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A. F. Seibert[a]; X. Py[a]; M. Mshewa[a]; J. R. Fair[a]
[a] Separations Research Program The University of Texas at Austin, Austin, Texas

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HYDRAULICS AND MASS TRANSFER EFFICIENCY OF A COMMERCIAL-SCALE MEMBRANE EXTRACTOR

A. F. Seibert, X. Py, M. Mshewa and J. R. Fair
Separations Research Program
The University of Texas at Austin
Austin, Texas 78712

ABSTRACT

In recent years there has been significant interest in utilizing microporous hollow fiber membranes for liquid-liquid extraction. The membrane extractor resembles the shell and tube heat exchanger with the tube section composed of 1000-2500 fibers/in^2. The diameter of each fiber is approximately 300 microns. In this process, the feed may be passed through the shell side, while the solvent is passed through the fiber side, or vice versa. Mass transfer occurs across the liquid-liquid interface formed in the pores of the fiber wall. The advantages of this technology are high throughput capacities, independence of density difference between the feed and solvent, and potentially high mass transfer areas. The mass transfer performance of an available commercial scale nonbaffled membrane extraction module was determined to be lower than expected from results obtained in smaller scale modules. Mass transfer studies of a commercial-scale membrane extraction module at the Separations Research Program have shown that a significant portion of the fibers are bypassed by the shell side fluid and consequently only a fraction of the total fiber surface area is utilized. A hydraulic study using a dye tracer technique verified this finding with an aqueous flow on the shell side. A model which incorporates mass transfer correlations reported by others has been developed and shown to have excellent agreement with the experimental data obtained. In this paper, the efficiency of the membrane extractor is compared with conventional spray, sieve tray, and packed columns; the effect of shell side bypassing is also presented.

INTRODUCTION

Membranes are species-selective barriers, and as such have found application as specialized separation media in gas purification, reverse osmosis and

ultrafiltration. Recently, microporous membranes have been shown to have application in traditional equilibrium-based separation processes such as liquid-liquid extraction (1-10), gas absorption (11,12) and distillation (13-15).

These equilibrium based processes require dispersion of one phase into a second immiscible phase. Non-proprietary contacting devices such as trays or packings are often used to provide intimate contact of the two phases. If necessary, mechanically-aided devices are used to improve the dispersion and consequently the mass transfer efficiency relative to that of trays or packings. Unfortunately, mechanically-aided columns are expensive and may require special installation and maintenance.

Dispersion such as that observed in many liquid-liquid systems often produces emulsions that lead to coalescence problems. In dispersive countercurrent extraction there is a size distribution of drops whose movement is limited to a difference in buoyant, gravitational and drag forces. Limitations of interfacial area and capacity are present in all dispersion-based systems. Recent advances in membrane technology have identified a method of using nondispersive solvent extraction with microporous hollow fibers. Previous studies with small-scale membrane module systems have demonstrated that a high mass transfer efficiency is possible. The high efficiency is attributed to the large amount of surface area per volume present in the module. Advantages of the membrane extraction process include:

(1) Dispersion-free operation. Membrane extraction does not require a density difference between phases.

(2) Potentially high efficiency due to the very large contact area which may be ten to a hundred times that of a conventional packed column.

(3) Modular design, which eases scale-up and retrofitting of equipment.

Disadvantages of the membrane extraction process include:

(1) The process is in the embryonic stage of development and has not been proven on the commercial scale.

(2) Penetration of shell side fluid into tube bundle may be difficult.

(3) The modules may produce emulsions by improper operation. Emulsion formation may be prevented by applying an appropriate pressure differential across the membrane.

(4) Chlorinated and ketone solvents are incompatible with the epoxy resin used in present modules.

(5) A prefilter is required to prevent plugging the micron-size flow passages in the module.

The membrane extractor studied in this work resembles a shell and tube heat exchanger. The tube side comprises thousands of micron-size diameter microporous hollow fibers. Mass transfer of solute occurs at a liquid-liquid interface located in the porous walls of the hollow fibers. If the fibers are composed of a hydrophobic material such as polypropylene, the organic phase preferentially wets the membrane material and as a consequence the non-wetting aqueous phase must be maintained at a higher pressure but one not exceeding the pressure required to displace the organic phase from the pores. In the membrane extraction process, one phase is passed through the shell side of the membrane module while the second phase is fed countercurrently through the tube side.

It is important to note that the membrane material used in this process does not function as a species selective barrier, but rather prevents dispersion of one phase into the other. In a sense, the membrane extractor behaves as a high efficiency packing with a high surface area for mass transfer without sacrifice in throughput capacity. Like the packed column, the membrane extractor may be treated as a differential contactor with a constant area for mass transfer. The efficiency of this device may also be described by the height of a transfer unit (HTU_{ow}) and the volumetric mass transfer coefficient (K_{ow} a) as shown in Equation (1).

$$HTU_{ow} = \frac{U_w}{K_{ow}\, a} \tag{1}$$

where

$$U_w = \frac{Q_w}{A_m} \tag{2}$$

While the membrane extractor may provide a potential of 10-100 times greater area for mass transfer than the conventional packed contactor, an additional resistance to mass transfer is present. Equation (3) may be derived for a hydrophobic microporous hollow fiber with the membrane-wetting organic phase on the shell side while the aqueous phase is in the fiber lumen (tube side) at a higher

pressure. The second mass transfer resistance given by Equation (3), which is not present in conventional dispersive extraction, is due to resistance of solute transfer in the membrane pore containing the liquid-liquid interface.

$$\frac{1}{K_{ow}\, d_o} = \frac{1}{k_{wt}\, d_i} + \frac{1}{k_{mo}\, d_{lm}} + \frac{1}{m\, k_{os}\, d_o} \qquad (3)$$

where, for Equations (1) - (3),

HTU_{ow} = Height of aqueous phase transfer unit, cm
U_w = Superficial velocity of the aqueous phase, cm^3/cm^2-s
Q_w = Volumetric flowrate of the aqueous phase, cm^3/s
A_m = Cross-sectional area of module, cm^2
a = Specific surface area of membrane module, cm^2/cm^3
K_{ow} = Overall coefficient based on the aqueous phase, cm/s
k_{os} = Shell side film coefficient for mass transfer through the organic phase, cm/s
k_{mo} = Film coefficient for mass transfer within the membrane pore, cm/s
k_{wt} = Tube side film coefficient for mass transfer through the aqueous phase, cm/s
d_i = Inner tube diameter, cm
d_{lm} = Log mean tube diameter, cm
d_o = Outer tube diameter, cm
m = Distribution coefficient, $(g/cm^3)/(g/cm^3)$

The objectives of this research were to obtain mass transfer data from a commercial scale membrane extractor for direct comparison with conventional extraction devices, and to identify and quantify the effects of shell side fiber bypassing, if present.

Previous Work

Initial membrane extraction studies were performed using flat microporous hydrophobic membranes (4,6) and hydrophilic and composite hydrophobic-hydrophilic membranes (2,5). Early application studies utilizing hydrophobic microporous hollow fibers include the extraction of alcohol from a fermentation broth (16,17) and protein and enzyme extractions using biphasic and reverse

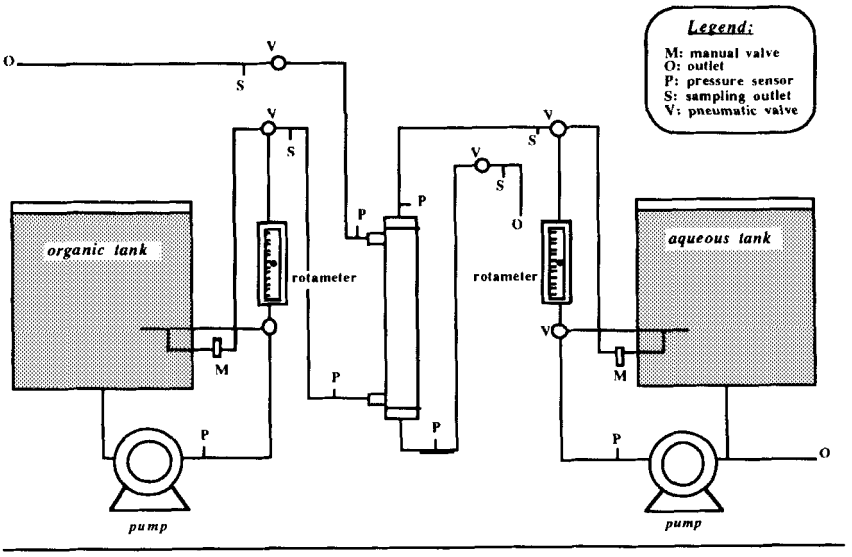

FIGURE 1. Membrane process flow system.

micelle systems (18,19). Other studies have included nondispersive metal extraction and back extraction (20). The mechanism of mass transfer in flat films and small-scale membrane extractors has been studied extensively by Sirkar and coworkers (1-6,8,9,10, 16,17).

EXPERIMENTAL METHOD

In this study, the Liqui-Cel™ MHF extractor modules were obtained from the Separations Products Division of Hoechst Celanese Corporation. A flow diagram of the experimental apparatus is given in Figure 1. The modules are solvent resistant and contain microporous hydrophobic hollow fibers of polypropylene in a nylon casing with epoxy tube sheets. The mass transfer efficiency and capacity of the Celgard X-10 module were studied in this work. Modules with fiber counts of 7500, 3000, and 1500 fibers were used in the investigation. The physical characteristics of these extraction modules are given in Table 1.

TABLE 1. MEMBRANE EXTRACTOR CHARACTERISTICS

Parameter	Characteristics		
Fiber Type	Celgard x-10		
Fiber Material	Polypropylene		
Fiber Diameter (i.d.), microns	240		
Fiber Wall Thickness, microns	30		
Effective Pore Size, microns	0.05		
Fiber Wall Porosity, %	30		
Maximum Operating Pressure, psia	60		
Temperature Operating Range °C	0-75		
Module Length, cm	61		
Module Inside Daimeter, cm	5.1		
Effective Fiber Length, cm	54.6		
Number of Fibers	7500	3000	1500
Surface Area, sq.cm/cu.cm	27.8	11.1	5.6
Packing Fraction	0.26	0.104	0.052

TABLE 2. PHYSICAL PROPERTIES OF THE MASS TRANSFER SYSTEMS

Physical Property	Toluene/Acetone/Water
Aqueous Phase	
viscosity, cp	0.92
density, g/cm^3	0.994
solute diffusion coefficient, cm^2/s	$1.29 \cdot 10^{-5}$
Organic Phase	
viscosity, cp	0.54
density, g/cm^3	0.86
solute diffusion coefficient, cm^2/s	$2.88 \cdot 10^{-5}$
slope of equilibrium line	0.82
interfacial tension, dynes/cm	22.0

The toluene/acetone/water system was chosen for study because of the availability of mass transfer data for conventional extraction contactors. The physical properties of this system are given in Table 2. Water was used to extract acetone from toluene with an initial feed composition of approximately 5 wt. % acetone. The epoxy used to seal the tube sheet was not chemically inert with acetone, and as a consequence, the lifetimes of the modules studied were limited. To extend the life of the module, at the end of each day the module was cleaned with water and dried with a nitrogen purge. This was necessary for the removal of residual acetone. (It is recommended that one question the vendor about the chemical compatibility before purchasing a module.)

The mass transfer data were obtained from a continuous, steady-state operation. Mass transfer performance of the membrane extraction device was characterized by calculating the volumetric mass transfer coefficient based on the aqueous phase. This volumetric coefficient $K_{ow}a$ was calculated as follows:

(1) The number of transfer units based on the aqueous phase (NTU_{ow}) was calculated from the flow ratio, equilibrium distribution coefficient, and steady state inlet and outlet compositions. A constant solvent/feed flow ratio was used and an average equilibrium distribution coefficient was assumed.

(2) The height of a transfer unit based on the aqueous phase (HTU_{ow}) was calculated from the contacting length of the module (Z) and the number of transfer units (NTU_{ow}) as follows:

$$HTU_{ow} = \frac{Z}{NTU_{ow}} \tag{4}$$

(3) The volumetric mass transfer coefficient ($K_{ow}a$) was calculated from the height of a transfer unit and the superficial velocity of the aqueous phase (U_w):

$$K_{ow}\,a = \frac{U_w}{HTU_{ow}} \tag{5}$$

During the shell side bypassing investigation, a dye-tracer technique was used to verify and quantify the degree of bypassing by measuring the actual residence time of the flowing shell side fluid and comparing with the calculated

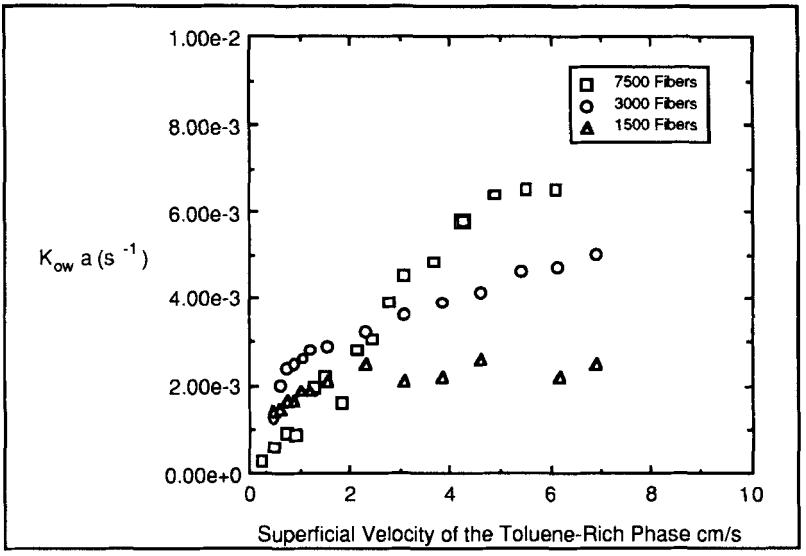

FIGURE 2. Mass transfer efficiency of the membrane extractor. System: toluene(shell)/acetone/water (tube). Shell side: organic phase. U_w = 0.22 cm/s. Direction of mass transfer: toluene--->water.

ideal residence time. The tracer solution consisted of 2 cm^3 of an aqueous solution saturated with methyl blue indicator. With stagnant conditions on the tube side, the tracer solution was injected into the flowing aqueous phase at the entrance of the shell side. The dye concentration was monitored at various locations using a spectrophotometer and recorded on a strip chart.

RESULTS AND DISCUSSION

The mass transfer efficiency of the commercial-scale membrane extractor and its dependence on the shell side flowrate are illustrated in Figure 2. The volumetric aqueous phase mass transfer coefficient ($K_{ow}a$) was observed to increase with the shell side superficial velocity with a constant aqueous superficial velocity of 0.22 cm^3/cm^2-s. The superficial velocity is the phase flowrate per cross sectional area of the module. At high shell side velocities, the efficiency eventually becomes independent of flowrate. At these conditions, the rate of mass transfer is controlled by the pore and tube side mass transfer resistances.

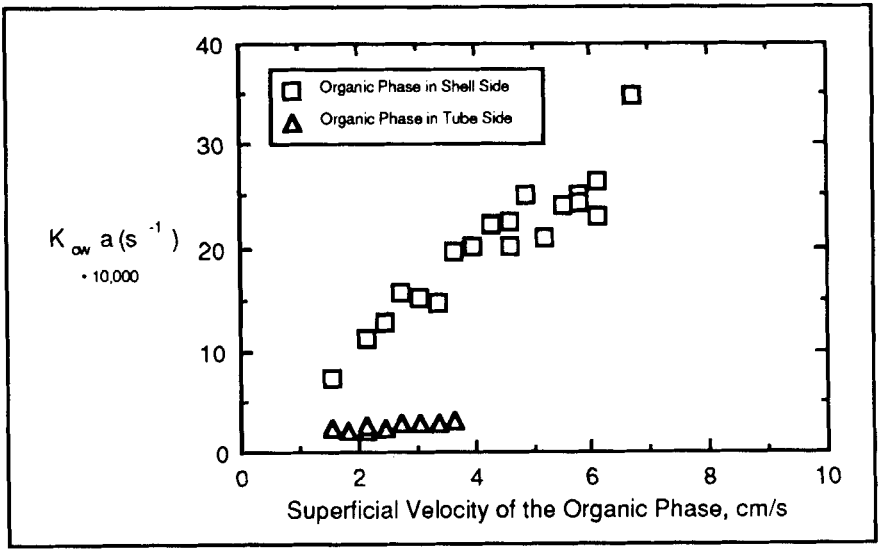

FIGURE 3. Effect of tube or shell side flow on the mass transfer efficiency. System: toluene/acetone/water. Aqueous phase velocity = 0.22 cm/s. Direction of mass transfer: toluene--->water. Fiber count = 7500.

As shown in Figure 3, for a constant aqueous phase superficial velocity of 0.22 cm/s the capacity and efficiency are greater when the organic phase is fed on the shell side. The increased capacity may be attributed to a lower pressure drop compared to passing the organic phase through the fiber side. In terms of maximizing capacity, it is generally preferred to feed the phase of significantly greater flowrate on the shell side. The efficiency was determined to be dependent on the shell side flow while being essentially independent of the tube side flow.

In Figure 4 the height equivalent to a theoretical stage (HETS) of the commercial scale membrane extractor is compared with that of conventional extractors such as the spray, sieve tray and packed (22). Surprisingly, the mass transfer performance of the membrane extractor is lower than the conventional contactors at toluene-phase superficial velocities less than 1.5 cm/s. The capacity of the membrane extractor, with the toluene-phase on the shell side, was much higher than the conventional contactors. The mass transfer efficiencies obtained in

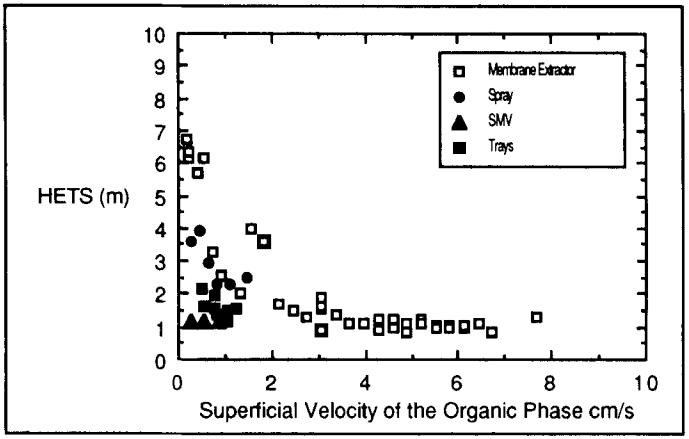

FIGURE 4. Mass transfer efficiency of the membrane extractor relative to conventional sieve trays and packings. System: toluene/acetone/water. Aqueous phase velocity = 0.22 cm/s. Direction of mass transfer:toluene--->water. Fiber count = 7500 fibers.

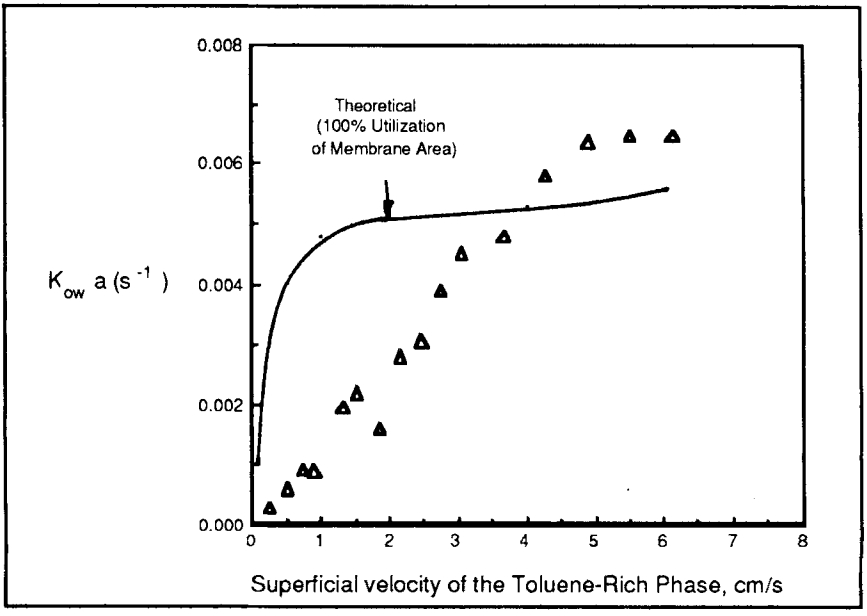

FIGURE 5. Comparison of experimental data with that predicted if all fiber area were utilized. Toluene (shell)/acetone/water (tube). Fiber count = 7500. $U_w = 0.22$ cm/s. Direction of mass transfer: toluene--->water.

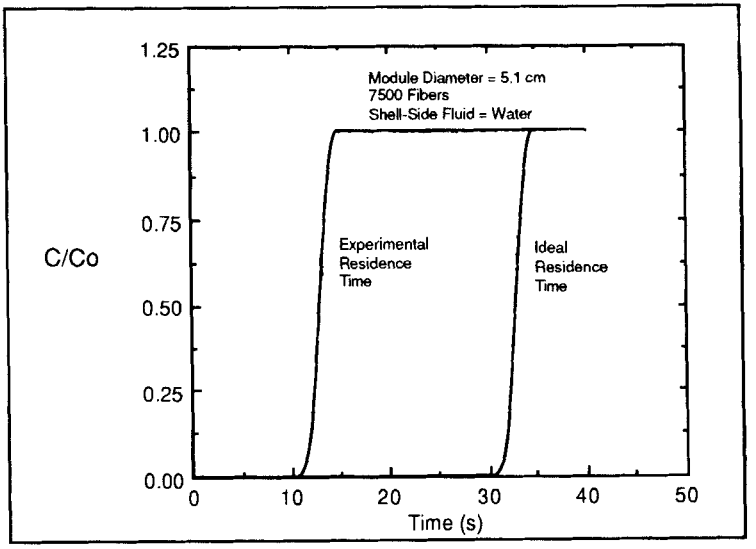

FIGURE 6. Typical residence time distribution on the shell side of a commercial size membrane extractor studied in this work.

this work were not consistent with those obtained from smaller-scale modules nor do they agree with those predicted by the previous mass transfer models (1,4) as shown in Figure 5. The comparison of theoretical mass transfer efficiency with 100% utilization of the fiber surface area is shown in Figure 5. It is assumed that for a commercial scale membrane extractor, this deviation is due to a lower fiber bundle penetration and consequently a lower effective mass transfer area. The hydraulics of the membrane extractor were investigated to verify if fiber bypassing was present.

Results from the dye tracer studies of the module with 7500 fibers indicated that the actual residence time was 3-4 times faster than the ideal residence time. A typical residence time distribution is shown in Figure 6. The ideal residence time is calculated from Equation (6). The significant deviation between the actual and ideal residence times provides verification that significant bypassing was present in the commercial-scale membrane.

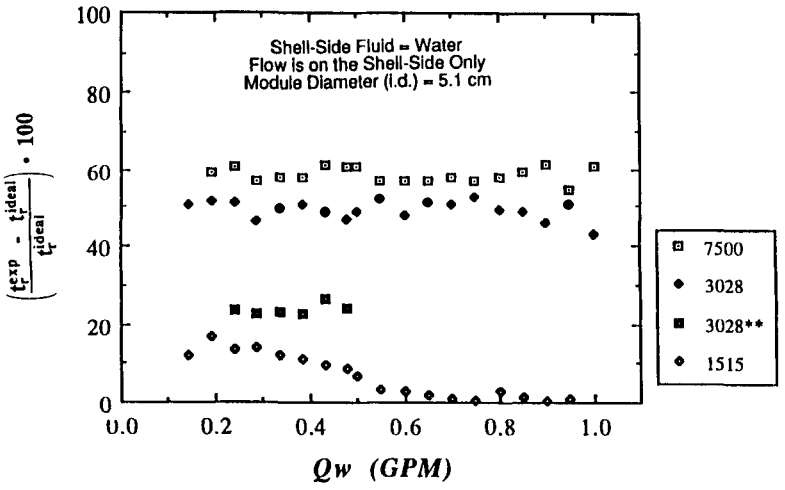

FIGURE 7. Effect of shell side flowrate on the residence time distribution deviation. The fiber count 3028** is for opposing inlet and outlet shell side nozzles.

$$t_{res} = \frac{\text{shell side void volume}}{\text{shell side flowrate}} \tag{6}$$

The effect of flowrate on the residence time deviation is shown in Figure 7. At the present time, hydraulic residence time measurements have not been performed with a commercially available module having lower fiber densities.

A simple model describing the fiber bypassing was developed and is illustrated in Figure 8. The model assumes that a fraction (α) of the shell side flow does not penetrate the bundle and merely bypasses all of the fibers along the periphery of the tube bundle. This results in a reduction in the effective interfacial area.

The dependence of the effective bypassing parameter α on the shell side rate and the fiber density is illustrated in Figure 9. The bypassing parameter was observed to decrease with shellside velocity to an asymptotic value of zero. A model for predicting the fraction of bypassed flow was developed assuming the

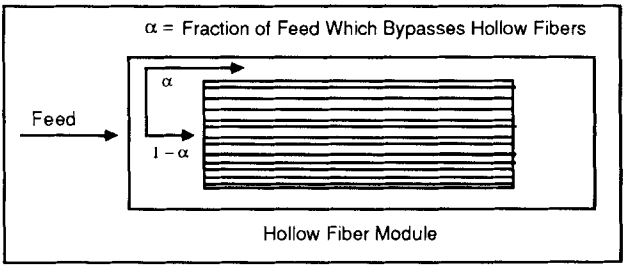

FIGURE 8. Bypassing model.

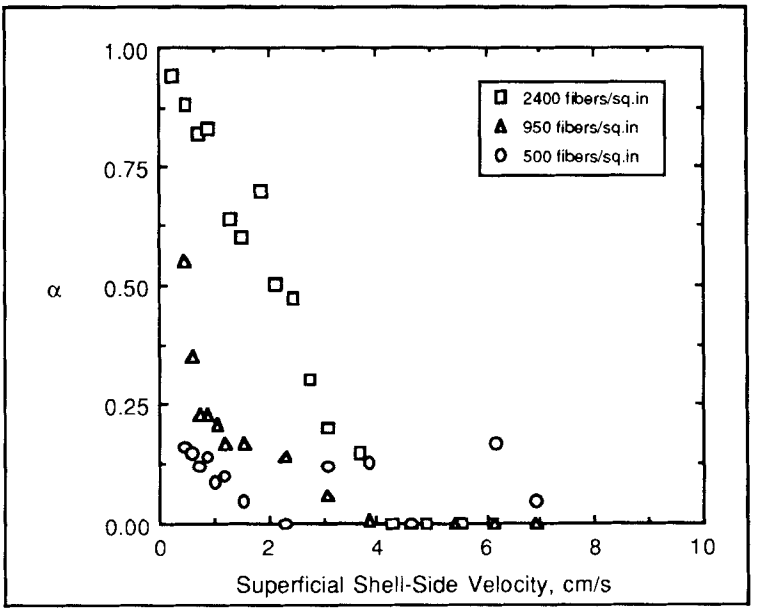

FIGURE 9. Effect of Shell-Side Velocity on the Bypassing Parameter. System: toluene (shell)/acetone/water(tube). $U_w = 0.22$ cm/s. Direction of mass transfer: toluene--->water.

TABLE 3. BYPASSING CONSTANTS FOR EQUATION (7) BASED ON THE TOLUENE/ACETONE/WATER

Fiber Count	Bypassing Constant C
7500	0.38
3000	1.4
1500	2.8

mass transfer model of Prasad and Sirkar (1,4) to be valid and determined from the experimental data of this work. The empirical correlation for predicting this parameter is given by Equation (7).

$$\alpha = e^{-CU_S} \tag{7}$$

where: U_S = shell side superficial velocity, cm/s

CONCLUSIONS

The microporous hollow fiber membrane extractor is a refreshing new device in a separation area which has been somewhat stagnant for years. It is simple and capable of handling high flowrates. At the present time, however, the supporting technology is under development and new advancements are on the horizon. While the capacity of the extractor was determined to be quite high, this occurred at the expense of a significant reduction in mass transfer efficiency. Under comparable conditions, the mass transfer performance of the first generation commercial-scale membrane extractor was less than the conventional packed, tray or spray extractor. These studies indicated that a considerable amount of fiber bypassing was occurring and as a result only a fraction of the available fiber surface area was being utilized. Approximately 10-30% of the surface area was effective based on theoretical calculations. The presence of shell side bypassing was verified by studying the deviation of the actual, experimental shell side residence time with the calculated, ideal residence time using a dye tracer technique. The actual residence time of the shell side fluid was 3-4 times shorter than the ideal residence time.

Further engineering improvements such as the elimination of the shell side bypassing and the utilization of internal baffling will likely be necessary to improve significantly the mass transfer performance. These improvements should allow the membrane extractor to become a competitive alternative to other contacting devices such as sieve trays and packings in terms of mass transfer while providing greater capacities.

Nomenclature

A_m	=	Cross-sectional area of module, cm^2
a	=	Specific surface area of membrane module, cm^2/cm^3
C	=	Empirical correlation constant for Equation (7)
d_i	=	Inner tube diameter, cm
d_{lm}	=	Log mean tube diameter, cm
d_o	=	Outer tube diameter, cm
HETS	=	Height equivalent to a theoretical stage, cm
HTU_{ow}	=	Height of aqueous phase transfer unit, cm
k_{mo}	=	Film coefficient for mass transfer within the membrane pore, cm/s
k_{os}	=	Shell side film coefficient for mass transfer through the organic phase, cm/s
k_{wt}	=	Tube side film coefficient for mass transfer through the aqueous phase, cm/s
K_{ow}	=	Overall coefficient based on the aqueous phase, cm/s
K_{ow} a	=	Volumetric mass transfer coefficient based on the aqueous phase, s^{-1}
m	=	Distribution coefficient, $(g/cm^3)/(g/cm^3)$
NTU_{ow}	=	Number of aqueous phase transfer units
Q_w	=	Volumetric flowrate of the aqueous phase, cm^3/s or gal/min
t_r	=	Residence time, s
U_s	=	Shell side superficial velocity cm/s
U_w	=	Superficial velocity of the aqueous phase, cm^3/cm^2-s
Z	=	Contacting (fiber) length, cm

Greek Symbol

α	=	Effective bypassing fraction

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REFERENCES

1. R. Prasad and K.K. Sirkar, "Dispersion-Free Solvent Extraction with Microporous Hollow-Fibers Modules", AIChE J. , 34, 177 (1988).

2. R. Prasad and K.K. Sirkar, "Microporous Membrane Solvent Extraction", Sep. Sci. Technol., 22, 619 (1987).

3. A. Sengupta, R. Basu, K.K. Sirkar, "Separation of Solutes from Aqueous Solutions by Contained Liquid Membranes", AIChE J., 34, 1698 (1988).

4. R. Prasad, A. Kiani, R.R. Bhave and K.K. Sirkar, "Further Studies on Solvent Extraction with Immobilized Interfaces in a Microporous Hydrophobic Membrane", J. Membr. Sci. , 26, 79 (1986).

5. R. Prasad and K.K. Sirkar, "Solvent Extraction with Microporous Hydrophilic and Composite Membranes", AIChE J. , 33, 1057 (1987).

6. A. Kiani, R.R. Bhave and K.K. Sirkar, "Solvent Extraction with Immobilized Interfaces in a Microporous Hydrophobic Membrane", J. Membr. Sci., 20, 125 (1984).

7. N.A. D'elia, L. Dahuron and E.L. Cussler, "Liquid-Liquid Extractions with Microporous Hollow Fibers", J. Membr. Sci., 29, 309 (1986).

8. R. Prasad, G.T. Frank and K.K. Sirkar, "Nondispersive Solvent Extraction Using Microporous Membranes", AIChE Symp. Ser., 84, 42 (1989).

9. R. Prasad and K.K. Sirkar, "Hollow Fiber Solvent Extraction of Pharmaceutical Products: A Case Study", J. Membr. Sci., 47, 235 (1989).

10. R. Prasad and K.K. Sirkar, "Hollow Fiber Solvent Extraction: Performance and Design", J. Membr. Sci. , 50, 153 (1990).

11. Z. Qi and E.L. Cussler, "Microporous Hollow Fibers for Gas Absorption II.Mass Transfer Across the Membrane", J. Membr. Sci., 23, 333 (1985).

12. M.C. Yang and E.L. Cussler, "Designing Hollow Fiber Contactors", AIChE J., 32, 1910 (1986).

13. K. Schneider and T.J. Van Gessel, "Membrane Distillation", Chem.-Ing.-Tech., 7, 514 (1984).

14. C.J.D. Fell, R.W. Schofield and A.G. Fane, "Membrane Distillation and Pervaporation as Alternatives to Conventional Distillation and Absorption Processes", I. Chem. E. Symp. Ser. No. 104, A371 (1987).

15. E. Drioli, V. Calabro and Y. Wu, "Microporous Membranes in Membrane Distillation", Pure Appl. Chem., 58, 1657 (1986).

16. G.T. Frank and K.K. Sirkar,"Alcohol Production by Yeast Fermentation and Membrane Extraction", Biotechnol. Bioeng. Symp. Ser., 15, 621 (1985).

17. G.T. Frank and K.K. Sirkar, "An Integrated Bioreactor Separator: In Situ Recovery of Fermentation Products by a Novel Dispersion-free Solvent Extraction Technique", Biotechnol. Bioeng. Symp. Ser., 17, 303 (1986).

18. L. Dahuron and E.L. Cussler, "Protein Extraction with Hollow Fibers", AIChE J., 34, 130 (1988).

19. M. Dekker, K. Van'T Riet, J.M.G.M. Wijmans and J.W.A. Baltussen, "Membrane Based Liquid/Liquid Extraction of Enzymes Using Reverse Micelles", paper 15-OA1210 presented at First International Congress of Membranes and Membrane Processes, Tokyo, Japan, June, 1987.

20. P.R. Alexander and R.W. Callahan, "Liquid-Liquid Extraction and Stripping of Gold with Microporous Hollow Fibers", J. Membr. Sci., 35, 57 (1987).

21. C.H. Yun, R. Prasad and K.K. Sirkar, "Hollow Fiber Solvent Extraction of Priority Pollutants", Paper presented at the Workshop on Advanced Aqueous Separations Techniques for Hazardous Waste Minimization, Santa Monica, Ca, April 24-25, 1989.

22. A.F. Seibert and J.R. Fair, "Hydrodynamics and Mass Transfer in Spray and Packed Extraction Columns", Ind. Eng. Chem. Res., 27, 470 (1988).