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The technology of SLM's for the Facilitated Extraction of Chromium ions from acidic medium: Comparison of extraction parameters and Complexation mechanism

Abdelkhalek Benjjar [a.b] *, Mohammed Riri [a], Mustapha Hor [a], Tarik Eljaddi [a], Laurent Lebrun [b], Miloudi Hlaibi [a.b]

[a] *Laboratoire Interface Matériaux et Environnement (LIME). Université Hassan II*
Faculté des Sciences Aïn Chock. B.P. 5366. Maârif 20101 Casablanca. Morocco.
[b] *Laboratoire des Polymères. Biopolymères. Surfaces. UMR 6270 du CNRS. Université de Rouen.*
Faculté des Sciences et Techniques. F-76821 Mont-Saint-Aignan. France.

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** Corresponding author; E-mail address: abdelkhalek.benjar@gmail.com*

Abstract

The technology of supported liquid membranes (SLM's) was used to achieve the facilitated extraction of Chromium ions (Cr(VI) and Cr(III)), using **Methyl Cholate (MC)** and **Resorcinarene (RESO)** as carriers, widely used for a facilitated extraction of carbohydrates. For our (SLM's), we use Toluene as an organic phase and PVDF microporous film as support. A kinetic model as well as an extraction mechanism have been developed and tested, in the first time, for the facilitated extraction of **Cr** ions from different acidic solutions. The macroscopic parameters, permeabilities **P** and initial fluxes $\mathbf{J_0}$ were determined and related to microscopic parameters, the association constant $\mathbf{K_{ass}}$, and apparent diffusion coefficient **D***, relating to the stability of the complex (Carrier-Substrate **TS**), formed at the membrane interface, and its diffusion through the SLM organic phase. The obtained results are important and used to determine the complexation nature of Cr ions in the organic phase of the studied SLM and to explain the high permeability of such membranes for facilitated extraction of these species. These studies show that these parameters $\mathbf{K_{ass}}$ and **D*** are changing significantly with different used carriers so the better extraction of these substrates is possible.

Keywords: supported liquid membrane, facilitated extraction, flux, association constant, apparent diffusion coefficient

Nomenclature

a	slope of the plot -ln $(C_0\text{-}2C_R) = f(t)$
$\mathbf{C_0}$	initial concentration of Cr ions in the feed phase (mol.L^{-1})
$\mathbf{C_r}$	concentration of transported Cr ions in the receiving phase (mol.L^{-1})
$\mathbf{C_s}$	concentration of Cr ions in the feed phase (mol.L^{-1})
P	the permeability of the SLM for Cr ions (cm^2.s^{-1})
$\mathbf{J_0}$	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})
$\mathbf{K_{ass}}$	association constant on the formation of the complex (**TS**).
l	the membrane thickness (mm or µm)
S	the membrane area (cm^2)
$\mathbf{[T]_0}$	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

The utilization of membrane technology has rapidly grown, due to increasing application domains. This development should be increased due to its good performance (low energy and utilization simple techniques), offered by membrane processes and due to the new requirements to protect the environment (wastewater treatment, clean processes ...). In parallel with these applications, further research is conducted to better understand the functioning of these membrane processes, to create and develop more effective or more specific methods in order to access new applications [1- 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 exist (mainly radioactive species). 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 charged aqueous media. This technique involves the use of complexing agents and large amounts of organic solvents which are often expensive and toxic [7-10]. It includes an extracting step by phase transfer, followed by re-extraction step so two steps are enough consumers of organic solvents, particularly when volatile solvents are involved. An alternative to liquid-liquid extraction is the development of artificial membrane systems that mimic the process of facilitated extraction across bio-membranes (by mobile carriers and more by ion channels). Liquid membranes incorporating specific complexing agents are artificial systems for the treatment of liquid media charged with metal ions [4, 5]. The novelty of this work is to propose and compare the architecture of complexes formed through supported liquid membranes prepared during the facilitated extraction of Cr(VI) and Cr(III) ions by using **Methyl Cholate** and **Resorcinarene** and also the determination of transport parameters specific to these ions. Our work will be limited to the supported liquid membranes (SLM's), made of a polymer film, inert, microporous polyvinylidene difluoride (PVDF), a thickness of 100 µm and 69% porosity with pores of 0.45 µm in diameter, containing the following amphiphilic carriers: **Methyl Cholate** and **Resorcinarene**, soluble in Toluene phase [5,6]. The description and operating principle of the SLM's was detailed in the publications [4, 11, 12].

2. Theory

2.1. Calculations of the macroscopic parameters: permeability P and flux J

At time **t**, $\mathbf{C_r}$ is the substrate concentration in the receiving phase, and the concentration of substrate in the source phase at this time is $\mathbf{C_s} = \mathbf{C_0} - \mathbf{C_r}$. $\mathbf{C_0}$ is the substrate initial concentration. Published studies show that the equation relating permeability **P** and flux **J** to $\mathbf{C_r}$ concentration of substrate **S,** is given by the relationship [6,11,12]:

$$\mathbf{P\ (t - t_L) = (l \times V/2S)\ ln\ [C_0 / (C_0 - 2C_r)]} \qquad (1)$$

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:

$$\mathbf{J} = \mathbf{P} \times \Delta C / l \qquad (2)$$

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

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

The initial flux $\mathbf{J_0}$ can be calculated as follows:

$$\mathbf{J_0} = \mathbf{P} \times C_0 / l \qquad (4)$$

*2.2. Calculations of microscopic parameters K_{ass} and D**

The complexation equilibrium in heterogeneous phases is written as follows:

$$\mathbf{S_{aq} \quad + \quad T_{org} \Longleftrightarrow TS_{org}}$$

$\mathbf{_{org}}$ and $\mathbf{_{aq}}$ represent respectively the membrane organic phase and the aqueous solution of the feed phase.

These same studies [6,11,12], show that the parameters, $\mathbf{J_0}$, association constant $\mathbf{K_{ass}}$, and the apparent diffusion coefficient **D*** are related to the initial concentrations of substrate **S** and to the carrier **T** by the Fick's second law:

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

$$\mathbf{1/J_0 = (l /D^*)\ x\ [(1 / [T]_0\ x\ K_{ass})\ x\ (1/C_0) + (1 / [T]_0)]} \qquad (6)$$

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

3. Experimental

The transport experiments were performed in the cell configured in [4, 11]. All used chemicals reagents and solvents were pure commercial products of analytical grade (Sigma-Aldrich, Fluka, and Redel-Dehaene). The used Chromium ions solutions are obtained by hydrolysis of $K_2Cr_2O_7$ and $CrCl_3$ salts. The support is a microporous polymer film, polyvinylidene difluoride (PVDF), with a thickness of 100 µm, 69% porosity and a pore diameter is 0.45 microns. The membrane liquid solution consists of the organic phase Toluene, containing 0.01 M carrier concentrations (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] is placed between two compartments of the transport cell (Figure 1) , in the feed phase (F), we introduce the substrate solutions with known concentration $\mathbf{(C_0)}$ and at pH = 1, 2 or 3 and in the receiving phase (R) a KCl solution at pH = 6. The two phases are subjected to the same agitation, and kinetic study on the transport of Cr ions is performed by regular sampling of a small amount from receiving phase at known time intervals. These samples were analyzed by standard Helios γ UV-Visible spectrophotometer, controlled by software VISION 32, at wavelengths of 260 nm for Cr(VI) and 215 nm for Cr(III), sometimes for Cr(III) the dosage is made by complexing with EDTA. The concentrations of substrate $\mathbf{(C_r)}$ in the receiving phase are calculated, and the evolution of the term **-Ln** $(\mathbf{C_0} \mathbf{-2C_r})$ versus time was studied.

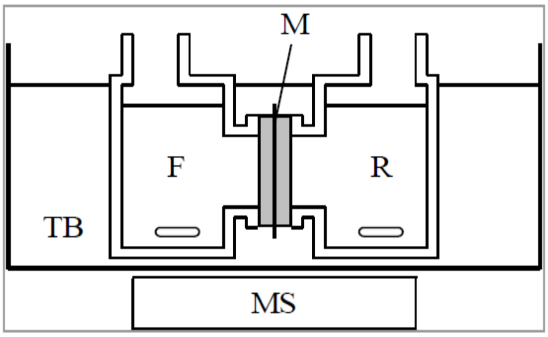

Figure 1: Scheme of the transport cell.

M: is the SLM.
F: is the feed phase. (Feed).
R: is the receiving phase.
TB: is the thermostated bath.
MS: is a multi-magnetic stirrer.

4. Results and Discussion

Various studies show that the nature and structure of the extractant are among the important and paramount factors for the facilitated extraction of metal ions and organic molecules through SLM's [13-16]. To check the influence of the nature and structure of the extractant, we conducted the same experiments under the same conditions with two SLM's each one containing two amphiphilic supramolecular the Methyl Cholate (MC) or Resorcinarene (RESO) as carriers. For both prepared membranes, the kinetic model and the mechanism for the facilitated extraction of chromium (VI and III) have been well established and verified.

4.1. facilitated extraction of hexavalent chromium (Cr(VI))

We compare the obtained results with the two prepared SLM's. Indeed, manipulations of the facilitated extraction of this substrate were performed under the same conditions by the two SLM's, each containing one of two carriers MC or RESO. The straight lines of function $-Ln\ (C_0 - 2C_R) = f(t)$ represented by the graph in **Figure 2** allows us to determine the macroscopic parameters.

Permeabilities **P** and initial fluxes J_0 are calculated for the four substrate concentrations and at different acidities by using equations (3) and (4). The obtained results are summarized in the table 1.

These results confirm that the macroscopic parameters **P** and J_0 depend on the initial concentration C_0 of ions Cr(VI) and that the Methyl Cholate is best extractant to extract these ions from concentrated acidic media. To determine the microscopic parameters K_{ass} and **D*** related to the phenomenon of extraction of these ions by the two SLM's, we trace the lines of Lineweaver-Burk (**Figure 3**). The slopes (**p**) and intercepts (**oo**), calculated from these line segments were used in the expressions of equation (7). The apparent diffusion coefficient **D*** and the association constant K_{ass} were thus determined for the three studied acidities. The overall results are grouped in **Table 2**. These results clearly show that the constant K_{ass} vary in the same direction as the acidity of the medium, while the coefficient **D*** vary inversely.

The values of these two microscopic parameters show that the complex (**TS**) formed in the organic phase of the membrane "SLM-MC" is more stable than that formed in the organic phase of the membrane "SLM-RESO" whereas diffusion of this complex through the organic phase of "SLM-MC" is more important, which clearly indicates that the facilitated extraction of these substrates is highly dependent on the chemical nature and structure of the extractant and the values of the parameters **D*** and K_{ass} are functions of the nature of the substrate and of the used SLM.

All the obtained results for the two prepared SLM indicate that the facilitated extraction of these ions by this type of membranes is very efficient and certainly more applications can be envisaged. The high values of the apparent diffusion coefficients **D*** indicate that the migration of the complex (**TS**) through the organic phase is not a pure diffusion and further studies are needed to elucidate the true movement of the complex through the SLM for these ions (Cr(VI)).

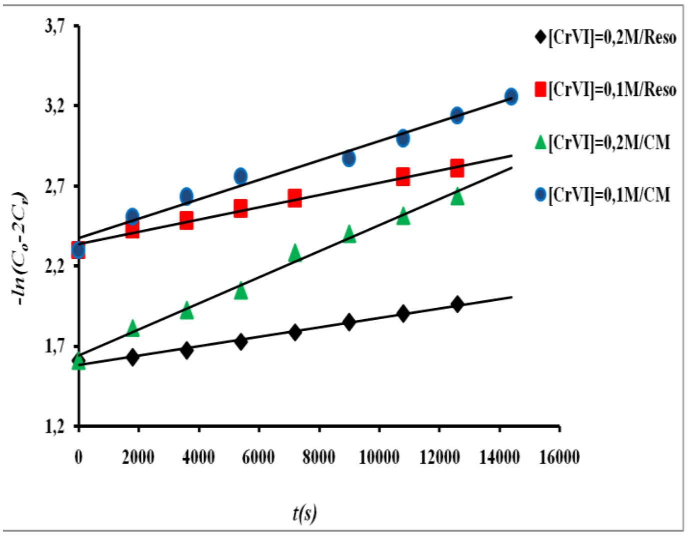

Figure 2: Evolution of ***-Ln*** $(C_0 - 2C_R) = f(t)$ for the extraction of Cr (VI), $pH_F = 2$ $pH_R = 6$, [MC] = [RESO] = 0.01 M phase Toluene and T = 298 K.

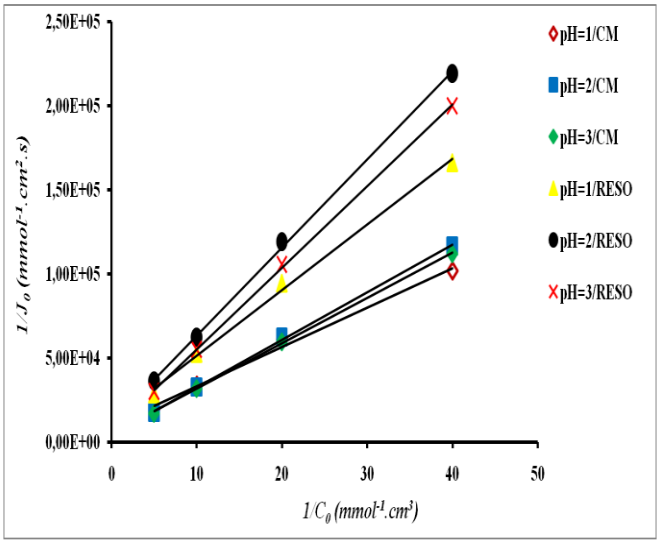

Figure 3: Lineweaver-Burk straight for the extraction of the ions Cr(VI) by the two SLM's [MC] = [RESO] = 0.01 M, $pH_F = 2$, $pH_R = 6$, Toluene phase and T = 298 K.

Table 1: Influence of the nature of the extractant on the macroscopic parameters **P** and $\mathbf{J_0}$ related to facilitated extraction of ions Cr(VI).

pH_F	$C_0 = [Cr(VI)]_0$ (M)	$P \times 10^7$ ($cm^2.s^{-1}$) MC/RESO	$J_0 \times 10^5$ ($mmol.cm^{-2}.s^{-1}$) MC/RESO
1	0.20 0.10 0.05 0.025	26.250/17.500 29.895/18.958 32.812/21.145 39.375/24.062	5.250/3.500 2.989/1.895 1.640/1.057 0.984/0.601
2	0.20 0.10 0.05 0.025	28.437/13.854 30.625/16.041 32.083/16.770 34.270/18.229	5.687/2.770 3.062/1.604 1.604/0.838 0.856/0.455
3	0.20 0.10 0.05 0.025	29.166/16.770 31.354/18.229 33.541/18.958 35.729/19.979	5.833/3.354 3.135/1.822 1.677/0.947 0.893/0.499

$pH_R = 6$, Toluene phase, T= 298 K.

Table 2: Influence of the nature of the extractant on the parameters **D*** and $\mathbf{K_{ass}}$ for the extraction of Cr(VI).

pH_F	*Extractant*	K_{ass} ($L. mol^{-1}$)	$D^* \times 10^5$ ($cm^2.s^{-1}$)
1	*MC/RESO*	4.23 / 3.23	10.08 / 7.95
2	*MC/RESO*	2.47 / 2.08	15.08 / 9.16
3	*MC/RESO*	1.69 / 1.31	21.83 / 15.67

$pH_R = 6$, Toluene phase, T= 298 K.

4.2. facilitated extraction of trivalent chromium (Cr(III))

In this section we develop a simple and efficient technical for the extraction of Cr(III) ions from acidic environments. We always use the same supported liquid membranes (SLM's). The kinetic model and the mechanism of extraction that have been developed have been checked for the facilitated extraction of Cr(III) ions from different acidic solutions. The macroscopic parameters permeabilities **P** and initial flux $\mathbf{J_0}$ were determined and related to microscopic parameters, the apparent diffusion coefficient **D*** and the association constant $\mathbf{K_{ass}}$ relating to the complex (TS) formed in the organic phase.

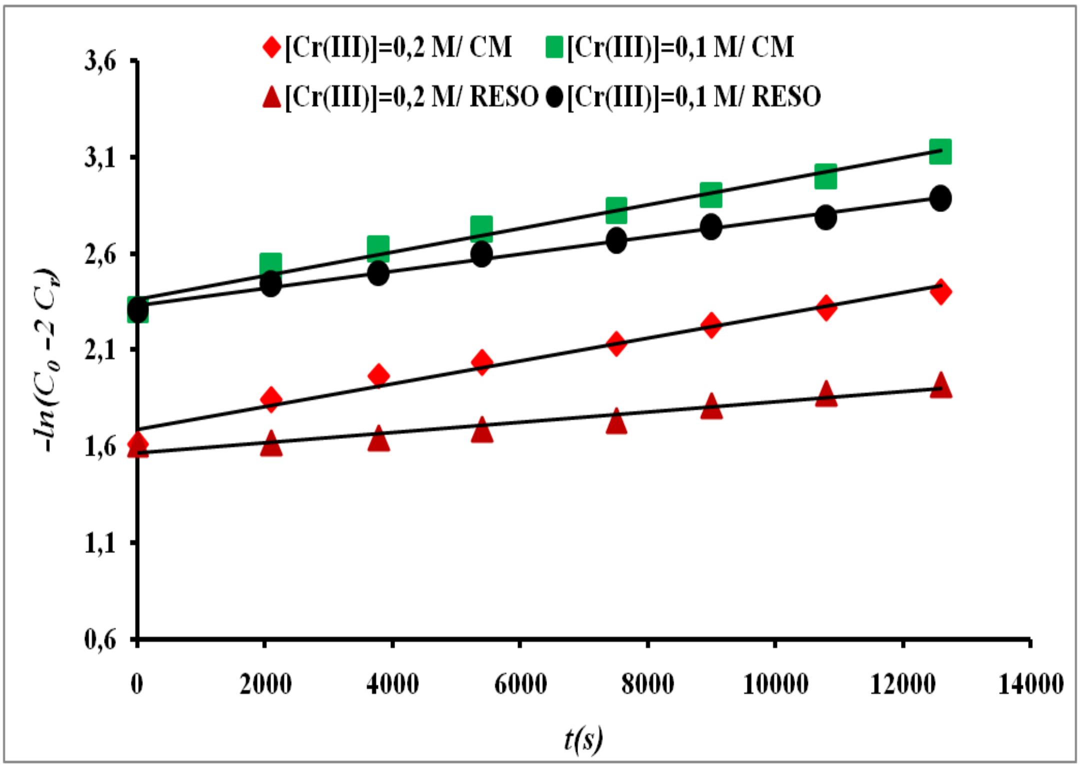

Figure 4: Evolution of the function ***-Ln*** $\boldsymbol{(C_0 - 2C_r) = f(t)}$ for the extraction of Cr(III) through the SLM's, $pH_F = 2$, $pH_R = 6$, [MC] = [RESO] = 0.01M, Toluene phase and T = 298 K.

Using the two extractants, MC and RESO, the suggested kinetic law is verified for the ions Cr(III). This is shown by the linearity of straight segments in **Figure 4**. Macroscopic parameters (**P** and $\mathbf{J_0}$) were calculated for the four substrate concentrations and at different acidities by using equations 3 and 4. The results are summarized in Table 3.

Table 3: Influence of extractant nature on macroscopic parameters for the extraction of Cr(III) ions.

pH (F)	$C_0 = [Cr(III)]_0$ *(M)*	$P \times 10^7$ $(cm^2.s^{-1})$ *MC/ RESO*	$J_0 \times 10^5 (mmol.cm^{-2}.s^{-1})$ *MC/ RESO*
1	0.20 0.10 0.05 0.025	14.583 / 06.125 16.843 / 08.968 19.979 / 10.791 21.875 / 12.979	2.916 / 1.225 1.684 / 0.896 0.998 / 0.539 0.546 / 0.324
2	0.20 0.10 0.05 0.025	16.770 / 14.583 19.177 / 17.645 21.875 / 21.000 23.625 / 23.516	3.354 / 2.916 1.917 / 1.764 1.093 / 1.050 0.590 / 0.587
3	0.20 0.10 0.05 0.025	18.375 / 17.572 21.145 / 20.927 23.552 / 22.750 25.520 / 24.937	3.675/3.514 2.114/2.092 1.177/1.137 0.638 /0.623

pH_R=6, Toluene phase, T= 298 K.

The results in this table show that the macroscopic parameters **P** and **J_0** depend on the initial concentration **C_0** for ions Cr(III) and in overall the Methyl Cholate is best extractant to extract these ions from concentrated acidic environments. However, these results clearly show that the acidity of the medium plays an important role in the extraction of Cr(III) ions, and the values of parameters **P** and **J_0** have been multiplied approximately by three for membrane "SLM-RESO" in increasing the pH, from pH=1 to pH=3 and an eventual separation of mixture (Cr(III) / Cr(VI)) by this type of membrane is possible. For more information on the facilitated extraction of these ions, we have established the rights of Lineweaver-Burk illustrated in **Figure 5**.

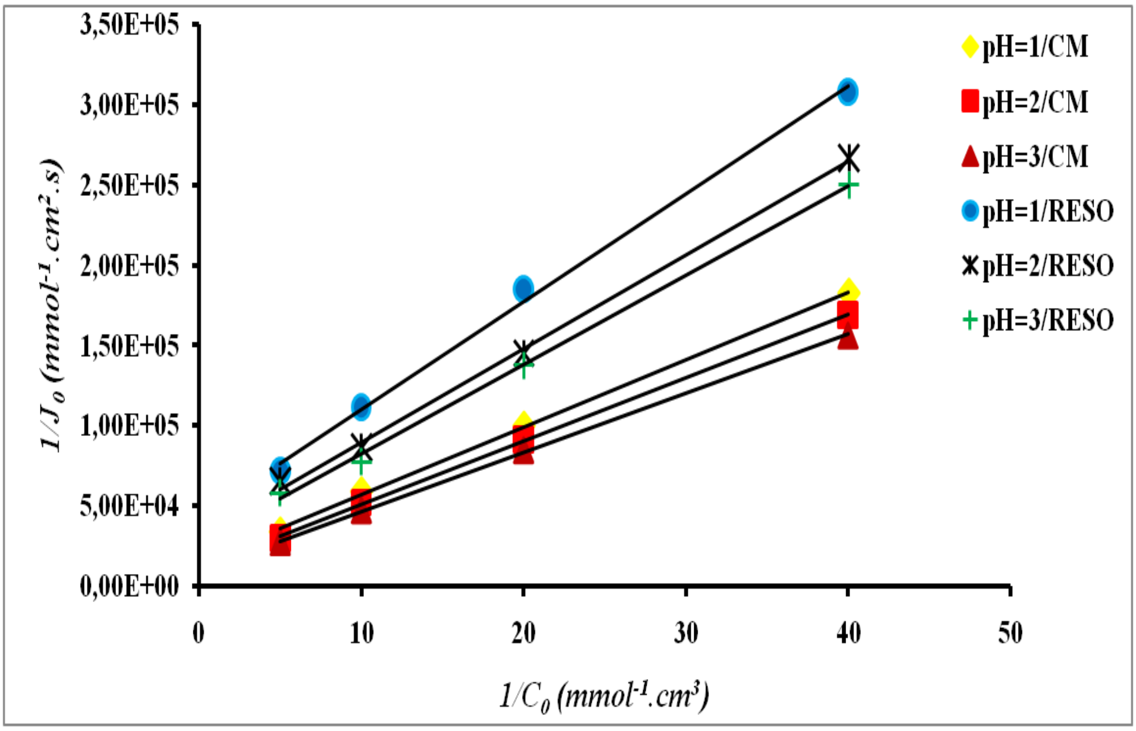

Figure 5: Lineweaver-Burk straight for the extraction of Cr(III) through the SLM's: [MC] = [RESO] = 0.01 M, pH_F = 2, Toluene Phase, and T = 298 K.

The microscopic parameters (**D*** and **K_{ass}**) were calculated using the slopes and intercepts of **Figure 6** by applying equation 7. **Table 4** summarizes the obtained results.

Table 4: Influence of the nature of the extractant on the parameters **D*** and **K_{ass}** relating to facilitated extraction of ions Cr (III).

pH_F	*extractants*	*K_{ass} (L. mol^{-1})*	*D* ×10^5 ($cm^2.s^{-1}$)*
1	*M C/RESO*	*3.66 / 7.60*	*6.51 / 2.02*
2	*MC/RESO*	*2.89 / 4.73*	*8.75 / 5.63*
3	*MC/RESO*	*2 .69 / 2.78*	*10.06 / 9.55*

pH_R=6, Toluene phase, T= 298 K.

These results show once again that there is a large variation in the values of the constant **K_{ass}** on the extraction of the substrate Cr(III) by the membrane "SLM-RESO", corresponding to a net evolution of parameters **J_0** and **P** and implies with great certainty that the thermodynamic parameter **K_{ass}** is an essential and crucial parameter for the facilitated extraction of a substrate by SLM.

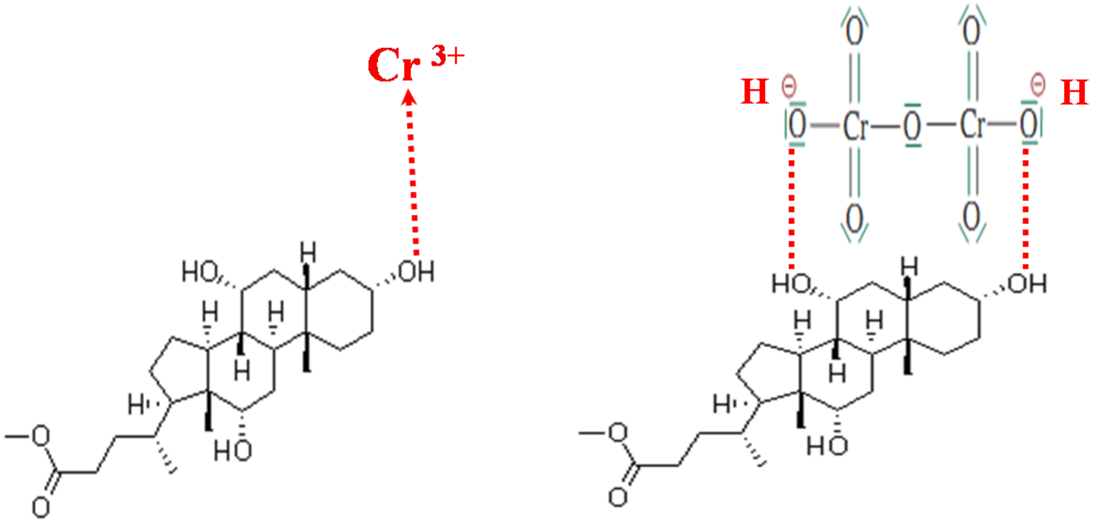

Figure 6: nature and type of liaison formed by the interaction of the ions (Cr(III) / Cr(VI)) with the extractant Methyl Cholate (MC).

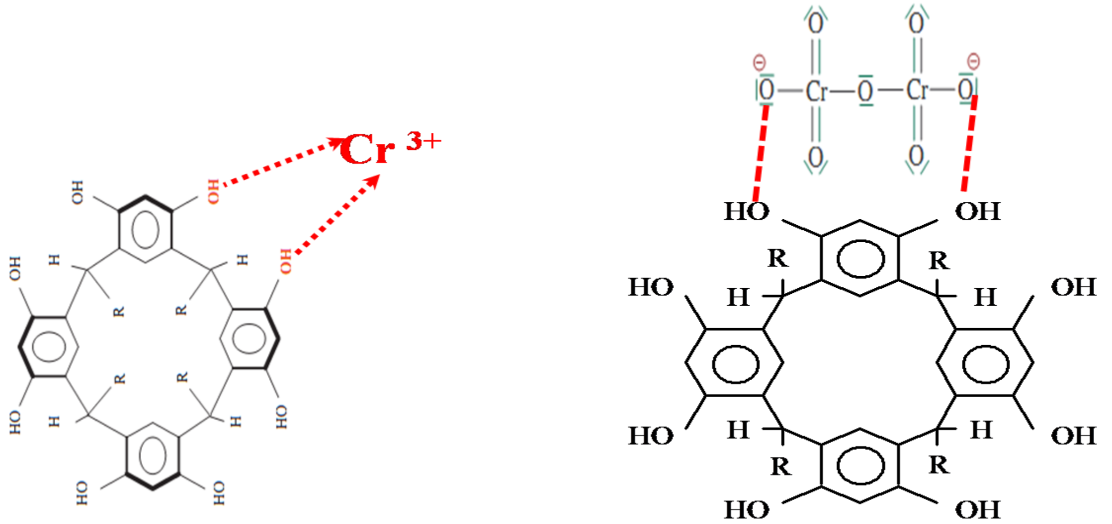

Figure 7: nature and type of liaison formed by the interaction of the ions (Cr(III) / Cr(VI)) with the extractant Resorcinarene (RESO).

Conclusion

The kinetic model, that has been developed and which considers the diffusion of ions-extractants through the membrane in the organic phase as rate-determining step, has been verified and which helped us to determine the permeability **P** and the flux $\mathbf{J_0}$ of ions Cr(VI) and Cr(III) across the elaborated membranes. The prepared SLM's are highly permeable for transported ions with high values of macroscopic parameters. The Methyl Cholate (MC) is a powerful new lipophilic agent for extracting anions Cr(VI) and cations Cr(III) from concentrated acidic media. The proposed mechanism has used to determine, for the first time, the microscopic parameters ($\mathbf{K_{ass}}$ and **D***) relating to the facilitated extraction of ions Cr(VI) and Cr(III) by two extractants. The experimental values (Table 2 and 4) show that the stability and diffusion of complex **TS** move in opposite directions and are closely linked to the nature of the substrate and the extractant and there is also establishing a heterogeneous equilibrium (Substrate-Extractant) in interface Feed phase/Membrane and the complex (Cr(III)-RESO) is more stable than its homologue formed with MC (Cr(III)-MC). This stability is reversed for pH values equal to 3, which shows that the acidity of the medium is certainly a determining factor for the selective extraction of a substrate by these types of membranes. These results also show that the extractant **Methyl Cholate** (MC) form by interaction with Cr(III) a strong liaison (dative type) and therefore more stable complex, while its interaction with ions Cr(VI) involves two weak liaisons (hydrogen type) and formation of an unstable complex. These results are certainly due to the fact that for environments with high acidity (low pH), the Cr(III) ions are in the free form Cr^{3+} presenting more affinity with one of the OH groups of the extractant while chromate ions Cr(VI) are protonated and are in the neutral form $Cr_2O_7H_2$ and it establishes the weak hydrogen liaison with two OH groups of MC. In addition, each one of studied ions form with the MC a complex of composition (1/1) (kinetic and thermodynamic models are verified), however, Cr(VI) can make two weak hydrogen liaisons, while Cr(III) establishes a single strong dative one with the MC (**Figure 6**). For the extractant Resorcinarene, the substrate Cr(VI) form the same number of weak hydrogen liaisons as the same formed with the extractant MC, therefore we have complexes with close stabilities. For the substrate Cr(III), the interaction with the extractant RESO leads to much more stable complexes than their counterparts formed with extractant MC, this result indicates that there are certainly much more affinity between the Cr(III) and RESO and the interaction between this latter and the substrate Cr(III) results in a stable complexes with two strong dative liaisons formed with two OH groups of the extractant RESO (**Figure7**).

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