

The possibility of using a mathematical model based on consecutive first-order reactions to describe the Cr(III) ions pertraction in DCSLM system

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Received: 30 January 2017 / Accepted: 25 March 2017 / Published online: 5 April 2017
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Abstract This paper discusses the use of double-carrier supported liquid membrane (DCSLM) for extraction of Cr(III) ions, using the D2EHPA/CYANEX272 mixture as the carriers. Based on the calculated value of the activation energy and on the assumption that the result of transport process in the DCSLM, in particular, depends on the accumulation of intermediate products in the membrane, the mathematical model of the chromium(III) ions separation based on consecutive first-order reactions has been proposed. Transport kinetics of chromium(III) in studied system for different carriers concentrations ratio and their comparison with theoretical prediction was analyzed. The obtained results confirmed the presence of a synergistic effect of selected carriers in DCSLM. Verification of the proposed model has been carried out in the article. Mathematical model describes correctly the membrane transport process only for most effective carriers ratio. It was found that depending on the carriers ratio in DCSLM the transport processes may be controlled by both chemical reaction and diffusion. The described model can be a useful tool for quickly and approximate determination of the transport process parameters in experimental works but is too simple to correctly describe the Cr(III) ions pertraction in supported liquid membrane system under the full range of process parameters (especially concentrations and proportions of the used carrier).

Keywords Cyanex272 · D2EHPA · Chromium(III) · Synergistic effect

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Abbreviations

SLM	Supported liquid membrane
DCSLM	Double-carrier supported liquid membrane
Z, M, O	The transport form in the feed, the membrane and the receiving phase, respectively
k_Z	Penetration coefficient of the substance to the membrane (1/s)
k_O	Penetration coefficient of the substance to the receiving phase (1/s)
C_Z	Transported substance concentration in the feed phase at a specific time (mol/dm^3)
C_P	Initial concentration of the transported substance in the feed phase (mol/dm^3)
C_O	Transported substance concentration in the receiving phase at a specific time (mol/dm^3)
R_Z, R_M, R_O	Reduced concentrations of the transported substance in the feed, membrane and receiving phase, respectively
J_Z	Flux of the Cr(III) ions penetrating into the membrane [$\text{mol}/(\text{m}^2 \text{ s})$]
V_Z	Volume of the feed phase (dm^3)
$F_{Z/M}$	The active surface of the membrane (m^2)
t	Process time (h)
E_a	The activation energy of transport process (kJ/mol)
R	The gas constant equal to 8314 (kJ/mol K)
T	The temperature (K)

Introduction

Chromium and its compounds are widely used in many industries (electroplating, tanning, dyes, textile). In tanning, chromium(III) is used as tannins, which enable the production of high-quality leather. 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 [2], 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.

The most widely method used for “pure form” metals (including chromium) separation is the solvent extraction. Separation methods based on solvent extraction usually consume large amounts of solvents and extractants. In order to reduce the amounts of reactants and energy needed for separations and to decrease the environmental and economic impact of extraction, several membrane-based separation techniques have been proposed [3–5].

Methods such as liquid membrane, due to significant reduction of organic solvents, are considered as a ‘green’ alternative to solvent extraction. Moreover, liquid membrane methods employ simultaneously extraction and stripping what make them very efficient. Out of the liquid membrane methods, supported liquid membrane (SLM) seems to be most attractive because, as the ligand inventory method, can be efficiently applied for separations of expensive reagents [3, 6].

The supported liquid membrane is a microporous polymeric support soaked with the membrane phase (solution of a specific substance—carrier in organic diluent). 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 stripping solution. The transport of ions in SLM is a combination of extraction and re-extraction processes which occur simultaneously in the same system [5, 6]. The coupled counter transport of hydrogen ions causes the effective transport of metal cations with acidic carrier in such system. The counter transport of hydrogen ions are promoted by lower acidity of the feed than the strip solution [5]. A schematic description of the membrane transport of metal cations with an organic acidic carrier is presented in Fig. 1.

The applications of SLMs with organophosphorus compounds as metal ions carriers (used for chromium concentration and separation) have been shown in several papers [7–9]. The most commonly used organophosphorus compounds as chromium(III) carriers in membrane systems are: di (2-ethylhexyl) phosphoric acid (D2EHPA) and bis (2,4,4-trimethyl) phosphine acid (Cyanex272). Moreover, Religa et al. [10] demonstrated that the addition of both carriers (D2EHPA/Cyanex272 mixture) into the membrane phase has a positive effect on improving of both the rate and selectivity of the chromium(III) ions transport. The double-carrier supported liquid membrane (DCSLM) with a selected carriers mixture enabled

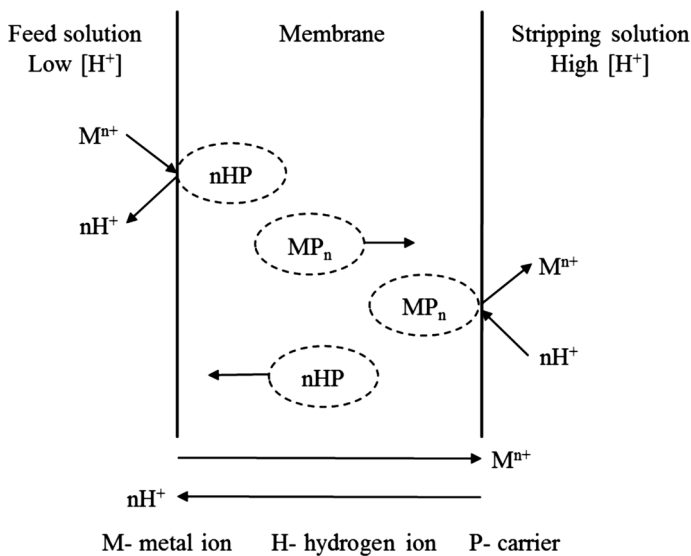


Fig. 1 Schematic description of coupled counter transport of metal ions through a SLM

more than threefold reduction of time processing in comparison to the membrane with only one carrier—D2EHPA. It was found also that the selecting of the appropriate carriers concentration ratio in DCSLM determined the transport rate.

Similar results were shown by the Biswas et al. [11], and Wojciechowski et al. [12]. The authors observed that for a specified carriers ratio in the membrane a synergistic effect—increasing of the rate and selectivity of the process—is obtained. Additionally, work Rajewski and Religa et al. [13] describe the transport mechanism in DCSLM. It was found that role of the D2EHPA in DCSLM is creation of the “transport tunnels” for chromium flow through the membrane. Whereas the role of the Cyanex272 in the membrane is both an extraction of the chromium(III) ions from feed phase and stabilization of the D2EHPA “transport tunnels”. Such stable “transport tunnels” facilitated flow of the Cr(III) ions through the membrane. This transport mechanism was called the “flow-type” transport.

In the present work, transport behavior of chromium(III) in the double-carrier (D2EHPA/Cyanex272 mixture) supported liquid membrane was continued and studied. First of all, the effect of the initial concentration of Cr(III) on the kinetics of the transport system of the double-carrier supported liquid membrane was examined. Kinetics experiments were performed to check, that the relations and observations described in work [10] at the initial concentration of Cr(III) = 0.002 mol/dm³ also occur at a higher concentration of Cr(III). All experiments were carried out for comparable experimental parameters, however, for other initial concentration of the Cr(III) = 0.006 mol/dm³. Moreover, for both initial concentrations of Cr(III) ions experiments were carried out in different process temperatures to determine the activation energy. In addition to the above, an attempt was made to develop a mathematical model to simulate the mass transfer process across the DCSLM from feed phase to receiver phase. Modeling of the mass transfer process may be useful in understanding of the phenomenon, it can help in scale-up of system and also it can minimize the experimental trials of further experiments. Moreover, carrier mediated transport has become an important area of study for engineers due to its applications in various biological and non-biological systems [4].

Various mathematical models have already been developed to simulate the transport of chromium(III) ion across SLM [5, 14] but none can be found in the literature for double carrier systems.

Many authors describe the mathematical models which take into account that the final effect of the transport process depends on the course of the subsequent stages, in particular the accumulation of intermediate substances in the membrane [6, 14, 15]. It is a typical feature of first order reaction kinetics. This model is most often used to describe the transport in the bulk liquid membrane systems (BLM). The model is very simple because it does not give insights into the boundary layer and support properties in SLM system.

Tested model assumes that the reactions at the interface dominate in the transport mechanism, so that the calculation does not need to determine the diffusion coefficient. What is often a cumbersome and time-consuming calculation element.

Thus, the model can be a useful tool for quickly determination of the most important transport process parameters. Therefore, the verification of the proposed model for SLM system has been carried out in the article.

The theoretical relation between mass transfer resistances and other parameters (membrane composition and initial chromium(III) concentration) have been fully discussed.

Theory

In the simplest case consecutive kinetic reactions take place in accordance with the following scheme [14, 16]:



where Z , M , O —the transport form in the feed, the membrane and the receiving phase, respectively, k_Z —penetration coefficient of the substance to the membrane, k_O —penetration coefficient of the substance to the receiving phase.

Using the reduced concentrations of transported substances:

$$R_Z = \frac{C_Z}{C_P}, \quad (2)$$

$$R_M = \frac{C_M}{C_P}, \quad (3)$$

$$R_O = \frac{C_O}{C_P}, \quad (4)$$

where C_Z —transported substance concentration in the feed phase at a specific time (mol/dm^3), C_P —initial concentration of the transported substance in the feed phase (mol/dm^3), C_O —transported substance concentration in the receiving phase at a specific time (mol/dm^3), R_Z , R_M , R_O —reduced concentrations of the transported substance in the feed, membrane and receiving phase, respectively.

Process rate under non-stationary conditions, (assuming the first order reactions) can be described by the following kinetic equations:

$$\frac{dR_Z}{dt} = -k_Z \cdot R_Z \quad (5)$$

$$\frac{dR_M}{dt} = k_Z \cdot R_Z - k_O \cdot R_O \quad (6)$$

$$\frac{dR_O}{dt} = -k_O \cdot R_O \quad (7)$$

And the material balance in the following way:

$$R_Z + R_M + R_O = 1 \quad (8)$$

After integration of the above equations with initial conditions: $t = 0$, $C_Z = C_P$, $C_M = 0$, $C_O = 0$: we get that:

$$R_Z = \exp(-k_Z \cdot t) \quad (9)$$

$$R_M = \frac{k_Z}{k_O - k_Z} \cdot [\exp(-k_Z \cdot t) - \exp(-k_O \cdot t)] \quad (10)$$

$$R_O = 1 - \frac{1}{k_O - k_Z} \cdot [k_O \cdot \exp(-k_Z \cdot t) - k_Z \cdot \exp(-k_O \cdot t)] \quad (11)$$

The solution of the model equations allows to determine the penetration coefficients (k_Z and k_O). Based on the algorithm stored in the Scilab program, the value of the chromium(III) ions penetration coefficient to the membrane (k_Z) was determined from the linear relationship of $\ln(C_Z/C_O)$ versus the elapsed time. The algorithm uses a golden ratio numerical method. It is one of the methods of one-dimensional optimization of the objective function.

Based on the value of the k_Z coefficient, the flux of the ions penetrating into the membrane was determined (J_Z):

$$J_Z = \frac{V_Z}{F_{Z/M}} \cdot k_Z \cdot C_P \quad (12)$$

where k_Z —penetration coefficient of the Cr(III) ion into the membrane, C_P —initial concentration of the Cr(III) ion (mol/dm^3), J_Z —flux of the Cr(III) ions penetrating into the membrane ($\text{mol}/\text{m}^2/\text{s}$), V_Z —volume of the feed phase (dm^3), $F_{Z/M}$ —the active Surface of the membrane (m^2), t —process time (h)

The knowledge of initial flux values at different temperatures allowed to establish the activation energy of transport process through DCSLM using the Arrhenius equation [17, 18]:

$$\log J = \log A - \frac{E_a}{2303RT} \quad (13)$$

where E_a is the activation energy of transport process (kJ/mol), R is the gas constant equal to $8314 \text{ kJ}/\text{mol K}$, T is the temperature (K) and A is a constant

Methods

Transport experiments were carried out in a vessel with two cylindrical chambers containing the feed and the stripping aqueous phases described in [10]. The volume of both chambers was 130 cm^3 . The solutions, feed with Cr(III) concentration equal to 0.002 and $0.006 \text{ mol}/\text{dm}^3$ (aqueous chromium(III) chloride solution, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and stripping ($6 \text{ M} \cdot \text{HCl}$) was separated by SLM. The active membrane area was equal to 15.2 cm^2 . The initial pH of the feed phase was equal to 4. The whole process was thermostated to ambient temperature ($T = 25 \pm 0.5 \text{ }^\circ\text{C}$). The solutions were mixed in both chambers by mechanical stirrers (IKA, OST20 digital). The

immobilized liquid membrane was a PTFE porous polymer film (Sartorius) with a pore size of 0.45 μm and porosity of 64%. The membrane was soaked for 24 h in a mixture of an organic phase consisting of kerosene (Dragon), *o*-xylene (Fluka) and carriers. In each experiment, stable and reproducible process conditions, which can affect the transport kinetics were assured. Also the composition of the membrane phase was easily reproducible.

Di (2-ethylhexyl) phosphoric acid (D2EHPA, Fluka) and bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, Cytec) were used as the ions carriers. The concentration of the carriers in the membrane was changed in the range of 0–1.2 mol/dm³. The volume ratio of the concentrations of the other ingredients (kerosene/*o*-xylene) was constant and equal to 2:1.

The analysis of the Cr(III) ions concentration in water phase was determined with a spectrophotometer (Spectrophotometer NANOCOLOR UV/VIS NUV480) using 1,5-difenylokarbazyde method with wave length $\lambda = 540 \text{ nm}$ after mineralization of samples. Each measurement was repeated three times. The standard deviation of the measured value determined by statistical methods was equal to ± 0.0003 .

Results and discussion

Comparison of the SLM with D2EHPA to SLM with Cyanex272

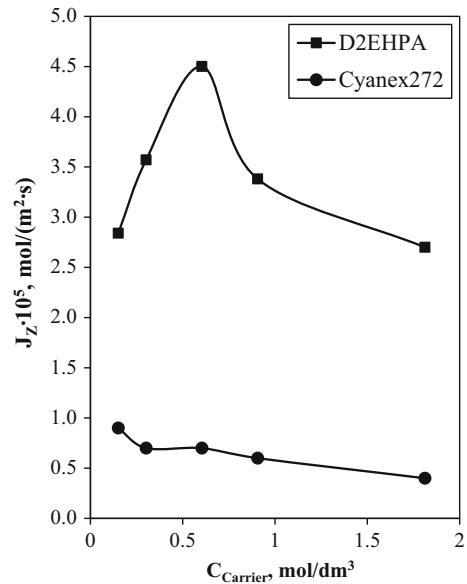
As reported by Religa et al. [10], the double-carrier supported liquid membrane (DCSLM) with a mixture of D2EHPA/Cyanex272 (0.15 mol/dm³ Cyanex272/0.9 mol/dm³ D2EHPA) enabled, for initial concentration of the Cr(III) = 0.002 mol/dm³, more than threefold reduction of time processing in comparison to the membrane with only one carrier—D2EHPA. The authors concluded that for a defined proportion of carriers concentration in the membrane, a clear synergistic effect is observed. Moreover, it was found that adding of the second carrier (Cyanex272), providing the possibility of better packing of the molecules D2EHPA and allows for increasing the concentration of D2EHPA in the membrane. Increasing the amount of carrier, which is responsible for the forming of a transport structure creates favorable conditions for the rapid penetration of Cr(III) ions to the membrane and their efficient transport [13]. It is also known that the initial concentration of transported ions have also significant impact on the transport efficiency in the SLM [3, 6, 7].

Therefore, to confirm this assumption we carried out similar studies for three times higher initial chromium(III) concentration = 0.006 mol/dm³.

According to the literature information [8, 11, 14, 18] in the SLM, for a specific concentration of the transported ions, the optimal concentration of a carrier can be found at which the transport of ions runs most effectively. Thus, at the beginning of the study the influence of the carriers concentrations (D2EHPA or Cyanex272) on the transport efficiency for initial concentration of the Cr(III) = 0.006 mol/dm³ has been investigated.

As can be seen on Fig. 2, for the initial concentration of chromium(III) ions equal to 0.006 mol/dm³, the most effective concentration of D2EHPA in the

Fig. 2 Effect of D2EHPA and Cyanex272 concentration in SLM on Cr(III) ions flux (J_C) penetrating to the membrane. $C_{Cr(III)} = 0.006 \text{ mol/dm}^3$; initial pH 4



membrane is 0.6 mol/dm^3 . At this concentration process was the most effective, which is in accordance with our previous observations. Such concentration of D2EHPA was chosen as the basic for tests with DCSLM system.

Next, it was to investigate whether Cyanex272 can acts as a carrier of chromium(III) in the SLM. During the experiments it was observed that the effectiveness of chromium(III) extraction was more than four times lower than in the SLM with D2EHPA (Fig. 2). Extraction was at the level of 20% (Fig. 3b), regardless of the Cyanex272 concentration in the membrane ($0.15\text{--}1.8 \text{ mol/dm}^3$). It is characteristic that the process was extremely intensive in the first phase that lasted about 1 h. In the later phase the process came to a stop. It is also significant that a considerable sudden decrease (from 4 to about 1.5) of pH in the feed solution was observed in the first phase of pertraction. In case of SLM with D2EHPA the optimal carrier concentration allowed for the complete extraction of Cr(III) (Fig. 3a). The pH in the feed solution did not decreased so sharply and remained at the level 2.1.

The rapid decrease of pH determines the forms of chromium(III) to be found in the solution—they will be hydrolyzed to a slight extent under the low pH. It is probably the reason for the fast decreasing of rate of extraction in the SLM system with Cyanex272.

Additionally, no presence of chromium(III) ions has been reported in the receiving phase in the SLM system with CYANEX272. Such result confirm the formation of stable, polymeric structures between chromium(III)-Cyanex272 molecules in the membrane [13]. Movement of these expanded structures in the membrane phase is significantly hampered. Moreover, high stability of the structure prevents an effective re-extraction of chromium(III). In studies on chromium(III) extraction by Cyanex272, Lanagan and Ibana [19] indicated that Cyanex272 can easily create stable forms with chromium(III). In case of formed structures, even

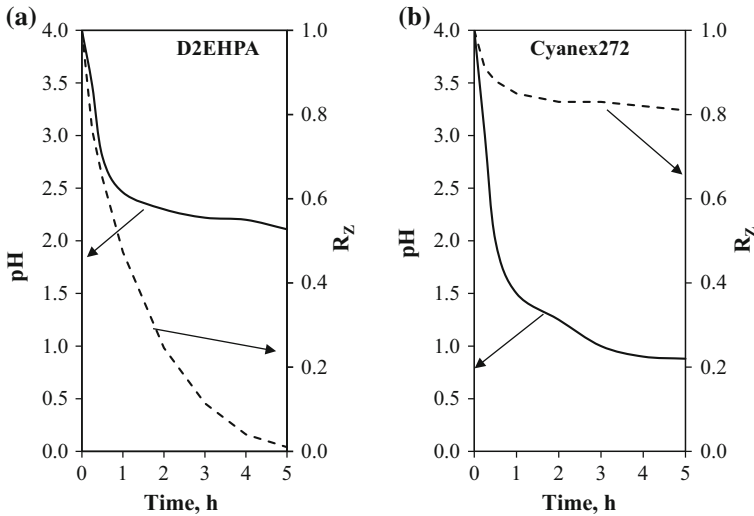


Fig. 3 Variation of chromium(III) concentration and the pH in feed phase versus time for SLM with **a** D2EHPA and **b** Cyanex272. Initial chromium(III) concentration in the feed phase $C_Z = 0.006 \text{ mol/dm}^3$; initial pH 4. R_Z —reduced concentrations of the Cr(III) in the feed phase

when $8 \text{ mol/dm}^3 \text{ HNO}_3$ is applied, the re-extraction of chromium was partial and possible only directly after the extraction process. Thus, the achieved results show that the ions of Cr(III) cannot be effectively transported by SLM containing only Cyanex272 as a carrier.

Synergistic effect in the double-carrier SLM

In the next step, a membrane with the constant concentration of D2EHPA and various concentrations of Cyanex272 was applied for investigations of the transport of chromium(III).

As it can be seen in Fig. 4a, the system with a certain concentration of CYANEX272 in the membrane containing 0.6 mol/dm^3 of D2EHPA achieves significantly higher effectiveness compared to the membrane containing only D2EHPA. This optimal concentration of Cyanex272 is equal to 0.15 mol/dm^3 and is 4 times lower than the concentration of D2EHPA. Moreover, the obtained result is the same as for initial concentration of Cr(III) = 0.002 mol/dm^3 [10, 13].

Based on the achieved results, the concentration of Cyanex272 equal to 0.15 mol/dm^3 —the most favorable for the speed of the process—has been selected for the next analyses. In this stage of the research various amounts of D2EHPA have been introduced to the membrane at a constant concentration of Cyanex272. The results (Fig. 4b) show that the presence of two carriers in a suitable ratio (0.9 mol/dm^3 D2EHPA and 0.15 mol/dm^3) causes a 2.5 fold increase process efficiency compared to the process carried out only with D2EHPA. As in case of the initial concentration of the Cr(III) = 0.002 mol/dm^3 it was also observed that adding a second carrier (CYANEX272) to DCSLM increase the threshold concentration of D2EHPA from

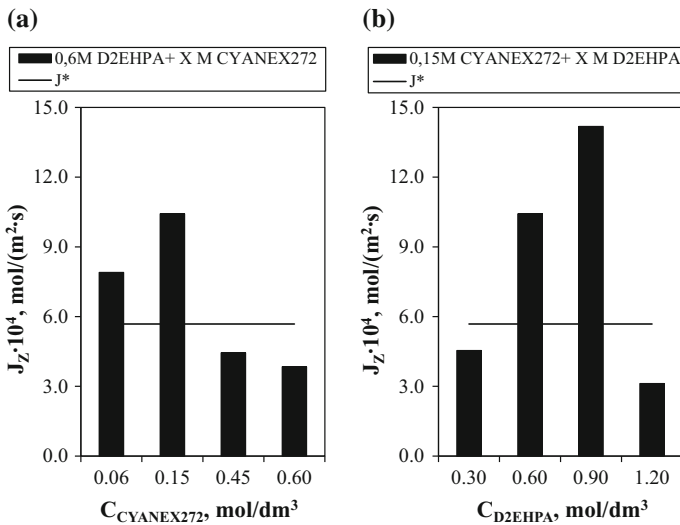


Fig. 4 Effect of carriers mixture proportion on Cr(III) ions flux (J_{Cr}) penetrating to the membrane: **a** addition of Cyanex272 to the membrane containing 0.6 mol/dm³ D2EHPA, **b** addition of D2EHPA to the membrane containing 0.15 mol/dm³ Cyanex272. J^* —flux of chromium(III) ions penetrating to the membrane containing only 0.6 mol/dm³ D2EHPA

0.6 mol/dm³ (Figs. 2, 4) to 0.9 mol/dm³. Addition of the second carrier (CYANEX272), provides the possibility of better packing of the molecules of the D2EHPA and stabilizes the transport structure on the membrane phase. It allows the increase in the D2EHPA concentration into the membrane. Increasing the amount of carrier, which is responsible for the forming of a transport structure, creates favourable conditions for the rapid penetration of Cr(III) ions to the membrane and their efficient transport [13].

This observation confirms that the role of the Cyanex272 in the membrane is both an extraction of the Cr(III) ions from feed phase and transfer the ions to the transport structure created by D2EHPA. Moreover, it can be concluded that the most effective carriers mixtures concentration ratio in the DCSLM are independent of the initial Cr(III) concentration.

Temperature effect on chromium(III) transport in DCSLM system

The temperature effect on chromium(III) transport was analyzed to verify the assumptions about reaction kinetic in the description of the model Cr(III) ion transport in DCSLM system. The study allowed to determine the activation energy, which confirmed that transport was limited by the kinetics reaction between the carrier and chromium(III) ions at the interface or by the diffusion of Cr(III) through the membrane [17, 18].

The experiment was carried out with the most effective DCSLM composition (0.15 mol/dm³ Cyanex272/0.9 mol/dm³ D2EHPA) for the initial concentrations of the $C_{\text{Cr(III)}} = 0.002$ and 0.006 mol/dm³ in the temperature range 293–313 K. Based

on the results the parameters of Cr(III) transport the activation energies were calculated (Table 1).

The obtained results show that the process rate increases with temperature regardless of the initial concentration of the Cr(III). In the case of the $C_{\text{Cr(III)}} = 0.002 \text{ mol/dm}^3$ the flux of the ions penetrating into the membrane increased from 7.33×10^{-5} at 293 K to $21.92 \times 10^{-5} \text{ mol/(m}^2 \text{ s)}$ at 313 K. In the case of the $C_{\text{Cr(III)}} = 0.006 \text{ mol/dm}^3$ the flux of the ions penetrating into the membrane increased from 14.13×10^{-4} at 293 K to $32.09 \times 10^{-4} \text{ mol/(m}^2 \text{ s)}$ at 313 K. Therefore, the increase of the temperature of the 20 K results in a threefold and twofold increase in the chromium(III) ions penetration rate into the membrane respectively for 0.002 and 0.006 mol/dm³ initial Cr(III) ions concentrations.

Figure 5 shows the initial flux variation for Cr(III) transport as a function of the process temperature. The relation $\log J_Z$ versus $1/T$ (a straight line) indicates that the process is controlled by chemical reaction and the constant rate is strongly dependent on temperature regardless of the initial concentration of Cr(III) ions [17, 21].

The activation energy (E_a) calculated from the Arrhenius equation Eq. (13) was equal to 114 ± 5 and $113 \pm 5 \text{ kJ/mol}$ respectively for 0.002 and 0.006 mol/dm³ initial Cr(III) ions concentrations. These values are consistent with that obtained by Kończyk et al. [17] and Lazarova et al. [20] for separation of the metal ions by supported liquid membranes systems. It is known that the E_a value is used as a criterion in the classification of the step-controlled mechanism. For diffusion-controlled processes the E_a 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 controlled by both diffusion and chemical reaction [17, 18, 21]. In our investigations, the value of the activation energy indicates that chromium(III) transport through DCSLM with D2EHPA/Cyanex272 mixture as an ion carrier is controlled by chemical reaction occurring at interface of boundary layers.

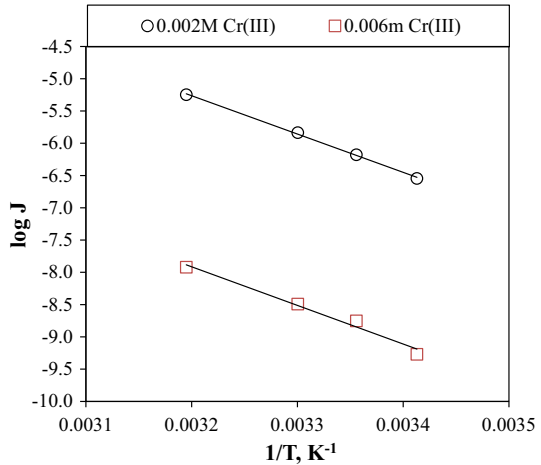
Comparison of the model and experimental results

In order to verify the possibility of using a mathematical model based on consecutive first-order reactions to describe the Cr(III) ions pertraction in DCSLM

Table 1 The parameters characterizing the Cr(III) transport in DCSLM at different temperatures for most effective membrane composition

Temperature (K)	$C_{\text{Cr(III)}} = 0.002 \text{ mol/dm}^3$		$C_{\text{Cr(III)}} = 0.006 \text{ mol/dm}^3$	
	$k_Z \times 10^{-4}$ (1/s)	$J_Z \times 10^{-5}$ [mol/(m ² s)]	$k_Z \times 10^{-4}$ (1/s)	$J_Z \times 10^{-4}$ [mol/(m ² s)]
293	3.03	7.33	14.13	14.18
298	6.53	13.83	17.77	20.74
303	8.47	17.21	21.03	29.24
313	10.58	21.92	32.09	52.60

Fig. 5 Arrhenius plots of Cr(III) transport across DCSLM with carriers mixture: (0.15 mol/dm³ Cyanex272/0.9 mol/dm³ D2EHPA) for the initial concentration of the $C_{Cr(III)} = 0.002$ and 0.006 mol/dm³



system the changes of chromium(III) concentration in DCSLM system with time for different proportions of the carriers concentrations in the membrane and its comparison with theoretical prediction were made.

The results (Figs. 6, 7) suggest that proposed mathematical model describes correctly the transport process in DCSLM with a D2EHPA/Cyanex272 mixture only in specific process conditions. For initial concentration of the Cr(III) ions, it is characteristic that satisfactory compatibility of experiments and model results were stated only for membranes with the most effective carriers ratio (Figs. 6b, 7d; Table 2).

In the other cases, the discrepancy between the experimental data and theoretical predictions increased. Moreover, decrease in the rate and efficiency of the ion transfer is observed. The effect was not dependent on the initial Cr(III) concentration. The same effect and identical correlation were observed for the initial concentration of the chromium(III) = 0.006 mol/dm³. Therefore, a full mathematical simulation is shown only for the selected Cr(III) concentration equal to 0.002 mol/dm³.

The carriers concentration and ratios are very important for the separation in the DCSLM system. Introduction to the membrane too small or too large amounts of carriers in inadequate ratios, on the one hand, results in a significant reduction in the rate of penetration (Table 2), and on the other hand prevents the complete re-extraction (Fig. 6, 7—blue points). The time of extraction and re-extraction becomes longer. Accumulation of the Cr(III) ions in the membrane is observed (Fig. 6, 7—yellow points). Probably, chromium accumulated in the membrane clogs the pores of the membrane and reduces the rate of the process.

Addition of the second carrier (Cyanex272), provides the possibility of better packing of the molecules of the D2EHPA. Increasing the amount of carrier, which is responsible for the forming of a transport structure, creates favorable conditions for the rapid penetration of Cr(III) ions to the membrane and their efficient transport [13]. Therefore, similarly as in the case of the SLM with only D2EHPA, the process

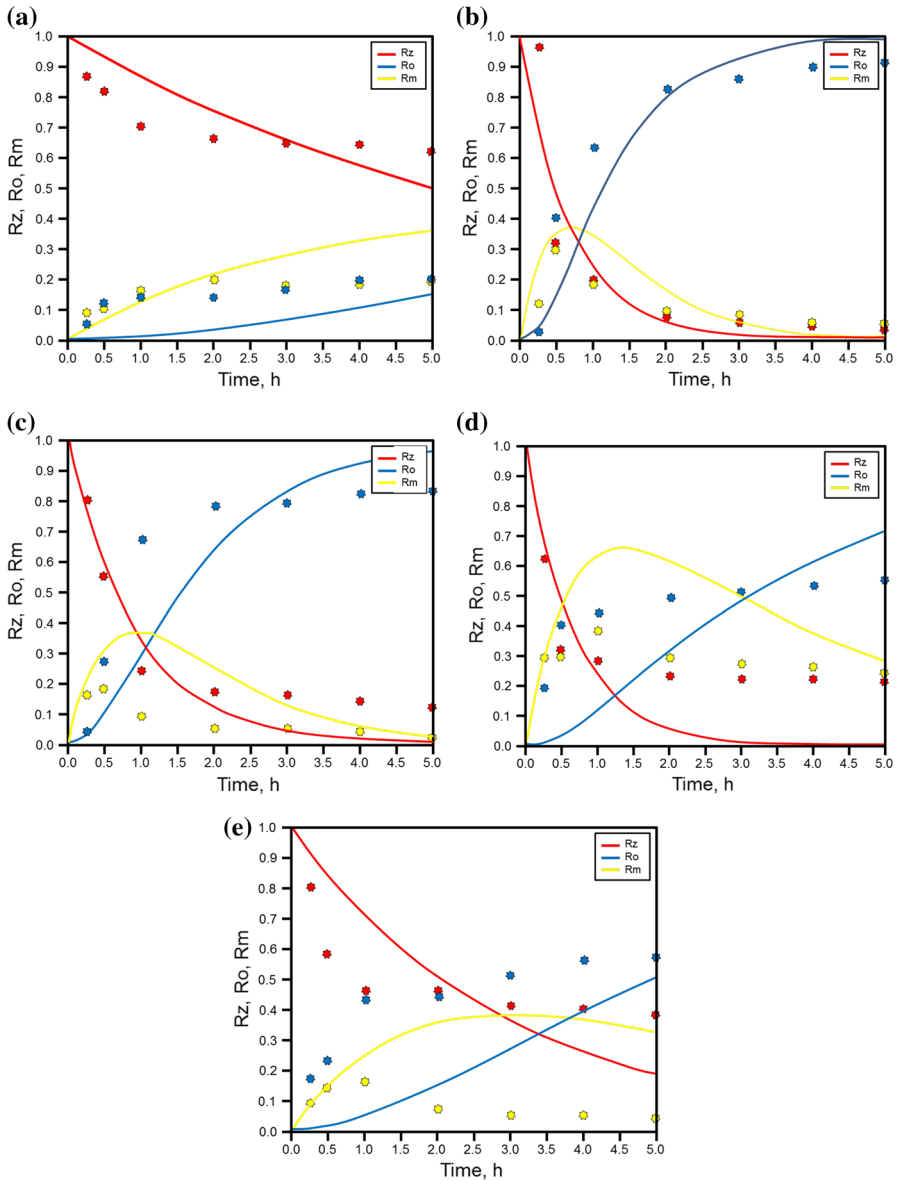


Fig. 6 Changes of Cr(III) concentration with time in: feed phase (R_Z), receiving phase (R_O) and membrane phase (R_M) for constant concentration of D2EHPA (0.45 mol/dm^3) and different concentrations of CYANEX272 (mol/dm^3): **a** 0.06; **b** 0.15; **c** 0.30; **d** 0.9; **e** 1.2. Initial chromium(III) concentration $C_{\text{Cr(III)}} = 0.002 \text{ mol/dm}^3$

should be carried out under “threshold” concentrations and ratios of the carriers. Therefore, it can be concluded that in the DCSLM system with the carrier concentration other than the “threshold”, transport structure does not provide conditions for facilitated transport of Cr(III) ions. This is illustrated in Fig. 8. In

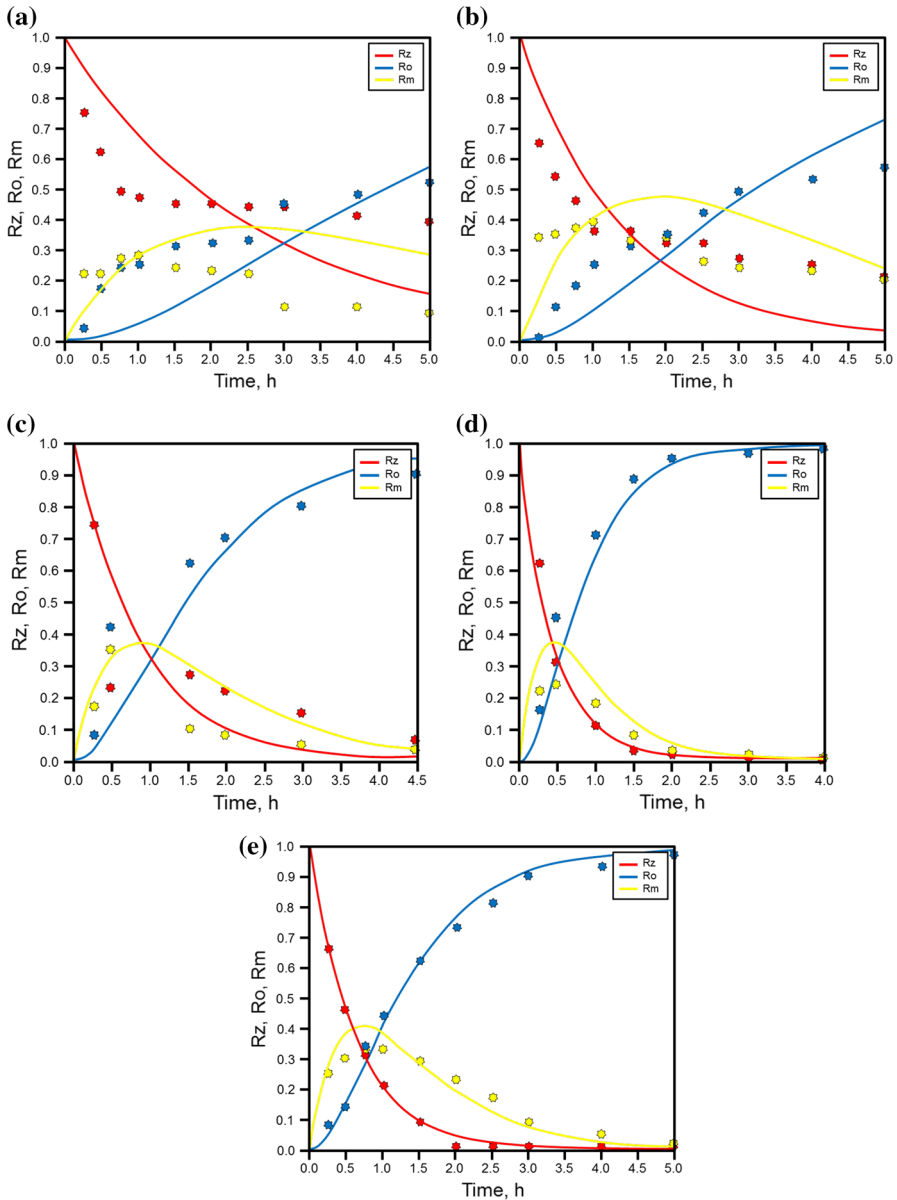


Fig. 7 Changes of Cr(III) concentration with time in: feed phase (R_Z), receiving phase (R_O) and membrane phase (R_M) for constant concentration of CYANEX272 (0.15 mol/dm^3) and different concentrations of D2EHPA (mol/dm^3): **a** 0.15; **b** 0.30; **c** 0.60; **d** 0.90; **e** 1.2. Initial chromium(III) concentration $C_{\text{Cr(III)}} = 0.002 \text{ mol/dm}^3$

case when transport structures areas overlap at “threshold” carrier concentration, the complexation reactions, releasing ions, and ions transport through the membrane are provided. When the carrier concentration is less than “threshold”, the transport

Table 2 Comparison of the coefficients (k_Z) of the Cr(III) penetrating to DCSLM with varying proportions of D2EHPA/Cyanex272

	$k_Z \times 10^{-4}$ (1/s)	Figures
$C_{Cr(III)} = 0.002 \text{ mol/dm}^3$		
0.45 mol/dm ³ D2EHPA/X mol/dm ³ Cyanex272		
0.06	0.12	6a
0.15	2.13	6b
0.30	1.51	6c
0.90	1.19	6d
1.20	0.42	6e
0.15 mol/dm ³ Cyanex272/X mol/dm ³ D2EHPA		
0.15	0.52	7a
0.30	0.96	7b
0.60	1.56	7c
0.90	3.03	7d
1.20	2.31	7e
	$k_Z \times 10^{-4}$ (1/s)	Figure
$C_{Cr(III)} = 0.006 \text{ mol/dm}^3$		
0.6 mol/dm ³ D2EHPA/X mol/dm ³ Cyanex272		
0.06	6.194	–
0.15	8.175	–
0.45	3.483	–
0.60	3.011	–
0.15 mol/dm ³ Cyanex272/X mol/dm ³ D2EHPA		
0.3	3.561	–
0.9	14.129	–
1.2	2.444	–

The initial concentration of $C_{Cr(III)} = 0.002; 0.006 \text{ mol/dm}^3$

of ions is limited (decrease in k_Z coefficient and extraction/re-extraction rate) probably because the transport structures areas overlap only partly. When the carrier concentration is more than “threshold”, the transport of ions is also limited. That’s because, as reported by Bouonomenna et al. [8], increasing the amount of carrier cause an increase in membrane phase viscosity. Thus, it can be concluded that the increase in viscosity of the membrane phase causes the accumulation of the chromium(III) ions in the membrane phase. As a consequence, this leads to process inhibition. This explains why the model based on the assumption of consecutive first-order reactions describes correctly the chromium(III) transport process in DCSLM with a D2EHPA/Cyanex272 mixture only with most effective carriers concentrations.

Moreover, we observed that in the case of most ineffective carriers concentration in DCSLM the influence of temperature on the process rate is minimal. We noted a decrease in the activation energy even to a value 24 kJ/mol. As reported Konczyk

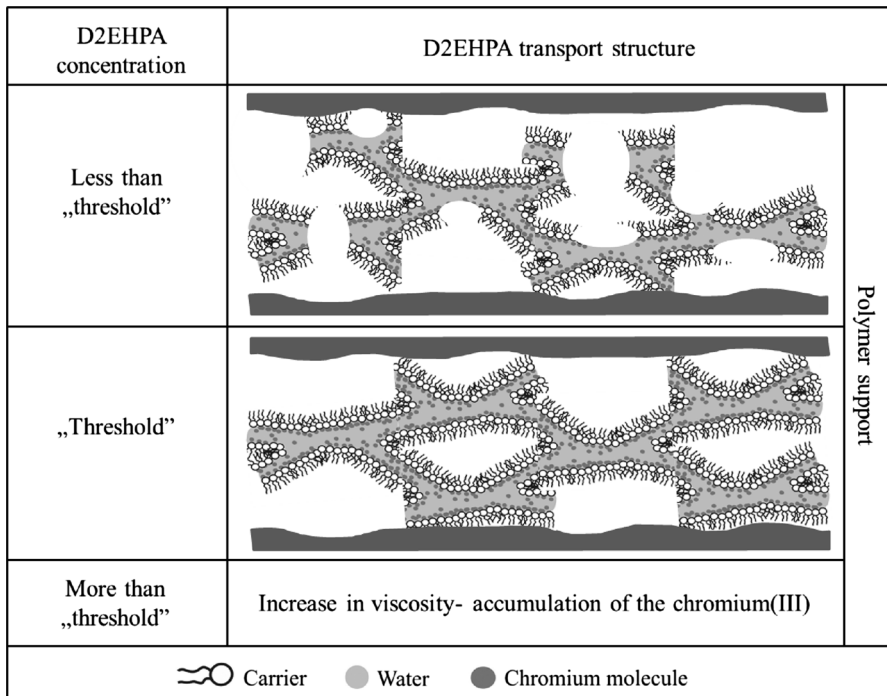


Fig. 8 Simplified scheme of D2EHPA transport structure in supported liquid membrane system. Based on [13]

et al. [17] and Lazarov et al. [21] in the liquid membrane system, under certain conditions and such values of activation energy the transport processes may be controlled by both chemical reaction and diffusion. Probably, in the DCSLM system with D2EHPA/Cyanex272 mixture the diffusion is significant at carriers concentrations ratio other than the most efficient.

This model is too simple to correctly describe the Cr(III) ions pertraction in supported liquid membrane system under the full range of process parameters (especially concentrations and proportions of the used carrier). It is necessary to develop and discuss the diffusion model which give insights into the boundary layer and support properties in SLM. Probably, it will be necessary to develop a model based on both the diffusion and chemical reactions. However, the described model can be a useful tool for quickly and approximate determination of the transport process parameters in experimental works.

Conclusion

In the discussed DCSLM system with D2EHPA/Cyanex272 mixture calculated value of the activation energy indicates that chromium(III) transport through membrane with optimum composition is controlled by chemical reaction occurring

at interface of boundary layers. For the description of the Cr(III) ions transport through the DCSLM, a model based on the assumption of consecutive first-order reactions was proposed.

The results of experiments confirm the presence of a synergistic effect of selected carriers in DCSLM. It was found that, the occurrence of the most effective concentration ratio of carriers mixtures (which guarantees the highest efficiency of the process) are independent of the initial concentrations of Cr(III) $\leq 0.006 \text{ mol/dm}^3$.

Proposed mathematical model describes correctly the transport process only in DCSLM with the most effective carriers ratio.

Probably, in the DCSLM system with D2EHPA/Cyanex272 mixture at the carriers concentrations ratio other than the most efficient the transport processes may be controlled by both chemical reaction and diffusion.

It is necessary to develop and discuss the diffusion model which give insights into the boundary layer and support properties in SLM and develop a model based on both the diffusion and chemical reactions.

Acknowledgements Many thanks are given to Cytec Canada Inc. for supplying Cyanex272.

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