Mass transfer modeling of membrane carrier system for extraction of Ce(IV) from sulfate media using hollow fiber supported liquid membrane

Ramakul Prakorn, Pattaweekongka Weerawat* and Pancharoen Ura[†]

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University,
Patumwun, Bangkok, Thailand. 10330
*Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University,
Nakhon Pathom, Thailand. 73000

Abstract−A theoretical and experimental study on the extraction and stripping of Ce(IV) ions from sulfate media using microporous hydrophobic hollow fiber supported liquid membrane has been performed. The experiments were made in the recycling mode. Tri-n-octylamine (TOA) was used as extractant diluted in kerosene and sodium hydroxide was use as strip solution. The mathematical model focused on the extraction side of a liquid membrane system. The aqueous feed mass transfer coefficient (k_i) and the organic mass transfer coefficient (k_m) which were calculated from the model were 9.47×10^{-2} and 6.303 cm/s, respectively. Therefore, the rate controlling step is the diffusion of the cerium complex across a liquid membrane. In addition, the mass transfer modeling was performed and the validity of the developed model was evaluated with experimental data and found to tie in well with the theoretical value when the concentration of TOA was higher than 5% (v/v).

Key words: Cerium, Extraction, Liquid Membrane, Hollow Fiber, Modeling

INTRODUCTION

Liquid membrane extraction is an attractive hydrometallurgical process for separate precious or rare earth metal ions from aqueous solutions. Metal ions can move from low to high concentration solutions by driving force. The membranes contain an extractant or a carrier which possesses the potential for selective permeation by using the facilitated transport mechanism [Gherrou and Hacene, 2002]. Liquid membrane extraction has received considerable attention due to the advantages of combining liquid-liquid extraction and membranes in a single operation.

The potential advantages of membrane extraction process are:

1. Only small amounts of complexing agent are required due to the continuous regeneration associated with the reversible reaction. As a consequence, operating costs can be reduced;

2. Extraction and stripping can be carried out simultaneously in one equipment, reducing investment costs;

3. Backmixing effects and loss of complexing agent can be minimized when an appropriate membrane configuration is used.

4. Highly selective separations are possible. This feature is most useful at low solute concentration whereas excess of complexing agent is present and the complexation reaction is very efficient. This is in contrast to other separation processes, which do not usually work well at low solute concentrations.

A new type of liquid membrane configuration, the membrane contactor [Kiani et al., 1984], with the potential to eliminate the shortcomings of supported liquid membranes while retaining its advantages is gaining importance. It has been applied to a large variety of systems including extraction of fermentation products [Hano et al., 1993; Basu and Sirkar, 1991; Dahuron and Cussler, 1988], pollutant [Basu et al., 1998; Yun et al., 1992; Tompkins et al., 1992] pharmaceutical products [Prasad and Sirkar, 1989; Basu and Sirkar, 1992] and metals [Alexander and Callahan, 1987; Matsumoto et al., 1987; Yi, 1995; Yang and Fane, 1999]. The advantages of Hollow Fiber Supported Liquid Membranes (HFSLMs), over traditional separation techniques include lower capital and operating costs, low energy and low extractant consumption factors and high fluxes compared to solid membranes [Loiacono et al., 1986; Sheng et al., 2004]. Due to these advantages, SLMs may be very useful for the recovery of metals from solutions.

In this paper, we focused on the modeling of hollow fiber supported liquid membrane to recover cerium ions from sulfate media. A model is presented which describes the transport mechanism, indcating different rate-controlling steps, the effect of TOA concentration on the permeability coefficient, the aqueous feed mass transfer coeffient (k_i) and the organic mass transfer coeffient (k_m), all of which were investigated by the model in order to find their value and the rate-controlling setp. Moerover, the theoretical and experimental data were compared.

THEORY

A liquid membrane composed of diluent and extractant was immobilized in the pores of a hydrophobic microporous supporter which binds one of the components very selectively from the feed solution. The SLM separated the aqueous feed solution and the strip solution. The species are accumulated in the strip at a concentration generally greater than that in the feed solution. The permeation of the species is due to a chemical potential gradient (the driving

[†]To whom correspondence should be addressed.
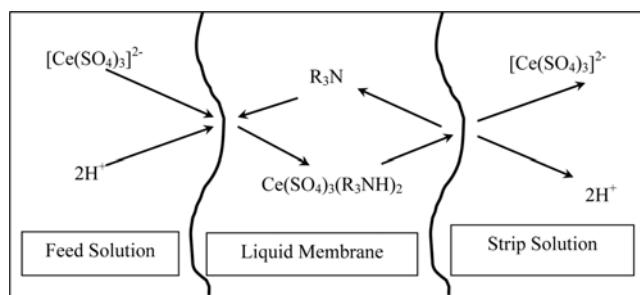E-mail: ura.p@chula.ac.th

**Fig. 1. Co-transport scheme for extraction of Ce(IV).**

force of the process) existing between two opposite sides of the SLM [Schulz, 1988; Ramakul and Pancharoen, 2003] and is described as follows [Porter, 1990]:

The metal ions are complexed by extractant at the interface feed-phase/membrane and the complex formed diffuses through the membrane phase to the interface membrane/strip-phase where the de-complexation of the metal ions occurs. In this case, the carrier is being a basic extractant. The transport mechanism of metal ions that occurs in this case, called co-transport, is shown in Fig. 1, and metal ions must be in anion complex form [Porter, 1990]. The chemistry of extraction is shown in Eq. (2) [Ramakul, 2002].

The hollow fiber module consists of a liquid membrane and two sides for aqueous solutions. The liquid membrane, solution of TOA in kerosene, was trapped in hydrophobic micropore due to capillary force [Schulz, 1988] and separated feed and strip solution. In this work, cerium sulfate as feed phase was flowing in tube side and sodium hydroxide as stripping phase was flowing in the shell side. Feed solution and strip solution flow countercurrently and liquid membrane was between them as shown in Fig. 2 [Ramakul and Pancharoen, 2003; Ramakul et al., 2004].

1. The Extraction Equilibruim

The extraction of Ce(IV) by TOA as extractant dissolved in kerosene has been studied and described elsewhere [Pattaweekongka, 2004]. The $Ce(SO_4)_2$ in presence of higher sulfuric concentration will result in $Ce(SO_4)_3^{2-}$ - type species [Chaudry, 1996]:

$$Ce(SO_4)_2 + H_2SO_4 \Leftrightarrow H_2Ce(SO_4)_2 \Rightarrow Ce(SO_4)_3^{2-} + 2H^+ \tag{1}$$
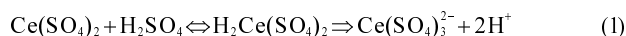
Amine molecules in an acidic aqueous solution will form a neutral
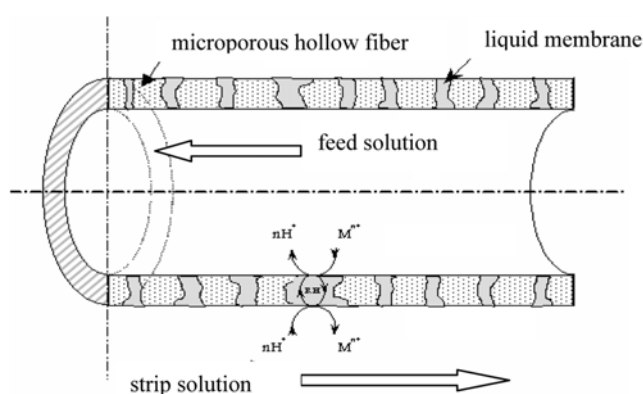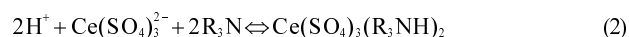

Fig. 2. Flow pattern in hollow fiber supported liquid membrane [Ramakul and Pancharoen, 2003].

species, which is extractable into the organic phase:

$$2H^+ + Ce(SO_4)_3^{2-} + 2R_3N \Leftrightarrow Ce(SO_4)_3(R_3NH)_2 \tag{2}$$

Ce(IV) ions in sulfuric acid can be extracted as $Ce(SO_4)_3^{2-}$.

In the presence of sodium hydroxide in the stripping phase the reaction on the stripping side membrane will be:

$$(R_3NH)_2Ce(SO_4)_3 + NaOH + R_3N$$
$$\Leftrightarrow Na_2Ce(SO_4)_3 + 2R_3N + N_2O \tag{3}$$
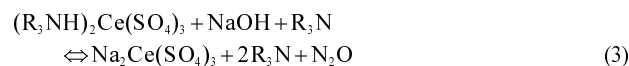
From the extract reaction in Eq. (2), the extraction equilibrium (K_{ex}) can be described as:

$$K_{ex} = \frac{[(R_3NH)_2Ce(SO_4)_3]_{org}}{[R_3N]_{org}^2[H^+]_{aq}^2[Ce(SO_4)_3^{2-}]_{aq}} \tag{4}$$

D, the distribution ratio for Ce(IV), is given by

$$D = \frac{[(R_3NH)_2Ce(SO_4)_3]_{aq}}{[Ce^{4+}]_{aq}} = K_{ex}[R_3N]_{org}^2[H^+]_{aq}^2 \tag{5}$$

The distribution ratio could be present as

$$\log D = \log K_{ex} + 2\log[R_3N]_{aq} - 2pH \tag{6}$$

The value of K_{ex} for Ce(IV) with TOA was found to be 0.653 [Pattaweekongka, 2004].

2. Determining of Permeability Coefficients

Considering linear concentration gradients, fast interfacial reactions and the distribution ratio of metal ions between feed and membrane phase being much higher than that between the membrane phase and stripping phase, the final equation obtained for permeability could be expressed as suggested by Danesi [1984].

$$-V_f\ln\left(\frac{C_f}{C_{f,0}}\right) = AP\frac{\beta}{\beta+1}t \tag{7}$$

where

$$\beta = \frac{Q_f}{PL\varepsilon\pi Nr_i} \tag{8}$$

P is permeability coefficient. C_f and $C_{f,0}$ are cerium ions concentration at time t and 0, respectively. A and V_f are effective area of the membrane and volume of the feed, respectively. Q_f is volumetric flow rate of feed solution that flows through the tube side. Plot $V_f\ln(C_f/C_{f,0})$ versus t. Therefore, $AP(\beta/\beta+1)$ is the slope and P can be obtained by analytical calculation. Where L, N, r_i, and ε are the length of the fiber, number of hollow fibers in the module, internal radius of hollow fiber and porosity of hollow fiber, respectively.

3. Mass Transfer Modeling

The mathematical model of a hollow fiber supported liquid membrane for the separation of cerium(IV) using permeability coefficient depends on three mass transfer resistances because the number of steps of the transport mechanism is three. One of them is the resistance when the liquid is flowing through the hollow fiber lumen. The second resistance is the diffusion of the cerium complex across liquid membrane that is immobilized in the porous wall of the fiber. The third resistance is due to the strip solution and organic interface at the outside of the fiber. The mass transfer resistance is the reciprocal of the mass transfer coefficient and the relation is given as the following [Rathore, 2001]:

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{P_m} + \frac{r_i}{r_o}\frac{1}{k_s} \qquad (9)$$

where r_{lm} is the log-mean radius of the hollow fiber, k_i and k_s are the aqueous and stripping mass transfer coefficient in tube and shell side, respectively. P_m is the membrane permeability, which is related to the distribution ratio (D)

$$D = \frac{[(R_3NH)_2Ce(SO_4)_3]_{aq}}{[Ce(SO_4)_3^{2-}]} = K_{ex}[R_3N]_{org}^2[H^+]_{aq}^2 \qquad (10)$$

and the relation of D and P_m is [Rathore, 2001]

$$P_m = Dk_m \qquad (11)$$

Combining Eqs. (10) and (11), we get

$$P_m = K_{ex}k_m[R_3N]_{org}^2[H^+]_{aq}^2 \qquad (12)$$

where k_m is the membrane mass transfer coefficient.

Substituting P_m in Eq. (12) into Eq. (9) and assuming the strip reaction is instantaneous, the contribution of stripping phase is neglected. Therefore, Eq. (9) is expressed as

$$\frac{1}{P} = \frac{1}{k_i} + \frac{r_i}{r_{lm}}\frac{1}{K_{ex}k_m[R_3N]_{org}^2[H^+]_{aq}^2} \qquad (13)$$

EXPERIMENTAL

1. Reagents

Ce(SO$_4$)$_2$·4H$_2$O and H$_2$SO$_4$ were used in feed solution. Tri-n-Octylamine was used as extractant and the diluent was kerosene and NaOH was used as strip solution. All chemicals were A.R. grade and supplied by Merck.

2. Apparatus

The Hollow Fiber, which is manufactured by Hoechst Celanese, Charlotte, NC (Liqui-Cel® Extra-Flow module), was used as a support material. This module uses Celgard® microporous polyethylene fibers that are woven into fabric and wrapped around a central tube feeder that supplies the shellside fluid. Woven fabric allows more uniform fiber spacing, which in turn leads to higher mass transfer coefficients than those obtained with individual fibers. The property of the hollow fiber module is specified in Table 1. The fiber is potted into a solvent-resistant polyethylene tubesheet and shell casing in polypropylene.
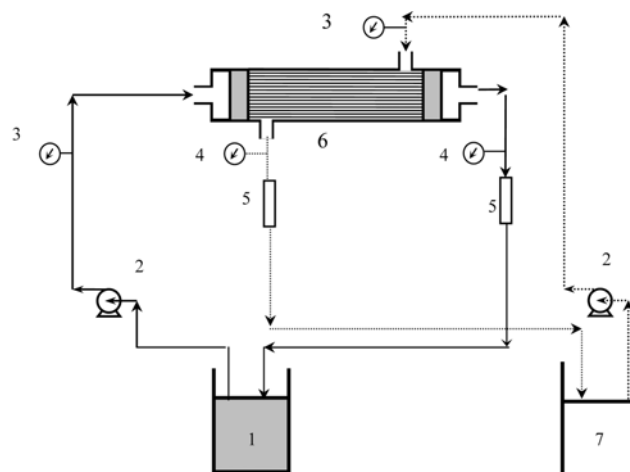
The Liqui-Cel® Laboratory Liquid/Liquid Extraction Systems

Fig. 3. Schematic counter-current flow diagram for recycling mode operation in hollow fiber supported liquid membrane.
1. Feed reservoir
2. Gear pump
3. Inlet pressure gauges
4. Outlet pressure gauges
5. Flow meters
6. Hollow fiber module
7. Strip reservoir

were used. They are composed of two gear pumps, two variable speed controllers, two rotameters and two pressure gauges. The flow diagram is shown in Fig. 3.

The concentration of cerium ions were measured by Inductively Coupled Plasma Spectroscopy (ICP).

3. HFSLM Preparation and Methods

The feed solution was made by dissolution of Ce(SO$_4$)$_2$·4H$_2$O and H$_2$SO$_4$. The concentration of Ce(IV) was 100 ppm and the concentration of H$_2$SO$_4$ was 0.5 M due to the optimized concentration [Chaudry, 1996]. The liquid membrane phase was prepared by dissolution of TOA in kerosene. The strip solution was NaOH. The organic solution which contained TOA was circulated in the tube and shell side for 20 minutes. After that, the experiment was started by flowing the feed solution into the tube side of both hollow fiber modules. Simultaneously, the strip solution was pumped into the shell side of hollow fiber module countercurrently, and once-through-mode operation was used. The module was operated in recycling mode and schematic of the process is shown in Fig. 3. In this work, feed containing 100 ppm Ce(IV) in sulfate media and strip containing 0.5 M NaOH was used. Samples of 2 cm^3 were taken out at different times from the feed and strip tanks Membrane permeabilities were determind by monitering Ce(SO$_4$)$^{2-}$ concentration by ICP in the raffinate and as a function of time.

RESULTS AND DISCUSSION

1. The Effect of TOA Concentration on the Extractability of Ce(IV)

Fig. 4 shows the relation of cerium concentration in feed solution versus time at different concentrations of TOA, which shows that the extractability was very poor when TOA concentration was lower than 5% (v/v) but abruptly increased when the TOA concentration was higher than 5% (v/v) to 10% (v/v).

2. Calculation of Permeability

Table 1. Property of hollow fiber module [Hoechst Celanese Corporation, 1995]

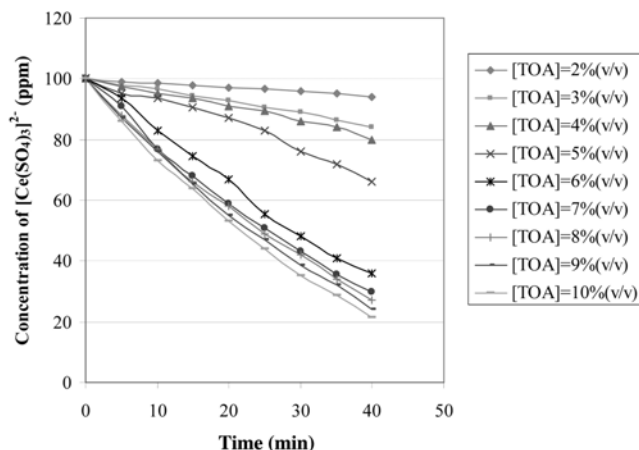| Properties	Description
Materials	Polypropylene
Fiber i.d.	240 μm
Fiber o.d.	300 μm
Size of pore	0.05 μm
Porosity	30%
Contact area	1.39 m^2
Area per unit volume	29.3 cm^2/cm^3
Module diameters	6.3 cm
Module length	20.3 cm

Fig. 4. Plot of cerium concentration in feed solution against time while using different TOA concentration.
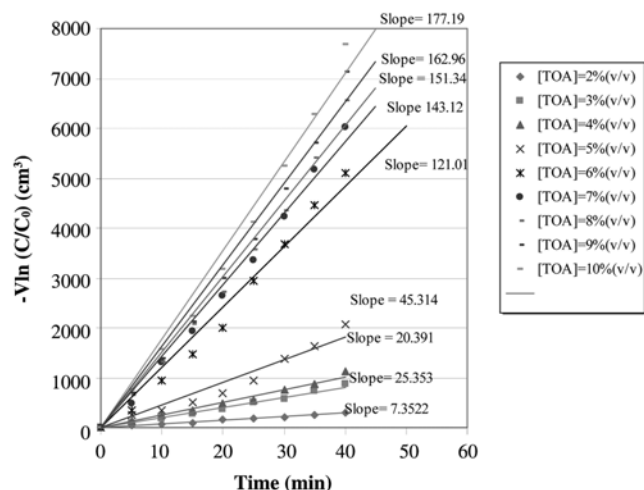

Fig. 5. Plot of $-V_f\ln(C_f/C_{f,0})$ of feed tank against time while using different TOA concentration.

The relation of $-V_f\ln(C_f/C_{f,0})$ versus time is shown in Fig. 5, and the permeability can be calculated from Eq. (7) and Eq. (8). The permeabilities of Ce(IV) which will be used with the calculation for the concentration of TOA of 2, 3, 4, 5, 6, 7, 8, 9, 10% (v/v) were 5.43×10^{-4}, 1.61×10^{-3}, 1.76×10^{-3}, 4.10×10^{-3}, 1.97×10^{-2} 3.04×10^{-2}, 3.60×10^{-2}, 4.77×10^{-2} and 7.12×10^{-2}, respectively.

3. Calculation of Mass Transfer Coefficients and Diffusion Coefficient

The aqueous and membrane mass transfer coefficient, k_i and k_m, respectively, can be evaluated by using Eq. (14) as follows:

$$\frac{1}{P}=\frac{1}{k_i}+\frac{r_i}{r_{lm}}\frac{1}{K_{ex}k_m[R_3N]^2_{org}[H^+]^2_{aq}} \tag{14}$$

When we plot(1/P) as a function of $1/[R_3N]^2$ for different concentrations of R_3N as shown in Fig. 6, a straight line with slope $r_i/r_{lm}K_{ex}k_m$ and ordinate of $1/k_i$ results. Therefore, from Fig. 6, the values of k_i and k_m can be calculated from the slope and ordinate as 9.47×10^{-2} and 6.303 cm/s, respectively. The membrane mass transfer coefficient (k_m) was much higher than the aqueous feed mass transfer co-
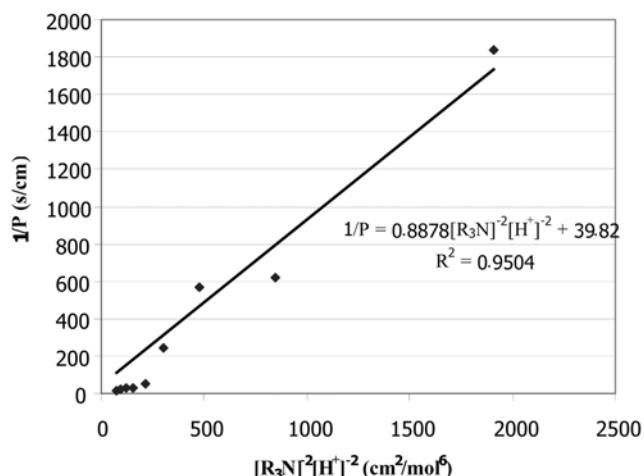
Fig. 6. Plot of 1/P as a function of $1/[H^+]^2[R_3N]^2$.

efficient (k_i). From this result, the rate controlling step is the mass transfer in aqueous film between feed solution and liquid membrane.

4. Flux Modeling of Cerium(IV)

We consider the reaction of extraction in Eq. (2). We denote $[Ce]_{org}$ and $[Ce]^{org}_i$ as the concentration of cerium complex in organic phase and at the interface between the feed and organic phase, respectively.

Where

$$[Ce]_{org}=[(R_3NH)_2Ce(SO_4)_3]_{org} \tag{15}$$

and from equilibrium constant in Eq. (4), we can rewrite that

$$[Ce]_{org,i}=K_{ex}[R_3N]^2_{org}[H^+]^2[Ce(SO_4)^{2-}_3]_{f,i} \tag{16}$$

From the relation [Aamrani, 1999]

$$J_m\theta_m=[Ce]_{org,i} \tag{17}$$

and

$$J_i\theta_i=[Ce(SO_4)^{2-}_3]_f-[Ce(SO_4)^{2-}_3]_{f,i} \tag{18}$$

where $\theta_0=1/k_m$ and $\theta_i=1/k_i$ are the aqueous and organic mass transfer resistances, respectively, and $[Ce(SO_4)^{2-}_4]_f$ and $[Ce(SO_4)^{2-}_4]_{f,i}$ are the concentration of cerium ion complex in feed solution and at interface at time t, respectively.

$[Ce]^{org}_i$ in Eq. (16) was substituted in Eq. (17) to obtain

$$[Ce(SO_4)^{2-}_3]_{f,i}=\frac{J_m\theta_m}{K_{ex}[R_3N]^2_{org}[H^+]^2} \tag{19}$$

Substituting this expression into Eq. (18) and assuming that $J_m=J_i=J$ due to steady state, the flux equation is

$$J=\frac{K_{ex}[R_3N]^2_{org}[H^+]^2}{\theta_m+\theta_iK_{ex}[R_3N]^2_{org}[H^+]^2}[Ce(SO_4)^{2-}_3]_f \tag{20}$$

According to the membrane phase

$$[R_3N]^{ini}_{org}=[R_3N]_{org}+2[Ce]_{org} \tag{21}$$

where $[R_3N]^{ini}_0$ is the total concentration of tri-n-octylamine and $[R_3N]_{org}$ is the free extractant concentration. We assume $[R_3N]_{org}$ can be neglected. Therefore,

$$[R_3N]^{ini}_{org}\cong2[Ce]_{org} \tag{22}$$

Combining Eq. (4), Eq. (15) and Eq. (22) and rearranging, we get

$$[R_3N]_{org}^2[H^+]^2 = \frac{[R_3N]_{org}^{ini}}{2K_{ex}[Ce(SO_4)_3^{2-}]_{f,i}} \tag{23}$$

Substituting Eq. (23) into Eq. (20) and rearranging, we obtain

$$J = \frac{[R_2N]_{org}^{ini}}{2\theta_m[Ce(SO)_3^{2-}]_{f,i} + \theta_i[R_3N]_{org}^{ini}}[Ce(SO_4)_3^{2-}]_f \tag{24}$$

Because the concentration of cerium at interface ($[Ce(SO_4)_3^{2-}]_{f,i}$) cannot be measured, Eq. (18) was substituted and rearranged into a quadratic equation.

$$2J^2\theta_m\theta_i - (2\theta_m[Ce(SO_4)_3^{2-}]_f + \theta_i[R_3N]_{org}^{ini})J$$
$$+ [R_3N]_{org}^{ini}[Ce(SO_4)_3^{2-}]_f = 0 \tag{25}$$

The flux equation was solved to

$$J = \frac{2\theta_m[Ce(SO_4)_3^{2-}]_f + \theta_i[R_3N]_{org}^{ini}}{2\theta_m\theta_i}$$
$$\frac{+\sqrt{(2\theta_m[Ce(SO_4)_3^{2-}]_f + \theta_i[R_3N]_{org}^{ini})^2 - 8\theta_m\theta_i[R_3N]_{org}^{ini}[Ce(SO_4)_3^{2-}]_f}}{2\theta_m\theta_i} \tag{26}$$

Due to $8\theta_m\theta_i[R_3N]_{org}^{ini}[Ce(SO_4)_3^{2-}] << (2\theta_m[Ce(SO_4)_3^{2-}]_f + \theta_i[R_3N]_{org}^{ini})^2$, the term of $8\theta_m\theta_i[R_3N]_{org}^{ini}[Ce(SO_4)_3^{2-}]$ can be neglected. Therefore, we get the final expression for cerium flux:

$$J = \frac{[Ce(SO_4)_3^{2-}]_f}{\theta_i} + \frac{[R_3N]_{org}^{ini}}{2\theta_m} \tag{27}$$

From the definition [Chaudry, 1996; Su-Hsia, 2001]

$$J = \frac{-d[Ce(SO_4)_3^{2-}]_f}{dt}\frac{V}{A} \tag{28}$$

Combining Eq. (27) and (28) to be

$$-\frac{d[Ce(SO_4)_3^{2-}]_f}{dt}\frac{V}{A} = \frac{[Ce(SO_4)_3^{2-}]_f}{\theta_i} + \frac{[R_3N]_{org}^{ini}}{2\theta_m} \tag{29}$$

and integrating with initial condition of t=0, $[Ce(SO_4)_3^{2-}]_f = [Ce(SO_4)_3^{2-}]_{f,o}$ the final equation of cerium ions concentration can be expressed as:

$$[Ce(SO_4)_3^{2-}]_f = \frac{-\theta_i[R_3N]_{org}^{ini}}{2\theta_m}$$
$$+ \left([Ce(SO_4)_3^{2-}]_{f,o} + \frac{\theta_i[R_3N]_{org}^{ini}}{2\theta_m}\right)\exp\left(-\frac{A}{V\theta_i}t\right) \tag{30}$$

In Fig. 7(a)-(e) is shown a comparison of the experimental data and the calculation from Eq. (31). When the concentration of TOA was lower than 5% (v/v), the mass transfer model was poor, but when the concentration of TOA was from 5% (v/v) and higher, the mass transfer model was valid as shown in Fig. 8(a)-(e).

Due to the result shown in Fig. 4, at a low concentration the separation result is very poor, but after increasing the concentration of the extractant to a certain level (5% (v/v)) the separation result comes out very good at this range, which hits the optimum condition of using the extractant concentration. Any higher than 10% (v/v) the
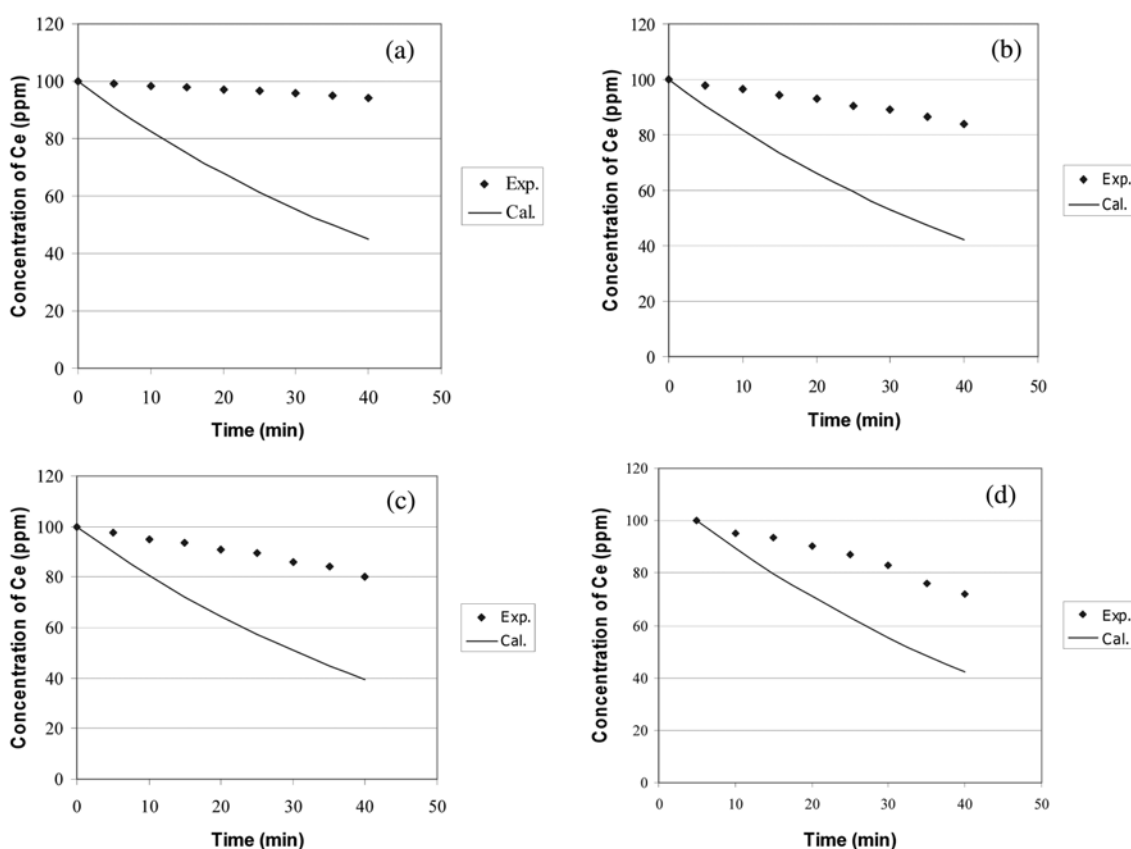

Fig. 7(a)-(d). Plot of concentration of Ce(IV) in feed solution and time when the concentrations of TOA were 2%, 3%, 4%, 5% (v/v), respectively. 100 ppm Ce(IV) in feed solution and 0.5 M H₂SO₄ and 0.5 M NaOH for feed and strip solution, respectively. Solid line is the result from experiment and the dashed line is from the calculation by Eq. (30).
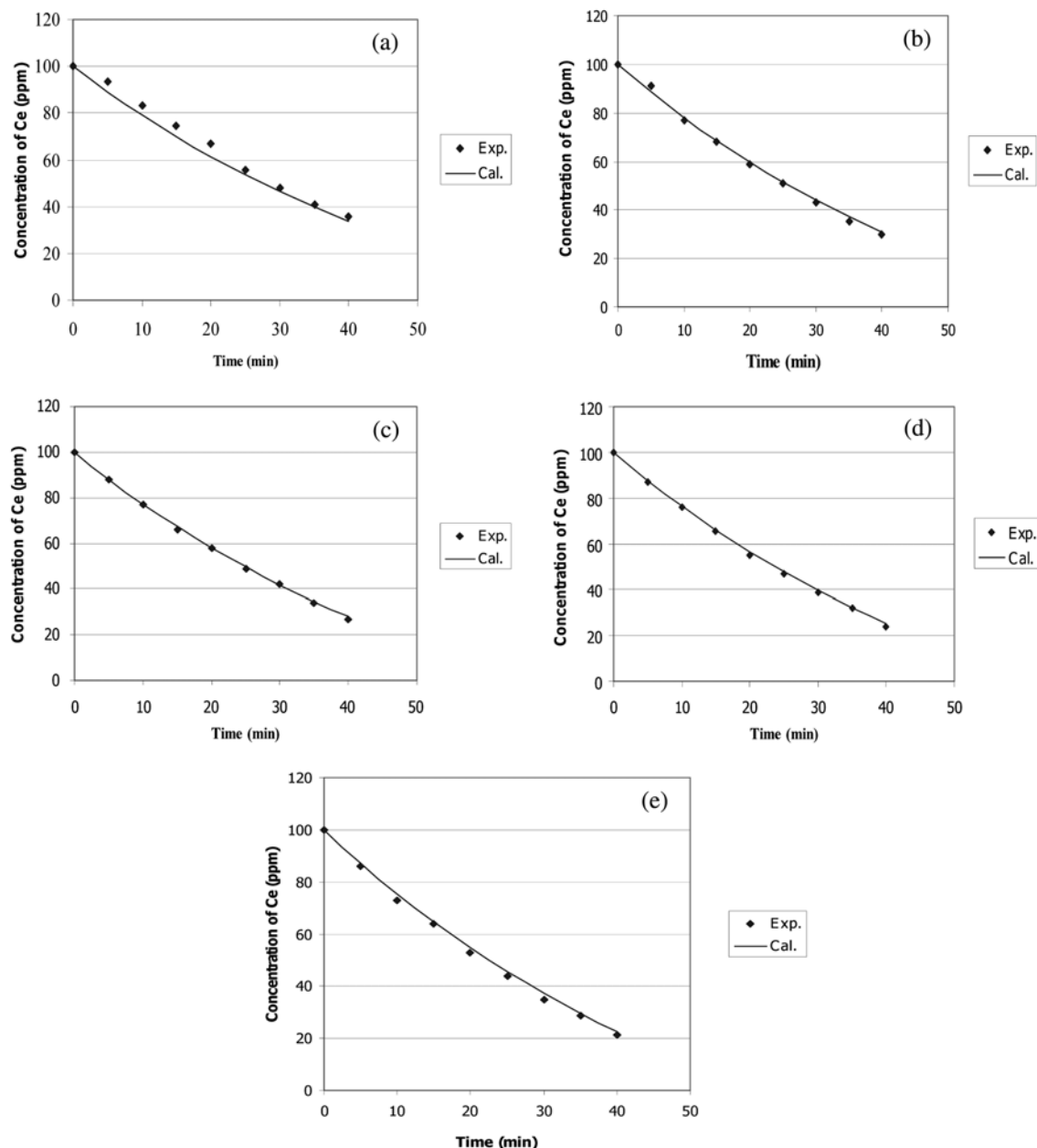
Fig. 8(a)-(e). Plot of concentration of Ce(IV) in feed solution and time when the concentrations of TOA were 6%, 7%, 8%, 9%, 10% (v/v), respectively, for the membrane. 100 ppm Ce(IV) in feed solution and 0.5 M H₂SO₄ and 0.5 M NaOH for feed and strip solution, respectively. Solid line is the result from experiment and the dashed line is from the calculation by Eq. (30).

extractant will increase the viscosity and slow down the membrane permeability [Ramakul et al., 2004].

CONCLUSIONS

The Ce(IV) ions in the from of $Ce(SO_4)_3^{2-}$ can be extracted and stripped by TOA as extractant from sulfate media by microporous hydrophobic hollow fiber supported liquid membrane. The aqueous feed mass transfer coefficient (k_i) and the organic mass transfer coefficient (k_m) which were calculated from the model were 9.47×10^{-2} and 6.303 cm/s, respectively. Therefore, the rate controlling step is the mass transfer in aqueous film between feed solution and membrane. The mass transfer modeling was performed and the va-

lidity of developed model was evaluated with experimental data and found to tie in well with the theoretical values when the concentration of extractant, TOA, was higher than 5% (v/v).

NOMENCLATURE

k_i : aqueous feed mass transfer coefficient [cm/s]
k_m : organic mass transfer coefficient [cm/s]
D_{eff} : effective diffusion coefficient [cm²/s]
K_{ex} : extraction equilibrium [-]
D : distribution ratio [-]
P_m : membrane permeability [cm/s]
t_m : thickness of the fiber membrane [cm]
r_{lm} : the log-mean radius of the hollow fiber [cm]
A : effective area of the membrane [cm²/s]
V_f : volume of the feed reservoir [cm³]
Q_f : volumetric flow rate of feed solution that flow through
    the tube side [cm³/s]
L : length of the fiber [cm]
N : number of hollow fiber in module [-]
r_i : internal radius of hollow fiber [cm]
r_o : external radius of hollow fiber [cm]

Greek Letters

τ : tortousity of the membrane [-]
ε : porosity, of hollow fiber [-]
θ_m : organic membrane mass transfer resistances [s/cm]
θ_i : aqueous and organic mass transfer resistances [s/cm]

Superscripts

ini : ini refer to at initial time
t : refer to at time t

Subscripts

f : refer to in feed phase
i : refer to at interface between feed and organic phase
org : refer to in organic phase

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