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The nature of the internal acid solution in sulfonated poly(styrene-*co*-divinylbenzene) resins

S. Koujout[a], B.M. Kiernan[b], D.R. Brown[a,*], H.G.M. Edwards[b], J.A. Dale[c], and S. Plant[c]

[a] *Department of Chemical and Biological Sciences, University of Huddersfield, Huddersfield HD1 3DH, UK*
[b] *Department of Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK*
[c] *Purolite International Ltd, Cowbridge Road, Pontyclun, Wales CF72 8YL, UK*

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The acidities of a series of fully hydrated sulfonated poly(styrene-*co*-divinylbenzene) resins with varying levels of sulfonation from 0.80 to 5.25 mequiv g^{-1} have been characterized. Enthalpies of neutralization with aqueous NaOH have been measured by titration calorimetry. The degrees of acid dissociation (α) have been measured using FT-Raman spectroscopy, based on the intensity of the $-SO_3^-$ stretching band at 1033 cm^{-1}. The same measurements have been made on aqueous solutions of *p*-toluenesulfonic acid (*p*-TsOH), on the basis that these solutions are analogs of the internal solutions in the hydrated resin gels. For resins with low levels of sulfonation, and therefore relatively dilute internal acid solutions, the internal and the equivalent *p*-TsOH solutions are similar. However, significant differences are seen in highly sulfonated resins where the internal solution concentration is above 4.0 mol kg^{-1}. At these concentrations, *p*-TsOH solutions show essentially complete dissociation and enthalpies of neutralization typical of a strong, fully dissociated acid in aqueous solution. In contrast, the acid groups in hydrated resins are largely undissociated and exhibit numerically higher enthalpies of neutralization, and catalytic activity measurements indicate that these acid groups are stronger than normal. It is proposed that this acidity enhancement is associated with networks of sulfonic acid groups which form in highly sulfonated resins. Although such networks have been previously proposed in dehydrated resins, this paper reports the first evidence for their existence in resins under conditions of full hydration.

KEY WORDS: ion-exchange resin; sulfonated polystyrene; acid catalysis; FT-Raman spectroscopy; titration microcalorimetry; acid dissociation; enthalpy of neutralization.

1. Introduction

Sulfonated poly(styrene-*co*-divinylbenzene) resins in their acid form are widely used as catalysts in liquid-phase processes [1,2]. In the 1970s Gates and co-workers [3] proposed a model to explain the relatively high catalytic activities of these resins, in terms of networks of interacting sulfonic acid groups which form when water is removed (figure 1). Acid groups participating in the networks (structures II and III) are largely undissociated and exhibit increased proton donating power compared to isolated sulfonic acid groups. It is worth noting that sulfonated resins invariably retain typically 1–2% by weight of water on drying [4,5]. The proposed model takes account of this by suggesting that networks form in both the complete absence of water (structure II) and in the presence of very low levels of water (structure III).

Commercially available resins are usually sulfonated at a level equivalent to approximately one sulfonic acid group per styrene monomer unit. Nowadays, most manufacturers also supply resins in which the polymer is sulfonated above this stoichiometric level. As well as increasing the concentration of acid sites, this usually has the additional effect of increasing the activity of the individual sulfonic acid groups, resulting in an apparently disproportionate overall rise in catalytic activity [6,7]. At first sight, this seems consistent with the model described above, and the idea that network formation is facilitated as the level of sulfonation is increased. However, it emerges very clearly from published work on these highly sulfonated resins that the dependence of activity on level of sulfonation is not restricted to dry resins but is also observed in resins fully solvated with water and other swelling solvents [5–12]. This would appear to require an alternative explanation and, to date, no satisfactory model has been proposed for the behavior of fully solvated or hydrated resins. In attempts to develop an understanding, however, a number of workers have observed a link between the relative activity of the sulfonic acid groups and the concentration of the so-called "internal solution" of the acid in the swollen resin gel. The evidence suggests that the sulfonic acid strength increases as the internal solution concentration increases [9–12].

Recently, we have investigated the importance of the internal solution concentration in hydrated resins. We measured the molar enthalpy of neutralization with aqueous NaOH of fully hydrated resins with varying levels of sulfonation [8]. Since sulfonic acids generally

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* To whom correspondence should be addressed.
E-mail: d.r.brown@hud.ac.uk

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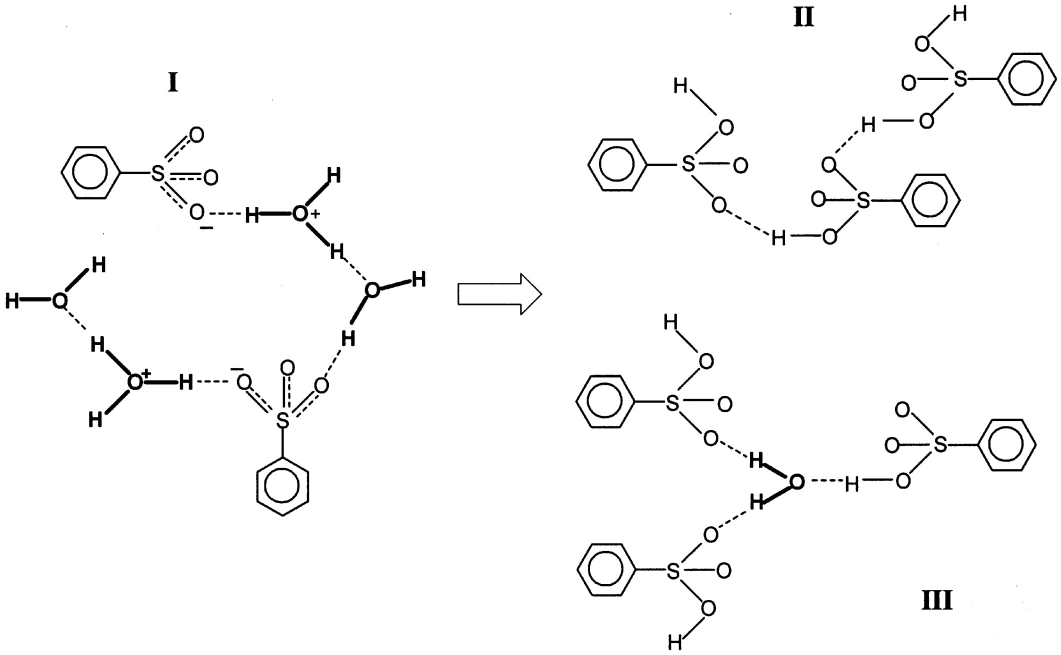


Figure 1. Proposed networks of sulfonic acid groups that form in sulfonated poly(styrene-*co*-divinylbenzene) resins as water is removed [3].

behave as strong acids in water, it seemed reasonable to expect that all the resins would exhibit the typical enthalpy of neutralization for a strong aqueous protonic acid. Resins with low levels of sulfonation, and therefore relatively dilute internal solutions, did indeed show the expected value, but, surprisingly, highly sulfonated resins showed progressively higher (exothermic) molar enthalpies of neutralization.

Changes were also seen in the FT-Raman spectra of the hydrated resins. Based on bands due to the sulfonate group and to the undissociated sulfonic acid group, the degree of dissociation of the acid group was found to decrease as the level of sulfonation was increased [13,14]. In resins sulfonated at the stoichiometric level and above, the sulfonic acid group was largely undissociated.

From this work it appeared that the undissociated form of the acid was responsible for the elevated catalytic activity of highly sulfonated resins, and that this form was dominant both in the dried and the fully hydrated resins. The most surprising aspect of this was that the sulfonic acid internal solution concentration was only 4.5–5.0 mol kg^{-1} even in the most highly sulfonated resins. The question addressed here is why the degree of acid dissociation is so low in this environment. The objective has been to establish whether it is simply the concentration of the internal solution that controls acid strength and catalytic activity, or whether other interactions in the gel matrix play a part in enhancing acidic properties. The study is based on a comparison between sulfonated poly(styrene-*co*-divinylbenzene) resins and homogeneous aqueous solutions of *p*-toluenesulfonic acid (*p*-TsOH) at concentrations equivalent to those existing in the resin internal solutions. The *p*-TsOH acid is a widely used monomeric analog of sulfonated poly(styrene-*co*-divinylbenzene) as shown in figure 2 [15].

In this work, a series of resins has been used with varying levels of sulfonation from 0.74 to 5.0 mequiv g^{-1}, corresponding to approximately 15–100% of the stoichiometric level. The hydrated resins have been compared with the aqueous solutions of *p*-TsOH in terms of enthalpies of neutralization and sulfonate bands in their FT-Raman spectra. Catalytic activities have been measured using the liquid-phase condensation

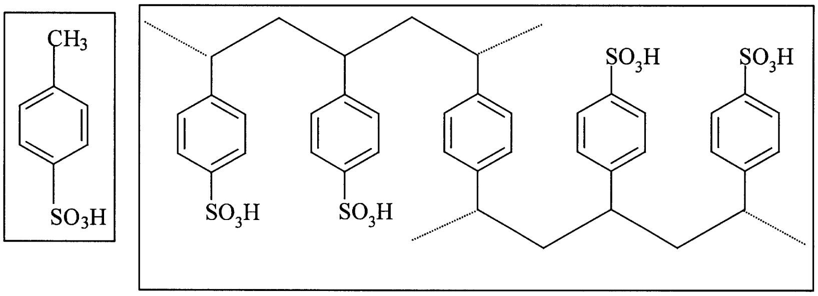
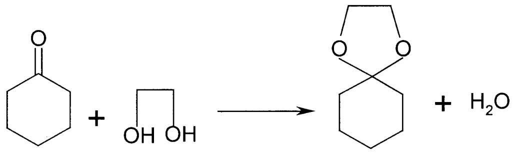


Figure 2. *p*-Toluenesulfonic acid as representative of the repeating unit in sulfonated poly(styrene-*co*-divinylbenzene).

of cyclohexanone with ethylene glycol to produce 2,2-pentamethylene-1,3-dioxolane and water in the swelling solvent 1,2-dichlorobenzene (scheme 1) [16,17].



Scheme 1.

2. Experimental

A series of gel resins was supplied by Purolite International Ltd (table 1), containing between 10% w/w divinylbenzene crosslinking agent. The resins were prepared using proprietary commercial processes, culminating in treatment with varying amounts of sulfuric acid to control levels of sulfonation. All resins were used in their H^+ forms. The sulfonic acid group concentrations were measured using a standard procedure of ion exchange with excess Na^+ followed by aqueous NaOH titration [18]. In selected cases, results were confirmed with elemental sulfur analysis. Water contents of the fully swollen resins were also determined using a standard method in which beads were dried at 100 °C for 2 h and weighed. They were then fully hydrated by immersion in water. The hydrated beads were centrifuged over glass frits to remove excess water, and re-weighed.

A sample of sulfonated linear polystyrene (soluble polymer) with a cation exchange capacity of 4.6 mequiv g^{-1} was also supplied by Purolite. Other reagents, including *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate, were used as supplied.

2.1. Aqueous titration microcalorimetry

A Setaram "Titrys" differential titration microcalorimeter was used for these experiments. In a typical experiment, 50 mg hydrated resin was suspended in 2 cm^3 water in the sample cell, with the same volume of water in the reference cell. The titrant, 0.100 mol dm^{-3} NaOH solution, was added to the sample cell in 0.20 cm^3 aliquots at one hour intervals, until neutralization was complete. Water was added to the reference cell in the same way (adding NaOH solution introduces small errors due to dilution). Titrant was delivered to both cells using a programmable twin syringe pump. The calorimeter was maintained at 30 °C and the titrant solutions were passed through pre-heating coils prior to addition to the cells, the temperature of which was set to ensure thermal equilibrium between titrant and sample/reference solutions. The heat output was measured for each addition and the cumulative heat plotted against the amount of added base. Solutions of *p*-TsOH were prepared at concentrations from approximately 0.1 to 5.0 mol kg^{-1}. Molar enthalpies of neutralization were measured in the same way as above. It was necessary to correct the measured heat outputs for the exothermic heats of dilution of the *p*-TsOH solution which were associated with the addition of the titrant to the acid solution. This was achieved in two ways and results from the two methods were used as a check on consistency. In the first method, the NaOH solution was

Table 1
Calorimetric, Raman and catalytic data for hydrated sulfonated resins, and solutions of sulfonated linear polystyrene and *p*-toluenesulfonic acid

Catalyst	Cation exchange capacity/mequiv g^{-1}	Water content/ %w/w	$-\Delta H^0_{neut}$/kJ mol^{-1} ($\pm$0.5)	Internal soln. concn./mol kg^{-1}	α/% ($\pm$10)	Initial rate/s^{-1} g^{-1} cat	Initial rate/s^{-1} mol^{-1} $-SO_3H$
Sulfonated poly(styrene-*co*-divinylbenzene) resins							
4075	0.80	26.7	53.1	2.2	100	0.20	0.24
4076	1.48	33.6	53.1	2.9	96	0.46	0.31
4074	1.98	38.5	53.4	3.2	92	0.67	0.34
4110	2.64	44.7	55.1	3.3	92	0.80	0.35
4042	3.04	47.0	55.3	3.4	96	1.1	0.37
4043	5.00	50.5	57.2	4.9	26	2.1	0.41
4044	5.11	50.7	57.2	5.0	18	3.1	0.42
C100	5.25	48.0	56.9	5.7	20		
Sulfonated linear polystyrene							
	4.6		53.7				
p-Toluenesulfonic acid (*p*-TsOH)							
			51.8	0.52	100		
			52.3	0.82	92		
			51.5	2.06	94		
			52.4	4.13	82		
			52.3	5.00	82		
HCl solution							
			52.8	0.1			

added to the acid solution in the sample cell, and water added to water in the reference cell. This was followed by measuring the heat of dilution in a separate experiment by adding water to *p*-TsOH solution in the sample cell and water to water in the reference cell. For each addition, the enthalpy of dilution was then subtracted from the enthalpy measured in the neutralization experiment. In the second method, the dilution correction was made automatically in the reference cell; NaOH solution was added to *p*-TsOH in the sample cell, and water to *p*-TsOH solution in the reference cell. Values for the molar enthalpies of neutralization calculated using the two methods were within experimental error of each other.

The molar enthalpy of neutralization for the soluble sulfonated linear polystyrene was measured in the same way, using 10 mg of polymer dissolved in 2 cm^3 of water. It was not necessary to correct this value for a dilution enthalpy.

2.2. FT-Raman spectroscopy

Raman spectra were run on fully hydrated resin beads and on the *p*-TsOH and sodium *p*-toluenesulfonate (TsONa) solutions. To allow comparison with spectra of fully dissociated sulfonates, the resins were ion exchanged with Na^+ ions, by passing 1.0 mol dm^{-3} NaCl solution repeatedly down a column of the resin beads. Aqueous solutions of TsONa were prepared at concentrations similar to those used for *p*-TsOH.

The Raman spectra were obtained using a Bruker IFS 66 infrared spectrometer with FRA 106 Raman module attachment and Nd^{3+}/YAG laser excitation in the near infrared at 1064 nm. Sampling was effected in a macroscopic mode using compacted resin beads in an aluminum sample "cup", and scattered radiation was collected from a 100 µm diameter sample "footprint". In previous work [13] we have used a dedicated Raman microscope attachment to measure spectra associated with individual beads, and we have shown that bead-to-bead homogeneity in resins of the type studied here is very high. Co-addition of sample spectra over 1000 scans, at 4 cm^{-1} spectral resolution and 200–3500 cm^{-1} shift range, was used to increase signal-to-noise ratios. Wavenumbers of spectral bands are accurate to ± 1 cm^{-1}, and band intensities are reported in arbitrary units.

2.3. Catalytic activities

Resin catalysts were dried at 120 °C for 20 h, and then allowed to solvate fully in 1,2-dichlorobenzene before use. These were found to be the optimum catalyst activation conditions. Typically, 0.55 mmol of the cyclohexanone and 0.55 mmol of ethylene glycol were dispersed in 1.5 g of 1,2-dichlorobenzene containing 16 mg (dry weight) of pre-swollen resin catalyst at 60 °C. The reaction mixture was stirred with a paddle stirrer. Samples were taken periodically and analyzed by GC, using the solvent peak as an internal standard. Reaction rate was measured in terms of peak area for the product 2,2-pentamethylene-1,3-dioxolane, and initial rates in s^{-1} are reported.

3. Results

3.1. Molar enthalpies of neutralization

A typical power vs. time output from the Titrys microcalorimeter for the neutralization of a hydrated sulfonated resin with aqueous NaOH solution is shown in figure 3. A plot of cumulative enthalpy against extent of neutralization is also shown. The average exothermic molar enthalpy of neutralization has been taken as the gradient of the straight line through the points corresponding to typically 80% neutralization, over which range linearity was invariably observed. Data collected in this way for the hydrated resins are shown in table 1.

Equivalent data for the neutralization of *p*-TsOH solutions are also given in table 1, corrected for enthalpies of dilution as indicated above. Data for the soluble sulfonated linear polystyrene are also included. It should be noted that the cation exchange capacity of the sulfonated linear polymer is close to those of the resins with the highest levels of sulfonation, and corresponds to approximately one acid group per styrene unit. It is noticeable, therefore, that the molar enthalpy of neutralization of this material at –53.7 kJ mol^{-1} is much closer to those of *p*-TsOH solutions than those of equivalent hydrated crosslinked resins such as specimens 4043 and 4044.

The water content of the fully hydrated gel resin beads is known accurately and the effective concentration of sulfonic acid groups in the internal solution can be calculated. The molar enthalpies of neutralization of the resins and the homogeneous solutions of *p*-TsOH are shown plotted against solution concentration (internal and homogeneous) in figure 4.

3.2. Raman spectra

Typical Raman spectra of a sulfonated resin in acid and Na^+ forms are shown in figure 5. The band seen in the 1020–1040 cm^{-1} region (at 1033 cm^{-1} in this case) has been observed in a number of sulfonated compounds and has been assigned to a symmetric SO_3^- stretching vibration [13,14]. Its intensity is therefore an indicator of the concentration of the dissociated form of the sulfonate group. By comparing the intensity of this band for the H^+ form of the resin with that for the Na^+ form, and assuming complete dissociation into $-SO_3^-$ for the Na^+ form, the degree of dissociation can be calculated.

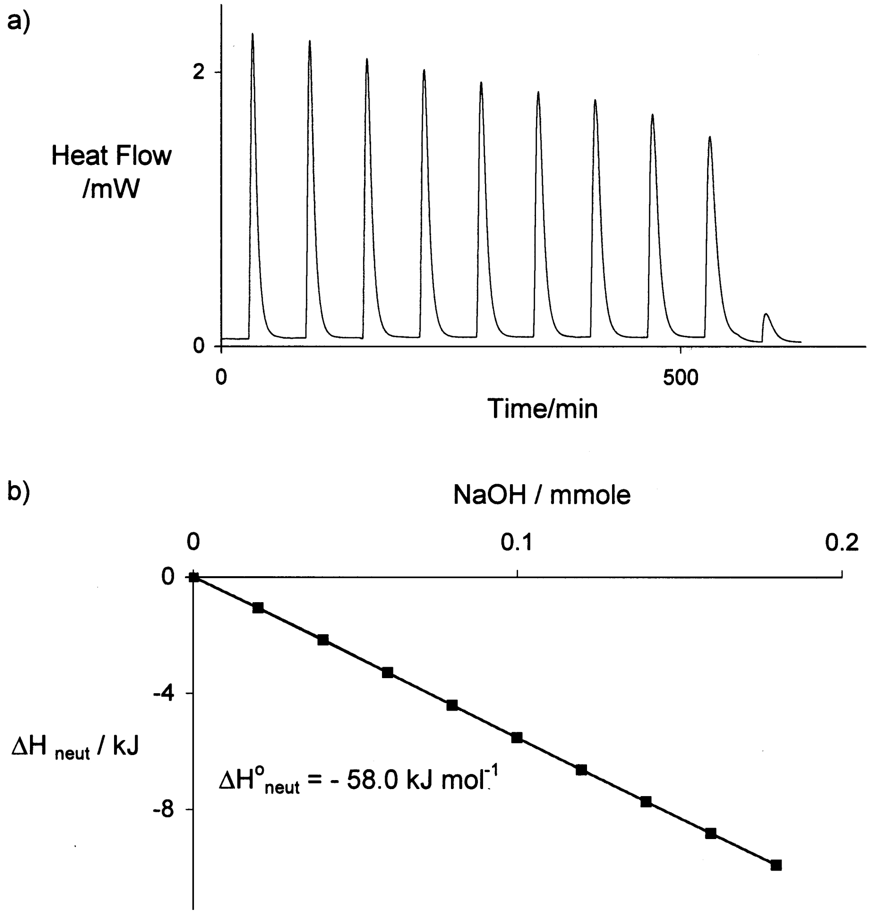


Figure 3. (a) Typical output from the Titrys differential microcalorimeter on neutralization of a hydrated sulfonated poly(styrene-*co*-divinylbenzene) resin (H^+ form) with aqueous 0.1 mol dm^{-3} NaOH solution, added in 0.2 cm^3 aliquots. (b) Derived cumulative enthalpy vs. extent of neutralization plot, showing how the molar enthalpy of neutralization is derived from the linear region of the plot.

Band intensities are normalized against the band at 1000–1010 cm^{-1} (aromatic CC stretch breathing mode) and the degree of dissociation (α) is taken as the ratio $I_{1033}(\mathrm{H^+}\ \mathrm{form})/I_{1033}(\mathrm{Na^+}\ \mathrm{form})$. Values of α (%) appear in table 1 and are plotted for both resins and *p*-TsOH against concentration in figure 6. In addition to the data for *p*-TsOH solutions in the figure, previously reported values of α for ethanesulfonic acid solutions

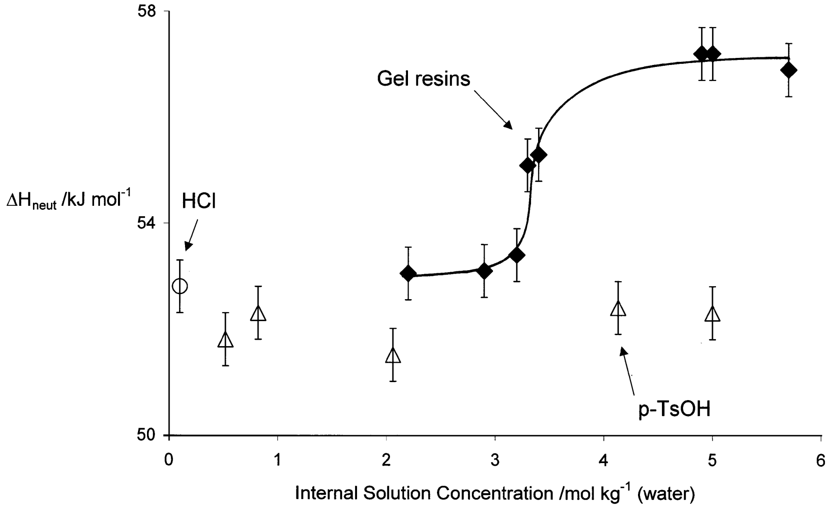


Figure 4. Dependence of the molar enthalpy of neutralization with aqueous NaOH on concentration for the internal solution in sulfonated poly(styrene-*co*-divinylbenzene) resins (◆), homogeneous aqueous solutions of *p*-TsOH (△) and a 0.1 mol kg^{-1} aqueous solution of HCl (○).

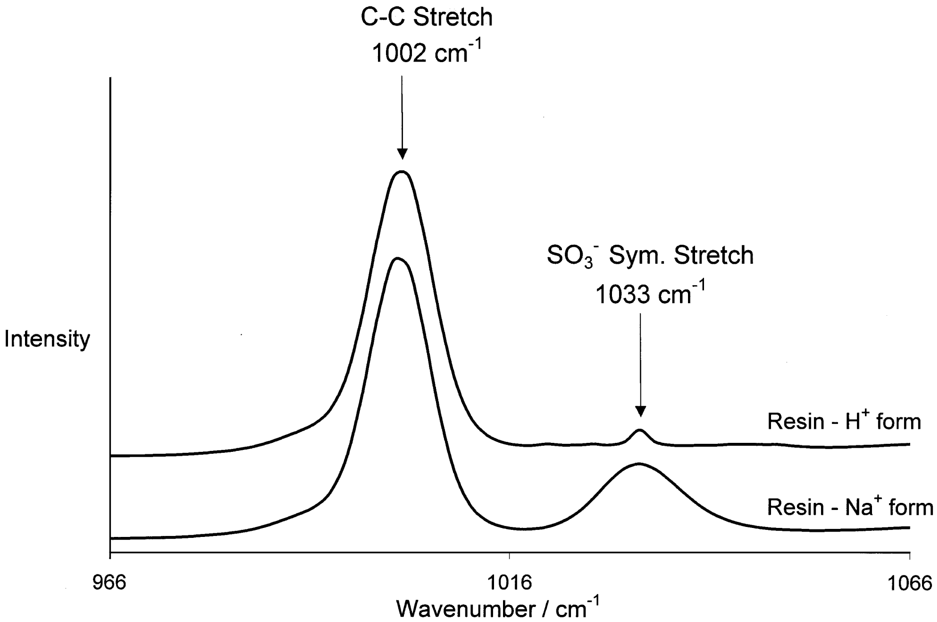


Figure 5. Part of the FT-Raman spectra of hydrated sulfonated poly(styrene-*co*-divinylbenzene) resins in the H^+ form and the Na^+ forms, showing the band associated with the $-SO_3^-$ ion.

(also obtained from the Raman spectra of the sulfonic acid groups) are shown [19].

3.3. Catalytic activities

Initial reaction rates are reported in Table 1, together with initial rates normalized for the concentration of sulfonic acid on the resin catalysts. The important observation from this data is that the activity per acid group rises progressively with the level of sulfonation across the range. This is consistent with results reported earlier [7] for resins sulfonated at levels from approximately 4.9 to 5.3 mequiv g^{-1} but, as far as we know, these results represent the first reported study of resins with levels of sulfonation extending to below 1 mequiv g^{-1}.

4. Discussion

Figure 4 shows that the *p*-toluenesulfonic acid solutions exhibit an exothermic enthalpy of neutralization typical of a strong acid in water, the same as that found for HCl, and essentially independent of concentration up to 5 mol kg^{-1}. The Raman spectra show that the acid is largely dissociated over this concentration range (figure 6). The data included for ethanesulfonic acid extend to higher concentration and this acid also remains almost fully dissociated throughout. In fact, ethanesulfonic acid is slightly weaker than *p*-toluenesulfonic acid in water (pK_a of -1.92 and -2.55 respectively) so we feel confident that *p*-TsOH would remain almost fully dissociated at concentrations higher than those examined.

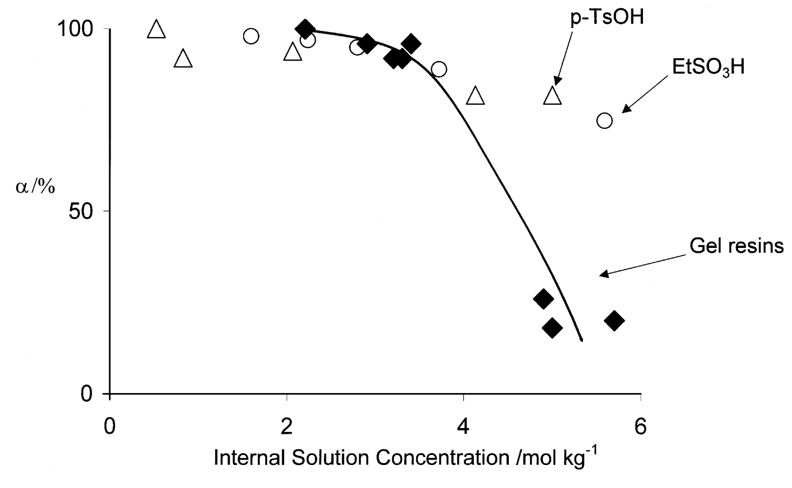


Figure 6. Dependence of the degree of dissociation of the $-SO_3H$ groups on concentration for the internal solution in sulfonated poly(styrene-*co*-divinylbenzene) resins (◆), and homogeneous aqueous solutions of *p*-TsOH (△) and ethanesulfonic acid (○).

Turning to the data for the hydrated sulfonated resins, it seems that those with low levels of sulfonation, up to approximately 1.5 mequiv g^{-1}, show behavior that is very similar to that of the equivalent homogeneous solutions of *p*-TsOH. Figure 6 shows that the sulfonic acid groups are almost fully dissociated and the enthalpies of neutralization (figure 4) are similar to those in homogeneous *p*-TsOH solution. This suggests that, in these resins for which the internal solution is relatively dilute, the sulfonic acid groups are in essentially the same environment as isolated sulfonic acid groups in a homogeneous aqueous solution. As the level of sulfonation is increased, however, the behavior deviates from that of the homogeneous solutions. For the resins, the molar enthalpy of neutralization becomes progressively more exothermic and the degree of dissociation falls dramatically. For resins with the highest level of sulfonation and an internal solution concentration of 4.5–5.0 mol kg^{-1}, the molar enthalpy of neutralization is almost -57 kJ mol^{-1}, compared to -52 kJ mol^{-1} for the equivalent solution of *p*-TsOH, and the degree of acid dissociation is only 20% or less, compared to more than 80% for *p*-TsOH.

Catalytic measurements made previously by us in excess water [7], and by others using a range of swelling solvents [9–12], together with the data in this study, show clearly that the catalytic activity of individual sulfonic acid groups increases as the level of sulfonation increases. Taking all the reported data together, it is clear that this trend is observed under virtually all reaction and solvation conditions, in the presence of both water and non-aqueous solvents.

It is clear that elevated activity is associated with the undissociated –SO_3H group. This is the dominant form of the acid group in resins sulfonated at close to the stoichiometric level, even when fully hydrated. Under these conditions the internal acid solution, which is typically 4 or 5 mol kg^{-1} in acid, is quite different to the equivalent homogeneous *p*-TsOH solution which shows behavior typical of a conventional strong aqueous acid.

The undissociated form of the acid only exists at high levels of sulfonation where the internal acid solution is relatively concentrated. Although the acidity measurements reported here all relate to hydrated resins, it is significant that disproportionate increases in catalytic activity with increasing levels of sulfonation are seen in solvents other than water, including the aprotic 1,2-dichlorobenzene studied in this work. This suggests that the presence of water may not in fact be essential to the generation of acid groups with enhanced acid strengths. The significance of this conclusion is that the idea of an internal solution may not, in fact, be as important as was previously thought in understanding the relationship between acid strength and extent of sulfonation for these systems.

Also of significance is the apparent absence, based on molar enthalpies of neutralization, of any enhancement to acid strength in the sulfonated linear polystyrene materials, when similar levels of sulfonation in the crosslinked polymer result in significantly higher acid strengths. Although not conclusive, this suggests that the nature of the polymer backbone, its structure and rigidity, are important features in conferring higher acid strengths to supported sulfonic acid groups.

In the light of the results reported here, we now offer a modified explanation for the unique behavior of sulfonic acid groups in highly sulfonated resins. We suggest that the structures II and/or III shown in figure 1 may not be restricted to dried resins as previously proposed [3], but may exist in hydrated resins, and also in resins solvated with other solvents. At high levels of sulfonation, they appear to be the dominant structures and, crucially, we now propose that their existence is largely independent of the presence of solvent. We suggest that interactions between neighboring sulfonic acid groups are the basis of enhanced acid strengths. These interactions occur only when (i) the concentration of sulfonic acid groups on the polymer is sufficiently high and (ii) the polymer support is sufficiently rigid and tightly confined to force neighboring acid groups into orientations in which interactions of this type are energetically favored over, for instance, more conventional solvation of the acid groups. Of course, these conditions are not met in fully dispersed homogeneous solutions of monomeric sulfonic acids, nor in solutions of the sulfonated linear polymer with no crosslinking where the polymer is highly flexible and the structure is spatially less restricted. The presence of crosslinking by divinylbenzene is evidently critical to ensuring that the sulfonic acid groups are brought into alignment.

Sulfonated poly(styrene-*co*-divinylbenzene) resins and *p*-TsOH have been the subjects of related studies by Arnett *et al.* using the solvent acetonitrile [15,20]. In this work, the enthalpies of neutralization were measured with a series of organic bases. They reported that the exothermic enthalpy of neutralization of the *p*-TsOH solution was almost always about 15 kJ mol^{-1} *higher* numerically than that of the sulfonated resins. This was attributed to an enhancement in the acid strength of the p-TsOH through strong hydrogen bonding stabilization of the sulfonate anion by excess sulfonic acid molecules. According to Arnett, this enhancement was not possible, or at least restricted, in sulfonated resins where the rigidity of the polymer matrix prevents the alignment of neighboring sulfonic acid groups with the sulfonate anion.

It is interesting that the trends we report here in water are the opposite to those in acetonitrile. In water the sulfonated resins are stronger acids than the monomeric arylsulfonic acids, whereas in acetonitrile the opposite appears to be true. But, importantly, the explanations for the difference in the two solvents both rely on the effect of the polymer backbone, in either directing the formation of favorable complexes (in water) or preventing their formation (in acetonitrile). The effect of the polymer matrix in controlling acid strength and therefore catalytic activity is evidently crucial, if subtle. It is clear from these results that there is the potential for additional control of catalytic properties through the careful design of polymer morphology and the nature in which they are sulfonated.

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