Preparation and Characterization of a Modified Ion-Exchange Resin

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A modified cationic-exchange resin by use of the conventional monomers was prepared and characterized. This resin consisted of relatively large particles (2–3 mm diameter) sulfonated only on an outside surface layer. The composite structure of the particles was demonstrated both by microscopic examination and by analysis of the sulfonation process. The active portion of the resin was highly porous and exhibited enhanced diffusion of low-molecular-weight species when compared with commercial resins of the same nominal extent of crosslinking.

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Commercially available styrene based ion-exchange resins are not prepared in sizes larger than about 1 mm diameter. During the course of a research project at this laboratory, it became necessary to prepare small quantities of cation-exchange resin particles from the conventional monomers which are considerably larger than commercially available resins and which have fixed ionogenic groups (—SO_3H) only on an outside surface layer. This paper relates a description of the preparative technique and discusses the chemical and physical properties of the modified resin.

The preparation of conventional microreticular ion-exchange resin beads ranging in diameter from 10μ to 1 mm has been described by numerous authors (Hohenstein and Mark, 1946; Pepper et al. 1952; Boyer, 1950; Helfferich, 1962; Wheaton and Harrington, 1952). The procedure generally involves the suspension polymerization at elevated temperatures of a suitable mixture of a monovinyl monomer and polyvinyl crosslinking agent with a small amount of a free radical catalyst to form small spherical beads. Commercial resins use styrene and divinylbenzene monomers. If the polymerized beads are preswollen in a suitable solvent prior to sulfonation, the stability of the final resin is greatly enhanced (Boyer, 1950; Wheaton and Harrington, 1952). The sulfonation generally can be carried out with any suitable acid in a suitable solvent or various sulfur trioxide complexes (Roth, 1957). After sulfonation, it is desirable to gradually decrease the ionic strength of the external solution.

When this technique was used in an attempt to prepare large fractionally sulfonated resins, it failed for two reasons:

- By suspension polymerization, it was not possible to prepare a significant fraction of the resin particles in spherical form and with diameters larger than 1 mm.
- Conventional polymerization techniques starting with the unreacted monomers and conventional sulfonation techniques by use of concentrated sulfuric acid yielded fractionally sulfonated resins unstable under end use conditions. The ultimate swelling of the particles to the final water swollen state caused the sulfonated portion of the particles to crack, chip, and decrepitate.

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Several modifications of the standard technique were necessary to prepare large particles (3 mm) in the fractionally sulfonated state. These modifications include:

- The preparation of a special prepolymer mixture consisting not only of the monomers but also of approximately 16 wt % pure linear molding grade polystyrene, following the technique of Abrams (1957)
- The development of a simple technique for extruding the prepolymer mixture into a density adjusted, highly viscous suspending medium so that drops of virtually any size can be formed
- The leaching out of this linear polystyrene after polymerization to form a porous matrix before sulfonation
- The use of dilute chlorosulfonic acid at room temperature as the sulfonating agent

Experimental

Preparative Technique. Approximately 16 wt % pure linear molding grade polystyrene (Union Carbide, Bakelite Styrene) was dissolved in the styrene monomer from which the inhibitor, *p-tert*-butyl catechol, had been removed by washing with 0.1*M* NaOH. Added were 8% inhibitor free divinylbenzene (based on the crosslinkable fraction excluding the linear polystyrene) and 1% benzoyl peroxide to make up the prepolymer mixture.

The chemical assays and prepolymer recipe are given in Table I. This mixture was placed in a polyethylene bottle to which 49–20 gage, 6-in. lengths of hyperdermic tubing had been placed on a 1 cm square lattice (Figure 1). By applying slight nitrogen pressure above the liquid, the prepolymer mixture could be forced slowly through the tubes. Because of the precision bore and equal length of each tube, nearly identical flows were obtained from each tube. The prepolymer mixture was forced into a solution of 2% methyl cellulose [Dow, Methocel 60HG (4000 cp at 25°C)] in a mixture of water and methyl alcohol which had the same density as the prepolymer mixture. By moving the flask of methyl cellulose solution up and down on a laboratory jack, the globules of prepolymer could be sheared from the ends of the tubing when they reached the desired size.

Because the globules and the dispersing medium were density equilibrated, there was no movement of the globules

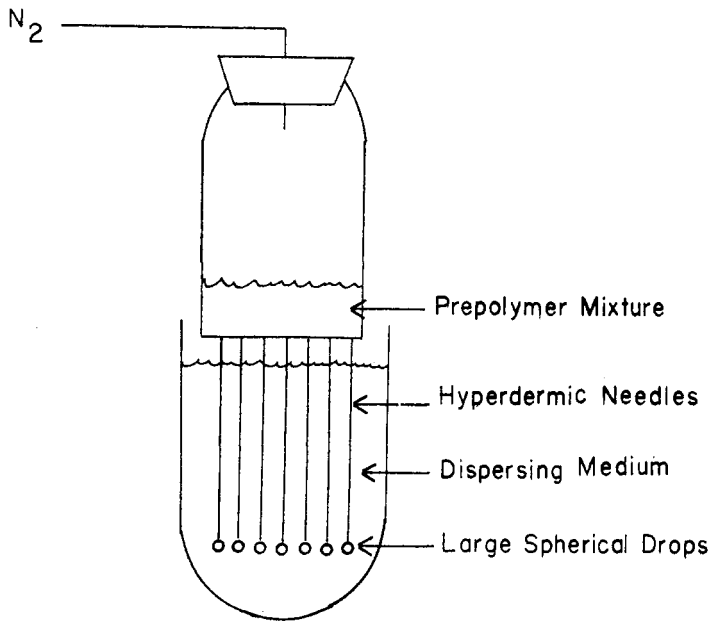

Figure 1. Apparatus for large particle polymerization technique

Table I. Chemical Assays and Prepolymer Mixture Recipe

Chemical assays

Styrene	10 ppm	*p-tert*-Butyl catechol
Divinyl benzene	0.1%	*p-tert*-Butyl catechol
	56.3%	Divinyl benzene
	38.4%	Ethylvinyl benzene
	3.5%	Dimethyl benzene
	1.7%	Unknown

Recipe for prepolymer mixture

	Wt %
Polystyrene	16.3
Divinyl benzene	13.9
Styrene	68.6
Benzoyl peroxide	1.2

during this preparation stage. Furthermore, no coalescence of the globules occurred, even when two globules were forced toward one another, because of the stabilizing influence of high-viscosity continuous-phase film. After the batch had been completely dispersed, the flask was heated to 80°C without stirring; during polymerization the density of the polymer spheres increased from about 0.91 g/cc to 1.06 g/cc. This density increase caused the spheres to settle slowly to the bottom of the flask; however, no agglomeration occurred. The settling facilitated removal of the beads from the methyl cellulose solution after polymerization had proceeded to completion (8–10 hr). The beads were washed with water to remove the suspending medium, oven dried, sieved, and swollen in toluene. After complete swelling, the beads were removed from the solvent and dried.

When the solvent was evaporated, the weight of the residual film corresponded closely to the weight of polystyrene originally added, strongly suggesting that no chain links were formed with the polystyrene added to the prepolymer mix and that it was completely dissolved from the beads, leaving a porous matrix for sulfonation. A 5*M* excess of 3% chlorosulfonic acid in ethylene dichloride at room temperature was used to yield sulfonated resins of good stability. The sulfonation time was precisely controlled to give variable capacity resins. Following sulfonation the resin particles were washed with an excess of ethylene dichloride to remove residual chlorosulfonic acid. Methanol was gradually added to the resin until the beads were in pure methanol solvent. This resin was then placed into a column and conditioned by cyclical exchange several times with 0.5*M* NaCl and 5% HCl.

Resin Characterization. Several resin physical properties were measured experimentally. The techniques which were used are summarized briefly below.

Visible Characterization. A statistical number of particles were examined under the microscope at 23.7×, 100× and 200×. The particles were examined for size, appearance of the interfacial region between the sulfonated shell and unsulfonated core within the particle, and thickness of the sulfonated outer shell.

Capacity. The experimental resin capacities were determined by passing 0.5*M* NaCl solution through a bed of resin which had been converted to the H^+ form with excess concentrated HCl and washed with an excess of deionized water to remove all traces of residual acid as determined by pH. The effluent from the bed was collected until the pH rose to 5.0 (Topp and Pepper, 1949). This effluent was titrated with 0.02*M* NaOH with a phenol red (end point pH = 6.8–8.4) indicator. The resin capacity was calculated by dividing the milliequivalents of titrated acid by the dry weight of the resin obtained by converting the resin back to the H^+ form and by drying the resin at 90–100°C and 750 mm Hg vacuum for at least 24 hr.

Resin Density and Porosity. The dry resin density was obtained pynometrically for a completely sulfonated and an unsulfonated (but preswollen) resin. The sulfonated resin density was obtained by displacing *n*-hexane, which is sorbed negligibly by the sulfonated resin. The unsulfonated resin density was obtained by displacing water. The wet resin density and porosity were obtained by using the well-documented centrifugation technique (Gregor et al., 1951, 1955; Pepper et al., 1952) for several liquids. The results (tabulated

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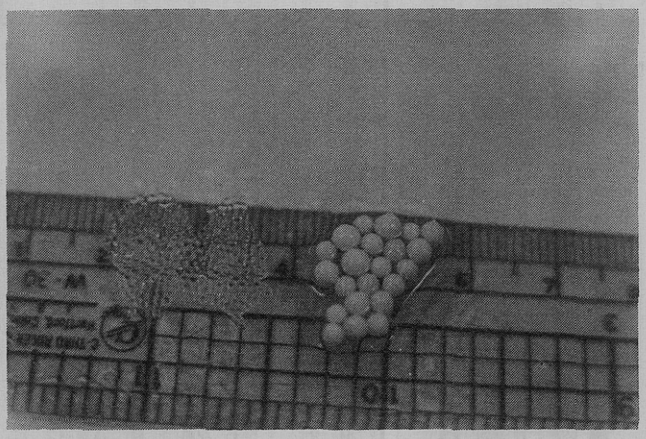

Figure 2. Comparison of DOWEX 50WX8, 20–50 mesh with resin prepared in this study (magnification = 1.17×)

Figure 3. Cut particle with core removed (13.5 hr sulfonation; magnification = 15.5×)

in Table II) were not corrected for the residual liquid film on the outside of the particles which has been estimated (Pepper et al., 1952) to amount to about a 4% error in the specific wet weight.

In the analysis of physical and transport properties of the resin, the sulfonated portion of the particles has been assumed to be a two-phase system—a three-dimensional network of polymer chains to which anionic groups are chemically bound, swollen by a liquid which constitutes an internal continuous liquid phase. The unsulfonated portion of the resin has also been assumed to be a porous solid. The porosities were computed by assuming the liquid density to be the same inside the resin as in the external solution and by assuming all the liquid to be free.

Experimental data for water indicate this assumption to be reasonably accurate except at low solvent uptakes (Myers and Boyd, 1956). The volume occupied by the wet resin used in the computation of the wet resin density and porosity was determined by measuring the volume displaced by the wet resin. The measurement of this volume was obtained by placing the centrifuged resin in a graduate cylinder; the volume of the swelling liquid which was required to fill the graduate cylinder to a particular level was measured via a calibrated burette. Consequently, the wet resin densities were computed as

$$\bar{\rho} = \frac{\text{Wet resin weight}}{\text{Wet resin volume}}$$

and the porosities were computed as

$$\nu = \frac{\text{Weight of liquid sorbed by resin/liquid density}}{\text{Wet resin volume}}$$

Diffusivity of Acetic Acid. The effective diffusivity of acetic acid diffusing through water within the partially sulfonated ion-exchange resin in the H^+ form was measured by a simple technique which utilizes the measurement of the desorption of acetic acid from the resin into a well-stirred solution of finite volume. By measuring the change in solution concentration via titration of the acetic acid with NaOH by using thymol blue indicator (end point 8.0–9.6) as a function of time, the diffusivity can be calculated. The resin particles were first equilibrated with an essentially infinite volume of 0.12*M* aqueous acetic acid. The resin was centrifuged on a porous disc to remove the external solution, thermally equilibrated with the liquid into which it was to be added, and then added to the well-stirred solution to start the diffusion experiment. Diffusivities were determined at 0°, 25.6° and 62.0°C.

The distribution coefficient of acetic acid at 25°C was also determined by eluting a bed of resin which had been equilibrated with 0.12*M* aqueous acetic acid and centrifuged to remove the external solution. The distribution ceofficient based on a heterogeneous model of the resin defined as

$$\lambda = \frac{C_R}{C_s} \tag{1}$$

where

C_R = concentration of acetic acid within the pore liquid of the resin

C_s = concentration of acetic acid in solution

$\lambda = 0.949$

It has been assumed that this distribution coefficient is independent of concentration. Indeed, Reichenberg and Wall (1956) found that acetic acid was salted out of Dowex resin, and the distribution coefficient was fairly independent of concentration between 0.5 and 2.0*M*, in agreement with the aforementioned result and assumption.

Table II. Resin Density and Porosity

Solvent	Density $\bar{\rho}_s$, g/cc	Density $\bar{\rho}_u$, g/cc	Specific wet wt ϕ_s	Specific wet wt ϕ_u	Porosity ν_s	Porosity ν_u
Dry	1.295	0.852	...	...	...	...
Methanol	1.079	...	1.860	1.179	0.636	0.184
Acetic acid	1.280	0.968	1.734	1.483	0.515	0.299
Water	1.176	0.852	2.262	1.088	0.657	0.069
Methyl acetate	1.257	...	1.567	1.708	0.504	0.453

Discussion of Results

General Resin Characteristics. Figure 2 shows a comparative photograph of the large particles prepared in this study and of the largest commercially available Dowex 50WX8 resin (20–50 mesh). Note not only the difference in size but also the difference in optical properties. The Dowex resin is nearly transparent whereas the resin of this study is opaque. The opacity is a result of a phase separation of the uncrosslinked polystyrene from the matrix copolymer during the course of the polymerization. The ultimate leaching of this uncrosslinked polystyrene from the crosslinked matrix leaves behind a porous particle with an average macropore size approaching the wavelength of light. Figure 3 shows a photo-

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Table III. Particle and Sulfonated Shell Sizes Microscopic Examination

Resin batch	dp,[a] mm	σ,[b] mm	n[c]	(1 − Ψ)[d] Shell	σ	n	Calcd from sieve fractions dp, mm	(1 − Ψ)
1	2.566	0.244	24	0.289	0.036	7	2.697	0.2335
2	2.733	0.242	20	...	...	..	2.751	0.2801
3	2.765	0.227	25	0.326	0.066	9	2.733	0.2644
4	2.868	0.203	27	0.490	0.060	12	2.924	0.4554
5	2.257	0.125	20	...	...	..	2.238	0.6135

[a] dp = particle diameter. [b] σ = standard deviation. [c] n = number of observations. [d] Ψ = core diameter/particle diameter.

micrograph of a single dry particle (15.5×) after the inert central core had been removed. This photograph shows quite explicitly the composite structure of these resins. By controlling sulfonation times, the thickness of the outer shell can be precisely controlled.

The resin was physically quite stable in the fully sulfonated state independent of the size of the particles. Large fractionally sulfonated resin particles were also reasonably stable so long as the ratio of the core diameter to the particle diameter did not increase significantly above 80%.

Particle Size and Shell Thickness. Table III summarizes the results of the microscopic examination of the particles from four different resin batches in the water swollen state. Besides the overall particle diameter, the thickness of the shell region was also measured by cutting the particles in half with a razor blade. Because the cutting action caused some splitting of the core region from the shell region, it was not possible to measure the shell thickness with the same precision as the particle diameter. Since the capacities of these resins were also measured, it is possible to make an independent estimate of the shell thickness from the fractional capacity of the resin by assuming all of the fixed ionogenic groups to lie in the outer shell. Assuming no volume change of the particles during sulfonation, the fractional capacity of the resin is related to the volume fraction sulfonated by

$$q_f = \frac{f_s}{f_s + (1 - f_s)\ \bar{\rho}_u/\bar{\rho}_s} \tag{2}$$

where

q_f = fractional resin capacity (experimentally measured capacity as meq H^+/g dry resin divided by the capacity of the fully sulfonated resin as meg H^+/g dry resin)
f_s = volume fraction of resin sulfonated in dry state
$\bar{\rho}_u$ = density of toluene preswollen dry unsulfonated resin
$\bar{\rho}_s$ = density of dry sulfonated resin

The radius of the unsulfonated core can now be calculated as

$$r_1/R_1 = \sqrt[3]{1 - f_s} \tag{3}$$

where

r_1 = radius of unsulfonated resin core in dry state
R_1 = radius of particle in dry state

Before the shell thickness can be computed in the water swollen state, account must be made of the swelling of the resin particle in water. The swelling of the unsulfonated core can be expressed as

Table IV. Fractional Sulfonation Results

Particle radius, mm	Capacity, meq/g	Sulfonation time, min	τ	f_s
1.18	2.37	240	0.356	0.367
1.18	1.23	60	0.177	0.175
1.18	1.34	120	0.252	0.191
1.18	1.08	120	0.252	0.152
1.18	0.35	20	0.103	0.046
1.18	4.73	780	0.642	0.905
1.18	2.37	130	0.262	0.366[a]
1.18	2.77	220	0.341	0.443[a]
1.18	2.74	220	0.341	0.437[a]
1.18	4.00	810	0.645	0.713[a]
0.37	3.35	49.3	0.521	0.562

[a] After swelling in methanol, broken beads were removed. This may tend to increase the average fraction sulfonated because the less durable broken particles probably have a lower degree of sulfonation than the average.

$$\left(\frac{r_2}{r_1}\right)^3 = \frac{\phi_u \bar{\rho}_u}{\bar{\rho}_u(w)} \tag{4}$$

where

r_2 = radius of core after swelling in water
ϕ_u = specific wet weight of unsulfonated resin (gram water + resin)/gram resin
$\bar{\rho}_u(w)$ = density of resin core after swelling in water

This swelling is not significant (r_2 is less than 3.0% greater than r_1), and one could equally well argue that the increase in the specific wet weight above unity amounts to the filling of pores formed during the leaching of the linear polystyrene. The particle radius of the solvent swollen particle is given by

$$\frac{R_2^3 - r_2^3}{R_1^3 - r_1^3} = \frac{\phi_s \bar{\rho}_s}{\bar{\rho}_s(w)} \tag{5}$$

where

R_2 = radius of the particle after swelling in water
ϕ_s = specific wet weight of sulfonated resin
$\bar{\rho}_s(w)$ = density of resin shell after swelling in water

Finally, the shell thickness as represented in Table III is computed as

$$1 - \Psi = 1 - r_2/R_2 \tag{6}$$

The density and specific wet weight data given in Table II were used in Equations 1–5 to compute the shell thicknesses. As Table III shows, reasonable agreement between the measured and calculated shell thicknesses is obtained considering the problems associated with obtaining accurate measurements and considering the assumptions involved in the computed shell thicknesses.

Resin Capacities. The theoretical capacity of the resin assuming one sulfonate group per benzene ring is 5.32 meg H^+/g dry resin in the H^+ form. The experimentally determined fully sulfonated capacity is 5.06 meg/g. Gregor (1951) obtained a quantitatively similar experimental capacity for a nominal 8% DVB resin. The small discrepancy between the theoretical and experimental capacity can be attributed to incomplete sulfonation of each benzene ring or to the formation of sulfone linkages (—SO_2—) between two benzene rings (Roth, 1957). The capacities of the fractionally sulfonated resins have been given in Table IV as a function of particle

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radius before swelling in a polar solvent and as a function of the sulfonation time.

Correlation of Degree of Sulfonation. From the previous results describing the character of the fractionally sulfonated resin, it is anticipated that a shell progressive mechanism (SPM) might give a good quantitative description of the sulfonation process. The shell progressive mechanism assumes that the rate of reaction is so rapid with respect to diffusion (Levenspiel, 1962; Carberry and Goring, 1966) that one can assume a reactant molecule reacts with the solid substrate as soon as it diffuses through the completely reacted shell to the interface between the completely reacted and unreacted zones of the particle. Thus, the mechanism assumes that a moving boundary exists between the reacted and unreacted zones of the particle; the rate of movement of the boundary is controlled in the general case by the relative resistances of three processes in series:

Diffusion of reactant through the liquid film from the bulk liquid to the solid surface

Diffusion of reactant through the completely reacted shell zone

Reaction with the substrate at the boundary between the reacted and the unreacted zones

Both Levenspiel (1962) and Carberry and Goring (1966) have derived the relevant equations for the SPM model for a first-order reaction. The total time to reach a particular degree of reaction is just the sum of the times for each of the three mechanisms described above, since the processes occur only in series with one another.

$$\Theta = \Theta_M + \Theta_D + \Theta_R \tag{7}$$

Solving for each of these times individually:

$$\Theta_M = \frac{(1 - \rho_i^3)RC_{st}}{3\,\nu_b k_l C_b} \tag{8}$$

$$\Theta_D = \frac{6\,R^2 C_{st}}{\nu_b \bar{D} C_b}(1 - 3\,\rho_i^2 + 2\,\rho_i^3) \tag{9}$$

$$\Theta_R = \frac{SC_{st}R(1 - \rho_i)}{\nu_b k_{1st} C_b} \tag{10}$$

In these equations

ν_b = stoichiometric coefficient for $A + \nu_b B \rightarrow$ product
A = diffusing reactant
B = solid substrate
C_b = bulk concentration of reacting species A
C_{st} = concentration of reacting sites on solid substrate
k_l = mass-transfer coefficient for external liquid film
ρ_i = r_i/R, dimensionless radial position of the moving interface
$\bar{D}$ = effective diffusivity of the diffusing reactant
S = solid substrate surface area/volume

Substituting Equations 8, 9, and 10 into Equation 7 yields the general result:

$$\Theta = \frac{C_{st}R^2}{\nu_b \bar{D} C_b}\left[\frac{(1 - \rho_i^3)}{3}\left(\frac{1}{N_{Sh}} - 1\right) + \frac{(1 - \rho_i^2)}{2} + \frac{(1 - \rho_i)}{N_{Da}}\right] \tag{11}$$

where

$N_{Sh} = k_l R/\bar{D}$, Sherwood no.

$N_{Da} = k_{1st}R/S\bar{D}$, Damköhler no.

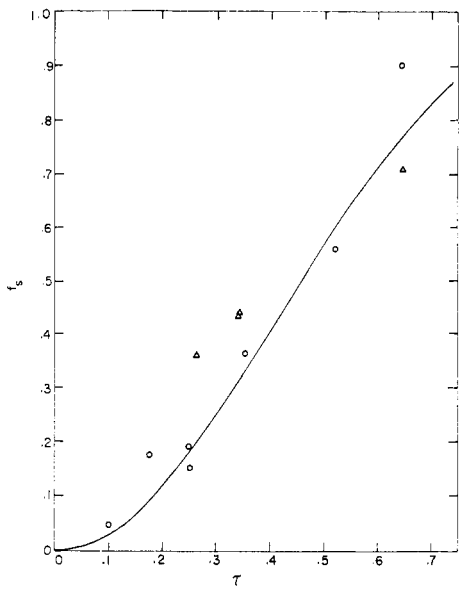

Figure 4. Plot of volume fraction sulfonated vs. dimensionless time (N_{Nu} = 127; N_{Da} = 1.08; Δ = Data points obtained by measuring capacity of resin which had broken beads removed)

To use this expression to correlate the experimental fractional capacity data, the mass transfer coefficient was estimated by using the correlation of Calderbank (1967):

$$k_l(N_{Sc})^{2/3} = 0.13\left[\frac{(P/V)\mu}{\rho^2}\right]^{1/4} \tag{12}$$

where

N_{Sc} = Schmidt no.
P/V = power input/volume
μ = viscosity
ρ = liquid density

Using the power input data of Rushton et al. (1950), using the Wilke-Chang equation to compute the molecular diffusivity of chlorosulfonic acid in ethylene dichloride, and assuming a tortuosity factor,

$$\tau = D_0/\bar{D} = 5.0$$

the effective diffusivity was estimated as $\bar{D} = 0.409 \times 10^{-5}$ cm²/sec, and the Sherwood number was estimated to be $N_{Sh} = 127$. The value of the Damköhler number was estimated by plotting:

$$f_s = 1 - \rho_i^3 \text{ vs. } T = \frac{1}{R}\sqrt{\frac{C_b\bar{D}\Theta}{C_{st}}}$$

A straight line was drawn through the data, and N_{Da} was estimated from Equation 11 at $f_s = 0.5$ to be $N_{Da} = 1.08$. By use of these values of N_{Sh} and N_{Da}, the experimental data given in Table III have been plotted in Figure 4 along with Equation 11. Although this plot shows some scatter, the correlation is reasonable considering the precision of the experiments. Note that the data which fall above the theoretical curve (indicated by triangles) were obtained from resin batches which had any broken particles removed. The reason for the breakage, of course, is that resin stability decreases as the shell becomes thin (f_s small) when the resin is swollen in a polar solvent. Consequently, one would expect that the unbroken resin for these batches might have a degree of sul-

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fonation larger than the true average for these batches. The datum point at $f_s = 0.713$ had less than 5% of the particles broken or cracked.

There are two assumptions necessary to derive Equation 11:

The rate of reaction must be rapid with respect to diffusion within the particle.

The rate of movement of the interface is much slower than the rate of diffusion.

Criteria can be established to determine if these assumptions are satisfied by the experimental system by considering slightly more complex versions of the full problem. To test the first assumption, a criterion for use of the SPM model can be obtained by an analogy with steady-state diffusion and catalytic reaction in a sphere (Carberry and Goring, 1966). The criterion established for this steady-state analog is that the concentration of reactant (assuming unimolecular first-order chemical reaction) should drop from its external concentration to 5% of that concentration within 5% of the sphere radius. Solving the simultaneous diffusion and chemical reaction equation for a sphere (Satterfield and Sherwood, 1963):

$$\frac{d^2C}{d_r^2} + \frac{2}{r}\frac{dC}{dr} - \frac{\phi_s^2 C}{R^2} = 0 \tag{13}$$

$$\phi_s = R\sqrt{\frac{k_{1st}}{\overline{D}}} \text{ Thiele modulus}$$

$$C = C_s \quad r = R$$

$$\frac{dC}{dr} = 0 \quad r = 0$$

yields:

$$C/C_s = \frac{R \sinh(\phi_s r/R)}{r \sinh \phi_s} \tag{14}$$

for $r/R \simeq 1.0$

$$C/C_s \simeq \frac{\exp\{-\phi_s(1 - r/R)\}}{r/R} \tag{15}$$

By substitution according to the criterion $C/C_s = 0.05$, $r/R = 0.95$,

$$\phi_{s\ \mathrm{crit}} = 61 \tag{16}$$

Thus, to satisfy this criterion at any stage in the sulfonation process, the effective ϕ_s for that degree of sulfonation must be greater than or equal to $\phi_{s\ \mathrm{crit}}$. To test this criterion on the experimental system, an estimate of the equivalent first-order rate constant must be obtained. Unfortunately, an accurate estimate of this rate constant is not available; however, the reaction rate expression for the sulfonation of benzene in nitrobenzene using SO_3 (Gilbert, 1965) is

$$r = k(C_6H_6)(SO_3)^2 \tag{17}$$

Rewriting as

$$r = \{k(A_RH)(SO_3) = k_{1st}(SO_3)\} \tag{18}$$

one obtains an equivalent first-order rate constant. It is quite obvious that, in general, the above lumping of varying concentrations may be in substantial error. However, there appear to be no data available for the homogeneous analog sulfonation of ethyl benzene in ethylene dichloride with chlorosulfonic acid. Data (Gilbert, 1965) indicate that rates of sulfonation increase with substitution on the benzene ring—that is, toluene sulfonates more rapidly than benzene. Consequently, the use of data on the sulfonation of benzene should supply a conservative estimate to verify the applicability of the SPM model. From the literature (Gilbert, 1965)

$$k = 1.59\ \mathrm{l.^2/mol^2\text{-}sec \text{ at } 25°C}$$

The equivalent aromatic concentration within the polystyrene matrix is

$$C_{st} = (A_RH) = \left(\frac{\rho}{M}\right) \times 10^3 = 9.68 \text{ mol/l.}$$

The initial chlorosulfonic acid concentration was 0.4715 mol/l. Because a 5M excess was used, the external bulk concentration did not vary significantly. Thus,

$$k_{1st} = 7.27 \text{ sec}^{-1} \tag{19}$$

By substitution of this value into the Thiele modulus, ϕ_s, one obtains at the beginning of the reaction

$$\phi_s = 156 > \phi_{s\ \mathrm{crit}} = 61 \tag{20}$$

Consequently, the SPM criterion is satisfied until the radius of the unreacted core reaches less than 40% of the initial radius ($f_s > 0.94$). All of the experimental data satisfy this criterion.

The criterion necessary for the satisfaction of the second assumption was established by Bischoff (1963). By considering transient diffusion rather than steady-state diffusion for any position of the interface with infinitely fast reaction and no bulk-phase mass-transfer resistance, he finds as a first approximation that the ratio of the actual position of the interface to the position computed with the SPM model is given by

$$\bar{\rho}_i/\rho_i = 1 + \frac{1}{6}\frac{C_b}{C_{st}}\frac{(1 - \rho_i)}{\rho_i^2} + \ldots \tag{21}$$

When $\rho_i = 0.40$, the error introduced by the first correction term amounts to only 3% so that the relative error caused by the second assumption is less than the relative error caused by the first assumption at $f_s = 0.94$.

If the rate constant given in Equation 18 is substituted into the Damköhler number obtained by the analysis of the experimental data, the surface area/volume can be computed:

$$S = 1.95 \times 10^5 \text{ cm}^2/\text{cm}^3$$

In the water swollen state the equivalent pore diameter becomes

$$d_{\mathrm{pore}} = \frac{4\,\nu_s(w)(1 - \nu_s(d))}{S(1 - \nu_s(w))} \simeq 3700 \text{ Å} \tag{22}$$

Goldring (1966), reporting the results of several experiments on average pore sizes in ion-exchange resins, states that the average pore size ranges from 120–220 Å with no pores larger than 1000 Å. Because measurements of average pore size based on transport properties generally indicate an average pore size of 20–30 Å, Goldring concludes that an ion-exchange resin must consist of a collection of multistaged charged voids interconnected by charged openings or capillaries whose minimum diameter is such as to limit passage of ions or molecules larger than 20–30 Å.

In any respect, the value of the pore diameter estimated from sulfonation results is larger than more directly computed values by a factor of 15–30. This suggests that either k_{1st} is too small or $\overline{D}$ too large in the Damköhler number. Either of these effects will tend to enhance even more the original hypothesis that the SPM model is applicable. That is, ϕ_s will be larger by a factor of 4–6. Note that outside mass transfer already contributes a small fraction of the overall resistance. Thus, a decrease in $\overline{D}$ will not affect the resistance to outside mass transfer.

Diffusivity of Acetic Acid Within Resin

Because the sorption of water into the unsulfonated portion of the resin particle is rather small (Table II), it seems reason-

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able to assume that a virtual no flux boundary exists at the interface between the sulfonated and unsulfonated regions within the particle. It has been assumed that Fick's law can be applied to the diffusion of the dilute acetic acid in the pore liquid within the resin. Although the solutions to the transient diffusion equation into a well-stirred finite volume from various solid shapes have been obtained by Patterson (1947), Carman and Haul (1954), Berthier (1952), and Ma and Evans (1968), the solution for a composite sphere capable of supporting a diffusive flux in the outside shell only has not been obtained. The pertinent equations in spherical coordinates are

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\bar{D}\frac{\partial C_R}{\partial r}\right) = \frac{\partial C_R}{\partial t} \tag{23}$$

with initial condition $C_R = C_0$, $a > r > b$, $t = 0$

and boundary conditions $\frac{\partial C_R}{\partial t} = 0$, $r = a$

$$C_R = \lambda C_s,\ r = b$$

Finally, equating the flux through the surface $r = b$ of all the particles to the increase in the concentration of the diffusing species in the well-stirred solution of volume V_s,

$$N\left(-\bar{D}\frac{\partial C_R}{\partial r}\Big|_b\right) 4\pi b^2 \nu_s = V_s\frac{\partial C_s}{\partial t} \tag{24}$$

where

$$N = \text{no. of particles} = V_R/(4/3)\pi b^3$$

$$C_R = \lambda C_s \text{ at } r = b$$

for particles of constant volume. Consequently, Equation 24 becomes

$$-\bar{D}\frac{\partial C_R}{\partial r}\Big|_b = \frac{V_s b}{3\lambda\nu_s V_R}\frac{\partial C_R}{\partial t}\Big|_b \tag{25}$$

Following the techniques of Patterson (1947) by use of the Laplace transform, the solutions to Equations 23 and 25 have been obtained in the form of an infinite series solution rapidly convergent at long times and two asymptotic solutions convergent at short times. Details of the solution have been given by McMaster (1969). The fractional approach to equilibrium given as the total mass of solute transferred from the resin to solution at time t to that measured at time infinity is the quantity measured experimentally. The solutions in terms of this quantity are:

Infinite series solution

$$\frac{M(\Theta)}{M\infty} = 1 + \frac{(1-\Psi^3)+3w}{(1-\Psi^3)}\sum_{n=1}^{\infty}\frac{2w\{(1-\Psi)^2+q_n^2\Psi^2\}\exp\{-q_n^2\Theta\}}{\{(2w+1)\Psi^3-(3w+1)\Psi^2-w^2\}q_n^2-(1-\Psi)^2(1+3w-\Psi^3)-w^2q_n^4\left(\frac{\Psi^2}{1-\Psi}\right)} \tag{26}$$

where

$$w = \frac{V_s}{3\lambda\nu_s V_R}$$

$$\Psi = a/b$$

$$\Theta = \bar{D}t/\{(1-\Psi)b\}^2$$

and q_n is the nth positive root of the characteristic equation

$$q_n \cot q_n = -\frac{\left\{w\left(\frac{1-\Psi}{\Psi}\right)+(1-\psi)\right\}q_n^2+\frac{(1-\Psi)^3}{\Psi}}{wq_n^2-\frac{(1-\Psi)^3}{\Psi}} \tag{27}$$

Short-time asymptotic solution by use of binomial expansion

$$\frac{M(\Theta)}{M\infty} = \frac{(1-\Psi^3)+3w}{(1-\Psi^3)}\Bigg[\frac{2(1-\Psi)}{w}\sqrt{\Theta}\,i\,\mathrm{erfc}(o) - \frac{4(1-\Psi)^2}{w^2}\{w+1\}\Theta i^2\mathrm{erfc}(o) + \frac{8(1-\Psi)^3}{w^3}\{1+2w\}\times\Theta^{3/2}i^3\mathrm{erfc}(o) - \frac{16(1-\Psi)^4}{w^4}\{w^2+3w+1\}\Theta^2 i^4\mathrm{erfc}(o) + \frac{32}{w^5}\{1+4w+3w^2\}(1-\Psi)^5\Theta^{5/2}i^5\mathrm{erfc}(o) - \frac{64}{w^6}\{1+4w+6w^2+w^3\}(1-\Psi)^6\Theta^3 i^6\mathrm{erfc}(o) + \ldots\Bigg] \tag{28}$$

where

$$i^n\,\mathrm{erfc}(x) = \int_x^\infty i^{n-1}\,\mathrm{erfc}(t)dt$$

$$i^0\,\mathrm{erfc}(x) = \mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-t^2}dt$$

The values of i^n erfc(o) have been tabulated by Carslaw and Jaeger (1959). Short-time asymptotic solution by use of partial fractions and binomial expansion

$$\frac{M(\Theta)}{M\infty} = \frac{(1-\Psi^3)+3w}{(1-\Psi^3)}\left[1-\sum_{i=1}^{3}\frac{\left(\alpha_i+\frac{1-\Psi}{\Psi}\right)\alpha_i e^{v_i^2}\mathrm{erfc}(v_i)}{3\alpha_i^2+2A\alpha_i+B}\right] \tag{29}$$

where

$$A = \frac{(1-\Psi)}{w\Psi}(w+\Psi)$$

$$B = \frac{(1-\Psi)^3}{w\Psi}$$

$$v_i = -\alpha_i\sqrt{\Theta}$$

and α_i, $i = 1, 2, 3$ are the roots of the cubic equation

$$\alpha^3 + A\alpha^2 + B(\alpha - 1) = 0 \tag{30}$$

By combining the solutions by use of these equations at long and short times, the full solution has been obtained for various values of w and Ψ. In many cases the active volume to external surface area characteristic length

$$b^* = b(1-\Psi^3) \tag{31}$$

can be substituted for the radius b in the transient diffusion problem for a uniform completely sulfonated sphere with negligible error in the computed diffusivity. There are other cases (w large, $\Psi \to 1.0$) where the error in the computed diffusivity by use of the active volume to surface area characteristic length can be as large as 100%.

By use of the experimental desorption results, the diffusivity was computed with Equations 26–30. The results are sum-

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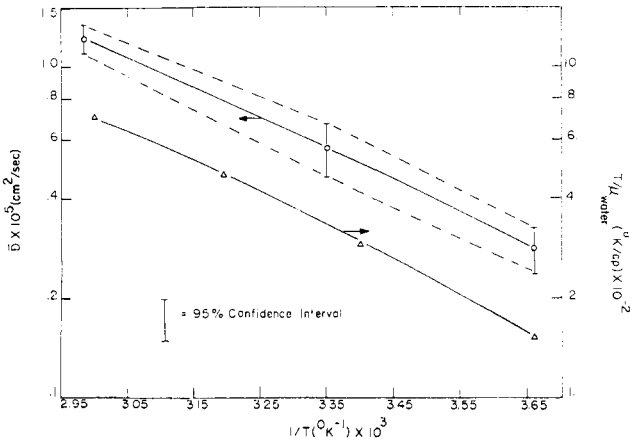

Figure 5. Effective diffusivity of acetic acid diffusing through water in ion-exchange resin

Table V. Experimental Diffusivity Data

No.	t, sec	$M(t)/M$	w	Ψ	b, mm	T, °C	$\bar{D} \times 10^5$, cm²/sec
1	30	0.582	1.730	0.386	1.119	61.5	1.39
2	180	0.810	1.730	0.386	1.119	25.6	0.62
3	30	0.315	1.730	0.386	1.119	0.0	0.31
4	60	0.682	1.776	0.386	1.119	62.0	1.08
5	60	0.705	1.776	0.386	1.119	61.5	1.19
6	300	0.890	1.776	0.386	1.119	25.6	0.54
7	60	0.402	1.776	0.386	1.119	0.0	0.28
8	120	0.803	1.608	0.386	1.119	62.0	0.89
9	120	0.843	1.608	0.386	1.119	61.5	1.07
10	420	0.919	1.608	0.386	1.119	25.6	0.45
11	120	0.586	1.608	0.386	1.119	0.0	0.35
12	37.5	0.565	1.793	0.386	1.119	62.0	1.03
13	60	0.690	1.997	0.386	1.119	62.0	1.14
14	30	0.414	1.997	0.386	1.119	25.6	0.61
15	180	0.597	1.997	0.386	1.119	0.0	0.25
16	120	0.879	2.765	0.386	1.119	62.0	1.36
17	60	0.516	2.765	0.386	1.119	25.6	0.55
18	300	0.766	2.765	0.386	1.119	0.0	0.33
19	60	0.846	2.252	0.386	1.119	62.0	2.27
20	120	0.626	2.252	0.386	1.119	25.6	0.44
21	420	0.768	2.252	0.386	1.119	0.0	0.23
22	90	0.843	2.043	0.386	1.119	62.0	1.47
23	45	0.536	2.043	0.386	1.119	25.6	0.77
24	120	0.497	2.043	0.386	1.119	0.0	0.24
25	120	0.862	1.728	0.386	1.119	62.0	1.18
26	60	0.737	1.596	0.386	1.119	62.0	1.34
27	30	0.603	1.596	0.386	1.119	62.0	1.52

marized in Table V. The logarithm of the computed diffusivities has been plotted in Figure 5 against inverse absolute temperature. Also given is the temperature dependent variable of the Wilke-Chang equation for predicting liquid phase diffusivities. The slopes of the two lines are nearly identical, suggesting that the diffusional process involves simple liquid phase diffusion in the pore liquid. The ratio of the molecular diffusivity to the effectivity diffusivity is just a measure of the tortuous path which the solute must follow within the solid. Table VI compares the computed tortuosity found for the resin of this study with tortuosities measured for commercial Dowex resins.

Consequently, the tortuosity measured in this study is substantially less than the tortuosity measured by other investigators in Dowex resins with both reaction and sorption techniques. Some of the discrepancy may be accounted for based on a relative size factor. For example, the sucrose molecule has an equivalent spherical diameter of approximately 9 Å (Gilliland et al., 1971). Based on apparent capacity measurements in microreticular resins for relatively large cations (Kunin, 1948, 1949), evidence exists that a fraction of the pores may have constrictions as small as 10 Å.

Consequently, a large tortuosity for sucrose may reflect a geometric constriction factor which inhibits the passage of large diffusing species. The tortuosity factor for methyl acetate may reflect adsorption of the methyl acetate molecule onto the surface of the resin pores. Haskell and Hammett (1949), Davies and Thomas (1952), and Frisch (1962) suggest that adsorption effects of this kind can lead to higher concentrations and corresponding higher rates of reaction than in the presence of homogeneous acid. Indeed, the molal phase distribution coefficient measured by Gregor et al. (1951) for aqueous methyl acetate was approximately 1.5 suggesting possible adsorption effects.

The comparison of the tortuosity factors for ethanol in Dowex 50 with the tortuosity factor of acetic acid in the resin of this study may reflect a difference in resin structure. The porosity of the resin of this study in water is larger than the porosity of an equivalently crosslinked Dowex resin. Because the preparative technique for the resin of this study involves the removal of the uncrosslinked portion of the resin matrix prior to sulfonation, it probably leads to larger and more uniform pores so that the constrictions suggested by Goldring do not exist. Whether the pore size distribution is fairly uniform or whether a bimodal distribution exists similar to that found for the macroreticular resins (Kunin et al., 1962) is beyond speculation at this time.

It is interesting to note that Peterson (1958) in a theoretical work estimates that an individual pore with a ratio of maximum to minimum diameters of 5–1 will have an increased resistance to diffusion of 3–1 over that of a pore of uniform cross sectional area and an identical volume. Based on the results of Goldring (1966) and Kunin (1948, 1949), it appears that conventional microreticular resins may have variations in maximum to minimum pore diameter as large as 25–1. Consequently, basic differences in resin morphology may be responsible for the enhanced diffusivities found for the resin of this study.

Conclusions

A modified ion-exchange resin using the conventional monomers has been prepared which consists of large particles (2–3 mm) active only on an outside surface layer. The H^+ capacity of this resin in the fully sulfonated state is identical with that of commercial microreticular resins. The composite structure of the particles has been demonstrated both by microscopic examination and by analysis of the sulfonation reaction with the shell progressive mechanism. The resin was highly porous and exhibited enhanced diffusion to low-molecular-weight species over commercial resins of the same nominal crosslink content suggesting the possibility of large and more uniform pores.

Nomenclature

A = constant in Equation 29 (0)
a = radius of core (cm)
B = constant in Equation 29 (0)
b = particle radius (cm)

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Table VI. Comparison of Tortuosities of Resin of this Work with Dowex

Resin	τ	Diffusing species	Solvent	Temp, °C	Technique	Investigator
This study	2.18	Acetic acid	Water	25–62	Desorption	...
Dowex 50 K^+ form (DVB content not specified)	33	Methyl acetate	Water	7–25	Desorption	Gregor et al. (1951)
Dowex 50 K^+ form (DVB content not specified)	14	Ethanol	Water	7–25	Desorption	Gregor et al. (1951)
Dowex 50X8 H^+ form	38	Sucrose	Water	50–70	Reaction	Gilliland et al. (1971)
Dowex 50 (DVB content not specified)	13	Ethanol	Ethanol/acetic reaction mixture	30–70	Reaction	Saletan and White (1952)

b^* = volume to surface area characteristic length (cm)
C = concentration (mol/cm^3)
C_b = bulk concentration (mol/cm^3)
C_R = concentration in resin pore liquid (mol/cm^3)
C_S = surface concentration (mol/cm^3)
C_s = external solution phase concentration (mol/cm^3)
C_{st} = concentration of reacting sites on solid substrate (mol/cm^3)
$\bar{D}$ = effective diffusivity (cm^2/sec)
D_0 = molecular diffusivity (cm^2/sec)
dp = particle diameter (cm)
d_{pore} = equivalent cylindrical pore diameter (cm)
f_s = $(1 - \rho_i^3)$, volume fraction sulfonated (0)
k = rate constant (l.^{2}/mol^2-sec)
k_{1st} = first-order rate constant (sec^{-1})
k_l = mass-transfer coefficient (cm/sec)
M = molecular weight (g/mol)
$M(\Theta)/M\infty$ = fraction of equilibrium uptake (0)
N_{Da} = $(k_{1st}R/S\bar{D})$, Damköhler no. (0)
N_{Sc} = $\mu/\rho D_0$, Schmidt no. (0)
N_{Sh} = $(k_lR/\bar{D})$, Sherwood no. (0)
P/V = power input/volume (ergs/cm^3)
R = particle radius (cm)
r = radius (cm)
q_f = fractional capacity of resin (0)
S = surface area/volume (cm^2/cm^3)
T = temperature (°K)
t = time (sec)
V_R = resin volume (cm^3)
V_s = solution volume (cm^3)
w = $V_s/3\lambda\nu_sV_R$ (0)

Greek Letters

α_i = roots of Equation 30 (0)
Θ = time (sec)
Θ = $\bar{D}t/\{(1 - \Psi)b\}^2$, dimensionless time (0)
Θ_D = time for diffusing through reacted shell (sec)
Θ_M = time for external mass transfer (sec)
Θ_R = time for chemical reaction (sec)
λ = C_R/C_s, distribution coefficient (0)
μ = viscosity (g/cm-sec)
ν_b = stoichiometric coefficient (0)
ν_s = sulfonated resin porosity (0)
ν_u = unsulfonated resin porosity (0)
ρ = density (g/cm^3)
ρ_i = r_i/R, dimensionless radial position of moving interface (0)
$\bar{\rho}_s$ = sulfonated resin density (g/cm^3)
$\bar{\rho}_u$ = unsulfonated resin density (g/cm^3)
τ = $D_0/\bar{D}$, tortuosity factor (0)
ϕ_s = Thiele modulus for sphere (0)
ϕ_s = specific wet weight of sulfonated resin (0)
ϕ_u = specific wet weight of unsulfonated resin (0)
Ψ = a/b, core radius/particle radius (0)

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