



## A novel polymer inclusion membrane applied in chromium (VI) separation from aqueous solutions

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### ABSTRACT

In the present work, we analyze the transport properties of a novel polymer inclusion membrane (PIM) containing a poly-vinyl chloride (PVC) polymer matrix and the organic anion exchanger Aliquat 336 as a specific carrier, without addition of plasticizers. The study was specifically focused on the transport properties of Cr(VI) in conditions simulating industrial wastewaters. We analyzed the impact of several parameters on the Cr(VI) transport process such as: the carrier content of the PIM, the pH, and the phases' composition. We concluded that efficient transport processes occur through a PIM containing 40% Aliquat 336/60% PVC (w/w). The process is very fast and efficient for solutions of initial Cr(VI) concentration smaller than  $10^{-3}$  mol/L, in which nearly all of Cr(VI) is removed within 3 h. The performed experiments prove that Cr(VI) transport through the membrane is a facilitated counter-transport process. The obtained results sustain that this novel non-plasticized membrane possesses enhanced transport properties towards other liquid membranes and plasticized PIMs previously reported as used for Cr(VI) transport. Additionally, it possesses an excellent reliability and a high selectivity for Cr(VI) from mixtures with other metal ions and anions existing in the real industrial effluents. The PIM characterization highlights the plasticizing role of the carrier Aliquat 336.

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### 1. Introduction

The chromium (Cr) is a heavy metal widely used in various industrial applications leading to an increase in Cr concentration in water (industrial discharges), air (coal combustion), and soils (waste disposal), where the metal is ends up in the Cr(III) and Cr(VI) forms. Chemical, leather and textile manufacturing, electro-painting and chromium plating are the main human activities leading to an increase in Cr(VI) concentrations in the environment. The health hazards associated with exposure to chromium are dependent on its oxidation state. Cr(III) is an essential element for organisms but the exceeded concentrations can cause negative effects in the human and animal bodies. The metal form of Cr is of low toxicity but its Cr(VI) form is toxic to humans, flora and fauna [1].

Hexavalent chromium removal from wastewaters is a problem of great and increasing significance nowadays. Plating baths in the electroplating process contain 100–200 g/L of Cr(VI), and low quantities of metal cations (i.e.,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ) and anions (nitrates, chlorides, phosphates and sulphates). Concentrations of Cr(VI) in the rinsing waters used after chromium plating need to be reduced from 100–500 to <1 mg/L before discharging it in the

environment. The treatment of electroplating effluents generally consists in a chemical reduction of Cr(VI) followed by a precipitation of Cr(III) as hydrates oxides, a recycling process involving anion-exchange resins followed by elution with NaOH and reverse osmosis, or solvent extraction methods. These techniques are costly and produce additional sludges. In this context, the possibility of recovering Cr(VI) for reuse makes very attractive the techniques of liquid membranes [2] (and references therein).

As the interest in this topic is increasing, many studies report possible applications of various liquid membranes such as: emulsion liquid membranes (ELMs), supported liquid membranes (SLMs), and PIMs in the removal of heavy metals from wastewaters [3–25]. Highly selective separations obtained by liquid membranes have shown interesting properties for PIMs such as a very good chemical and mechanical resistance and comparable and even higher membrane fluxes than those of SLMs [12,16,26]. By eliminating the disadvantage of using flammable solvents in the extraction processes as well as high quantities of expensive reagents in the ELM processes, the PIM embedded transport cells have many advantages over conventional methods, and are currently investigated for possible applications on large industrial scale [4].

Because of Cr(VI) extreme toxicity, a number of studies have been devoted to its removal using liquid and activated composite membranes (ACMs) [9–11,25,27–34]. Despite the fact that PVC-based PIMs are more stable and possess higher usage duration than CTA-based PIMs [3] there is a scarcity of results in the literature

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concerning these membranes. In fact, to our knowledge, there are only two papers regarding the transport processes of Cr(VI) through PIMs consisting of PVC polymer matrix, one considering tri-*n*-octyl amine (TOA) and the other one Aliquat 336 as ion carriers, and containing also different plasticizers [21,30]. Moreover, there are not any that we are aware of studies concerning the Cr(VI) separation by non-plasticized PIMs.

In a previous paper [35], we studied the transport process of Pb(II) ions by a PVC-based non-plasticized PIM. We found that the transport properties of a PIM containing 50% D2EHPA/50% PVC are enhanced over that of other plasticized PIMs previously reported for Pb(II) separation from aqueous solutions. In this context, the preparation of novel non-plasticized PIMs based on PVC and their investigation regarding the efficiency of the Cr(VI) recovery is a research direction of increased interest.

The goal of the present study was to prepare a novel PVC-based PIM, without addition of plasticizers, with enhanced transport properties for Cr(VI) ions comparing to the plasticized PIMs previously reported. Considering that the plasticizers used in PIMs preparation are expensive chemicals, the novel PVC membrane studied in this work is significantly cheaper compared with the plasticized ones. This fact makes it a good candidate in the continuous search of cheaper and non-polluting separation methods for recovery of different useful components from the industrial effluents. In the mean time, our study was aimed to establish the optimal conditions for the recovery of Cr(VI) using the least possible aggressive chemicals, from solutions with similar composition like real industrial effluents [28]. For this purpose, we studied the effect of different parameters on the transport process of Cr(VI) from source solutions prepared without pH buffer, and using as receiving phases the less possible aggressive and diluted reagents. Thus, the obtained data are presented and discussed in terms of identifying suitable conditions for using the developed membrane in applications at a larger scale. The work provides also a characterization of the newly prepared membrane, as well as selectivity and reliability studies. Also a membrane transport mechanism strongly supported by the experimental data is proposed.

## 2. Experimental

### 2.1. Chemicals/reagents

High molecular weight PVC, tri-*n*-capryl-methyl-ammonium chloride (Aliquat 336),  $K_2CrO_4$ , HCl, NaOH, tetrahydrofuran (THF), were supplied by Sigma-Aldrich, Germany. These chemicals and other necessary reagents were of analytical reagent grade and used as received. Highly purified water (resistivity  $18.2 M\Omega cm$ ) was used for the preparation of the aqueous solutions.

### 2.2. Membrane preparation and characterization

The non-plasticized PIMs were prepared by dissolving fixed quantities of PVC and Aliquat 336 in THF under continuous magnetically stirring until a homogeneous solution was obtained. The solution was then poured into a 9.0 cm diameter Petri dish and the organic solvent was allowed to evaporate overnight at the room temperature. The prepared membranes containing maximum 45% Aliquat 336 (w/w) were homogeneous, flexible and transparent with good strength, while those containing more than 45% carrier were soft, sticky and less mechanically resistant. The thickness of the membrane containing 40% Aliquat 336/60% PVC (w/w) was  $70 \pm 4 \mu m$  (measured with a VEGA II SBH electron microscope).

Information regarding membrane morphology was obtained by scanning electron microscopy (SEM), images being recorded with a VEGA II SBH electron microscope manufactured by TESCAN. The

surface chemical composition of the 40% Aliquat336/60% PVC PIM was analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI-5000 Versa Probe photoelectron spectrometer ( $\Phi$  ULVAC-PHI, INC.) with a hemispherical energy analyzer (0.85 eV binding energy resolution, for organic materials). A monochromatic Al  $K\alpha$  X-ray radiation ( $h\nu = 1486.7 eV$ ) was used as excitation source. The standard take-off angle used for analysis was  $45^\circ$ , producing a maximum analysis depth in the range of 3–5 nm. High-resolution spectra were recorded in 0.1 eV steps with 58.7 eV analyzer pass energy.

### 2.3. Solid/liquid extraction experiment

Studies on the Cr(VI) retention properties of the prepared PIMs, were carried out using batch equilibrium extraction method. Equal quantities of cut membranes with different carrier concentration were placed in 100 mL Cr(VI) solution under continuous magnetic stirring (400 rpm). The equilibrium concentration of metal ion was determined by AAS Perkin Elmer 3300, after appropriate dilution of the samples collected at preselected times. All the experiments were performed in triplicate under thermostatic conditions ( $25.0 \pm 0.1^\circ C$ ).

### 2.4. Transport study

The membrane transport experiments were performed in a double-cell device containing the membrane tightly clamped between the two cell compartments [3], under thermostatic conditions ( $25.0 \pm 0.1^\circ C$ ) and under continuous mechanically stirring with Teflon pads (400 rpm). Each compartment is sealed and has an individual volume of  $75 cm^3$ , with an exposed membrane area of  $8.7025 cm^2$ . The first compartment was filled with the source phase (solutions of the interest metals) and the second compartment contained the solution which represents the stripping (receiving) phase. Because both compartments are closed, the source and receiving solutions are isolated against the ambient atmosphere during the transport experiment. The pH of the solutions was adjusted with HCl and NaOH.

The Cr(VI) transport process was investigated under various conditions of the stripping phase composition, pH, the Cr(VI) concentration in the source phase and the carrier content of the PIM.

The membrane stability study was performed by subsequent transport experiments of 4 h each, under the same optimal conditions previously established. The same membrane was kept in the membrane-transport cell, being washed, dried and then reused, both phases being renewed after each experiment.

The pH of the source solution was continuously monitored within the transport experiments. To determine the kinetics of the metal ion transport, samples from both compartments were collected at preselected times. Concentrations of metal ions were determined by AAS after appropriate dilution of the samples.

The kinetic of the metal ion transport process through a PIM is described by a first-order reaction [36]:

$$\ln \left( \frac{C_{source}}{C_{0,source}} \right) = -k \times t, \quad (1)$$

where  $C_{0,source}$  and  $C_{source}$  represents the metal ion concentrations in the source solution at time  $t=0$  and at a particular time (mol/L),  $k$  is the transport process rate constant ( $s^{-1}$ ) and  $t$  is the transport time (s).

The membrane transport parameters were calculated as follows:

$$P = \left( \frac{V}{A} \right) \times k \quad (2)$$

$$J_i = P \times C_{0,source} \quad (3)$$

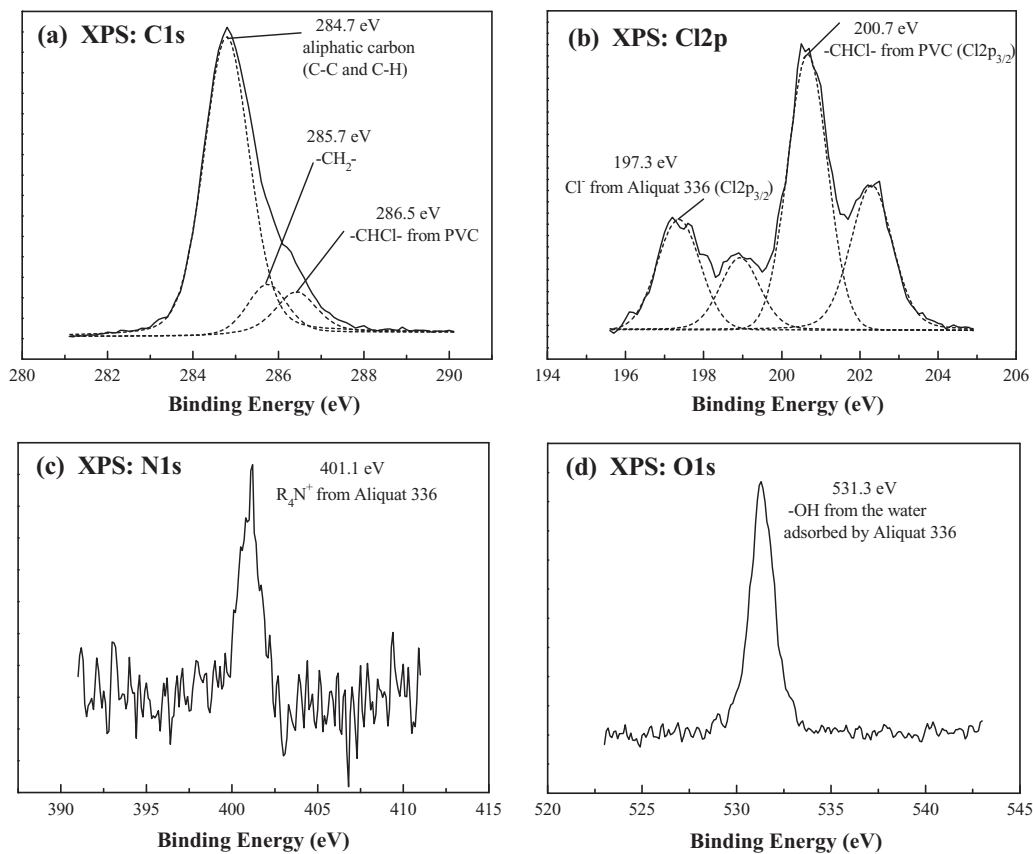


Fig. 1. XP spectra acquired from the surface of the 40% Aliquat 336/60% PVC membrane.

$$\text{Removal (\%)} = \left[ \frac{C_{0,\text{source}} - C_{\text{source}}}{C_{0,\text{source}}} \right] \times 100 \quad (4)$$

$$\text{Recovery (\%)} = \left[ \frac{C_{\text{strip}}}{C_{0,\text{source}}} \right] \times 100 \quad (5)$$

with the following notations:  $P$  – permeability coefficient (m/s),  $V$  – volume of the source solution ( $\text{m}^3$ ),  $A$  – exposed area of the membrane ( $\text{m}^2$ ),  $J_i$  – initial flux ( $\text{mol}/\text{m}^2\text{s}$ ),  $\text{Removal (\%)}$  – removal factor,  $\text{Recovery (\%)}$  – recovery factor,  $C_{\text{strip}}$  – metal concentration in the strip compartment at a particular time ( $\text{mol}/\text{L}$ ).

### 2.5. Selectivity study

For the optimal 40% Aliquat 336/60% PVC (w/w) membrane, its selectivity has been investigated towards the competitive transport of  $\text{Cr(VI)}$ ,  $\text{Co(II)}$ ,  $\text{Zn(II)}$ ,  $\text{Cu(II)}$  and  $\text{Ni(II)}$  metal ions, the transport process of some anions generally existed in the industrial effluents, namely nitrate, chloride and sulphate being also investigated. The source solution consisted in a mixture of metal ions in approximately equal concentrations of  $10^{-3}$  M each, and containing also great quantities of the above mentioned anions, further experimental steps following similar sequences as indicated in Section 2.4. The concentrations of the anions (nitrate, chloride and sulphate) were determined by ion chromatography (Shimadzu Model Prominence 2010).

The reported values for all the experiments represent an average of three experiments performed under identical conditions, the relative standard deviation being up to 4%.

## 3. Results and discussion

### 3.1. Membrane surface analysis

In order to detect the elements existing on the 40% Aliquat 336/60% PVC PIM's surface, the XP high resolution spectra of C, H, N and O was acquired from this PIM (Fig. 1). The obtained binding energy peaks was assigned to the correspondent species (as depicted in Fig. 1), the values obtained in these spectra being in good agreement with those previously reported in the literature [37]. Thus, the  $\text{C1s}$  (Fig. 1a) and the  $\text{Cl2p}$  (Fig. 1b) spectra highlight the existence of three carbon species and two chlorine species respectively, as showed by the deconvolutions of those spectra. The large amount of aliphatic carbon confirms the presence of Aliquat 336 on the PIM's surface. The  $\text{Cl2p}$  spectrum contains a pair of peaks  $\text{Cl2p}_{1/2}$  and  $\text{Cl2p}_{3/2}$  for each chlorine species, the higher intensity ones from each pair being the  $\text{Cl2p}_{3/2}$  peaks, as depicted in Fig. 1b. The values of the binding energies obtained for N and O cases (Fig. 1c and d), highlight the presence of quaternary  $\text{N}^+$  from Aliquat 336, and of the  $-\text{OH}$  groups from water adsorbed by the carrier respectively [37,38]. Therefore, the XPS analyses confirm the presence of both Aliquat 336 and PVC on our PIM's surface.

The SEM image of the 40% Aliquat 336/PVC membrane surface (Fig. 2) shows two separate domains which alternate on the PIM's surface (the dark zones and the light ones), corresponding to the PVC and Aliquat 336 respectively, previously evidenced by XPS. This assignment of the light and dark zones on PIM's surface is based on our previous study, which demonstrates by AFM the carrier domains' presence as "haystacks" on the flat PVC film in a non-plasticized PIM [39]. The polymer chains support the carrier micro domains, and the latter are interposed between the polymer chains, leading to an increase of the distance between them and disrupting

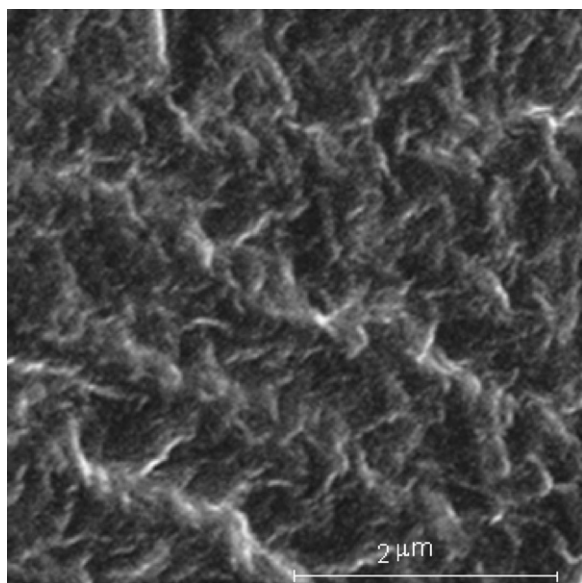


Fig. 2. SEM image acquired from the surface of the 40% Aliquat 336/60% PVC membrane.

the physical bonding between the PVC chains. In this way, Aliquat 336 micro-domains also have a plasticizing effect on the polymer matrix, which could explain the very good transport properties of the 40% Aliquat336/60% PVC PIM (see Section 3.3) even if it does not contain an additionally added plasticizer.

### 3.2. Solid/liquid extraction experiment

The kinetics of the metal ion retention was analyzed by placing equal quantities of cut membranes with different carrier concentration in 100 mL Cr(VI) solution of 100 mg/L at pH 4.0, and with the equilibrium concentration of Cr(VI) being measured at different contact durations. In order to establish the membrane extraction capacity for Cr(VI), and what the extracted species are (i.e. what is the stoichiometry of the metal-carrier ion-pair in the membrane), the equilibrium ratios between the mole numbers of the adsorbed Cr(VI), and those of the Aliquat 336 were calculated for different carrier contents in the membranes (Fig. 3).

From the data presented in Fig. 3, it can be observed that at low concentrations of Aliquat 336 in the PIM the metal is not quantitatively retained, and membrane extraction capacity increases with

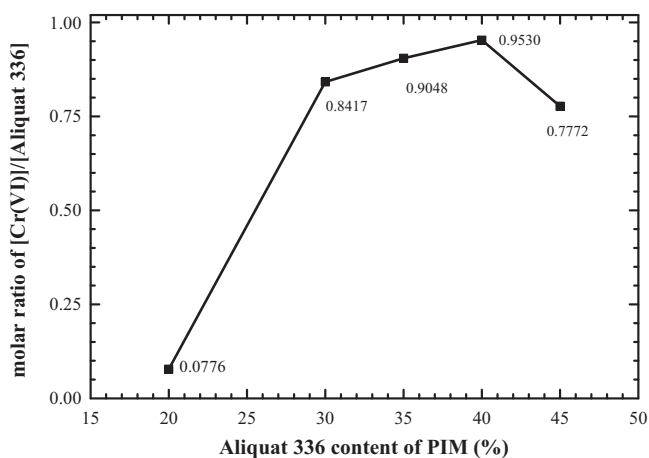


Fig. 3. Influence of Aliquat 336 concentration in the membrane on the Cr(VI) extraction efficiency (100 mL Cr(VI) solution 100 mg/L, pH 4.0;  $130 \pm 2$  mg PIM).

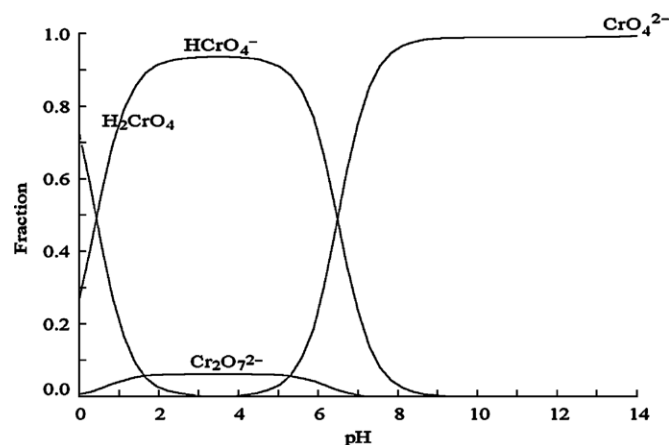
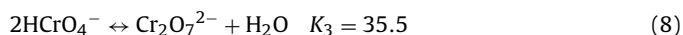
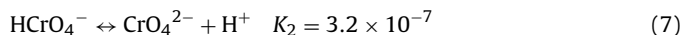
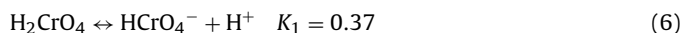


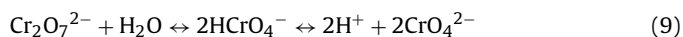
Fig. 4. Chromium (VI) speciation diagram.

increasing the carrier content in the PIM until 40% (w/w) with equilibrium settled in about 30 h. Furthermore, this ratio decreases with increasing the carrier content above 40%. All these observations are explained below.

Because Cr(VI) exists in solutions in various forms depending by the solution pH and Cr(VI) concentration, the extraction and transport of Cr(VI) ions is strongly dependent by their chemical forms. As chromium exist in solution in different anionic forms such as:  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HCr}_2\text{O}_7^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ , the working conditions, i.e. metal concentration range and the pH of the solutions will determine the mechanism of the extraction and transport processes. The main equilibriums for the Cr(VI) species in aqueous solutions [40] are presented below:



In an aqueous solution containing Cr(VI) ions, the following general equilibrium is realized [41]:

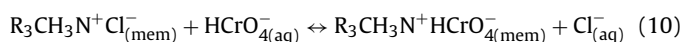


and this is a highly mobile equilibrium process depending on the pH of the solution.

From the above presented equilibriums (6)–(8) and from suggestions from the literature, results that  $\text{CrO}_4^{2-}$  prevails in basic solutions ( $\text{pH} > 7$ ) while  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  prevails in acidic solutions, the anions' ratio depending on species concentrations [40,41]. Additionally, at total Cr(VI) concentration lower than  $(1.26\text{--}1.74) \times 10^{-2}$  M,  $\text{Cr}_2\text{O}_7^{2-}$  converts to  $\text{HCrO}_4^-$ , while at higher Cr(VI) concentrations, the  $\text{HCrO}_4^-$  dimerization occurs, and  $\text{Cr}_2\text{O}_7^{2-}$  became the major species in the solution [25]. From the reactions (6)–(8), the speciation diagram for the  $10^{-3}$  M Cr(VI) solution is presented in Fig. 4.

As in our study the metal ion concentration is in the range of  $(1\text{--}5) \times 10^{-3}$  M we may suggest that Cr(VI) existed mainly as  $\text{HCrO}_4^-$  anion, while only a small fraction of  $\text{Cr}_2\text{O}_7^{2-}$  coexisted also in the aqueous solution.

As shown in Fig. 3, for the 40% Aliquat 336/PVC PIMs the mentioned molar ratio is 0.953. It indicates that the membrane extracted species is  $\text{HCrO}_4^-$ , the extraction process being represented below:



where  $\text{R}_3\text{CH}_3\text{N}^+\text{Cl}^-$  represents the Aliquat 336 molecules.

In this case almost all of the positive charged active sites of the carrier molecules are neutralized with  $\text{HCrO}_4^-$  and the alkyl

groups of Aliquat 336 molecules are serving as plasticizer, as is known that Aliquat 336 possesses this property in PVC-based PIMs [3,42]. Our findings prove that  $\text{HCrO}_4^-$  is the extracted species in the membrane phase.

The 20% Aliquat 336/PVC PIMs case can be explained by the theory of the “percolation threshold”, which is based on the idea that the accessibility of the metal ions inside PIMs depends on a minimal carrier concentration value (threshold). This concentration is necessary to create continuous pathways (liquid micro-domains containing carrier) necessary to carry out the adsorbed metal ion across the PIM [43]. For the 30–35% and 45% Aliquat 336/PVC (w/w) membranes, the values obtained for the ratios between the moles number of Cr(VI), and Aliquat 336 highlight the incomplete formation of the liquid pathways inside the membranes due to the insufficient carrier quantity (for 30–35% carrier in PIM), or the carrier excess loss and steric hindrance in the membrane (case of 45% Aliquat 336/PVC PIM). The steric hindrance effect is realized by the voluminous alkyl groups of the carrier molecules which limit the accessibility of Cr(VI) ions to the active sites. If the carrier content in PIM is over 40% not all the reactive sites of the carrier molecules are involved in the membrane extraction or transport. Similar behaviour was also observed by Navarro et al. [14] and Martinez et al. [44].

Under these circumstances, the conclusion is that the maximum retention capacity against Cr(VI) is reached by using PIM contains 40% Aliquat 336/60% PVC (w/w).

### 3.3. Transport study

#### 3.3.1. Effect of concentration of the stripping phase

The stripping process of metal ions at the membrane/receiving phase interface plays an important role in the transport process. If the stripping process is not efficient the metal-carrier ion-pair accumulates in the membrane and the permeation rate decreases. The effect of the stripping phase composition was investigated using a pH 2.0 source solution of 50 mg/L Cr(VI) and different NaOH concentration solutions as stripping phase.

From the distribution of the data presented in Fig. 5 we can observe that the removal efficiency (*Removal* (%)) is almost 100% for all NaOH studied solutions, while the Cr(VI) recovery efficiency values (*Recovery* (%)) are increasing with the increasing of NaOH concentration from 0.01 M to 0.05 M. The increasing of the *Recovery* (%) is determined by the increasing of the  $\text{OH}^-$  concentration in the stripping phase, which leads to an increasing of the driving force represented by the  $\text{OH}^-$  concentration gradient. For further NaOH concentration increase over the value of 0.05 M, the recovery

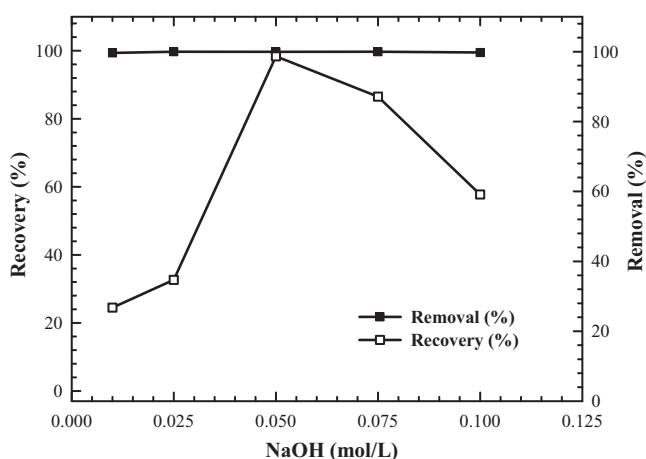


Fig. 5. The effect of strip solution on the Cr(VI) transport process (source solution: 50 mg/L Cr(VI), pH 2.0; PIM: 40% Aliquat 336/60% PVC (w/w)).

Table 1

Fluxes, permeability and recovery factors at different initial pH value of the source solution.

Initial pH of the source solution	$P \times 10^6$ (m/s)	$J_i$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )	Recovery (%)
2	$15.48 \pm 0.47$	$15.21 \pm 0.48$	72.97
3	$18.76 \pm 0.61$	$18.75 \pm 0.57$	80.32
4	$26.32 \pm 0.72$	$27.26 \pm 0.81$	98.36
5	$13.44 \pm 0.36$	$14.00 \pm 0.52$	95.80

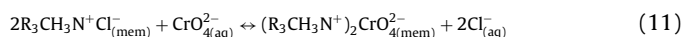
Note: Source solution  $10^{-3}$  M Cr(VI); receiving phase: 0.05 M NaOH; PIM: 40% Aliquat 336/60% PVC.

of Cr(VI) decreases probably due the PIM degradation in aggressive NaOH solutions. Thus, for further investigations the optimal NaOH 0.05 M stripping solution will be used.

#### 3.3.2. Effect of initial pH of the source phase

In order to simulate the electroplating effluents and industrial wastewater from metallic powder plants (which have a real pH values in the 3.5–6 range) [28] and to avoid the other metallic species hydrolysis which occurs at  $\text{pH} > 6$  [6], the transport experiments were performed from source solutions with initial pH of 2, 3, 4, and 5 prepared without pH buffers. The obtained results (Table 1) highlights that Cr(VI) recovery efficiency *Recovery* (%), the initial flux  $J_i$  and the membrane permeability ( $P$ ) are increasing with increasing the pH to 4. In the  $4 < \text{pH} < 5$  range the recovery efficiency remains almost constant while  $J_i$  and  $P$  are decreasing. In all cases, the pH of the source solutions changed during the transport experiments due the counter-transport of  $\text{OH}^-$  (as showed in Section 3.3.4), the values for  $P$  and  $J_i$  presented in Table 1 being obtained in these experimental conditions. These observations could be explained as follows:

- The source solution pH is adjusted with HCl. At low pH values, the high  $\text{Cl}^-$  concentration leads to an inhibition of the formation of the metal-carrier ion-pair by Eq. (10). As Fig. 4 shows, a protonation effect of  $\text{HCrO}_4^-$  may also be considered at pH 2.0, which leads to a small decreasing of the concentration of this species. Therefore, the extraction of Cr(VI) in the membrane is reduced when the source solution pH decreases.
- At initial pH 5.0 the transport parameters decrease sharply comparing to the pH 4.0 case, due to the fact that the increasing of pH over 7 as a consequence of the counter-transport of  $\text{OH}^-$  ions is much faster than in the case of the source solutions at initial pH 4.0. Thus, in this case  $\text{CrO}_4^{2-}$  is very fast formed in the source solution, the extraction of  $\text{CrO}_4^{2-}$  species in the membrane being represented by Eq. (11):



Therefore, the formation of this metal-carrier ion-pair reduces to a half the number of Cr(VI) ions transported by the same number of carrier molecules compared with the pH 4.0 identical process (Eq. (10)). Additionally, the formed ion-pair is voluminous and with a reduced mobility and therefore it accumulates in the membrane phase.

Considering these observations, we decided further investigations to be carried out from source solutions with the initial optimal pH 4.0.

#### 3.3.3. Effect of carrier concentration in the membrane

In order to establish the optimal membrane composition for Cr(VI) transport, PIMs with various content of Aliquat 336 (20–45% w/w) was tested in membrane transport experiments under optimal conditions previously established, the obtained transport parameters being presented in Table 2.

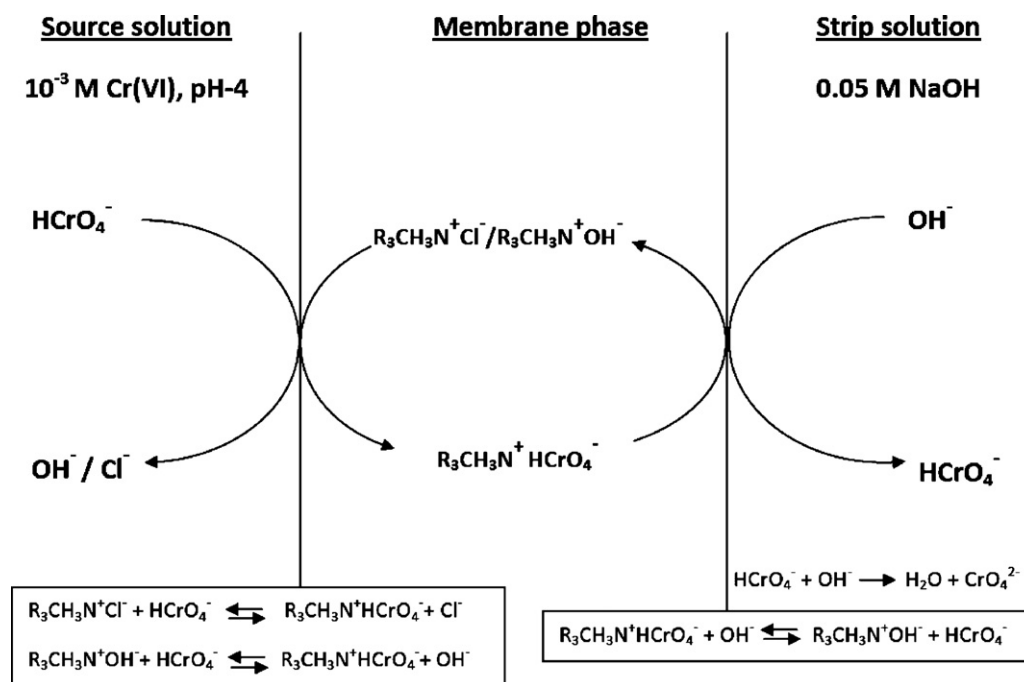


Fig. 6. The proposed mechanism for Cr(VI) transport process.

The results show that the 40% Aliquat 336/PVC membrane ensures in  $\approx 4$  h the most effective Cr(VI) removal from the source solution and also its recovery into the strip phase. Additionally, it leads to the highest values for the membrane flux and permeability. The 20% Aliquat 336/PVC membrane is not transporting the metal ion into the stripping phase, the carrier concentration being below the “percolation threshold” limits [43]. The variations of the parameters for the 30, 35 and 45% carrier follows the same trend like the solid-phase extraction experiments results, the explanations from Section 3.2 being also consistent with the results of the transport experiments for these PIMs.

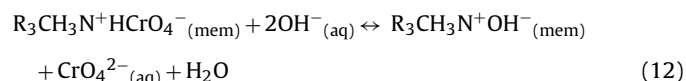
Thus, the optimal conditions for Cr(VI) transport are: (i) source solutions at initial pH 4.0; (ii) receiving phase consisting of NaOH 0.05 M; (iii) the optimal membrane composition is 40% Aliquat 336/60% PVC (w/w).

### 3.3.4. Transport mechanism

Based on the above presented results, the following mechanism for the Cr(VI) transport by our PIM can be suggested (Fig. 6). This mechanism involves the following stages:

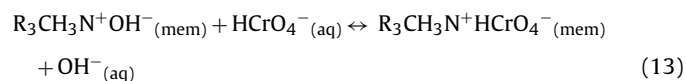
- i. The displacement of  $\text{Cl}^-$  and  $\text{OH}^-$  by  $\text{HCrO}_4^-$  ions at the source solution/membrane interface (represented by Eq. (10)) which leads to a metal-carrier ion-pair formed in the membrane phase (see Fig. 6).
- ii. The diffusion of the formed metal-carrier ion-pair through the PIM [3].

- iii. The substitution of  $\text{HCrO}_4^-$  on the membrane/receiving phase interface, determining Cr(VI) release into the receiving phase, as follows:



After the release of  $\text{HCrO}_4^-$  into the strip phase, the  $\text{R}_3\text{CH}_3\text{N}^+\text{OH}^-(\text{mem})$  species restart the transport process.

Therefore, the Cr(VI) transport by PIMs containing a quaternary ammonium salt like Aliquat 336 as carrier is a facilitated counter-transport process, the Cr(VI) transport from the source solution into the receiving phase being coupled with a reverse transport of  $\text{OH}^-$  (Fig. 6). Therefore, the pH of both solutions must change due the transport process. Indeed, by continuous monitoring of the pH during the transport experiments a change in the pH value of the source solution from  $\text{pH}_i$  4.0 to  $\text{pH}_f$  11.0 was measured after 3 h from the start of the transport process. It corresponds to  $10^{-3}$  M  $\text{OH}^-$  transported on stage (iv) and its release into the source solution by reaction (13):



Under these circumstances, the membrane transport process requires as optimal conditions a difference in  $\text{OH}^-$  concentration between the two solutions (source and receiving). This concentration gradient represents the driving force of the Cr(VI) transport

Table 2

Values of the transport parameters for different Aliquat 336/PVC membranes.

Aliquat 336 percentage in PIM	Rate constant $k \times 10^4$ ( $\text{s}^{-1}$ )	$R^2$	$P \times 10^6$ (m/s)	$J_i$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )	Removal (%)	Recovery (%)
20	–	–	–	–	72.17	1.73
30	0.42	0.9910	$3.64 \pm 0.14$	$3.91 \pm 0.15$	77.48	25.63
35	1.05	0.9980	$9.05 \pm 0.31$	$10.14 \pm 0.32$	99.52	96.24
40	3.05	0.9965	$26.32 \pm 0.72$	$27.26 \pm 0.81$	99.97	98.31
45	2.50	0.9960	$21.54 \pm 0.67$	$23.56 \pm 0.78$	99.94	85.81

Note: Source phase  $10^{-3}$  M Cr(VI), initial pH 4.0; receiving phase: 0.05 M NaOH.

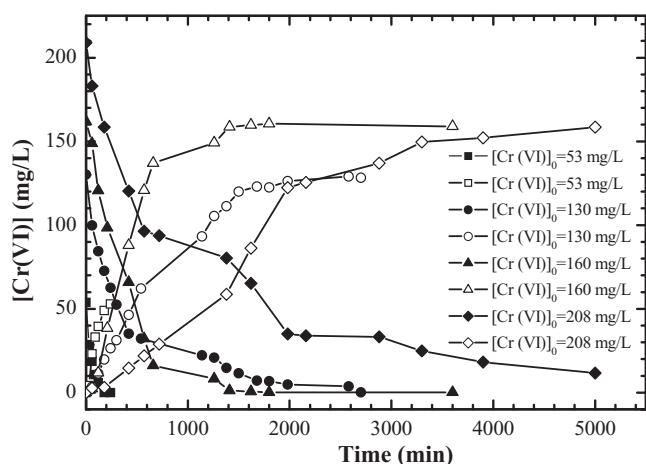


Fig. 7. Effect of initial metal ion concentration on the Cr(VI) transport process (source solution of pH 4.0; stripping phase: NaOH 0.05 M; The full symbols represent the Cr(VI) concentrations in the source phase and the empty symbols represent the Cr(VI) concentrations in the receiving phase).

process, which enable the transport of the metal ions to be carried out even at very low solute concentrations in the source phase, against their concentration gradient.

### 3.3.5. Effect of Cr(VI) concentration

The transport experiments performed under optimal conditions from solutions with different Cr(VI) initial concentration in the 50–208 mg/L range highlighted in all cases a transportation of the metal ions into the stripping phase (Fig. 7). The data presented in Fig. 7 and Table 3 show that the transport parameters decrease with the increasing of the Cr(VI) initial concentration. Therefore a higher Cr(VI) concentration in the source phase induces a slower transport of metal ions into the stripping phase. This experimental observation is in disagreement with Eq. (3), with similar data being reported elsewhere [28]. Our explanation for this behaviour is based on the pH increasing during the transport process as mentioned in Section 3.3.4. Thus, after the transport of about  $10^{-3}$  M Cr(VI), the pH of the source solution became more than 8.0. From the speciation diagram (Fig. 4) is evident that at  $\text{pH} > 8$  the single species in the source solution is  $\text{CrO}_4^{2-}$ . As we already explained in Section 3.3.2, the transport process of this divalent species by PIM is very slow, due to the reduced mobility and temporary accumulating in the membrane phase of the voluminous metal-carrier ion-pair  $(\text{R}_3\text{CH}_3\text{N}^+)_2\text{CrO}_4^{2-}(\text{mem})$ . Therefore, at Cr(VI) initial concentrations higher than  $10^{-3}$  M, an increasingly higher quantity of Cr(VI) is transported as  $\text{CrO}_4^{2-}$  ions, which leads to the reducing of the transport rate with the increase of the metal initial concentration in the source solution.

Data in Table 3 highlights that Cr(VI) concentration in the source solution is reduced to below the permissible limit of 1 mg Cr(VI)/L for Cr(VI) initial concentrations below 160 mg/L, Recovery (%) being also very high. However, for the solution with less than 53 mg/L Cr(VI), the process is faster and very efficient (as Fig. 7 shows). The

Table 3  
Transport parameters corresponding to different Cr(VI) initial concentration.

[Cr(VI)] <sub>0</sub> (mg/L)	Removal (%)	Recovery (%)	$P \times 10^6$ (m/s)	$J_i$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )
53	99.92	98.31	$26.32 \pm 0.72$	$27.26 \pm 0.81$
130	99.92	98.58	$4.50 \pm 0.17$	$11.26 \pm 0.38$
160	99.92	98.26	$3.15 \pm 0.12$	$9.79 \pm 0.31$
208	94.43	75.91	$1.95 \pm 0.07$	$7.84 \pm 0.29$

Note: Source solution of initial pH 4; receiving phase: 0.05 M NaOH; PIM: 40% Aliquat 336/60% PVC.

transport time required to reduce the Cr(VI) concentration in the source phase from about  $10^{-3}$  M to below the permissible limit was  $\approx 3$  h, the recovery efficiency in the stripping phase after  $\approx 4$  h being about 99%. Therefore, the real effluents containing more than about  $10^{-3}$  M Cr(VI) may be diluted until this concentration is reached, in order to realize the most efficient chromium separation process.

These quantitative results demonstrate that the 40% Aliquat 336/PVC PIM possesses very good separation and recovery properties against Cr(VI) even without an added plasticizing agent. In the same time, the receiving solution (0.05 M NaOH) has very good stripping properties, being in addition, under our knowledge, the most less aggressive stripping solution used in Cr(VI) liquid membrane studies (see Table 4).

### 3.3.6. Selectivity study

The industrial discharges generally contain mixtures of heavy metal ions and other anionic species, the separation and reusing of the individual metals being necessary. For this purpose, transport experiments were conducted from mixtures of Cr(VI), Co(II), Cu(II), Zn(II), Ni(II) and the anions sulphate, chloride and nitrate, using NaOH 0.05 M as stripping phase. To avoid other species precipitation which occur at  $\text{pH} > 6$ , the source phase was prepared at pH 1.25 value (adjusted with HCl).

The results in Table 5 show that Co(II), Cu(II), Zn(II) and Ni(II) ions are not transported through the optimal PIM. At the same time, only Cr(VI) ions are totally removed from the source solution and transported in the stripping phase in 6 h, while the other metal ions extraction in the membrane seems to be within the experimental error limits. This behaviour can be explained by the anionic forms of Cr(VI) in the working conditions, opposite to the cationic forms of the other metal ions from the studied mixture. Also, there was no transport process of the anionic species from the source solution into the receiving phase, even if their initial concentrations are greater than the Cr(VI) ones. However, a small quantity of chloride was transported by PIM, probably due to the great concentration gradient of this species (see Table 5). Thus, at the membrane/source solution interface the carrier is interacting most probable with the Cr(VI) (in solution as anion  $\text{HCrO}_4^-$  mainly).

Therefore, the optimal 40% Aliquat 336/PVC membrane is selective for Cr(VI) by mixtures of Cr(VI), Co(II), Cu(II), Zn(II), Ni(II) metal ions, in the presence of great amounts of sulphate, chloride and nitrate.

### 3.3.7. Membrane stability and reusability

Strength and stability are among the greatest advantages of PIMs over other liquid membranes, being one of the membrane properties that would ensure its applicability on industrial scale [3].

Data presented in Fig. 8 show that the initial flux (and therefore the membrane permeability), and the Recovery (%) also, are almost the same during 15 cycles (4 h each) of transport experiments by the optimal PIM. These results highlight that the membrane possesses very good transport properties, without significant alteration in its properties and appearance. Thus, PIM changes his colour from colourless to yellow in one transport cycle, and then gradually darkening up to red-brown colour until the 15th transport cycles on the same PIM. Therefore, the transport process is reproducible under the conditions above. The Cr(VI) concentration in the source phase was reduced below the permissible limit ( $< 1$  mg/L) and an efficient transport in the stripping phase occurred in all 15 experiments, the Cr(VI) recovery in the strip phase being  $\geq 98\%$ . These observations are consistent with the previous observations that reported enhanced reusability properties of PVC-based PIMs besides the CTA ones especially under extreme caustic and acidic mediums [3], and indicate that the non-plasticized PIMs can be used in the long-term separation experiments. The very good reusability of the studied PIM can be explained by the reduced quantity

**Table 4**  
Comparison of the Cr(VI) transport parameters by different membranes.

[Cr(VI)] <sub>0</sub> (mol/L)	Source solution pH	Membrane type/base polymer	Carrier/Plasticizer	Strip solution	$J_{EXP,M}$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )	Membrane thickness $\delta_M$ ( $\mu\text{m}$ )	$J_N$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )	Ref.
$2.0 \times 10^{-3}$	1.0	SLM	Aliquat 336/-	0.1 M NaOH	12.25	25	12,250	[30]
$2.0 \times 10^{-3}$	1.0	PIM/CTA	Aliquat 336/o-NPPE	0.1 M NaOH	8.84	28	9,901	[30]
$2.0 \times 10^{-3}$	1.0	PIM/CTA	TOA/o-NPPE	0.1 M NaOH	12.99	28	14,549	[30]
$2.0 \times 10^{-3}$	1.0	SLM	TOA/-	0.1 M NaOH	14.16	25	14.10	[30]
$2.0 \times 10^{-3}$	1.0	PIM/PVC	TOA/o-NPPE	0.1 M NaOH	10.67	27	11,524	[30]
$2.0 \times 10^{-3}$	1.0-2.5	PIM/CTA	TOA/o-NPPE	0.1 M CH <sub>3</sub> COONH <sub>4</sub>	11.00	28	12,320	[9]
$2.3 \times 10^{-4}$	1.2	PIM/CTA	Aliquat 336/2-NPOE	0.1 M NaOH	3.11	80	9,952	[21]
$2.3 \times 10^{-4}$	1.2	PIM/PVC	Aliquat 336/2-NPOE	0.1 M NaOH	3.15	80	10,080	[21]
$1.0 \times 10^{-3}$	0.3	PIM/CTA	TOA/o-NPPE	0.5 M CH <sub>3</sub> COONa	6.62	28	7,414	[11]
$1.0 \times 10^{-3}$	0.3	PIM/CTA	TDPNO/o-NPPE	0.5 M CH <sub>3</sub> COONa	16.01	28	17,931	[11]
$1.8 \times 10^{-6}$	2.0	PIM/CTA	Aliquat 336/DOP	1 M NaNO <sub>3</sub>	0.02	62	0,050	[29]
$1.8 \times 10^{-6}$	8.0	PIM/CTA	Aliquat 336/DOP	1 M NaNO <sub>3</sub>	0.002	62	0,005	[29]
$1.0 \times 10^{-3}$	1.0	SLM	Cyanex 923/-	0.5 M NaOH	11.94	25	11,90	[5]
$1.0 \times 10^{-3}$	1.0	ACM	Cyanex 923/-	0.5 M NaOH	3.03	90	10,908	[5]
$5.0 \times 10^{-3}$	1.0	ACM	Cyanex 923/-	0.5 M NaOH	8.15	90	29,340	[5]
$1.0 \times 10^{-3}$	4.0 (initial pH of the source solution)	PIM/PVC	Aliquat 336/-	0.05 M NaOH	27.26	70	76,328	This study

**Table 5**  
Initial fluxes, Removal (%) and Recovery (%) values in the selectivity study.

Ion	Initial ion concentration (mg/L)	Removal (%)	Recovery (%)	$J_i$ ( $\mu\text{mol}/\text{m}^2\text{s}$ )
Cr(VI)	52.10	99.91	98.54	25.94
Co(II)	61.15	1.20	0	-
Ni(II)	60.97	0.17	0	-
Zn(II)	68.37	0.39	0	-
Cu(II)	67.91	2.04	0	-
Cl <sup>-</sup>	7600	2.63	1.51	-
SO <sub>4</sub> <sup>2-</sup>	201	0.27	-	-
NO <sub>3</sub> <sup>-</sup>	252	0.59	-	-

Note: Source phase of initial pH 1.25; receiving phase: 0.05 M NaOH; PIM: 40% Aliquat 336/60% PVC.

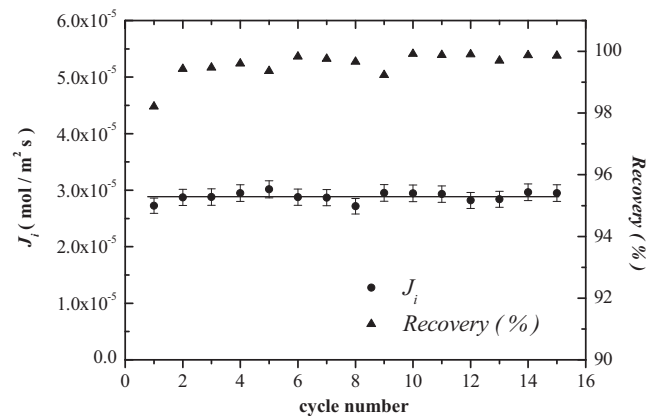
of liquid components from its composition (due to the lack of the plasticizers) and by the mild working conditions used in this study.

Table 4 summarizes some comparative working conditions and the obtained parameters for Cr(VI) transport, based on the results previously reported in literature and own results reported in this study for the optimal 40% Aliquat 336/60% PVC PIM.

Taking into account the fact that transport process is enhanced when the membrane thickness decrease [3], the flux obtained for each membrane ( $J_{EXP,M}$ ) with an average thickness  $\delta_M$ , was normalized considering the thinnest membrane presented in Table 4 as reference ( $\delta_{REF} = 25 \mu\text{m}$ ). The normalized flux ( $J_N$ ) was calculated as:

$$J_N = J_{EXP,M} \times \frac{\delta_M}{\delta_{REF}} \quad (14)$$

As Table 4 shows, the values of the membrane flux and permeability reported in this work are higher than those reported in the literature for other PIMs (containing plasticizers), SLMs and ACMs used for Cr(VI) transport. An explanation for these results may be the replacing of the plasticizing agent from our 40% Aliquat/PVC membrane with the carrier itself, which allows including a much higher amount of carrier in this PIM comparing to the plasticized ones. Indeed, as revealed by SEM analysis, the distribution of the carrier between the polymer chains leads to a plasticizing effect even in this PIM (see Section 2.2). Thus, the entire quantity of liquid component from the membrane (Aliquat 336) is involved in Cr(VI) transport process by their active sites, the alkyl groups of the carrier acting simultaneously as plasticizer of the polymer matrix. Therefore, by eliminating the classical plasticizers from our PIM's composition we obtained a membrane that is both cheaper, and with better transport properties compared to the plasticized PIMs.

**Fig. 8.** Fluxes and recovery factors in consecutive transport experiments performed on the same membrane (source solution: 53 mg/L Cr(VI), pH 4.0; stripping phase: NaOH 0.05 M; PIM: 40% Aliquat 336/60% PVC,  $70 \pm 4 \mu\text{m}$  thickness).



#### 4. Conclusions

In the present study, a novel PIM containing 40% Aliquat 336/60% PVC without added plasticizers was investigated towards the Cr(VI) transport from aqueous matrices. In the optimal membrane, the carrier Aliquat 336 is also showing plasticizing properties for PVC, the membrane characterization revealing the carrier being well dispersed in physical form in the polymer matrix.

The Cr(VI) transport was influenced by various factors like the pH of the source solution, membrane and phases' composition, as well as the metal ion concentration in the source phase. We found out that the prepared PIM without added plasticizers may effectively transport Cr(VI) from aqueous solution with initial pH 4.0 into 0.05 M NaOH receiving phase. The transport process was very fast and efficient for Cr(VI) concentration in the source phase until to  $10^{-3}$  M. Under these optimal conditions the flux of Cr(VI) ions through the membrane ( $27.26 \mu\text{mol}/\text{m}^2 \text{ s}$ ) is enhanced over the values reported in other studies dealing with Cr(VI) transport by plasticized PIMs, ACMs and SLMs.

The performed experiments demonstrated that the mechanism of Cr(VI) transport in the non-plasticized 40% Aliquat 336/60% PVC membrane is a facilitated counter-transport mechanism.

The Cr(VI) ions were preferably transported from mixtures with other heavy metal ions and with great amount of common anions existing in real industrial effluents (chloride, nitrate, sulphate). The optimal membrane possesses in addition a very high stability and very good reusability capacity, being able to be used at least 15 times without any significant alteration of its transport properties.

All these properties revealed by using the less aggressive reagents and closely resemble solutions with those from industry, recommend the investigated membrane as suitable material for applications in long-term separation processes of interest in cleaning technologies of residual and waste waters. The absence of the plasticizers from the membrane composition determines besides the enhanced properties—a high potential to reduce the price compared to the plasticized ones. Moreover, the reduced use of reagents – due to the lack of buffer solutions from the source phase—and the use of cheap and diluted stripping phases, are in line with the goals of today's research to develop cheap and non-polluting separation methods.

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