-Hill–Kogakusha, Tokyo, 1970).
- [11] C.H. Rochester, *Acidity Functions* (Academic Press, London, 1970).
- [12] M. Liler, *Reaction Mechanisms in Sulphuric Acid* (Academic Press, London, 1971).
- [13] R. Stewart, *The Proton in Chemistry* (Academic Press, London, 1985).
- [14] G.A. Olah, G.K. Surya Prakash and J. Sommer, *Superacids* (Wiley, New York, 1985).
- [15] N.C. Marziano, G. Cimino and R. Passerini, *J. Chem. Soc. Perkin Trans. 2* (1973) 1915.
- [16] N.C. Marziano, P. Traverso, A. Tomasin and R. Passerini, *J. Chem. Soc. Perkin Trans. 2* (1977) 309.
- [17] N.C. Marziano, A. Tomasin and P. Traverso, *J. Chem. Soc. Perkin Trans. 2* (1981) 1070.
- [18] M. Sampoli, A. De Santis and N.C. Marziano, *J. Chem. Soc. Chem. Commun.* (1985) 110.
- [19] N.C. Marziano, M. Sampoli and M. Gonizzi, *J. Phys. Chem.* 90 (1986) 4347.
- [20] N.C. Marziano, A. Tomasin and C. Tortato, *J. Chem. Soc. Perkin Trans. 2* (1991) 1575.
- [21] N.C. Marziano, C. Tortato and R. Bertani, *J. Chem. Soc. Perkin Trans. 2* (1992) 955.
- [22] N.C. Marziano, C. Tortato, A.A. Sheikh-Osman, J. Riego and J.M. Zaldivar, *Org. React. (Estonia)* 30 (1996) 49.
- [23] N.C. Marziano, C. Tortato, A.A. Sheikh-Osman, J. Riego and J.M. Zaldivar, *Org. React. (Estonia)* 31 (1997) 87.
- [24] Unpublished results.
- [25] Present work.
- [26] J.M. Riego, Z. Sedin, J.M. Zaldivar, N.C. Marziano and C. Tortato, *Tetrahedron Lett.* 37 (1996) 513.
- [27] R.B. Borade, A. Adnot and S. Kaliaguine, *J. Catal.* 125 (1990) 6.