Hollow Fiber Contained Liquid Membrane Separation of Citric Acid

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Citric acid was successfully separated from an aqueous solution using the hollow fiber contained liquid membrane (HFCLM) technique. In this technique, the organic liquid membrane is contained in the shell side between two sets of hollow fibers; feed solution flows through one set of fibers and the strip solution flows through the other set. Tri-n-octylamine diluted in various organic solvents was used as a complexing agent for facilitated transport of citric acid from an aqueous solution. Pure water and aqueous sodium hydroxide were used as stripping agents. Membrane life and stability problems encountered in supported liquid membranes are eliminated. A mathematical model of facilitated solute transport through HFCLM that accounts for the interfacial reversible reaction kinetics and diffusion process inherent in carrier-facilitated transport is presented. Experimental data agreed well with the theoretical predictions for permeators achieving almost complete solute recovery.

Introduction

Citric acid is the largest bulk chemical produced via fermentation of sugar juice and cane or beet molasses by *Aspergillus niger* in submerged cultures. Acid concentrations of the order of 15% w/v are achieved (Boey et al., 1987). Conventionally, the fermentation broth is first filtered. The acid is next precipitated as calcium salt by the addition of lime and is then liberated as a fairly pure compound by adding sulfuric acid. It is further purified by ion exchange and decolorized by active carbon. The final product is obtained after evaporation and crystallization (Yu-Ming et al., 1983).

The repeated precipitations, filtrations, hot water washes, and disposal of unsalable $CaSO_4$ are the main drawbacks of the conventional process. An alternate route, liquid extraction using reversible chemical complexation, has been tried. Several patents disclose the use of amines and amide as complexing agents (Baniel et al., 1973, 1981; Alter and Blumberg, 1981). Wennersten (1980) reported a number of solvents as diluents and their distribution coefficients, and proposed using different temperatures for extraction and stripping. But these investigators failed to overcome the emulsion problems when a fermentation broth was used instead of a pure citric acid solution (Yu-Ming et al., 1983). Yu-Ming and coworkers paid special attention to the key problems for the successful use of solvent extraction to obtain citric acid for edible purposes from fermentation broth.

The emulsion liquid membrane (ELM), invented by N. N. Li (1971), has recently been applied successfully to industrial phenolic wastewater treatment in China (Xiujuan et al., 1988) and to commercial-scale extraction of zinc in the viscose industry at Lenzing AG of Austria (Draxler et al., 1988). Citric acid recovery by ELM has been studied by Boey et al. (1987); a significant increase in the internal phase volume and some mycelium entrainment was observed. Babcock et al. (1986) investigated the recovery of citric acid using the simpler configuration of a supported liquid membrane (SLM). They found that citric acid flux was greatest under the following conditions: 60°C, trilauryl amine concentration of 38 vol. % in alkyl aromatic oil, or 50 vol. % in Shell Sol 71, and 15 vol. % *n*-dodecanol in the membrane as a modifier.

However, SLMs have not been adopted for industrial operations, primarily due to a lack of long-term stability resulting from loss of membrane by solubility, osmotic flow of water across the membrane, progressive wetting of the support pores, and pressure differential across the membrane (Danesi, 1984–1985; Danesi et al., 1987). To overcome such shortcomings, a new liquid membrane structure using microporous hollow fi-

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bers called the hollow fiber contained liquid membrane (HFCLM) has been employed in gas separation (Majumdar et al., 1988, 1989) and in solute separation from aqueous solutions without any reaction (Sengupta et al., 1988a,b). Since many liquid membrane systems of interest involve facilitated transport, it would be natural to study the HFCLM with facilitated transport. Citric acid recovery by such an HFCLM technique is explored here. An efficient citric acid recovery process may be a model for recovering fermentation-based organic acids (Kertes and King, 1986; Kuo and Gregor, 1983).

The HFCLM permeator was built out of two sets of identical hydrophobic microporous hollow fibers well mixed throughout the permeator but separated at the ends. One fiber set carried the feed aqueous solution of citric acid; the other set had the strip solution flowing in the lumen. The liquid membrane in the interstices of the two sets of fibers on the permeator shell side contained a mobile complexing agent (a tertiary amine, R_3N) in organic diluents. The interface between the organic liquid membrane and the feed aqueous solution is located on the inside diameter of the feed fiber set since the organic membrane wets the hydrophobic fiber pores. At this interface, the complexing agent reacts selectively with citric acid; the complex then diffuses across the organic liquid membrane and dissociates at the hydrophobic strip fiber aqueous-organic interface, releasing citric acid.

Tri-*n*-octyl amine (TOA) diluted in organic solvents—xylenes, heptane, methyl isobutyl ketone (MIBK)—was used as the complexing agent for facilitated transport of citric acid from an aqueous solution since the nonfacilitated flux is quite low. Pure water as well as aqueous sodium hydroxide were used as the stripping agent. The roles of the complexing agent concentration and diluent were investigated. The effects of feed-side and strip-side boundary layer resistances on mass transfer were studied. Membrane life and stability characteristics of the HFCLM was explored by means of long-term runs. A mathematical model of facilitated solute transport through the HFCLM accounting for interfacial reversible reaction kinetics and diffusion process inherent in carrier-facilitated transport is presented. The theoretical predictions for different permeators are compared with the experimental data. The permeator productivity behavior as a function of a dimensionless area-flow rate parameter is reported and compared with model results. The long-term objective in such studies is to develop a general membrane separation technique for efficiently recovering carboxylic acids from fermentation broths.

Theoretical Model

In the facilitated transport of citric acid from an aqueous feed solution through a hydrophobic HFCLM permeator containing trioctylamine in an organic diluent on the shell side of the HFCLM permeator, water or aqueous sodium hydroxide was used as the stripping or receiving phase. Both mobile phases are in cocurrent flow through the lumen of the two separate fiber sets. The general assumptions for analysis of a nonreactive HFCLM permeator are similar to those in Sengupta et al. (1988a). We focus now on the role of the chemical reaction.

In the following analyses, the overall complexation reaction under consideration and its symbolic representation are respectively

$$\mathrm{C_6H_8O_7(aq)} + 3R_3\mathrm{N(org)} \rightleftharpoons (R_3\mathrm{NH})_3\mathrm{C_6H_5O_7(org)} \tag{1a}$$

$$A(\mathrm{aq}) + 3B(\mathrm{org}) = C(\mathrm{org}) \tag{1b}$$

where R represents $CH_3(CH_2)_7$. It can also be assumed that component A partitions into the organic membrane phase (from the feed side) according to its distribution coefficient in the pure organic diluent, given by

$$C_{Ao} = m_i^F C_{Aw} \tag{2}$$

and reacts with three molecules of B to form complex C:

$$A(\mathrm{org}) + 3B(\mathrm{org}) = C(\mathrm{org}) \tag{3}$$

Species B and C are essentially insoluble in water or aqueous solutions and therefore cannot leave the organic membrane phase. Playne and Smith (1983) have reported that the water solubility of trioctyl amine and xylene is 0.0012 and 0.19 μL/mL respectively. The presence of three carboxylic acid groups and one hydroxyl group makes citric acid extremely hydrophilic and therefore its distribution in pure organic diluent is very small (King, 1987). It is also assumed that reactions 1a and 3 are sufficiently fast that the reacting species are present in equilibrium concentrations everywhere. The reaction rate between citric acid and amine is expected to be very rapid because of a neutralization reaction (Yu-Ming et al., 1983). Since $m_i^F << 1$ for water-citric acid-pure organic diluent, it is expected that the complexation reaction occurs essentially at the interface. However, interfacial reaction is not a necessary assumption here.

The local value of the total flux of A, N_A^T, across an organic film of thickness δ that contains the water-insoluble species B and C is obtained by an analysis similar to those by Olander (1960), Ward (1970), and Cussler (1971). They studied analytically a system involving mass transfer and equilibrium chemical reaction. If D_{Bo} and D_{Co} are assumed to be equal, the total local flux of A through a film of thickness δ is

$$N_A^T = \frac{D_{Co}}{\delta}(C_{Co}^F - C_{Co}^S) + \frac{D_{Ao}}{\delta}(C_{Ao}^F - C_{Ao}^S) \tag{4}$$

However, it is to be kept in mind that depending on cases, D_{Bo}/D_{Co} may differ greatly from one. Under most circumstances, D_{Bo}/D_{Co} is greater than one. When $D_{Bo}/D_{Co} > 1$, the actual facilitation factor would be less than that predicted by a simplified model assuming $D_{Bo}/D_{Co} = 1$ (Basaran et al., 1989). Moreover, the effect of hindered diffusion of the complex molecules through the micropores has not been considered in this analysis.

For facilitated transport through an HFCLM, if one assumes negligible aqueous phase boundary layer resistances, the local value of the organic-phase-based overall transfer coefficient, K, for each species C and A can be obtained from single-species transport (Sengupta et al., 1988a,b) as

$$\frac{1}{K_{o,C}} = \frac{d_i}{d_{lm}} \frac{2}{D_{Co}\epsilon_s/[\tau_s(d_o - d_i)/2]} + \frac{d_i}{d_o} \frac{1}{D_{Co}/\delta_m} = \frac{t_{eff}}{D_{Co}} \tag{5}$$

and

$$\frac{1}{K_{o,A}} = \frac{d_i}{d_{lm}} \frac{2}{D_{Ao}\epsilon_s/[\tau_s(d_o - d_i)/2]} + \frac{d_i}{d_o} \frac{1}{D_{Ao}/\delta_m} = \frac{t_{eff}}{D_{Ao}} \quad (6)$$

Since diffusion in the organic liquid in hollow fiber pores and in the organic contained liquid membrane of effective thickness δ_m are in series, it is obvious that (D_{Co}/t_{eff}) is $K_{o,C}$ and (D_{Ao}/t_{eff}) is $K_{o,A}$. Consequently, in the expression for N_A^T in Eq. 4, (D_{Co}/δ) may be replaced by either (D_{Co}/t_{eff}) or $K_{o,C}$, and (D_{Ao}/δ) by (D_{Ao}/t_{eff}) or $K_{o,A}$. Note that it is illustrative to represent $K_{o,C}$, for example, by D_{Co}/t_{eff} instead of the complete expression in Eq. 5. The above developments assume:

1. There are no interfacial resistances
2. τ_s is same for both species since the pore sizes are orders of magnitude larger.

We now focus on the differential equations for the HFCLM module.

Pure water as receiving phase in the permeator

When pure water is used as the receiving phase (stripping solution), the differential mass balances on species A at any point along the length of the HFCLM permeator are written for the feed solution and the strip solution as

$$-Q_F \frac{dC_{Aw}^F}{dA_m} = K_{o,C}(C_{Co}^F - C_{Co}^S) + m_i K_{o,A}(C_{Aw}^F - C_{Aw}^S) = Q_S \frac{dC_{Aw}^S}{dA_m} \quad (7)$$

Further, at the feed interface,

$$C_{Bo}^F + 3C_{Co}^F = C_{To} \quad (8)$$

$$K_{eq} = \frac{C_{Co}^F}{C_{Aw}^F C_{Bo}^{F^3}} \quad (9)$$

and at the strip interface,

$$C_{Bo}^S + 3C_{Co}^S = C_{To} \quad (10)$$

$$K_{eq} = \frac{C_{Co}^S}{C_{Aw}^S C_{Bo}^{S^3}} \quad (11)$$

Here C_{To} is the initial amine concentration without complexation.

The conditions at the permeator inlet are:

$$C_{Aw}^F = C_{A,in}^F \quad \text{and} \quad C_{Aw}^S = 0 \quad \text{at } A_m = 0 \quad (12)$$

The mass transfer coefficients are given by Eqs. 5 and 6.

Equations 8 and 9 can be combined to form a cubic equation in C_{Bo}^F that can be solved in terms of K_{eq}, C_{To}, and C_{Aw}^F. Similarly, Eqs. 10 and 11 are combined to form a cubic in C_{Bo}^S that can be solved in terms of K_{eq}, C_{To}, and C_{Aw}^S.

Differential Eqs. 7 can be integrated numerically along the HFCLM permeator length using the initial conditions, Eqs. 12, and algebraic solutions for C_{Bo}^F, C_{Bo}^S, and expressions for C_{Co}^F and C_{Co}^S from Eqs. 8 and 10, respectively (Basu, 1989).

Aqueous sodium hydroxide as receiving phase

The following strip-side instantaneous reaction occurs when aqueous sodium hydroxide is used as the stripping agent:

$$(R_3NH)_3C_6H_5O_7(\text{org}) + 3\text{NaOH(aq)} = C_6H_5O_7Na_3(\text{aq}) + 3R_3N(\text{org}) + 3H_2O \quad (13)$$

Because of the instantaneous reaction, $C_{Co}^S = 0$ and $C_{Ao}^S = 0$. Therefore, differential mass balances for A and A^{3-} (citric acid and citrate ion) at any point along the length of the HFCLM permeator are

$$-Q_F \frac{dC_{Aw}^F}{dA_m} = K_{o,C}\, C_{Co}^F + m_i K_{o,A} C_{Aw}^F = Q_S \frac{dC_{Aw}^{S_{3-}}}{dA_m} \quad (14)$$

and further

$$C_{Bo}^F + 3C_{Co}^F = C_{To} \quad (15)$$

$$K_{eq} = \frac{C_{Co}^F}{C_{Aw}^F C_{Bo}^{F^3}} \quad (16)$$

The initial conditions are given by:

$$C_{Aw}^F = C_{A,in}^F \quad \text{and} \quad C_{Aw}^{S_{3-}} = 0 \quad \text{at } A_m = 0 \quad (17)$$

The mass transfer coefficients are again represented by Eqs. 5 and 6. Equations 15 and 16 can be combined to form a cubic in C_{Bo}^F. Differential Eqs. 14 can be integrated numerically along the length of the HFCLM permeator along with the initial conditions Eqs. 17, the algebraic Eq. 15, and the cubic in C_{Bo}^F (Basu, 1989).

From this theoretical analysis, the HFCLM permeator productivity can be determined. The productivity can be expressed as the fraction of citric acid removed from the feed to the strip stream. This will be a function of the membrane surface area–feed flow rate parameter A_m^+, which is defined as $A_m K_o/Q_F$. Here A_m is the membrane surface area of the permeator module, Q_F is the feed flow rate, and K_o is a reference mass transfer coefficient. K_o is taken as $K_{o,C}(=D_{Co}/t_{eff})$. This aspect of permeator productivity is discussed later in connection with its experimental verification.

Experimental Materials and Procedure

All chemicals were used as received. Xylenes (ACS grade), *n*-hexane (HPLC grade), *n*-heptane (HPLC), *n*-octanol (ACS), sodium hydroxide (ACS), oxalic acid, dihydrate (ACS), orthophosphoric acid, 85% (HPLC), and ammonium dihydrogen phosphate (HPLC) were all from Fisher Scientific, Fairlawn, NJ. Citric acid, anhydrous (Puriss p.a. grade) and trioctylamine (Pract. grade) were from Fluka Chemical Corporation, Ronkonkoma, NY. Acetic acid, glacial reagent (Electronic grade) was from Du Pont, Wilmington, DE.

Hydrophobic polypropylene (PP) Celgard X-10 hollow fibers (Questar, Charlotte, NC) were used to make three permeator modules. Details of module making are available elsewhere (Sengupta et al., 1988a). The geometric characteristics of the fibers and permeators are shown in Table 1.

Table 1. Geometric Characteristics of HFCLM Permeators

	Hydrophobic HFCLM Modules 1, 2, 3
Fibers	Celgard $X-10$ polypropylene
Porosity, ϵ_m	0.2*
Tortuosity, τ_m	3.5*
Fiber dia.,** μm	
OD, d_o	150
ID, d_i	100
No. of fibers	
Feed, N_F	300
Strip, N_S	300
Eff. CLM thickness, δ_m, μm	110†
Eff permeator length, cm	
Modules 1, 2	10
Module 3	48
Mass transfer area/vol, a, cm^{-1}	32.2
Fraction of shell cross-sectional area occupied by the two fiber sets	0.36

*Sengupta et al. (1988a)
**Manufacturer's data
†Majumdar et al. (1989)

To determine the effective liquid membrane thickness, δ_m, of the permeator, pure CO_2 permeation was carried out through pure water as a liquid membrane following the method described in Majumdar et al. (1989). The permeated CO_2 gas was allowed to flow countercurrent to the feed gas; it exited the permeator essentially at atmospheric pressure.

Sodium hydroxide concentration was measured by titration against standard oxalic acid using phenolphthalein as the indicator. Acetic acid concentration was determined by titration against standard NaOH solution using phenolphthalein as the indicator. Both titration and HPLC analysis procedures were adopted to measure citric acid concentration. In some cases, analyses by these two methods were compared and were found to be quite close. For the HPLC method of analysis, an HP 1090 liquid chromatograph was used. A 20 cm Chromsphere C18 (5 μm) chromsep analytical column (Chrompack Inc., Bridgewater, NJ) was used. The filter photometric detector wavelength was set at 210 nm. The mobile phase was aqueous ammonium dihydrogen phosphate (15 gm/L, adjusted to pH 1.85 with orthophosphoric acid) at a flow rate of 0.4 cm^3/min. To determine the organic phase citric acid concentration, the acid was first extracted out into standard NaOH. The acid concentration was then determined either by back-titrating the remaining NaOH or by HPLC. Glucose was analyzed by a Dionex liquid chromatograph with a pulsed amperometric detector (Dionex Corp., Sunnyvale, CA). The analytical HPLC column was Dionex Carbopack PA 1 and the mobile phase was 100 mM NaOH at a flow rate of 1.0 cm^3/min.

A diagram of the experimental setup is available in Sengupta et al. (1988a) and the experimental procedure was essentially similar to the procedure described there. However, in the case of long-term stability runs it was necessary to refill the feed and strip supply reservoirs several times during the course of the experiments. To refill these reservoirs, the permeator feed and strip outlet valves were closed first. Then the permeator inlet valves were closed. The liquid reservoirs were depressurized, opened, and refilled. Feed and strip inlet samples were collected during this time. After closing and pressurizing the reservoirs, the permeator feed and strip inlet valves were opened first. Then the permeator outlet valves were opened. The entire refilling operation was done within 10 min. In one long-term stability experiment, 2–4 cm^3 of membrane liquid was withdrawn per day through the permeator 3 shell-side outlet port.

Results and Discussion

Any fermentation broth containing citric acid also contains glucose. To ensure that the extraction system does not remove any glucose, an experiment was performed at the beginning with an aqueous feed containing 100 gm/L glucose and 100 gm/L citric acid. TOA 10% v/v in xylenes was used as the liquid membrane and pure water was used as the stripping solution. It was observed that while citric acid permeated to the strip side as expected, HPLC analysis of the strip outlet stream did not show any glucose. All other experiments were therefore performed with a feed containing only citric acid. Table 2 illustrates the pressure conditions of the feed side, strip side, and membrane liquid for all experiments with hydrophobic HFCLM permeators. The membrane phase pressure was always lower than those of the feed or the strip since the membrane phase wetted the pores of the hollow fiber (Sengupta et al., 1988a).

The initial time-dependent permeation behavior of citric acid in HFCLM permeator 1 containing TOA in MIBK as the liquid membrane is reported first. Experiments were then made in detail to determine the following:

1. The effect of keeping TOA as complexing agent and pure water or aqueous sodium hydroxide as stripping agent
2. The effect of changing TOA concentration on overall mass transfer coefficient
3. The influence of feed and strip flow rate variation
4. The consequences of TOA concentration variation in different diluents with water as strip
5. The effect of aqueous sodium hydroxide as strip for a fixed concentration of TOA in different diluents
6. The effect of varying feed concentration and flow rate for a fixed concentration of TOA in the liquid membrane and aqueous sodium hydroxide as strip.

Results of membrane stability studies are presented at the end of this section.

The initial time-dependent citric acid permeation behavior in permeator 1, presented in Figure 1, shows that steady-state concentrations are reached in about 10–12 h. A higher percentage of TOA in the membrane liquid increases the time to

Table 2. Pressure Conditions of Hydrophobic HFCLM Permeator Studies

System	Pressure, KPa				
Solute-Membrane	Feed Inlet	Feed Outlet	Membrane Phase	Strip Inlet	Strip Outlet
Citric acid–TOA/organic diluent	41–55	28–38	7–17	41–55	28–38

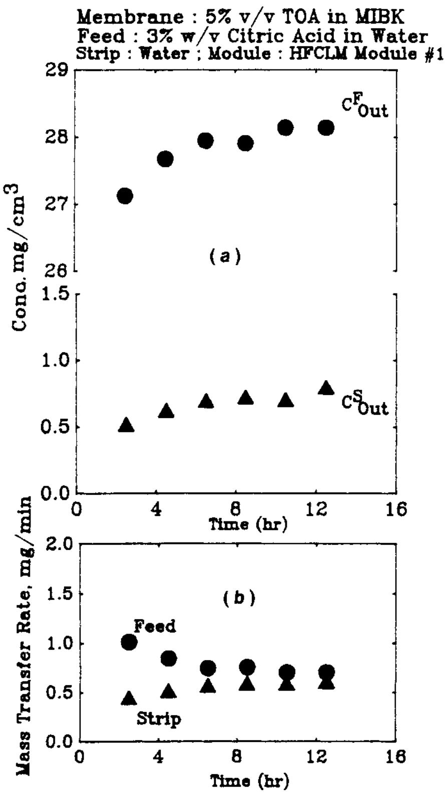

Figure 1. Time-dependent behavior for 5% v/v TOA in MIBK as membrane liquid.

a. Citric acid concentrations in feed and strip outlets
b. Mass transfer rate based on feed and strip sides

reach steady state. As the TOA concentration is increased, the membrane liquid takes more time to be loaded with the complex. When aqueous sodium hydroxide is used as strip, with 10% v/v TOA in MIBK as the membrane liquid, the steady state is reached in about 5-6 hours. With an instantaneous reaction at the strip side, the driving force for solute transport increases to enhance the mass transfer rate and the steady state is achieved much earlier.

Figure 2 illustrates the time-dependent citric acid permeation behavior in permeator 2 for two cases:

1. Solute permeation with or without complexing agent (TOA) in the membrane liquid
2. Solute permeation with or without chemical reaction in the permeator strip side when there is a complexing agent in the membrane liquid.

Line 3 in Figure 2 indicates the mass flux of citric acid through pure MIBK as the membrane. This mass flux was an average of those based on the feed side and strip side. Line 2 shows the enhancement of mass flux due to 10% v/v TOA in the membrane. Line 2 clearly demonstrates the usefulness of facilitated transport for removal of solutes in an HFCLM permeator. Line 1 shows further enhancement of solute transport via sodium hydroxide in the strip stream.

Figure 3 shows the variation of overall mass transfer coefficients for citric acid transport with variation of membrane TOA concentration. Two opposing factors act on K_o as the complexing agent concentration is varied. An increase in the complexing agent concentration increases the ability for complex formation in the membrane, leading to enhanced driving force for mass transfer. But this enhancement of mass transfer driving force will reach a limit because of the stoichiometric limit of chemical complexation. On the other hand, as TOA concentration is increased, the viscosity of the membrane liquid increases since long-chain amines are extremely viscous. This increase of viscosity reduces the diffusion coefficient of the complex, the amine, and the citric acid. This phenomenon opposes the mass transfer enhancement due to a higher driving force. Figure 3 clearly demonstrates this behavior.

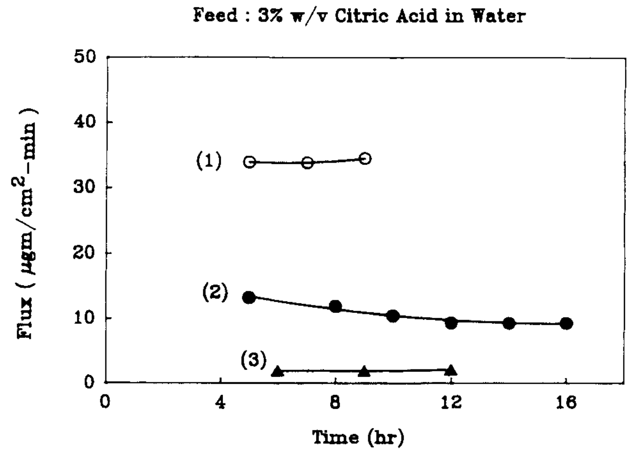

Figure 2. Change in citric acid flux under different experimental conditions.

1. Membrane: 10% v/v TOA in MIBK; strip: 0.5 M NaOH (complexing agent and downstream instantaneous reaction)
2. Membrane: 10% v/v TOA in MIBK; strip: water (complexing agent only)
3. Membrane: Pure MIBK (no amine); strip: water (no reaction)

As the operating aqueous phase Reynolds numbers are low, it is necessary to verify experimentally whether the feed side and strip side boundary layer mass transfer resistances may be neglected. Figure 4 shows the data regarding influence of feed flow rate on overall mass transfer coefficient. Both strategies of pure water and aqueous sodium hydroxide strip at a constant flow rate (to completely eliminate the strip-side resistance with an instantaneous reaction; Basu et al., 1990) were adopted to

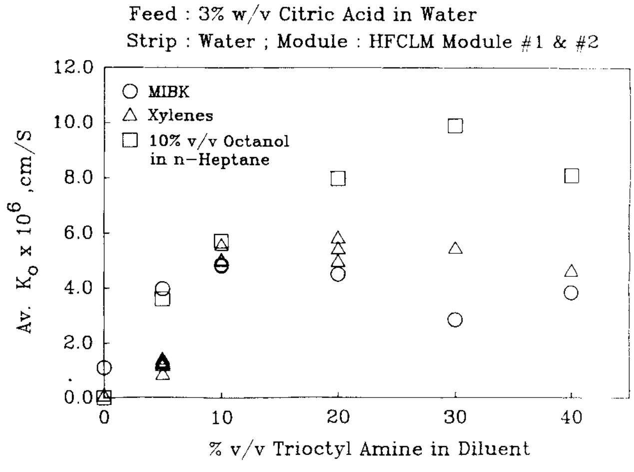

Figure 3. Effect of trioctyl amine concentration on overall mass transfer coefficient for different organic diluents as membrane liquid.

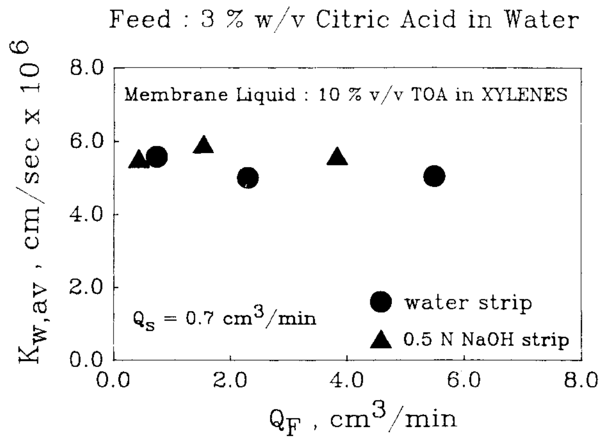

Figure 4. Effect of feed flow variation on overall mass transfer coefficient, HFCLM module 1.

verify this. The figure clearly demonstrates that there is no significant influence of feed flow rate on the overall mass transfer coefficient. Figure 5 shows that the influence of strip flow variation on overall mass transfer coefficient is also insignificant, justifying the assumption of negligible aqueous phase boundary layer resistances in the theoretical model.

Figures 6a, b, and c represent the influence of TOA concentration and different diluents on the transfer rate of citric acid in permeators 1 and 2. The opposing effects of increased amine concentration and membrane liquid viscosity are clear in these data for all three cases. The solid lines in Figures 6a, b, and c represent the theoretically predicted mass transfer rates as a function of TOA concentration for the respective diluents. The theoretical predictions are based on the mathematical model developed for pure water as receiving phase in the permeator. The mass transfer coefficients, $K_{o,C}$ and $K_{o,A}$, necessary for this mathematical treatment were taken as D_{Co}/t_{eff} and D_{Ao}/t_{eff}, respectively. Here t_{eff} was determined by citric acid and acetic acid permeation studies through the pure diluents. This aspect is discussed in detail later in this section.

Experiments with either hexane or heptane as diluent showed almost negligible citric acid permeation. The low polarity of aliphatic hydrocarbons creates low solubility of citric acid as well as the complex in the membrane. Since this does not completely explain negligible permeation behavior, a batch equilibrium study was performed between an aqueous phase of citric acid and an organic phase of 20% TOA in n-heptane. Citric acid indeed partitions into the organic phase. This equilibrated organic phase was next equilibrated with an excess of aqueous sodium hydroxide to back-extract citric acid from the organic phase. It was observed that citric acid did not come back to the aqueous phase for this case. Therefore, it is presumed that the polarity of the diluent plays a significant role. When the polarity of the diluent is low, the solvation of the complex is very weak. The acid-amine complex may selfassociate strongly in the presence of the apolar diluent; then it becomes difficult for the stripping agent to reverse the chemical reaction and unload citric acid from the membrane.

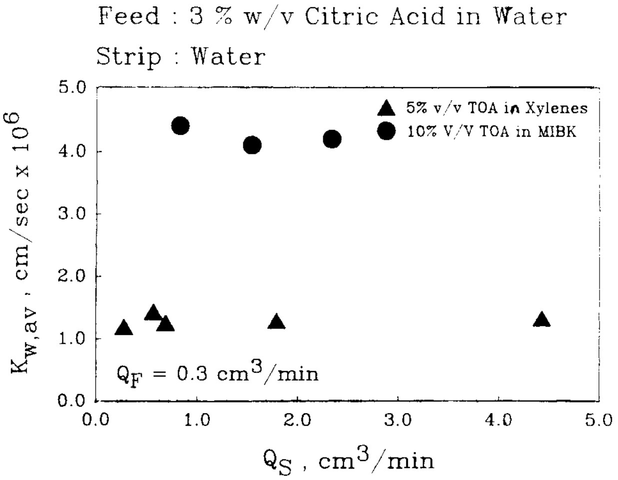

Figure 5. Effect of strip flow variation on overall mass transfer coefficient, HFCLM module 1.

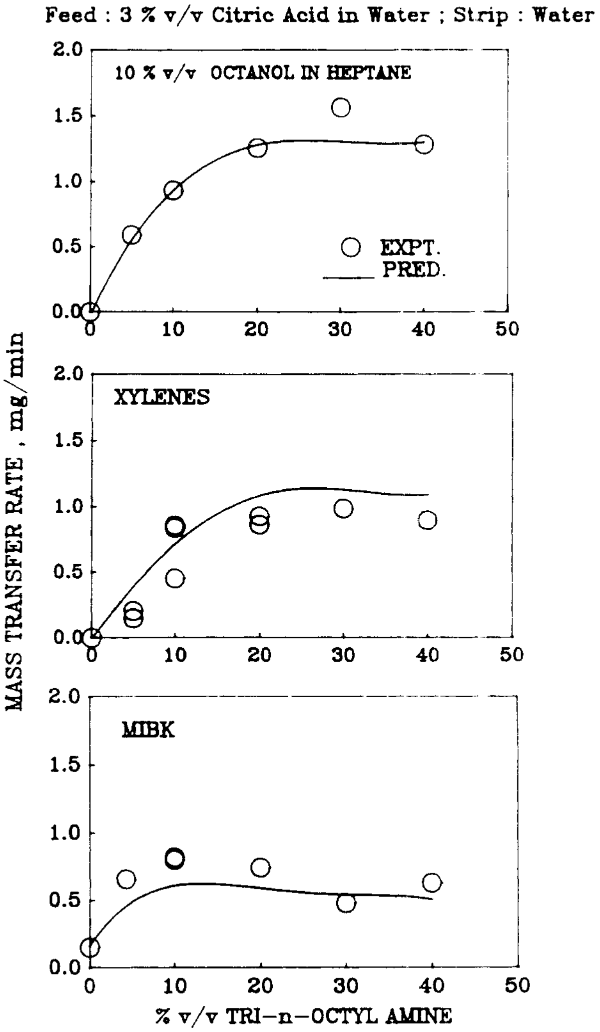

Figure 6. Citric acid mass transfer rate vs. concentration of complexing agent in different organic membrane liquids.

When a small amount of n-octanol is added to the diluent, the organic medium becomes polar and the extent of self-association of the acid-amine complex is drastically reduced. The complexation reaction can then be reversed. This was verified by batch extraction studies, where it was possible to

Table 3. Measured Equilibrium Constants for Citric Acid–TOA Complexation Reaction

Diluent	K_{eq} $(\text{gmol/cm}^3)^{-3}$
MIBK	5.33×10^{13}
Xylenes	4.85×10^{11}
10% v/v octanol in *n*-heptane	5.24×10^{11}

*$K_{eq} = C_{Co}/C_{Aw}C_{Bo}^3$, according to Eq. 1b

Table 4. Effect of Organic Diluents on Mass Transfer Rate of Citric Acid with Instantaneous Reaction on the Strip Side

Diluent	Flow Rate, cm^3/min		Mass Transfer Rate mg/min	
	Feed	Strip	Exp.	Theory
Xylenes	1.0	0.7	1.05	0.91
10% v/v octanol in heptane	1.8	0.4	1.23	1.25
MIBK	0.5	1.1	2.98	1.54

Feed: 3% w/v citric acid in water
Strip: 2% w/v aqueous NaOH
Membrane liquid: 10% v/v trioctyl amine in diluent
Module: Hydrophobic HFCLM module 2

unload citric acid from the organic medium by an excess of sodium hydroxide in the aqueous phase.

Increased polarity of the diluent has the advantage of a higher solubility of acid-amine complex in the liquid membrane. But it may give rise to two disadvantages:

1. When the polarity of the diluent increases, its solubility in the aqueous feed and strip streams also increases, leading to a considerable loss of membrane liquid in the aqueous streams. This may give rise to long-term stability problems unless other corrective actions are taken.
2. An increased polarity of the diluent indeed gives an increased partitioning of the acid into the organic phase. This gives rise to a higher equilibrium constant for the complexation reaction. However when pure water is used as the stripping agent, because of the higher equilibrium constant, loading of acid from the feed stream is easier but unloading the acid from the membrane to the strip stream becomes equally difficult. So, while the membrane remains loaded with the acid, the permeation rate through the liquid membrane declines. However, this disadvantage can be overcome by using sodium hydroxide in the strip stream. With sodium hydroxide in the strip stream, an instantaneous reaction takes place at the phase interface and the acid is easily unloaded from the membrane at the strip-side phase interface.

That an increased equilibrium constant will cause a decline in acid permeation rate, when water is used as the stripping agent, is evident from a comparison of Figures 6a, b, and c. Table 3 shows the measured equilibrium constants for different diluents. When xylenes or octanol in *n*-heptane is used as the diluent, the equilibrium constants are quite close. When MIBK is used as the diluent, the equilibrium constant is much higher. Therefore, for xylenes or octanol in *n*-heptane as diluent, permeation rates are close. For MIBK as diluent the permeation rate has declined. The reversal of the situation in the presence of an instantaneous reaction at the strip-side phase interface in the presence of sodium hydroxide is evident from Table 4. Now the permeation behavior has been reversed: for MIBK as the diluent, permeation rate has increased while it is close for xylenes or octanol in *n*-heptane as diluent.

Some comments are necessary about these experiments. MIBK is significantly soluble in water while xylenes, octanol, and heptane are much less soluble in water. TOA also is practically insoluble in water. Therefore, when MIBK is used as the diluent, during the course of the experiment MIBK is preferentially lost (compared to TOA) to the feed and strip streams, causing the membrane liquid to concentrate in the TOA. This creates considerable unsteadiness in the mass transfer rate. But this unsteadiness in mass transfer was not observed for a reasonable length of time in the case of other diluents studied. Therefore, all experiments with MIBK as diluent were done with aqueous streams previously saturated with the membrane liquid. Dramatic improvements in mass transfer were observed. More deliberations on stability are provided at the end of this section.

A few remarks need to be made regarding the mathematical model of the present study and facilitated transport of citric acid through the hydrophobic HFCLM permeator. Since the equilibrium constant of the system is very high and experimental evidence shows negligible influence of aqueous phase boundary layer resistances on mass transfer, the mass transport rate becomes diffusion limited through the membrane. The very high equilibrium constant allows considerable error latitude in predicting mass transfer rates. Two other important parameters are the estimated diffusion coefficients and estimated overall membrane thickness. The present case involves diffusion of large and complex molecules through a viscous nonionic medium. Since the Wilke-Chang correlation is used to estimate the diffusion coefficient of solute molecules, the accuracy of these estimates will depend upon the accuracy of the estimates of viscosities. Loeb's method of estimating the viscosity of liquid mixtures was adopted. In the absence of any experimental data for this system, the accuracy of adopting Loeb's method for viscosity prediction was checked using Ricker's (1978) experimental data on a liquid mixture of Alamine 336 and di-isobutyl ketone (DIBK). It has been found that Ricker's experimental data and prediction by Loeb's method match within 15%.

The theoretical model developed needs mass transfer coefficients $K_{o,C}$ and $K_{o,A}$ defined by Eqs. 5 and 6. The magnitudes of $K_{o,C}$ and $K_{o,A}$ only differ due to the diffusion coefficient values, D_{Co} and D_{Ao}. Equations 5 and 6 also show that mass transfer coefficients $K_{o,C}$ and $K_{o,A}$ can be expressed in terms of D_{Co}, D_{Ao}, and an effective HFCLM thickness t_{eff} where

$$t_{eff} = \frac{d_i}{d_{lm}} \frac{\tau_s (d_o - d_i)}{\epsilon_s} + \frac{d_i}{d_o} \delta_m \tag{18}$$

One can also express t_{eff} for hydrophobic membrane substrates by

$$t_{eff} = m_i D_{Ao} \left(\frac{1}{K_{w,A}} - \frac{1}{k_{w,A}^F} - \frac{1}{k_{w,A}^S} \right) \tag{19}$$

where $K_{w,A}$ is the overall mass transfer coefficient for simple permeation of species A, and $k_{w,A}^F$, $k_{w,A}^S$ are the two aqueous

Table 5. Values of t_{eff} for Different Hydrophobic HFCLM Permeators

System	Module No.	t_{eff}, cm	
		Eq. 18	Eq. 19
Citric acid-MIBK-water	1	0.0783	0.32
Citric acid-MIBK-water	2	0.0783	0.30
Citric acid-MIBK-water	3	0.0783	0.30
Acetic acid-xylene-water	3	0.0783	0.35
Citric acid-xylene-water	2	0.0783	0.37

Table 6. Effective Membrane Thickness*, δ_m for HFCLM Permeators

HFCLM Module No.	δ_m, μm	
	Exp.	Lit.**
1	365.8	110
2	452.1	110
3	76.2	110

*Determined by pure CO_2 permeation through water
**Majumdar et al., 1989

film transfer coefficients for the feed and the strip stream of the permeator (Sengupta et al., 1988a).

To estimate $K_{o,C}$ and $K_{o,A}$, one can make use of the estimate of t_{eff} from individual estimates of τ_s, ϵ_s, and δ_m, whose values and sources are given in Table 1. However, t_{eff} can also be estimated from measurements of $K_{w,A}$ and estimates of $k^F_{w,A}$ and $k^S_{w,A}$. To estimate t_{eff} by the latter method, experiments were done with aqueous acetic acid or citric acid as feed, water as strip, and pure MIBK or xylenes as membrane liquid.

The estimates of t_{eff} by Eqs. 18 and 19 are shown in Table 5 for different HFCLM permeators. Note that t_{eff} determined by Eq. 19 is ~4.2 times larger than that determined by Eq. 18. The possible reasons for this difference are:

1. The actual values of δ_m are much larger than those predicted theoretically
2. The actual value of τ_s is larger than that obtained from literature
3. There may be interfacial mass transfer resistance not considered in Eq. 18.

Pure-component gas permeation studies, discussed in the experimental section, were carried out to determine δ_m. Table 6 shows that δ_m varied from 76.2 to 452.1 μm for different permeators. If the fibers were configured in the regular fashion, then the theoretical estimate of δ_m for these permeators would be 110 μm (Majumdar et al., 1989). However, assuming that the contributions of the resistances of the substrates are accurate, even this large variation of δ_m does not explain the large value of t_{eff} obtained by Eq. 19. Therefore, it can be concluded that the major discrepancy comes from either using a wrong estimate of τ_s or is due to ignoring the interfacial resistance.

If it is assumed that there is no interfacial resistance to mass transfer, then from the experimental values of t_{eff} using Eq. 19 and δ_m values obtained by gas permeation studies, one can use Eq. 18 to calculate τ_s. The values of τ_s determined this way vary from 13.4 to 14.6. This is a rather high value. Therefore it can be postulated that there is some interfacial resistance present. This kind of interfacial resistance is often reported in literature on the solvent extraction of organic acids. Pratt (1983) has reported the influence of interfacial resistance in the case of extraction of carboxylic acids from water into nonpolar solvents, for example, the extraction of benzoic acid from water into benzene. However, he provides no quantitative estimate of the interfacial resistance. Grosjean and Sawistowski (1980) have made some preliminary calculations for estimating interfacial resistance in the transfer of propionic acid from toluene to aqueous sodium hydroxide. However, they argue that since the interfacial resistance is obtained by the difference between predicted and experimental values, it is subject to much error.

In separate experiments on the dispersion-free extraction and back-extraction studies of citric acid using one set of hollow fibers in a module, it was observed that back-extraction rates were considerably lower than the extraction rates under identical conditions (Basu, 1989). Therefore it may be presumed that an interfacial mass transfer resistance exists at the strip-side phase interface. Further, the citric acid transfer rate in an HFCLM permeator was found to be quite similar to that in the back extractor made out of one set of hollow fibers (Basu, 1989).

In the theoretical model, t_{eff} was obtained from the experiments with pure membrane liquids, for example, MIBK and

Table 7. Effect of Feed Flow Variation on Removal and Mass Transfer Rate of Citric Acid

Feed Conc. % w/v	Feed Flow Rate cm^3/min	Mass Transfer Rate mg/min		Removal %	
		Exp.	Theory	Exp.	Theory
3*	1.0	10.20	13.60	34.0	45.3
3*	2.0	10.40	13.73	17.3	22.9
3*	4.0	11.04	13.79	9.2	11.5
10**	0.12	11.60	12.00	96.7	~100.0
10**	0.4	11.97	14.71	29.9	36.8
10**	1.4	10.96	14.81	7.8	10.6
10**	4.1	12.78	14.84	3.1	3.6

Membrane liquid: 40% v/v tri-octyl amine in xylenes
Module: Hydrophobic HFCLM module 3
*Strip flow rate: 1.0 cm^3/min (2% w/v aqueous NaOH)
**Strip flow rate: 1.2 cm^3/min (2% w/v aqueous NaOH)

xylenes, and using Eq. 19. The advantage of estimating t_{eff} this way is that all the uncertain parameters are lumped into one; further, t_{eff} can be determined fairly accurately by careful experiments. The assumption of course remains that the mechanism of the interfacial resistance is the same in the presence or absence of the complexing agent.

Table 7 shows the experimental and theoretically predicted mass transfer rate and percent removal of citric acid in the larger HFCLM module 3 for different feed flow rates at feed concentrations of 3 and 10% w/v of citric acid. In both cases, the strip was 2% w/v aqueous sodium hydroxide and the membrane liquid was 40% v/v TOA in xylenes. It is clear that the experimental values of mass transfer rates are reasonably close to those theoretically predicted. It is also to be noticed that the mass transfer rates do not change significantly with increase of feed flow rate and feed concentration.

Figure 7 shows the theoretically predicted and experimentally obtained permeator productivity behavior as a function of the dimensionless area-flow rate parameter A_m^+. The permeator productivity is defined as the fraction of citric acid removed from the feed to the strip stream. For this theoretical analysis and experimental verification, a simulated fermentation broth, 10% w/v citric acid in water, was considered. The model predictions appear to be quite close to the experimentally obtained productivity values. This figure also shows that more than 99% recovery is obtained for $A_m^+ = 2.3$. For module 3, which has a surface area of 454 cm^2, the permeator can treat 0.14 cm^3/min of feed stream for more than 99% recovery. Since the permeator productivity appears to be a linear function of A_m^+, it is possible to treat a larger volumetric feed rate by using larger surface area modules and keeping these modules in parallel. Note that the substrate resistance contributes significantly to the overall mass transfer resistance. Therefore, using larger diameter fibers (e.g., X-20, 240 μm ID) having higher porosity and lower tortuosity will probably increase the mass transfer rate. Moreover, larger surface area per module may be achieved with these fibers.

The next question is: how stable is this HFCLM? Danesi et al. (1987) have reached the following conclusions regarding the stability of supported liquid membranes (SLM):

1. When the electrolyte concentrations of the aqueous solutions separated by the organic membrane are approximately equal and the solubility of the organic carrier in water is low, stable SLMs are obtained
2. When the electrolyte concentrations of these aqueous solutions are very different, resulting in a large osmotic pressure gradient, SLMs become unstable and their lifetime decreases with the applied osmotic pressure gradient, the amount of water extracted, and the wettability of the SLM
3. The ability of SLMs to transport water parallels their instability; the amount of water transported is an indication of instability.

Danesi et al. (1987) also propose the following mechanism of water transport through SLMs:

1. In the presence of an osmotic pressure gradient, water tends to flow through the organic filled pores of the SLM, provided the organic phase can appreciably solubilize water; this initial water flow can be imagined as the diffusion of water molecules through a stationary organic diluent.
2. When the amount of flowing water becomes massive and the SLM is easily wetted by the aqueous phases, the organic phase is eventually displaced from the support pores and replaced by water; at this point the membrane behaves as a semipermeable diaphragm containing water-filled micropores.

The unfilled circles in Figure 8 represent the data for a stability run of 60 days in module 3 for a 10% w/v aqueous citric acid feed and a 0.5 M aqueous NaOH strip. The membrane liquid was 40% v/v TOA in xylenes. These data show that the mass transfer rate drops somewhat and then reaches asymptotically a steady value. Since both constituents of the organic membrane are practically insoluble in water, the water transport due to osmotic pressure difference is not the cause of mass transfer reduction. The work of Danesi et al. shows evidences of water transport through the organic membrane when the osmotic pressure differences between the two aqueous streams are more than 100 atm. The osmotic coefficient for 0.5 M NaOH is 0.937 (Robinson and Stokes, 1959) and the partial molar volume of water is 18.05 cm^3/gmol. The osmotic pressure of 0.5 M NaOH is 22.85 atm. Therefore the maximum osmotic pressure difference between the two aqueous streams, in the present case, is 22.85 atm. It is postulated that even though the constituents of the membrane liquid are practically insoluble in water, they have different numerical values of

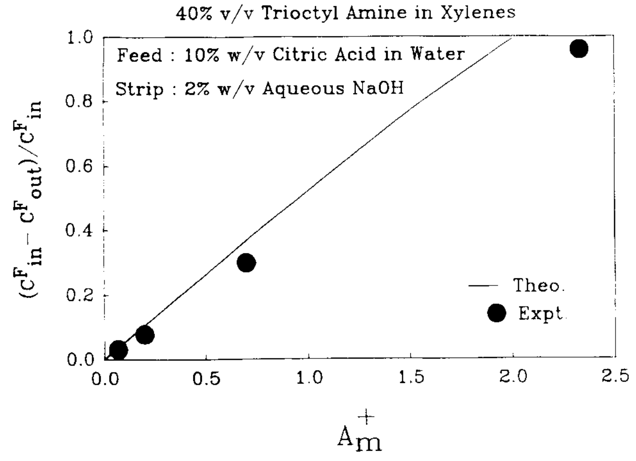

Figure 7. Performance analysis of HFCLM permeators in terms of dimensionless variables.

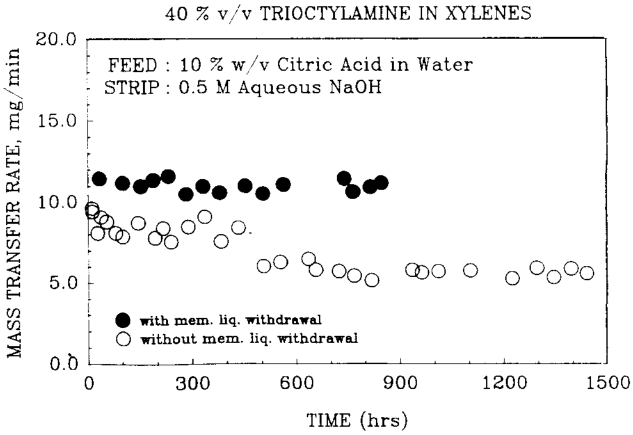

Figure 8. HFCLM stability studies: mass transfer rate vs. time with and without membrane liquid withdrawal once a day.

solubility, however small those values may be: xylene is two orders of magnitude more soluble than TOA. Therefore the membrane loses xylene at a faster rate than TOA. Even though the HFCLM is connected to a membrane liquid reservoir, that liquid has to diffuse along the length of the permeator to bring back the initial uniform concentration. Therefore, after a long time, a pseudosteady state is reached between the loss of membrane liquid to the mobile aqueous phases and the supply of it from the reservoir.

To verify this phenomenon, one 16 h experiment was performed in module 3 with 60% v/v TOA in xylenes as membrane liquid. The feed was 10% w/v aqueous citric acid and the strip was 0.5 M aqueous NaOH. At steady state, a constant mass transfer rate of 4.0 mg/min, close to the asymptote of unfilled circles in Figure 8, was observed.

Figure 8 also shows via filled circles a highly stable mass transfer performance of a separate 35-day stability run in the same module 3. All conditions were identical to those of the 60-day run (unfilled circles) except for a discharge of 2–4 cm^3 of the membrane liquid every day during this run. This procedure of discharging a small amount of membrane liquid showed a radical improvement in the stability of mass transfer rate for a long time. The discharged liquid can be reused by adding the diluent xylene.

Conclusions

The HFCLM permeation technique has been successfully employed to separate citric acid from an aqueous solution. Trioctyl amine diluted in various organic diluents was used as a complexing agent for facilitated transport of citric acid from an aqueous solution. Pure water as well as aqueous NaOH was used as the stripping agent. Membrane life and stability problems encountered in supported liquid membranes (SLM) are essentially eliminated. A mathematical model of facilitated solute transport through an HFCLM accounting for interfacial reversible reaction kinetics and diffusion process inherent in carrier-facilitated transport is presented for the whole permeator. There is considerable indirect evidence for an interfacial resistance in the citric acid back-extraction step. Experimental data agree well with the theoretical predictions when such an interfacial resistance obtained from experiments with no facilitation is incorporated in the model. This agreement was found to be valid over a variety of diluents and a wide concentration range of TOA. The extent of citric acid recovery of up to 99% is linear with the membrane area in an HFCLM permeator, suggesting easy scale-up.

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Notation

a = mass transfer area per unit permeator volume, cm^{-1}
A_m = membrane area, cm^2
A^{3-} = citrate ion
C_{io}, C_{iw} = concentration of i in organic, aqueous phase, mol/cm^3
C_{To} = total initial amine concentration in the membrane liquid, mol/cm^3
d_i, d_o = inner, outer diameter of a hollow fiber, cm
d_{lm} = log mean diameter of a hollow fiber, cm
D_{io}, D_{iw} = diffusion coefficient of i in organic, aqueous phase, cm^2/s
k_w^F, k_w^S = feed, strip phase mass transfer coefficients, cm/s
K_{eq} = equilibrium constant, Eq. 1b, $(mol/cm^3)^{-3}$
K_o, K_w = overall mass transfer coefficient for total citric acid transport based on organic phase, aqueous phase, cm/s
m_i = distribution coefficient of solute A between organic and aqueous phase, C_{Ao}/C_{Aw}, $(gmol/cm^3)/(gmol/cm^3)$
N_A^T = total flux of species A, $mol/cm^2 \cdot s$
Q = total mobile phase flow rate, cm^3/s
t = thickness, cm

Greek letters

δ = any organic liquid membrane thickness, cm
δ_m = contained liquid membrane thickness, cm
ϵ, τ = porosity, tortuosity, respectively

Subscripts

A = citric acid
B = trioctyl amine
C = citric acid–trioctyl amine complex
m = membrane
o = organic phase
s = membrane substrate
w = aqueous phase

Superscripts

F = feed side
S = strip side
in = inlet
$+$ = dimensionless

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