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A new supported liquid membrane (*SLM*) with *methyl cholate* for facilitated transport of dichromate ions from mineral acids: parameters and mechanism relating to the transport [**].

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Abstract

The technique of supported liquid membranes (***SLM***) was used to achieve the facilitated transport of $Cr_2O_7^{2-}$, using an amphiphilic organic molecules as carriers, ***methyl cholate***, widely used for facilitated transport of metal ions and carbohydrates (sugars and alditols). For our prepared ***SLM***, toluene as organic phase and film of polyvinylidene difluoride (***PVDF***), as microporous and hydrophobic polymer support with 100µm in thickness and 0.45µm as the diameter of the pores. The *macroscopic parameters*, permeability ***P*** and initial flux J_i, on the facilitated transport of the $Cr_2O_7^{2-}$ anions were determined for several acidities of the medium of the three mineral acids: *hydrochloric acid (HCl)*, *nitric acid (HNO_3)* and *sulfuric acid (H_2SO_4)*. For the different studied environments, the prepared ***SLM*** is highly permeable for the transported substrate ($Cr_2O_7^{2-}$), and a clear evolution of these parameters was observed for the used carrier. The initial flux on the facilitated transport of the $Cr_2O_7^{2-}$ anions is related to the initial concentration of this substrate in the feed phase by a saturation law, which allowed the determination of the *microscopic parameters*, apparent diffusion coefficient ***D**** and the association constant K_{ass} of the (carrier-substrate) complexes, formed in the organic phase for the used ***SLM***. The experimental results clearly indicate that the (carrier-substrate) complexes formed in the organic phase are unstable, which results in higher apparent diffusion coefficients ***D**** and thus a high permeability of this membrane type, to facilitated transport on this type of oxygen anions ($Cr_2O_7^{2-}$).

Keywords: Supported liquid membrane (SLM); Methyl Cholate, Permeability; flux, association constant, apparent diffusion coefficient.

1. Introduction

Chromium is a naturally occurring element found in rocks, soils, plants, animals, and volcanic emissions. Chromium can exist in several chemical forms in the environment and under different oxidation states. Generally, the most experienced oxidation states are respectively, metal, trivalent and hexavalent chromium (Cr (0), Cr (III), Cr (VI)). Hexavalent chromium can exist in aquatic environments, as water soluble anionic complexes and can persist in these environments. It is the only element relative to other heavy metals that can exist as cationic and anionic species, depending on the pH of the medium [1]. The metal chromium is very important in industry and its main applications are: electroplating, leather tanning (tanning) and industrial metal alloys. It is a toxic element and a strong oxidant; it has proved mutagenic and carcinogenic. Several methods have been used for the elimination of chromium Cr (VI) from industrial effluents, in particular, liquid-liquid extraction [2, 3], the ion exchange processes [4] and supported liquid membranes (SLMs).

Currently, different membranes are used for many industrial applications, either to recover or separate the components of a mixture or to selectively control the exchange of material between different environments. The use of membrane technology in recent years experiencing rapid growth, it is mainly due to the increasing number of application domains. This development should increase, due to the emerging needs of environmental protection (pollution effluent, clean processes...) due to energy efficiency and techno-economic increasingly competition offered by membrane processes. In parallel to these different applications, research increasingly advanced and aim to better understand the operation of membranes, to create more efficient or more specific one, and also to develop processes providing access to new applications [5,6].

Nowadays for drilling in this domain it became necessary and certainly obligatory to draw up highly selective systems, which are considered essential to the achievement of certain separation and recovery of metal ions very environmentally damaging (especially when it comes to radioactive species) from complex aqueous mixtures. For this use, the liquid-liquid extraction was the first widely used separation technique with agents that are more or less adapted with recovering metallic ions from aqueous environments charged and complex. This technique implies the use of chelating agents and large amounts of organic solvents which are often expensive and toxic. It consists an extraction step by phase transfer, followed by a reextraction step; these two steps can be quite consuming organic solvents, especially when dealing with volatile solvents. An elegant alternative to liquid-liquid extraction is the elaboration of artificial membrane systems that reproduce the processes of facilitated transport through bio-membranes (carried out by mobile carriers and still more by ionic channels). Liquid membranes incorporating specific complexes represent artificial systems of choice for the treatment of liquid mediums charged with metal ions.

Among these membranes, the supported liquid membranes (SLM) systems are frequently used for these applications. These systems are elaborated from an inert polymer support. In fact, the organic solution containing a specific complexing molecule is incorporated, usually by impregnation of the polymer support. Polypropylene is for these purposes the most widely used polymer support due to its high porosity, which generates the best flux of metallic ions through the SLM. The supported liquid membrane process, have several advantages compared to liquid-liquid extraction. They are considerably less consumers of organic solvents, which is an important factor today in relation to the constraints of environmental protection and limitation of toxic discharges. These processes permit a continuous operation in a single stage because the two stages of extraction and reextraction are so coupled to the two interfaces. In fact the membranes are thin films separating two fluids; an essential membranes property is their permeability, i.e. their capacity to permit the passage of only certain species from one medium to another, while they are a barrier for other species [7 - 10].

The main advantages of SLMs are the small amounts of organic phase and extractant (carrier) used, one-step mass transfer, the possibility of achieving high separation factors, concentration of extracted compound(s) during separation, and low separation costs.

For this work we try to develop a simple and effective technique for the extraction of $Cr_2O_7^{2-}$ ions from acid mediums by changing their natures. This technique is based on a set of work on membrane transport phenomena, including facilitated transport.

Our work will be limited to supported liquid membranes (SLM), consisting of an inert and microporous polymer support *polyvinylidene difluoride* (**PVDF**), with 100 µm in thickness, 69% in porosity and 0.45µm in pores diameter, containing an amphiphilic carrier: ***methyl cholate*** (Figure 1), soluble in toluene phase**.**

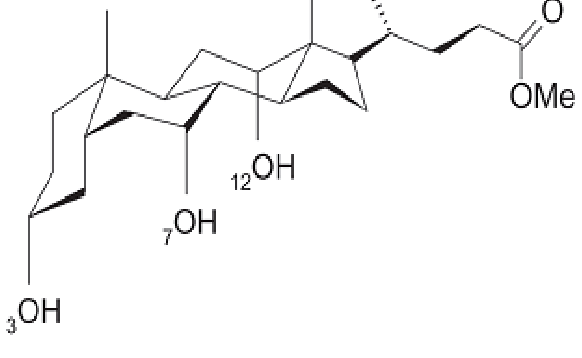

Figure 1: Structure of methyl cholate in 3D.

2. Description and functioning mode of SLM

The SLM is constituted of an organic solvent immobilized by capillary forces in the pores of a support separating the feed phase from the receiving phase. The support of these membranes is generally an inert, microporous and hydrophobic polymer, and is characterized by a low thickness of the order of 25 to 100 microns and the pore diameter from 0.12 to 1 micron [11, 12]. The passage of chemical species across these membranes is an interfacial phenomenon, the use of a support highly porous is necessary to increase the contact area and the selectivity of passage species, and therefore very important to ensure the best transport and separation conditions through SLM [13]. To improve the separation process, the researchers added to the SLM organic phase, mobile carriers accelerate and facilitate the species transport, while increasing the membranes selectivity [5,14]. The SLM technique is an approach widely used for the extraction and enrichment of metallic ions and organic compounds [15-17].

In fact this technique has been used to study transport and apply it to the selective extraction and enrichment of very different organic compounds, such as amino acids [18,19], the aromatic aminophosphate [20] sugars [21-23], herbicides [24,25] or organic acids [26,27].

This process which is called facilitated transport across supported liquid membranes is based on the recognition of a substance (**S**) by a carrier molecule (**T**). This process involves the mobility within the membrane complex (**ST**) produced by a reversible formation reaction between the carrier (**T**) and the species transported (**S**) at the interfaces of the membrane with the feed and receiving phases.

This transport phenomenon across SLM is a cyclical process that is carried out in five consecutive steps:

1 - Diffusion of the substrate (**S**) in the feed phase to the interface of the membrane.

2 - Formation of the complex substrate-carrier (**ST**) at the interface of the membrane with the feed phase.

3 - Diffusion of the complex (**ST**) through the organic phase of the membrane to the interface of the membrane with the receiving phase.

4 - Dissociation of the complex (**ST**) at the interface of the membrane with the receiving phase.

5 - Distribution of free substrate (**S**) in the receiving phase and the carrier (**T**) in the membrane organic phase to participate in the following cyclic process (complexation/diffusion/dissociation). These five steps are represented by the scheme of the Figure 2 and provide the transport mechanism through a SLM, with step three as a kinetically determining step.

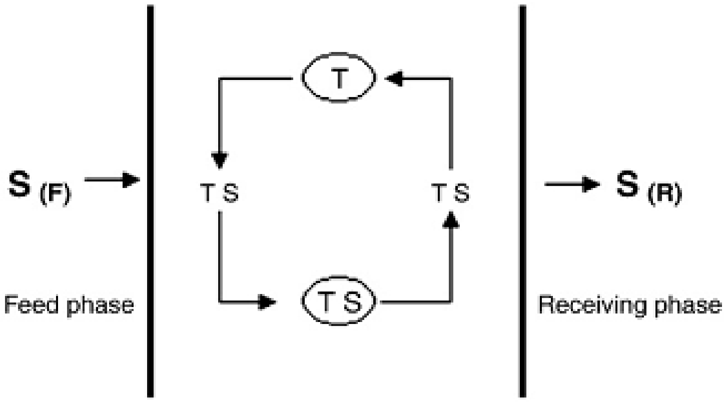

Figure 2: transport mechanism across a SLM.

3. Experimental design and theoretical model

3.1. Conditioning of the SLM

The transport of a model solution of dichromate ions ($Cr_2O_7^{2-}$) (0.20M in feed phase), was achieved through a SLM in which the membrane phase was a 0.01M solution of *methyl cholate* in pure Toluene solvent, supported by a microporous polyvinylidene difluoride (PDVF) film.

When the SLM was used for transporting immediately the substrate after its preparation, its flux is remained small for a long initial period, typically 8 to 10 h. After this time, the rate of transport increased and the concentration of dichromate ions ($Cr_2O_7^{2-}$) in the receiving phase C_r, increased rapidly over several hours. This behaviour has been observed previously with a SLM containing some lipophilic carriers [20,21], and was attributed to the slow incorporation of water into the membrane to form presumably a carrier–water complex. After this initial period (induction period), the transport of dichromate ions ($Cr_2O_7^{2-}$) increases, probably because the substrate rapidly exchanges with water at the interfaces, to form the carrier–substrate complex, or possibly a ternary carrier–substrate–water complex that is the active species for the transport process. The presence of water in the SLM was reported to be important phenomenon for the transport of carbohydrates through plasticized cellulose triacetate membranes containing ion-pair carriers [28, 29].

The existence of this induction period complicates the analysis of the kinetic studies, because it makes it difficult to approximate the exact value of the slope of the plots drawn for a first-order reaction [25].In this study, in order to suppress this period of slow transport, the prepared SLM was conditioned for 18 h in the cell between two phases of pure water. After this time, the induction period was not observed and the transport of dichromate ions ($Cr_2O_7^{2-}$) began just after its introduction in the feed phase.

3.2. Transport cell

The transport experiments were performed in the cell represented by the diagram in Figure 3. This cell has two compartments with a volume of each is 175 mL, separated by the micro porous membrane (M). This transport unit is immersed in a thermostated bath (TB) and a multi-magnetic stirrer; allow stirring the solutions in both compartments.

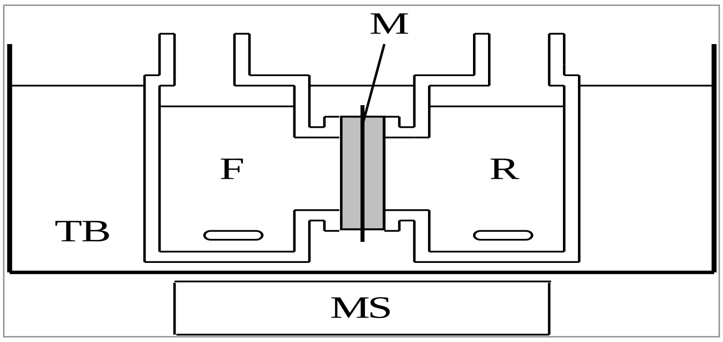

Figure 3: Scheme of the transport cell.

**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.**

3.3. Determination of permeability and flux

The SLM is placed between two compartments (Figure 3). Into the feed compartment, a known volume of a substrate solution (**S**) with a concentration C_0 is introduced, and we place the same volume of water in the receiving compartment. Small aliquots (v=1.0 mL) of the receiving phase were withdrawn at known intervals. If C_r is the concentration of substrate in the receiving phase at a time t, the substrate concentration in the feed phase C_s at this time t is: $C_s = C_0 - C_r$. The evolution of the concentration C_r of substrate (**S**) in the receiving phase vs. time is related to the flux J by the following equation:

$$dC_r / dt = J \times S / V \quad (1)$$

With, S as the diffusion surface of the membrane and V the volume of receiving phase.

For a quasi-stationary state, the flux is related to the difference of the concentrations of two compartments, $\Delta C = C_s - C_r$, by the Fick's first law:

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

P is the permeability of the membrane and l its thickness.

As $C_s = C_0 - C_r$; therefore $\Delta C = C_s - C_r = C_0 - 2C_r$ (3)

By combining Eqs. (1),(2) and (3), we find the following equation:

$$P \times dt = (l \times V/S) \times dCr / C_0 - 2C_r) \qquad (4)$$

After integration:

$$P\,(t - t_L) = (l \times V/ 2S)\ ln\ [C_0 / (C_0 - 2C_r)] \qquad (5)$$

This equation shows that after an induction period (t_L), which can last several hours, if the term $-ln(C_0 - 2\,C_r)$ of Eq. (5), follows a linear evolution as a function of the time, then, the diffusion rate of the substrate (***S***) through the SLM, is carried out by a kinetic law of first order. The permeability is calculated from the slope "***a***" of the right $(-ln\ (C_0 - 2C_r) = f(t))$, using the following equation:

$$P = a \times V \times l / 2S \qquad (6)$$

And that the initial flux J_i, which can be calculated from the permeability ***P*** according to Eq. (7):

$$J_i = P \times C_0 / l \qquad (7)$$

While, equality $C_s = C_r = C_0/2$ of the concentrations in both compartments, reflects a dynamic equilibrium state, with equal diffusion rates of the substrate (**S**) through the SLM in the two opposite directions, and indicates the end of the transport process.

3.4. Model and theoretical calculations:

The phenomenon of facilitated transport depends on the formation and dissociation of the complex carrier–substrate (**TS**) at the solution–membrane interfaces. The carrier (**T**) is insoluble in the aqueous phase, while the substrate (**S)** is insoluble in the organic phase of the membrane. The complexation equilibrium is:

$$T_{org} + S_{aq} \Leftrightarrow TS_{org}$$

$_{Org}$ and $_{aq}$ represent respectively, the organic phase of the membrane and the feed aqueous phase. The concentration $[TS]_i$ of carrier– substrate complex (**TS**) at the membrane-source phase interface, is expressed from the mass action law according to the equation:

$$[TS]_i = K_{ass} \times [T]_i \times [S]_i \qquad (8)$$

$[T]_i$ and $[S]_i$ are respectively the concentrations of the carrier and the substrate at the feed phase membrane interface. K_{ass} is the association constant of the complex (**TS**), is also the constant of the heterogeneous equilibrium established at this interface. In kinetically determining step, the flux ***J*** is determined by Eq. (9), derived from the Fick's first law, which implies that the concentration of the complex is negligible at the receiving phase membrane interface (dissociation of complex).

$$J = (D^*/l) \times [TS] \qquad (9)$$

D^* is the apparent diffusion coefficient and ***l*** is the thickness of membrane.

However, at the feed phase membrane interface, $[TS]_i << [S]_i$ (excess of substrate relative to the carrier) and at any moment, the concentration $[S]_t$ of the substrate in the feed phase is equal to the concentration $[S]_i$ at the interface of the membrane ($[S]_i = [S]_t$). The total carrier concentration $[T]_0$ immobilized in the membrane is constant, equal to the sum of the concentrations $[T]_i$ and $[TS]_i$.

$$[T]_0 = [T]_i + [TS]_i = [TS]_i \times [(1 + K_{ass} \times [S]_i) / (K_{ass} \times [S]_i)] \qquad (10)$$

$$[TS]_i = [T]_0 \times K_{ass} \times [S]_i / (1 + K_{ass} \times [S]_i) \qquad (11)$$

But in the initial conditions, the substrate is in excess of the carrier and at the source phase-membrane interface, we can write $[S]_i = [S]_0 = C_0$ and $[TS]_i \approx [T]_0$.
Using Eqs. (9) And (11), the expression of initial flux $J_i = (D^*/l) \times [TS]_i$ is given by the following relationship:

$$J_i = (D^*/l) \times ([T]_0 \times K_{ass} \times [S]_i) / (1 + K_{ass} \times [S]_i)$$

Hence the final expression of J_i from the initial concentration, $[T]_0$ and C_0 with an excess of substrate ($C_0 >> [T]_0$):

$$J_i = (D^*/l) \times ([T]_0 \times K_{ass} \times C_0) / (1 + K_{ass} \times C_0) \qquad (12)$$

This expression allows to calculate the permeability P as a function of $[T]_0$, C_0 and K_{ass} using the following equation:

$$P = J_i \times l / C_0 = (D^*) \times ([T]_0 \times K_{ass}) / (1 + K_{ass} \times C_0) \qquad (13)$$

We note that the evolution of J_i and P is proportional to the initial substrate concentration C_0, and it is a Michaelis–Menten type, since for high concentrations of substrate, these two macroscopic parameters reaching the limit values. To determine the microscopic parameters D^* and K_{ass}, the relationship given by Eq. (12) is linearized according to the Lineweaver–Burk plot $1/J_i = f(1/C_0)$, Eq. (14):

$$1/J_i = (l/D^*) \times [(1/[T]_0 \times K_{ass}) \times (1/C_0) + (1/[T]_0)] \qquad (14)$$

And values of K_{ass} and D^* are calculated from the relationships:

$$K_{ass} = \text{Intercept (OO)} / \text{slope } (p) \text{ and } D^* = (l / OO) \times (1 / [T]_0) \qquad (15)$$

4. Experimental section

All chemicals, reagents and solvents were pure commercial products (Aldrich or Fluka) of analytical grade, used as received. The SLM support was a micro porous **PVDF** film (Millipore) of thickness 100 µm. Characteristic values are porosity 69% and the pore size 0.45 µm. The membrane area available for diffusion was 20 cm^2 (diameter 5.0 cm). The acidic solutions of $Cr_2O_7^{2-}$ ions are obtained by hydrolysis of $K_2Cr_2O_7$ in bidistilled water.

The transport cell (Figure 3) is made of two compartments of equal volumes (175 mL) separated by the SLM, prepared by soaking a square portion of the polymer film into an 0.01 M organic solution of the carrier **methyl cholate** in pure toluene, during 06 h. The cell is immersed into a thermostated bath (T=298°K). Initially, the feed phase is a solution of dichromate ions ($Cr_2O_7^{2-}$), with an initial concentration C_0 and a fixed value of pH, in this work we try with three values of pH=1; 2 and 3 at one cycle and at each cycle the pH is adjusted by one of the following mineral acids: HCl, HNO_3 or H_2SO_4, while the receiving phase are solutions of KCl, KNO_3 or K_2SO_4 at pH=6. The solutions in both compartments are stirred with magnetic bars, using a Multimatic-9 S apparatus. The technique is used to study the facilitated transport of substrate (dichromate ions ($Cr_2O_7^{2-}$)) through the SLM.

− In the first one (mode a), for the study of the lifetime of the membrane and the reproducibility of the results, we used for each of the experiments a new substrate solution with the same fixed concentration. With this procedure, we have verified that the results are reproducible with the same membrane which was used during 10 days without showing any sign of failure.

− In the second one (mode b), to study the effect of the concentration of the substrate on the parameters of transport, the same membrane and the same solution have been used for all runs. At equilibrium after each run, the contents of both compartments were withdrawn and mixed together, then 175 mL of the resulting solution which were introduced in the feed compartment and 175 mL of solutions of KCl, KNO_3 or K_2SO_4 at pH=6 in the receiving compartment and the following run was started. This economic procedure for dichromate ions solutions ($Cr_2O_7^{2-}$) was typically repeated four or five times.

In these techniques, small aliquots (v =100µL) of the receiving phase were withdrawn at known intervals. These samples were analyzed by standard Helios γ UV–visible spectrometer, the concentrations C_r of dichromate ions in the receiving phase are calculated and the evolution of the function $-ln\ (C_0-2C_r)$ is determined as a function of time. The following table (table 1) lists an example of results on the facilitated transport of dichromate ions ($Cr_2O_7^{2-}$) from acidic medium with pH = 2 adjusted by mineral acids mentioned above.

Some experiments were continued for 24 h, when samples of both aqueous phases were withdrawn and analyzed to ensure that equal concentrations were present, indicating that equilibrium was reached.

Table 1: Facilitated transport of substrate ($Cr_2O_7^{2-}$) through an SLM.

t (min)	C_r (M)			$-ln\ (C_0-2C_r)$		
	HCl	HNO_3	H_2SO_4	HCl	HNO_3	H_2SO_4
60	0.0140	0.0147	0.0112	2.632	2.651	2.554
90	0.0184	0.0192	0.0145	2.763	2.785	2.644
120	0.0218	0.0231	0.0180	2.875	2.922	2.748
150	0.0251	0.0267	0.0209	2.997	3.064	2.842
180	0.0285	0.0296	0.0238	3.144	3.197	2.946

$C_0 = [Cr_2O_7^{2-}]_0 = 0,10$ M, pH=2, [Methyl Cholate] = 0,01 M and T = 298 K

5. Results and discussion

5.1. Influence of the HNO_3 acidity of the feed phase:

Under the same experimental conditions, using the SLM with 0.01 M of the carrier (**methyl Cholate**) dissolved in the organic phase(toluene), facilitated transport of substrate ($Cr_2O_7^{2-}$) was carried out from different nitric acid solutions with the successive acidity, pH(HNO_3)=1, 2 and 3. The kinetic model proposed for this type of transport, indicates that the evolution of the term $-ln\ (C_0-2\times C_r)$ should be linear with time, which is verified by the straight lines represented by the graph in Figure 4.

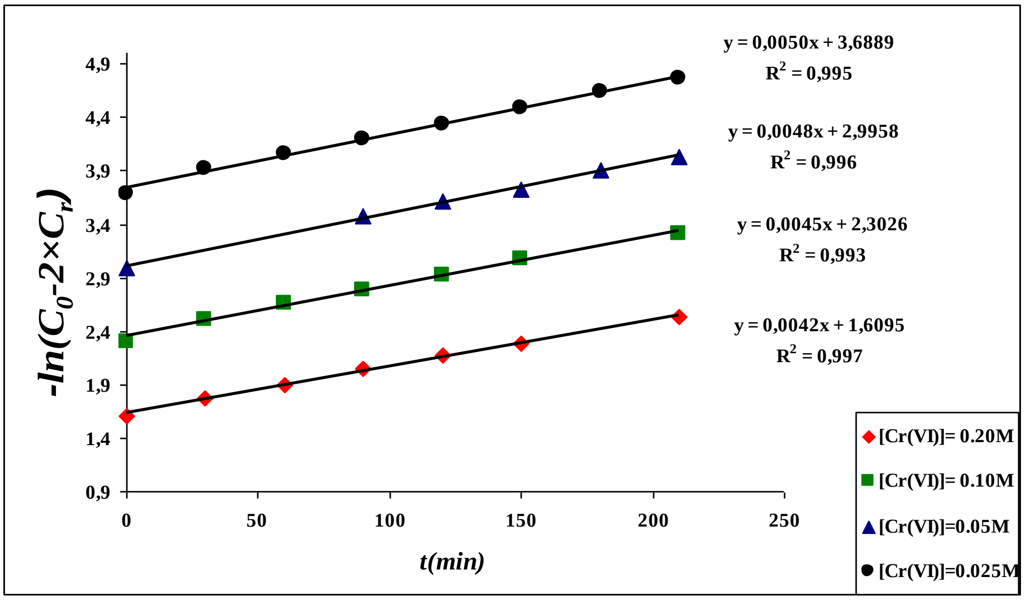

Figure 4: Plots of $-ln\ (C_0-2C_r)$ vs. time t for the transport of $Cr_2O_7^{2-}$ ions through the SLM, pH (HNO_3) =2, T= 298K.

The slopes determined by these straight lines, allow calculating the permeabilities ***P*** of this SLM for dichromate ions ($Cr_2O_7^{2-}$) *of* different studied *HNO*$_3$solutions (Eq. (6)), while the initial fluxes $\boldsymbol{J_i}$ through the SLM for these ions, are calculated with the Eq. (7). The results relating to these parameters obtained of the different studied solutions are summarized in Table 2.

Table 2: Influence of the medium acidity on the macroscopic parameters of the transport.

pH (feed phase)(HNO$_3$)	$C_0 = [Cr_2O_7^{2-}]$ ***M***	$P \times 10^7$ $(cm^2.s^{-1})$	$J_i \times 10^5$ $(mmol.cm^{-2}.s^{-1})$
1	**0.20** **0.10** **0.05**	**29.896** **32.084** **33.542**	**5.980** **3.209** **1.678**
2	**0.20** **0.10** **0.05**	**30.625** **32.813** **35.000**	**6.125** **3.282** **1.750**
3	**0.20** **0.10** **0.05**	**32.084** **34.271** **36.313**	**6.417** **3.428** **1.816**

[Methyl Cholate]=0.01 M, Permeability P is calculated from Eq. (6). Initial flux J_i *is calculated from Eq. (7). For the PVDF film, the area S is 20.0 cm*^{2}*, the thickness l is 0.01 cm, toluene phase and T=298 K.*

These results show that the permeability ***P*** of the SLM varies inversely with the initial concentration $\boldsymbol{C_0}$ of dichromate ions ($Cr_2O_7^{2-}$) and an increase in $\boldsymbol{C_0}$ results in a decrease of ***P***. In contrast, the initial flux $\boldsymbol{J_i}$ of these ions ($Cr_2O_7^{2-}$) through the SLM increases with the initial concentration $\boldsymbol{C_0}$ of the substrate in the feed phase [21, 22]. The study of the *Lineweaver–Burk* plots ($\boldsymbol{1/J_i=f\,(1/C_0)}$) provided by Eq. (14), allows to verify the proposed mechanism for the facilitated transport of dichromate ions ($Cr_2O_7^{2-}$) by the studied SLM and to determine *microscopic parameters* ***D**** and $\boldsymbol{K_{ass}}$, for the three studied acidity. The obtained straight lines are represented by the graph of Figure 5.

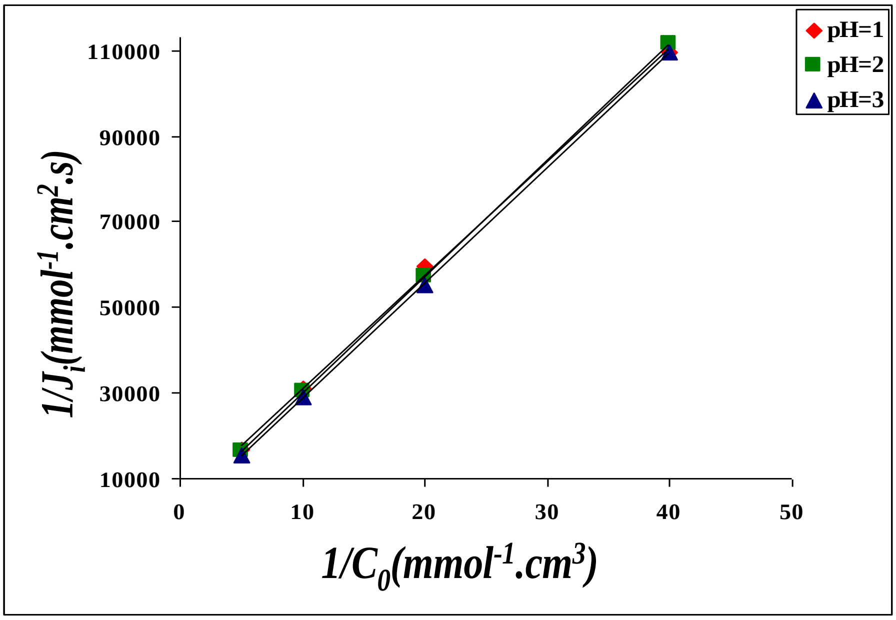

Figure 5: Plots of $1/J_i$ vs. $1/C_0$ for the transport of $Cr_2O_7^{2-}$ ions across the SLM, pH (*HNO*$_3$) =2, T= 298K.

The results show that the proposed mechanism is verified, the carrier–substrate complex (***TS***) formed in the organic phase of the SLM is the composition (1/1) and the migration of this complex through the organic phase is the kinetically determining step for the mechanism on the transport of dichromate ions ($Cr_2O_7^{2-}$). The slopes (***p***) and the intercepts (***OO***) were determined by straight lines in Figure 5 and using the expressions given by Eq. (15), the apparent diffusion coefficients ***D**** and the association constants $\boldsymbol{K_{ass}}$ were calculated. However, these results summarized in Table 3 show that these two parameters (***D**** and $\boldsymbol{K_{ass}}$) vary slightly with the acidity of the medium. The formation of the complex and its diffusion through the organic phase of the SLM are affected by the acidity of the feed phases.

Table 3: Evolution of the microscopic parameters D^* and K_{ass} depending on the acidity.

pH (feed phase) (HNO_3)	***K_{ass} ($L.mol^{-1}$)***	***$D^*. 10^5$ ($cm^2.s^{-1}$)***
1	**1.75**	**21.46**
2	**1.05**	**33.89**
3	**0.75**	**49.51**

[Methyl Cholate]=0.01 M; $K_{ass} \pm 0.01$ *and* $(D^* \pm 0.01)\times10^{-5}$; K_{ass} *is the association constant for the heterogeneous equilibrium:* $T_{org} + S_{aq} \leftrightarrow TS_{org}$.

According to these results, we find that the values of apparent diffusion coefficients ***D**** obtained (about 10^{-4} $cm^2.s^{-1}$) for the transport of the ($Cr_2O_7^{2-}$) ions in nitric acid medium, are higher compared to literature values (about 10^{-6} $cm^2.s^{-1}$) [30, 31]. The same remark was made for the transport of some alditols and sugars [24, 25].

To explain this phenomenon, we suggested in the transport of alditols [25], that the diffusion process is perhaps accompanied by a convection movement, which would be responsible for accelerating the diffusion of complexes in the membrane. While the hypothesis of "fixed-site jumping" proposed by *Smith et al.* in the transport of sugars through a plasticized membrane of triacetate cellulose [28,32] is another suggestion, more likely to clarify this point. This theory assumes that the substrate moves by jumping from site to site inside the membrane. In this case, the transport mechanism has the same kinetic profile as the facilitated transport; nevertheless, its characteristic is to be faster than the diffusion [28].

5.2. Influence of the nature of mineral acids: *HCl, HNO_3 and H_2SO_4*.

Several studies indicate that the nature of the mineral acid is an important and essential factor for the facilitated transport across the SLM of metal ions [33, 34]. To complete our results and check the influence of the nature of the three studied acids, we performed the same experiments under the same conditions with the same MLS that contains **cholate** as carrier. The kinetic model and the mechanism of dichromate ions transport have been well verified. The graph in Figure 6 allows us to determine the permeability and then the initial flux.

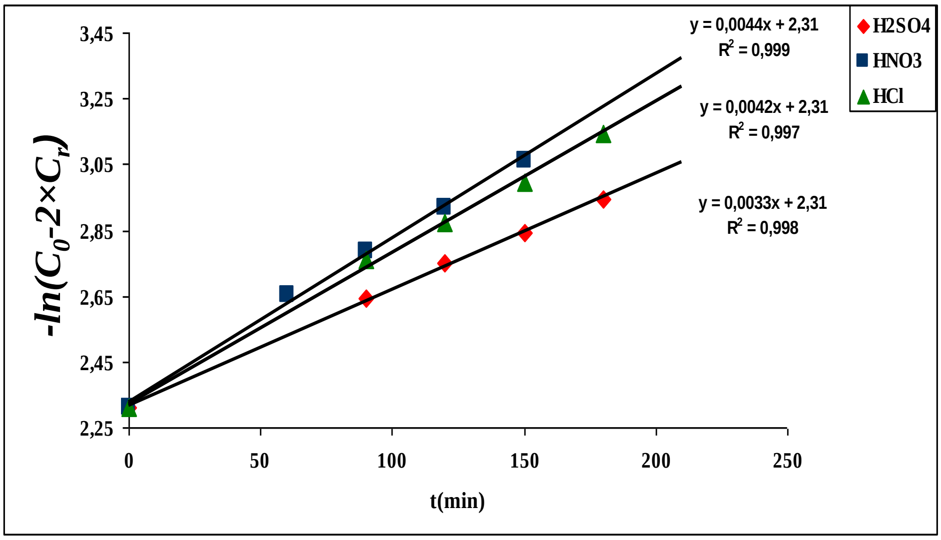

Figure 6: Plots of $-ln\ (C_0-2C_r)$ vs. time t for the transport of $Cr_2O_7^{2-}$ ions through the SLM, C_0= $[Cr_2O_7^{2-}]_0$ = 0,10M, pH=2, T= 298K.

For this new solutions, the kinetic model proposed for the evolution of the concentration C_r of dichromate ions ($Cr_2O_7^{2-}$), carried in the receiving phase, as a function of time was verified (Figure 5). All determined permeabilities and initial fluxes for the facilitated transport of substrate through this new condition with the agents HCl, HNO_3 and H_2SO_4, are summarized in Table 4.

Table 4: Evolution of the transport parameters which depending on the nature of mineral acids.

pH (feed phase) (HCl, HNO_3, H_2SO_4)	***$C_0 = [Cr_2O_7^{2-}]$ M***	***$P \times 10^7$ ($cm^2.s^{-1}$)***			***$J_i \times 10^5$ ($mmol. cm^{-2}.s^{-1}$)***		
		HCl	*HNO_3*	*H_2SO_4*	*HCl*	*HNO_3*	*H_2SO_4*
1	0.20	26.250	29.896	21.875	5.250	5.980	4.375
	0.10	29.895	32.084	23.334	2.989	3.209	2.334
	0.05	32.812	33.542	27.709	1.640	1.678	1.386
2	0.20	28.437	30.625	23.115	5.687	6.125	4.623
	0.10	30.625	32.813	23.699	3.062	3.282	2.370
	0.05	32.083	35.000	24.938	1.604	1.750	1.247
3	0.20	29.166	32.084	21.667	5.833	6.417	4.334
	0.10	31.354	34.271	22.500	3.135	3.428	2.250
	0.05	33.541	36.313	23.334	1.677	1.816	1.167

[Methyl Cholate]=0.01 M, similar experimental conditions to Table 2.

In the same way as for the previous acid (HNO_3), the study of the Lineweaver–Burk plots (**$1/J_i=f(1/C_0)$**) provided by Eq. (14), allows to verify the proposed mechanism for the facilitated transport of substrate for the three acids and to determine microscopic parameters ***D**** and K_{ass}, for each studied agent, *HCl*, HNO_3 and H_2SO_4. The obtained straight lines are represented by the graph of Figure 7:

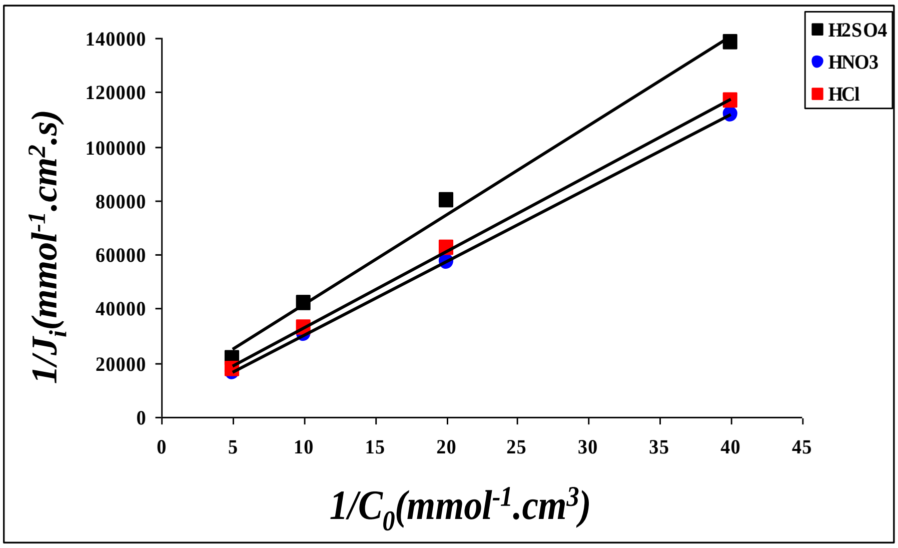

Figure 7: Plots of $1/J_i$ vs. $1/C_0$ for the transport of $Cr_2O_7^{2-}$ ions across the SLM, for the three acid agents *HCl*, HNO_3 and H_2SO_4. pH =2, T= 298K.

From straight lines in Figure 7, the intercepts (***OO***) and the slopes (***p***) were determined and using the expressions given by Eq. (15), the apparent diffusion coefficients ***D**** and the association constants K_{ass} were calculated. For the studied acids, all results are summarized in Table 5. These results show that the constant K_{ass} decreases with the acidity of the medium, while the apparent coefficient ***D**** increases, for all three mineral acids.

Table 5: Microscopic parameters K_{ass} and D^* according to the acidity with the acid agents: HCl, HNO_3 and H_2SO_4.

pH(feed phase)	K_{ass} **(L.mol^{-1})**			D^***. 10^5 (cm^2.s^{-1})**		
	HCl	HNO_3	H_2SO_4	*HCl*	HNO_3	H_2SO_4
1	4.23	1.75	4.70	10.08	21.46	07.70
2	2.47	1.05	2.65	15.08	33.89	11.46
3	1.69	0.75	1.82	21.83	49.51	14.69

[Methyl Cholate]=0.01 M; $K_{ass} \pm 0.01$ *and* $(D^* \pm 0.01) \times 10^{-5}$; K_{ass} *is the association constant for the heterogeneous equilibrium:* $T_{org} + S_{aq} \Leftrightarrow TS_{org}$.

The presence of the HNO_3 in the feed phase is more effective for facilitated transport of $Cr_2O_7^{2-}$ ions from the concentrated acid solutions, through supported liquid membranes, and the extraction of this substrate ($Cr_2O_7^{2-}$) from these solutions is more important in the presence of the stripping agent HNO_3, as its two counterparts *HCl* and H_2SO_4. The extraction of dichromate ions is highly important in the presence of the *HCl* than the presence of H_2SO_4.

The comparison of the values of these microscopic factors (K_{ass} and D^*), shows that the less stable complexes migrate rapidly through the membrane (medium with HNO_3). $D^*_{HNO3} > D^*_{HCl} > D^*_{H2SO4}$ and $K_{ass\ H2SO4} > K_{ass\ HCl} > K_{ass\ HNO3}$. As a result, the association constants vary inversely in relation with the apparent diffusion coefficients.

The obtained results for prepared SLMs, under the above conditions, clearly show that facilitated transport of dichromate ions ($Cr_2O_7^{2-}$) in this type of membranes is very effective and certainly more applications can be envisaged.

This result can be explained by the hypothesis of “fixed-site jumping” proposed by Smith [28], or the transport of substrate is by skipping one carrier to another. Indeed, when the stability of complexes is low, their dissociation constants are large; therefore, the passage of the substrate from one carrier to another is easy. The apparent diffusion coefficients in this case are larger than those observed in the case of a simple diffusion. The study of all results shows that the migration of complexes (Carrier–Substrate) through the organic phase of the membrane depends on the stability of these complexes, and low stability (small K_{ass}), results in a large diffusion (high D^*) through the membrane and a high permeability of the used SLM for transported dichromate ions ($Cr_2O_7^{2-}$). However, we can propose three types of movements associated with the migration of these complexes through the organic phases of the SLM.

1) Movement of pure diffusion (D^* order 10^{-6}) for a very stable complexes in organic phase.
2) Composed movement (diffusion + jump from site to site) for unstable complexes in organic phase of the SLM (D^* order 10^{-5})
3) Movement characterized by the displacement of the substrate by jumping from site to site (with high D^*, at around 10^{-4}).

This hypothesis of “fixed-site jumping” advanced by Smith for the transport of sugars [32], explains the rapid migration through the organic phase of the SLM for these dichromate ions ($Cr_2O_7^{2-}$) complexes with low stability.

6. Conclusion

A supported liquid membrane (*SLM*) was prepared with the polymer support (*PVDF*), the organic phase (toluene) and the carrier *Methyl Cholate*. This SLM has been used for the facilitated transport of dichromate ions ($Cr_2O_7^{2-}$) from the concentrated acid mediums. On the one hand, these experimental results confirm the recent work on the transport of Dy^{3+} and Tm^{3+} ions [34, 35, 36], which clearly indicate that the permeability P of the membrane increases when the concentration of each substrate Dy^{3+} or Tm^{3+} decreases, the acidity and the nature of the studied mineral acids are important factors for the feed phase and the transport parameters depend on these agents. Moreover, these results verify the proposed kinetic model, allowing for determining the permeability P and initial flux J_i for the adopted SLM. The obtained results show that the used SLM is very permeable for $Cr_2O_7^{2-}$ ions, which resulted in significant fluxes of transported substrate. To understand this facilitated transport phenomenon through this type of liquid membranes we developed a mechanism based on the formation of a complex carrier–substrate at the interface of the membrane and the migration of this complex through the organic phase of the SLM, to explain the migration of $Cr_2O_7^{2-}$ ions from the feed phase to the receiving phase. This mechanism has been verified, thus determining the microscopic parameters $\boldsymbol{K_{ass}}$ and ***D****, for the reaction of complex formation and its diffusion through the organic phase of the SLM. Low values of the constants $\boldsymbol{K_{ass}}$ and high values of the coefficients ***D****, can fully explain the large permeabilities and fluxes, obtained for facilitated transport of $Cr_2O_7^{2-}$ ions in this type of SLM. Indeed, the microscopic parameters $\boldsymbol{K_{ass}}$ and ***D**** vary inversely and the low values of association constants $\boldsymbol{K_{ass}}$, correspond to the high values of apparent coefficients ***D****. This important result shows that these high values of the apparent coefficients do not reflect a pure movement of diffusion of the complex (*TS*) through the organic phase of the SLM. Recent studies [37,38] on the facilitated transport of metal ions by the same type of membranes, confirm the high values of these apparent diffusion coefficients ***D****.They explain this result by the nature of the movement of the substrate (**S)** in the organic phase of the SLM during its migration from the feed phase to the receiving phase.

Various studies [39–42], show that some supported liquid membranes containing specific carriers, are also very effective for the facilitated transport of some organic compounds (sugars, organic acids), and can be fully operational for the separation of mixtures of these compounds. All these results clearly indicate that the SLMs may be potential tools for several applications, particularly the specific extraction of compounds from mixtures, or the general extraction of toxic heavy metals from industrial waste.

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