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# ABEXPERIMENTAL ANALYSIS OF THE TRANSPORT MECHANISM OF CHROMIUM (III) IONS IN THE POLYMER INCLUSION MEMBRANE SYSTEM STRACT

**Key words**

PIM, chromium(III), “jumping” mechanism, D2EHPA.

## Abstract

The paper presents an experimental analysis of the mechanism of chromium(III) ion transport in a polymer inclusion membrane (PIM). First of all, the influence of the carrier concentration on chromium(III) transport kinetics through polymer inclusion membranes is investigated. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) was used as a carrier. The initial Cr(III) concentration was changed. The authors indicate that the transport efficiency of Cr(III) depends on the D2EHPA concentration in the PIM. Regardless of the initial chromium(III) concentration, for experimental conditions, there was an optimal range of carrier concentration, somewhere between 30–50% v/v, for which the process was the most effective. The authors propose the “jumping” transport as the dominant transport mechanism in the investigated system.

## Introduction

Chromium is one of the heavy metals, which are often used in compounds in many industrial processes. More often than not, chromium compounds are applied in tanning and galvanizing industries [1]. In tanning, chromium(III) is used as tannins, which enable the production of high-quality leather [2]. In the galvanizing plants, chromium helps to produce very tight and effective coatings [1]. In spite of the many advantages of chromium, spent tannings threaten environment, because of the toxic effect of chromium ions, in particular chromium(VI) ions. Therefore, wastewater containing chromium ions should be purified before discharge.

Furthermore, according to the European Commission Report of 2010 [3], chromium belongs to the "critical elements." This means, that it is characterized by limited resources and the lack of substitutes, while simultaneously being essential for economic and industry development. Taking into consideration the above factors, it requires the exploration and development of methods for the efficient separation of chromium from aqueous solutions.

There are many different methods for chromium separation from the wastewater [4]. However, traditional methods used for the purification of aqueous solutions containing chromium (i.e.: precipitation methods, ion exchange, adsorption, crystallization, liquid extraction etc.) are often inefficient and costly, especially in the case of low concentrations of chromium in the wastewater. The ability to effectively remove and recover chromium and other toxic or radioactive metals by liquid membranes [1–3] and, in particular, polymeric inclusion membranes (PIM) [4, 5] was demonstrated in recent years by many researchers.

A PIM membrane is formed by physical immobilization of the ion carrier with a plasticizer on a polymer matrix. The membrane is a barrier separating two aqueous solutions, i.e., the feed and stripping phases. The carrier facilitates the transfer of transported ions from the feed to the stripping solution. The transport of ions in SLM is a combination of extraction and reextraction processes which occur simultaneously in the same system. The effective transport of metal cations with an acidic carrier and the counter transport of hydrogen ions are promoted by the lower acidity of the feed rather than that of stripping solution.

Selective transport through a membrane can be accomplished when the carrier/extractant in the PIM is properly chosen. In the case of carrier transport in the PIM, the carrier (P) has a high affinity to transporting substance (S), which, as a result of the reversible reaction, forms compounds (PS) that easily diffuse through the membrane (Fig. 1a). Depending on the type and structure of the carrier and the kind of the substance transported, descriptions of the various transport mechanisms can be found in literature [5]. Other than a simple carrier transport, a coupled carrier transport, characterized as a co-transport (Fig. 1b), and a counter-transport (Fig. 1c) are distinguished; the latter has greater importance and is described as a dominant mechanism in publications [6].

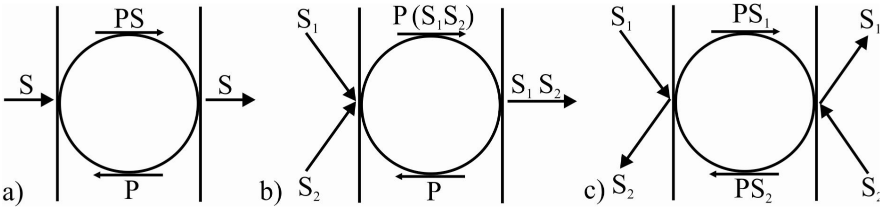

Fig. 1. Schematic transport mechanism in liquid membranes: a) simple facilitated transport, b) coupled carrier transport, c) counter-transport

Analysing the data on mechanisms occurring during the PIM`s transport available in the literature, descriptions of a "jumping" transport can also be found [7, 8]. The mechanism has been proposed and described by Cussler et al. [9] and confirmed by many other authors [10–13]. For a system with the PIM, which assumes a certain mobility of carrier molecules, possible due to the presence of the appropriately selected plasticizer [14], the assumption of this transport mechanism seems to be correct.

The aim of this study is an experimental analysis of the transport mechanism of chromium (III) ions in a polymer inclusion membrane (PIM). Based on the previous experience [15–17], kinetic studies on the system, and the review of the literature, the "jumping" mechanism was proposed. A description of the mechanism is very interesting, not only due to an educational value of the process itself, but also because it provides a theoretical basis for the development of a mathematical model describing the transport of Cr (III) ions in the system with the PIM developed by the authors of the article.

## 1. Materials and methods

In our investigation, we used a reactor described elsewhere [16] consisting of two cylindrical chambers divided by a PIM. The feed phase contained an aqueous solution of chromium(III) chloride ($CrCl_3 \cdot 6H_2O$, POCH) at a concentration from $5\times10^{-4}$ M to $2\times10^{-3}$ M with an initial pH of 4, while the stripping phase was made up of an aqueous solution of sulphuric acid (96% $H_2SO_4$, Lach-Ner) with the concentration of 4 mol/dm$^3$. The volume of both solutions amounted to 130 cm$^3$. The PIM membrane was formed by the physical immobilization of the ion carrier with the plasticizer (2-nitro phenyl-octyl ether or 2-nitro phenyl-pentyl ether, Fluka) on a polymer matrix made of triacetate of cellulose (CTA, Fluka). After evaporation of the solvent, the membrane was conditioned by immersing it in distilled water for 12 hours. The active membrane surface area amounted to 15.2 $cm^2$. Di(2-ethylhexyl) phosphoric acid (D2EHPA, Merck) (Fig.1b) was used as a carrier. The whole investigation process was thermostated ($T$ = 25°C±1°C) using a Julabo CF41 Circulator. During the experiments, the solutions used were mixed in both chambers with mechanical stirrers (IKA Yellow Line OST 20 digital) working at a constant speed of 300rpm. The samples were collected from the feed and stripping phase in the defined time intervals. The concentration of Cr(III) was measured with a spectrophotometric method with 1.5-diphenyl-carbazide, after previous oxidation of Cr(III) to Cr(VI) at a wave length equal to 540 nm (Spectrophotometr NANOCOLOR UV/VIS NUV480).

## 2. Flux and Activation Energy calculation

It was assumed that the transport of Cr(III) ions runs according to the consecutive first-order reaction [12]. Based on this assumption, the Cr(III) extraction kinetics can be described by the following formula:

$$-\frac{dc_{(f)}}{dt} = k \cdot c_O \tag{1}$$

The integration of Eq. (1) leads to:

$$ln\frac{c_{(f)}}{c_0} = -k \cdot t \tag{2}$$

The reaction constant rate ($k$) can be determined from the linear relationship of $\ln(c_{(f)}/c_0)$ vs. the elapsed time. The temporary flux ($J_f$) of chromium(III) ions transported through the membrane from the feed to the stripping phase was calculated for the initial stage of process, when the process runs most quickly. At t = 0, when the concentration of chromium in the feed phase is equal to the initial concentration ($C_f = C_0$), the flux $J_f$ assumes the following form [12]:

$$J_f = \frac{V_{(f)}}{A_{(f/m)}} k \cdot c_0 \tag{3}$$

The knowledge of initial flux values at different temperatures allowed us to establish the activation energy of transport process through PIM using the Arrhenius equation [18, 19]:

$$\log J = logA - \frac{E_a}{2,303RT} \tag{4}$$

where Ea is the activation energy of transport process (kJ/mol), R is the gas constant equal to 8,314 kJ/mol K, T is the temperature (K), and A is a constant.

## 3. Results and discussion

First, the influence of carrier (D2EHPA) concentration in PIM on chromium(III) ion transport at the initial ion concentration of $5\times10^{-4}$ M was investigated. The results of these studies are shown in Fig. 2. As indicated, the carrier concentration has a very large impact on the kinetics of the process. In this system, there is no transport of chromium(III) ions without the carrier in the membrane.

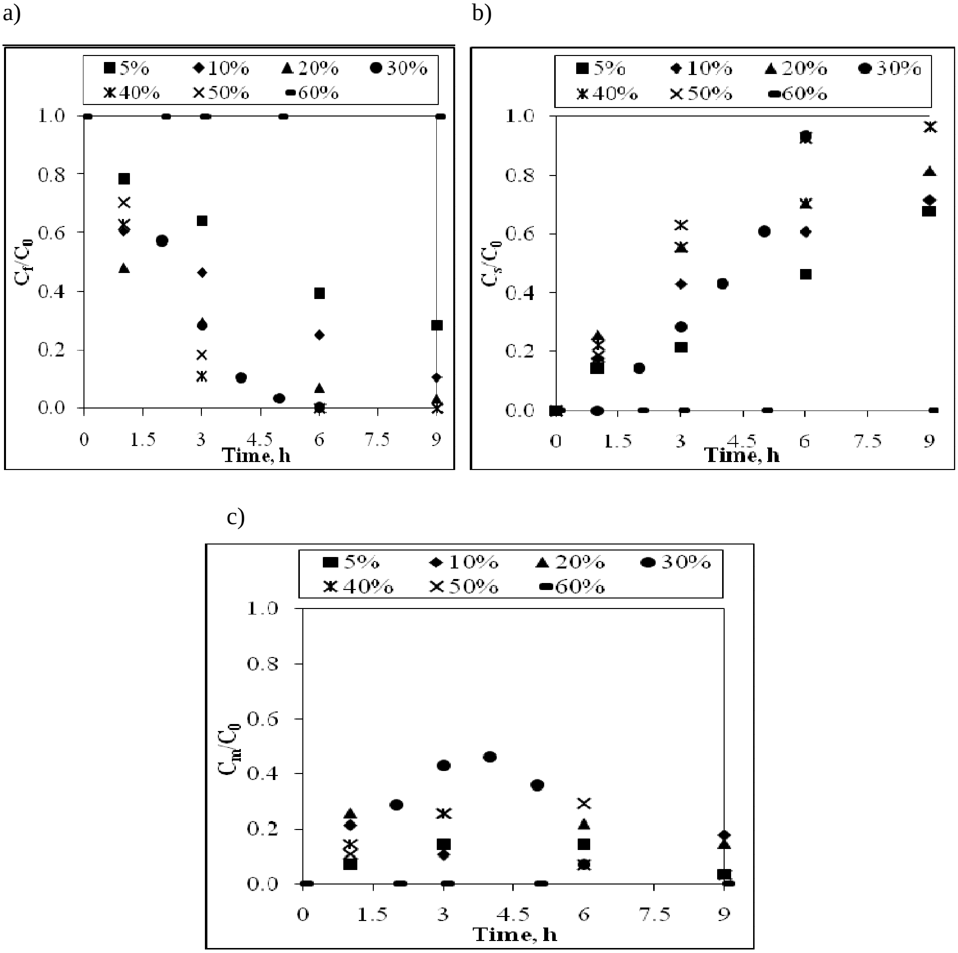
a)
b)
c)

Fig. 2. Variation of chromium(III) concentration vs. time in feed (a), stripping (b) and membrane (c) phase, for different concentration of D2EHPA in membrane. Initial concentrations of Cr(III)=$5\times10^{-4}$ M. $C_0$- initial concentration of the Cr(III) ions; $C_f$- current concentration of the Cr(III) ions in feed phase; $C_s$- current concentration of the Cr(III) ions in stripping phase $C_m$- current concentrations of the Cr(III) ion in membrane phase

A partial extraction and reextraction, at an initial concentration of the carrier in the range of 5–20% v/v D2EHPA, was observed. The effective and fast process was provided by gradually increasing the D2EHPA concentration in the membrane up to 30–50% v/v. When the concentration of D2EHPA in the membrane was above 50%, due to the limitations of the mutual solubility of the carrier and the plasticizer, the membrane did not maintain its properties; e.g., the tarnishing of the membrane surface could be observed, which resulted from the crystallization of plasticizer in the membrane structure.

Similar results were obtained for other initial concentrations of Cr(III). Therefore, in the case of the PIM, regardless of the initial concentration of the transported substance, there is a range of D2EHPA concentrations in the membrane that helps to reach the highest efficiency. In our investigation, this concentration is in the range of 30–50% v/v, in which both the penetration of Cr(III) ions and pertraction were the fastest (Fig. 2c). Kebiche-Senhadji et al. [20] and Kavitha and Palanivelu [21], who studied the transport of metals through PIM including alkyl derivatives of phosphoric acid as a carrier, made a similar observation.

The rate of the process with the PIM, with an optimal amount of a carrier, depends on the initial concentration of Cr(III) ions, as illustrated in Fig. 3. Increasing the initial concentration of Cr(III) ions had a negative impact on the extraction and reextraction (Fig. 3a, b), resulting in slower transport of Cr(III) ions through the membrane (Fig. 3c).

The presence of some fixed range of D2EHPA concentration in PIM, for which the transport of chromium (III) occurs most efficiently, confirms the results of instantaneous changes in the flow of Cr(III) ions penetrating into the membrane as a function of the carrier concentration at different initial content of Cr(III) ions (Fig. 4).

To explain the results, Cussler et al. (1989), who developed the transport mechanism through the membrane with a physically immobilized carrier, adopted a layered structure of a polymeric inclusive membrane. This theory is also supported by many other researchers [7, 8, 10–13]. According to this concept (Fig. 5), the molecules of plasticizer are arranged in the membrane in layers at certain distances from each other. A carrier added to the membrane gradually fills the areas of the individual layers. Assuming mobility of the plasticizer chains in the membrane, the substance transported across a single layer can only occur with a minimum concentration of the carrier. Transport takes place based on the "transfer" between the adjacent carrier particles.

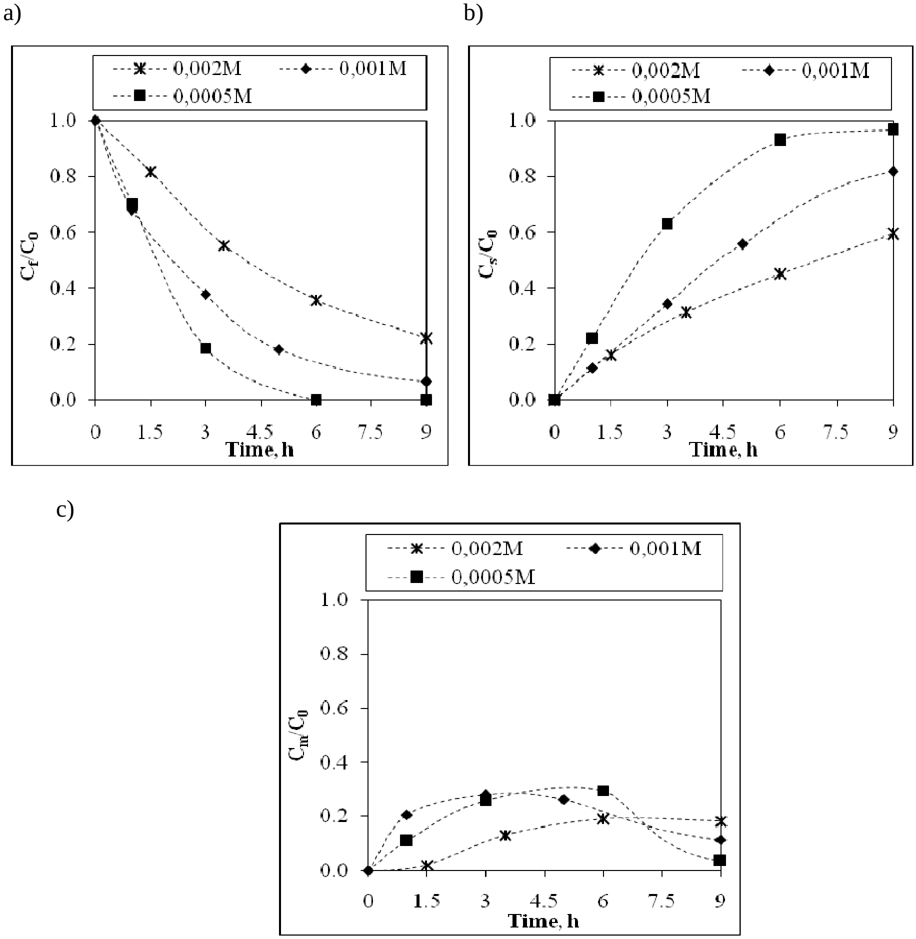

Fig. 3. Variation of chromium(III) concentration vs. time in feed (a), stripping (b), and membrane (c) phase for initial Cr(III) concentration Cr(III) = $2\times10^{-3}$; $1\times10^{-3}$; $5\times10^{-4}$ M. D2EHPA concentration was constant = 40% v/v. $C_0$- initial concentration of the Cr(III) ions; $C_f$- current concentration of the Cr(III) ions in feed phase; $C_s$- current concentration of the Cr(III) ions in stripping phase $C_m$- current concentration of the Cr(III) ion in membrane phase

In order to verify the assumptions about jumping transport of Cr (III) through the PIM, the effect of temperature on the transport kinetics was analysed. Implementation of studies on the effects of temperature allows one to determine the activation energy and confirms whether the transport is limited by the kinetics of the reaction between the carrier and the Cr (III) ions at the interface, or the diffusion of Cr (III) through the membrane.

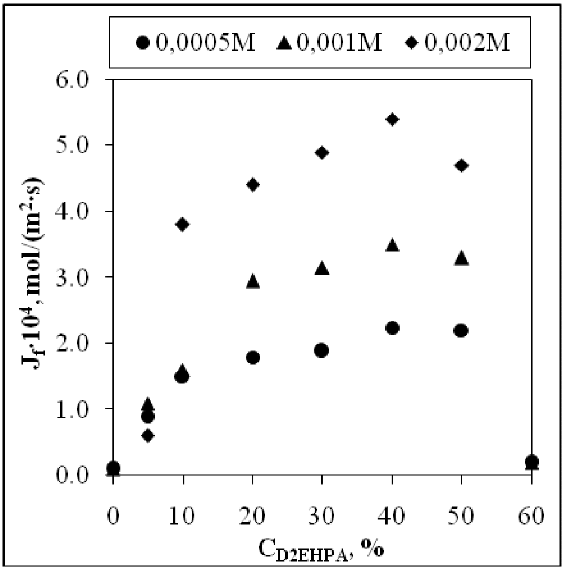

Fig. 4. Variations in the temporary flux of chromium(III) ions penetrating into the membrane, as a function of carrier concentration, for different initial concentrations of chromium (III)

The study was conducted at the most effective composition of the PIM, at an initial concentration of Cr(III), C = 0.002M ,in the temperature range of 293-313K.

Figure 5 shows the initial flux variation for Cr(III) transport as a function of the process temperature. The relation log J vs. 1/T indicates that the process is controlled by the formation of a metal complex in membrane phase. The activation energy (Ea) calculated from the Arrhenius equation, Eq. (4), was equal to 108±5 kJ/mol. This value is consistent with that obtained by [19] for chromium(III) transport through PIM with D2EHPA as an ion carrier and Aliquat 336 as a plasticizer. It is known that the Ea value is used as a criterion in the classification of the step-controlled mechanism. For diffusion-controlled processes, the Ea values are lower than 20 kJ/mol, while those for processes controlled by chemical reaction are higher than 42 kJ/mol. In the case when the activation energy values are in the range from 20 to 42 kJ/mol, the transport processes are controllable by both diffusion and chemical reaction [18, 19]. In our investigations, the value of the activation energy indicates that chromium(III) transport through PIM with D2EHPA as an ion carrier is also controlled by chemical reactions occurring at interface of boundary layers. That is a confirmation of our assumptions about the “jumping” transport mechanism in the studied system.

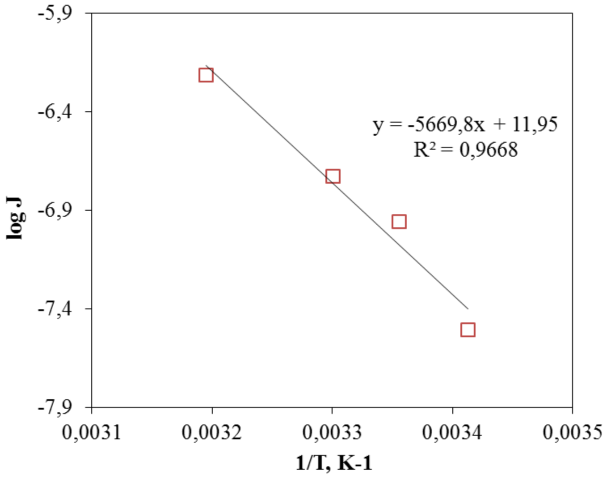

Fig. 5. Arrhenius plot of Cr(III) transport across PIM. The initial Cr(III) concentration is Cr(III) = 0.002 M. The D2EHPA concentration was constant = 40% v/v

Cussler et al. [9] singled out two major cases in the transport mechanism. In the first, illustrated in Fig. 6a, when $l > l_0$, the areas of the mobility of carrier molecules do not overlap. Therefore, it is impossible to transport ions between particles of the carrier in the membrane, because the flux $J = 0$. The second case is illustrated in Fig. 6b, where it is assumed that $l < l_0$. In this case, areas of the mobility of neighbouring molecules partly overlap. This enables multiple complexation reactions, releasing ions, and transporting particles through the membrane ($J \neq 0$).

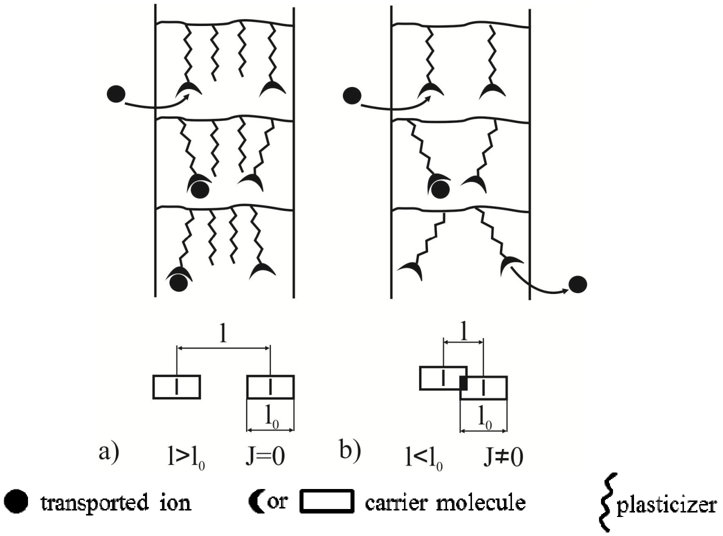

Fig. 6. Transport mechanism in a polymer inclusion membrane: $l$ – the distance between carrier molecules, $l_0$ – the length of the carrier molecules

However, our results demonstrate that, apart from the two above-mentioned cases, there may be even more options. In Fig. 4, the effect of carrier concentration, D2EHPA on the flow of Cr(III) ions through a polymeric inclusion membrane for different initial concentrations of chromium ions is demonstrated. It is clearly seen that, in the case of the PIM, transport efficiency improves with the increase in the concentration of the carrier in the membrane. The most preferred flux was obtained for a carrier concentration of 40%. Therefore, there is a certain limit concentration of the carrier in the membrane that guarantees the most preferred flux, as shown in Fig. 7a. In this case, the distance between the carrier molecules, located in the membrane, is much smaller than the range of movement that the carrier can perform ($l << \underline{l_0}$), which guarantees efficient ion transport. This mechanism is a variation of the coupled-carrier transport and is schematically shown in Fig. 8. Increasing the concentration of the carrier in the membrane by more than 40% resulted in a greater flux decrease. It can be assumed that the excess of the optimal concentration of carrier in the membrane leads to a situation in which the particles are overlapping and hence limiting or preventing its movement ($l=0$; $l_0=0$) and the transport of ions ($J = 0$) (Fig. 7b).

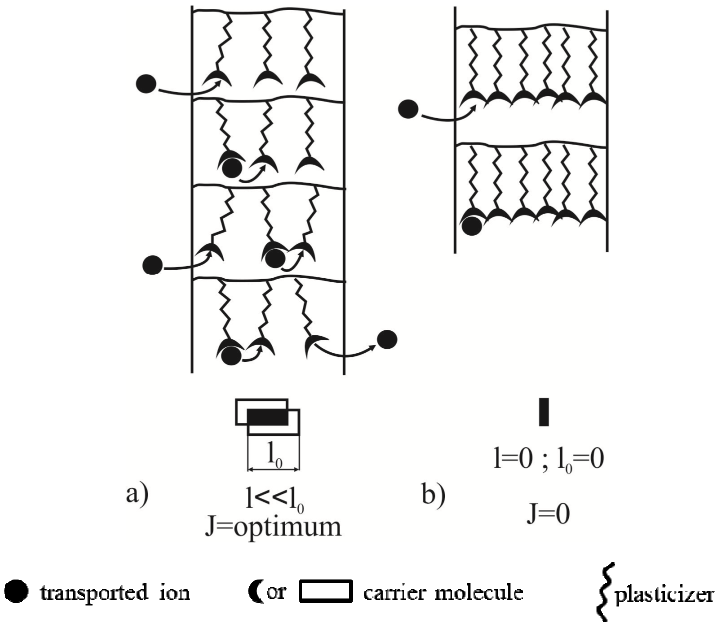

Fig. 7. Transport mechanism in polymer inclusion membrane: $l$ – the distance between carrier molecules, $l_0$ – the length of the carrier molecules

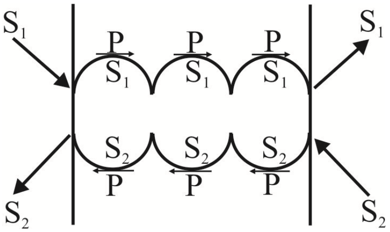

Fig. 8. Schematic transport mechanism in a system with PIM

## Conclusion

The polymer inclusion membrane containing di(2-ethylhexyl)phosphoric acid as a carrier enables efficient release of chromium(III) ions from aqueous solutions. The transport efficiency of Cr (III) through PIM, and directly the speed of the "transfer" of Cr (III) ions through the membrane, depends mainly on the carrier concentration in a membrane. In the case of PIM, regardless of the initial concentration of the transported substance, there is a range of D2EHPA concentration in a membrane for which the highest efficiency can be obtained. For the system studied the optimal concentration of D2EHPA varies from 30 to 50% v/v. To explain the transport mechanism of chromium (III) ions through the PIM, layered membrane structures were proposed. Observations suggest that the dominant mechanism of transport is the “jumping” mechanism. For the conditions of the experiments the assumption seems to be correct.

## SYMBOLS

$A_{(f/m)}$ – the interfacial area ($m^2$),
$C_0$ – the initial chromium(III) concentration in the feed solution ($mol/dm^3$)
$C_{(f)}$ – the current concentration of chromium(III) in the feed solution ($mol/dm^3$)
$C_m$ – current concentration of the Cr(III) ion in membrane phase
$C_s$ – current concentration of the Cr(III) ions in stripping phase
$J_f$ – temporary flux of chromium(III) ions transported through the membrane
$k$ – reaction constant rate ($h^{-1}$)
$t$ – the elapsed time (h)
$V_{(f)}$ – the volume of the feed phase ($m^3$).

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## Eksperymentalna analiza mechanizmu transportu jonów Cr(III) w polimerowej membranie inkluzyjnej

### Słowa kluczowe

PIM, chrom (III), mechanizm przeskokowy, D2EHPA.

### Streszczenie

W pracy dokonano eksperymentalnej analizy mechanizmu transportu jonów chromu(III) w polimerowej membranie inkluzyjnej (PIM). W pierwszej kolejności zbadano wpływ stężenia przenośnika na kinetykę transportu jonów chromu (III) przez polimerową membrane inkluzyjną. Jako przenośnika jonów Cr(III) użyto kwasu di(2-etylkoheksylo) fosforowego (D2EHPA). Badania prowadzono przy różnym stężeniu początkowym jonów chromu. Autorzy wskazują, że efektywność transportu jest zależna od stężenia D2EHPA w PIM. Niezależnie od początkowego stężenia Cr(III) w warunkach prowadzenia badań wyznaczono zakres stężeń przenośnika 30–50% v/v, przy których transport zachodził najefektywniej. Zaproponowano mechanizm przeskokowy jako transport dominujący.