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Sulfonated poly(styrene-co-divinylbenzene) ion-exchange resins: acidities and catalytic activities in aqueous reactions

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Abstract

A series of sulfonated poly(styrene-co-divinylbenzene) ion-exchange resins with varying levels of sulfonation has been prepared. The acidities of these resins in the hydrated form have been characterised microcalorimetrically by titration with aqueous NaOH solution. The resultant molar enthalpies of neutralisation have been compared with acid strengths of the same resins measured in the absence of water by ammonia adsorption microcalorimetry, and catalytic activities in two test reactions, the dehydration of 1-hexanol and the hydration of propene. The molar enthalpies of neutralisation of hydrated resins with aqueous NaOH have been shown to increase with increasing sulfonation level. This has been explained in terms of an increasing concentration of sulfonic acid in the internal gel solution, generating stronger acid sites and higher specific catalytic activities. A similar trend of increasing acid strengths has been observed in anhydrous resins, but this has been explained in terms of structural features such as di-substitution of sulfonic acid groups on styrene units, giving rise to intrinsically stronger acid sites. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Sulfonated poly(styrene-co-divinylbenzene) resins are widely used as acid catalysts in liquid phase reactions. They are generally supplied in the form of polymer beads of diameters between 0.3 and 1.0 mm. They do not exhibit a catalytically active surface in the conventional sense; their activity is dependent on reactants diffusing into the solvated-polymer gel to access acid sites. In this respect, their behaviour can be described as a combination of conventional heterogeneous and homogeneous catalysts. They offer advantages over many inorganic solid acids in terms of ease of handling, structural uniformity and high abundance of acid sites [1,2]. They are, however, limited in application because of their intolerance to temperatures greater than 140–150 °C, and their acid sites are generally weaker than those found on zeolitic and similar solid acid catalysts [3].

Most commercially available sulfonated polystyrene ion-exchange resins (IERs) are sulfonated at a level equivalent to approximately one acid group per styrene or divinylbenzene (DVB) monomer unit (stoichiometric sulfonation). In recent work, we have studied IERs with both lower and higher levels of sulfonation [4,5]. We measured the concentrations and strengths of acid sites on these resins by microcalorimetric studies of ammonia adsorption at 100 °C. The results showed that the average acid site strengths (in terms of molar enthalpies of ammonia adsorption)

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increase as the level of sulfonation is increased, and those with greater than stoichiometric levels of sulfonation ("persulfonated" resins) exhibit significantly stronger sites than conventional, stoichiometrically sulfonated resins.

We compared these measured acid strengths for conventional and persulfonated resins with their catalytic activities in both the hydration of propene and the dehydration of 1-hexanol. We found that the specific activities (per acid site) of persulfonated resins were very much higher than those of conventional resins, in line with the differences in acid strengths [5].

The surprising aspect of this correlation is that the acid strengths measured by ammonia adsorption were associated with dehydrated resins (probably containing not more than 1% (w/w) water [6,7]) and yet the catalytic activities were measured for resins in an aqueous reaction medium, in which the resins would be hydrated. Typically resins of the type studied contain 50% (w/w) water when fully hydrated and the sulfonic acid groups are assumed to be fully hydrated in the gel region of the resin bead. Under these conditions, the water might be expected to have a levelling effect on the strength of the acid groups. In principle, therefore, differences in acid strength seen in dehydrated resins might be expected to disappear once water is introduced to the system. The objective of the work reported here has been to study differences in acid strength for resins containing varying levels of sulfonation, in the presence of water, in an attempt to explain the differences in catalytic activity seen in this series of resins in aqueous media.

2. Experimental

2.1. Sulfonated poly(styrene-co-divinylbenzene) resin catalysts

The following macroporous resins were provided by Purolite International:

(a) two specially prepared resins with less than the stoichiometric levels of sulfonation (D4034 and SP21-51);
(b) CT-175, a standard, normally sulfonated material and Amberlyst 15 (Rohm and Haas) with which it is roughly analogous. Both are sulfonated at a level equivalent to approximately one sulfonic acid group per styrene or DVB monomer unit (stoichiometric sulfonation);
(c) two persulfonated resins, based on CT175, but with higher levels of sulfonation (CT-275 and CT-375).

A series of gel-type resins with varying levels of sulfonation was also studied, provided by Purolite International. These differ from the macroporous resins in that they exhibit no permanent porosity. Some were prepared with 4% (w/w) DVB cross-linking agent in the polymer support, and some with 10% DVB. The former swell more than the latter and have higher water contents under full hydration.

All resins were used in their H^+ forms. The sulfonic acid group concentrations were measured by Purolite International, using a standard procedure of ion-exchange with Na^+ followed by the aqueous titration with standard NaOH solution [8]. Water contents of the fully swollen resins were also determined by Purolite International.

2.2. Base adsorption/titration microcalorimetry

Ammonia adsorption by dry resins. A Setaram C80 differential microcalorimeter coupled to an evacuable glass gas-handling system was used to monitor ammonia adsorption and associated enthalpies of adsorption. Measurements were made only on the macroporous series of resins because, in the dehydrated state, the gel resins adsorb very little ammonia and meaningful comparisons from enthalpies of adsorption are difficult to make. Resin samples (150 mg dry weight) were conditioned in the calorimeter at 100 °C under vacuum for 2 h, with an empty reference cell. Successive pulses of ammonia (ca. 0.06 mmol) were introduced to the sample at 100 °C. The amount of ammonia adsorbed was measured for each pulse using the recorded pressure of ammonia (typically ca. 25 Torr) in the dosing volume (ca. 40 cm^3) before exposure, and the pressure in the combined cells/dosing volume (ca. 75 cm^3) on reaching equilibrium. Enthalpy changes associated with each dose were converted to molar enthalpies of adsorption and expressed as functions of resin coverage. Further details of the technique have been reported previously [5].

Aqueous titration microcalorimetry. A Setaram "Titrys" microcalorimeter was used for these experiments. This instrument is based on the C80 microcalorimeter as described above, with modifications to allow continuous stirring of liquid samples. The titrant is added to both sample and reference cells simultaneously using a programmable twin syringe pump. The solution is passed through preheating coils prior to addition to the cells, the temperature of which is set to ensure thermal equilibrium between titrant and sample/reference solutions.

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. Experiments were performed at 30 °C. The titrant, 0.100 mol dm^{-3} standard NaOH solution, was added to the sample cell in 0.20 cm^3 aliquots at 1 h intervals, until neutralisation was complete. Water was added to the reference cell in the same way (adding NaOH solution introduces small errors due to dilution in the reference cell). The heat output was measured for each addition and the cumulative heat plotted against amount of added base. The gradient (which was essentially constant up to complete neutralisation in all the cases) was calculated and is reported as the molar enthalpy of neutralisation in kJ mol^{-1}. Molar enthalpies of neutralisation were also measured for 0.10 mol dm^{-3} HCl solution and 0.50 mol dm^{-3} *p*-toluenesulfonic acid (*p*-TsOH) solution.

2.3. Catalytic activities

Catalytic measurements were only made on four of the macroporous resins, as reported previously [5]. Propene hydration was carried out in batch mode in a pressure vessel (maximum pressure typically 300 bar) at 140 °C, using an excess of water. Reaction progress was monitored using the pressure in the reaction vessel. Dehydration of 1-hexanol was carried out in a trickle bed flow reactor, also at 140 °C, but at atmospheric pressure. Conversion was measured by GC analysis of the products. Details of these methods appear in a previous paper [5].

3. Results

3.1. Resin acidities

Ammonia adsorption on dehydrated resins. Plots showing the molar enthalpies of ammonia adsorption at 100 °C as a function of acid site coverages for the six dehydrated macroporous resins are shown in Fig. 1.

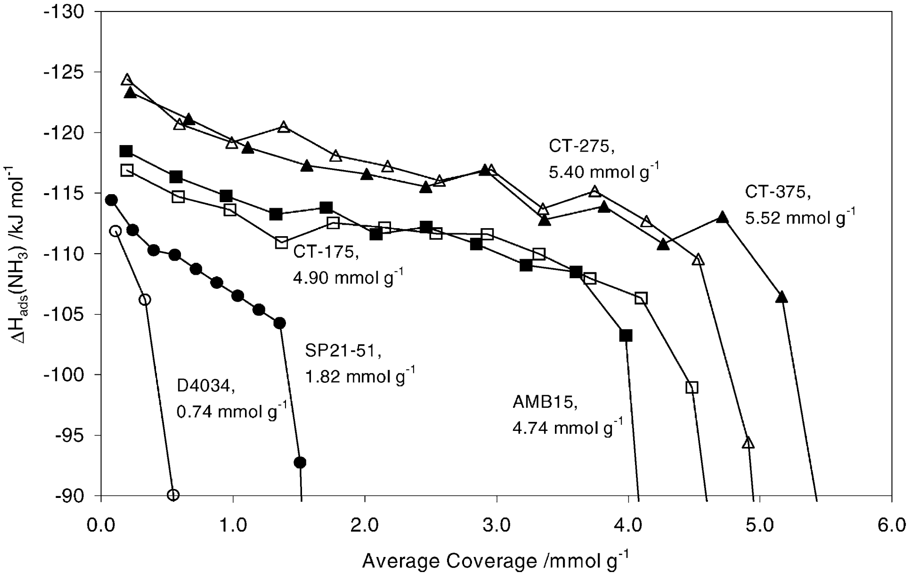

Fig. 1. Molar enthalpies of adsorption of ammonia (100 °C) with coverage for macroporous resins CT-275, CT-375, Amberlyst 15, CT-175, D4034 and SP21-51. Sulfonic acid concentrations are shown for each resin.

Table 1
Macroporous sulfonated poly(styrene-co-divinylbenzene) ion-exchange resins: water contents, sulfonic acid levels, acid strengths in terms of molar enthalpies of neutralisation by (a) ammonia adsorption (dry resins) and (b) titration with aqueous 0.100 mol dm^{-3} NaOH solution, and specific catalytic activities

Macroporous resin	Moisture (%, w/w)	[–SO_3H] (mmol g^{-1}) (dry weight)	ΔH_{ads} (NH_3) (kJ mol^{-1}) (±1)	ΔH_{neut} (NaOH) (kJ mol^{-1}) (±0.5)	Rate (a) (h^{-1}) (1-hexanol dehydration)	Rate (b) (h^{-1}) (propene hydration)
D4034	47.5	0.74	−105.4	−52.2	–	–
SP21-51	51.9	1.82	−110.3	−54.6	–	–
AMB15	52.5	4.74	−112.7	−58.3	0.49	2.7
CT-175	55.0	4.90	−114.2	−58.6	0.52	2.7
CT-275	56.6	5.40	−119.2	−61.2	1.40	5.7
CT-375	53.0	5.56	−117.6	−60.9	–	5.6
HCl (0.1M)				−52.8		
p-TsOH (0.5 M)				−52.4		

Note that, in each case, the profile falls abruptly at a coverage close to the sulfonic acid content of the resin, showing that the interaction with ammonia is essentially stoichiometric. The persulfonated resins exhibit higher (numerical) enthalpies of adsorption than the stoichiometric resins which, in turn, show higher values than the resins with reduced levels of sulfonation. For comparative purposes, it is convenient to plot the cumulative enthalpies against coverages and determine mean gradients up to saturation coverage. This gives average molar enthalpies of ammonia adsorption for each catalyst and these are shown in Table 1.

Aqueous NaOH titrations. A typical microcalorimeter output is shown in Fig. 2 for an aqueous NaOH titration of one of the resins. The molar enthalpy of neutralisation calculated for each addition of NaOH solution is essentially constant throughout the neutralisation and a plot of total heat against added NaOH gives a straight line to the point of complete neutralisation. A precise single value for the molar enthalpy of

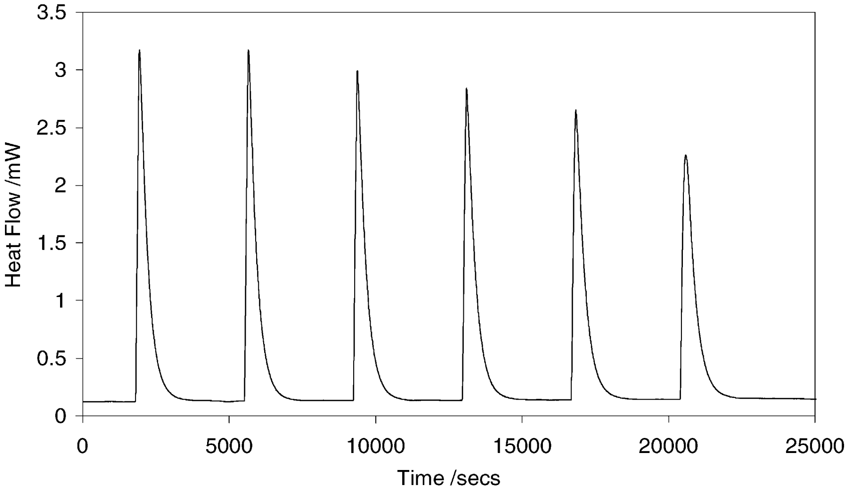

Fig. 2. A typical output from the Titrys microcalorimeter, in which a sample of fully hydrated sulfonated IER is being titrated with 0.100 mol dm^{-3} aqueous NaOH solution. Titrant is added in 0.2 cm^3 pulses at 1 h intervals.

Table 2
Gel-type sulfonated poly(styrene-co-divinylbenzene) ion-exchange resins, with 4 and 10% DVB cross-linking agent: water contents, sulfonic acid levels and acid strengths in terms of molar enthalpies of neutralisation by aqueous 0.100 mol dm^{-3} NaOH solution

Gel resin	Moisture (%, w/w)	[–SO_3H] (mmol g^{-1}) (dry weight)	ΔH_{neut} (NaOH) (kJ mol^{-1}) (±0.5)
4% DVB			
D4072	39.1	1.31	−53.4
D4073	56.0	2.61	−54.4
D4079	62.2	3.45	−54.7
D4078	64.1	5.04	−55.8
10% DVB			
D4075	26.7	0.80	−50.6
D4076	33.6	1.48	−53.1
D4074	38.5	1.98	−53.4
D4110	44.7	2.64	−55.1
D4042	47.0	3.04	−55.3
D4043	50.5	5.00	−57.2
D4044	50.7	5.11	−57.1
HCl (0.1 M)			−52.8
p-TsOH (0.5 M)			−52.4

neutralisation for each resin can therefore be obtained and are shown in Tables 1 and 2. Also shown are the molar enthalpies of neutralisation for 0.10 mol dm^{-3} HCl and 0.50 mol dm^{-3} TsOH solutions. The second of these acids, TsOH, is a close monomeric analogue of the polymeric sulfonated polystyrene.

3.2. Catalytic activities

The specific rate constants, corrected for differences in concentrations of acid sites on the resin catalysts, are shown for both propene hydration and 1-hexanol dehydration in Table 1 [5]. In both reactions, the activities of the persulfonated resins are very much higher than those of the stoichiometrically sulfonated resins. In the case of the propene hydration reaction, there is little doubt that the resins would be fully hydrated throughout the reaction. In the second reaction, the dehydration of 1-hexanol, water is generated as a product within the beads so that the resins would be at least partially hydrated, but it is possible that the resins were not in a *fully* hydrated state throughout the reaction. However, there is consistency between the two reactions in terms of the way rates vary with catalyst, so we do not believe that this affects the overall conclusions about the behaviour of the catalysts in the presence of water.

4. Discussion

It can be seen from both the tables that, for dehydrated resins, the average strength of the sulfonic acid groups, measured as the enthalpy of ammonia adsorption, increases as the level of sulfonation increases. In our previous work, we have suggested that this increase in strength is linked to structural features which enhance the acid strength of the sulfonic acid groups such as di-sulfonated phenyl groups [5], through-space interactions between neighbouring sulfonic acid groups [9], and sulfone bridges between neighbouring phenyl groups [10], all of which would be more abundant at high levels of sulfonation.

Although these structural features would certainly increase the *intrinsic* acid strength of supported sulfonic acid groups under anhydrous conditions, the presence of (bulk) water would be expected to change the acid behaviour. When the resin is hydrated, the sulfonic acid can be thought of as an internal solution within the gel bead. Because alkyl and aryl sulfonic acids are mostly strong acids in aqueous solution, it might be thought that the presence of water would level the acid strengths of all the sulfonated resins studied here to that of the hydronium ion. However, based on the molar enthalpies of neutralisation with NaOH, which are generally different from those of dilute HCl

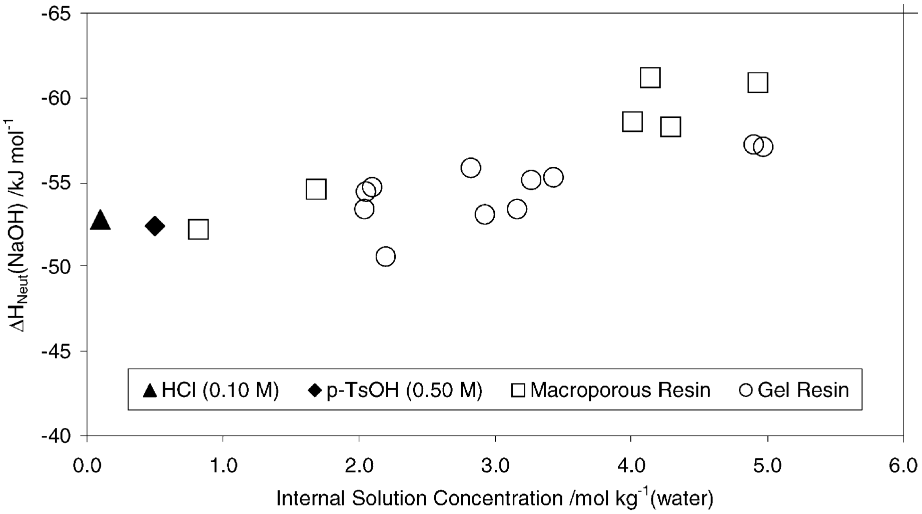

Fig. 3. The molar enthalpy of neutralisation by aqueous 0.100 mol dm^{-3} NaOH solution for a range of macroporous and gel-type sulfonated resins plotted against the effective sulfonic acid concentration in the internal gel solution. Data for dilute HCl and p-$CH_3C_6H_4SO_3H$ solutions are also shown for comparison.

and TsOH solutions, this does not appear to be the case. This may be because there is a fundamental difference between sulfonic acid groups in the internal gel solution and sulfonic acids in dilute homogeneous solution, or it may simply be a consequence of the high concentration of sulfonic acid in the internal solution.

To examine these possibilities, we have calculated the concentrations of the internal solutions in the resins studied here, using the water contents of the hydrated resins and the sulfonic acid contents. In Fig. 3, the molar enthalpies of neutralisation by aqueous NaOH are plotted against the effective internal solution concentration. Note that this calculation of internal solution concentration is based on the assumption that all the water in the resin is in the gel region. This is a good assumption for gel-type resins but not necessarily valid for macroporous resins where some of the measured water may be held outside the gel in the macropores. This may result in under-estimation of the internal solution concentration for macroporous resins, and may be responsible for the points for these resins lying slightly above those for the gel resins in the graph as drawn.

The molar enthalpies of neutralisation of the IERs are higher than for the dilute aqueous strong acid solutions, but fall as the level of sulfonation falls (and the internal solution becomes more dilute). The homogeneous acid solution values are also shown in Fig. 3 (at low concentration), and it seems that the data for the resins and for the dilute TsOH and HCl solutions would fit reasonably well on a single trend line linking the enthalpies of neutralisation to concentration. It therefore seems likely that the variation in enthalpy of neutralisation with level of sulfonation can be satisfactorily explained in terms of the varying concentration of the internal solution of the gel.

Further evidence showing the influence of internal solution concentration on the acid strength of sulfonic acid groups has been provided by a recent FT–Raman study of the same series of resins, in which we have identified vibrational S–O bands associated with both protonated and “free” sulfonate groups [11]. This spectroscopic work on fully hydrated resins has shown that the degree of dissociation of the sulfonic acid groups decreases as the level of sulfonation (and hence internal solution concentration) increases.

These results are consistent with a body of work by others in which the link between the concentration of the internal gel solution and acid catalytic activity has been investigated, in each case by examining the effect of IER water content on catalytic activity [12–15]. In all these studies, catalytic activity has been found to increase as the water content is reduced.

These combined results give a consistent model for the acid catalytic behaviour of hydrated sulfonated resins. As the level of resin sulfonation is increased, the concentration of sulfonic acid groups in the internal solution also increases. This leads to a reduced degree of acid dissociation, an increase in the strength of the supported-sulfonic acid groups, and an increased molar enthalpy of neutralisation with hydroxide ion. This in turn increases the catalytic activity of the resin.

5. Conclusions

The acid catalytic activity of sulfonated polystyrene ion-exchange resins shows a pronounced dependence on the degree to which the polymer is sulfonated. This is, in part, due to the increased concentration of acid sites, but a more significant factor is that the acid strength also increases with level of sulfonation. When the resins are used as anhydrous catalysts (as far as they can be), this increased acid strength is a direct result of structural features such as the degree of di-substitution, the presence of sulfone bridges and interactions between neighbouring groups. In the presence of water, the enhanced-acid strength is due mainly to the increased acid concentration in the internal gel solution, driving the acid groups towards the associated state which is evidently stronger than the hydronium ion which predominates in dilute solution.

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