Coupled Transport of Zr Ions from Different Acid Feed Aqueous Solutions using Carboxylic Acids as Stripping Agents

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Summary: Transport of Zr ions through tri-n-octylamine and di-cylohexylamine xylene based liquid membranes supported in polypropylene microporous films has been studied and found that HNO_3 is a better acid in the feed and water and methyl-succinic acid are the stripping agents which can be used to transport Zr ions. The values of flux (J) and permeability coefficient (p) for Zr (IV) ions under optimum conditions from HNO_3 feeds to water stripping phase across the membranes are 19.4×10^{-6} mol.m^{-2}.s^{-1} and 19.90×10^{-10} m^2.s^{-1}respectivley. In case of methyl succinic acid as stripping agent the values of J and P are 1.9×10^{-6} mol.m^{-2}.s^{-1}and 1.78×10^{-11} m^2.s^{-1} respectively. Di-cyclo-hexylamine is not a suitable carrier to separate Zr ions using coupled transport system.

Introduction

Liquid Membranes (LM) techniques have been applied for the separation of various cations [1-5]. The association of metal ions in cationic or anionic form with the extracting molecules (in the liquid membrane) supported in hydrophobic films or tubes, diffusion through the membrane phase and stripping on the other face of the membrane are the basic steps, which take place to transport the selected ions across SLM membrane. The ions association with metal ions and travelling across the membrane is called coupling of ions. The ions, which normally couple with metal ions are like H^+, NO_3^-, Cl^-, SO_4^{2-} .These ions provide chemical energy for transport of the metal ions. The extraction and stripping steps take place simultaneously in liquid membrane systems. In the earlier works [6-13] this technique has been successfully applied on U (VI), Cr (VI), Mo (VI), Be (VI), Ti (VI), Hf (VI), W (VI) and Ce (VI) using the extractants like tri-n-butyl phosphate, tri-n-octyl-amine, diethyl-hexyl-phosphoric acid, acid and tri-n-octylphospine oxide. These authors worked with uranium high concentrations (28.5 %) even in their work and added significantly to the separation technique utilizing the coupled transport liquid membrane system.

Zr ions have been selected for investigation for this work to study the transport of Zr (IV) ions using tri-n-octylamine (TOA) and dicyclohexylamine (DCA) as organic carriers while HNO_3 and HCl are used in the feed at different concentration levels. Mandelic acid, ascorbic acids, methylsuccinic acids aqueous solutions and water were used as strippents. The work with these stripping agents has not been performed before in supported liquid membrane systems for Zr ions transport.

Theoretical

In the acid solution (1-6 M) the Zr ions exist at Zr^{4+} ions and not as ZrO^{2+}. In case of tri-n-octylamine (R_3N) the chemical reactions occurring at the membrane phase on the feed side is as under to form a complex species (1).

$$Zr\,X_6^{-2} + 2H^+ + 2R_3N \rightleftharpoons Zr(X)_6.(HNR_3)_2 \qquad 1$$

Here X^- is a univalent anion, as used in the present case. On the other side of the membrane (the metal ions) stripping the following reaction takes place, when water is used as a stripping agent, the reaction is as under.

$$Zr\,(X)_6.(R_3NH)_{2\,org} \rightleftharpoons 2R_3N_{org} + Zr\,X_{6\,aq}^{-2} + 2H^+_{aq}$$

$$\downarrow 2H_2O$$

$$ZrO_2Cl_2 + 4\,HCl \qquad 2$$

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If mandelic acid and ascorbic acids are present in the stripping phase, the reduction reaction occurring is as under.

$$RCH(OH)COOH + Zr(IV) \longrightarrow RCHO + CO_2 + H^+ + Zr(III) \quad 3$$

This is a free radical reaction involving RCH-$O^{\bullet}$ type free radial species.

|
COOH

Ascorbic acid and di-methyl-succinic acids also act likewise to reduce the Zr (IV) ion to Zr (III) state. It can be described as:

$$\log J\eta = \log AT + n\log(H^+)_{aq} + m\log b[X^-] + n\log[E] + \log C^0_t \quad 4$$

Where n, m and b represent the moles of H^+, X^- and E taking part in the chemical reaction, on the feed solution side on the membrane face. A is a constant and T, the absolute temperature. J is the metal ions flux and [E] represents the extracting molecule activity and C°_t is the metal ions concentration at time t in the bulk feed phase. η is the viscosity of the organic membrane phase.

The permeability coefficient, p, is represented as:

$$-\ln C^{\circ}_t / C^{\circ} = apt / Vd \quad 5$$

and has been determined from the plot of $-\ln C^{\circ}_t / C^{\circ}$ versus t, the time for the transport. C°_t and C° represent concentration of Zr ions in the feed solution at time t and at the start of experiment at t = 0

Results and Discussion

Two extractants were used to make the supported liquid membranes (SLM)

Tri-n-octylamine (TOA) and 2) Di-cyclohexylamine (DCH) dissolved in xylene as diluent.

The following aspects of extraction, stripping and transport were studied in the case of TOA.

Effect of TOA concentration on the membrane.

Effect of HNO_3 and HCl on the feed solution.

Effect of ascorbic acid, mandelic acid and methyl-succinic acid on the stripping solution.

In the case of DCH, only the effect of HNO_3 the transport of Zr ions in the solution on across the membrane was studied.

a) Effect of TOA Concentration in the Membrane

Fig. 1 represents a decrease in the concentration of Zr ions in the feed solution, as a function of time at various concentrations of TOA in the membrane. Fig. 2 is a plot of Zr ions flux and permeability coefficient across the membrane as a function of TOA concentration. Beyond 1.16 M concentration of TOA in the membrane, the xylene phase, the flux and permeability decrease, after a maximum increase up to this concentration, which is the optimum concentration triggering the transport of Zr ions. This is due to the hindered diffusion with an increase in the viscosity due to the extracting concentration increase.

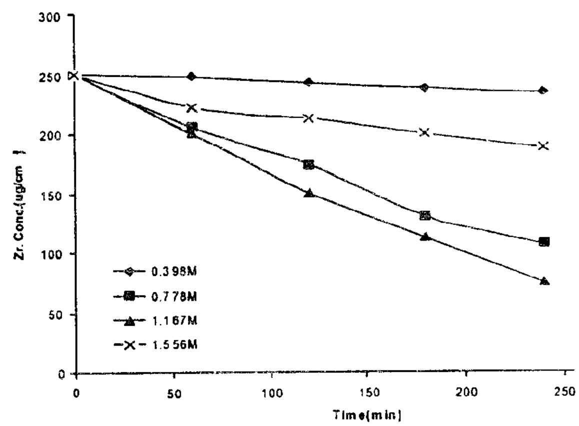

Fig.1: Effect of TOA-Xylene on transport of Zr through

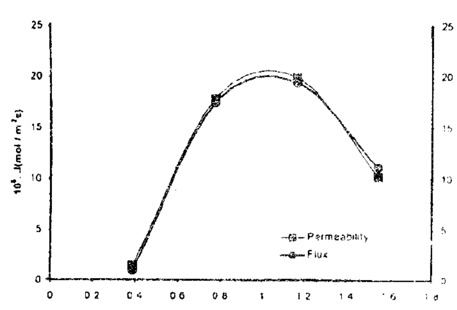

Fig. 2: Pot of Zr ions flux(J) and permeability(p) versus TOA conc. In the membrane.

b) Effect of Different Acids on the Feed

Fig. 3 (a and b) represents the plot of Zr concentration in the feed versus time at varied acids' concentrations (HCl and HNO_3). Fig. 4 is the plot of J and p versus HNO_3 concentration, representing a continuous increase in flux and permeability values with the increase in acid concentration. As described in Eq: 4, Zr ions flux is increased with an increase in acid (H^+) concentration. Where A is a constant. As J is indirectly proportional to η, so it is expected to decrease with an increase in viscosity like increase in TOA concentration. The absence of viscosity factor should observe a continuous increase in J subsequently increasing the TOA concentration.

It has been observed experimentally that the transport rate of Zr ions in the presence of HNO_3 in the feed is almost equivalent to the one when HCl was used in the feed solution. The comparison of data is shown in Table-1.

Table-1. Zr ions conc. in the feed solution as a function of time with 4M HCl and HNO_3 in the feed.

Zr feed concentration	= 250 g/ cm^3
Stripping solution	= distilled water
TOA conc. in the membrane	= 1.167 M
Temperature	= 298 ± 20 °C
HCl/ HNO_3 conc. in the feed	= 4M

Time (Minutes)	HCl	Zr. Conc. in the feed with HNO_3
0	250	250
30	232	230
60	243	221
90	225	220
120	229	-
150	210	210
180	218	-
240	-	192

Not much change in the feed concentration in the feed compartment was observed where HCl and HNO_3 concentration reached 4M, though HNO_3 medium supports the transport relatively better than HCl, due to the extent of dissociation of $R_3NH^{\cdot}Cl$ or $R_3NH^{\cdot}NO_3$ species, which may vary from species to species as is appeared from the results in Table-1.

Fig. 5 represents the effect of HCl concentration on the flux and permeability of Zr ions. It is evident that up to 1M HCl, there is an increase in the values of flux and permeability, followed by a continual decrease in the values of J and p. This is possible due to -type reaction.

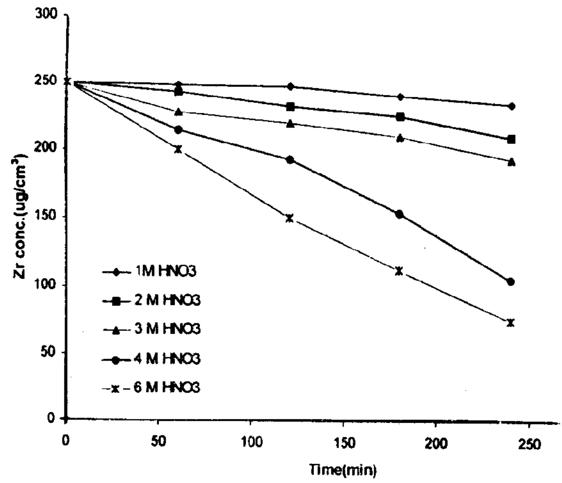

Fig. 3a: Plot of Zr. Con. Ersus time with different HNO_3 concentrations.

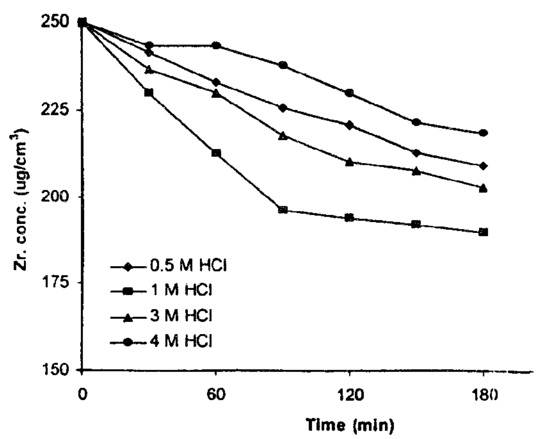

Fig. 3b: Plot of Zr concentration in the feed versus time at various HCl concentrations.

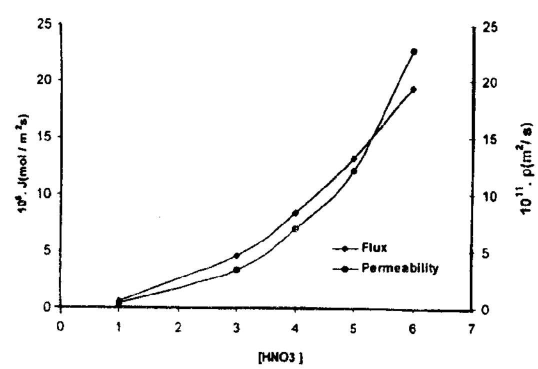

Fig. 4: Plot of Flux and Permeability for Zr(IV) ions Vs NO_3

$$ZrO^{2+} + nHCl \leftrightarrow ZrOCl_2 + nH^+ + (n-2)Cl^-$$
$$\downarrow$$
$$ZrOCl_n.H_{n-2} \quad \text{(II)}$$

Species (II) may not ionize to get associated with protonated, positively charged amine ions.

c) Effect of Strippers

The effect of various stripping agents on the transport of Zr ions is shown in the Table-2.

Table-2. Zr conc. in the feed versus time with different strippers

Time (min)	Concentration of Zr in the feed versus time with different strippers			
	H_2O	0.3M mandelic acid	0.3M ascorbic acid	0.3M succinic acid
0	250	250	250	250
60	200	233	243	202
120	150	218	236	161
180	112	208	230	138
240	75	199	224	113

It can be seen from the results that water is the best strippers. The complex formed with TOA on the feed side membrane phase is not stable at the lower acid concentration and even in water.

So the complex $Zr(NO_3)_n(HR_3N)_{n-4}$ is broken into simple ZrO^{2+} and R_3N components resulting into Zr ions stripping. In case of HCl, the complex may be $Zr(Cl)_n.(HR_3N)_{n-4}$.

In the case of mandelic acid and ascorbic acid, there may be a reduction of Zr (IV) ions, after breakage of the TOA-Zr (IV) complex into simple components, resulting into stripping.

Effects of mandelic acid and ascorbic acid concentration on the flux and permeability are shown in Fig. 6 (a and b). The decrease in the flux is attributed to the higher proton conc., which lowers the ionization of the Zr complex, coupled with R_3NH^+. It also appears that stripping through the reducing mechanism is comparatively a slower step.

Di-methyl-succinic acid (DMSA) is the second best strippers, resulting into Zr ions flux of $1.9X10^{-5}$ mol.m^2.s. at 0.3M concentration in the stripping solution. This may be due to the better reducing action of this compound on Zr (IV) ions. Effects of DMSA concentration on the flux and permeability of Zr ions are shown in Fig. 7.

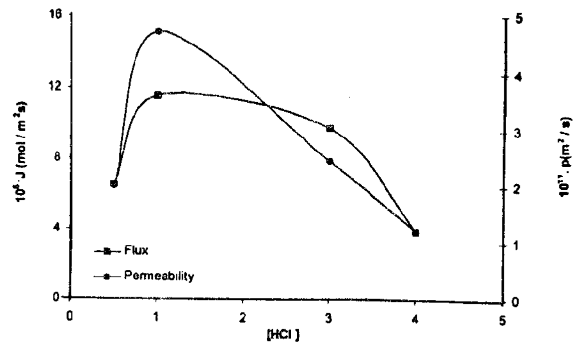

Fig. 5: Effect of HCl conc. In feed of Zr(IV) ions with 1.16 m TOA in the membrane and water as strippent.

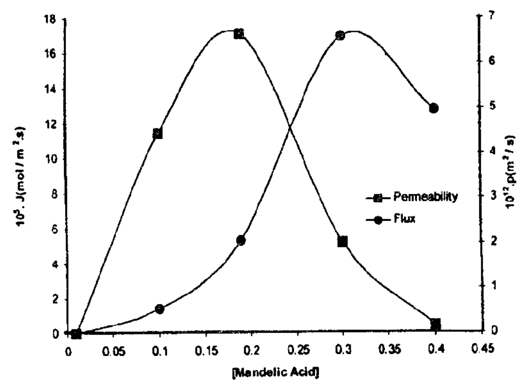

Fig. 6a: Plot of Flux (J) and permeability p of Mandelic Acid in the stripping phase.

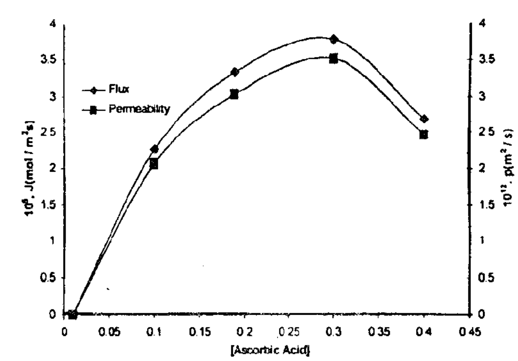

Fig. 6b: Plot of flux (J) and permeabity, p versus ascorbic acid concentration.

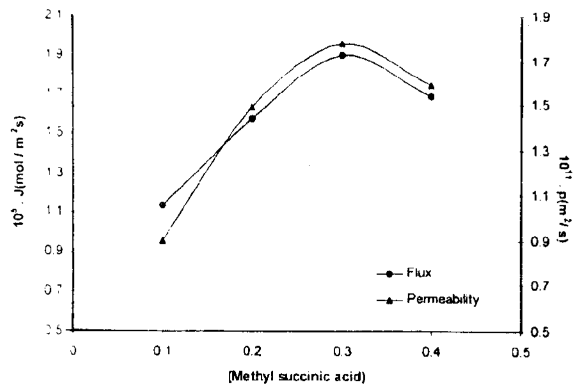

Fig. 7: Plot of flux (J) and permeability (p) versus methylsuccinic acid concentration.

Table 3 indicates that the presence of DCA at all the HNO_3 concentrations in the feed may inhibit the transport of Zr. It means that DCA is not a good extractant or membrane to extract and isolate Zr ions from the feed solution.

Table-3: Effect of HNO_3 conc. on the transport of Zr (IV) ions with DCA as the membrane

Strippers = water
Zr. Feed conc. = 250 $\mu g/cm^3$
Membrane = 1.167M DCA in Xylene
Temperature = 298 ± 2 °C

	HNO_3 conc. in Feed (M)			
Time(min)	1	2	3	4
0	250	250	250	250
60	249	249	247.8	248
90	247	248	247.6	246
120	248	247	246.5	244
180	248	247	245.5	242

This shows that DCA, the secondary amine, is not a good agent in the membrane formation unless it is protonated to form $(C_6H_{11})_2N^+H_2$ species, which may not be possible in the present conditions. Hence, the expected $Zr(NO_3)_n.(R_2NH_2)_{n-4}$ type complex may not be formed to get diffused through the membrane. Here, R represents $C_6H_{11}^-$ group.

Experimental

Chemicals

Nitric acid, $ZrOCl_2.8H_2O$, tri-n-octylamine, NaOH, HCl, ascorbic acid and mandelic acid were of AnalaR grade, BDH or equivalent grades. Water used was purified by the reverse osmosis-cum-ion-exchange Milli-Q system to get rid of all the metal ions impurities.

Reagents

Zr (IV) solution and stripping solution of carboxylic acids were prepared from $ZrOCl_2$ $8H_2O$ by taking appropriate amounts. TOA and DCA solutions were prepared in xylene in the required concentration.

Membranes and Flux Measurement

Membranes

Celgard 2400 hydrophobic films having 25μm thickness and 0.02μm pore size were used as supports to absorb extractants like TOA and DCH dissolved in xylene in a given amount.

Flux Measurement

The stripping and the feed Zr(IV) solutions were filled in the two halves of the cell containing membrane supporting in the middle as shown in Fig. 8. The solutions were stirred with electric stirrers fitted in both the half-cells.

The samples collected from feed or strip solutions were analyzed to monitor the concentration in the feed and strip solutions.

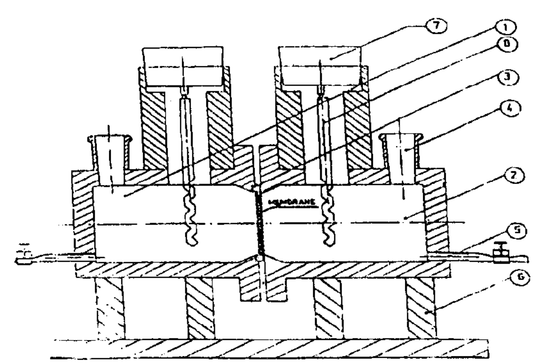

Fig. 8: Supported Liquid membrane Cell.

1. Feed solution compartment.
2. Product solution compartment.
3. O-ring and supported liquid membrane.
4. Sample solution outlets.
5. Out-lets for drain.
6. Stand for cell.
7. Electric motors for stirring.
8. Perspex stirrer.

Chemical Analysis

Spectrophotometric analysis was performed with 4-2 pyrideylazo-2-naphthol as described by Chaudry et al[14].

Conclusions

Zr ions can be transported from acid feed in both HCl and HNO_3 media, but gives better results with HNO_3 in the feed. Water is a better stripping agent than all other strippers used in this study, followed by succinic acid as being the second best option. DCA, the secondary amine, is not a good carrier of Zr ions.

The optimum conditions facilitating transport of Zr ions across the membrane are found to be 6M HNO_3 in feed, 1.167M TOA in the membrane, 0.3M methyl-succinic acid or mandelic acid. If HCl is used in the feed, 1M HCl with water as stripping agent is the optimum feed condition.

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