J. Am. Chem. Soc., **96,** 1236 (1974). σ_I and σ_R^+ values of SEt and N(Et)$_2$ have been supposed equal to those of SMe and N(Me)$_2$. σ_I for OEt and CCl$_3$ and σ_R^+ for CCl$_3$ come from ref 28, p 189. σ_I for CH$_2$Br has been calculated from $\sigma^*(\sigma_I = \sigma^*/6.23)$. σ_R^+ for Et, *i*-Pr, *t*-Bu, OEt, and SEt have been calculated from ν(CO) of para-substituted acetophenones and benzoic acids [C. Laurence and M. Berthelot, *J. Chem. Soc., Perkin Trans. 2*, in press] according to the equations

$$\sigma_R^+ = 0.012 + 0.0949(\nu - \nu_0) - 1.1505\sigma_I$$
(acetophenones $R = 0.989$, $n = 14$)

$$\sigma_R^+ = 0.049 + 0.1092(\nu - \nu_0) - 1.3664\sigma_I$$
(benzoic acids $R = 0.994$, $n = 13$)

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Acidity Function of Solid-Bound Acids[1,2]

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Abstract: A new method has been developed to determine the acidity of acids bound to solids and hence compare their acidity with that of homogeneous acid systems. A model was set up to relate the sorption of indicators onto proton-carrying solids with the protonation of these indicators in acid solutions. The resulting relationship allows calculation of the acidity function of solid-bound acids. For a strongly acidic ion exchanger, e.g., Amberlyst-15, dispersed in water, the calculated acidity corresponds to an acidity of 35 wt % aqueous sulfuric acid.

The proton-donating ability (Brønsted acidity) of solid materials is an important consideration concerning their behavior in ion-exchange processes and in heterogeneous acid catalysis. The most useful measure of the acid strength of concentrated acid solutions is Hammett's H_0 function[3-7] which relates to primary aromatic amines, and is defined as

$$H_0 = -\log (a_{H^+}f_B/f_{BH^+}) = pK_{BH^+} - \log ([BH^+]/[B]) \qquad (1)$$

where a_{H^+} is the activity of the hydrogen ion, f_B and f_{BH^+} are the activity coefficients for a neutral (i.e., uncharged) base and its conjugate acid, respectively, pK_{BH^+} is the negative logarithm of the acidity constant of the protonated base, and [B] and [BH$^+$] are the concentrations of the neutral base and its conjugate acid, respectively. Analogous functions, such as H_R, H_-, and so on, have been developed for other families of acids and bases.[4]

Acidity functions have been an enormous aid in the study of the rates and mechanisms of organic reactions in solution. Various attempts have also been made to determine the H_0 values of acidic solids. Such an H_0 scale for solid-bound acids is important not only for investigations of the mechanisms of heterogeneous acid-catalyzed reactions but also in the determinations of possible reactivity differences between solid-bound and dissolved acids caused by the solid matrix. The present methods[8,9] to determine surface acidities of cracking catalysts, clays, and a variety of acids mounted on silica gel allow only a semiquantitative estimation of H_0. These methods consist of bringing separate samples of the solid under study into contact with various indicator solutions and noting the resulting colors of the adsorbed indicators.

The present study introduces a new method for an improved quantitative determination of H_0 in solid materials. This method is based on the sorption model SINA (sorption of indicators for the determination of the acidity of solid materials). It enables $f_B f_{H^+}/f_{BH^+}$, and therefore H_0, to be determined from the sorption isotherms of indicator bases onto acidic solid materials. The applicability and usefulness of this new method for determining the H_0 of a sulfonated polystyrene ion-exchange resin in its acidic form (Amberlyst-15) are shown.

Experimental Section

Indicators. The following compounds were obtained from Fluka AG, Switzerland, and were used without further purification (mp, pK_{BH^+}): 2-nitroaniline (70–72 °C, −0.29); 3-nitroaniline (112–113 °C, 2.47); 4-nitroaniline (148–149 °C, 1.00); 2,4-dinitroaniline (179–181 °C, −4.53); 4-chloro-2-nitroaniline (114–116 °C, −1.03). Commercially available (Fluka AG and Aldrich Chemical Co.) samples of the following compounds were recrystallized from ethanol/water mixtures to constant melting point (mp, pK_{BH^+}): 2-methyl-5-nitroaniline (103–105 °C, 2.32); 2-methyl-4-nitroaniline (130–132 °C, 1.04); 4-methyl-2-nitroaniline (114–115 °C, 0.43); 2,6-dichloro-4-nitroaniline (190–192 °C, −3.27); 2-chloro-6-nitroaniline (73–75 °C, −2.46). All melting points were obtained on a FP61 melting point apparatus from Mettler AG, Switzerland, and are uncorrected. The pK_{BH^+} values are taken from the literature.[10]

Solid Substrates. The acidic solid material used was Amberlyst-15 (Rohm and Haas Co.), a sulfonated polystyrene ion-exchange resin in its H$^+$ form, having[11,12] an exchange capacity of 4.3 equiv/L of imbibed water, a porosity of 0.36, an inner surface area of 54 m^2/g, an apparent density of the dried resin bead of 1.012 g/cm^3, a true density of the polystyrene matrix of 1.513 g/cm^3, and an average pore size of 8×10^{-7} cm.

The ion-exchange resin for the sorption experiments was prepared by successive washing with methanol, ethanol, and distilled water until each wash was colorless. Afterwards, the resin was converted into its H$^+$ form by treating it with a 2 M hydrochloric acid solution. The excess acid was removed by extensive washing with distilled water. For the sorption experiments from organic solvents the resin was first predried in air and then at 90 °C under vacuum at 0.1 mmHg. The remaining water content was determined using the method of Karl Fischer. Before the sorption experiments the resin was carefully preconditioned with the appropriate solvent.

The solid substrates used as reference materials were Amberlite XAD-2 (Rohm and Haas Co.), a nonsulfonated polystyrene resin, and Amberlyst-15 in its partial or its total exchanged Na$^+$ form.

Solvents. The solvents were the purest grade products from Merck AG, West Germany. They were used without further purification.

Technique. The sorption isotherms were determined by adding between 0.1 and 1 g of the preconditioned ion-exchange resin to a solution of the appropriate indicator. After the sorption equilibrium was established at 25 °C (24 h), the resin beads were filtered. The amount of the sorbed indicator was then determined spectrophotometrically either by measuring the decrease in the concentration of the indicator in the remaining solution or by extracting the resin with

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Table I. Sorption Equilibria between Various Indicators and Amberlyst-15 (H^+ Form) in Various Solvents and Solvent Mixtures at 25.0 °C

		water			ethanol			methanol		
	pK_{BH^+}	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$	$\log \frac{K_a'}{L/mol}$	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$	$\log \frac{K_a'}{L/mol}$	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$	$\log \frac{K_a'}{L/mol}$
2,4-dinitroaniline	−4.53	2.2×10^{-3}	1.0×10^{-4}	0.71	1.1×10^{-2}	7.0×10^{-3}	−0.45			
2,6-dichloro-4-nitroaniline	−3.57				1.9×10^{-2}	7.0×10^{-3}	−0.20	6.8×10^{-3}	5.0×10^{-3}	−0.50
2-chloro-6-nitroaniline	−2.46	3.5×10^{-3}	1.3×10^{-4}	0.80	2.6×10^{-2}	7.5×10^{-3}	−0.10			
4-chloro-6-nitroaniline	−1.09	5.0×10^{-3}	1.3×10^{-4}	0.95	5.5×10^{-2}	8.0×10^{-3}	0.20	3.1×10^{-3}	9.0×10^{-4}	−0.10
2-nitroaniline	−0.29	8.0×10^{-2}	1.0×10^{-3}	1.27	1.8×10^{-1}	1.0×10^{-2}	0.65	9.9×10^{-3}	6.0×10^{-4}	0.58
4-methyl-2-nitroaniline	0.43	4.1×10^{-1}	8.2×10^{-5}	2.07	2.4×10^{-1}	5.0×10^{-3}	1.05	2.7×10^{-2}	8.0×10^{-4}	0.90
4-nitroaniline	1.00	1.4×10^{-1}	1.0×10^{-4}	2.53	3.5×10^{-2}	1.0×10^{-4}	1.91	6.2×10^{-2}	2.0×10^{-4}	1.86
2-methyl-4-nitroaniline	1.04	6.7×10^{-2}	7.0×10^{-5}	2.35	3.0×10^{-1}	1.0×10^{-3}	1.85	7.6×10^{-2}	2.8×10^{-4}	1.80
2-methyl-5-nitroaniline	2.32	8.5×10^{-1}	5.0×10^{-5}	3.60	3.1×10^{-1}	4.0×10^{-5}	3.27			
3-nitroaniline	2.46	9.5×10^{-1}	5.0×10^{-5}	3.65	3.3×10^{-1}	3.6×10^{-5}	3.34	2.1×10^{-1}	3.3×10^{-5}	3.16

		ethanol/water								
		4:1			1:1			1:4		
	pK_{BH^+}	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$	$\log \frac{K_a'}{L/mol}$	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$	$\log \frac{K_a'}{L/mol}$	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$	$\log \frac{K_a'}{L/mol}$
4-methyl-2-nitroaniline	0.43	1.5×10^{-2}	7.0×10^{-3}	−0.30	1.0×10^{-1}	8.0×10^{-3}	0.45	3.7×10^{-3}	3.0×10^{-5}	1.45
4-nitroaniline	1.00	7.7×10^{-2}	4.8×10^{-3}	0.57	2.3×10^{-1}	3.3×10^{-3}	1.20	2.8×10^{-1}	6.0×10^{-4}	2.04
2-methyl-4-nitroaniline	1.04	1.0×10^{-2}	1.0×10^{-3}	0.40	3.8×10^{-2}	3.0×10^{-3}	1.10	8.7×10^{-3}	2.0×10^{-5}	2.00
2-methyl-5-nitroaniline	2.32	1.2×10^{-1}	4.0×10^{-4}	1.85	2.9×10^{-1}	3.0×10^{-4}	2.35	4.9×10^{-1}	5.7×10^{-5}	3.33
3-nitroaniline	2.46	2.8×10^{-1}	4.0×10^{-4}	2.21	7.8×10^{-2}	4.0×10^{-5}	2.65	2.5×10^{-1}	2.0×10^{-5}	3.50

ammonia solution or dimethyl sulfoxide and measuring the concentration of indicator in the extracts. For the determination of the isotherm this procedure was repeated for various indicator concentrations.

Results and Discussion

The Basic Concept of the SINA Model. If a neutral indicator base is sorbed by an acidic solid porous material, such as a sulfonated ion-exchange resin, the total concentration of the sorbed base $[\bar{B}]_{tot}$ is given by

$$[\bar{B}]_{tot} = [\bar{B}] + [\overline{BH}^+] + [Res,B] + [Res\text{-}SO_3H,B] \quad (2)$$

where $[\bar{B}]$ and $[\overline{BH}^+]$ are the concentrations in the pore liquid of the mobile (not adsorbed) base and its conjugate acid, respectively, and [Res,B] and [Res-SO$_3$H,B] are the concentrations of the immobilized (adsorbed) base onto the resin matrix and the fixed sulfonic acid groups, respectively. The immobilization of the base can be caused by various kinds of intermolecular interactions, such as dispersion interactions, hydrogen bonding, or strong Coulombic interactions leading to intimate ion-pair formation.

All the concentration terms in eq 2 are interrelated as shown in the equations

$$[Res\text{-}SO_3H]_0 = [Res\text{-}SO_3H] + [Res\text{-}SO_3^-] + [Res\text{-}SO_3H,B] \quad (3)$$

$$[Res\text{-}SO_3^-] = [\bar{H}^+] + [\overline{BH}^+] \quad (4)$$

$$K_{Res} = \frac{[Res\text{-}SO_3^-][\bar{H}^+]}{[Res\text{-}SO_3H]} \frac{\bar{f}_{SO_3^-}\bar{f}_{H^+}}{\bar{f}_{SO_3H}} \quad (5)$$

$$K_{BH^+} = \frac{[\bar{B}][\bar{H}^+]}{[\overline{BH}^+]} \frac{\bar{f}_B\bar{f}_{H^+}}{\bar{f}_{BH^+}} \quad (6)$$

$$K_S = \frac{[Res,B]}{[\bar{B}][Res]} \frac{\bar{f}_{Res,B}}{\bar{f}_B\bar{f}_{Res}} \quad (7)$$

$$K_{IP} = \frac{[Res\text{-}SO_3H,B]}{[Res\text{-}SO_3^-][\overline{BH}^+]} \frac{\bar{f}_{SO_3H,B}}{\bar{f}_{SO_3^-}\bar{f}_{BH^+}} \quad (8)$$

$$\frac{K_{IP}K_{Res}}{K_{BH^+}} = \frac{[Res\text{-}SO_3H,B]}{[Res\text{-}SO_3H][\bar{B}]} \frac{\bar{f}_{SO_3H,B}}{\bar{f}_{SO_3H}\bar{f}_B} \quad (9)$$

Table II. Sorption of 3- and 4-Nitroaniline on Amberlite XAD-2 and Amberlyst-15 (Na^+ Form) at 25.0 °C[a]

indicator	substrate	solvent	$\frac{[\bar{B}]_{tot}}{mol/L}$	$\frac{[B]}{mol/L}$
4-nitroaniline	1	ethanol	9.4×10^{-3}	6.7×10^{-3}
4-nitroaniline	2	ethanol	1.7×10^{-2}	6.5×10^{-3}
4-nitroaniline	2	water	2.7×10^{-3}	3.0×10^{-4}
3-nitroaniline	2	ethanol	1.0×10^{-2}	7.0×10^{-3}
3-nitroaniline	2	water	2.0×10^{-3}	7.0×10^{-4}

[a] Substrate 1, Amberlite XAD-2; substrate 2, Amberlyst-15 (Na^+ form).

where $[Res\text{-}SO_3H]_0$ is the total ion-exchange capacity, [Res-SO$_3$H] and [Res-SO$_3^-$] are the concentrations of the matrix-bound sulfonic acid and sulfonate groups, respectively, $[\bar{H}^+]$ is the proton concentration within the pore liquid, and f represents the activity coefficient.

In the present study it is assumed that $[\bar{B}] = [B]$, i.e., that in the equilibrium state the concentrations of the free base in the solution surrounding the ion-exchange resin and in the pore solution are equal. Measurements of the sorption of nonelectrolyte into ion-exchange resin show that, as a first approximation, this assumption is justified.[13] In the imbibed solution the sorbed free base is subject to further reactions with the proton and the resin residue. These reactions can adequately be treated as adsorption-desorption processes whose equilibrium states are described by eq 10. Formally, eq 10 is equivalent to the expression for a Langmuir adsorption isotherm.

$$[\bar{B}_a] = [S]_0 \frac{K_a[\bar{B}]}{1 + K_a[\bar{B}]} \quad (10)$$

$[\bar{B}_a]$ and $[\bar{B}]$ are the concentrations of the adsorbed and the free base, respectively, $[S]_0$ is the concentration of the total available adsorption sites of the same type, and K_a is the adsorption constant.

If the inner surface of the resin matrix, the fixed sulfonic acid groups, and the protons are the three different types of "adsorption" sites, eq 11–13 can be derived from eq 10.

Table III. Sorption Isotherms of 2-, 3-, and 4-Nitroaniline on Amberlyst-15 (H^+ Form) in Water and Ethanol at 25.0 °C

2-nitroaniline		4-nitroaniline		3-nitroaniline	
$[\bar{B}]_{tot}$, mol/L	$[B]$, mol/L	$[\bar{B}]_{tot}$, mol/L	$[B]$, mol/L	$[\bar{B}]_{tot}$, mol/L	$[B]$, mol/L
		Water			
3.2×10^{-3}	4.0×10^{-5}	2.4×10^{-2}	1.5×10^{-5}	3.3×10^{-1}	1.0×10^{-5}
4.0×10^{-3}	5.2×10^{-5}	7.2×10^{-2}	5.0×10^{-5}	7.0×10^{-1}	3.0×10^{-5}
6.0×10^{-3}	7.5×10^{-5}	9.0×10^{-2}	6.0×10^{-5}	1.0	5.4×10^{-5}
7.0×10^{-3}	8.0×10^{-5}	1.2×10^{-1}	8.1×10^{-5}	1.4	1.0×10^{-4}
8.0×10^{-3}	1.0×10^{-4}	1.4×10^{-1}	1.0×10^{-4}	1.9	2.0×10^{-4}
1.0×10^{-2}	1.2×10^{-4}	2.0×10^{-1}	1.5×10^{-4}	2.2	3.0×10^{-4}
1.6×10^{-2}	2.0×10^{-4}	2.5×10^{-1}	2.0×10^{-4}	2.5	5.0×10^{-4}
2.4×10^{-2}	3.0×10^{-4}	3.0×10^{-1}	2.5×10^{-4}	3.0	1.0×10^{-3}
6.5×10^{-2}	8.0×10^{-4}	5.0×10^{-1}	5.0×10^{-4}	3.2	2.0×10^{-3}
8.0×10^{-2}	1.0×10^{-3}	6.5×10^{-1}	7.0×10^{-4}	3.4	3.6×10^{-3}
1.6×10^{-1}	2.0×10^{-3}	8.4×10^{-1}	1.0×10^{-3}	3.4	4.0×10^{-3}
1.8×10^{-1}	2.5×10^{-3}	1.0	1.4×10^{-3}	3.5	6.0×10^{-3}
2.2×10^{-1}	3.0×10^{-3}	1.2	2.0×10^{-3}	3.5	7.0×10^{-3}
3.8×10^{-1}	5.0×10^{-3}	1.5	3.0×10^{-3}	3.5	8.0×10^{-3}
4.0×10^{-1}	6.0×10^{-3}	1.7	4.0×10^{-3}		
5.0×10^{-1}	7.5×10^{-3}	1.8	4.5×10^{-3}		
		Ethanol			
1.9×10^{-3}	1.0×10^{-4}	1.9×10^{-2}	5.0×10^{-5}	1.8×10^{-1}	2.0×10^{-5}
6.0×10^{-3}	3.2×10^{-4}	3.5×10^{-2}	1.1×10^{-4}	3.6×10^{-1}	4.0×10^{-5}
1.9×10^{-2}	1.0×10^{-3}	1.8×10^{-1}	4.9×10^{-4}	5.4×10^{-1}	7.2×10^{-5}
9.5×10^{-2}	5.0×10^{-3}	2.6×10^{-1}	8.2×10^{-4}	7.1×10^{-1}	1.0×10^{-4}
1.8×10^{-1}	1.0×10^{-2}	3.1×10^{-1}	1.0×10^{-3}	1.1	1.9×10^{-4}
3.5×10^{-1}	2.0×10^{-2}	5.4×10^{-1}	1.9×10^{-3}	1.3	3.0×10^{-4}
4.8×10^{-1}	3.0×10^{-2}	9.3×10^{-1}	5.0×10^{-3}	1.5	5.0×10^{-4}
5.8×10^{-1}	4.0×10^{-2}	1.3	1.0×10^{-2}	1.9	1.0×10^{-3}
6.8×10^{-1}	5.0×10^{-2}	1.8	2.0×10^{-2}	2.5	3.0×10^{-3}
7.6×10^{-1}	6.0×10^{-2}	1.9	3.0×10^{-2}	2.7	5.0×10^{-3}
8.3×10^{-1}	7.0×10^{-2}	2.1	4.0×10^{-2}	3.0	1.0×10^{-2}
9.0×10^{-1}	8.0×10^{-2}	2.2	6.0×10^{-2}	3.1	4.0×10^{-2}
9.5×10^{-1}	9.0×10^{-2}	2.3	8.0×10^{-2}	3.1	9.0×10^{-2}

$$[\text{Res,B}] = [\text{Res}]_0 K_S \frac{\bar{f}_B \bar{f}_{Res}}{\bar{f}_{Res,B}} [\bar{B}] \Big/ \left(1 + K_S \frac{\bar{f}_B \bar{f}_{Res}}{\bar{f}_{Res,B}} [\bar{B}]\right) \quad (11)$$

$$[\text{Res-SO}_3\text{H,B}] = ([\text{Res-SO}_3\text{H}]_0 - [\text{Res-SO}_3^-]) \times \frac{(K_{IP}K_{Res}/K_{BH^+})(\bar{f}_{SO_3H}\bar{f}_B/\bar{f}_{SO_3H,B})[\bar{B}]}{1 + (K_{IP}K_{Res}/K_{BH^+})(\bar{f}_{SO_3H}\bar{f}_B/\bar{f}_{SO_3H,B})[\bar{B}]} \quad (12a)$$

$$[\text{Res-SO}_3\text{H,B}] = [\text{Res-SO}_3\text{H}]_0 \times \frac{K_{IP}(\bar{f}_{SO_3^-}\bar{f}_{BH^+}/\bar{f}_{SO_3H,B})[\overline{BH}^+]}{1 + K_{IP}(\bar{f}_{SO_3^-}\bar{f}_{BH^+}/\bar{f}_{SO_3H,B})[\overline{BH}^+] + (1/K_{Res})(\bar{f}_{SO_3^-}\bar{f}_{H^+}/\bar{f}_{SO_3H})[H^+]} \quad (12b)$$

$$[\overline{BH}^+] = ([\text{Res-SO}_3\text{H}]_0 - [\text{Res-SO}_3\text{H,B}] - [\text{Res-SO}_3\text{H}]) \frac{(1/K_{BH^+})(\bar{f}_B\bar{f}_{H^+}/\bar{f}_{BH^+})[\bar{B}]}{1 + (1/K_{BH^+})(\bar{f}_B\bar{f}_{H^+}/\bar{f}_{BH^+})[\bar{B}]} \quad (13)$$

Acidity of Strongly Acidic Ion-Exchange Resin. With the help of eq 11–13, all the concentration terms which sum up to the total concentration of the sorbed indicator (eq 2) can now be expressed as functions of the concentration of the free base. The relative share of these terms depends on the properties of the acidic solid substrates. There is enough evidence to assume that, for the strongly acidic ion-exchange resin Amberlyst-15 under study, the sulfonic acid groups and their salts with monovalent cations are, in protic solvents, fully ionized[14-17] as well as dissociated.[15,18,19] From this it follows that [Res-SO$_3$H] and [Res-SO$_3$H,B] can be neglected. This leads to the equation

$$[\overline{BH}^+] = [\bar{B}]_{tot} - [\bar{B}] - [\text{Res,B}] = [\text{Res-SO}_3\text{H}]_0 \frac{(1/K_{BH^+})(\bar{f}_B\bar{f}_{H^+}/\bar{f}_{BH^+})[\bar{B}]}{1 + (1/K_{BH^+})(\bar{f}_B\bar{f}_{H^+}/\bar{f}_{BH^+})[\bar{B}]} \quad (14)$$

Comparing eq 14 with eq 10 gives

$$K_a = (1/K_{BH^+})(\bar{f}_B\bar{f}_{H^+}/\bar{f}_{BH^+}) \quad (15)$$

As $[\bar{B}]_{tot}$ rather than $[\overline{BH}^+]$ is the experimentally measurable quantity, it is useful to define

$$K_a' = \frac{[\bar{B}]_{tot}}{([\text{Res-SO}_3\text{H}]_0 - [\bar{B}]_{tot})[\bar{B}]} \quad (16)$$

It then follows that

$$K_a' = K_a + ([\text{Res,B}] + [\bar{B}]) \frac{1 + K_a[\bar{B}]}{([\text{Res-SO}_3\text{H}]_0 - [\bar{B}]_{tot})[\bar{B}]} \quad (17)$$

Equation 18 follows from eq 15 and 17:

$$\log \left[K_a' - ([\text{Res,B}] + [\bar{B}]) \frac{1 + K_a[\bar{B}]}{([\text{Res-SO}_3\text{H}]_0 - [\bar{B}]_{tot})[\bar{B}]}\right] = pK_{HB^+} + \log \frac{\bar{f}_B\bar{f}_{H^+}}{\bar{f}_{BH^+}} \quad (18)$$

Therefore, if a plot of log K_a' vs. pK_{BH^+} gives a straight line with a slope of one, it can be assumed, according to eq 16 and 18, that $[\bar{B}]_{tot} \gg ([\text{Res,B}] + [\bar{B}])(1 + K_a[\bar{B}])$. This is the case if $([\text{Res,B}] + [\bar{B}])$ is negligible compared to $[\overline{BH}^+]$. As the curves in Figure 1 show for Amberlyst-15, such a situation is expected for the sorption of indicators with pK_{BH^+} values between −0.5 and 3.0, e.g., of 2-, 3-, and 4-nitroaniline.

The experimental data for the curves in Figure 1 are given in Table I. Some control experiments in the linear part of the relationship (18) show that the sorption onto the inner surface of the resin matrix, given in Table II by $[\bar{B}]_{tot}$ for either a

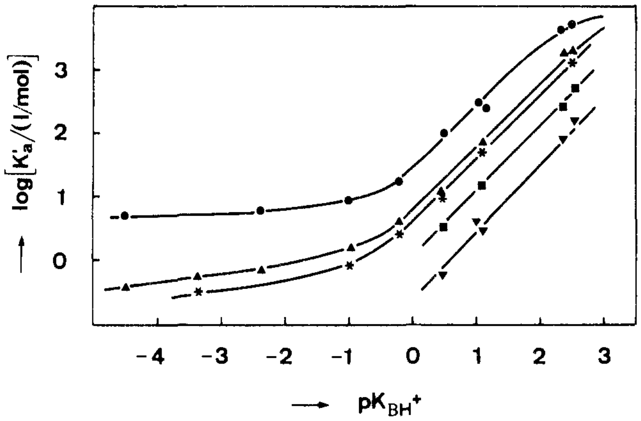

Figure 1. Sorption constants K_a' as a function of the pK_{BH^+} values of various indicators in various solvents and solvent mixtures (●, water; ▲, ethanol; ✱, methanol; ■, 50 vol % ethanol/water; ▼, 80 vol % ethanol/water).

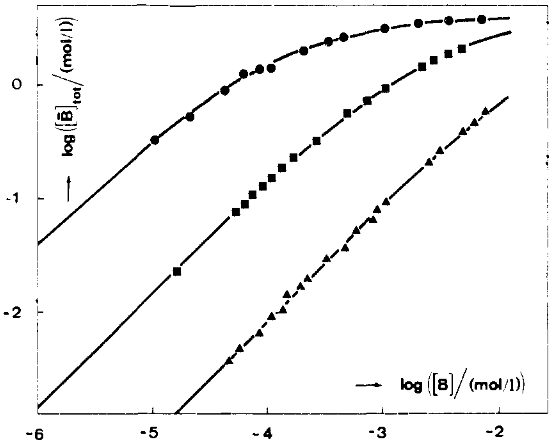

Figure 2. Sorption isotherms of 2- (▲), 3- (●), and 4-nitroaniline (■) on Amberlyst-15 in water at 25.0 °C.

nonsulfonated resin or an entirely Na$^+$-exchanged sulfonated resin, is in fact much smaller than $[\bar{B}]_{tot}$ for the H$^+$ form of Amberlyst-15 (Table III). In this case, the ratio of the activity coefficients can be calculated from the isotherms, i.e.

$$\frac{\bar{f}_B\bar{f}_{H^+}}{\bar{f}_{BH^+}} = \frac{([\bar{B}]_{tot} - [\bar{B}])K_{BH^+}}{[\bar{B}]([\text{Res-SO}_3\text{H}]_0 - [\bar{B}]_{tot} + [\bar{B}])} \quad (19)$$

Figures 2 and 3 give the sorption isotherms of 2-, 3-, and 4-nitroaniline on Amberlyst-15 in water and ethanol, respectively. In Figure 4 the logarithm of the activity coefficient ratio, calculated using eq 19, is plotted against the concentration of the total sorbed indicator. The results show that Hammett's postulate, namely, that bases with similar structure have similar activity coefficient ratios in homogeneous acid solutions also holds within the pore solution of strongly acidic ion-exchange resins. Furthermore, as long as $[\bar{B}]_{tot} < 0.2$ mol/L imbibed solution, the presence of the indicator does not influence the measured proton activity. In this concentration range the H_0 and the M_c values for Amberlyst-15 can be calculated using the equations

$$H_0 = -\log\frac{a_{H^+}\bar{f}_B}{\bar{f}_{BH^+}} = -\log\frac{([\bar{B}]_{tot} - [\bar{B}])K_{BH^+}}{[\bar{B}]} \quad (20)$$

$$M_c = -\log\frac{\bar{f}_B\bar{f}_{H^+}}{\bar{f}_{BH^+}} = -\log\frac{([\bar{B}]_{tot} - [\bar{B}])K_{BH^+}}{[\bar{B}]([\text{Res-SO}_3\text{H}]_0 - [\bar{B}]_{tot} + [\bar{B}])} \quad (21)$$

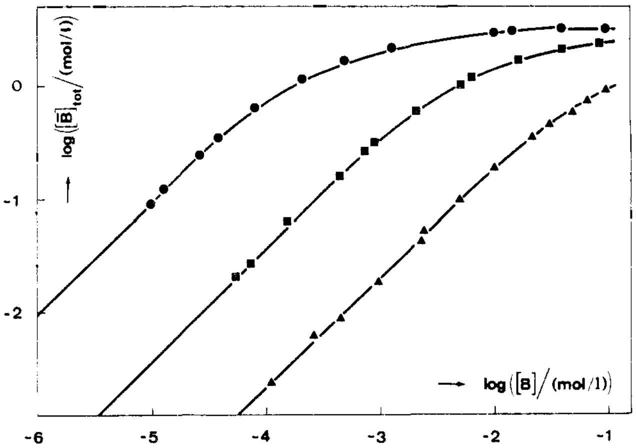

Figure 3. Sorption isotherms of 2- (▲), 3- (●), and 4-nitroaniline (■) on Amberlyst-15 in ethanol at 25.0 °C.

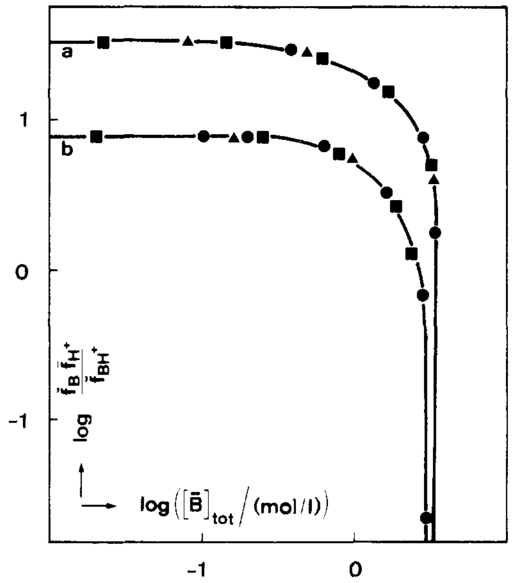

Figure 4. Activity coefficient ratio as a function of the concentration of the total sorbed indicator by Amberlyst-15 in water (a) and ethanol (b). ▲, 2-nitroaniline; ●, 3-nitroaniline; ■, 4-nitroaniline.

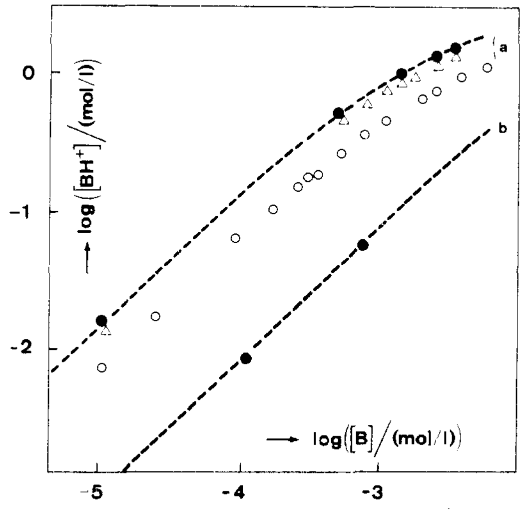

Figure 5. Degree of protonation of 2- (b) and 4-nitroaniline (a) in Amberlyst-15 (dotted line) and in sulfuric acid (●, 35 wt %; △, 34 wt %; ○, 30 wt % H_2SO_4).

Table IV. Acidity Function of Amberlyst-15 (H^+ Form) in Ethanol/Water Mixtures at 25.0 °C[a]

ethanol vol %	indicator	$[\overline{B}]_{tot}$ mol/L	$[B]$ mol/L	$-H_0$
100	A	1.8×10^{-3}	1.0×10^{-4}	1.54
	B	1.8×10^{-1}	2.0×10^{-5}	1.50
	C	3.5×10^{-2}	1.0×10^{-4}	1.54
97	B	1.2×10^{-1}	5.0×10^{-5}	0.93
	C	1.6×10^{-2}	2.0×10^{-4}	0.90
95	B	1.7×10^{-1}	1.0×10^{-4}	0.76
	C	1.1×10^{-2}	2.0×10^{-4}	0.74
90	B	1.4×10^{-1}	1.5×10^{-4}	0.50
	C	1.4×10^{-2}	5.0×10^{-4}	0.46
80	B	5.1×10^{-2}	1.0×10^{-4}	0.25
	C	7.7×10^{-2}	4.8×10^{-3}	0.21
70	B	1.7×10^{-1}	2.6×10^{-4}	0.36
	C	1.1×10^{-2}	5.0×10^{-4}	0.33
60	B	1.8×10^{-1}	2.0×10^{-4}	0.50
	C	1.4×10^{-2}	5.0×10^{-4}	0.46
50	B	7.8×10^{-2}	4.0×10^{-5}	0.83
	C	6.5×10^{-2}	5.0×10^{-4}	0.85
40	B	1.4×10^{-1}	5.0×10^{-5}	1.00
	C	1.9×10^{-2}	2.0×10^{-4}	0.98
30	B	1.9×10^{-1}	3.0×10^{-5}	1.34
	C	4.5×10^{-2}	2.0×10^{-4}	1.35
20	B	2.5×10^{-1}	2.0×10^{-5}	1.63
	C	1.4×10^{-1}	3.0×10^{-4}	1.66
10	B	2.3×10^{-1}	1.0×10^{-5}	1.90
	C	1.5×10^{-1}	2.0×10^{-4}	1.88
0	A	8.0×10^{-3}	1.0×10^{-4}	2.18
	B	4.2×10^{-2}	1.0×10^{-6}	2.16
	C	1.4×10^{-1}	1.0×10^{-4}	2.15

[a] A, 2-nitroaniline; B, 3-nitroaniline; C, 4-nitroaniline.

This gives values in water of $H_0 = -2.16$ and $M_c = -1.53$, and in ethanol of $H_0 = -1.54$ and $M_c = -0.91$. Comparing the H_0 value with the acidity function of aqueous sulfuric acid it follows that the acidity of Amberlyst-15 in its H^+ form corresponds to an acidity of either 35[20] or 38 wt %[21] sulfuric acid. A comparison of the M_c value with the M_c function of aqueous sulfuric acid[22] gives an acidity for Amberlyst-15 corresponding to a 37 wt % sulfuric acid.

Figure 5 shows a comparison between the degree of protonation of 2- and 4-nitroaniline in sulfuric acid[23] and in Amberlyst-15. The results confirm that the acidity in Amberlyst-15 corresponds to an acidity of a 35 wt % sulfuric acid. In addition, from the similarity of the curves for Amberlyst-15 and sulfuric acid one can conclude that the sharp drop in the activity coefficient ratio at higher indicator concentrations (Figure 4) is not caused by invalidation of the assumption $[\overline{B}] = [B]$.

A control experiment was carried out to determine the catalytic activity of the protons in Amberlyst-15 by measurement of the rate of the acid-catalyzed hydrolysis of ethyl acetate. A comparison of the observed rate constant $k = 1.14 \times 10^{-3}\ s^{-1}$ with the kinetic data in sulfuric acid[24] confirms once more that the acid form of Amberlyst-15 has an acidity which is equal to that of 35 wt % sulfuric acid.

In Table IV the H_0 values of Amberlyst-15 are given for various ethanol/water mixtures.[25] In Figure 6 these acidity functions are compared with the acidity functions of a 1 M hydrochloric acid solution.[26] Both acidity functions show a minimum around 80 vol % ethanol/water. In Table V are listed H_0 values[25] which have been determined using the presented SINA model for various common solvents.

The addition of salts to acidic solutions changes their H_0 values. The resulting salt effect ΔH_0 is defined[10] in the equation

$$\Delta H_0 = H_0(\text{with salt}) - H_0(\text{without salt}) \qquad (22)$$

The salt effects for ion-exchange substrates can be determined by partially neutralizing its acidic form and measuring the H_0 of the remaining acid. The salt effect for partially neutralized Amberlyst-15 is shown in Figure 7 and listed in Table VI. The solid line in Figure 7 corresponds to the acidity function of sulfuric acid.[3] If, for Amberlyst-15 with a total exchange capacity of $[\text{Res-SO}_3\text{H}]_0 = 4.3$ mol/L imbibed water, the acidity of $H_0 = -2.16$ is taken as the reference point, and it is assumed that the relative change of H_0 is the same for sulfonated polystyrene as for sulfuric acid, the salt effect ΔH_0 can be determined by plotting the H_0 values of the partially neutralized Amberlyst-15 against the concentration of the remaining

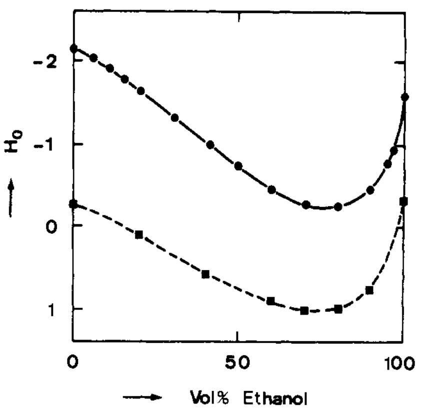

Figure 6. Acidity function of Amberlyst-15 (●) in its acid form and of a 1 M hydrochloric acid solution (■) in ethanol/water mixtures.

Table V. Acidity Function of Amberlyst-15 (H^+ Form) in Various Solvents at 25.0 °C[a]

solvent	indicator	$[\overline{B}]_{tot}$ mol/L	$[B]$ mol/L	$-H_0$
ethanol	A	1.8×10^{-3}	1.0×10^{-4}	1.54
	B	1.8×10^{-1}	2.0×10^{-5}	1.50
	C	3.5×10^{-2}	1.0×10^{-4}	1.54
methanol	A	9.9×10^{-3}	6.0×10^{-4}	1.50
	C	6.2×10^{-2}	2.0×10^{-4}	1.49
1-propanol	C	1.9×10^{-1}	2.0×10^{-4}	1.97
1-propanol (95%)	B	1.4×10^{-1}	1.0×10^{-4}	0.69
	C	1.0×10^{-2}	2.0×10^{-4}	0.70
2-propanol	C	2.0×10^{-1}	2.0×10^{-4}	2.00
2-propanol (95%)	B	1.8×10^{-1}	1.0×10^{-4}	0.80
	C	1.3×10^{-2}	2.0×10^{-4}	0.80
acetone	A	4.5×10^{-2}	7.1×10^{-4}	2.10
	C	2.8×10^{-1}	1.4×10^{-4}	2.30
tetrahydrofuran	A	1.0×10^{-2}	3.0×10^{-4}	1.81
	C	2.6×10^{-1}	5.0×10^{-4}	1.72
nitromethane	A	1.0×10^{-1}	6.2×10^{-4}	2.80
acetonitrile	A	6.1×10^{-2}	4.9×10^{-4}	2.40
	C	3.2×10^{-1}	1.0×10^{-4}	2.50
chloroform	A	1.4×10^{-2}	9.4×10^{-4}	1.44
diethyl ether	A	5.1×10^{-2}	5.7×10^{-4}	2.21
water	A	8.0×10^{-3}	1.0×10^{-4}	2.18
	B	4.2×10^{-2}	1.0×10^{-6}	2.16
	C	1.4×10^{-1}	1.0×10^{-4}	2.15
dimethyl sulfoxide	A	0	1.0×10^{-3}	
dimethylformamide	A	0	1.0×10^{-3}	
pyridine	A	0	1.0×10^{-3}	

[a] A, 2-nitroaniline; B, 3-nitroaniline; C, 4-nitroaniline.

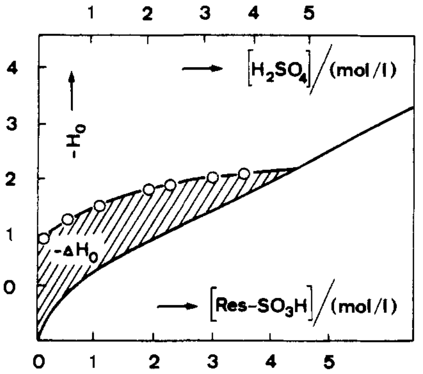

Figure 7. Salt effect (ΔH_0) in partially neutralized Amberlyst-15 measured with 4-nitroaniline in water at 25.0 °C.

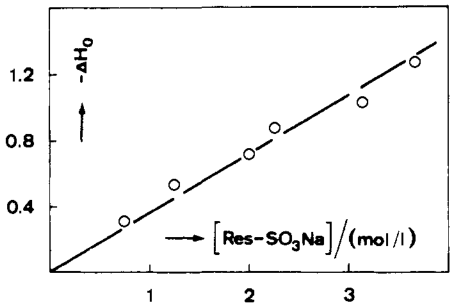

Figure 8. Salt effect (ΔH_0) in partially neutralized Amberlyst-15 measured with 4-nitroaniline in water at 25.0 °C.

Table VI. Salt Effect (ΔH_0) in Partially Neutralized Amberlyst-15 Measured with 4-Nitroaniline in Water at 25.0 °C

$[Res\text{-}SO_3Na]/[Res\text{-}SO_3H]_0$	$[Res\text{-}SO_3H]$ mol/L	$[Res\text{-}SO_3Na]$ mol/L	$-H_0$	$-\Delta H_0$
0.00	4.30		2.17	
0.17	3.57	0.73	2.12	0.32
0.29	3.05	1.25	2.04	0.54
0.46	2.32	2.00	1.92	0.72
0.57	1.85	2.25	1.82	0.87
0.74	1.12	3.18	1.57	1.02
0.86	0.60	3.70	1.27	1.27
1.00		4.30	0.95	

sulfonic acid groups. The salt effect determined by this procedure increases linearly with increasing neutralization, as shown in Figure 8.

Conclusions

The results obtained in this investigation show that the acid strengths of solids can be quantitatively determined from the sorption isotherms of Hammett indicators. This technique can furnish useful information not readily obtainable by other means and has also a general applicability in the determination of possible reactivity differences, caused by the solid matrix, between solid-bound and dissolved reactants. While the acidity function which we have determined strictly relates, like those determined in solutions, to one family of bases, the method described obviously has more general applicability.

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References and Notes

(1) This paper is dedicated, for their 60th birthdays, to Professor H. Zollinger in recognition of his contributions to physical organic chemistry, and to Dr. P. B. Weisz, whose discovery of the catalytic capabilities of acidic zeolites opened new areas of research and technology.
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