

## Separation of chromium and nickel ions by supported liquid membranes using TOA as carrier

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### ABSTRACT

The extensive use of chromium in leather tanning, metallurgy, electroplating and other industries has resulted in the release of aqueous chromium to the subsurface at numerous sites. Cr (VI) has received considerable attention owing to its extensive industrial applications and has long been recognised as a toxic substance due to its strong oxidising potential and the ease with which it can cross the biological membranes. In recent years the application of various solvent extraction technologies to the removal and concentration of chromium have been widely studied; chemical precipitation, ion exchange, reverse osmosis, diffusion dialysis, adsorption, liquid membrane technique are some of the alternatives that have been reported in the literature. Recently supported liquid membrane (SLM) extraction is an alternative to conventional solvent extraction due to its advantages like high selectivity, operational simplicity, low solvent inventory, low energy consumption, zero effluent discharge and combination of extraction and stripping into one single unit. In this work the selective separation of chromium from acidic media, containing the mixtures of chromium and nickel by SLM was investigated using TOA (tri-octylamine) as carrier. The liquid membrane was consisted of the desired concentration of an extractant (TOA), a modifier (TBP), and a diluent (chloroform, kerosene, cyclohexane). The membrane support was microporous hydrophobic polypropylene Celgard 2500. Such parameters as, the solvent type, feed solution pH, extractant (TOA) concentration, modifier (TBP) concentration and temperature were experimentally studied and the optimum conditions were determined. The permeation coefficients (P) and the initial fluxes of chromium ( $J_0$ ) were calculated. Separation factors of chromium over nickel was calculated from the experimental measurements.

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### 1. Introduction

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liquid membrane technique are some of the alternatives that have been reported in the literature [1].

Recently supported liquid membrane (SLM) extraction is emerging as an alternative to conventional solvent extraction due to its advantages like high selectivity, operational simplicity, low solvent inventory, low energy consumption, zero effluent discharge and combination of extraction and stripping into one single unit.

In this work the selective separation of chromium from acidic media, containing the mixtures of chromium and nickel by SLM was investigated using TOA (tri-octylamine) as carrier. The liquid membrane was consisted of the desired

concentration of an extractant (TOA), a modifier (TBP), and a diluent (chloroform, kerosene, cyclohexane). The membrane support was microporous hydrophobic polypropylene Celgard 2500. Such parameters as, the solvent type, feed solution pH, extractant (TOA) concentration, modifier (TBP) concentration and temperature were experimentally studied and the optimum conditions were determined. The permeation coefficients (P) and the initial fluxes of chromium ( $J_0$ ) were calculated. Separation factors of chromium over nickel was calculated from the experimental measurements.

## 2. Experimental

### 2.1. Chemicals

As ion carrier of chromium, TOA (Merck) was used.  $K_2Cr_2O_7$ ,  $NiSO_4 \cdot 6H_2O$ , NaOH, chloroform, xylene, n-decanol, TBP are of analytical grade (Merck) and all the stock solutions for chromium and nickel were prepared by dissolving the salts in distilled water.

### 2.2. Flat-sheet supported liquid membrane preparation and measurements

The permeation coefficient (P) and initial flux ( $J_0$ ), from C-t curves, were calculated from Eqs. (1) and (2) :

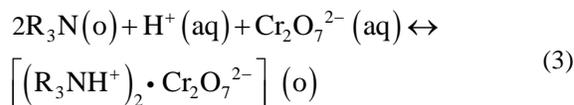
$$\ln \frac{C}{C_0} = - \frac{A\varepsilon}{V_F} P t \quad (1)$$

$$J_0 = - \left( \frac{dC}{dt} \right)_0 \left( \frac{V_F}{A\varepsilon} \right) \quad (2)$$

where  $V_F$  is the volume of the feed phase,  $\varepsilon$  is the porosity of membrane support, C and  $C_0$  are the concentrations of cobalt in the feed phase at elapsed time and time zero, respectively, and t is the elapsed time.  $(dC/dt)_0$  is the slope at  $t = 0$ ,  $V_F$  is the volume of the feed solution. A is the membrane area.

Amines are the general reagents among the extractants which form ion-pairs and known as basic extractant types, and extract metal ions according to an ion association principle. The chemical reactions occurring on the feed and stripping side of membrane are given below :

Feed side reaction:



If the complex formed, as shown in Eq. 3, diffuses through the membrane toward the strip side, the stripping reaction for the complex with an alkaline solution is expressed by Eq. 4:

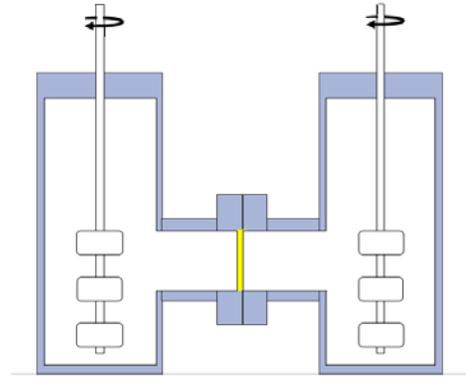
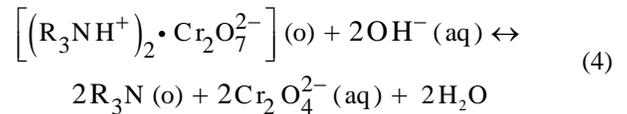


Figure 1. Schematic diagram of experimental apparatus.

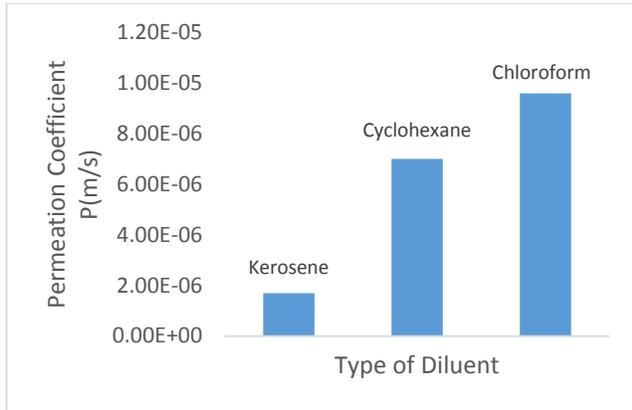
Competitive transport of the equimolar and non-equimolar mixture of Cr and Ni ions across the SLM from the aqueous solutions were studied using a two-compartment permeation cell, made from a pyrex glass, with flat-sheet membranes of  $12.56 \text{ cm}^2$  area (A), as shown schematically in Fig. 1. In all experiments the supports used for the liquid membranes were microporous hydrophobic polypropylene Celgard 2500 (Celgard Inc., USA)  $25 \mu\text{m}$  thick,  $0.209 \mu\text{m} \times 0.054 \mu\text{m}$  pore size and 55 % porosity. The support was soaked for 18 hours in a membrane solution of the desired composition, then leaving them to drip for a few seconds before being placed in the SLM cell. TBP was used as a modifier to improve the membrane performance. The volumes of both aqueous feed and strip phases were 250 mL. Various feed solutions were prepared by adding both chromium and nickel salts to study the effect of feed composition. The feed and stripping phases were mechanically stirred at the desired mixing speeds at  $20 \pm 1^\circ\text{C}$  to avoid concentration polarisation conditions at the membrane interfaces and in the bulk of the solutions. During the transport experiments in SLM system, the samples of feed and strip phases (about 1 mL) were periodically removed for determination of Cr and Ni concentration by atomic absorption spectroscopy (Shimadzu 6701GF, Japan). The feed phase pH measurements were determined with a Schott model CG840 pH meter (Germany). Membrane permeabilities were determined by monitoring chromium and nickel concentrations in the feed phase as a function of time.

## 3. Results and discussion

### 3.1. Effect of diluent

The influence of the diluent on both the stability and efficiency of supported liquid membranes for the transport of metal ions has been reported [2-5]. Experiments were carried out for separation and extraction of chromium from the

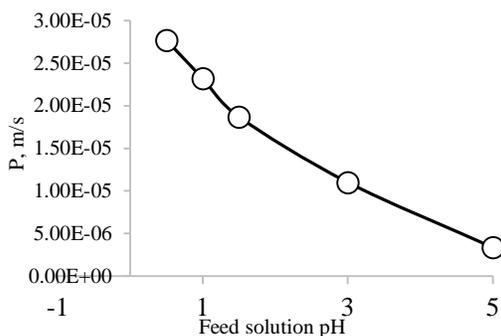
aqueous solutions. The results obtained indicate that TOA with TBP is a more effective carrier for chromium in chloroform than others as indicated in Fig. 2.



**Figure 2.** The effect of diluent (Extractant (TOA): 5 % w/w; TBP: 20 w/w %; Feed phase: 500 mg/L  $Cr^{6+}$ ; 500 mg/L  $Ni^{2+}$ ; Feed soln.pH: 0.5; Feed stirring speed: 1200  $min^{-1}$ ; Strip phase stirring speed: 1200  $min^{-1}$ ; Strip solution: 2 w/w % NaOH; Temp.: 20°C; Membrane support: Celgard 2500)

### 3.2. Effect of feed solution pH

In order to assess the role of the pH on separation of chromium from the equimolar and nonequimolar mixtures of chromium and nickel, pH variation studies in the range of 0.5-5 were carried out, as indicated in Fig. 3. As seen from Fig. 3, the permeation coefficient decreased from  $2.77 \times 10^{-5}$  to  $0.34 \times 10^{-5}$  m/s with increase of pH from 0.5 to 5.0. The increase in proton concentration, that is a decrease in pH, will lead to increased formation of the complex,  $(R_3NH^+)_2 \cdot Cr_2O_7^{2-}$  that causes to increase the diffusional resistance and hence the permeation coefficient decreases [5]. On the other hand, the decrease in the coefficient with the increase in pH can be explained by the fact that the concentration of the protonated tertiary amine,  $R_3NH^+$  decreases due to the less availability of proton and thus the adduct,  $(R_3NH^+)_2 \cdot Cr_2O_7^{2-}$  concentration will decrease, as described by Eq. 3. As a result, the flux will decrease.

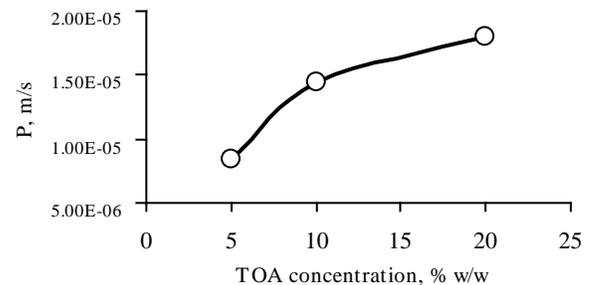


**Figure 3.** Effect of feed pH on Cr permeation coefficient ( Diluent (Chloroform): 75 % w/w; Extractant (TOA): 5 % w/w; TBP: 20

w/w %; Feed phase: 500 mg/L  $Cr^{6+}$ ; 500 mg/L  $Ni^{2+}$ ; Feed stirring speed: 1200  $min^{-1}$ ; Strip phase stirring speed: 1200  $min^{-1}$ ; Strip solution: 2 w/w % NaOH; Temp.: 20°C; Membrane support: Celgard 2500)

### 3.3. Effect of TOA concentration.

As shown in Eq. (3), the chromium extraction and thereby the transport rates are dependent the carrier concentration. In order to understand the effect of carrier (TOA) concentration on the transport of chromium, the experiments were carried out at varying concentration of TOA. As shown in Fig. 4, the permeation coefficient increases with increasing carrier concentration. In facilitated transport, the metal ion transport is expected to increase with the carrier concentration which is in conformity with the behaviour at least at lower concentration range.



**Figure 4.** Effect of carrier (TOA) concentration on the permeation coefficient (Diluent (Chloroform): 55-95 %; Feed phase: 500 mg/L  $Cr^{6+}$ ; 500 mg/L  $Ni^{2+}$ ; Feed soln.pH: 0.5; Feed stirring speed: 1200  $min^{-1}$ ; Strip stirring speed: 1200  $min^{-1}$ ; Strip soln: 2 w/w % NaOH; Temperature: 20°C; Membrane support: Celgard 2500).

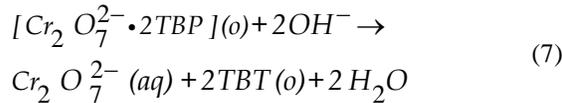
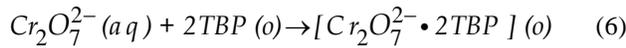
### 3.4. Synergistic effect of solvation extractant (TBP).

The combination of amines and neutral or solvation extractants was studied in a potential extracting system for metal ions [6]. TBP variation studies in the range of 0-40 % w/w were carried out, as indicated in Fig. 5. Fig. 5 shows that there is a synergic effect, from which the flux of cobalt,  $J_o$  is increased when carriers are used. The increase in TBP concentration increases the Cr flux since the complex diffusivity, as described by Eq. (5), in the membrane phase increases due to a decrease in the membrane viscosity [7]. According to Marcus [8], however, an adduct between the complex of Eq. (6) a neutral ligand, like TBP, could also be formed in the SLM. This view is also supported by Biswas and Basu [9] that the nature of the extracted adduct in presence of combined extractant can be expected to be  $[(R_3NH^+)_2 \cdot Cr_2O_7^{2-} \cdot B]$ , B represents neutral extractant. Thus, the effect of B, may be described in terms of the replacement of water molecules from  $[(R_3NH^+)_2 \cdot Cr_2O_7^{2-} \cdot xH_2O]$ . This leads an adduct formation which is responsible for the enhanced extraction into the organic phase. However, De Haas et al. [10] give the

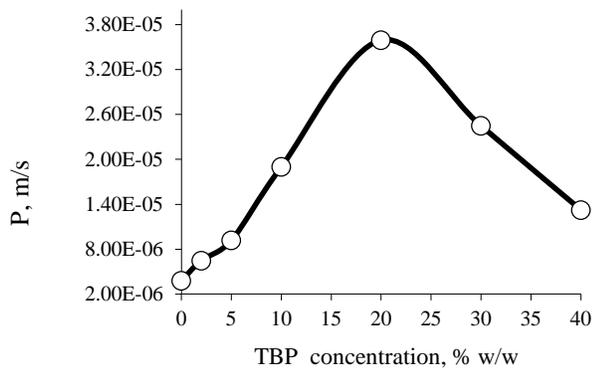
extraction and stripping reactions for TBP by Eqs. (6) and (7), respectively.

$$D = kT / \eta \quad (5)$$

where  $D$ : diffusion coefficient,  $\eta$ : viscosity and,  $T$ : temperature.



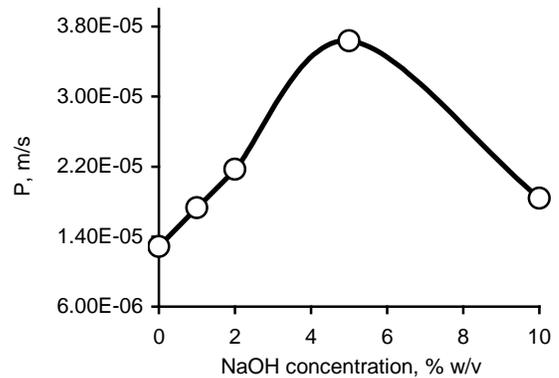
From Fig. 3 it can be seen that the value of the flux increases up to 25 % w/w TBP in the membrane and then it decreases. The increase in TBP concentration, in fact, causes the viscosity of membrane solution, having TOA as extractant, to decrease and thus the Cr flux increases up to a certain level that the membrane solution becomes saturated or viscous again.



**Figure 5.** Synergistic effect of neutral or solvation extractant (TBP) conc. on permeation coefficient (Diluent (Chloroform): 55-95 %; Extractant (TOA): 5 %; Feed phase: 500 mg/L  $Cr^{6+}$ ; 500 mg/L  $Ni^{2+}$ ; Feed soln.pH: 0.5; Feed stirring speed: 1200  $min^{-1}$ ; Strip stirring speed: 1200  $min^{-1}$ ; Strip soln: 2 w/w % NaOH; Temperature: 20°C; Membrane support: Celgard 2500).

### 3.5. Effect of strip phase (NaOH) concentration.

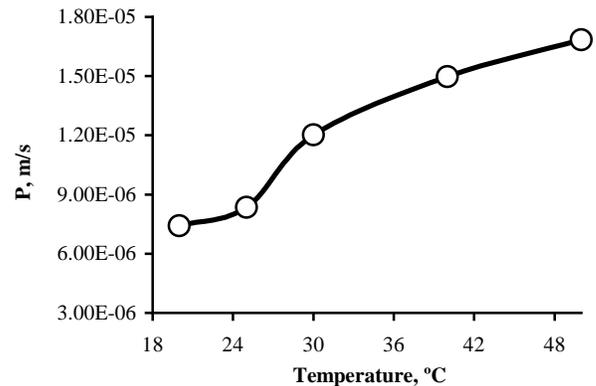
The strength of the strip phase for the transported Cr (VI) could have a significant effect on the efficiency and selectivity of the Cr (VI) transport. The stripping efficiency of the sodium hydroxide solution in the receiving phase was studied in the range 0-10 % w/v (0-2.5 M). The results are shown in Fig. 6. The figure indicates that with increase in concentration of NaOH, the permeation of chromium increases up to 5 % NaOH concentration and decreases after that. This may be due to the saturation of the driving force for diffusion through the SLM owing to an increase of chromium complexes concentration at the membrane-strip interface, as reported also elsewhere [11].



**Figure 6.** Synergistic effect of neutral or solvation extractant (TBP) conc. on permeation coefficient (Diluent (Chloroform): 55-95 %; Extractant (TOA): 5 %; Feed phase: 500 mg/L  $Cr^{6+}$ ; 500 mg/L  $Ni^{2+}$ ; Feed soln.pH: 0.5; Feed stirring speed: 1200  $min^{-1}$ ; Strip stirring speed: 1200  $min^{-1}$ ; Strip soln: 2 w/w % NaOH; Temperature: 20°C; Membrane support: Celgard 2500).

### 3.6. Effect of system temperature.

The chromium permeation through SLM was also examined against temperature, between 25°C and 50°C, as shown in Fig. 7. From Fig. 7, the Cr permeation or flux increases with the increase of temperature. The increase in temperature causes the complex diffusivity in the membrane phase to increase and the membrane viscosity to decrease, as given in Eq. 5, and thus the Cr flux increases. This indicates that the diffusional resistance to mass transfer is of prime importance.



**Figure 7.** Effect of temperature on permeation coefficient (Diluent (Chloroform): 90 %; Extractant (TOA): 5 %; Feed phase: 500 mg/L  $Cr^{6+}$ ; 500 mg/L  $Ni^{2+}$ ; Feed soln. pH: 2; Feed stirring speed: 1200  $min^{-1}$ ; Strip stirring speed: 1200  $min^{-1}$ ; Strip soln: 2 w/w % NaOH; Membrane support: Celgard 2500).

### 3.7. Optimum conditions.

The following results were obtained from examining the experimental parameters :

- Diluent: Chloroform

- Feed solution pH: 0.5
- Feed solution stirring rate: 1200 min<sup>-1</sup>
- Stripping solution stirring rate: 1200 min<sup>-1</sup>
- Extractant (TOA) concentration: 10 % w/w
- Neutral or solvation extractant (TBP) concentration: 20 %
- Temperature: 50°C
- Stripping solution: 2 % w/w NaOH
- Polymer support: Celgard 2500 ( $\epsilon = 0.55$ ;  $\Phi = 0.29$  x 0.054  $\mu\text{m}$ ;  $\delta = 25$   $\mu\text{m}$ )

### 3.8. Membrane selectivity.

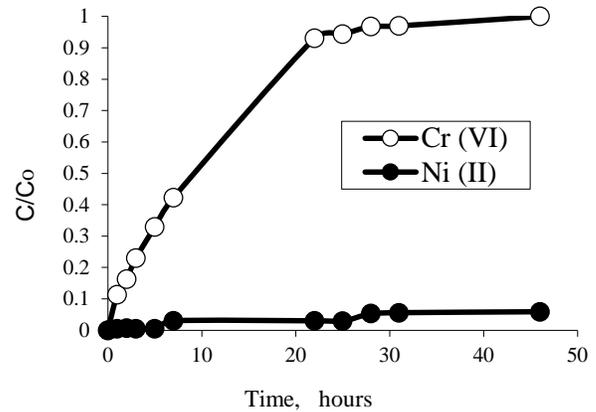
Under the optimum conditions, the effect of feed concentration, both equimolar and non-equimolar, on the extraction rate or separation of chromium over nickel have been experimentally studied. The separation factors,  $\alpha_{Cr/Ni}$ , Eq. 8, of Cr over Ni, based on the initial feed composition, have been determined for 8 hours, under the optimum conditions, and shown for the both equimolar and non-equimolar feed mixtures in Table 1.

**Table 1.** Separation factors,  $\alpha_{Cr/Ni}$  of Cr over Ni, based on the initial feed solutions, under the optimum conditions.

| Equimolar feed mixtures,    | $\alpha_{Cr/Ni}$ | Nonequimolar feed mixtures, | $\alpha_{Cr/Ni}$ |
|-----------------------------|------------------|-----------------------------|------------------|
| 100 mg/L Cr + 100 mg/L Ni   | 8.0              | 100 mg/L Cr + 1000 mg/L Ni  | 43.4             |
| 200 mg/L Cr + 200 mg/L Ni   | 18.3             | 200 mg/L Cr + 1000 mg/L Ni  | 50.2             |
| 500 mg/L Cr + 500 mg/L Ni   | 27.6             | 400 mg/L Cr + 1000 mg/L Ni  | 71.7             |
| 700 mg/L Cr + 700 mg/L Ni   | 36.3             | 600 mg/L Cr + 1000 mg/L Ni  | 44.8             |
| 1000 mg/L Cr + 1000 mg/L Ni | 28.0             | 800 mg/L Cr + 1000 mg/L Ni  | 34.8             |

$$\alpha_{Cr/Ni} = \frac{(C_{Cr}/C_{Ni})_{strip}}{(C_{Cr}/C_{Ni})_{feed,o}} \quad (8)$$

The concentration-time profiles of Cr (VI) and Ni transport for equimolar feed mixtures of 2000 mg/L each, was also studied over a time period of 46 hours, in the optimum conditions, as depicted in Fig. 8. From Fig. 8, it is confirmed that under the optimum conditions, almost all Cr (VI) was transported from the feed phase into the receiving phase. On the other hand, the selective separation of chromium from nickel is reasonably possible, as indicated in Fig. 8.



**Figure 8.** Relative transport rates of Cr and Ni through Celgard 2500 membrane containing 10 % TOA and 20 % TBP in chloroform (Feed phase: 2000 mg/L Cr<sup>6+</sup>; 2000 mg/L Ni<sup>2+</sup>; optimum conditions).

## 4. Conclusions

Supported liquid membrane process using TOA plus TBP to extract and separate Cr from the acidic feed solutions has been studied. From this study the following conclusions can be drawn:

- The optimum conditions are determined experimentally as stated above.
- At the optimum conditions, the extraction of chromium is achieved with the efficiencies of 97.6 % and 57.1 % for the equimolar feed mixtures of 200 mg/L Cr + 200 mg/L Ni, and 700 mg/L Cr + 700 mg/L Ni, respectively, within 8 hours, and the separation factors of Cr over Ni are 18.3 and 36.3. For nonequimolar feed mixtures of 100 mg/L Cr + 1000 mg/L Ni, and 800 mg/L Cr + 1000 mg/L Ni, the extraction efficiencies of cobalt are 100.0 % and 66.4 %, respectively, and the separation factors of Cr are 43.4 and 34.8 in 8 hrs.
- The extraction rate of cobalt increases with the increase of system temperature. The initial mass flux of Cr increased from  $3.79 \times 10^{-6}$  kg/m<sup>2</sup>s to  $9.25 \times 10^{-6}$  kg/m<sup>2</sup>s, as the temperature increased from 20°C to 50°C. The separation factor  $\alpha_{Cr/Ni}$  also increases from 21.3 to 27.8 in 8 hours. It also shows that the diffusional resistance in the liquid membrane phase is of a great importance.

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