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Studies on the transport of chromium(III) through a supported liquid membrane containing D2EHPA as carrier

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ABSTRACT

The facilitated transport of chromium(III) through a flat-sheet supported liquid membrane (FSSLM) containing di(2-ethylhexyl) phosphoric acid (D2EHPA) as ionophore is studied. A buffered Cr(III) solution was used as a source phase, whereas HCl solution was used as a receiving phase. The incidence of several parameters such as feed phase pH, carrier concentration, polymeric support nature and diluent chemical nature on the transport efficiency has been investigated. Overall experiments, a feed pH decrease has been observed due probably to proton permeation. Therefore, pH was manually maintained during the run at the initial value by adding NaOH concentrated solution to the feed phase. After 48 h transport, a trivalent chromium transport efficiency of almost 67% has been obtained through a D2EHPA-2-octanol based SLM when source pH was maintained constant around 4.5. Under the optimum experimental conditions an initial flux value of 4×10^{-6} mol.m^{-2}.s^{-1} has been estimated. Transport of hexavalent chromium across the D2EHPA based FSSLM was also examined, and a very slight amount not exceeding 5% was transported.

Keywords: Chromium(III); D2EHPA; Facilitated transport; Flat-sheet supported liquid membrane (FSSLM); Transport efficiency

1. Introduction

A growing interest in the investigation of more suitable techniques for the processing of liquid solutions has been shown in the past decades. Nowadays, the recovery of valuable or toxic metals from these solutions can be considered as a primordial objective for industrial clean production and resource recovery.

Considerable attention throughout the past three decades has been dedicated to membrane techniques for the separation and concentration of metal ions due to some interesting characteristics such as ease of operation, some energy and selectivity advantages, and low cost operation factors. From a practical point of view, applications in the industrial [1,2], and analytical fields [3,4] as well as in wastewater treatment [5,6] have been stated for membrane techniques. Consequently, continual efforts are being made to improve the performance of these membranes. Nevertheless, liquid membranes were the most investigated category for the recovery of metal ions [7] and organic compounds [8]. In fact, these membrane processes combine extraction and stripping into one single stage and thus non-equilibrium mass transfer characteristic where the separation is not limited by the conditions of equilibrium [9]. Various configurations of liquid membranes such as bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM) were searched for different applications [10,11]. Among these configurations, the use of SLM is

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an interesting alternative to liquid–liquid extraction for the removal of contaminants, and a manner of complying with environmental regulations that have become more and more strict.

Di(2-ethylhexyl) phosphoric acid (D2EHPA) is available commercially as a 97% pure liquid. It has been widely used in the extraction of a range of metals including nickel, cobalt, zinc and chromium [7,10]. Contrary to the extraction of chromium(III) with D2EHPA across SLMs, its liquid–liquid extraction has received the most attention in the literature [12–15]. Pandey et al. [12] used an experimental time of 5 min to ensure attainment of equilibrium. Contact times between 15 and 35 min were reported by other authors [13,15]. The transport efficiency of a D2EHPA system was governed by the operating pH. The pH required for maximum extraction of Cr(III) with D2EHPA is 4.5–5 although significant extraction occurs at pH values as low as three [12,13].

The work of Beneitez and Ayllon [16] focused on the nature of the extracted species. The extracted species was reported in the pH range 0.85–1.20 as $CrX_3(H_2O)_2Y$ where Y is D2EHPA and X the de-protonated form of D2EHPA. The structure suggested by these authors was similar to the CrX_3 reported by Islam and Biswas for the pH range 2.5–5.5 [14]. The choice of diluent has received some attention but the results are conflicting. Islam and Biswas [14] concluded that aliphatic diluents produced higher extraction at a given pH than aromatic diluents whereas Rao and Hariharan [13] concluded that the most efficient extraction occurred with benzene as diluent. The extraction efficiency does not seem to follow any identifiable physical property of the diluent, e.g. dielectric constant or viscosity.

The stripping of Cr(III) extracted with D2EHPA has been studied by Pandey et al. [12]. They found that stripping of chromium(III) from the organic phase with hydrochloric acid was dependent on the acid strength. Maximum recovery around 70% could be achieved with HCl solution up to 3 $mol.L^{-1}$. Schügerl et al. [15] reported near-complete stripping of organic phases that have low Cr(III) loading. In their study, the loaded organic phase contained 4×10^{-5} $mol.L^{-1}$ chromium(III) and 1.5 $mol.L^{-1}$ D2EHPA in kerosene.

The aim of this work is the use of a lower cost commercially available extractant (D2EHPA) to study the transport of chromium(III) through a flat-sheet SLM (FSSLM). Results are compared to the literature liquid–liquid extraction available results. Several operational variables such as feed pH, carrier concentration, metal concentration, chemical diluent nature and polymeric support nature were investigated.

2. Experimental

2.1. Reagents and solutions

2-nitrophenyl octyl ether (NPOE), decane, 2-octanol and kerosene were purchased from Fluka. Cyclohexane was obtained from Merck. Toluene and *p*-xylene were purchased from Prolabo. Viscosity and dielectric constant of organic solvents are presented in Table 1.

Table 1
Viscosity and dielectric constant of organic solvents [17]

Solvent	Viscosity (cP)	Dielectric constant ε_r
Cyclohexane	0.980 (20°C)	2.02 (25°C)
Decane	0.838 (25°C)	1.991 (20°C)
Kerosene	1.6 (20°C) [18]	2.2 (20°C) [18]
NPOE	13.80 (25°C) [19]	24.2 (25°C) [19]
2-octanol	6.125 (30°C)	8.13 (20°C)
Toluene	0.523 (30°C)	2.385 (20°C)
p-xylene	0.603 (25°C)	2.273 (20°C)
D2EHPA	197.24 (30°C)*	—

*Measured by a capillary viscosimeter

Table 2
Physical characteristics, experimental and normalized Cr(III) fluxes of used polymeric supports. Feed solution: acetate buffer, $[Cr(III)] = 5\times10^{-4}$ M kept constant around pH 4.5 by NaOH addition; Supports: Accurel and Durapore; Organic phase: D2EHPA (50% v/v) in 2-octanol; Stripping phase: HCl pH = 1

Polymeric support	Accurel® PP 2E-HF (Membrana, Germany)	Durapore (Millipore, USA)
Material	Polypropylene	Polyvinylidene difluoride
Thickness d_0, µm	160	120
Pore diameter d_0, µm	0.2	0.2
Porosity ε, %	75	65
Tortuosity ($\tau = 1 - \ln \varepsilon$) [20]	1.29	1.43
$\varepsilon/d_0\tau$ ($\times10^{-3}$ μm^{-1})	3.63	3.79
J_{exp} ($\times10^6$), mol m^{-2} s^{-1}	4.0	2.68
J_N ($\times10^6$), mol m^{-2} s^{-1}	4.0	2.57

Chromium(III) salt as chromium(III) chloride hexahydrate $[CrCl_2(OH_2)_4]Cl$, $2H_2O$ and di(2-ethylhexyl) phosphoric acid (D2EHPA) were procured from Fluka. 2-[*N*-morpholino] ethane sulfonic acid (MES) was procured from Sigma. All chemical compounds were of analytical grade or higher.

Two different flat-sheet polymeric supports were evaluated. Their physical characteristics are collected in Table 2.

2.2. SLM preparation and transport procedure

FSSLMs consist of a polymeric inert support impregnated with D2EHPA (50% v/v) diluted in different organic diluents for at least 24 h. The organic phase is immiscible with the aqueous media. Obtained SLMs were placed in the middle of a two-compartment permeation cell described elsewhere [21–23].

The feed solution (50 mL) was a 5×10^{-4} mol.L^{-1} Cr(III) aqueous solution buffered at pH 4.8 (acetate buffer). The stripping solution (50 mL) was an HCl aqueous solution adjusted to pH 1. Both aqueous feed and stripping solutions were magnetically stirred (600 rpm was selected, from a preliminary study, as the optimal stirring speed to obtain the best transport efficiency) at 25±1°C. All experiments were carried out in duplicate and S.D.s were less than ±10%.

The transport efficiency, (% Transport), was calculated according to Eq. (1):

$$\%\ \text{Transport} = \frac{[\text{M}]_{\text{aq,strip}}}{[\text{M}]_{\text{aq,init}}} \times 100 \qquad (1)$$

where $[\text{M}]_{\text{aq,strip}}$ is the concentration of the metal ions released in the stripping solution, and $[\text{M}]_{\text{aq,init}}$ is the initial concentration of Cr(III) ions in the feed solution.

From the slope of the straight line (at time tending to zero, negligible diffusion lag time) obtained when plotting the metal concentration in the stripping phase as a function of time, the initial flux (*J*) can be calculated according to the following equation [21–24]:

$$J = \left(\frac{V}{A}\right) \cdot \left(\frac{\text{d}[\text{M}]}{\text{d}t}\right) \qquad (2)$$

where *V* is the volume of the aqueous stripping solution (L), *A* is the effective exposed surface area of the membrane (m^2), and [M] is the concentration of the metal in the stripping phase (mol.L^{-1}) at elapsed time (s).

1 mL sample of each feed and stripping solutions was periodically taken and chromium concentration was determined by flame atomic absorption spectrophotometry (Analytikjena AAS vario 6). The flow times of the binary mixture liquids and pure D2EHPA were measured by a capillary viscosimeter from Schott thermostated in a water bath and equipped with an electronic timer (Visco-Clock, Schott). Viscosities of binary mixtures of D2EHPA (% v/v) and 2-octanol or cyclohexane at θ = 30°C are reported in Table 3.

Table 3
Viscosities (η) of binary mixtures of D2EHPA (% v/v) and 2-octanol or cyclohexane at θ = 30°C

D2EHPA (%, v/v)	η (cP)	
	2-octanol	Cyclohexane
20	13.71	2.04
23	20.13	2.26
27	27.31	2.58
30	39.54	2.90
40	52.45	4.35
50	66.79	6.60
60	79.75	11.75
80	84.12	43.85

Chloride concentrations were determined in the aqueous solution by a potentiometric automatic titration using a Metrohm 716 DMS Titrino. Each experiment is replicated twice.

3. Results and discussion

The mass transfer of trivalent chromium across the membrane will be described by considering only diffusional parameters because of the fast reaction between the metal ions and the carrier molecules at the interfaces [25].

In all the experiments, the ionic strength of the source and receiving phases was constant at 0.1 M. This constant value provides better membrane stability conditions and avoids osmotic flux of water.

3.1. Effect of the feed pH

Even though transport efficiency through the SLM system is directly influenced by interfacial pH, the effect of bulk solution pH is discussed below. In fact, due to concentration gradients at interfacial diffusion layers, interfacial pH can be different from that in the bulk solution but it depends on its value.

The feed solution has been buffered at two different pHs using MES buffer (5×10^{-2} M, pH 5.5) or acetate buffer (5×10^{-2} M, pH 4.8). The receiving phase was an aqueous HCl solution at pH 1. The organic phase is composed of D2EHPA (50% v/v) diluted in cyclohexane or 2-octanol. Fig. 1 shows the Cr(III) transport efficiency as a function of transport time.

It can be observed that in both cases, acetate buffer demonstrates higher transport efficiency than MES buffer. In fact, when the feed solution is buffered at pH 4.8 (acetate buffer) we are in the pH range (4.5–5) suggested by several authors in Cr(III) liquid–liquid extraction with D2EHPA as the maximum extraction pH range

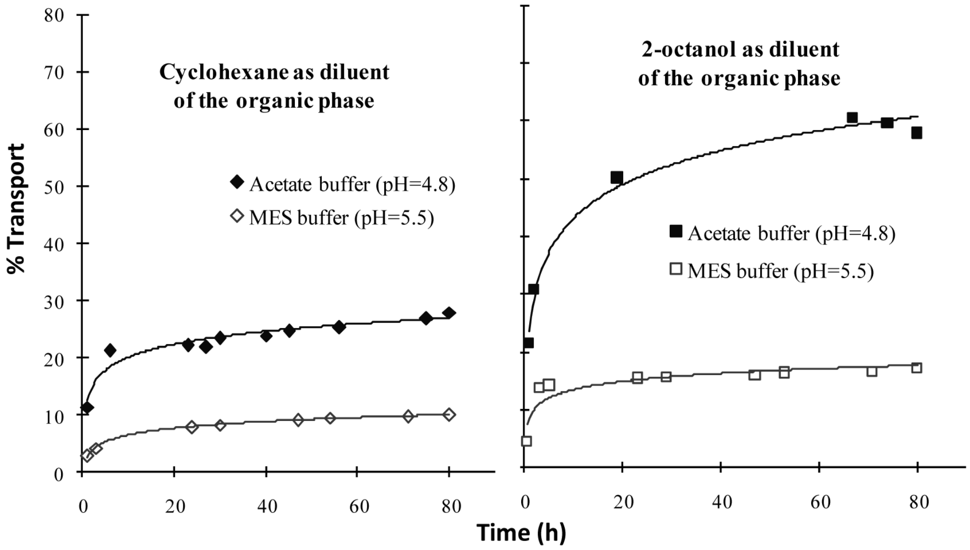

Fig. 1. Effect of feed pH on Cr(III) transport efficiency. Feed phase: [Cr(III)] = 5×10^{-4} M at pH 4.8 and 5.5; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in cyclohexane or in 2-octanol; Stripping phase: HCl pH = 1.

[12,14,15]. On the other hand, when the feed phase pH is adjusted to 5.5 using acetate buffer (5×10^{-2} M), a comparable transport efficiency of around 20% was attained as using MES buffer. This could attest that the effective buffer nature has no effect on Cr(III) transport efficiency. This former depends only on the Cr(III) species present in the feed phase which depend on the feed pH. Taking into account that predominant Cr(III) species in the pH range (4.5–5) are $\mathrm{Cr(OH)}_2^+$ [26], the extraction equilibrium can be described as follows:

$$\mathrm{Cr(OH)}_{2aq}^{+} + \mathrm{LH}_{org} \rightleftharpoons \mathrm{Cr(OH)}_2\mathrm{L}_{org} + \mathrm{H}_{aq}^{+} \qquad (3)$$

where LH_{org} is D2EHPA and $\mathrm{Cr(OH)}_2\mathrm{L}_{org}$ is the complex formed between Cr(III) predominant species and D2EHPA.

It can be also noticed that under the two different feed pHs, Cr(III) is better transported using 2-octanol as diluent. The dependence of the transport efficiency on the diluent chemical nature will be discussed largely below.

In all experiments studied and by measuring the pH after 80 h of transport, a feed decrease was observed. For example, using 50% 2-octanol as a diluent membrane solution, acetate buffer as a feed solution, and HCl solution of pH 1 as a receiving phase, the time courses of the concentration changes of Cr(III) and pH in both phases are shown in Fig. 2a and 2b.

As is evident from Fig. 2a, facilitated transport was

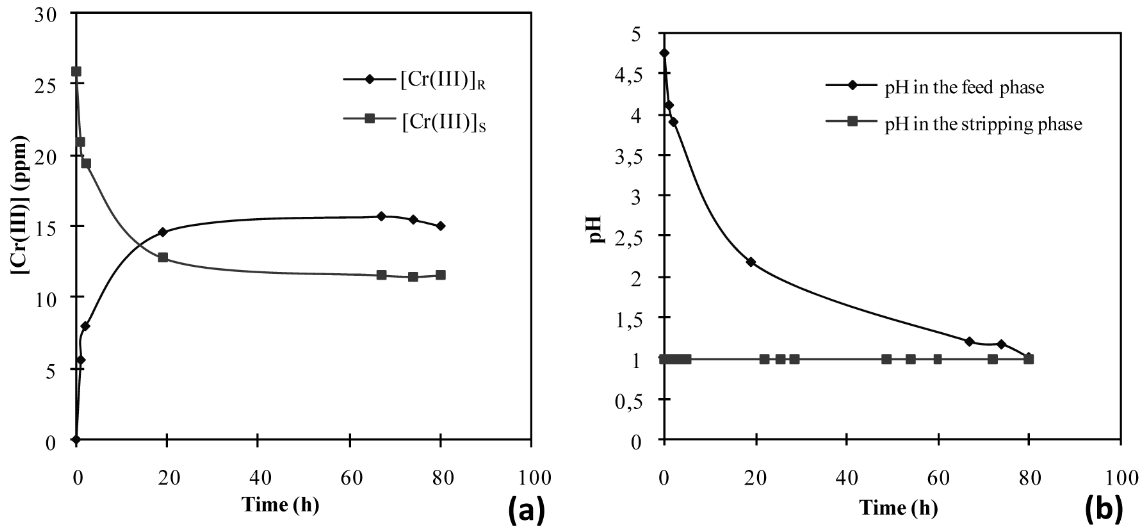

Fig. 2. Time courses of Cr(III) concentration (a) and pH (b) in feed and receiving phases. Feed phase: acetate buffer, [Cr(III)] = 5×10^{-4} M; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in 2-octanol; Stripping phase: HCl pH = 1.

not observed. The same behaviour was viewed using cyclohexane as diluent. This was probably caused by disappearing of the pH difference required to ensure uphill facilitated transport due to proton permeation, as shown in Fig. 2b. The proton permeation will normally lead to a feed pH decrease and a receiving pH increase. Fig. 2a shows only a feed pH decrease; in contrast, receiving pH remained almost constant at pH 1. This fact can be explained by the stronger acidity of the receiving phase which is insignificantly changed by the addition of protons.

In order to understand the proton permeation origin, a blank experiment was performed in which the feed phase contained no metal ions. In both phases, pH and chloride concentration were measured as a function of time. No detectable variation in pH and chloride concentration was mentioned confirming the counter-coupled transport of Cr(III) ions using D2EHPA as carrier. By the way, a feed pH decrease due to proton permeation is only observed when Cr(III) is transported towards the receiving solution. To avoid this feed pH decrease, the buffer concentration is increased using more concentrated acetate buffer solutions (10^{-1} and 5×10^{-1} M). Although this buffer concentration increases, the feed pH decrease persists (a profile of pH time course similar to Fig. 2b was obtained) limiting the counter-coupled transport of Cr(III).

Based on our previous work [22], the feed pH was manually kept constant around pH 4.5 during the experiment by adding some drops of a concentrated NaOH solution. This addition had insignificant change in the concentration of Cr(III) in the feed phase. The time courses of the concentration changes of Cr(III) in the feed and receiving phases are shown in Fig. 3.

As can be seen in Fig. 3, uphill facilitated transport driven by pH difference between the feed solution and the receiving solution was observed. It can be also noticed that an HCl solution of pH 1 ensures an approximately total release of Cr(III) complexed at the interface feed solution–membrane.

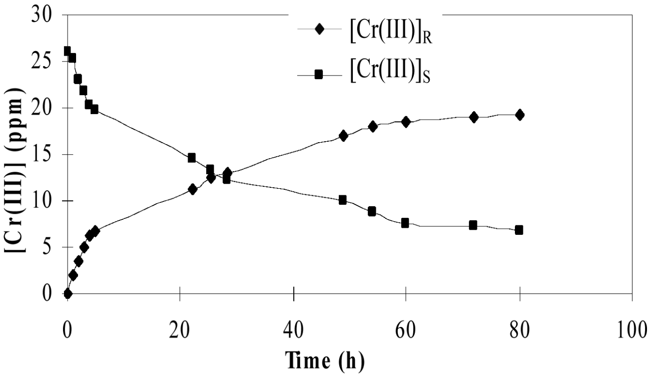

Fig. 3. Time courses of Cr(III) concentration in feed and receiving phases with feed pH control. Feed phase: acetate buffer, [Cr(III)] = 5×10^{-4} M kept constant around pH 4.5 by NaOH addition; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in 2-octanol; Stripping phase: HCl pH = 1.

3.2. Effect of metal concentration

Table 4 shows the variation in the chromium initial flux against the concentration of Cr(III) ranging from 10^{-4} to 5×10^{-3} M in acetate buffered feed solution. This study was carried out using organic solutions of 50% (v/v) D2EHPA in 2-octanol and receiving solutions of 0.1 M HCl. It can be observed that under these experimental conditions, the metal flux increased with the increase of the initial chromium concentration in the feed phase and membrane saturation phenomenon was not perceived. Similar behaviour was mentioned in our previous work dealing with binary Pd(II) and Au(III) extraction by a SLM system containing thiacalix[4]arene derivative as ionophore [27]. In the same way, Chaudry et al. [28] revealed that the initial Cr(III) flux across a triethanolamine-cyclohexanone based SLM is enhanced when the metal concentration in the source phase increases from 10.22×10^{-4} to 30.72×10^{-4} M.

3.3. Effect of the type of stripping acid

Chromium(III) complexes are kinetically slow to be formed in the aqueous phase because of the thermodynamic stability of the aqueous complexes. The rate of exchange of ligands on the chromium(III) centre is extremely low and depends on the concentration of the ligand in the solution, the pH and the affinity for coordination of the ligand towards the chromium(III) centre. On the other hand, due to the weakness of knowledge of the nature of the carrier–metal complex formed in the membrane (ignorance of values of its complexation and acidity constants), it is difficult to confirm that the decomplexation in the receiving phase is only due to the strong presence of the protons (with low pH), but that can be also due to the complexation of chromium with the ligand of the acid. On other hand, the rate at which Cr(III) establishes equilibrium, depends on the concentration and pH of the receiving solutions and the affinity of coordination characteristics of different ligands.

Table 4
Effect of the metal concentration on the on the initial Cr(III) flux. Feed solution: acetate buffer, [Cr(III)] at different concentrations; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in 2-octanol; Stripping phase: HCl pH = 1.

Metal concentration (mol.L^{-1})	Initial flux ($\times10^5$) (mol.m^{-2}.s^{-1})
10^{-4}	0.2
5×10^{-4}	0.4
10^{-3}	4.0
5×10^{-3}	11.8

Therefore, the probability to complex Cr(III) with the counter ion of the acid was investigated. Several acid solutions were tested as the stripping phase to recover the extracted Cr(III) in the organic phase. The efficiency of transport of Cr(III) ions across the D2EHPA-SLM was studied using HCl, H_2SO_4, HNO_3 and $HClO_4$ to adjust the pH of the strip solutions at pH 1. The feed phase was a 5×10^{-4} M Cr(III) aqueous acetate buffered solution. The organic membrane phase was a 50% D2EHPA solution in 2-octanol. The transport efficiencies (% transport) changing the acid type are given in Table 5. Cr(III) complex formation constants with chloride, sulphate, nitrate, and perchlorate ions estimated by Neuhoff [29] are also given in this table. At the membrane–stripping solution interface, the stripping acid could protonate D2EHPA in order to release trivalent chromium ions. Chloride, sulphate, nitrate, and perchlorate each has a lone-pair of electrons to donate to Cr(III) and therefore it is possible for these ions to act as ligands and to complex with Cr(III).

According to the experimental results, a slight transport efficiency difference among tested acids was observed with respect to the Cr(III) complex formation constants with chloride, sulphate, nitrate or perchlorate ions. A 0.1 M HCl stripping solution was found as required and sufficient to obtain the maximum Cr(III) transport efficiency.

3.4. *Effect of the carrier concentration*

The efficiency of Cr(III) transport through a SLM containing D2EHPA as carrier was studied at different concentrations ranging from 20 to 80% (v/v) diluted with cyclohexane or 2-octanol.

Fig. 4 shows that the transport efficiency is dependent on the D2EHPA concentration in the membrane organic phase. Indeed, for both cases the transport efficiency increases with increasing D2EHPA concentration until an optimal value. Above this value, the Cr(III) amount released in the stripping phase decreases. Furthermore, when the polymeric support is impregnated with an organic solution composed of 50% D2EHPA-50% 2-octanol (v/v), a transport percentage towards 60% was obtained after 80 h of transport. This transport percentage does not exceed 4% using a 80% D2EHPA-20% 2-octanol (v/v) as organic solution. On the other hand, in the case of cyclohexane, the transport percentage shifts from 49.5% (30% D2EHPA) to 7.5% (80% D2EHPA). The transport efficiency increase until an optimal value may be explained keeping in view the increasing availability and formation of extractable complex with Cr(III) ions and hence its extraction into membrane organic phase. The further transport efficiency decrease is probably due to the increase of the viscosity of the organic solution at higher ionophore concentrations that leads to an increase of the liquid membrane resistance to the diffusion of metal-carrier species [30,31]. In this case, the increase of the carrier concentration at this point does not compensate for the increase in the solution viscosity (Table 3). The abrupt fall of the transport efficiency at 60% D2EHPA (v/v) using 2-octanol as diluent can be attributed to the more pronounced viscosity increase of the resultant membrane solution (79.75 cP) compared to cyclohexane (11.75 cP).

The carrier concentration effect on Cr(III) transport efficiency was carried out once again while maintaining constant the feed solution pH. The results are given in Fig. 5.

This figure shows, in both cases, a noticeable improvement of the transport efficiency especially at a lower carrier concentration. In fact, when using 20% carrier, the transport efficiency shifts from 22.6% to 49.1% with 2-octanol and from 12.9% to 43.5% with cyclohexane as diluent. Maximum transport efficiencies of 73.8% (50% D2EHPA) and 60.3% (30% D2EHPA) were found using 2-octanol or cyclohexane, respectively. These observations confirm once again that the pH required for maximum Cr(III) transport through a SLM containing D2EHPA as carrier is 4.5–5.

Results concerning feed pH and carrier concentration effects on chromium(III) transport efficiency confirm literature liquid–liquid extraction observations concerning the dependence of transport efficiency on the chemical diluent nature.

3.5. *Effect of chemical diluent nature*

It is recognized that organic diluents influence the

Table 5
Effect of the stripping acid type on the Cr(III) transport efficiency and estimation of the Cr(III) complex formation constants [29]. Feed solution: acetate buffer, [Cr(III)] = 5×10^{-4} M; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in 2-octanol; Transport time: 80 h

Stripping solution (0.1 mol.L^{-1})	% transport	Ion	log K_1	log K_2	log K_3
HCl	59.6	Cl^-	1.279	0.978	0.740
H_2SO_4	54.0	SO_4^{2-}	1.397	1.114	—
HNO_3	50.6	NO_3^-	0.903	0.519	—
$HClO_4$	49.0	ClO_4^-	0.568	—	—

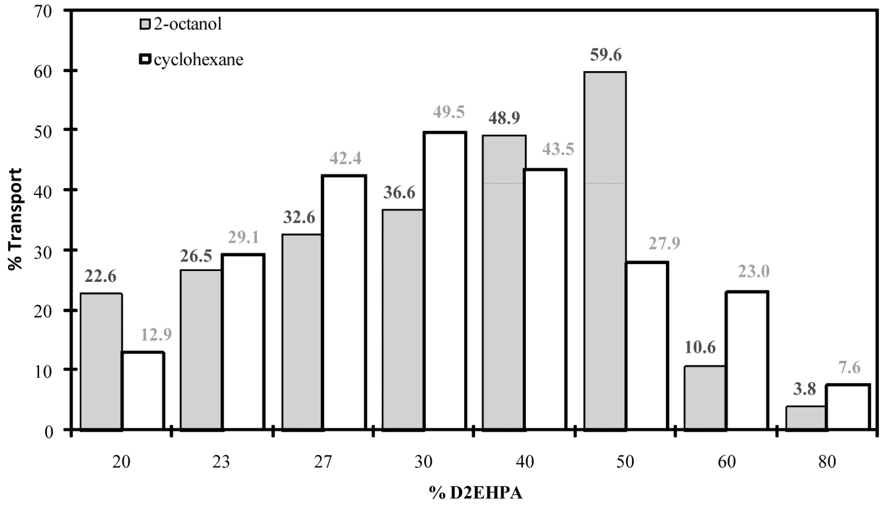

Fig. 4. Effect of D2EHPA concentration on Cr(III) transport efficiency. Feed phase: acetate buffer, [Cr(III)] = 5×10^{-4} M; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in cyclohexane or in 2-octanol; Stripping phase: HCl pH = 1. Transport time: 80 h.

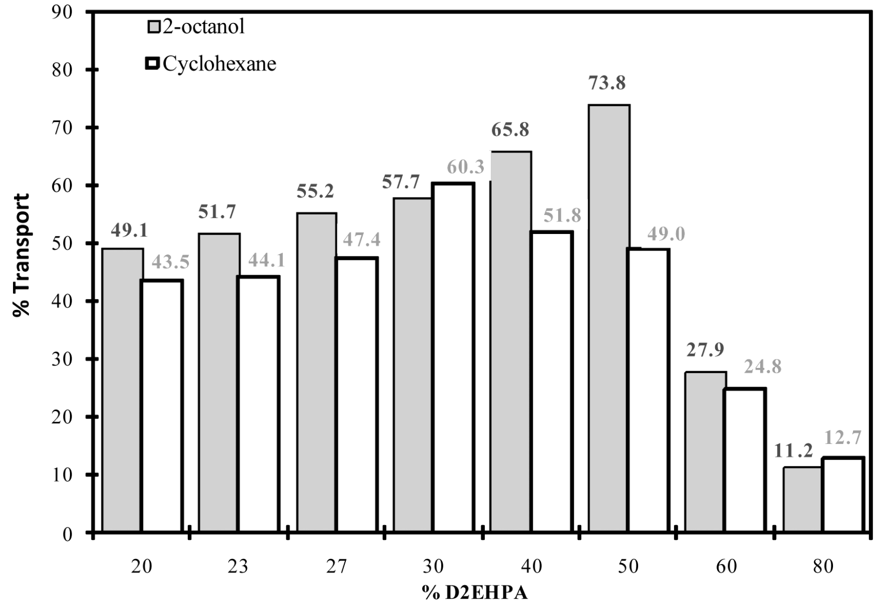

Fig. 5. Effect of D2EHPA concentration on Cr(III) transport efficiency with feed pH control. Feed solution: acetate buffer, [Cr(III)] = 5×10^{-4} M kept constant around pH 4.5 by NaOH addition; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in cyclohexane or in 2-octanol; Stripping phase: HCl pH = 1. Transport time: 80 h.

performance of supported liquid membrane systems. To determine their effect on the present system, experiments were carried out with solutions of 50% (v/v) D2EHPA in different diluents as organic membrane phase, solution of 5×10^{-4} M Cr(III) buffered at pH 4.8 (kept manually constant) as aqueous feed phase and HCl solution of pH 1 as aqueous receiving phThe incidence of the chemical diluent nature on the transport efficiency depends on its viscosity, but also on its dielectric constant which influences the balance between the efficiency of the association and dissociation steps for the uptake of the metal ion by the carrier and its release from the complex at the receiving interface [32]. Nevertheless, it is difficult to ascribe the transport of the metal to any particular physical property of the organic diluent.

Fig. 6 shows the time courses of the transport efficiency using different diluents of the membrane phase. This figure shows that among studied diluents, the weakest transport efficiency was obtained when the highest diluent viscosity NPOE was used. It can as well be perceived

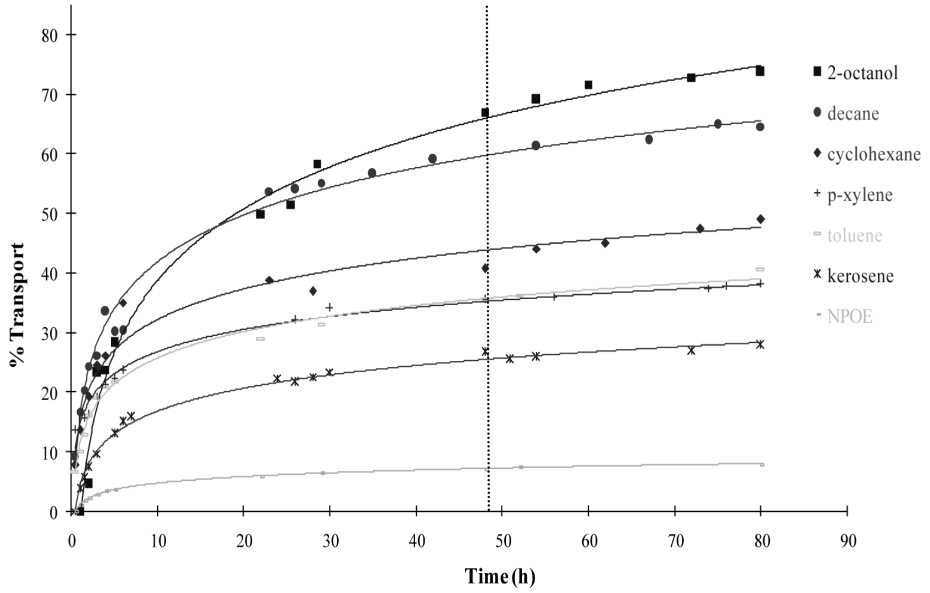

Fig. 6. Effect of chemical diluent nature on Cr(III) transport efficiency. Feed solution: acetate buffer, [Cr(III)] = 5×10^{-4} M kept constant around pH 4.5 by NaOH addition; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in different diluents; Stripping phase: HCl pH = 1.

that cyclohexane and decane present comparable viscosity and dielectric constant values, likewise *p*-xylene, toluene and kerosene provide similar Cr(III) FSSLM transport efficiencies (Table 1). On the other hand, 2-octanol, an alcohol diluent, provides the highest transport efficiency among the tested diluents and a transport percentage of 67% was attained after only 48 h of continuous running.

Furthermore, the increase of the effective exposed surface area of the membrane could increase the transport efficiency of the system.

Due to the higher transport efficiency obtained using 2-octanol as diluent, this latter has been chosen to estimate the initial Cr(III) transport flux (*J*). According to Eq. (2), the obtained linearity between Cr(III) concentration in the receiving solution and transport time allowed us to estimate the flux under optimum experimental conditions. An initial flux in the order of 4×10^{-6} mol.m^{-2}.s^{-1} has been found. This flux value is almost 10 times higher than the one obtained when using Lasalocid A as hydrophobic ionophore in FSSLM trivalent chromium transport experiments [22].

3.6. *Effect of the polymeric support type*

In this study, two supports with different chemical composition and physical properties were tested under the same experimental conditions.

Thickness, porosity, and tortuosity of the support are fundamental parameters that act on the mass fluxes of the metallic ions. Table 2 collects both experimental ($J_{\exp}$) and normalized Cr(III) fluxes (J_N) obtained with Durapore related to the thickness $d_{0,A}$, porosity ε_A and tortuosity τ_A of Accurel 2E-HF support, as described in the following equation [33,34]:

$$J_N = J_{\exp}\frac{d_0\tau}{\varepsilon}\frac{\varepsilon_A}{d_{0,A}\tau_A} \tag{5}$$

Durapore would normally provide higher fluxes than Accurel 2E-HF due to its higher ratio $\varepsilon/d_0\tau$, whereas in our case, the latter showed the best flux value as well as the best chromium recovery. Similar results were obtained in previous works [27,35] where it was reported that not only the physical parameters but both chemical composition and physical parameters of the support affect the metal transport efficiency through an SLM system.

3.7. *Transport of Cr(III)–Cr(VI)*

The transport of Cr(III) and Cr(VI) through an Accurel SLM containing D2EHPA in 2-octanol was investigated using as feed solution each metal ions separately.

The percentage of metal transported to the stripping phase against time is presented in Fig. 7. After 48 h of transport and under individual studies, recoveries around 67% and less than 5% were reached for Cr(III) and Cr(VI), respectively.

As it can be seen, Cr(VI) permeation is poor and only Cr(III) was effectively transported. Accordingly, recovery of chromium(III) species can be performed using a D2EHPA-2-octanol based FSSLM for the practical aspect of direct transport of Cr(III) ions, without its prior oxidation to Cr(VI).

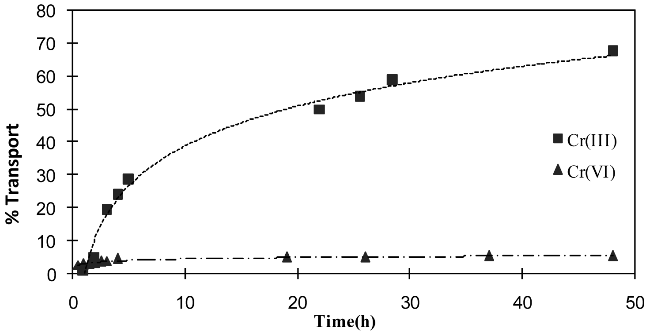

Fig. 7. Variation in Cr(III) and Cr(VI) concentrations in receiving phase vs. time using 2-octanol as diluent and with feed pH control. Feed solution: acetate buffer, [Cr(III)] or [Cr(VI)] = 5×10^{-4} M kept constant around pH 4.5 by NaOH addition; Support: Accurel PP 2E-HF; Organic phase: D2EHPA (50% v/v) in 2-octanol; Stripping phase: HCl pH = 1.

4. Conclusion

A D2EHPA based SLM for the extraction of Cr(III) from aqueous solution has been described. The presented data show that transport efficiency depends widely on the chemical diluent nature and the pH of the source phase. It has been observed that a disappearance of the pH difference is required to ensure uphill facilitated transport due to proton permeation. Consequently, pH was manually preserved during the run around pH 4.5 by adding NaOH concentrated solution to feed phase. In this case, 2-octanol can be considered as the most efficient diluent. Chromium transport comparison between Cr(III) and Cr(VI) was also studied and our system proved a particular preference to Cr(III) ions. Although no stability study was conducted, the present study permits us to predict a possible industrial application of the described system, especially when the effective exposed surface area of the membrane could be considerably increased using a hollow-fiber SLM (HFSLM) system, to the removal of Cr(III) ions from tannery effluents.

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