Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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John D. Lamb[a]; Ronald L. Bruening[a]; David A. Linsley[a]; Cheri Smith[a]; Reed M. Izatt[a]
[a] Department of Chemistry, Brigham Young University, Provo, Utah

To cite this Article Lamb, John D. , Bruening, Ronald L. , Linsley, David A. , Smith, Cheri and Izatt, Reed M.(1990) 'Characterization of a Macrocycle-Mediated Dual Module Hollow Fiber Membrane Contactor for Making Cation Separations', Separation Science and Technology, 25: 13, 1407 — 1419

To link to this Article: DOI: 10.1080/01496399008050400

URL: http://dx.doi.org/10.1080/01496399008050400

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 1407-1419 (1990)

CHARACTERIZATION OF A MACROCYCLE-MEDIATED DUAL MODULE HOLLOW FIBER MEMBRANE CONTACTOR FOR MAKING CATION SEPARATIONS

John D. Lamb, Ronald L. Bruening, David A. Linsley, Cheri Smith, and Reed M. Izatt.
Department of Chemistry
Brigham Young University
Provo, Utah 84602

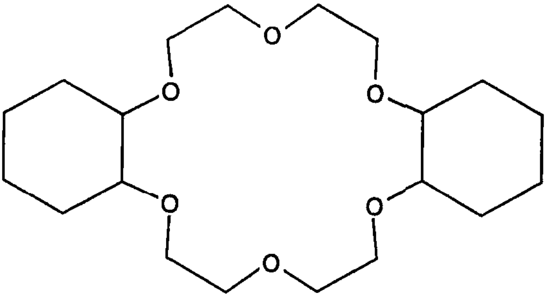
ABSTRACT

Separation of metal cations in aqueous solution by a macrocycle-mediated Dual Hollow Fiber Membrane Contactor is described. The advantages of this type of supported liquid membrane configuration include easily accessible source, receiving and membrane phases; transport rates competitive with those of other types of membranes; and the potential for continuous operation. The new system was investigated to determine the effect of aqueous solution flow rate and membrane solvent stirring rate on Na^+ and K^+ transport using dicyclohexano-18-crown-6 as the carrier. The results demonstrated that transport increases with increasing stirring speed, but remains constant with increased aqueous flow rate through the fibers within the range of four to twelve ml/min. The membrane solvents hexane, toluene, octane, 1-octanol, 4-methyl-2-pentanone, octanal, and 2-octanone were tested for their ability to preserve membrane integrity in the presence of aqueous solutions of low pH, and to maximize transport. Of these solvents, 2-octanone was found to be most effective in minimizing acid diffusion across the membrane, while giving the highest facilitated K^+ transport rate. Quantitative transport using 18-crown-6 was observed for K^+ over Na^+ (all solvents studied) and Ba^{2+} and Sr^{2+} over Ca^{2+} (only octanol was studied).

INTRODUCTION

The potential for wide application of liquid membranes has made them the subject of detailed study in recent years (1). For example, environmental concerns have led to increased interest in economical methods for removing harmful or valuable metals from solution (2-4). Liquid membranes have been investigated as possible devices to deal with these and other needs.

In many cases, it is desireable to incorporate cation selectivity into separation systems (5). Of particular promise for improving selective cation transport is the use of macrocyclic ligands, which solubilize ionic salts in non-polar liquids by sequestering the cation in a polar ligand cavity. This partitioning facilitates rapid transport through an otherwise impermeable phase. Certain macrocycles of the crown ether type, such as DC18C6, interact preferentially with specific cations (3,6-10), resulting in selective transport in liquid membrane systems. Selectivity for particular cations can be controlled by the type of macrocycle incorporated into the membrane thus making it possible to design cation selectivities into these systems.



Dicyclohexano 18-Crown-6
(DC18C6)

Several macrocycles with one or two ionizable protons have been synthesized (11-14). These crowns can exchange their protons for cations at the source interface, and then release the cations at a receiving phase interface of low pH in exchange for protons. Thus, the gradient-driven transfer of cations from high concentration to low concentration can be supplemented or completely driven by the proton transfer from low to high pH, in the reverse direction.

There are many physical configurations that liquid membranes can assume. Of the types which have been studied, the hollow fiber supported systems stand out as having promise for industrial application (15). These latter systems use porous polymeric hollow fibers as supports for the membrane solvent and macrocycle. Hollow fiber supported systems (15-19) exhibit advantageous properties such as stability, large transport rates, and easy operation with the potential to be run continuously.

In the present study, a hollow fiber membrane configuration similar to that described by Sirkar and his coworkers (18) has been tested in an attempt to improve performance over that of other hollow fiber systems. This new membrane system exhibits high fluxes, good control of individual phases, and stability over long periods of time. This system also allows for easy replenishment of membrane solvent and carrier when needed without system downtime. This is a particularly important parameter for industrial use of liquid membrane systems. The new system is described and discussed with respect to the effect of membrane solvent type, the rate at which the solvent reservoir is stirred, and the rate at which the aqueous phases are circulated through the membrane on cation transport and system stability.

EXPERIMENTAL

All chemicals were reagent grade and used as supplied from the manufacturer without further purification. Solvents used were 1-octanol (Aldrich), octane (Aldrich), toluene (Fisher), hexane (Mallinckrodt), octanal (Aldrich), 4-methyl-2-pentanone (Fisher), and 2-octanone (MCB). Dicyclohexano-18-crown-6 (Aldrich, mixture of isomers) was used as the carrier molecule in all facilitated transport experiments. Source phases were prepared from $NaNO_3$ (Fisher), KNO_3 (J.T. Baker, Fisher), $Ca(NO_3)_2$ (J.T. Baker), $Sr(NO_3)_2$ (B&A), and $Ba(NO_3)_2$ (J.T. Baker) using distilled, deionized water. Source phases of experiments using K^+ and Na^+ were 0.5 M in each cation, and those of experiments using Ba^{2+}, Ca^{2+}, and Sr^{2+} were 0.1 M in each cation. Receiving phases consisted of either distilled, deionized water; 1.0 M HNO_3 prepared from concentrated HNO_3 (Mallinckrodt); or 1.0 M HCl prepared from concentrated HCl (Mallinckrodt).

Each Dual Hollow Fiber Membrane Contactor (Figure 1) consisted of a glass 250 ml reservoir containing the source phase, and another of equal volume containing the receiving phase. These aqueous phases were circulated by means of C-Flex or Norprene (Cole-Parmer) tubing and a Masterflex (Cole-Parmer) peristaltic pump through the lumen of a fiber bundle. Each fiber bundle was constructed of 60 lengths of polypropylene microporous hollow fibers secured in a bundle using polyethylene tubing connectors and silicone glue (Dow Corning and Mechanics Helper, Inc.). The fibers used, Celgard X20 (Hoechst Celanese), have an inside diameter of 400 μm, an outside diameter of 456 μm, an effective pore size of 0.03 μm, and 40% porosity (manufacturer's specifications). Each fiber bundle was four inches in length, excluding the polypropylene tubing connectors. Two fiber bundles were held in a U-shape and immersed in a 60 ml membrane reservoir containing 30 ml of the membrane solvent. The average outside surface area of each bundle that was exposed to the solvent was 49 cm^2. This surface area is based on the manufacturer's specifications which were found to be accurate by us according to

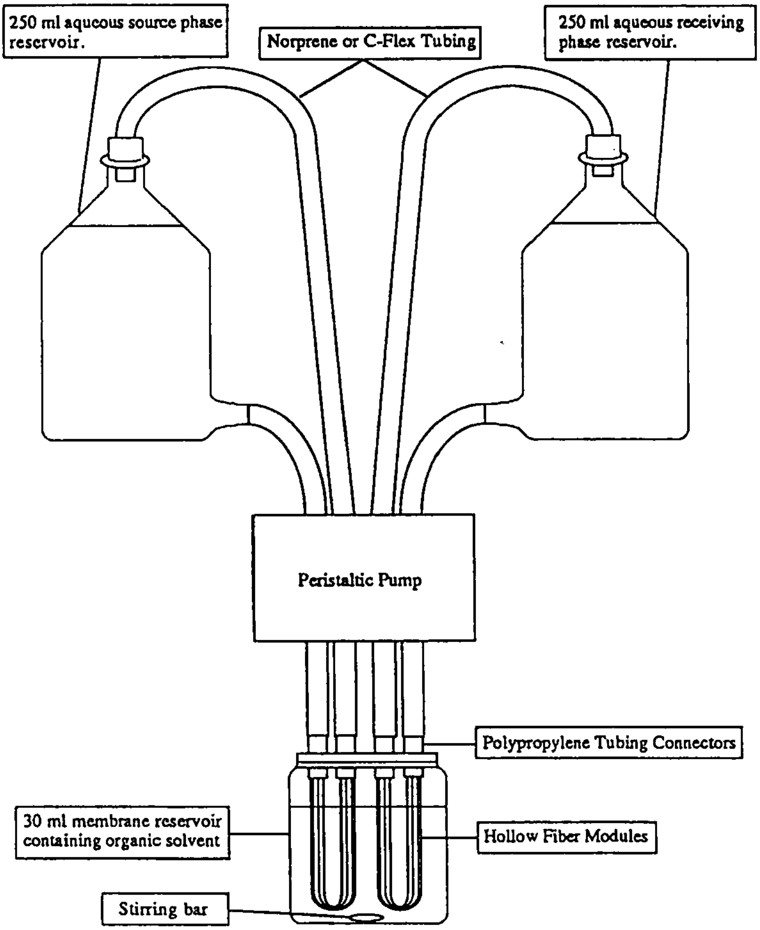


Fig. 1. Schematic of Dual Hollow Fiber Membrane Contactor.

measurements made at beginning and end of the experiments. Solvent and aqueous reservoirs were stirred with teflon-coated magnetic stirring bars and synchronous stirring motors (Hurst Manufacturing Co.).

Prior to developing this particular arrangement of the Dual Hollow Fiber Membrane Contactor, several different configurations were tried. In the first two of these configurations, no reservoirs were involved. Commercially prepared hollow fiber modules were used in the first configuration. In these modules (Microdyn Filtration Module, manufactured by Enka America, Inc.), the macrocycle, dissolved in 1-octanol, was forced into the pores of the fibers, and the excess washed off. The source and receiving solutions were then circulated through the module; the source phase was pumped through the lumen of the fibers (contained in a polypropylene shell) and the receiving phase was pumped through the outside of the fibers in the shell. Irreplaceable loss of macrocycle from the fiber pores and breakdown of the potting material at each end of the module in contact with the solvent (1-octanol) were problems encountered with this process. In the second configuration used, the same process was repeated with a new commercial module. This module was a polypropylene microporous hollow fiber membrane manufactured by Hoechst-Celanese. The same problems with potting material and loss of macrocycle were experienced with this module.

Using the Hoechst-Celanese modules, the procedure was changed so that the solvent and macrocycle were contained in a reservoir and circulated through the lumen of two modules in series. The source and receiving phases were also contained in reservoirs, and each was circulated through the outside of the fibers in a shell. This procedure eliminated the effects of losing small amounts of solvent and macrocycle, but did not eliminate problems associated with breakdown of the potting materials.

In an attempt to eliminate problems with potting materials, polypropylene microporous hollow fibers provided by Hoescht-Celanese were used to fabricate modules similar in design to the ones tested previously. Silicone glue was used to secure the fibers in the shell, but once again, after circulating the solvent through the lumen of the fibers, it was found that the silicone was not resistant to the solvent.

The configuration now in use was successful in keeping the solvent from destroying the potting material. This arrangement, shown in Figure 1, removes the potting material from direct contact with the solvent reservoir. Thus, although solvent vapors can cause the silicone cement to soften in places, serious degradation of the silicone is not a problem. This configuration allows the method to be evaluated without resorting to a long search for a resistant potting material.

Experiments were run for periods of approximately 24 hours, and samples were taken periodically of the receiving phase. New hollow fiber bundles were made for each experiment. Samples containing alkali metal ions were analyzed by AA spectrophotometry (Perkin Elmer Model 603) and those containing alkaline earth metal ions by ICP Spectrophotometry (Perkin Elmer Model Plasma II). Three experiments for each system were run simultaneously. These experiments were identical except that it was difficult to make the contact area between the solvent and the membrane the same in each experiment. This difficulty is probably the reason for the large uncertainties in the flux values. Blanks, run under identical system conditions, except for the absence of macrocycle, showed that virtually no transport occurs without the aid of a carrier molecule.

RESULTS AND DISCUSSION

Solvent, Stirring, and Flow Rate Effects

The solvent used in supported liquid membranes must be hydrophobic enough to pose an effective barrier to cation permeation. At the same time, it must be hydrophilic enough to allow the moderately polar macrocycle to favorably partition to the organic solvent over the aqueous phases and for the desired cation to be readily extracted so facilitated transport can take place (19-21). In the present system, the ratio of total aqueous volume (500 ml) to organic volume (30 ml) is about 17:1, and the solvent reservoir is accessible, so that any macrocycle lost to the aqueous phases can be replenished. These factors make solvent considerations less critical than they are in supported liquid membranes that have larger aqueous/organic ratios such as thin sheet supported membranes, no solvent reservoir, and where the means of replenishing the carrier while an experiment is in progress are difficult. Even so, in anticipation of using proton-ionizable macrocycles in the future, the effect of solvent on transport was examined carefully. A solvent was needed that would minimize diffusion of hydrogen ions from a receiving phase of low pH to a source phase of high pH in the absence of the macrocycle, but would provide high facilitated cation fluxes with no cation leakage. In the experiments performed for this study where the aqueous phases are completely recycled, no loss of DC18C6 from the organic phase was detected. Future studies with greater aqueous to organic volume ratios will need to be made to quantify macrocycle loss and needed replenishment.

Several solvents of varying hydrophobicity were employed in the Dual Hollow Fiber Membrane Contactor under the following conditions: Na^+ and K^+ in the aqueous source phase, solvent (without macrocycle) in the membrane, and 1.0 M HNO_3 in the receiving phase. The pH of the source phase was then observed over time. It was found that the drop in pH was least with hexane, octane and toluene, solvents containing no functional groups capable of interacting with protons. The drop in pH was most extreme with the solvents 1-octanol (alcohols are known to be proton acceptors to a slight degree) and 4-methyl-2-pentanone. Source phases in the Dual Hollow Fiber Membrane Contactors containing either 2-octanone or octanal as the solvent showed a drop in pH intermediate between those of octane and 1-octanol (Table 1). Ketones and aldehydes interact less with hydrogen ions (higher pKa values) than do alcohols. Therefore one would expect that they would be more impermeable to unaided acid transport than 1-octanol. 4-Methyl-2-pentanone is less hydrophobic than 2-octanone and octanal because it contains six carbons instead of eight, and so its resistance to unaided acid transport across the membrane is less than that of either of the other two solvents.

The same solvents (except for 4-methyl-2-pentanone) were then incorporated into Dual Hollow Fiber Membrane Contactors with K^+ and Na^+ in the source phase, DC18C6 at a concentration of 0.10 M as the carrier, and water in the receiving phase. The K^+ fluxes for each solvent are reported in Table 2. No Na^+ flux was observed that can be determined to be greater than analytical error. Even though a very hydrophobic solvent is desired to minimize unaided acid diffusion, one that is too hydrophobic will not allow cation transport to take place due to the difficulty of extracting aqueous ionized species into very hydrophobic phases, even with the help of a hydrophobic carrier molecule. For this reason, the solvents hexane, octane, and toluene gave poor transport. Higher flux values were obtained with 1-octanol as the membrane solvent, and even higher fluxes were observed with 2-octanone and octanal.

The effect of changing the stiring rate of the organic membrane was studied. We, and others, in modeling liquid membranes have hypothesized that there is an unstirred boundary layer between the source and membrane phases, and between the receiving and membrane phases (21-24). One of the factors influencing flux is the rate at which molecules can diffuse across these boundary layers, which is a function of solvent viscosity and stirring rate (21-24). Stirring the solvent reduces the thickness of the boundary layer and shortens the diffusion path length. Only a minimal stirring speed is necessary to effectively equilibrate the concentrations of the bulk of the organic phase. The effect on K^+ flux of the speed at which the solvent reservoir was stirred in a Dual Hollow Fiber Membrane Contactor containing Na^+ and K^+ in the source phase, 0.10 M DC18C6 in 1-octanol in the membrane reservoir and water as the receiving phase was determined. Results are shown in Table 3. The flux was found to increase as stirring speed increases, reinforcing the hypothesis that reducing the diffusion pathlength through stirring the solvent influences transport rate. It can be seen that there is a substantial difference in the K^+ fluxes at 200 and 400 revolutions per minute, but there is little

TABLE 1

Effect of Solvent on Membrane Integrity in a Dual Hollow Fiber Membrane Contactor Using an Acidic Receiving Phase[a]

Solvent	Average mM/hour rise in $[H^+]$[b]
Hexane	<0.001
Octane	<0.001
Toluene	<0.001
2-Octanone[c]	0.053
Octanal[d]	0.43
4 Methyl-2-pentanone	4.0
1-Octanol	6.0

[a] Rise in source phase $[H^+]$ in a 250 ml, H_2O source phase/30 ml organic solvent membrane/ 250 ml, 1.0 M HNO_3 receiving phase system.

[b] All determinations were made over 20-25 hour periods, except for 4-methyl-2-pentanone, which was over a three hour period.

[c] Source phase contained 250 ml 0.5 M $NaNO_3$, 0.5 M KNO_3, and receiving phase contained 1.0 M HCl.

[d] Source phase contained 250 ml 0.1 M $Ba(NO_3)_2$, 0.1 M $Ca(NO_3)_2$, 0.1 M $Sr(NO_3)_2$.

TABLE 2

K^+ Fluxes in 1:1 Na^+/K^+ Mixtures as a Function of Solvent in a Macrocycle-Mediated Dual Hollow Fiber Membrane Contactor[a]

Solvent	K^+ Flux x 10^8 [b]	Std. Dev.
Hexane	0.06	0.02
Octane	22	9
Toluene	117	17
1-Octanol	483	44
Octanal	780	100
2-Octanone	824	70

[a] Transport in a 250 ml, 0.5 M $NaNO_3$, 0.5 M KNO_3 source phase/30 ml, 0.1 M dicyclohexano-18-crown-6 in the organic solvent membrane/250 ml H_2O receiving phase system.

[b] Units of flux are $mol \cdot s^{-1} \cdot m^{-2}$

TABLE 3

Effect of Solvent Reservoir Stirring Speed on Cation Flux[a] in a Macrocycle-Mediated Dual Hollow Fiber Membrane Contactor

Stirring Speed	K^+ Flux x 10^8 [b]	Na Flux x 10^8 [b]
200 rpm	309±25	21±6
400 rpm	441±46	28±15
600 rpm	483±44	32±10

[a] Transport in a 250 ml (0.5 M $NaNO_3$, 0.5 M KNO_3) source phase/30 ml (0.1 M dicyclohexano-18-crown-6) 1-octanol membrane/250 ml H_2O receiving phase system.

[b] Units of flux are $mol \cdot s^{-1} \cdot m^{-2}$

difference between the K^+ fluxes at 400 and 600 revolutions per minute. This indicates that there is an upper limit to how much the diffusion path length can be reduced and that stirring the solvent reservoir at 400 rpm yields satisfactory fluxes.

The flow rates of the aqueous phases through the lumen of the fibers were varied to see if a faster aqueous flow rate also reduces the diffusion pathlength. The K^+ fluxes in the system with flow rates of four, six, and twelve ml/min were compared, all other conditions being identical. No identifiable trend was found, indicating that circulating the aqueous phases more rapidly in this range does not improve transport. Flow rates above twelve ml/min cause the pressure in the fibers to exceed that of the solvent reservoir to the point that water leaks through the pores of the fibers into the solvent reservoir. However, taking into consideration the point that the hollow fibers are hydrophobic it would be expected that the boundary layers at the surfaces of the fibers would primarily involve the hydrophobic membrane phase. Thus, varying aqueous flow rates would do little to decrease the diffusion path length.

Maintenance of Macrocycle Effects

Figure 2 shows the selective transport of Ba^{2+} and Sr^{2+} over Ca^{2+} from a solution containing equimolar quantities of these cations. These results, along with the large K^+:Na^+ separation

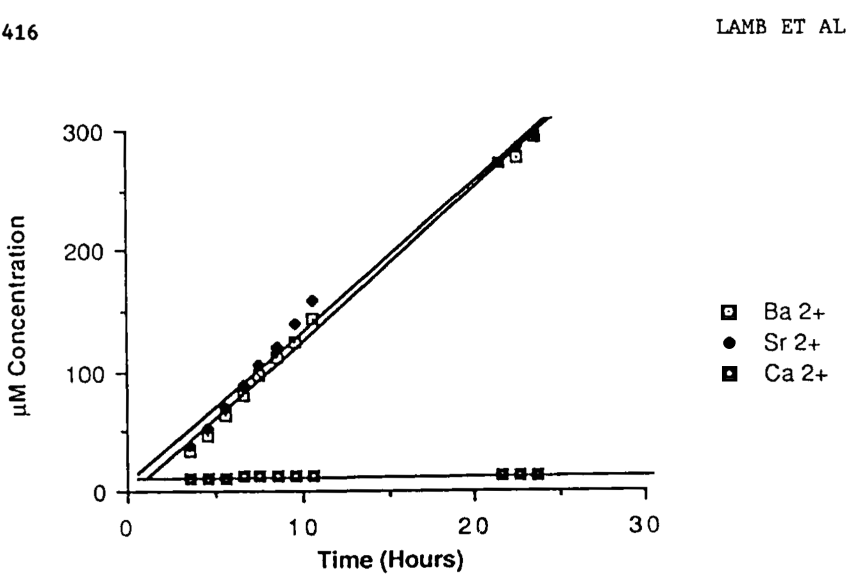


Fig. 2. Plot of Ba^{2+}, Sr^{2+}, and Ca^{2+} DC18C6-mediated transport vs. time using a Dual Hollow Fiber Membrane Contactor. Source phase: 250 ml solution containing 0.1 M $Ba(NO_3)_2$, 0.1 M $Sr(NO_3)_2$, and 0.1 M $Ca(NO_3)_2$. Membrane phase: 0.1 M DC18C6 in 30 ml 1-octanal. Receiving phase: 250 ml water.

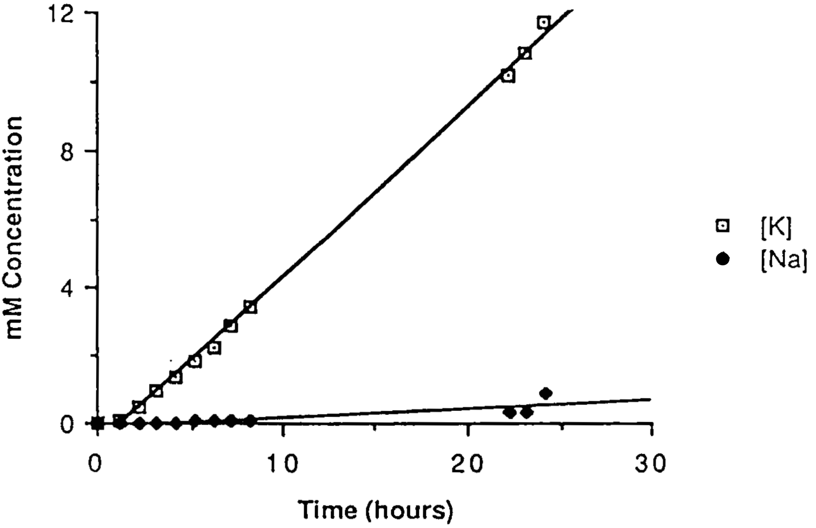


Fig. 3. Plot of K^+ and Na^+ DC18C6-mediated transport vs. time using a Dual Hollow Fiber Membrane Contactor. Source phase: 250 ml solution containing 0.5 M KNO_3 and 0.5 M $NaNO_3$. Membrane phase: 0.1 M DC18C6 in 30 ml octanal. Receiving phase: 250 ml water.

evident from the data in Figure 3 demonstrate that the cation selectivities determined previously using DC18C6 in bulk and emulsion membranes also apply to the Dual Hollow Fiber Membrane Contactor (6,15,19,20). This retention of selectivities is essential so that new macrocycles that are developed for a particular application can be characterized and tested using the minimal quantities available.

The flux of any cation transported selectively (i.e. K^+, Sr^{2+}, and Ba^{2+} in this study) by a crown ether macrocycle in previous similar systems has been shown to be directly proportional to the concentration of the crown (21). To determine if the same relationship between crown concentration and flux is observed in the Dual Hollow Fiber Membrane Contactor, the flux of K^+ in a system containing 0.5 M K^+ and 0.5 M Na^+ in the source phase, water in the receiving phase and DC18C6 at a concentration of 0.10 M in 2-octanone was compared to a similar system containing DC18C6 at a concentration of 0.01 M. The flux of K^+ in the former system was 780 mol $\cdot$ s^{-1} $\cdot$ m^{2} x 10^{-8}, and the flux of the same cation in the latter system was 107 x 10^{-8} mol$\cdot s^{-1} \cdot m^{2}$, or 0.14 times the value of the first. The good agreement between the ratios of the K^+ fluxes and the ratios of the macrocycle concentrations implies that this new system preserves the proportionality with a slope of one between flux and macrocycle concentration.

Despite the fact that the Dual Hollow Fiber Membrane Contactor can be run for days without loss of integrity, there are some problems with stability of the overall system. The aqueous phases are pumped through the small volume of the fiber lumen, so the pressure of the aqueous phases inside the fiber is greater than the pressure of the organic phase outside the fibers. As a result, some of the aqueous phase is forced through the pores of the fibers, into the solvent reservoir. The amount of leakage was observed to increase as the rate of pumping the aqueous phases through the fibers was increased or the hydrophobicity of the solvent in the reservoir was decreased.

CONCLUSIONS

The Dual Hollow Fiber Contactor has been shown to retain the selectivities of macrocycles observed with other membrane systems, as well as provide transport rates competitive with those of other systems. Increasing the speed that the solvent reservoir is stirred causes observed transport rates to increase, as the unstirred boundary membrane layers are reduced in thickness. The accessible aqueous and organic reservoirs are advantageous for long-term operation. A disadvantage of the system is that pressure differences between the source/receiving solution and solvent phases, resulting in seepage from one reservoir to another over a period of time. However, this seepage can be minimized by reducing the aqueous flow rates through the fibers.

ACKNOWLEDGMENT

We wish to thank Alan Van Orden for doing much of the ICP and AA analyses, and The Department of Energy, Office of Basic Energy Sciences, who funded this research under Grant #DE-FG02-86ER-13463.

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