Copper Selective Adsorption with a Microemulsion-Based Resin

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Cross-linked terpolymers of allyl acetylacetone, 2-hydroxyethyl methacrylate, and ethylene glycol dimethacrylate were synthesized in the oil phase of a bicontinuous microemulsion stabilized with didodecyldimethylammonium bromide. The resulting material is porous, with a surface area of 58 m^2/dry g. It selectively adsorbs copper, picking up 0.07 meq/dry g from a 0.1-M solution. This is less than the total apparent capacity of 0.65 meq/dry g inferred from titration with base and much less than the amount in conventional, nonselective resins, which is typically 5 meq/dry g. Breakthrough curves in packed beds and across membranes of this material seem consistent with uptake controlled by chemical reaction compromised by dispersion. Nonporous membranes of this material do not show facilitated transport.

Introduction

In this article, we report efforts to synthesize a new type of microporous adsorbent selective for transition metal ions. Conventional ion-exchangers are rarely selective between ions of the same valence, though exceptions do occur (Schmuckler, 1987; Tremillon, 1968). Our adsorbent is based on allyl acetylacetone, which when polymerized has the potential for selective separation of transition metal ions (Stary, 1964).

Polymers of allyl acetylacetone are too hydrophobic to allow effective contact with aqueous solutions of the metal ions, so we made copolymers with hydrophilic 2-hydroxyethyl methacrylate (HEMA). We carried out these copolymerizations in the oil phase of a bicontinuous microemulsion. In earlier studies (Burban et al., 1994a,b), we showed that such microemulsion-based polymerizations could yield solids with high specific surface areas.

In this article, we begin by describing the synthesis of allyl acetylacetone in porous polymers. We then present evidence of selective adsorption by these polymers. We determine two different kinds of breakthrough curves: those in beds packed with small particles and those for flow across microporous membranes. Finally, we discuss how these new ion-exchange materials might be improved.

Experimental

Materials

To synthesize allyl acetylacetone, we adapted the procedure of Davis and Hurd (Davis and Hurd, 1955; Yang, 1993), which reacts acetylacetone with allyl bromide (Aldrich). We purified the product by two vacuum distillations. Commercially available 2-hydroxyethyl methacrylate (Aldrich) and ethylene glycol dimethacrylate (Aldrich) were also purified by vacuum distillation. Other materials were reagent grade and were used as received.

One typical adsorbent was made in a glove bag as follows. We first added 0.005 g of 2,2′-azobisisobutyronitrile (Kodak) to a glass vial. Next, we added an oil phase of 1.0 g of allyl acetylacetone, 0.33 g of hydroxyethyl methacrylate, and 0.17 g of ethylene glycol dimethacrylate. After the initiator dissolved in the oil phase, we added 2.75 g of didodecyldimethylammonium bromide (Eastman) and 0.75 g of deionized water to the mixture. After stirring to form the transparent bicontinuous microemulsion, we sparged the microemulsion with nitrogen to remove dissolved oxygen, pipetted it onto a glass plate, and drew a casting blade across the plate to form a 0.020-in. (0.5-mm) film. We placed a quarter-inch-thick greased gasket along the edge of the plate and set another glass plate on top of the gasket to seal the microemulsion. The microemulsion was removed from the glove bag and polymerized at 90°C for 24 hours. The resulting adsorbent film, about 100 μ thick, was washed repeatedly with denatured alcohol to remove the surfactant and stored in deionized water. The specific surface area of this film measured with an Automated BET Sorptometer (Porous Materials), was 58-m^2/g dry polymer after freeze drying. Its skeletal density was 0.76-g dry polymer per cubic centimeter. Since the average polymer weight fraction of the water-swollen film is 0.24, the porosity in the material is 0.70. Nitrogen adsorption and mercury porosimetry data show a broad distribution of pore sizes (Yang, 1993).

Procedure

To determine the total capacity of the porous polymer, we placed water-swollen polymer samples in polyethylene vials containing 10 cm^3 of 0.1-M NaCl (Mallinckrodt) and a specified amount of 0.0485 M NaOH (Mallinckrodt). After a week, we determined the hydroxide concentration of the adsorbent-free solution by titration with HNO_3 (EM Science). The difference between the final and initial base concentrations determined the number of sites neutralized at equilibrium. The resin was then treated with 0.05 M HNO_3 to convert it to the protonated form; it was air dried to obtain the dry sample weight.

The binding of metal ions was measured in a similar way. A known mass of water-swollen adsorbent, blotted dry, was placed in vials containing various concentrations of either $Mg(NO_3)_2$, $Ni(NO_3)_2$, or $Cu(NO_3)_2$ (Baker, Baker, and Mallinckrodt, respectively). No buffers, acids, or bases were added to alter the pH of the nitrate solutions. After at least one week we removed the adsorbent from solution and rinsed it with deionized water to remove unbound ions, and placed it in HNO_3 solutions of pH 2.1 for at least 12 hours. The final equilibrium cation concentrations in the adsorbing and the stripping solutions were determined with a Varian-1475 atomic adsorption spectrophotometer.

For our packed bed experiments, we first stacked polymer films in an 8-cm^3 plastic cubic mold filled with TissueTek, a polyethylene glycol-based embedding compound (Miles). The plastic cube was frozen in dry ice. We then took the frozen cube out of the mold, placed it on a microtome (Bright Instrument Co.), and sliced 100-μm-thick layers. The ion-exchange material is now, in essence, adsorbent spaghetti. The polymer spaghetti was rinsed free of embedding compound and stored in deionized water. When we packed beds of this spaghetti under vacuum in a 3-cm stainless steel tube (0.65-cm OD, 0.48-cm ID), the interparticle porosity of the bed was 0.23, possibly reflecting breakage and compression of the adsorbent.

For our membrane experiments, we mounted the polymer film just described in a glass diaphragm cell made from an O-ring pipe joint 2.5 cm in diameter and about 20 cm long. To mount the membrane in the cell, we first applied stopcock grease (Dow Corning Corporation) on the rim of the permeate side of the pipe joint. We put a polypropylene screen (FilmTec) on this rim and set the membrane on top of this screen. We greased the rim of the feed side and placed an O-ring on this rim. We greased the exposed side of the gasket and clamped the two half-cells together.

Breakthrough curves with the packed beds and with the membrane "beds" were measured in similar ways. We washed a bed by pumping deionized water through overnight, often at 0.5 cm^3/min. We then switched to a feed solution containing $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Mg(NO_3)_2$, and/or blue dextran (Sigma Chemical) at the desired flow rate. For the packed bed, the pumping was provided by a Spectra-Physics IsoChrom LC Pump. For the membrane bed, the flow was effected by pressurizing the feed pipe joint with a cylinder of nitrogen. We analyzed the blue dextran output spectrophotometrically (Milton Roy SpectroMonitor 3100 UV/visible detector set at 254 nm). The salt solutions were analyzed by atomic adsorption. When each experiment was finished, we regenerated the bed with HNO_3 at a pH of 2.1 and rinsed it with deionized water.

Results

The results of this work are conveniently split into three groups: equilibrium measurements, selectivity measurements, and adsorption kinetics measurements. We discuss these sequentially.

The equilibrium measurements center on the determinations of the isotherms of cupric nitrate solutions from 10^{-6} to 10^{-1} M. We found no simple isotherm that fits our data over this entire range. Below 10^{-5} M, the data fit the Langmuir isotherm

$$q = \frac{0.02c}{6.5\times 10^{-6} + c} \tag{1}$$

where q is the concentration in the adsorbent, in meq/g dry polymer; and c is the concentration in solution, in moles per liter. Above 10^{-5} M, the data are closer to a Freundlich isotherm

$$q = 0.10c^{0.18}. \tag{2}$$

The data supporting this latter result are shown in Figure 1. Data for magnesium and nickel nitrates show 20 times less adsorption at a concentration of 10^{-5} M (Yang, 1993). These data are more scattered, a possible consequence of less sensitive atomic absorption.

While this selective adsorption is encouraging, the amount of selective adsorption is not: the maximum amount adsorbed is around 0.07 meq/g dry polymer. This is less than the 0.65

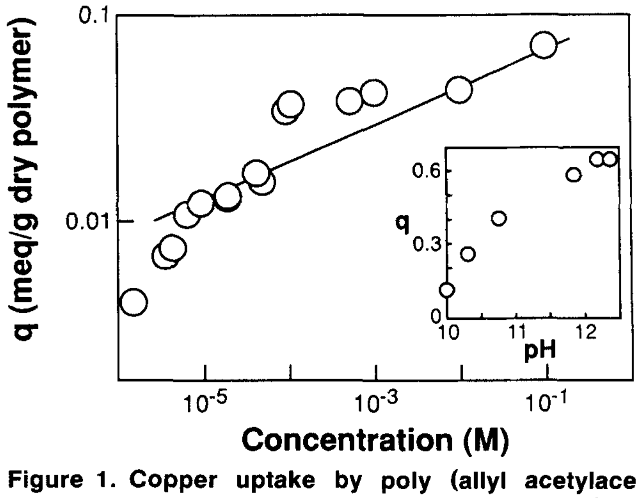

Figure 1. Copper uptake by poly (allyl acetylacetone-co-hydroxyethylmethyl methacrylate).

The data fit a Freundlich isotherm at high concentrations, but a Langmuir isotherm at lower concentrations. The capacity is higher at higher pH, as shown in the inset.

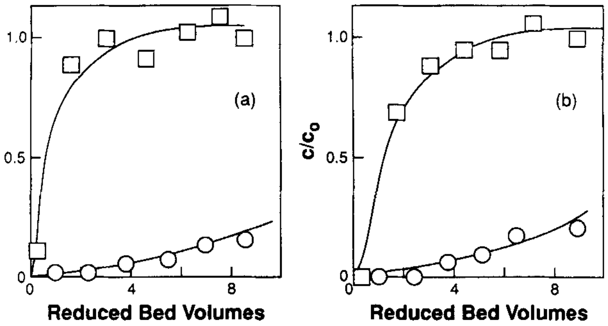

Figure 2. Selective breakthrough in a packed bed.

Cupric ions, shown as the circles, are selectively adsorbed over magnesium or nickel ions, shown as the squares in (a) and (b), respectively.

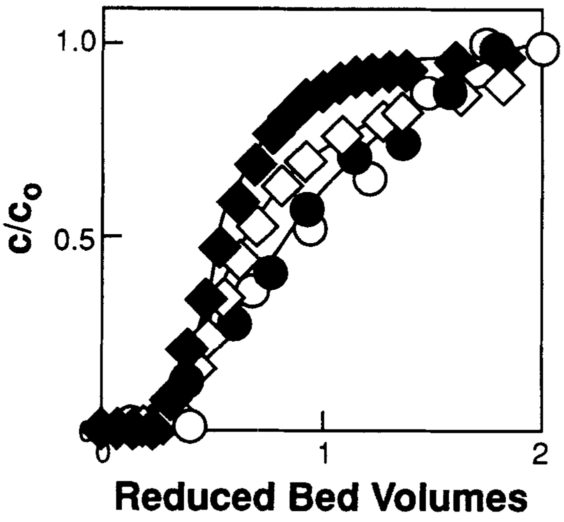

Figure 3. Breakthrough curves of nonadsorbing species.

Blue dextran, shown as diamonds, breaks through more rapidly than Cu^{++} at pH 2.1, shown as circles. At this pH, Cu^{++} is not adsorbed. The open symbols are at 0.055 cm/min; the closed symbols are at 2.7 cm/min.

meq/g dry polymer found by titration of this material to pH of 12, as shown in the inset of Figure 1. We expect that we could increase the amount adsorbed by using a feed of Cu^{++} in aqueous ammonia to increase the pH. In contrast, the feed in our isotherm measurements had a pH of 5. Even with a more basic feed, however, the capacity of 0.65 meq/g is much less than the 5 meq/g typically found in ion-exchange materials. We will return to this point in the discussion section below.

We now turn to our second group of experiments, aimed at showing selective adsorption in packed beds. Typical breakthrough curves with a feed of 10^{-5}-M $Cu(NO_3)_2$ and of 10^{-5}-M $Mg(NO_3)_2$ or $Ni(NO_3)_2$ are shown in Figure 2. The figure plots the exit concentration c per feed concentration c_0 vs. the reduced bed volume, defined as the volumetric flow Q times the time t divided by bed volume V. The few results at small reduced bed volumes are a consequence of the need to get samples of a significant volume from these small beds.

The breakthrough curves in Figure 2 show that adsorption in these columns is selective. For a nonadsorbed solute in an ideal bed, we expect that c/c_0 would be zero when $Qt/\epsilon V$ is less than one. (The void fraction in the bed is ϵ.) We expect that this concentration ratio would jump to one when $Qt/\epsilon V$ exceeds one. The data in Figure 2 qualitatively support this expectation.

For an adsorbing solute in an ideal bed, we expect that c/c_0 will be zero when $Qt/V[\epsilon+(1-\epsilon)K]$ is less than one, where K is an apparent linear equilibrium constant for adsorption (Ruthven, 1984). We also expect that c/c_0 will jump to one when $Qt/V[\epsilon+(1-\epsilon)K]$ exceeds one. The concentration of copper does remain low, much less than that of other ions, at smaller reduced volumes. However, the copper concentration being eluted is not zero. This nonzero concentration is a measure of kinetic processes in the bed, including diffusion, reaction, and dispersion.

Measurements of these kinetic processes are the third and largest group of experiments reported in this article. To introduce this subject, we first explore the effect of molecular size on the breakthrough curve. We choose as test solutes blue dextran (molecular weight 2×10^6 daltons) and nonadsorbed Cu^{++} at pH 2.1. The exit concentrations for these solutes are shown in Figure 3, again as a function of reduced bed volume. The inlet concentrations of blue dextran and Cu^{++} are 0.05 g/L and 1×10^{-5} M, respectively. Both solutes are run at two superficial velocities, 0.055 and 2.7 cm/min. The results in Figure 3 imply that the small Cu^{++} ions diffuse into the pores of the adsorbent more quickly than the much larger blue dextran molecules. As a result, the copper ions are retained longer, as in size exclusion chromatography (Wankat, 1990).

We next examine the effects of feed flow and feed concentration on the breakthrough curves in packed beds. To measure the effects of feed flow, we fix the concentration at 1×10^{-5}-M Cu^{++} but vary the flow from 0.01 to 0.5 cm^3/min. This implies superficial velocities from 0.055 to 2.7 cm/min. The resulting breakthrough curves, shown in Figure 4, show that breakthrough occurs at around one-third the volume when the flow is increased 50 times. Note that the range of the reduced bed volumes is much greater in Figure 4 than it was in Figures 2 and 3.

The effects of changing feed concentration are much greater than those caused by changes in feed velocity. To show this, we fix the feed velocity at 0.53 cm/min and measure the breakthrough at Cu^{++} feed concentrations of 0.5×10^{-5}, 1.0×10^{-5}, and 2.0×10^{-5} M. The results, given in Figure 5, show that this fourfold change in feed concentration has a larger effect on the breakthrough than the fiftyfold change in velocity shown in Figure 4. Note that the values at 1.0×10^{-5} M and 0.53 cm/min are the same in Figures 4 and 5; note also that the range of reduced volumes in Figure 5 is again much larger than that in Figure 2.

An alternative to adsorption in packed beds is to carry out adsorption in microporous membranes. Such "membrane chromatography" may avoid mass-transfer restrictions (Brandt et al., 1988; Henis, 1988), though it may also be compromised by polydispersity of membrane pores (Schisla et al., 1993). The breakthrough curves for the microporous membranes are qualitatively similar to those for the packed beds,

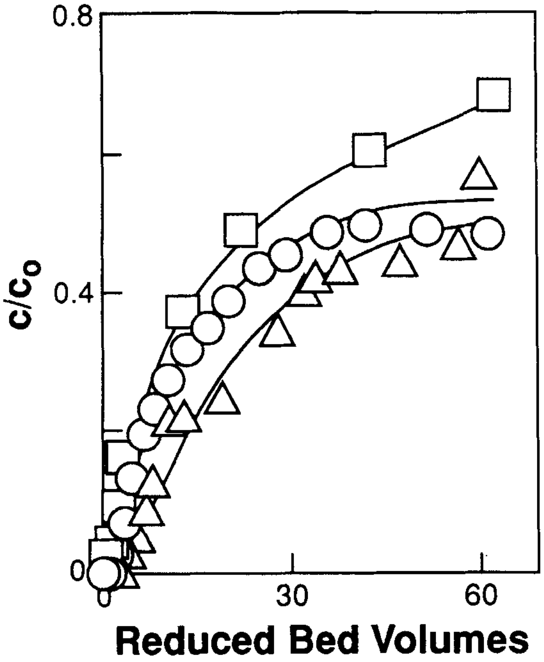

Figure 4. Packed bed breakthrough curves vs. feed velocity.

The triangles, circles, and squares refer to 0.055 cm/min, 0.53 cm/min, and 2.7 cm/min, respectively. The feed concentration was 10^{-5} M Cu^{++} in all cases.

though the smaller volume of the membranes forces us to make measurements at somewhat larger reduced volumes *Qt/V*. The breakthrough occurs earlier at higher velocity, as shown in Figure 6; it takes place earlier at higher feed concentration, as shown in Figure 7. Both the velocity and concentration dependences seem similar to those observed in

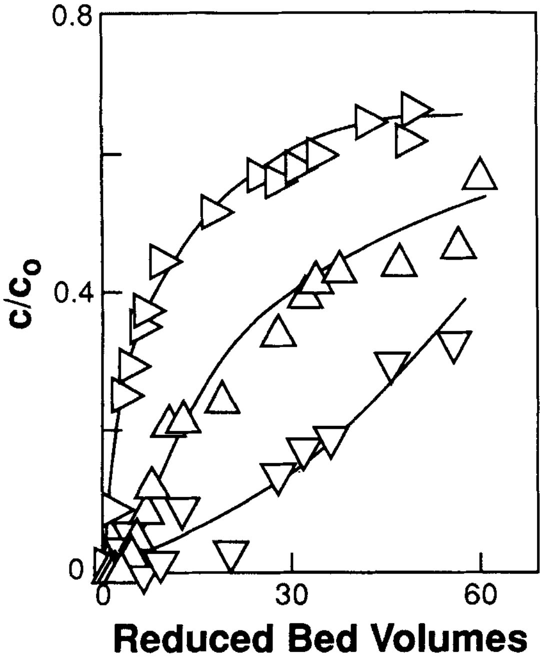

Figure 5. Packed bed breakthrough curves vs. feed concentration.

The inverted triangles, regular triangles, and right-pointing triangles are for 0.5×1.0^{-5} M, 1.0×10^{-5} M, and 2.0×10^{-5} M Cu^{++}, respectively. The flow was 0.055 cm/min in all cases.

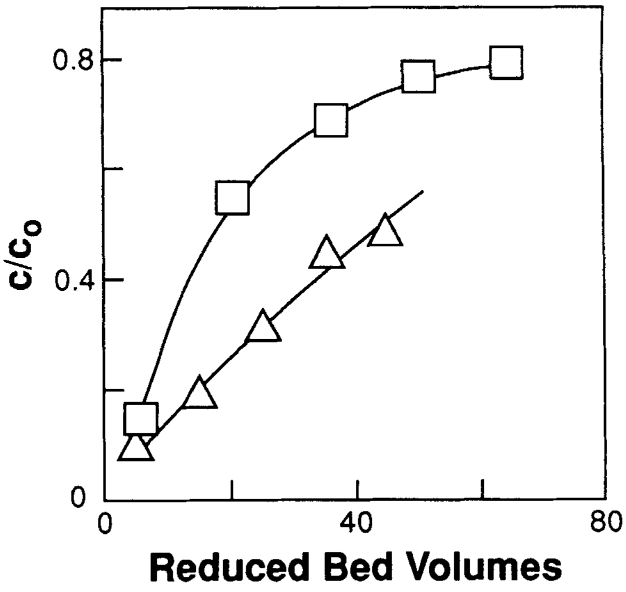

Figure 6. Membrane breakthrough curves vs. feed velocity.

The triangles and squares refer to superficial velocities of 0.0025 cm/min and 0.0037 cm/min, respectively. The feed concentration was again 10^{-5} M Cu^{++}.

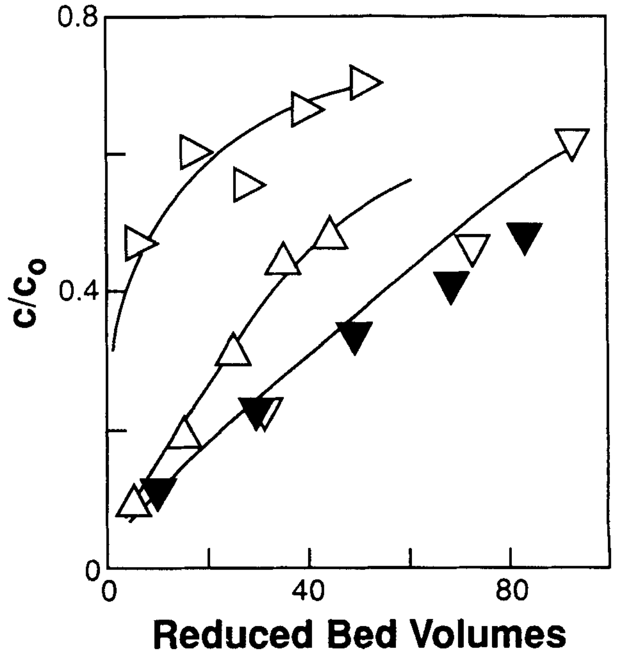

Figure 7. Membrane breakthrough curves vs. feed concentration.

The inverted triangles, regular triangles, and right-pointing triangles refer to Cu^{++} concentrations of 0.5×1.0^{-5} M at a superficial velocity of 0.0023 cm/min; 1.0×10^{-5} M at 0.0025 cm/min; and 2.0×10^{-5} M at 0.0022 cm/min, respectively. The open and filled inverted triangles are experiments on two different membranes.

packed beds, even though the channels for flow through the membranes are orders of magnitude smaller than the channels for flow in the packed beds. The data in Figure 7 include two experiments made under the same conditions but with two different membranes. The agreement between these experiments shows that we can make these membrane structures reproducibly, as detailed elsewhere (Yang, 1993). The significance of these and the earlier results is explored in the next and final section of this article.

Discussion

The preceding results show that porous polymers of allyl acetylacetone, hydroxyethyl methacrylate, and ethylene glycol dimethacrylate can be used for selective ion exchange of cupric ions. The selectivity, which is easily more than an order of magnitude, is substantially greater than that in more conventional resins. We believe that this selectivity could be further enhanced by a more careful choice of the pH selected for adsorption. The adsorbed Cu^{++} is quickly and easily eluted with HNO_3 at a pH of 2.1. Elution at this pH does not irreversibly alter the resin, which can be used repeatedly.

The capacity observed for these new resins is disappointingly low, around 0.07 meq/g dry resin at 0.1 M Cu^{++}. This is much less than the value of 0.65 meq/g obtained from titration to high pH (cf. Figure 2) and a still smaller fraction of the 5 meq/g expected for conventional, nonselective resins. We had hoped from our original monomer composition to get a capacity for our new material close to that of the conventional resin, but we think it likely that not all the allyl acetylacetone reacted (Liable et al., 1987). Still, we are bothered by why our capacity is so low.

One possibility is that the capacity of this new material reflects the surface area of 58 cm^2/dry g that we obtained in these experiments. If we assume that our material consists of small spheres, then we can infer from the void fraction of 0.70 and the skeletal density of 0.76 g/cm^3 that the spheres have diameters of 410 Å. If we use measurements of flow rate across our membranes under a given pressure drop, then we infer a particle size of 460 Å, in good agreement (Yang, 1993). These diameters are close to the 500 Å size observed for similar polymers studied with small-angle X-ray scattering (Burban et al., 1994a). These sizes may seem small, but they are substantially greater than the size of around 40 Å that exists in the original microemulsion (Burban et al., 1994a,b).

The 410 Å size characteristic of our new material seems consistent with our observed capacity. In particular, the area of a copper-selective site s^2 can be estimated from

$$s^2\left[\frac{7\times10^{-5}\ eq}{g}\right]\frac{6.02\times10^{23}}{eq}=\left(\frac{58\times10^{4}\ \text{cm}^2}{g}\right)$$

$$s=12\ \text{Å}. \qquad (3)$$

Thus the observed capacity suggests a possible site for a cupric ion located in every 12×12 Å space under the experimental conditions used. If the entire capacity observed at high pH could be used, the sites would be in each 4×4 Å space.

Achieving greater capacity thus seems to require a larger surface area. We had originally hoped that these microemulsion-based materials would show the larger areas implied by their 40 Å characteristic size. Other parallel experiments (Burban et al., 1995a,b), however, have shown that this size is destroyed in making our material. Interestingly it survives the polymerization, for it is still detectable by small-angle X-ray scattering after the reaction is complete. It does not survive the extraction of the detergent after polymerization, however. The 40 Å peak disappears even while the 500 Å peak, which appears during the reaction, remains unaltered by the detergent extraction.

We are less successful in analyzing the breakthrough curves given earlier. Because our data show considerable scatter, we are reticent to apply models of adsorption that use more than a very few adjustable parameters. We investigate two such models, each of which requires approximating our isotherm as linear. First, we assume that diffusion within the resin controls the adsorption, a limit sometimes called the "Rosen model" (Rosen, 1952). While we can successfully fit our breakthrough curves with this model, the apparent diffusion coefficient used in these fits is flow dependent. Because this does not make physical sense, we reject the use of the Rosen model.

Second, we assume that mass transfer and reaction from the fluid onto the polymer surface controls adsorption (Ruthven, 1984). This assumption leads to good fits of the breakthrough curves if we also include a dispersion coefficient (Lapidus and Amundson, 1952). Our rate constants for adsorption vary from 10^{-4} to 0.02 s^{-1}, which is slow for diffusion control but consistent with chemical kinetics control. Our values of the dispersion coefficient E vary widely, from 3×10^{-7} to 1×10^{-4} cm^2/s in the membrane, and from 2×10^{-2} to 2 cm^2/s in the packed bed. The turbulent Péclet numbers, however, vary only from 0.1 to 0.8 in both the membrane and the bed. This dimensionless group is defined as bed length times superficial velocity divided by E (Suen et al., 1992). We feel any more analysis without more data is excessively speculative.

We should confess that our original objective in this research was not to make selective ion exchangers, but rather to make solid membranes capable of facilitated diffusion. Facilitated diffusion occurs when a reactive group, somehow restrained within a membrane, reacts with the solute of interest and enhances—"facilitates"—that solute's transport across the membrane. Because these reactions are often highly selective, the resulting membrane separations could have commercial value.

Many membranes that show selective facilitated diffusion have been carefully described in the literature (Noble et al., 1989; Cussler, 1990, 1994). These membranes are almost exclusively thin layers of immiscible liquids or of liquid-swollen gels. Within these liquid layers, the reactive species diffuse freely, so that the selective fluxes may be fast. Past liquid membranes, however, are rarely stable for more than a few days. The resulting unstable behavior means that the commercial promise of facilitated diffusion has not been realized.

One obvious way to seize the promise of these separations is to develop solid membranes capable of facilitated diffusion. Such membranes often have been claimed to exist. Theories showing that such membranes are feasible appear sporadically (Cussler et al., 1989; Noble, 1990). Still, when the claims of facilitated diffusion in solid membranes are critically examined, the claims vanish, at least to date.

We had hoped that ultrathin, nonporous films of the materials used in this work would at last be membranes capable of facilitated diffusion in solids. They are not. When such films are operated in steady state, they do not show selective transport (Yang, 1993). They have fluxes that vary linearly with the concentration difference across the membrane, and so do not show the "saturation" that is the hallmark of the facilitated mechanism. When these films are operated in unsteady state, they do show transiently selective fluxes and they can give data that implies saturation (Yang, 1993; Cussler, 1994). This fosters our suspicions that many earlier reports of facilitated transport in solid membranes are nothing more than artifacts of unsteady-state experiments.

Acknowledgments

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