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Separation of zirconium and hafnium using hollow fibers
Part I. Supported liquid membranes

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Abstract

A supported liquid membrane system using hollow fiber membranes as supports (HFSLM) has been studied for the separation of zirconium and hafnium, which are typical metal pairs with extreme similarity in chemistry. Tri-*n*-octylamine (TNOA) and trioctylmethyl ammonium chloride (Aliquat 336) were used as carriers. The effect on the transport and separation of Zr and Hf of HCl concentrations in the feed and stripping solutions, hollow fiber length, flow rate of aqueous phases was investigated. The mechanism of transport through the HFSLM is discussed. The controlling step for the liquid membrane process was the diffusion in the membrane, except at low flow rates. The HFSLM acquires a maximum Zr/Hf flux ratio of about 160, which is 20 times than that of a flat-sheet system reported previously.

Keywords: Zirconium; Hafnium; Hollow fiber-supported liquid membrane; Transport; Separation

1. Introduction

Zirconium (Zr) and hafnium (Hf) are two of the most important nuclear materials; the use of Zircaloy in the construction of fuel elements and other structural components in reactor cores meets many physical and technological requirements. One advantage of Zr in nuclear applications is its low thermal neutron capture cross-section (0.18 b/a), whereas Hf has 640 times higher neutron absorption. Therefore, the amount of Hf present in Zr has a direct effect on the efficiency of the reactor core and thus on the cost of producing nuclear power. Moreover, the total amount of Hf in the reactor core affects the reactor shutdown margin, a major safety concern. In other technical applications in geochemistry and cosmochemistry, the precise measurement of the Hf isotopic ratio (^{176}Hf/^{177}Hf) is an important chronometering tool which requires pure Hf separated from the associated Zr.

The chemical similarity of Zr and Hf, both in their metallic and compound states, is greater than that between any other homologous elements in the periodic table (the atomic and ionic radii of Zr and Hf are virtually identical; atomic radius: Zr $= 1.45$ Å, Hf $= 1.44$ Å; ionic radius: $Zr^{4+} = 0.74$ Å, $Hf^{4+} = 0.75$ Å) [1]. In recent years, the problem of Zr/Hf separation has acquired significant importance. The separation of Zr and Hf can be achieved in solvent extraction technology in multi-stages of two separate steps (extraction and stripping) using tri-*n*-butylphosphate (TBP) as extractant [2,3]. These two processes can be combined in a single step by the use of a liquid membrane (LM), which potentially offers high selectivity in a single operation. However, the use of LMs for the difficult Zr and Hf separation has been very limited. Supported liquid membrane (SLM) using microporous membranes eliminates the major disadvantages of solvent extraction such as emulsification, flooding and loading limits, phase disengagement and large solvent inventory. Chaudry and Malik investigated transport of Zr(IV) [4] and Hf(IV) [5] through SLMs consisting of flat-sheet polypropylene microporous membranes impregnated with TBP–xylene. The maximum fluxes of 12.9×10^{-6} mol/m^2 s (Zr) and 2×10^{-6} mol/m^2 s (Hf) were found and a Zr/Hf flux ratio of about 8 was obtained at the optimized conditions of TBP concentration <2.93 M, HNO_3 concentration 5–6 M and temperature 10 °C [5]. If a practical Zr/Hf process based on SLMs is to be developed, it is likely to use hollow fiber membranes as substrates. The hollow fiber-supported liquid membrane (HFSLM) is characterized by high surface/volume ratio and low organic extractant inventory and there has been no report on this approach for Zr/Hf separation. Liquid anionic exchangers such as tri-*n*-octylamine (TNOA) and tri-*n*-octyl-monomethyl ammonium chloride

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Nomenclature

aq	aqueous phase
A	membrane area (m^2)
C	concentration (mol/l)
D	diffusion coefficient (m^2/s)
J	flux ($mol/m^2\,s$)
k	mass transfer coefficient (m/s)
K_d	distribution coefficient
org	organic phase
SF	separation factor
t	time (s)
V	volume (l)

Greek letters

δ	membrane thickness (m)
ε	porosity (%)
τ	tortuosity

Subscripts

F	feed
m	membrane
S	strip

(Aliquat 336) have higher selectivity than TBP for Zr/Hf separation [6–9] and have been investigated for flat-sheet SLM extraction of metals such as Cr, Cd, V, W, Rh, Au, Pt [10–18]. In this study, TNOA and Aliquat 336 were used as mobile carriers in the membrane phase immobilized in the walls of hollow fiber membranes for Zr/Hf separation.

2. Principles of SLM

SLM employ a thin microporous membrane that has been impregnated with an organic solvent to separate the feed and stripping solutions. In a specific application, the organic solvent, feed and stripping solutions can be the same as used in the solvent extraction. At the feed/membrane interface, the extraction takes place and the formed metal complex diffuses to the membrane/stripping interface where the stripping occurs. The features of the SLM compared to the conventional solvent extraction are that the extraction and stripping are simultaneously carried out in such a way that equilibrium limitation is not applicable, no limitations of the aqueous/organic ratio are required, and emulsification, flooding and loading limits, phase disengagement and large solvent inventory are avoided.

3. Experimental

3.1. Materials and chemicals

TNOA, tri-*n*-octyl-monomethyl ammonium chloride (marketed as Aliquat 336, molecular weight: 404.17), kerosene (b.p.: 175–325 °C), 2-ethyl-1-hexanol (FW: 130.23, b.p.: 183–186 °C) were obtained from Aldrich Chemical, USA. Zirconium and Hafnium standard solutions (Aldrich Chemical, USA) were 1000 μg/ml. All other chemicals used were of analytical grade, and all the chemicals were used as received. Water with a resistivity of 18 MΩ purified using a Milli-Q (Millipore) system was used throughout.

The hollow fiber membranes, kindly supplied by Akzo, have an inner diameter of 600 μm and a wall thickness of 200 μm (mean value). The pore size and porosity of the fiber are 0.2 μm and 69%, respectively. The material of the fiber is polypropylene.

3.2. Preparation of hollow fiber membrane module

The fibers were arranged into a bundle and the ends were embedded into a glass tube (diameter: 18 mm) by means of epoxy resin potting material. When the epoxy resin became hard, the plug was sliced open at the glass tube end. The module was placed vertically and the organic membrane phase (carrier + diluent + modifier: 0.5 M TNOA–1 M 2-ethyl-1-hexanol or 0.2 M Aliquat 336–1 M 2-ethyl-1-hexanol in kerosene) was fed into the lumen of the fibers from the top of the module until all the fibers were impregnated. A compressed air flow was passed through the module for a few minutes to remove the excess organic liquid. The modules prepared are listed in Table 1.

3.3. Solvent extraction

Equal volumes of the aqueous zirconium and hafnium mixture in the HCl medium (6–10 M) and the organic solution were shaken for 10 min in a tube and then centrifuged for 5–10 min at a speed of 1000 rpm. The concentrations of Zr and Hf in the aqueous phase were determined by the ICP-AES method described below. The distribution coefficient (K_d) is calculated by

$$K_d = \frac{C(\text{org})}{C(\text{aq})} \tag{1}$$

and the separation factor (SF_{sx}) by

$$SF_{sx} = \frac{K_{d\,Zr}}{K_{d\,Hf}} \tag{2}$$

Table 1
Characterization of HFSLM modules

	Module			
	1	2	3	4
Number of fibers	35	118	118	118
Packing density (%)	13.7	46.1	46.1	46.1
Length (mm)	300	100	200	300
Carrier	TNOA	Aliquat 336	Aliquat 336	Aliquat 336

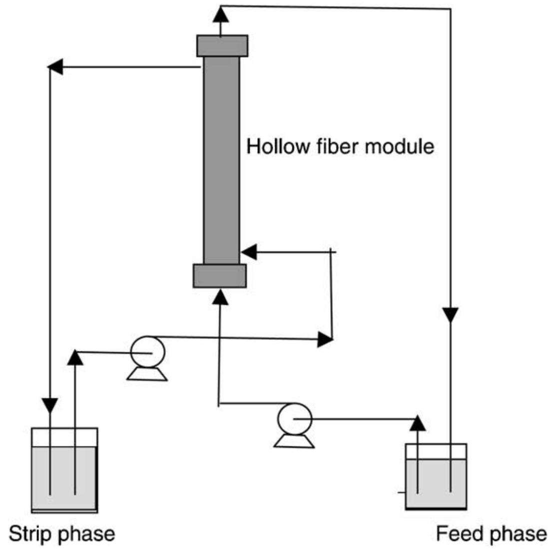

Fig. 1. Schematic diagram of HFSLM. The microporous polypropylene hollow fiber membranes (600 μm i.d., 200 μm thick and 69% porosity) were arranged into a glass tube (18 mm o.d.) and were impregnated with 0.5 M TNOA–1 M 2-ethyl-1-hexanol or 0.2 M Aliquat 336–1 M 2-ethyl-1-hexanol in kerosene. The module was placed vertically and the feed (8 M HCl) and stripping (2 M HCl) solutions were pumped co-currently through the lumen and the shell side of the fibers, respectively. The feed and strip solutions were stirred with magnetic bars.

3.4. LM transport

The experimental setup is shown in Fig. 1. The feed and strip solutions were pumped co-currently through the lumen and the shell side of the fibers, respectively, in upward flow at flow rates of 0.8–8.8 ml/min by a peristaltic pump. All the experiments were carried out at a constant temperature (22 ± 2 °C). Samples (0.5 ml) from the feed and strip tanks (100 ml) were taken at the given time intervals and analyzed by ICP-AES. The HCl concentrations in the feed and stripping solutions were measured by standard NaOH titration.

The extraction % and recovery % were calculated by

$$\text{Extraction (\%)} = \frac{C_{F,0} - C_{F,t}}{C_{F,0}} \tag{3}$$

$$\text{Recovery (\%)} = \frac{C_{S,t} V_S}{C_{F,0} V_F} \tag{4}$$

Mass flux of Zr (or Hf) is expressed by

$$J = \frac{V_F}{A} \frac{dC_F}{dt} \tag{5}$$

where C_F is the Zr (or Hf) concentration in the feed solution at time t, V_F the volume of the feed solution and A the contact area of the membrane.

The overall mass transfer coefficient (k) can be estimated from

$$-\ln \frac{C_{F,t}}{C_{F,0}} = \frac{kA}{V_F} t \tag{6}$$

where $C_{F,0}$ is the initial concentration in the feed solution.

The selectivity of the HFSLM can be expressed by the separation factor (SF) of Zr and Hf after the transport experiments obtained from

$$SF = \frac{(C_{Zr}/C_{Hf})_{strip}}{(C_{Zr}/C_{Hf})_{feed}} \tag{7}$$

or by the Zr/Hf flux ratio

$$S = \frac{J_{Zr}}{J_{Hf}} \tag{8}$$

3.5. Analytical method

The concentrations of Zr and Hf were determined by an ICP-AES instrument (Jobin-Yvon 70 II, Longjumeau, France) at Zr(II) 343.823 nm and Hf(II) 232.247 nm.

4. Results and discussion

4.1. Solvent extraction

The solvent extraction was investigated by varying shaking time and HCl concentration. The extraction and strip reached equilibrium within 30 s (8 M HCl feed and 2 M HCl strip concentration). The separation factor as a function of HCl concentration is presented in Fig. 2. It was observed that a third phase was produced between the aqueous and organic phases if no phase modifier (2-ethyl-1-hexanol) was added. The third phase disappeared with the presence of the modifier; however, the aqueous phase turned cloudy even after centrifugation. This is a major disadvantage of amine extractant (also known as liquid ion-exchangers) in solvent extraction.

4.2. Transport of Zr and Hf through HFSLM

The Zr and Hf transport processes through the HFSLM using module 1 are shown in Fig. 3. The extraction of Zr and Hf increased very rapidly with time in the initial stage and that of Zr reached >85%, and that of Hf reached about 15% within 1 h at initial HCl and Zr (or Hf) concentrations

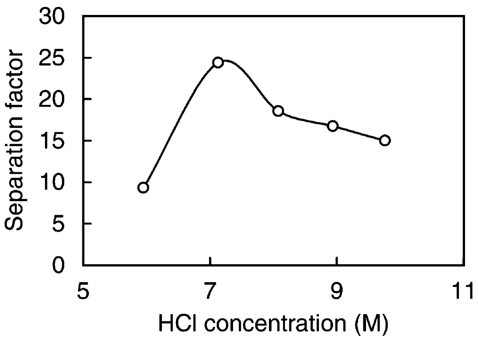

Fig. 2. Separation factor as a function of HCl concentration by solvent extraction (organic phase, 0.5 M TNOA; phase ratio, A/O = 1:1; contact time, 10 min).

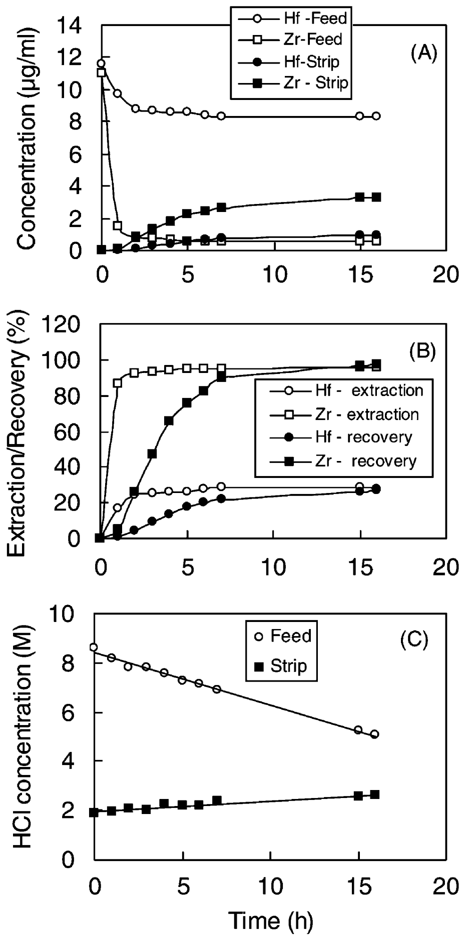

Fig. 3. Selective transport of Zr and Hf through HFSLM. Module 1 (35 fibers × 300 mm long): membrane phase 0.5 M TNOA; co-current up flow rate = 2.1 ml/min; feed solution, 20 ml of 8.6 M HCl; strip solution, 80 ml of 1.9 M HCl. (A) Zr and Hf concentrations change in the feed and stripping solutions; (B) extraction and recovery; (C) HCl concentration changes as a function of time.

of 8.6 M and 12 μg/ml, respectively. Then the extraction leveled-off. This was due to the decrease in Zr, Hf and HCl concentrations in the feed solution. Fig. 3 indicates that the HCl concentrations of the feed solution decreased linearly with time and that of the stripping solution increased linearly suggesting that the extraction of Zr (or Hf) and HCl by the carrier TNOA takes place simultaneously. It is evident that the Zr was transported against its concentration gradient (the concentrations in the stripping phase rapidly became higher than in the feed phase) through the SLMs (Fig. 3A). It should be noted that the recovery of Zr and Hf did not match their extraction percentage until 10 h (Fig. 3B).

In general, there are the following mass transfer resistances in LM processes:

1. boundary layer resistances including feed/membrane and membrane/strip interfacial films ($1/k_{S1}$ and $1/k_{S2}$);
2. chemical reaction resistance including extraction and back-extraction ($1/k_r$);
3. membrane diffusion resistance ($1/k_m = \delta_m \tau / D_m \varepsilon$).

Therefore, the overall mass transfer resistance ($1/k_{overall}$) has the following contributions:

$$\frac{1}{k_{overall}} = \frac{1}{k_m} + \frac{1}{k_{S1}} + \frac{1}{k_{S2}} + \frac{1}{k_r} \tag{9}$$

In the present system, we consider the extraction and strip reactions as rapid in terms of the solvent extraction (the extraction and stripping can reach equilibrium within 30 s in solvent extraction). The initial mass transfer coefficient through the bulk feed phase to the membrane phase was measured as 7.5×10^{-4} m/s (Zr) and 1.1×10^{-4} m/s (Hf). The mass transfer coefficient within the membrane was estimated as 4.9×10^{-7} m/s by assuming $D_m = 2 \times 10^{-10}$ m^2/s, $\varepsilon = 0.69$, $\tau = 1.4$, $\delta_m = 2 \times 10^{-4}$ m under the present dynamic conditions. Therefore, we would consider the membrane resistance ($1/k_m$) as dominated for the overall transport process in the present HFSLM system.

4.3. Effect of HCl concentration

The effect of HCl concentration of the feed phase on the initial flux and separation factor is shown in Fig. 4A and B, respectively. The HCl concentration of the feed solution plays a very important role in the extraction of Zr and Hf. The overall fluxes of Zr and Hf between 8 and 10 M HCl were found to be 9.4–11.3 × 10^{-5} and 0.58–3.2 × 10^{-6} mol/m^2 s, respectively. The selectivity (flux ratio) is 163 at 8 M HCl. In contrast, the Zr/Hf flux ratio was found

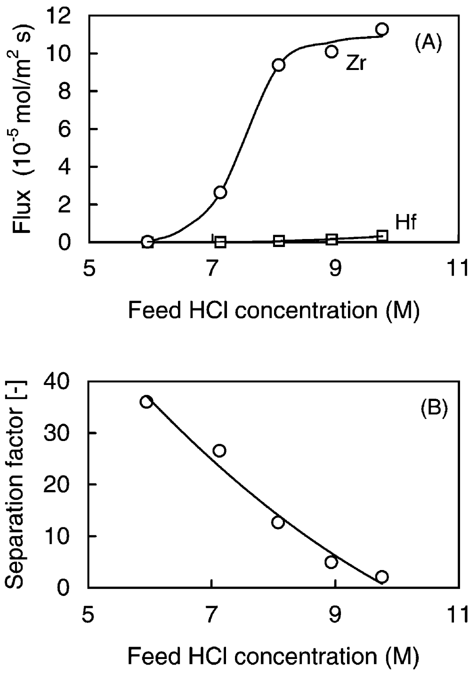

Fig. 4. Effect of HCl concentration of the feed solution on (A) initial flux (1 h) and (B) separation factor of Zr and Hf (7 h). Module 1 (35 fibers × 300 mm long): membrane phase, 0.5 M TNOA; feed phase, 15 ml of 50 μg/ml Zr and Hf in various HCl concentrations; stripping solution, 70 ml of 1.99 M HCl; flow rate = 2.2 ml/min.

to be 8 in the flat-sheet Celgard 2400-TBP–xylene system at optimum conditions [5]. The separation of Zr and Hf decreased with increasing HCl concentration of the feed phase (Fig. 4B). By comparing the result of solvent extraction (Fig. 2), it can be seen that the separation by LMs is comparable to a single stage of solvent extraction. It should be noted that the separation factor for solvent extraction passed through maximum value at a HCl concentration of 7 M compared to the monotonic decrease in the HFSLM process. A plausible explanation could be the physical entrainment in solvent extraction because of emulsification and phase disengagement difficulties.

The effect of HCl concentration in the stripping solution is given in Fig. 5. The HCl concentration in the stripping solution has much less significant influence on the transfer rate and separation than in the feed solution.

4.4. *Effect of flow rate*

The effect of flow rates on the mass transfer coefficient and separation factor is shown in Fig. 6A and B, respectively. The mass transfer coefficient for Zr increases noticeably with flow rate in the low flow rate range where liquid film resistances are expected to be significant. For laminar flow conditions, the film mass transfer coefficient varies according to $k \propto (\text{flow rate})^{0.25}$ for flow rates up to about 4 ml/min. This suggests a gradual transition to membrane resistance control which is confirmed by the insensitivity to flow rate in the range 4.5–8.8 ml/min. For Hf, the overall coefficients are lower but sensitive to flow rates up to about 4 ml/min. The separation factors in Fig. 6B reflect the gradual transition to membrane resistance control at higher flow rates. These data (Fig. 6A and B) show that HFSLM for Zr/Hf separation can be operated with negligible impact of concentration polarization.

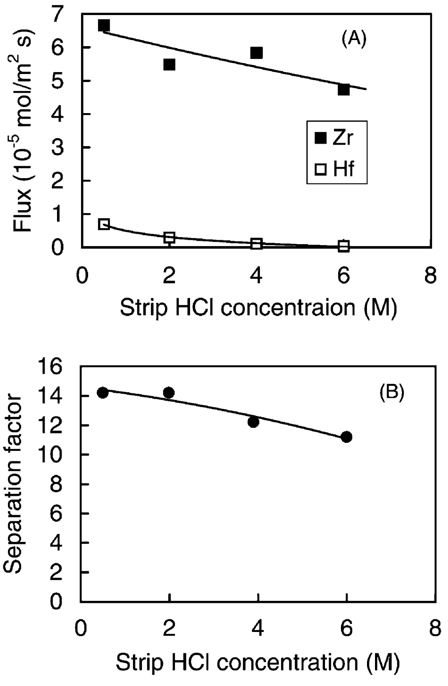

Fig. 5. Effect of HCl concentration of the stripping solution on (A) initial flux (1 h) and (B) separation factor of Zr and Hf (1 h). Module 1 (35 fibers × 300 mm long): membrane phase, 0.5 M TNOA; feed phase, 20 ml of 25 μg/ml Zr and Hf in 8.08 M HCl concentration; stripping solution, 80 ml of 0.5–6 M HCl; flow rate = 2.2 ml/min.

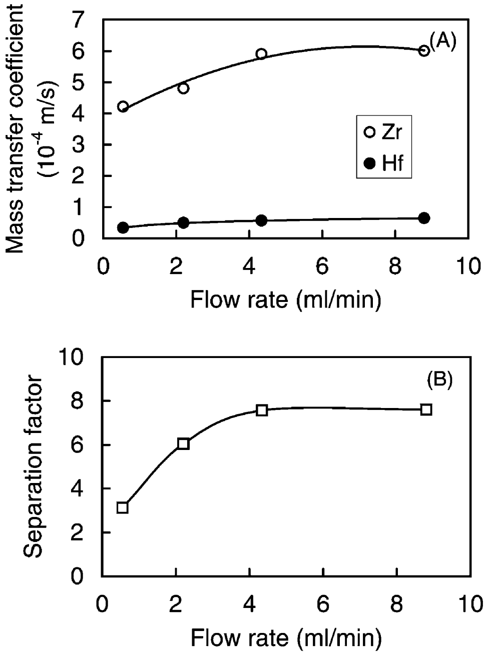

Fig. 6. Effect of aqueous flow rate on (A) mass transfer coefficient and (B) separation factor of Zr and Hf. Module 1 (35 fibers × 300 mm long): organic membrane phase, 0.5 M TNOA; feed phase, 15 ml of 25 μg/ml Zr and Hf in 8.08 M HCl; striping phase, 80 ml of 1.99 M HCl. Data obtained at an operating time of 1.5 h.

4.5. *Effect of fiber length*

In other separation processes, the separation efficiency can be improved significantly by employing multiple stages in solvent extraction or increasing the column length in ion-exchange and liquid chromatography. In hollow fiber membrane-based processes, increase in fiber length means increasing transfer area, but this could lead to decrease in mass transfer coefficient in laminar flow ($k \propto (d_\text{h}/L)^{0.33}$). In addition, for the HFSLM longer fibers need more LM inventory and, as a result, it is likely to have more metal-complex accumulation within the membrane phase. To date, there have been no reports on the experimental determination of the effect of fiber length on the separation efficiency in an HFSLM system.

Fig. 7A shows that the Zr and Hf concentrations in the strip solution are in proportion to the contact area of the fibers for similar batch conditions. The extraction and recovery of Zr with various fiber lengths are shown in Fig. 7B.

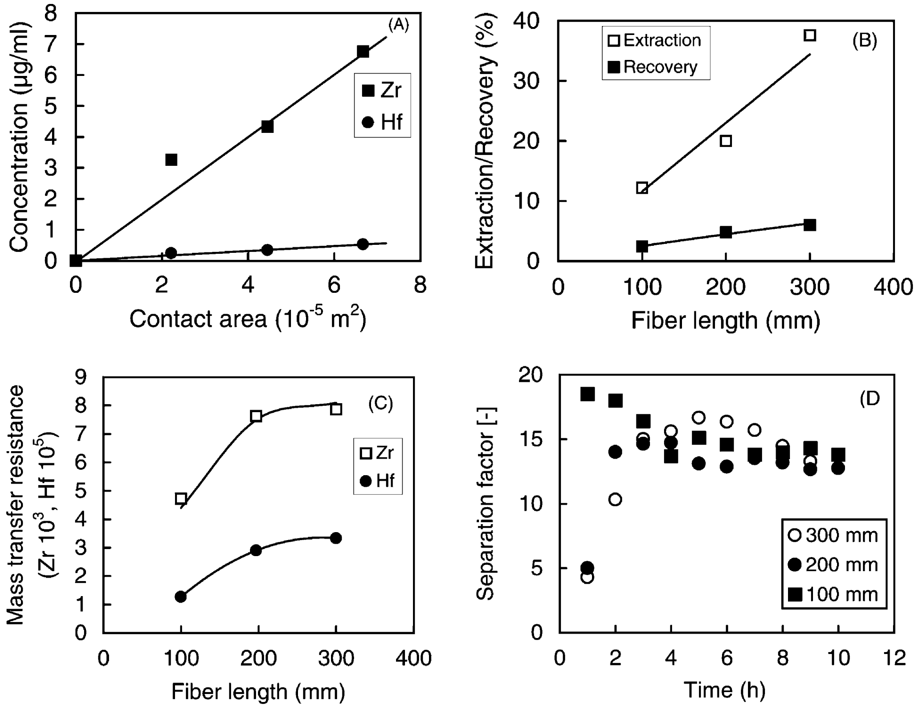

Fig. 7. Effect of fiber length. Modules 2–4: organic membrane phase, 0.2 M Aliquat 336; feed phase, 60 ml of 25 μg/ml Zr and Hf in 8.08 M HCl concentration; stripping phase, 60 ml of 2 M HCl; flow rate = 3.5 ml/min; batch time = 10 h. (A) Zr and Hf concentrations in the strip solution as a function of contact area; (B) Zr extraction and recovery vs. fiber length; (C) mass transfer resistance in various fiber lengths ($t = 3$ h); (D) separation factor with different fiber lengths as a function of time.

The extraction is in proportion to the fiber length and the recovery increases with increasing fiber length, but is not in proportion suggesting that the accumulation in the membrane is more serious in the case of increased organic inventory. The overall fluxes and separation factors are summarized in Table 2. The fluxes for 200 and 300 mm long fibers are almost the same, but the 100 mm fiber has higher fluxes implying that shorter fiber has higher mass transfer resistance (see Fig. 7C). The separation factor as a function of time using different lengths of fiber is shown in Fig. 7D. It can be seen that separation factors for shorter fibers are higher than those for longer fibers within 2 h and are identical for various length fibers after 3 h operation. Fig. 7C and D suggests less liquid film resistance for short fibers; this is compatible with laminar flow mass transfer. Accumulation in the membrane for longer fibers was due to the greater liquid film resistance and organic inventory, which leads to a low separation factor within 2 h. By comparing the values for solvent extraction (Fig. 2), the separation factor data also reflects the fact that the LM process is a combination of single extraction and stripping steps, and the separation efficiency in the HFSLM cannot be improved by increasing fiber length or membrane area. The separation has also been investigated in such a configuration that the feed solution and the stripping phase flow through the fiber's lumen successively. In that case, the length of the fiber has a dominant effect on the separation efficiency. These findings are presented in Part II.

Table 2
Flux and separation efficiency of Zr and Hf through HFSLM

	Fiber length (mm)		
	100	200	300
Contact area (m^2)	2.22×10^{-5}	4.45×10^{-5}	6.67×10^{-5}
Overall flux (mol/m^2 s), $t = 10$ h			
Zr	2.24×10^{-6}	1.48×10^{-6}	1.55×10^{-6}
Hf	8.28×10^{-8}	6.64×10^{-8}	6.18×10^{-8}
Separation factor	13.80	12.74	12.75

4.6. Mechanism of Zr and Hf transport through HFSLM

The extraction of Zr(IV) and Hf(IV) in HCl medium by TNOA and Aliquat 336 is an anion exchange mechanism (so-called liquid anionic exchanger), which may be represented as [19,20]

$$\mathrm{R_3N(org) + HCl(aq) = R_3NH^+ \cdot Cl^-(org)} \tag{10}$$

$$\mathrm{2R_3NH^+ \cdot Cl^-(org) + MCl_6{}^{2-}(aq) = (R_3NH^+)_2 \cdot MCl_6{}^{2-}(org) + 2Cl^-(aq)} \tag{11}$$

$$\mathrm{R_3R'N^+ \cdot Cl^-(org) + MCl_6{}^{2-}(aq) = (R_3R'N)_2{}^+ \cdot MCl_6{}^{2-}(org) + 2Cl^-(aq)} \tag{12}$$

where $M = Zr (Hf)$, R_3N = TNOA, $R_3R'N^+ \cdot Cl^-$ = Aliquat 336, R = octyl group and R′ = methyl group, and org = organic phase, aq = aqueous phase.

Back-extraction at the strip side interface could be expressed by

$$(R_3NH^+)_2 \cdot MCl_6^{2-}(org) \rightarrow 2R_3N(org) + MCl_6^{2-}(aq) + 2H^+(aq) \quad (13)$$

$$(R_3NH^+)_2 \cdot MCl_6^{2-}(org) + H_2O \rightarrow 2R_3N(org) + MOCl_4^{2-}(aq) + 4H^+ + 2Cl^-(aq) \quad (14)$$

$$(R_3R'N)_2^+ \cdot MCl_6^{2-}(org) + 2HCl \rightarrow 2R_3R'N^+ \cdot Cl^-(org) + MCl_6^{2-}(aq) + 2H^+ \quad (15)$$

$$(R_3R'N)_2^+ \cdot MCl_6^{2-}(org) + H_2O \rightarrow 2R_3R'N^+ \cdot Cl^-(org) + MOCl_4^{2-}(aq) + 2H^+ \quad (16)$$

Therefore, the mechanism of Zr and Hf transport through LMs may be described as follows: the extraction occurs as shown in Eqs. (10)–(12) at the feed–membrane interface, and the complex species $[(R_3NH^+)_2 \cdot MCl_6^{2-}, (R_3R'N)_2^+ \cdot MCl_6^{2-}]$ formed diffuse through the membrane under their concentration gradients. As the complexes reach the stripping side of the membrane where the HCl concentration is very low compared with the feed side, Zr and Hf are released into the stripping solutions, as shown in Eqs. (13)–(16). The regenerated amine molecules are left in the organic membrane phase and diffuse back to the feed–membrane interface. As the extraction mechanism for TNOA requires the association of hydrochloric acid, HCl moves in the same direction as Zr and Hf ions from the feed to the stripping phases (refer to Fig. 3C). This is a coupled co-transport process. The coupled transport of Zr (or Hf) and Cl^- ions through the membrane is represented in Fig. 8.

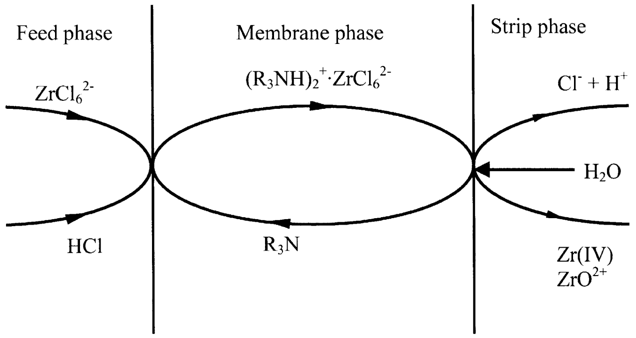

Fig. 8. Transport mechanism of Zr and Hf through SLMs using TNOA as carrier.

From the extraction mechanism of Aliquat 336 (Eq. (12)), it seems that Aliquat does not extract HCl and it is an ion-exchange mechanism [22]. Therefore, it should be expected that the HCl concentration of the feed phase in the Aliquat 336 system remains the same during the transport process; however, we did observed HCl concentration changes in the Aliquat system. Hence, the stripping mechanism for Aliquat is more likely to be expressed by Eq. (16), and this needs to be confirmed by further studies.

5. Conclusions

The HFSLM with TNOA or Aliquat 336 as carriers is very effective for separation of Zr and Hf. The maximum flux ratio (Zr/Hf) with TNOA was 160, which is 20 times than reported previously for SLMs. It was observed that the separation factor decreased with increase in HCl concentration of feed solution. The selectivity of HFSLM is equivalent to one single solvent extraction stage. The flow rate and fiber length play important roles in the transfer rate and separation; however, the mutual separation of Zr/Hf is independent of the fiber length. It seems impossible to increase separation efficiency of LMs by increasing the membrane area or contact time due to the characteristics of non-equilibrium mass transfer, i.e., the combination of extraction and stripping into one single step. Except for low flow conditions, the controlling step for the mass transfer is diffusion in the membrane. The transport mechanism is a coupled co-transport of Zr (or Hf) with chloride ions, which means that a continuous make-up of chloride ions in the feed could help to maintain flux of Zr. Conversely, low levels of HCl in the feed can lead to a chemical resistance control of the process.

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