



## Zirconium and Hafnium Separation by Novel Green Emulsion Liquid Membrane Containing an Environmentally Benign Diluent

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Green liquid emulsion membrane (LEM) was developed for separation of zirconium and hafnium from nitric acid medium. The membrane is based on the use of CYANEX-272 diluted with corn oil (green diluent) as a carrier, span 80 as a surfactant and citric acid as a stripping agent. The factors affecting the stability of the LEM were investigated under chosen conditions. The parameters affecting the permeation of Zr and Hf from nitrate medium were also studied. The metal ion content in the inner phase obtained by demulsifying the loaded CC-LEM using the freeze-thaw method is 22.8 g/l Zr and 2.05 mg/l Hf i.e. the contamination of the recovered Zr is 89.91 mg Hf/ kg Zr which is below the limit for the use of zirconium in nuclear applications.

**Keywords:** Green Liquid Emulsion Membrane; Corn Oil; Zirconium; Hafnium; CYANEX-272.

### Introduction

Zirconium (Zr) is considered as vital material in the nuclear industry [1]. This metal and its alloys are utilized as a construction material for nuclear reactors and as fuel rod cladding [2-4]. Zirconium has a unique combination of the physical and chemical characteristics such as suitable thermal conductivity, corrosion resistance, and low thermal neutron capture cross-section (0.18 barns) [1, 5]. The nuclear industry consumes around 90% of the total world production of zirconium [6]. Hafnium and zirconium have extremely similar chemical and physical properties thus hafnium is constantly co-existed, 1-3 wt%, in natural zirconium minerals [1, 3, 7]. Hafnium has high thermal neutrons capture cross-section, 102 b, more than a hundreds of times higher than that of Zr [4, 8]. Therefore, the embedded hafnium in zirconium used in the nuclear field, must be below 100 mg/kg [2, 4]. Accordingly, the separation of hafnium from zirconium is of utmost importance for the utilization of zirconium for nuclear applications. Nonetheless, due to the incredible chemical

similarity of Zr and Hf, their separation is difficult and requires elaborate processes [2, 4]. Liquid-liquid extraction methods have been proven to be much better among known commercial processes [2, 4]. The literature review indicates that selective extraction with efficient separation of Zr from Hf occurs from nitric or hydrochloric acid [6] media with organophosphorous extractants such as DEHPA, PC 88A and Cyanex-272 [2-4, 6-10].

Liquid membranes (LMs) are the advanced forms of the solvent extraction with the difference that extraction and stripping processes occur simultaneously in one stage, which improves the selectivity and separation ability [11-12]. Due to its high selectivity, low energy consumption and ease of use and scaling-up, the liquid membrane technique has attracted a lot of consideration for the pre-concentration and separation of metal ions [5]. Despite of these advantages, there are very few studies on the use of LMs to separate Zr from Hf. Chaudry and Ahmed [13] explored the separation of Zr and Hf ions from the HNO<sub>3</sub> solutions via a

flat-sheet supported liquid membrane (FSSLM) impregnated with TBP-xylene. While, the utilization of the hollow fiber supported liquid membrane (HFSLM) impregnated with tri-n-octylamine, TNOA, and tri-octyl methyl ammonium chloride, Aliquat 336, as carriers for the separation of Zr/Hf from chloride medium was examined by Yang et al [14]. They concluded that the selectivity of the supported liquid membrane (SLM) is equal to a single solvent extraction stage with a separation factor up to 38, from 6.0 mol L<sup>-1</sup> HCl solution. Recently, A.Yadollahi et al [5] used a hollow fiber renewal liquid membrane (HFRLM) loaded with synergistic mixture of Cyanex-272 and TBP for the separation of Zr/Hf from HNO<sub>3</sub> media. The results obtained prove the efficiency of the proposed HFRLM technique for selective extraction of Zr over Hf.

So far, there have been no studies on using the liquid emulsion membrane (LEM) for zirconium and hafnium separation.

As compared with other separation methods, LEM has the same advantage of LMs, especially with selectivity. In addition, LEM use limited extractant quantities, low production costs, short operation time, high surface area for mass transfer, simple operation method, and can be operated continuously [11, 12, 15]. The diluent is an essential component in the composition of the LEM which represents the largest part of the LEM constituents and directly affects the stability of the membrane [16]. Traditional diluents used in the preparation of LEM are petroleum derivatives and synthetic chemicals such as kerosene and hexane [11]. These organic chemicals are harmful to living organisms and environment [11, 16]. Due to the recent greater stringent environmental regulations [17], studies on extraction methods have directed to the more eco-friendly diluents (green diluents) such as vegetable oils [16]. The bio-degradability, nontoxicity, non-volatility, and inflammability with the other green features of the vegetable oils, like palm, sunflower, cotton, coconut, corn, and peanut oils make them a strong competitor for the traditional diluents [15-16, 18-19]. Furthermore, the aliphatic properties of these vegetable oils and their low dielectric constant make them non-polar and immiscible with aqueous solutions [16]. Many vegetable oils also have a high viscosity, which

can improve the emulsion stability [16]. The unlimited biological resources and relatively simple vegetable oils extraction process makes them cheaper than the traditional organic diluents [18].

Several studies were carried out to investigate the effectiveness of using vegetable oil as a green diluent with various extractants [12,15-19]. Ahmad et al (2015) [11] examined the efficiency of using some vegetable oils (sunflower, corn, and palm oil) as a diluent in the formation of LEM consisting of Aliquat 336 (carrier), Span 80 (surfactant) and NaOH (internal phase). They concluded that vegetable oils are effective in producing the Aliquat 336-LEM system. Sanna Björkegren and Rose Fassihi Karimi [12] used palm oil as an organic diluent to develop stable TOMAC-LEM which was used effectively in the extraction of Cr(VI) and As(V).

This work address two aspects; the first focus on the development of a novel green CYANEX 272-LEM by replacing the fossil-fuel based diluent such as kerosene in the LEM with renewable vegetable oil as well as the use of other LEM constituents as environmentally friendly materials as possible. The second part is to develop, a CYANEX 272-LEM system for separation of zirconium from hafnium. In this concern, different factors that affect the stability, efficiency and selectivity of CYANEX 272-LEM are studied to obtain the optimal conditions for the separation of Zr(IV) from Hf(IV).

## Materials and Method

### Chemicals

A commercial grade of corn, sunflower and flaxseed oils have been used. CYANEX-272 (bis 2,4,4-trimethylpentyl phosphinic acid) is kindly supplied by Cyanamid Canada, Inc and used as received. Citric acid was supplied by Sigma Aldrich while Span 80 and HNO<sub>3</sub> were purchased from Merck. Alfa Aesar is the producer of ZrOCl<sub>2</sub>.8H<sub>2</sub>O (99.9%) and HfOCl<sub>2</sub>.8H<sub>2</sub>O (+98%). Kerosene is obtained from Misr Petroleum Ltd and the orange dye from Fluka. Double distilled water was used for dilution.

**Table 1: Separation factors of Zr/Hf with CYANEX-272 dissolved in kerosene or corn oil.**

Acid conc., mol L <sup>-1</sup>	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Kerosene	7.0	12.9	15.2	17.6	16.9	12.3	10.1	5.4
Corn oil	7.4	13.1	15.1	17.9	17.3	12.7	10.3	5.5

#### *Preliminary investigations*

The stability constants for complexes of Zr(IV) and Hf(IV) with some inorganic ligands decrease in the order of  $\text{OH}^- > \text{F}^- > \text{SO}_4^{2-} \gg \text{Cl}^- \geq \text{NO}_3^-$  [6, 20]. As chloride and nitrate ions exhibit fewer tendency to form complexes with Zr(IV) or Hf(IV), nitrate is chosen to be the extraction medium. The extraction ability of any extractant depends to some extent on the used diluent [21]. In this concern, a preliminary investigation was carried out using a conventional liquid-liquid extraction method to select a suitable vegetable oil as a green diluent for CYANEX-272. The corn, sunflower and flaxseed oils are the investigated vegetable oils. The extraction efficiency of Zr(IV) and Hf(IV) with CYANEX-272 in vegetable oil is compared with that in kerosene as the most common organic diluent from a medium of different  $\text{HNO}_3$  concentrations, Fig 1. From this figure, it is clear that the extraction of both Zr(IV) and Hf(IV) increases, in the following order, flaxseed oil < sunflower oil < corn oil. Furthermore, the behavior of CYANEX-272 dissolved in Corn oil is almost identical for that in kerosene. These results are comparable with that obtained by Ahmad et al [11] and Chang et al [18] who studied the use of different vegetable oils as diluents for Aliquat 336 and D<sub>2</sub>EHPA, respectively. They concluded that corn oil is effective and does not affect the extraction ability of the extractant. Separation factors of Zr(IV)/Hf(IV) with CYANEX-272 in kerosene or corn oil at various  $\text{HNO}_3$  concentrations are presented in Table 1. The results obtained are in agreement with the reported data [3, 6-7] which indicates that 2.0-2.5 mol L<sup>-1</sup> nitric acid is the optimum acid concentration to separate Zr(IV) from Hf(IV) with CYANEX-272.

Depending on the above results, corn oil is selected as a diluent in this study in the preparation of the green CYANEX-272 -LEM and extraction experiments were conducted from the feed phase of 2.0 mol L<sup>-1</sup>  $\text{HNO}_3$ .

#### *Green CYANEX-272/Corn oil LEM (CC-LEM)*

##### *Preparation method*

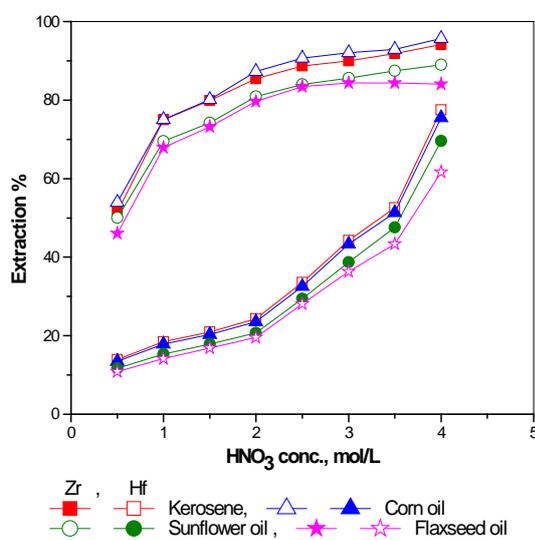
In order to obtain a green sustainable LEM, all components should be relatively available, not expensive and as environmentally friendly as possible. Table 2 shows the examined components and preparation conditions for the corn oil-CYANEX-272 LEM (CC-LEM). Corn oil is mainly composed of aliphatic polyunsaturated fatty acids, where the major components are linoleic and oleic acids [23]. The non-ionic surfactant Span 80 is classified as environmentally friendly because it is sugar-based, produced from renewable sources and biodegradable [24]. Citric acid is a green acid. It is selected as a stripping agent because zirconium citrate complex is approximately 7.5 times more stable than hafnium citrate (stability constants:  $348 \pm 43$  for Hf citrate and  $2600 \pm 432$  for Zr citrate) [21] which expected to enhance the separation between the two metals. The CC-LEM is prepared by mixing the organic and internal phases in a double jacket glass vessel which was thermostated at  $25 \pm 1$  °C by a water bath of the type MGW, LAUQA, R2OK (Germany), Fig 2. The mixture containing the two phases is emulsified mechanically using an ultra-high-speed homogenizer (IKA, Ultra-Turrax T25, Germany) coupled with a stainless steel stirring rod.

##### *Stability of CC-ELM*

The stability of the formed CC-LEMs was examined using the tracer method. In this concern, an orange dye, which is an inert material, has no interaction with either organic or aqueous molecules, and cannot be diffused through the membrane, was added to the stripping phase. 10 ml of this LEM contains the inert dye is placed in a measuring test tube tightly sealed at room temperature. The separation of the emulsion phases by the naked eye inspection and the time for the physical separation of the orange aqueous phase and oil phase was recorded.

**Table 2: Different components and preparation conditions of the CC-LEM**

Components of W/O CC-LEM		Investigated Range	Limitation conditions formed stable LEM
Organic phase	Carrier: CYANEX-272 dissolved in corn oil	$5 \times 10^{-3} - 0.1 \text{ mol L}^{-1}$	$5 \times 10^{-3} - 0.1 \text{ mol L}^{-1}$
	Surfactant: Span 80 (sorbitan monoolete)	1.0 – 5.0 wt%	2.0 – 4.0 wt%
Aqueous internal phase: citric acid		0.5 – 3.5 mol/L	0.5 – 3.5 mol/L
Organic/internal phase ratio		0.75:1 – 3:1	1:1 – 3:1
Emulsification time		5 – 20 min	10 – 15 min
Homogenization speed		2000 – 8000 rpm	3000 – 5000 rpm



**Figure 1: Effect of diluents on the liquid-liquid extraction (%) of  $0.01 \text{ mol L}^{-1}$  Zr(IV) and  $1 \times 10^{-3} \text{ mol L}^{-1}$  Hf(IV) using  $5 \times 10^{-3} \text{ mol L}^{-1}$  CYANEX-272 dissolved in kerosene and various vegetable oils at different concentrations of  $\text{HNO}_3$ .**

The obtained results indicated that a homogenous CC-LEM can be created with acceptable stability, where the emulsion retains without showing any significant phase separation for at least 2 hrs. at limitation conditions shown in Table 2.

On the other side, when the CC-ELM is mixed with the aqueous feed phase, breaking of the emulsion can be occurred which was recorded at different investigated operating conditions using the relation;

$$BK(\%) = \frac{[O_f]_t}{[O_{int}]_0} \times 100 \quad (1)$$

where  $[O_f]$  is the orange dye concentration in the feed phase after the time ( $t$ ) of the mixing process; whereas  $[O_{int}]_0$  represents the initial dye concentration in the internal phase. Breaking percentages, after 30 min of operation with a  $2.0 \text{ mol L}^{-1}$   $\text{HNO}_3$  feed solution, are shown in Table 3. The results show that in most of the experimental conditions, the breaking percentages are lower than 3%. Only low Span 80 concentrations in the membrane phase and high stirring speeds led to higher breakage values. Since the low surfactant concentration induces emulsion breakage and the high surfactant concentration enhances the emulsion swelling and the membrane resistance to the mass transfer of the metal ions [22], Span 80 concentration is maintained at 3% for all extraction experiments.

Figure 3 represents the microscopic studies of the developed CC-LEM droplets. As shown from the figure the emulsion is of good stability and the emulsion globules are mostly spherical with an average size of  $\sim 1\text{-}3 \mu\text{m}$ , Fig.3a. Some of the emulsion globules containing one internal droplet while the others containing more than one, Fig.3b. The average size of the internal phase droplets is ranged between  $0.1\text{-}0.2 \mu\text{m}$  (Fig 3c) that is fully covered by a layer of the organic phase with an acceptable thickness which is suitable for stable globules and in the same time does not retard the transport of metal ions.

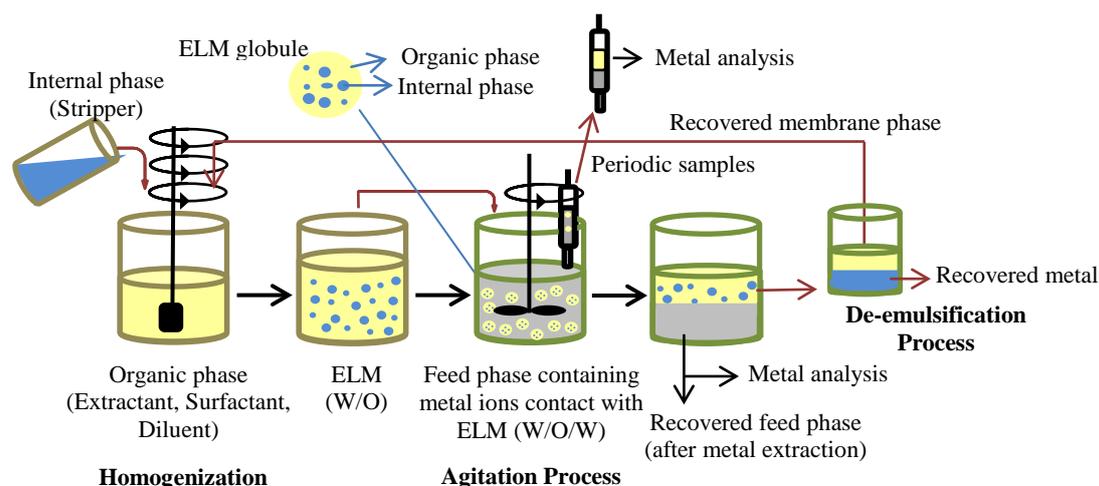


Figure 2: A schematic diagram of the emulsion liquid membrane preparation and application for metal

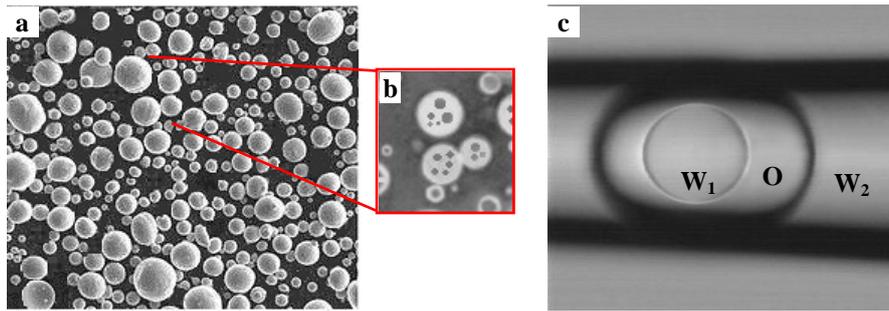
### Extraction procedure

Steps of the metal extraction process with CC-LEM are described in details in the schematic diagram shown in Fig. 2. Fresh aqueous solutions of Zr(IV) and Hf(IV) are used at concentrations of 0.01 mol L<sup>-1</sup> and 0.001 mol L<sup>-1</sup>, respectively. During the extraction process, the external feed phase was periodically sampled at predetermined time and the samples were allowed to settle for 3 min to separate the (w/o) emulsion phase from the

external aqueous phase. All experiments were performed at room temperature and repeated twice at different times and the results obtained showed a maximum deviation of 3%. Atomic absorption spectroscopy (AAS 6 VARIO, Analytical Jena GmbH, Germany) and Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES), Shimadzu Sequential Type, Kyoto "Japan" analyzer were employed to measure the concentrations of metal ions in the aqueous phase.

Table 3: Breaking percentage of the CC-LEM after 30 min mixing time at different operating conditions

Parameter	BK, %	Parameter	BK, %
CYANEX-272 conc., mol L <sup>-1</sup>	0.005	Citric acid conc., mol L <sup>-1</sup>	0.5
	0.01		0.6
	0.05		1.5
	0.07		1.3
	0.1		1.7
Span 80, wt%	2.0	Stirring speed, rpm	100
	2.5		0.7
	3.0		200
	3.5		1.3
	4		0.9
Organic/internal phase ratio	1:1	$V_{\text{emulsion}}/V_{\text{feed}}$	300
	1.5:1		1.9
	2:1		400
	2.5:1		2.8
	3.0		0.7
			500
			5:100
			0.7
			10:100
			0.8
			15:100
			1.1
			20:100
			1.7
			25:100
			2.2



**Figure 3: Microscopic images of corn oil-CYANEX-272 LEM. a) emulsion globules, b) planar W/O with presentation of the internal droplets, c) micro-capillary photo showing the composition of the W/O/W CC-LEM ( $W_1$  internal aqueous phase; O membrane phase; and  $W_2$  external phase)**

The effect of different parameters on the efficiency of CC-LEM permeation of Zr or Hf was investigated by “one-factor-at-a time” method. With this method one factor is changed while keeping other parameters constant.

Unless otherwise stated; the general conditions used for such investigation were as follows:

-The aqueous phase contains of  $0.01 \text{ mol L}^{-1}$  Zr(IV) and  $0.001 \text{ mol L}^{-1}$  Hf(IV) in  $2.0 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution.

-The membrane phase was  $0.005 \text{ mol L}^{-1}$  CYANEX-272 dissolved in corn oil and 3% Span 80, while the inner phase is  $1.0 \text{ mol L}^{-1}$  citric acid with an organic/inner phase ratio 1.5:1.

The stirring speed is 300 rpm and treat ratio ( $V_{\text{emulsion}}/V_{\text{feed}}$ ) equal 15:100. Where  $V_{\text{emulsion}}$  is the volume of the emulsion phase and  $V_{\text{feed}}$  is the volume of the feed solution.

## Results and Discussion

Since the extraction and stripping reactions occur simultaneously in the LEM systems in a single step, the transport of solute is controlled by kinetic parameters instead of equilibrium parameters, as in the case of liquid-liquid extraction process. In this regard, the flux (J) and the permeability (P) parameters are used to describe the performance of liquid membranes for the extraction and separation of metal ions. Flux is defined as, the rate of the mass transfer of metal ions through the membrane, which can be expressed as follows:

$$J = -\frac{V_f}{A} \frac{dC_{f,t}}{dt} \quad (2)$$

where J is the flux of metal ions through the membrane,  $C_{f,t}$  is the metal concentration in the feed solution at time t,  $V_f$  is the volume of the

aqueous feed solution, A is the effective membrane area. In the case of LEM, A is proportional to the volume of emulsion ( $V_E$ ) [23]. Hence, Eq. (2) is modified as following;

$$J = -\frac{V_f}{V_e} \frac{dC_{f,t}}{dt} \quad (3)$$

Permeability is related to the flux (J) as  $P = \frac{J}{C_{f,0}}$

where  $C_{f,0}$  is the initial metal concentration in the feed solution. Substituting P in Eq. (3) and integrating the equation leads to:

$$\ln \frac{C_{f,t}}{C_{f,0}} = -\frac{V_E}{V_f} P t \quad (4)$$

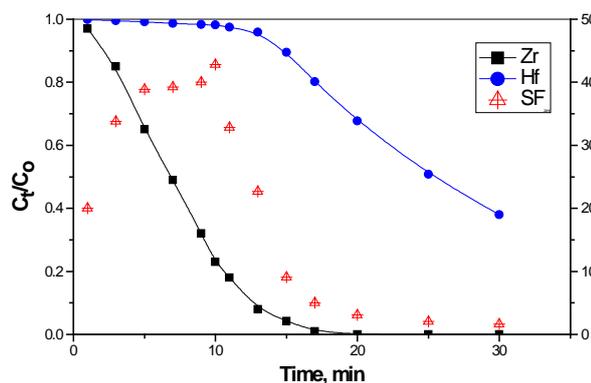
The  $V_E/V_f$  is the treatment ratio. Experimentally, by plotting  $\ln(C_{f,t}/C_{f,0})$  vs. t, a linear relation is obtained with slope equals  $(-P \cdot V_E/V_f)$  from which P and consequently J can be calculated. Equation (4) is used for the calculation of apparent P with the following assumptions: stripping reaction at liquid membrane/internal phase interface is very fast and there is no accumulation of the solute in the membrane phase, uniform size of emulsion globules produced under similar emulsion preparation conditions. The separation factor of Zr(IV) and Hf(IV) ( $SF_{Zr/Hf}$ ) using LEM is calculated from;

$$SF_{Zr/Hf} = \frac{E_n(Zr)}{E_n(Hf)} \quad (5)$$

The  $E_n$  is the enrichment factor of the metal ions in the internal phase which equals  $\frac{C_{int,t}}{C_{f,0}}$  where,  $C_{int,t}$  is the concentrations of metal ions in the internal phase at time t.

### Effect of contact time

Experiments were conducted to determine the time required to achieve the maximum extraction and separation of metal ions. The concentration of Zr(IV) and Hf(IV) in the feed phase was measured against time, Fig. 4. Hafnium concentration is decreasing with time up to 30 min. Zirconium is extracted almost completely at 17 min then feed phase remains almost free of Zr(IV) for further ~13 min. As metal ion separation is the main target, the best separation factor between zirconium and hafnium is found to be ~ 42.7 at 10 min as shown in Fig 4.



**Figure 4:** Effect of contact time on the extraction and separation factor of Zr(IV) and Hf(IV) by CC-LEM (0.005 mol L<sup>-1</sup> CYANEX-272, 2.0 mol L<sup>-1</sup> citric acid, 100 rpm, V<sub>d</sub>/V<sub>f</sub> = 10/100).

### Effect of stirring speed

As shown in Table 3, the membrane breakage increases with increase of the stirring speed. There is a “critical stirring speed” (400 rpm) above which membrane breakage is greatly increased. Therefore, the effect of stirring speed on the permeation of Zr(IV) and Hf(IV) was investigated in the range from 100 to 400 rpm. It was observed that as the stirring speed increases the permeability of both Zr(IV) and Hf(IV) gradually increase, Fig. 5a, but the increase in the case of Hf(IV) is greater. The increase in the permeability is due to the increase in the number of smaller emulsion droplets, which increased the interfacial area between the feed phase and the membrane phase, resulting in an increase the surface area for mass transfer. Besides, permeability increase may be attributed to the reduction in the thickness of the boundary diffusion layer for metal ions at the feed phase–liquid membrane interface with increasing the stirring speed. With respect to metal separation, 200 rpm obtained S<sub>Zr/Hf</sub> of 52.8 after 10 min and it is fixed for all other CC-LEM studies.

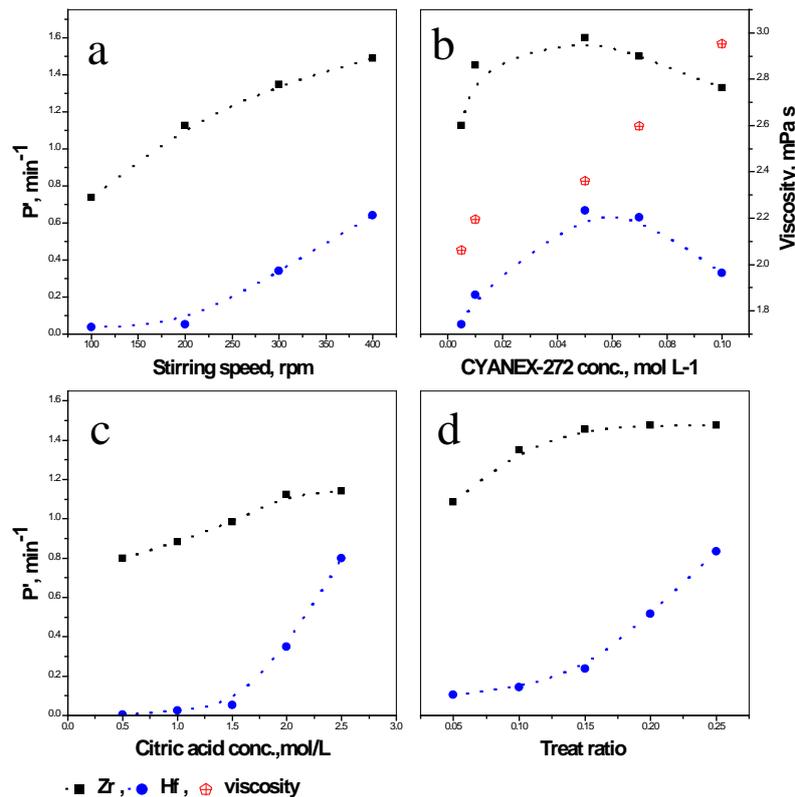
### Effect of extractant concentration

Results illustrated in Fig 5b represent the permeability of Zr(IV) and Hf(IV) at different concentrations of CYANEX-272. The Zr(IV) and Hf(IV) permeability increased as the extractant concentration increased in the membrane phase from 0.001 to 0.05 mol L<sup>-1</sup>. Further increase in the CYANEX-272 concentration, decreases the metal flux. This is results from two opposite effects: (i) increasing the extractant concentration generates a higher number of active sites available for metal complexes at the membrane/feed phase interface. This produces a higher metal concentration gradient in the membrane phase between membrane/feed phase and membrane/internal phase interfaces which enhance the metal diffusion and obtain more flux of metal towards the internal phase. (ii) The increase in the extractant concentration produces a slight increase in the emulsion viscosity Fig. 5b, causing higher resistance for the transport of metal ions across the liquid membrane. Also, the higher viscosity increases the size of the emulsion globules with a corresponding decrease in the mass transfer surface area, resulting in a decrease in the metal flux.

The concentration of 0.01 mol L<sup>-1</sup> of CYANEX-272 provides a separation factor of Zr(IV) and Hf(IV) of ~ 59.9 after 10 min which is used in the following CC-LEM studies.

### Effect of stripper concentration

The change in permeability of Zr(IV) and Hf(IV) via the ELM with the variation in citric acid concentration in the internal aqueous phase was studied in the concentration range of 0.5 to 2.5 mol L<sup>-1</sup>, Fig. 5c. The permeability of Zr(IV) increases as the citric acid concentration increased from 0.5 – 2.0 mol L<sup>-1</sup> as a result of the increase in the stripping capacity of the inner phase. At concentration range 2.0 – 2.5 mol L<sup>-1</sup>, the permeation rate of Zr(IV) is almost constant. The permeation of Hf(IV) is very slightly increased with the change in the citric acid concentration up to 1.5 mol L<sup>-1</sup> followed by a sudden increase. For the concept of metal separation, the concentration of 1.5 mol L<sup>-1</sup> citric acid is considered a critical concentration which gives good permeability to Zr(IV) with good metal ion separation (~ 63.7).



**Figure 5: Effect of stirring speed (a), CYANEX-272 conc. (b), citric acid conc. (c), and treat ratio (d) on the permeation of Zr(IV) and Hf(IV) across CC-LEM (Span 80 3%, 2.0 mol L<sup>-1</sup> HNO<sub>3</sub>; equilibrium time 10 min, Organic/internal phase ratio 1.5:1).**

#### Effect of treat ratio (TR)

The rise in the treat ratio ( $V_e/V_f$ ) is generally expected to increase the extraction capacity of the emulsion for metal ions present in the feed solution, which may be affecting on the separation efficiency of the LEM. The effect of treat ratio on the permeation of Zr(IV) and Hf(IV) was studied by varying the volume of the CC-LEM added to the feed phase and keeping the volume of the later constant. The treat ratio was varied from 0.05 ( $V_e/V_f = 5:100$ ) to 0.25 ( $V_e/V_f = 25:100$ ) and the obtained results were shown in Fig. 5d. It is observed that there is a steady increase in the flux of Zr(IV) and Hf(IV) with raising values of treat ratio from 0.05 to 0.15. In the treat ratio range of 0.15-0.25, the Hf(IV) flux is highly increased with almost quantitative extraction and recovery of Zr(IV). Therefore, to reduce the contamination of Zr(IV) with respect of Hf(IV) in the inner phase with the acceptable recovery of Zr(IV), 0.1 can be considered as the optimal value ( $S_{Zr/Hf} \sim 75.9$ ).

#### Zirconium recovery

Separation of zirconium from hafnium is one of the main objective of this investigation. From this point of view, the obtained data is carefully analyzed. It can be concluded that the optimal experimental conditions for Zr(IV)/Hf(IV) separation by CC-LEM from 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> are 0.01 mol L<sup>-1</sup> CYANEX-272 dissolved in corn oil and 3% Span 80, while the inner phase is 1.5 mol L<sup>-1</sup> citric acid with an organic/inner phase ratio 1.5:1, for emulsion preparation. For extraction process, the stirring speed is 200 rpm as well as the treat ratio ( $V_e/V_f$ ) is equal 10:100.

To recover the extracted zirconium, CC-LEM was firstly separated from the external phase after extraction process using a separating funnel. De-emulsification of W/O emulsion is the final step for the Zr recovery. The freeze - thaw method is used for the de-emulsification of CC-LEM. In this concern, the loaded emulsion freezes at  $268 \pm 1$  K°. The frozen emulsion was left to melt at room temperature,  $98 \pm 3$  K°. With the slow melting

process, the difference between the melting points of the organic phase and the aqueous inner phase gives a clear phase separation. The separated aqueous inner solution was analyzed and the loaded amount of zirconium, under the optimum separation condition, found to contain 22.8 g/l Zr and 2.05 mg/l Hf. This reflects that, the contamination factor is 89.91 mg of Hf for one kg of Zr which is below the limit of using zirconium in nuclear applications.

The separated organic phase is reused by adding fresh citric acid and re-emulsified, which found to give a good satisfactory results to obtain stable emulsion for further use for extraction of metal ions through new cycle.

### Conclusions

The incorporation of corn oil as a green diluent instead of kerosene in the formation of CYANEX-272 LEM was studied and the stability of the CC-LEM produced was carefully investigated. Corn oil was found to have no effect on the extraction ability of the extractant and form LEM with good stability for at least 2 h. The obtained green CC-LEM was used for the extraction and separation of Zr(IV) and Hf(IV) from 2.0 mol L<sup>-1</sup> HNO<sub>3</sub>. The effect of different parameters on the extraction process was examined and from the obtained results it is concluded that:

- Increasing the stirring speed has positive effect on the extraction of both Zr and Hf but the best metal separation is attained at 200 rpm stirring speed.

- 0.05 mol L<sup>-1</sup> CYANEX-272 is a critical concentration above which the viscosity of the membrane reached a limit that retards the permeation of the metal ions. 0.01 mol L<sup>-1</sup> CYANEX-272 provides a good separation between the investigated metal ions

- Above 1.5 mol L<sup>-1</sup> citric acid as a stripping agent the permeation of hafnium is highly increase which badly affect the separation of Zr/Hf

De-emulsification of the loaded CC-LEM was achieved using the freeze-thaw method and the contamination factor in the recovered zirconium is found to be 89.91 mg Hf/ kg Zr, which is below the limit of using zirconium in nuclear applications. The demulsified organic phase is successfully re-emulsified and re-used in another extraction cycle.

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