

INFLUENCE OF SOME FACTORS ON THE PARAMETERS OF FACILITATED TRANSPORT FOR CHROMIUM IONS ACROSS SUPPORTED LIQUID MEMBRANES CONTAINING METHYL CHOLATE AS CARRIER

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Abstract

The technique of supported liquid membranes (SLM's) was used to achieve the facilitated transport of Chromium ions (Cr(VI) and Cr(III)), using **Methyl Cholate** as carrier, widely used for a facilitated transport of carbohydrates. For our (SLM's), we use toluene as an organic phase and microporous film of PVDF as support. **Permeability P** and **initial flux J₀** were determined for different studied factors and the prepared membranes are highly permeable. The mechanism based on the complexation of the substrate by the carrier and the diffusion of the complex (ST) was developed. The results of this phenomenon are used to determine the **association constant K_{ass}** and the **apparent diffusion coefficient D***. These studies show that these parameters **K_{ass}** and **D*** are changing significantly with different studied factors, and better extraction of this substrate is possible.

Keywords:

Supported liquid membrane, facilitated transport, flux, association constant, apparent diffusion coefficient.

Nomenclature	
a	slope of the plot $-\ln(C_0 - 2C_R) = f(t)$
C₀	initial concentration of Cr ions in the feed phase (mol.L ⁻¹)
C_r	concentration of transported Cr ions in the receiving phase (mol.L ⁻¹)
C_s	concentration of Cr ions in the feed phase (mol.L ⁻¹)
P	the permeability of the SLM for Cr ions (cm ² .s ⁻¹)
J₀	initial flux on the facilitated transport of substrate (mmol.cm ⁻² .s ⁻¹)
D*	apparent diffusion coefficient of the complex (TS) (cm ² .s ⁻¹)
K_{ass}	association constant on the formation of the complex (TS).
l	the membrane thickness (mm or μm)
S	the membrane area (cm ²)
[T]₀	concentration of carrier in the membrane (mol.L ⁻¹)
[TS]	concentration of the complex in the organic phase (mol.L ⁻¹)
T	temperature (K or °C)
t	time (s)
V	volume of the receiving compartment (cm ³)

1. INTRODUCTION

Currently, different membrane types are used for many industrial applications, to recover or separate the constituents of a mixture, or to selectively control the exchange of material between different media. The use of membrane technology has recently rapidly grown, particularly because of the increasing application areas. This development should be increased because of its good performance (low energy and use simple techniques), offered by membrane processes and due to the emerging needs of environmental protection (effluent treatment, clean processes,...). Meanwhile, these different applications, a research increasingly pushed to better understand the functioning of these membrane processes, create and develop more efficient or more specific and new methods to access new applications¹⁻⁶.

Today, it became necessary and certainly required to develop highly selective systems that are essential, considering that the realization of separations and recoveries of very harmful metal ions to the environment where complex aqueous mixtures (mainly radioactive species) exist. For this purpose, the liquid-liquid separation technique was first widely used, with more or less suitable agents, for the recovery of metal ions from complex and loaded aqueous media. This technique involves the use of complexing agents, and large amounts of organic solvents which are often expensive and toxic⁷⁻¹⁰. It includes an extracting step by phase transfer, followed by back extraction step and two steps are enough consumers of organic solvents, particularly when volatile solvents are involved. A stylish alternative to liquid-liquid extraction is the development of artificial membrane systems that mimic the process of facilitated transport across bio-membranes (by mobile carriers and more by ion channels). Liquid membranes incorporating specific complexing agents are artificial systems of choice for the treatment of liquid media charged with metal ions^{4,5}.

Our work will be limited to the supported liquid membrane (SLM), made of a polymer film, inert, microporous polyvinylidene difluoride (PVDF), a thickness of 100 μm and 69% porosity with pores of 0.45 or 0.22 μm in diameter, containing the **Methyl Cholate (MC)**, soluble in toluene phase^{5,6}. A kinetic model as well as a transport mechanism have been developed and tested, for the first time, for the facilitated transport of Crions from different solutions. The macroscopic parameters, permeabilities **P** and initial fluxes **J₀** were determined and related to microscopic parameters, the association constant **K_{ass}**, and apparent diffusion coefficient **D***, relating to the stability of the complex (Carrier-Substrate), formed at the membrane interface, and its diffusion through the SLM organic phase. The obtained results are important and will determine the movement nature of Crions through the organic phase of studied SLM, and explain the high permeability of such membranes for facilitated transport of these species.

2. THEORETICAL MODELS

2.1. Transport cell

The transport experiments were performed in the cell configured in^{4,11}.

2.2. Determination of the macroscopic parameters: permeability **P** and flux **J**

At time **t**, **C_r** is the substrate concentration in the receiving phase, and the concentration of substrate in the source phase at this time is **C_s = C₀ - C_r**. **C₀** is the substrate initial concentration. Published studies show that the equation relating permeability **P** and flux **J** to **C_r** concentration of substrate **S**, is given by the relationship^{6,11,12}:

$$P(t - t_i) = (l \times V / 2S) \ln [C_0 / (C_0 - 2C_r)] \quad (1)$$

S is the membrane active surface in contact with the source phase solution, **V** is the receiving phase volume and **l** is the membrane thickness.

For a quasi-static state applying the Fick's first law:

$$J = P \times \Delta C / l \quad (2)$$

$$\text{and } P = a \times V \times l / 2S(3)$$

With, **a** is the slope experimental value of the line $-\ln(C_0 - 2C_r) = f(t)$,

The initial flux **J₀** can be calculated as follows:

$$J_0 = P \times C_0 / l \quad (4)$$

2.3. Modelling and calculations of microscopic parameters **K_{ass}** and **D***

The complexation equilibrium in heterogeneous phases is written as follows:



S_{org} and **S_{aq}** represent the membrane organic phase and the aqueous solution of the feed phase respectively.

These same studies^{6,11,12}, show that the parameters, **J₀**, association constant **K_{ass}**, and the apparent diffusion coefficient **D*** are related to the initial concentrations of substrate **S** and carrier **T** by the Fick's second law:

$$J = (D^*/l) \times [TS](5)$$

$$1/J_0 = (1/D^*) \times [(1/[T]_0 \times K_{ass}) \times (1/C_0) + (1/[T]_0)] \quad (6)$$

$$\text{With: } K_{ass} = \text{intercept (OO)} / \text{slope (p)}, \text{ and } D^* = (l / \text{OO}) \times (1 / [T]_0) \quad (7)$$

3. Experimental section

All used chemicals reagents and solvents were pure commercial products of analytical grade (Sigma-Aldrich, Fluka, Redel-Dehaene). The Chromium ions' solutions used are obtained by hydrolysis of $K_2Cr_2O_7$, $Cr(NO_3)_3$ salts. The support is a microporous polymer film, polyvinylidenedifluoride (PVDF), a thickness of 100 μm , 69% porosity and pore diameters are 0.22 or 0.45 microns. The membrane liquid solution consists of the organic phase toluene, containing 0.01M carrier concentration (Methyl Cholate). Acidic solutions of chromium ions (0.20 - 0.025M) were prepared from a stock solution in doubly distilled pure water. After conditioning the prepared SLM^{2,4,11}, it is placed between two compartments of the transport cell, in the feed phase (F), the substrate solutions with known concentration (**C₀**), at pH = 1, 2 or 3 and in the receiving phase (R) KNO_3 solution at pH = 6. Both phases are subject to the same agitation and the kinetic monitoring of Crions transport occurs through regular sampling from the receiving phase in known time intervals. These samples were analyzed by UV-Visible spectrophotometer. Substrate concentrations (**C_r**) in the receiving phase are calculated, and the evolution of the term $-\ln(C_0 - 2C_r)$ versus time was studied.

4. Results and Discussion

4.1. Influence of the PVDF pore diameter

In an evident manner, we think that the permeability of a SLM must increase when the pore diameter increases. In an analogue fashion, instability should increase and less solvent being retained within large pores¹³. However, the literature reports contradictory results concerning the influence of the pore diameter, e.g the permeability of a PTFE membrane for the uranyl ion decreases when the pore diameter increases¹⁴. On the contrary, some authors have investigated the transport of chromium ions through two PTFE membranes containing tri-n-butyl phosphate (TBP) as a carrier and they showed that the membrane with a pore diameter of 1.0 micron is more permeable than the membrane with pore diameter of 0.5 micron¹⁵. Our results show a great permeability when the pore diameter increases.

4.1.1. Influence of pore diameter on P and J_0

The macroscopic parameters P and J_0 have been determined for each of the pH values for an initial concentration of substrate $C_0 = 0.20M$. The results (Fig. 2 and Fig. 3) show that the values of permeability and initial flux related to the support PVDF (0.22 microns) are smaller than those of the support PVDF (0.45 microns) for the three studied pH, knowing that both types of support have the same porosity, 69%.

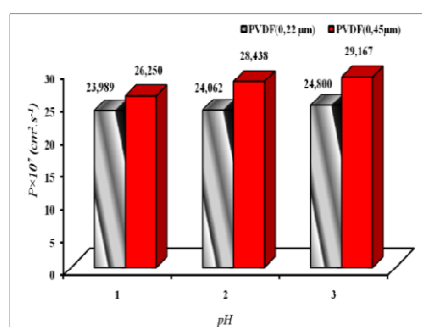


Fig. 1: Influence of pore diameter on permeability on facilitated transport of Cr(VI) ions. (0.20M). Toluene phase, $T = 298 \text{ K}$.

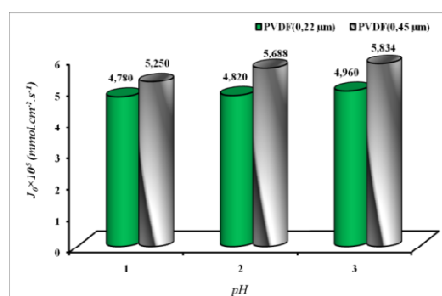


Fig. 2: Evolution of the initial flux on the transport of Cr(VI) (0.20M) as function the pore diameter. Toluene phase, $T = 298 \text{ K}$.

4.1.2. Influence of pore diameter on D^* and K_{ass}

The microscopic parameters are also determined for each values of the pH and for the two used supports, Fig. 4 and Fig. 5. SLM's with large pore diameters are generally more permeable and more stable than those with reduced pore diameters.

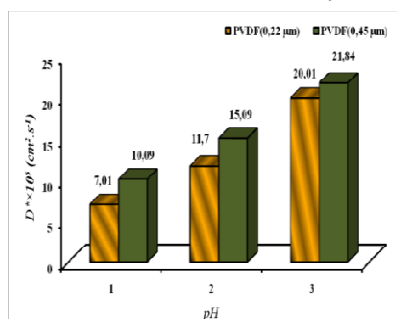


Fig. 3: Influence of the pore diameter on the values of the **apparent diffusion coefficient** for facilitated transport of Cr(VI) (0.20M). Toluene phase, T = 298 K.

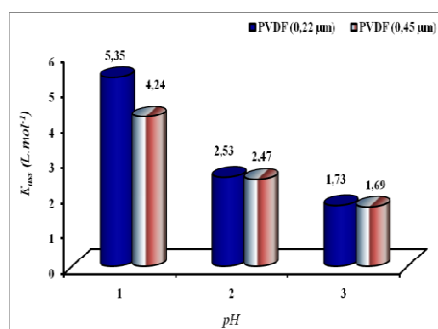


Fig. 4: Effect of pore diameter on the values of the **association constants** for the facilitated transport of Cr(VI) (0.20M). Toluene phase, T = 298 K.

4.2. Influence of substrate concentration

For facilitated transport, the mechanism in which the migration of the complex carrier-chromium (TS) is the rate-determining step, this phenomenon is characterized by saturation kinetic law. In this case, the initial flux of the chromium ion J_0 is proportional to the carrier concentration $[T]_0$, but depends on the initial chromium concentration C_0 by type law Michaelis-Menten.

The parameters (macroscopic and microscopic) relating to the transport were determined for different chromium ions concentrations. To examine the influence of the chromium ion configuration, so transport of this element under the two oxidation states Cr(VI) and Cr(III). Their facilitated transport was studied under similar conditions. The solvent is toluene, the carrier concentration is 0.01M and the support is PVDF 0.45 microns (the best support).

Table I: Permeability P and initial flux J_0 for different initial concentrations (C_0) of Chromium element.

oxidation states	Cr(VI)		Cr(III)	
$C_0 = [\text{Cr}]_0$ ($\text{mmol} \cdot \text{cm}^{-3}$)	$P \times 10^7$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	$J_0 \times 10^5$ ($\text{mmol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$)	$P \times 10^7$ ($\text{cm}^2 \cdot \text{s}^{-1}$)	$J_0 \times 10^5$ ($\text{mmol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$)
0.20	28.437	5.687	22.012	4.404
0.10	30.625	3.062	24.281	2.428
0.05	32.084	1.604	26.834	1.341
0.025	34.271	0.856	29.677	0.742

$\text{pH}_F=2$, $\text{pH}_R = 6$, Toluene phase and T = 298 K.

Table I presents the values of permeabilities and initial fluxes on the transport of two studied ions. These results show clearly that the permeability P of the SLM varies inversely with the chromium ions concentration and an increase in substrate concentration leads to a reduction in permeability. In contrast, the fluxes J_0 of Cr ions through the SLM follow the same direction as the substrate concentration C_0 ^{16,11}. It is deduced that the complex (Cr(III)-MC) formed in the organic phase of the SLM by association (substrate-carrier) is more stable than that formed by association of Cr(VI) with the same carrier (Cr(VI)-MC), and therefore migration of the second complex through the organic phase of the SLM is more important (P and J_0 for Cr(VI) \gg P and J_0 for Cr(III)).

To verify the developed model for explaining the mechanism relating the facilitated transport of chromium ions (VI and III) by the prepared SLM's and to determine the coefficients D^* and constants K_{ass} we plotted the straight of Lineweaver-Burk, $1/J_0 = f(1/C_0)$ provided by equation (6). Fig. 6 presents the straight of Lineweaver-Burk for two studied elements.

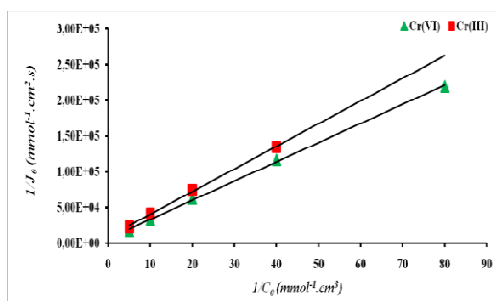


Fig. 5: Lineweaver-Burk lines on the transport of Cr (VI) and Cr (III) ($C_0 = 0.20, 0.10, 0.05, 0.025$ M), $[MC] = 0.01$ M, $pH_F = 2$, Toluene phase and $T = 298$ K.

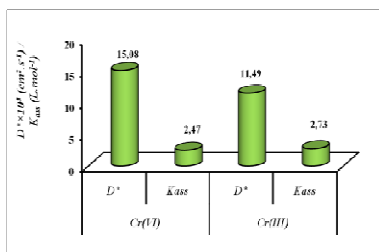


Fig. 6: Histogram of the parameters K_{ass} and D^* relating to facilitated transport of Cr (VI) and Cr (III), $[MC] = 0.01$ M, $pH_F = 2$, Toluene Phase and $T = 298$ K.

The obtained results show clearly that the proposed model to explain the transport mechanism is verified and there is interaction between the substrate and the carrier for forming a complex (TS) of composition (1/1) in the SLM organic phase and the migration of the complex through this phase constitutes the rate-determining step of the mechanism relating to the transport of chromium (VI and III) ions. The slopes (p) and intercepts (oo) were calculated from straight in Fig. 6 and by using the expression of equation (7), the coefficients D^* and constant K_{ass} were determined. The results are represented in Fig. 7 and make it clear that both microscopic parameters are different for both types of studied Chromium ions. Therefore the Cr(III) provides the most stable complex and the Cr(VI) forms the less stable complex in the organic phase.

In conclusion, the permeabilities (and eventually the initial fluxes) of the different forms of Chromium ions vary in the same order as the apparent diffusion coefficient D^* , but in reverse of association constants K_{ass} (Fig. 7). So, for each element, the permeability is resulting by a compensation between the values of parameters K_{ass} and D^* , which explains why the permeabilities are approximately similar, of a concentration to another for both elements, despite the significant difference between the association constants.

4.3. Influence of the nature of mineral acids on the transport of Cr(III)

The nature of mineral acids proved as an important factor on facilitated transport of metal ions through the liquid membranes^{4,17}.

For this study, we carried out the similar experiences under the same conditions with the same SLM containing Methyl Cholate as carrier. In this section, we tested the effect of the nature of some usual inorganic acids (HCl, HNO₃) and especially the effect of co-ions: Cl⁻, NO₃⁻ on the facilitated transport of Cr(III) ions. To do this, we set the pH_F at 2, and pH_R at 6, the pH is adjusted with an acid of the two aforementioned acids. In the receiving phase we put a salt corresponds to the same co-ion of feed phase. Under the same operating conditions as the Cr(VI)¹⁸, Cr(III) was transported by the same SLM and from acidic environments (HCl and HNO₃) for comparing the mechanism of the two elements by changing the nature of the acid and consequently by changing the conjugated co-ion.

The straight presented by Fig. 8 are linear, this means that the suggested kinetic law is verified in this case, and we can calculate the macroscopic parameters on facilitated transport for Cr(III).

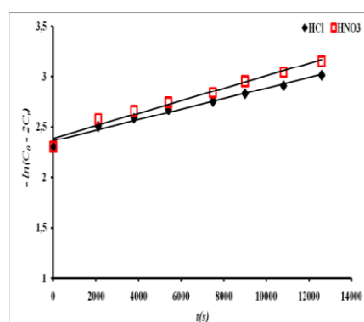


Fig. 7: Evolution of $-\ln(C_0 - 2C_r) = f(t)$ for the transport of $[Cr(III)]_0 = 0.10M$, $pH_F = 2$ $[MC] = 0.01 M$ and $T = 298K$.

The determined permeabilities and fluxes for the facilitated transport of ions Cr(III) in these new solutions are summarized in Table II.

Table II: Influence of the nature of acids and the acidity of the medium on the transport parameters for the Cr(III).

pH _F (HCl, HNO ₃)	C ₀ = [Cr(III)] ₀ (mmol.cm ⁻³)	P × 10 ⁷ (cm ² .s ⁻¹)		J ₀ × 10 ⁵ (mmol.cm ⁻² .s ⁻¹)	
		HCl	HNO ₃	HCl	HNO ₃
1	0.20	14.583	14.875	2.916	2.975
	0.10	16.843	17.281	1.684	1.728
	0.05	19.979	20.854	0.998	1.042
2	0.20	16.770	16.916	3.354	3.383
	0.10	19.177	19.468	1.917	1.946
	0.05	21.875	22.166	1.093	1.108
3	0.20	18.375	19.760	3.675	3.952
	0.10	21.145	25.958	2.114	2.442
	0.05	23.552	24.427	1.177	1.297

[MC] = 0.01 M, pH_R=6, Toluene phase and T = 298 K.

The results in this Table allow us to plot the straight of Lineweaver-Burk, $1/J_0 = f(1/C_0)$ provided by equation (6), the resulting segments are linear and represented by the graph Fig. 9 for both studied acids.

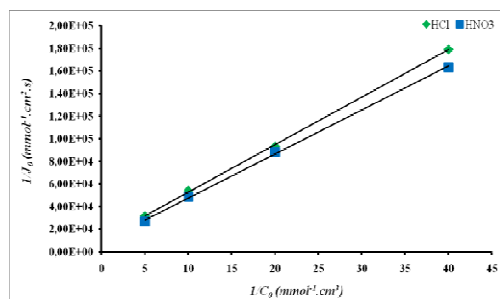


Fig. 8:Lineweaver-Burk lines for the transport of Cr(III). [MC] = 0.010M, Toluene phase, $pH_F = 2$ and $T = 298K$.

Using equation (7), the apparent diffusion coefficient D^* and the association constants K_{ass} has been determined for the three acidities of the two used acids. The results of the facilitated transport of Cr(III) ions under these conditions are represented by Fig. 10 and Fig. 11. These results verify that the values of the constant K_{ass} vary in the same direction as the acidity of the medium for the two studied acids, while the values of the coefficient D^* vary inversely.

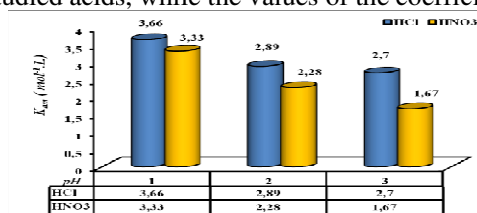


Fig. 9: Histogram of the evolution of K_{ass} depending on the nature of studied acids,[MC] = 0.01 M, $pH_F = 2$, Toluene phase and $T = 298K$.

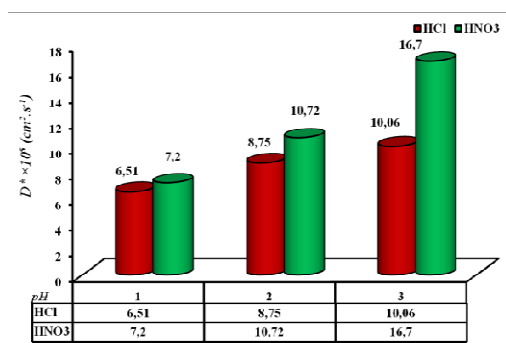


Fig. 10: Histogram of the evolution of D^* depending on the nature of studied acids,[MC] = 0.01 M, $pH_F = 2$, Toluene phase and $T = 298K$.

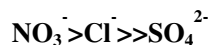
These results show once again that the values of the parameters D^* and K_{ass} on the transport of Cr(III) ions through the SLM-MC are functions of acidity of the medium and depends on the nature of the used acid and so of the co-ion present in this medium. Indeed, nitric acid is the best to use and the presence of co-ion of nitrate (NO_3^-) in the medium provides the best results with decrease in values of the constants K_{ass} and so the increase in values of the coefficients D^* . This evolution is more clear in the case of transport of the substrate Cr(VI)¹⁸ than for the substrate

Cr(III), this is probably due to the nature of the liaisons in the two complexes (TS) formed by interaction Methyl Cholate (MC) with the substrates (Cr(VI) or Cr(III)).

From these results, it is clear that the co-ion NO_3^- accompanies each of the two substrates within the organic phase and its presence in this phase makes each complex (TS) less stable, thus a more weak liaisons and significant improvement of the migration of the substrate across the SLM. This influence is certainly due to the formation of a less stable **ternary complex** with engagement with co-ion, this feebleness is much more marked for the complex (Cr(VI)-MC) than for its homologue Cr(III)-MC.

Discussion

The rate of facilitated transport of Cr(VI)¹⁸ across the SLM-MC in a medium containing anions NO_3^- is higher than that of a medium containing the anions Cl^- , and in third-order is the medium enclosing the anions SO_4^{2-} . The same evolution is observed for the facilitated transport of Cr(III) ions through SLM-MC in medium containing the same anions (NO_3^- and Cl^-). In general, the efficiency of ions in the phenomenon of coupled transport increases in the opposite order of their hydration:



This behaviour of the SLM-MC membrane toward Chromium ions seems to be governed by two factors:

- (i) The hydrophobicity and nucleophilicity / electrophilicity of the carrier in this SLM-MC led to an increase in the instability of MC-anions complex and to the stability of MC-cations complex¹⁹.
- (ii) the solubility of anions in the hydrophobic organic phase of the SLM-MC, is depending on the hydration of the anions²⁰, the selectivity of the used membrane for this system, is not only defined by the local extraction constant, but also by the degree of hydration of the transported anion (Table III).

Table III: the values of the free hydration energy ($-\Delta G_h$) for the three studied co-ions²¹

Anions	NO_3^-	Cl^-	SO_4^{2-}
$-\Delta G_h$ (kJ.mol ⁻¹)	0.0024	0.32	0.47

$-\Delta G_h$: free Gibbs' energy: free energy of hydration of free ion in water.

Previous studies indicate that the order of the limits of permeability is correlated with the molar free hydration energy of free ions in water (Gibbs' energy)²².

The driving force across a SLM-MC system is based mainly on the substrate-carrier interactions and the concentration gradient of metal species or other species known as co-ion in the coupled transport phenomenon²³⁻²⁶. Consequently the nature of these interactions and the ionic composition of the aqueous solutions (feed and receiving phases), represent an essential role in the facilitated transport governance of these metal ions. This finding is observed on the one hand, from our experimental results that show that there is certainly formation of a less stable ternary complex in the organic phase of the SLM-MC with presence of the co-ion NO_3^- than counterparts Cl^- and SO_4^{2-} , on the other hand from several studies in which transport experiments are carried out with several different ions in coupled transport and under a similar concentration gradient²⁷.

In these studies, a better transport of targeted metal ions is systematically reported when we have decrease free hydration energy of present ions in medium. However, it should be noted that most of ions in coupled transport can act like complexing agents. Therefore, the phenomena discussed here are further complicated by the fact that the types of metal species present in the medium are often functions of the concentration²⁸ and the facilitated transport of targeted metal ion can be influenced by competition with other ions in the aqueous phase. As indicated in the literature, in the majority of cases^{29,30}, the efficiency's order of simple inorganic anions on coupled transport should follow the order of free energy of hydration of these anions, thus their degree of participation in the formation of the **ternary complex** in the organic phase of the SLM (ST-Co-anion).

5. CONCLUSIONS

The mechanism established and adopted kinetic model was verified by all the experimental results related to the process of facilitated transport of these metal ions by using the prepared membranes. The parameters **P**, **J₀** and **K_{ass}**, **D*** were determined for different experimental conditions and the influence of factors: the initial substrate concentration (**C₀**), the effect of the pore diameter of used films and the nature of co-ions and their concentration on the evolution of these parameters were studied. The results have allowed us to establish relationships expressing the evolution of each of these parameters (**P**, **J₀** and **K_{ass}**, **D***) depending to studied factor.

Studies related to the influence of the presence of co-ions in the feed phase (anions **NO₃⁻**, **Cl⁻**, **SO₄²⁻**) show unambiguously that the nature of these anions and their presence has an enormous influence on the evolution of the facilitated transport parameters of these metal ions. In fact the results have revealed a strong influence of the presence of nitrate anions **NO₃⁻** on **K_{ass}**, and **D*** and the increase in concentration of these anions in feed phase results in decrease stability of the complex (TS) formed in the organic phase of the membrane and therefore more low values of **K_{ass}** and more high values of **D*** and so a more efficient membrane.

These results are very important and indicate unambiguously that in this process of facilitated transport on the one hand; the presence of the nitrate anions in the feed phase allows for the participation of these anions to the substrate-carrier interactions for forming the complex (TS) and it accompany the substrate within the membrane organic phase. The results also indicate that this participation makes the low stability of the complex (TS) and affects the stability and the nature of the established liaisons between the substrate and the carrier. On the other hand, these results enabled us to be certain that the migration of the substrate through the organic phase (rate-determining step) is not a simple diffusion movement of the complex (TS). In fact, if it was the case there was no reason that the presence of these anions in the feed phase and their participation for forming the complex (TS) leads an increasingly important diffusion of this complex, but contrary would block the participation of the diffusion movement and would cause a less efficient membrane.

Consequently, the obtained results indicate clearly that this presence and participation of these anions for formation-dissociation reactions (substrate/carrier) at source / membrane interfaces and in membrane phase reduce more the stability of the formed complex, increase the rates of these reactions and allow increasingly important diffusion of the substrate according a consequence of dissociation-association reactions by the successive jumps of substrate from one site to another on mobile carriers in the used membrane.

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