Fractional Extraction with Hollow Fibers with Hydrogel-Filled Walls

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Extractions using hollow fibers can be faster and more efficient than those in conventional equipment. These advantages, due to the large area per volume possible with fibers, can be compromised by accidental convection through the fibers' pores. When these pores are filled with gels of crosslinked polyvinyl alcohol, convection through the pores is stopped but the overall mass transfer is unaltered. The separations across these gel-filled fiber walls provide excellent yield and purity, especially in the case of fractional extraction.

Introduction

Modules made with microporous hollow fibers are an efficient method of effecting gas adsorption and liquid extraction. They have mass transfer coefficients similar to those in conventional equipment, but they provide larger surface area per volume. As a result, they usually can achieve the same performance as conventional equipment in a smaller volume.

The advantages of hollow fiber modules are great especially in liquid-liquid extraction (Lee et al., 1976; Ho et al., 1976; Kiani et al., 1984; D'Elia et al., 1986; Prasad et al., 1986; Dahuron and Cussler, 1988). The reason is that the flows of feed and solvent can be adjusted independently. In contrast, in conventional differential extractors, these flows are fixed by the density differences between feed and solvent. In hollow fibers, they can be individually adjusted even when feed and solvent have the same density. These advantages seem useful especially in the extraction and purification of antibiotics, where hollow fiber modules are already a proven alternative to expensive centrifugal extractors (Prasad and Sirkar, 1988, 1990).

In this article, we want to develop hollow fiber extraction in two important ways. First, we want to test the performance of microporous hollow fibers whose pores are filled with hydrogel. Second, we want to use fiber modules for fractional extractions. Each of these goals merits discussion.

We want to test hollow fibers with gel-filled walls to avoid the disadvantages of past fiber-based extractions. To date, the better hollow fiber extractions have used microporous hydrophobic hollow fibers. These fibers are typically wet by the organic extractant, but not by the aqueous feed. They sometimes allow some solvent to leak into the aqueous solution, leading to entrainment and emulsion formation. In some cases, this entrainment can be avoided by applying a static pressure to the aqueous phase which doesn't wet the fibers (Prasad et al., 1986; Prasad and Sirkar, 1988). This static pressure presumably forces the solvent-water interface back into the pores, away from any shear forces which might cause entrainment.

Applying a static pressure on the nonwetting phase improves hollow fiber extractions in the laboratory. Such a static pressure is often successful at larger scales. Still, it can be inconvenient or difficult in large modules, where the pressure drop along the module length can be as big as the static pressure difference. In addition, surface active species in either the feed or the extract can wet the fiber. Such "wet-out," which sometimes occurs after days of successful operation, can lead to entrainment, emulsification, and a compromised extraction.

We want to test hollow fibers with hydrogel-filled walls to avoid both the "wet-out" and the need for static pressure. The pores in these fibers are filled with cross-linked polyvinyl alcohol which prevents either the feed or the solvent from accidently flowing across the walls. Still, while we may avoid the usual entrainment problems, we know that we may seriously retard the mass transfer. Thus, our first goal is to determine both the merits and demerits of these gel-filled fibers.

Our second goal, developing fractional extraction, comes from the past focus on high-value-added antibiotics, steroids, and proteins. The value of these products justifies extensive purification. Often, the price willingly paid for this purification is dilution with a solvent or water. For example, in chromatography, a pulse of mixed solutes is dramatically diluted to separate the solutes as distinct eluted peaks. This dilution involves many theoretical plates or many transfer units, and so provides extensive purification.

Similar purification can be provided by fractional extraction

(Belter et al., 1988). In such an extraction, water and solvent flow countercurrently in either a differential extractor or a hollow-fiber module. When two solutes are injected continuously near the center of the module, one is eluted from one end of the module, and the other flows out the other end. As in chromatography, the quality of the purification depends on the number of stages or transfer units (Lo et al., 1983; Young, 1989). Conventional extractors commonly have fewer than five transfer units; hollow fiber extractors routinely promise ten or more. Our second goal is to test this promise.

In the rest of this article, we pursue these two goals of gel-filled fibers and of fiber-based fractional extractions. In the theory below, we show how gel-filled fibers compare both with conventional extractions and with other hollow fiber extractions. We show how fiber-based fractional extraction parallels conventional, staged, fractional extraction. We then compare the performance anticipated from this theory with experiments using microporous hollow fibers, with and without hydrogel-filled walls.

Theory

Liquid-liquid extractions in microporous hollow fibers are described by the same basic equations used for conventional liquid-liquid extractions. In particular, the length of an extractor ℓ is given by (Belter et al., 1988):

$$\ell = HTU \cdot NTU \tag{1}$$

The number of transfer units NTU is a measurement of the difficulty of the extraction:

$$NTU = \frac{E}{E-1} \ln \left[\frac{Ky_\ell - x_\ell}{Ky_o - x_o} \right] \tag{2}$$

in which $E(=KL/H)$ is the extraction factor; H and L are the flows of water and solvent, taken as constant; y_ℓ and x_ℓ are the concentrations in water and solvent at the end of the module where the water enters; y_o and x_o are the corresponding concentrations where the water exits; and K is an equilibrium partition coefficient, the solute concentration in the solvent divided by the aqueous solute concentration at equilibrium. The height of a transfer unit HTU refers not to the difficulty of the process, but to the efficiency of the equipment:

$$HTU = \frac{v_H}{ka} \tag{3}$$

in which v_H is the water velocity, a is the surface area per volume, and k is an overall mass transfer coefficient.

The success of extractions based on hollow fibers with gel-filled pores hinges critically on the overall mass transfer coefficient k contained within the HTU. This coefficient is given by (Cussler, 1984; Yang and Cussler, 1986):

$$\frac{1}{k} = \frac{1}{k_H} + \frac{1}{k_M} + \frac{K}{k_L} \tag{4}$$

where k_H, k_M, and k_L are the mass transfer coefficients in the water, across the membrane, and in the solvent, respectively. In conventional equipment, the term involving k_M is missing. However, because k_M is often large (Prasad et al., 1986; D'Elia et al., 1986; Dahuron and Cussler, 1988), its presence rarely has a dramatic effect of hollow-fiber extraction.

Gel-filled hollow fibers make the situation more complicated. In the case considered here, the hollow fibers are microporous, and their pores are filled with cross-linked, hydrophilic polyvinyl alcohol. In this case,

$$k_M = \frac{D}{\delta} \tag{5}$$

where δ is the thickness of the fiber's wall and D is an effective diffusion coefficient (Cussler, 1984). The value of D includes any fiber void fraction and tortuosity. In contrast, in the past hollow-fiber extractions, the fibers are usually hydrophobic, wet by the solvent but not by the water. In this past case,

$$k_M = \frac{DK}{\delta} \tag{6}$$

Because K is often much greater than one, this change in fiber wetting may significantly alter the overall mass transfer coefficient k, and hence the module performance. We will explore this point experimentally later.

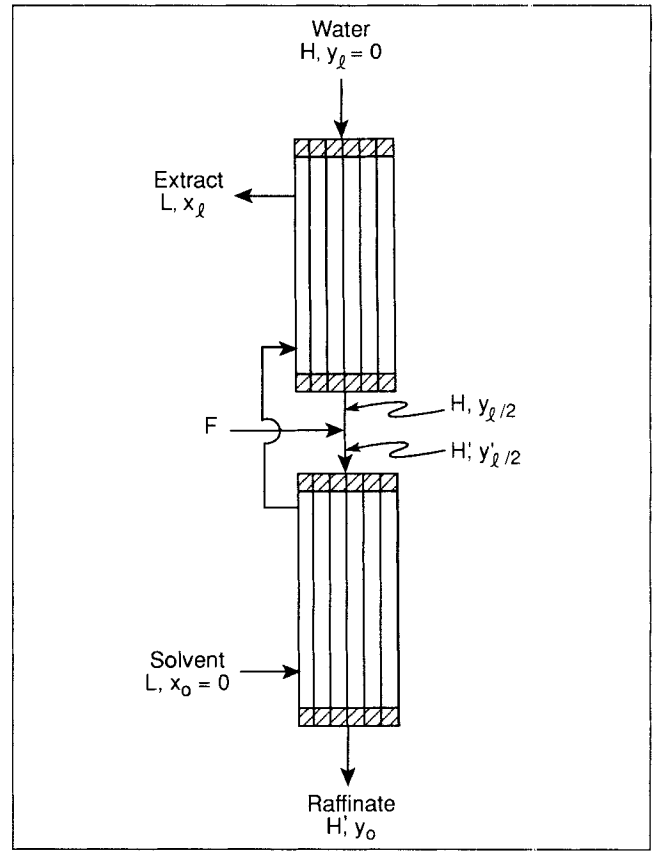

Figure 1. Fractional extraction.

Water inside the hollow fibers flows countercurrently to solvent flowing outside the hollow fibers. Solutes are fed to the aqueous stream between the two hollow fiber modules.

We can most easily adapt this analysis to fractional extraction by imagining that the hollow fiber module is split into two equal sections, shown schematically in Figure 1. The restriction to equal sections is made only to simplify the algebra and can be easily removed by paralleling developments in the literature (Lo et al., 1983). The two modules shown in Figure 1 are connected in series; water and solvent flow countercurrently through each module at the rates and concentrations shown. A small amount of aqueous solution flows into the aqueous stream between the modules. As a result, the solute concentration in the water coming out of one module is not equal to that going into the next module:

$$F + Hy_{\ell/2} = Hy'_{\ell/2} \tag{7}$$

where F represents the feed rate of solute. Note that the solute concentration reaches a maximum near this feed point, and drops where H and L enter and leave.

We expect that the performance of each half-module will be described by Eq. 1. Thus, for the lower rectifying section, we find:

$$\frac{NTU}{2} = \frac{E}{E-1}\ln\left[\frac{Ky'_{\ell/2} - x_{\ell/2}}{Ky_o}\right] = \frac{E}{E-1}\ln\left[\frac{(E-1)y'_{\ell/2} + y_o}{Ey_o}\right] \tag{8}$$

For the upper stripping section,

$$\frac{NTU}{2} = \frac{E}{E-1}\ln\left[\frac{Ey_\ell^*}{Ey_\ell^* - (E-1)y_{\ell/2}}\right] \tag{9}$$

where y_ℓ^* equals x_ℓ/K. Combining Eqs. 7, 8 and 9, we find the ratio of concentrations:

$$\frac{y_\ell^*}{y_o} = \left[\frac{e^{\frac{NTU(E-1)}{2E}} - 1}{E - e^{-\frac{NTU(E-1)}{2E}}}\right] \tag{10}$$

This ratio is easily related to the yield Y:

$$Y = \frac{Lx_\ell}{F} = \frac{LX_\ell}{Lx_\ell + Hy_o} = \frac{1}{1 + \frac{y_o}{Ey_\ell^*}} \tag{11}$$

Equations 10-11, which are similar to those developed for staged operations (Brian, 1972), describe the performance of fractional extraction using hollow fiber modules.

Several limits of these results may clarify their physical significance. These limits depend on our expectation that hollow fiber modules will have a large value for the NTU. In this case, the key in Eqs. 10-11 is the sign of the term $(E-1)$. When this is positive, we find:

$$Y \doteq \frac{1}{1 + e^{-\frac{NTU(E-1)}{2E}}} \tag{12}$$

When the term $(E-1)$ is negative,

$$Y \doteq Ee^{\frac{NTU(1-E)}{2E}} \tag{13}$$

These results predict that a plot of Y vs. E should have the shape of a titration curve, a prediction that can be tested experimentally.

Experimental Studies

Materials

All chemicals were from Aldrich, except as noted. Benzoic acid was recrystallized once from water. Acetylfuran, o-vanillin and 3-nitrobenzoic acid were reagent grade and used as received. Divinylsulfone, polyvinyl alcohol (MW = 10 ~ 30 $\times 10^3$, Air Product and Chemicals, Inc., Allentown, PA), and polyoxyethylene sorbitan monosterate (Tween 60, Sigma) were used without further purification. 1-Octanol and 2,2,4-trimethylpentane were HPLC grade and were used as received. Water was distilled twice and buffered with suitable amounts of reagent grade of acetic acid, boric acid, phosphoric acid and sodium hydroxide.

Experiment

Experiments with a single hollow-fiber module followed the procedure used in earlier extraction studies (Prasad and Sirkar, 1988; Dahuron and Cussler, 1988), and so are not reviewed here. The equipment used in fractional extraction is shown schematically in Figure 2. In this equipment, two hollow-fiber modules are connected together in series. One module functions as a rectifying column and the second as a stripping column. Two pumps [FMI metering pumps model RP-G6 with 1/8 in. (3.2 mm) piston heads] force the two immiscible liquids to flow countercurrently through the modules. The aqueous phase is in the lumen of the hollow fibers, and the organic phase is on the shell side. Aqueous solutes are fed with a third identical pump into a tee in the aqueous stream between the two columns. The output of either the aqueous or the solvent stream can be attached to a UV-visible spectrophotometer (Micrometrics, Model 787 A) attached to an Apple Macintosh data analysis system. Details of this analysis, developed for the studies of high-pressure liquid chromatography, are given by Schisla (1990). For benzoic acid and 3-nitrobenzoic acid, concentrations were measured at 233 nm; for o-vanillin and acetylfuran, they were monitored at 255 nm.

The key to these experiments is the hollow-fiber modules. The modules, constructed as detailed elsewhere (Ding et al., 1989; Schisla, 1990), use microporous polypropylene hollow fibers (Celgard, Hoechst-Celanese Separations Products, Charlotte, NC). These fibers have inner diameters from 100 to 400 μm, with a wall thickness around 25 μm and a void fraction of around 35%. After the modules are made, the pores in the fibers are filled with a gel made of cross-linked polyvinyl alcohol. This filling involves three steps. First, the fibers are made water-wettable by washing with a solution of 1 g TWEEN 60, 40 cm^3 of distilled water and 60 cm^3 of methanol. After

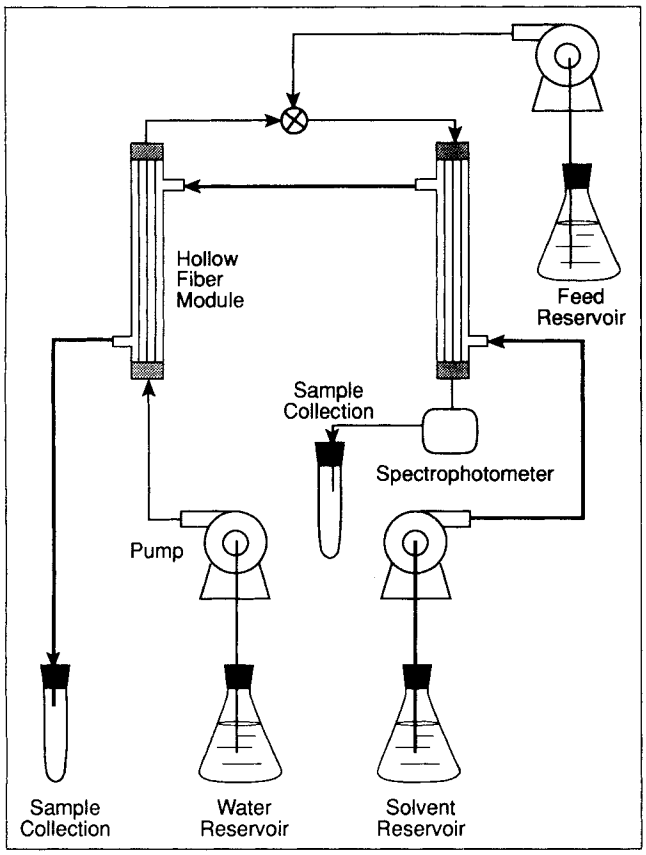

Figure 2. Experimental apparatus.

A feed containing two solutes can be continuously separated even when the solutes have very similar partition coefficients.

this washing, the module is dried. In the second step, the fibers are filled by pumping a solution of 1.1 wt. % divinylsulfone, 5.6 wt. % polyvinyl alcohol, and 93.3 wt. % water through the fibers' lumens. This is followed by pumping distilled water through the fibers to remove the polymer not captured in the fiber wall. In the third step, the polyvinyl alcohol is cross-linked by pumping a 55°C solution of 20 wt. % NaOH and 80 wt. % water through the fibers. The gel forms within seconds. After a few minutes of treatment with base, the module is carefully washed. This procedure gives gel-filled fibers with diameters within ± 2 μm, a variation similar to the unfilled fibers. The resulting gel-filled fibers will stand pressure drops across the wall of at least five atmospheres without failure. We did not investigate higher pressures because they are not needed for our experiments.

Procedure

Modules made with gel-filled fibers require no special precautions in their use. The only potential difficulty might occur if the modules were allowed to dry, which we did not permit. However, experiments with unfilled fibers do require a definite procedure to avoid emulsification and entrainment. First, the solvent is slowly pumped into the shell side of each module; and then the aqueous phase is slowly loaded. A static pressure on the aqueous phase was then applied, following the guidelines established by Sirkar and coworkers (Kiani et al., 1984; Prasad and Sirkir, 1988). This static pressure is often around 70 kPa, substantially less than that expected from the nominal pore size of 30 nm. Determining an appropriate static pressure is often tedious, but straightforward, for the single module used for conventional extraction, but annoyingly difficult for the two modules in series used for fractional extraction.

The results from simple extraction experiments are most easily summarized in terms by a mass transfer coefficient k, calculated from

$$k = \frac{v_H}{\ell a}\left\{\frac{E}{E-1}\ln\left[\frac{y_\ell - x_\ell/K}{y_o}\right]\right\} \tag{14}$$

where v_H is the feed velocity, ℓ is the module length, a is the surface area per module volume, and E is the extraction factor KL/H. The concentrations y_ℓ and y_o are in the aqueous feed and raffinate, respectively; the concentration x_ℓ is in the extract leaving the module. Note that the quantity in braces corresponds to the number of transfer units under the experimental conditions. The results from fractional extractions are not reported as mass transfer coefficients, but as the yield.

Results

This work tests two new features of hollow-fiber extraction. The first test is to determine mass transfer coefficients for microporous hollow fibers with hydrogel-filled pores. Such gel-filled fibers promise more routine liquid extraction, but at potentially compromised performance. The second aim of this work is to use the filled hollow fibers for fractional extraction. This fractional method promises continuous purification of similar solutes at a price of dramatically diluting both solutes. Fractional extraction is clumsy in conventional equipment.

Mass transfer coefficients

The chief characteristics of hydrogel-filled hollow fibers are shown in Figure 3. This figure gives the mass transfer coefficient k, calculated from Eq. 14, as a function of the aqueous velocity in the hollow-fiber lumen. The data in Figure 3a, for four different modules constructed in the same way, test the reproducibility of the gel coating. Three of the columns agree closely: they show a mass transfer coefficient which increases with the cube root of the aqueous velocity. The fourth column seems to give a more constant mass transfer coefficient, slightly *larger* than the values of the other three columns. The scatter in the data, typical of mass transfer measurements, prevents more exact conclusions. The data suggest that the gel filling is uniform and reproducible, at least in three of the four columns. The suggestion is also supported by liquid chromatography experiments, where the uniformity of the filling can be tested more exactly (Schisla, 1990).

The mass transfer coefficients for gel-filled fibers are close to the values for unfilled fibers, as shown in Figure 3b. In particular, the open circles for the gel-filled fiber, which are the most complete data set in Figure 3a, agree with results on unfilled fibers, shown as filled symbols. The data on unfilled fibers were obtained for similar solutes, but with different procedures. All these data are for organic acids; some data for phenol and nitrophenol were obtained for unfilled fibers by Dahuron and Cussler (1986); and more data for unfilled

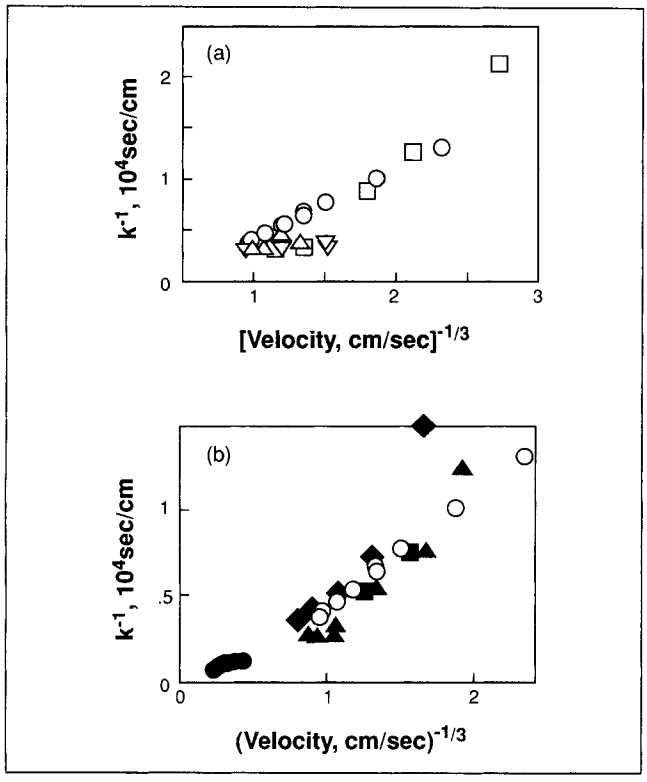

Figure 3. Performance of gel-filled and unfilled hollow fibers.

Part a tests the reproducibility of extractions from water at pH 5.0 across gel-filled fibers into 10% octanol—90% octane (○ and ▽, benzoic acid; □ and △, 3-nitrobenzoic acid).
Part b compares filled fibers (open symbols) and unfilled fibers (closed symbols). [○ and ▲, benzoic acid (this work); ●, phenol (Basu et al., 1990); ●, *p*-nitrophenol (Dahuron and Cussler, 1986).]

fibers were obtained by Basu et al. (1990). All data seem in agreement.

Thus, in these experiments, hollow fibers whose pores are filled with hydrogel give the same mass transfer coefficients as hollow fibers that are not filled. This means that for the systems studied here, filled fibers should provide the same rapid extractions as unfilled fibers. They will do so without the inconvenient static pressures required in unfilled fibers.

We recognize that, in cases not studied here, filled fibers may sometimes give smaller mass transfer coefficients and hence compromise performance. Obviously, this would be true for macromolecular solutes that diffuse freely through the 30-nm pores, but which can't diffuse through the cross-linked gel filling. More subtly, this might be true for strongly hydrophobic solutes being extracted from a rapidly flowing aqueous feed. In this second case, the resistance to mass transfer in the feed and stripping solutions might be minor, and the resistance of the gel-filled membrane might dominate performance.

Our surprised delight at the mass transfer coefficients in Figure 3 is also tempered by a broader concern common to both filled and unfilled fibers. In Figure 3, we plotted the inverse of the mass transfer coefficient vs. the inverse cube root of feed velocity because previous studies suggest this as a means of linearizing data (Yang and Cussler, 1986; Prasad et al., 1986). Such a plot should give an intercept related to the diffusional resistances of the membrane and stripping solution. Such a plot should give a slope related to the diffusion resistance in the feed solution and close to that estimated by the Lévèque analysis (1928).

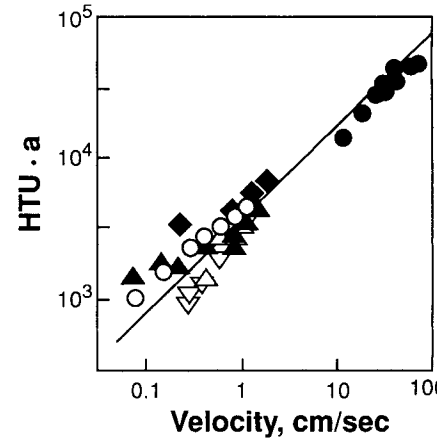

Figure 4. Height of a transfer unit of hollow fiber modules.

These data replotted from Figure 3 appear to show less scatter. The symbols refer to the same systems as in the earlier figure; the quantity ($HTU \cdot a$) is dimensionless.

Plotting the data as shown in Figure 3 does effectively organize the data, and so seems superficially consistent with those earlier studies. However, the intercept on these plots may be negative, especially in Figure 3a. A negative intercept makes no physical sense. The slope of these data may increase at low velocities, especially for the unfilled fiber results in Figure 3b. These problems may mean that the analysis of mass transfer should include ionization, which can explain apparently negative intercepts (Semmens et al., 1990). These problems may reflect polydispersity of the hollow-fiber diameters, which causes smaller values of k at low velocities (Cussler, unpublished).

Mass transfer data can also be plotted as *HTU*'s, the "height of a transfer unit" basic to earlier analyses of chemical engineering separations. Such a plot is given in Figure 4 for the same data given in Figure 3b. Again, filled and unfilled fibers

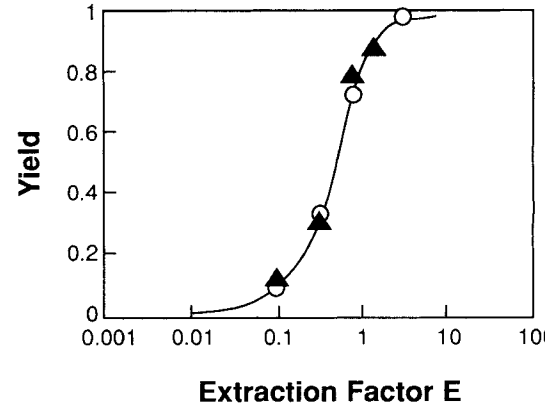

Figure 5. Conventional extraction with coated hollow fibers.

The aqueous feed at pH 5.0, containing benzoic acid, is extracted with 10% octanol-90% octane. The open and closed symbols refer to velocities of 0.28 and 0.15 cm/s, respectively.

give equivalent results. The *HTU*'s are often described as a measure of the efficiency of a separation and are closely related to the height of an equivalent theoretical plate used to describe chromatography. A small *HTU*, representing efficient contacting, is viewed as good. A large *HTU*, possibly caused by channeling in a badly packed tower, is viewed as bad.

However, while *HTU*'s sometimes give a convenient description of conventional separation equipment, they give a flawed description of a hollow-fiber extraction for two reasons. The first reason comes from the definition of the *HTU*, given in Eq. 3: the *HTU* varies linearly with the velocity. When the velocity in the fibers goes to zero, the mass transfer coefficient k remains finite, so the *HTU* goes to zero. But having a *HTU* equal to zero doesn't imply efficient equipment; it merely implies equipment without flow, producing nothing. This limit doesn't occur in conventional separation equipment, where density differences force flow.

The second flaw in the *HTU*'s for hollow fibers is that their use can make bad data look good. The data in Figure 4 do show some scatter, but apparently less than the same data in Figure 3b. The reason for the apparently smaller scatter is that the *HTU*'s are proportional to the velocity, perturbed by the dependence on velocity of the mass transfer coefficient k. Thus, Figure 4 is close to a plot of velocity vs. velocity, so smaller apparent scatter is hardly surprising.

Extractions

Thus, the mass transfer coefficients across hydrogel-filled hollow fibers are within experimental error of these found for unfilled hollow fibers. We now turn to the extractions possible with these filled hollow fibers.

Typical results for conventional extractions are shown in Figure 5. These results are like these found for other hollow-fiber extractions. They were obtained on a single, gel-filled hollow-fiber module containing 60 fibers, 40-cm-long and of 240-μm internal diameter. An aqueous feed containing 0.16 wt. % benzoic acid at pH 5.5 flows through the fibers' lumens; a solvent stream of 10 wt. % octanol in octane flows outside the fibers. When the extraction factor E is much greater than one, the fraction extracted—the "yield"—is near 100%; when E is much less than one, the yield is small.

The results in Figure 5 include experiments at two different velocities of 0.15 and 0.28 cm/s. The results agree fairly closely, showing that the curves are not a dramatic function of the number of transfer units. From the mass transfer coefficients in Figure 3 and Eqs. 1 and 3, we find this number is around 9 for the slower velocity and 5 for the faster velocity. The curves predicted from Eq. 2 are similar and agree reasonably well with the data. This result for conventional extraction implies that fractional extraction will be dominated by the extraction factor and influenced less by the height of a transfer unit.

The results for fractional extraction are given in Figures 6–7. The benzoic acid and nitrobenzoic acid experiments used to two identical modules, each of which was 31-cm-long and contained 96 gel-filled fibers 240 μm in diameter. The acetyl furan-vanillin experiments also used two identical modules, each of which was 30-cm-long and contained 120 unfilled fibers 240 μm in diameter.

The results in Figure 6, for an equimolar feed of benzoic acid and 3-nitrobenzoic acid, show that the yield is a strong function of the pH. At pH less than three, the acids are protonated and more soluble in the organic phase than in water. As a result, the yield is high, near 100%. At pH greater than five, the acids are ionized and the yield is low. The differences between benzoic acid and 3-nitrobenzoic acid reflect different values of the acids' pKa's and can produce highly selective fractional extractions. For example, at a pH of 4.2, the extract contains 97% of the benzoic acid at a purity greater than 99%; and the aqueous phase contains 99% of the 3-nitrobenzoic acid with a purity of about 98%.

The separations shown in Figure 6 are due to differences in extraction factor caused in turn by differences in the pH-dependent partition coefficient. To show that this is so, we can replot the data in Figure 6 as a function of the extraction factor. The new plot, Figure 7, shows that these data collapse to a single curve predicted reasonable closely by Eq. 11. The superposition of these data and their agreement with the prediction provide support for the theory developed in the first section of this article. Figure 7 also contains results for the fractional extraction of acetyl furan and vanillin using unfilled hollow fibers. The results for these solutes agree roughly with

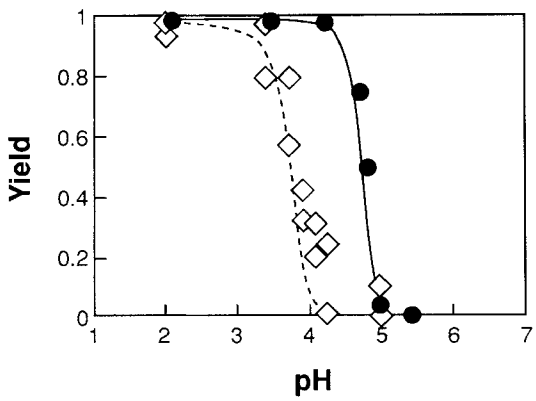

Figure 6. Fractional extraction with gel-filled hollow fibers.

The open and closed symbols refer to 3-nitrobenzoic acid and benzoic acid, respectively.

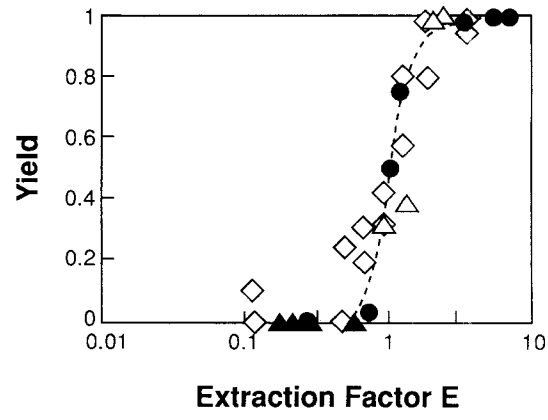

Figure 7. Fractional extraction vs. extraction factor.

The filled triangles are for vanillin and the open triangles are for acetylfuran; other symbols are those in Figure 6. When the results in Figure 6 are replotted vs. extraction factor, they fall on a single curve predicted from Eqs. 10–11, assuming that *NTU* equals 22.

those for the benzoic acids. This agreement implies that the number of transfer units, and hence the mass transfer coefficients, are similar for gel-filled and unfilled fibers. Thus, Figure 7 is consistent with Figure 3.

However, the results in Figure 7 say nothing about the relative difficulty of gel-filled and unfilled experiments. The gel-filled fibers give reliable results without special precautions, but the unfilled fibers require exquisite adjustment of pressures on the nonwetting, aqueous phase. While these pressures are relatively easily adjusted for a single module, they are much harder to discover for the twin modules used in fractional extraction. This is especially true for solutes that are surface active, like the benzoic acids. In fact, the data for the unfilled fibers in Figure 7 represent only those experiments where no entrainment occurred. This was about one tenth of the experiments made. Such entrainment never occurs with the gel-filled fibers.

Discussion

This research has two goals. The first is to determine the value of gel-filled hollow fibers in extraction, especially as reflected in the mass transfer coefficients. The second goal is to test the fibers for fractional extraction. In this section, we explore the extent to which we have realized these goals.

We have shown that gel-filled hollow fibers have considerable promise in extraction. They do not require careful adjustment of static pressures to avoid entrainment and emulsification, as unfilled fibers do. We believe that the mass transfer coefficients across these gel-filled fibers will not be much less than those unfilled fibers; indeed, in our experiments, they are indistinguishable.

We should stress that we do not always expect filled and unfilled fibers to have indistinguishable coefficients. As suggested by Eq. 4, the mass transfer resistance in extraction will be the sum of three resistances: that in the feed, that across the membrane, and that in the extract. The resistance across the membrane is that affected by the gel. This altered membrane resistance will occur because of changes in diffusion coefficient and changes in partition coefficient. For most solutes, especially those of modest molecular weight, we expect that changes in the diffusion coefficient will be less important than changes in partition coefficient. Thus, we recommend that the hollow fibers be filled with hydrogels for the extraction of hydrophilic solutes and that they be filled with organic-swollen gels for hydrophobic solutes. We must emphasize that this recommendation is not directly tested in this work, for we studied no gels other than cross-linked polyvinyl alcohol. Still, this recommendation parallels that successfully used for extractions with unfilled fibers. In making it, we demonstrate our confidence in having achieved our first goal.

We are less sanguine about achieving our second goal, the test of filled hollow fibers for fractional extraction. To be sure, we have shown that fractional extraction works well and that its performance can be predicted using the theory developed above. However, we do not know whether hollow-fiber fractional extraction provides a new practical, large-scale separation process because we haven't tried it at large scale. We are encouraged that conventional hollow fiber extraction can outperform conventional extraction equipment, including centrifugal extractors (Prasad and Sirkar, 1990). However, we share the frustration of the reviewers of this article, who urged a broad quantitative comparison with conventional equipment. We really don't know how to make such a comparison without a lot of guessing.

We can identify two competing methods for fractional extraction using hollow fibers. The first of these is the well established Craig extractor (Belter et al., 1988). In this device, an extracted fraction in one tube is repeatedly shaken with fresh solvent and then partly decanted into a new tube. The result, often involving hundreds of shakings and hundreds of tubes, is a roughly Gaussian profile distributed along the array of tubes. This method can be automated, but is sufficiently complex mechanically so that it has rarely been used to purify more than gram quantities.

The second competing method is the Ito helical chromatograph (Bhushan and Ito, 1988). This method uses an epicyclically rotating helical column to periodically mix and separate two liquids that are flowing countercurrently. The apparatus works well, as demonstrated in spectacular photographs. It is not uncommonly used analytically. However, the mechanical complexity of the epicyclically rotating helix caused nervous giggles from the engineers with whom we have discussed its scale-up. The consensus seems to be that such scale-up is risky.

We are uncertain how we can directly compare our fractional hollow-fiber extractions with these two competing methods, especially because our experience with them is meager. Instead, we can use our results to estimate the performance of two larger modules and allow those using the Craig or Ito apparatus to make their own comparison. To do so, we assume two modules, each 1.5-m-long containing 20,000 fibers of 240-μm-diameter. The fibers' pores would be filled with the hydrogel used here. If each module were half full of fibers, it would have a volume of about 3 L and a surface area per volume of 125 cm^2/cm^3. If the flow through the fiber were 0.3 cm/s, the overall mass transfer coefficient in each module would be around 1.4×10^{-4} cm/s (cf. Figure 3), and the number of transfer units would be about nine, again in each module. This is close to that observed in Figure 5.

We now assume that equal amounts of two solutes are injected into the water flowing between the modules, as suggested by Figure 2. We adjust the water and solvent flows so that the extraction factors are 4/3 and 2/3; this implies a separation factor of two. In this case, the exiting water will contain over 99% of one solute at a purity of over 99.99%; and the solvent will leave with over 99% of the second solute at a purity of 98.9%. These values are consistent with Eqs. 10–11 and with Figure 7. If each exiting solution contains 0.5 wt. % of product, then the unit will produce about 1 kg/d of each material. While these values are speculative, other more specific values are easily estimated.

Thus, we are sure that fractional extraction works well in hollow fibers whose porous walls are filled with hydrogel. We are sure that mass transfer across these walls can be unaffected by the gel. We are less sure how to compare this method with its competition, but we look forward to learning these comparisons.

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Notation

a = area per module volume (Eq. 3)
D = diffusion coefficient
E = extraction factor (Eq. 2)
F = solute feed (Eq. 7)
H = water flow
HTU = height of transfer unit (Eq. 3)
k = overall mass transfer coefficient (Eq. 4)
k_H, k_L, k_M = individual mass transfer coefficients in the water, solvent, and membrane, respectively
K = partition coefficient
ℓ = extractor length (Eq. 1)
L = solvent flow
NTU = number of transfer units (Eq. 2)
v_H = water velocity
x = solute concentration in solvent
y = solute concentration in water
Y = yield (Eq. 11)
δ = membrane thickness

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