New Supported Liquid Membrane for Studying Facilitated Transport of U(VI) Ions Using Tributyl Phosphate (TBP) and Tri-n-Octylamine (TOA) as Carriers from Acid Medium

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Abstract

Our objective is to develop a new supported liquid membrane (SLM) for recovering uranyl ions (substrate) from concentrated industrial solutions of phosphoric acid. In this paper, we have prepared SLMs membrane using Tributyl phosphate (TBP) and Tri-n-octylamine (TOA) as carriers, and the polymer polyvinylidene difluoride (PVDF) as a hydrophobic support for studying facilitated transport of uranyl ions from acidic solutions. Then, a kinetic model is used to calculate the macroscopic parameters (permeability $P$ and initial flux $J_0$) relating to transport of uranyl ions and a thermodynamic model is used to determine the microscopic parameters (association constant $K_{as}$ and apparent diffusion coefficient $D^*$) relating to migration of the complex (Substrate-Carrier) formed through the membrane phase of the SLM. The experimental results verify these models, and they determine the different parameters relating to effect of the nature of carrier, initial concentration of substrate and temperature. In addition, the determination of activation parameters ($E_a$, $\Delta H^*$ and $\Delta S^*$) relating to the transition state for the reaction of association between carrier and substrate at interface phase (source-membrane) give more information about nature of migration of these high values of the coefficients $D^*$ and therefore the high permeability for transported ions by this type for SLM.

Keywords: supported liquid membranes; facilitated transport; uranium; TBP; TOA; activation parameter; permeability; apparent diffusion coefficient; association constant

Introduction

Membrane processes are the most important and widely technologies used in many industrial applications for recovering and separating the components of a mixture or to control selectively the material exchange between different environments. In recent years, the use of these techniques grew rapidly. This development is expected to increase, due to environmental protection requirements and the energy performance and technical-economic increasingly competitive offered by these processes. Alongside, research aims to better understand the functioning of the membranes, to create the materials more efficient or more specific and also to develop new methods for different applications.

Nowadays, it became necessary required to develop highly selective systems, which are essential to consider the implementation of certain separations and recoveries of metal ions very harmful to the environment (especially radioactive species) from complex aqueous mixtures like uranium ions from phosphoric acid (0.05 to 2 g/L) [1] because this metal is very important for many industrial applications like nuclear energy or others applications in medicine, metallurgy…. However, this metal is radioactive which is harmful for all vivant species [2]. For this use, the liquid-liquid extraction was the first dividing technique widely used with more or less suitable agents, for recovering metal ions from aqueous media loaded and complex. This technique involves the use of extractive agents and large quantities of organic solvents which are often expensive and toxic. It comprises a step of extracting phase transfer, followed by re-extraction step; these two steps can be quite consuming organic solvents, especially when dealing with volatile solvents. An alternative to liquid-liquid extraction is the development of artificial membrane system that reproduces the facilitated transport process through bio-membranes (made by mobile carriers and more by ion channels).

As liquid membranes are used in different fields of environmental protection [3], we mention supported liquid membranes (SLM) [4] which are the most used systems for these applications [5-11], for example the separation of organic molecules [12-14] or metallic ions [15-19]. Parhi summarize several applications in wastewater treatment, hydrometallurgical and waste recycling process [20].

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Sub Date: July 21, 2015, Acc Date: August 17, 2015, Pub Date: August 20, 2015

Citation: Eljaddi T, Hor M, Benjjar A, Riri M, Mouadili H, et al. (2015) New Supported Liquid Membrane for Studying Facilitated Transport of U(VI) Ions Using Tributyl Phosphate (Tbp) and Tri-n-Octylamine (Toa) as Carriers from Acid Medium. BAOJ Chem 1: 003.

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These systems are made from an inert polymeric support; the organic solution containing a specific extractive molecule is incorporated, usually by impregnating the polymeric support in this solution. Polypropylene for such purposes is the polymeric support most used due to its high porosity, which produces the best flux of metal ions through SLM. The supported liquid membrane processes have several advantages compared to liquid-liquid extraction. They are much less consumers of organic solvents, that today is an important criterion with regard to environmental constraints and control toxic discharges, these processes enable continuous operation in one step, since both steps extraction and re-extraction are so coupled to two interfaces of membrane. Indeed, the supported liquid membrane (SLM) has shown enormous potential for various applications.

Several studies have described the use of certain lipophilic agents such as the Tri-n-octyl amine (TOA) [20-23], or Tributyl phosphate (TBP) [24-27], which allow dissolution of certain metal ions in organic phase for extracting them from concentrated solutions. With the same aim, we try to develop a simple and effective technique for extracting ions (UO$_{2}^{3+}$) from acidic medium. This technique is based on a set of work on membrane transport processes and in particular the facilitated transport. Our work will be limited to the supported liquid membranes (SLM), consisting of an inert carrier polymer microporous polyvinylidene difluoride (PVDF), containing two amphiphilic carriers Tri-Octyl Amine (TOA) and Tributylphosphate (TBP) that are soluble in toluene solvent. A kinetic model and a transport mechanism have been developed and verified for the transport of these ions from different solutions. The macroscopic parameters permeability $P$ and initial flux $J_0$ were determined and linked to microscopic parameters, (apparent diffusion coefficient $D^*$ and the association constant $K_{ass}$) related to complex (carrier-substrate) formed in organic phase, finally, the determination of activation parameters ($E_a$, $\Delta H^*$ et $\Delta S^*$) relating to the transition state for the complexing reaction to the source-membrane interface.

**Experimental**

**Reagents**

All chemicals reagents and solvents used in this study, were pure commercial products (Aldrich, Panreac Quimica, Fluka, Redel-deHaen) of analytical grade. The prepared solutions of U(VI) ions (0.0125 M to 0.1 M), are obtained by hydrolysis of UO$_2$(CH$_2$COO)$_2$.2H$_2$O. In the receiving phase an acetic acid, the pH of two aqueous phases is adjusted to 1 by HCl acid solution.

**Preparation of the membrane**

For development of adopted membranes, we used as commercial support a microporous flat paper of polyvinylidene difluoride polymer (PVDF), a thickness of 100 µm, porosity 69% and a pore size of 0.45 µm. The SLM organic phase consists of toluene polymer (PVDF), a thickness of 100 µm, porosity 69% and a pore size of 0.45 µm. The carrier dissolved in toluene is immobilized in pores of PVDF under the capillary forces action. Then, prepared membrane is placed between two compartments of transport cell (Figure 1). Before using each of prepared membranes, we need to condition them in distilled water for 15 to 20 hours; to remove the induction time, to reduce the experience time and get a better experimental results [29]. Kinetic study of facilitated extraction process was carried out by taking samples from the receiving phase at known time intervals. These samples were analyzed by absorption spectrophotometer UV-visible (Helios γ, Shimadzu), and urany 1 ions concentrations were determined for these known time intervals.

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**Figure 1: structure of carriers:**

(a) Tri-Octyl Amine (TOA)  
(b) Tributhyle phosphate (TBP)

**Transport cell**

Experiments of transport phenomenon were performed in cell represented by the diagram in Figure 2. This cell consists of two same volume compartments, separated by the microporous membrane (M). The cell is immersed in a water bath (TB), and a multi-agitator can stir at same speed solutions in both compartments.

**Calculation models**

**Kinetic model and calculation of permeability P and initial flux $J_0$:** The membrane is placed between two compartments of transport cell, a known volume of a solution containing $C_S$ concentration of the substrate $S$, is introduced into the source phase compartment, and the same volume of water in the receiving phase compartment, at known values of pH [18,19]. We collected several successive small quantities, from the receiving phase at known time intervals,
if $C_{\text{org}}$ is the substrate concentration in the receiving phase at a time $t$, the substrate concentration in the feed phase at this time is given by the relationship $C_{\text{org}} = C_{\text{org}} - C_{\text{aq}}$ (very thin film).

The equation that relates the flux $J$ of the substrate through the each SLM and its concentration $C_{\text{org}}$ in the receiving phase is given by the relation:

$$\frac{dC_{\text{org}}}{dt} = J \times S/V$$

(1)

S: diffusion membrane surface, V: the receiving phase volume.

When the system reaches a quasi-steady state, the flux $J$ is related to the difference between the concentrations of substrate S in the feed and receiving phases $\Delta C = C_{\text{org}} - C_{\text{aq}}$ and the membrane thickness $I$ by Eq. (2) derived from Fick's First Law

$$J = P \times \Delta C/I$$

(2)

$P$ is the permeability of the membrane and $I$ its thickness

As $C_{\text{org}} = C_{\text{aq}}$ therefore $\Delta C = C_{\text{org}} - C_{\text{aq}} = C_{\text{org}} - 2C_{\text{aq}}$

(3)

Combining equations (1), (2) and (3), we obtain the following relation:

$$P \frac{dt}{C_{\text{org}}}(I \times V/S) \frac{dC_{\text{org}}}{(C_{\text{org}} - 2C_{\text{aq}})}$$

(4)

After integration:

$$P \left( t-t_{i} \right) = (I \times V / 2S) \ln \left( C_{\text{org}} / (C_{\text{org}} - 2C_{\text{aq}}) \right)$$

(5)

This equation shows that after an induction period ($t_{i}$), which can reach several hours, the term $-\ln \left( C_{\text{org}} - 2C_{\text{aq}} \right)$ must be a linear function of time $t$.

The slope “$a$” of this line allows calculating the macroscopic parameter $P$ according to equation (6).

$$P = a \times V / 2S$$

(6)

The initial flux $J_{i}$ can be calculated from the permeability $P$ according to the equation:

$$J_{i} = P \times C_{\text{org}} / I$$

(7)

The facilitated transport process ends with a dynamic equilibrium, that is established between the two compartments with $C_{\text{org}} = C_{\text{aq}} = C_{\text{org}}/2$ and equal diffusion rates in the two opposite directions.

**Thermodynamic model and calculations of microscopic parameters $K_{i}$ and $D^{*}$:** Facilitated transport of the substrate $S$ is related to the formation and dissociation of the complex Carrier-substrate ($TS$), at solution-membrane interfaces and its migration through the SLM organic phase. It should be noted that the carrier $T$ is insoluble in aqueous phases and the substrate $S$ is insoluble in the membrane organic phase. Equilibrium “association-dissociation” at interfaces, is written:

$$T_{\text{org}} + S_{\text{aq}} \leftrightarrow TS_{\text{org}}$$

org and aq indices represent respectively the membrane organic phase and the source and receiving aqueous phases. Complex concentration $[TS]$, at the interfaces of the membrane is governed by the mass action law according to the equation (8)

$$[TS] = K_{\text{ass}} [T]_{i} [S]_{i}$$

(8)

$K_{\text{ass}}$ the association constant substrate carrier to form the complex TS, by heterogeneous reaction at the interface membrane source phase.

$$[T]_{i}$$: Carrier concentration at the interface of the membrane

$[S]_{i}$: Substrate concentration in the source phase at the interface of the membrane.

In the rate determining step (migration of the substrate through the SLM organic phase), the flux $J$ is determined by the equation (9), derived from Fick’s first law, which assumes that the complex concentration is substantially zero at the membrane receiving phase interface (complex dissociation)

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

(9)

$D$: The diffusion coefficient of the complex TS through the organic phase. $l$: the membrane thickness.

However, at the membrane source phase interface, $[TS]_{i} << [S]_{i}$, (excess of the substrate relative to the carrier) and the concentration $[S]_{i}$ is equal to the substrate concentration $[S]_{i}$ at a time $t$ and $[S]_{i} = [S]_{i}$. The total carrier concentration $[T]_{i}$ immobilized in the membrane is expressed by the following equations

$$[T]_{i} = [T]_{i} + [TS] = [TS] \times \left[ (1 + \frac{K_{\text{ass}}}{[S]_{i}}) / K_{\text{ass}} \times [S]_{i} \right]$$

(10)

$$[TS] = [T]_{i} \times \frac{K_{\text{ass}}}{[S]_{i}} \times [S]_{i} / (1 + K_{\text{ass}} \times [S]_{i})$$

(11)

But in the initial conditions, we operate with a substrate excess relative to the carrier, and at interface membrane feed phase, we have: $[S]_{i} = [S]_{i} = C_{0}$ and $[TS] = [T]_{i}$. Therefore the expression of the initial flux $J_{i} = (D^{*} / l) \times [TS]$, as a function of concentrations $[T]_{i}$ and $C_{0}$ according to equation 11 is given by the following expressions

$$J_{i} = (D^{*} / l) \times ([S]_{i} \times K_{\text{ass}} / (1 + K_{\text{ass}} \times [S]_{i}))$$

Or

$$J_{i} = (D^{*} / l) \times ([T]_{i} \times K_{\text{ass}} \times C_{0} / (1 + K_{\text{ass}} \times C_{0}))$$

(12)

This expression is used to calculate the permeability as a function of $[T]_{i}, C_{0}$ and $K_{\text{ass}}$

$$P = J_{i} \times l / C_{0} = (D^{*} \times ([T]_{i} \times K_{\text{ass}} / (1 + K_{\text{ass}} \times C_{0}))$$

(13)

We note that the evaluation of parameters $J_{i}$ and $P$ is proportional to the $C_{0}$ initial concentration of substrate and is Michaelis-Menten type, since for high substrate concentrations, these two parameters evolve into limits.

To determine the microscopic parameters $D^{*}$ and $K_{\text{ass}}$, we draw the Lineweaver-Burk straight line $1/J_{i} = f(1/C_{0})$, from equation (14):

$$1/J_{i} = (l / D^{*}) \times ([1 / [T]_{i} \times K_{\text{ass}}] \times (1 / C_{0}) + (1 / [T]_{i}))$$

(14)

With:

$$K_{\text{ass}} = \text{intercept} \times (OO) / \text{slope} (p)$$

and

$$D^{*} = (l / OO) \times (1 / [T]_{i})$$

(15)

**Determination of activation parameters:** Studies relating to the...
facilitated extraction process of ions across membranes [30, 31], indicate that the initial flux is related to temperature factor by Arrhenius law, according to the following equation (16):

$$J_0(T) = A \exp(-E_a/RT)$$

(16)

$R$ is the gas constant (8.314 J.mol$^{-1}$.K$^{-1}$). $A$, a constant (pre-exponential factor), and $E_a$ is the transition state activation energy on the formation-dissociation reaction of complex (T-S) at the membrane interfaces and in the SLM organic phase, during the migration of the substrate through the membrane, which is the rate-determining step relative to the apparent diffusion of the complex (T-S). After linearization we get equation (17):

$$\ln J_0 = (-E_a/R)(1/T) + \ln A$$

(17)

Thus the terms of activation energy ($E_a$) and pre-exponential factor ($A$) are determined from the slope and intercept for the linear function $\ln(J_0)$ versus $1/T$. According to the activated complex theory (Eyring theory), we can calculate the activation parameters, enthalpy $\Delta H^*$ and entropy $\Delta S^*$, according to the expressions in the equation (18):

$$\Delta H^* = E_a - 2500 \text{ (J. mol}^{-1}) \text{ and } \Delta S^* = R (\ln A - 30.46) \text{ (J.K}^{-1}.\text{mol}^{-1}) \text{ at } 298 \text{ °K}$$

(18)

**Results and discussion**

**Influence of nature of carrier on the facilitated transport of uranyl ions**

The nature and type of the carrier are one of the most important factors that have an influence on transport process and facilitated extraction of the substrates through supported liquid membranes, because this process is based on established interactions between the two elements (substrate and carrier agent). Several studies have been realized to study and understand this effect [32-36]. In order to study and examine the influence of carrier nature on this facilitated extraction process of uranyl ions U (VI) through SLM adopted, we have worked with same operating conditions (pH = 1, $T = 298 \text{ K}$, PVDF support, Toluene as an organic solvent, ...) for the initial concentrations of substrate $C_s$ from 0.1 M to 0.0125 M and a fixed concentration of the carrier agent of 0.01 M.

Graphs of Figure 3 represent the evolution of kinetic terms $\ln(C_s - 2C_o)$ versus time, provided by the kinetic model developed for the facilitated transport phenomenon of uranyl ions through the membrane SLM-TOA and SLM-TBP. From this graphs, we can see clearly that evolution of these kinetic functions $\ln(C_s - 2C_o) = f(t)$ are straight whatever the nature of carrier, the kinetic model is checked for this process of ion studied through different membranes SLMs adopted. From the slopes of these lines, we could calculate the values of macroscopic parameters $P$ and $J_0$ according to the expressions of equations (6) and (7) under the kinetic model, and all values obtained for these two macroscopic parameters are grouped in Table 1

**Table 1**: macroscopic parameters ($P$, $J_0$) relating to facilitated transport of uranyl by SLM-TBP and SLM-TOA

| carrier | $C_s$ (mol/L) | $P \times 10^5$ (cm$^2$.s$^{-1}$) | $J_0 \times 10^5$ (mmol/s.cm$^2$) |
|---------|--------------|---------------------------------|----------------------------------|
| TOA     | 0.1          | 17.50                           | 1.75                             |
|         | 0.05         | 19.98                           | 1.00                             |
|         | 0.025        | 23.77                           | 0.59                             |
|         | 0.0125       | 27.34                           | 0.34                             |
| TBP     | 0.1          | 28.58                           | 2.86                             |
|         | 0.05         | 33.76                           | 1.69                             |
|         | 0.025        | 36.02                           | 0.90                             |
|         | 0.0125       | 37.70                           | 0.47                             |

The results in Table 1 show that the SLM membrane based on the agent TBP (SLM-TBP) is more efficient than the SLM-TOA for this facilitated process of uranyl ions ($\text{UO}_2^{2+}$), and provides the highest values of the macroscopic parameters P and $J_0$. All these results clearly indicate that the nature of extractive agent, and structure of interaction site supported by this agent, are essential for the extraction a substrate through SLMs adopted, hence the importance of choosing the carrier for improving the properties, efficiency and performance of this type of supported liquid membranes SLMs.

To explain and understand the evolution of these macroscopic parameters (permeability P and initial flux $J_0$), the thermodynamic model was developed to determine the microscopic parameters for this facilitated extraction of metal ions, Kass association constants and apparent diffusion coefficients $D^*$ concerning the association between substrate $S$ (uranil) with the carrier(T) (TOA and TBP) used to form S-T units, and diffusion of these entities through the organic phases of each SLM membranes adopted. The graph of Figure 4 shows the Lineweaver-Burk representation of the function $1 / J_0 = f(1 / C_s)$ provided by this thermodynamic model (equation 14), for extraction facilitated U (VI) ions through the two types of membranes prepared: SLM-TBP and SLM-TOA. This figure has allowed us to verify the proposed model for this process, and the rate-determining step is the migrations of S-T entity (Substrate-Carrier) through membrane phase. The slopes and intercepts of obtained straight, used to calculate the values of microscopic parameters $K_{ass}$ and $D^*$ according to the expressions of the equation

![Figure 3: the evolution of -$\ln(C_s - 2C_o)$ versus time for facilitated transport of uranyl ions through membranes SLM-TOA and SLM-TBP](image-url)

**Figure 3**: the evolution of $-\ln(C_s - 2C_o)$ versus time for facilitated transport of uranyl ions through membranes SLM-TOA and SLM-TBP $[T]=10^{-2} \text{M}, \text{pH}_i=\text{pH}_o=1, T=25^\circ \text{C et } C_s=0.0125\text{M.}$
corresponding to a low value of the constant $K_{ass}^*$ which explains the high values of the parameters $P$ and $J_0$ related to SLM-TOA, so the good performance of the SLM-TBP membrane. This last result is probably related to the fact that Uranium is a natural part of phosphate rock.

For comparing the efficiency of different membranes adopted for the studied process must be based on the values of macroscopic parameters permeability $P$ and initial flux $J_0$. It means the most efficient membrane for this process is that the values of parameters $P$ and $J_0$ are the largest in specific experimental conditions. These results were announced by Benjjar in his thesis work about facilitated extraction of Cr (III) ions and Cr (VI) with different types of membranes and also Hassoun in his thesis work, which showed that for transport facilitated of four sugars (Galactose, Mannose, Glucose, Xylose) by SLM membranes, it has been found values close to the permeability parameter ($P$), by against very different values for the parameters $D^*$ and $K_{ass}^*$ which depend on the structure each of the four sugars studied [37-38].

Finally, according to experimental results, we can confirm that this extraction process facilitated of these metal ions across SLM membranes prepared depends on two key elements: type of substrate to be extracted, nature and structure adopted the extractive agent, because the stability of interactions established between these two elements are different and specific to this pair of elements.

**Influence of substrate concentration on the facilitated transport of uranyl ions**

In this section, we will examine the effect of the initial concentration of metal ions $U$ (VI) on the evolution of macroscopic parameters $P$ and $J_0$. In order to conduct a comparative study, we have realized studies under the same experimental conditions and we have change the initial concentration of substrate from 0.0125M to 0.1M.

For our studies, the thermodynamic model adopted is based on the mechanism of the formation of an entity by interaction of substrate with extractive agent, and migration of this entity through the organic phase of membrane as a rate-determining step ($r.d.s$). This phenomenon is characterized by a kinetic law of saturation, so the flux is proportional to the concentration of the extractive agent and it depends to the substrate concentration to be extracted, in this case $U$ (VI) ion. The obtained values are summarized in Table 1. We have found the calculation model is verified and we were able to determine the values of macroscopic parameters $P$ and $J_0$. Figure 6 shows that the permeability obtained for this type of membrane varies inversely with initial concentration $C_0$ of the substrate, that it means an increase in the concentration $C_0$ causes a reduction of the parameter $P$ permeability of the membrane, by against the initial flux parameter $J_0$ moving in the same direction of the evolution of the $C_0$ concentration factor. Several studies by researchers about the phenomenon of facilitated extraction of compounds such as metal ions or organic compounds confirm this evolution [39-41]. Furthermore, representations of straight-Line weaver Burk $(1/J_0 = f(1/C_0))$ (found in the previous paragraph “the effect of the nature
of the carrier”) allowed us to validate the thermodynamic model, based on the formation of an entity (Substrate-carrier) composition (1/1) by interaction of substrate with extractive agent. Therefore, this study clearly indicates that this extraction process depends on two initial concentrations noted $C_0$ of substrate and extractive agent noted $[T]_0$.

Effect of temperature on the facilitated transport of uranyl ions

In this study, the transport of $UO_{2}^{2+}$ ions was performed at different temperatures (20, 25 and 30 °C), using the same type of membrane (SLM) with TOA carrier and initial concentration of metal ions which varied from 0.0125 to 0.1M in the same experimental conditions. The kinetic model proposed for this type of transport, in which we consider the diffusion of carrier-substrate complex is the rate-determining step indicates that the evolution of the term $- \ln (C_0 - 2C_R)$ must be linear in function of time that is always checked by straight segments represented at graph Figure 7.

The slopes of straight lines Figure 7 have allowed calculating the permeability $P$ of the membrane relating to uranyl ions for different solutions tested (equation 6); while the initial flux $J_0$ of uranyl ions through SLM are calculated using the equation 7. The results obtained for the different temperatures are grouped in table 3.

| $T$ (°K) | $C_0$ M | $P$, $10^7$ (cm$^2$ s$^{-1}$) | $J_0$, $10^5$ (mmole/s·cm$^2$) |
|----------|---------|-------------------------------|-------------------------------|
| 293      | 0.1     | 14.00                         | 1.40                          |
|          | 0.05    | 16.26                         | 0.81                          |
|          | 0.025   | 19.03                         | 0.48                          |
|          | 0.0125  | 22.39                         | 0.28                          |
|          | 0.1     | 17.50                         | 1.75                          |
|          | 0.05    | 19.98                         | 1.00                          |
|          | 0.025   | 23.77                         | 0.59                          |
|          | 0.0125  | 27.34                         | 0.34                          |
|          | 0.1     | 20.42                         | 2.04                          |
|          | 0.05    | 23.77                         | 1.19                          |
|          | 0.025   | 27.05                         | 0.68                          |
|          | 0.0125  | 31.43                         | 0.39                          |

On the one hand, the results show that increasing of temperature is accompanied with the increase of permeability and flux which indicates that this transport process needs energy. On the other hand, these results confirm that permeability $P$ of the SLM varies inversely with the concentration of the uranyl ions; an increase in the substrate concentration causes a decrease in permeability. However, the flux $J_0$ of uranyl ions through the SLM is evolving in the same direction as the substrate concentration $C_0$.

To verify the mechanism proposed for the facilitated transport of these ions prepared by the SLM and identify microscopic parameters (coefficients $D_*$ and constants $K_{ass}$), we plotted Lineweaver-Burk lines $1 / J_0 = f(1 / C_0)$ provided by equation (14), the line segments obtained are represented by the graph of Figure 8 for the three temperatures studied for SLM-TOA.

The obtained results show that the proposed mechanism is verified and there is formation of a complex S-T with (1/1) composition in the organic phase of the SLM, and also, the migration of
formed complex through this phase constitutes 'rate-determining step of the mechanism of transport of uranyl ions by this type of membrane. The slopes (p) and intercepts (oo) were calculated from these straight lines and using the expressions of the equation (14), we have determined the microscopic parameters (coefficients D* and constants K\textsubscript{ass}). The results for studied carrier are summarized in Table 4 and show that these two microscopic parameters vary little with the medium temperature.

**Table 4: Effect of temperature on microscopic parameters D* and K\textsubscript{ass} for facilitated transport of uranyl ions by SLM-TOA**

| T en °K | D* \times 10\textsuperscript{5} (cm\textsuperscript{2}.s\textsuperscript{-1}) | K\textsubscript{ass} (L.mol\textsuperscript{-1}) |
|---------|-----------------------------|-----------------------------|
| 293     | 2.55                        | 9.73                        |
| 298     | 3.31                        | 9.10                        |
| 303     | 4.05                        | 8.49                        |

From Table 4 and Figure 9, the apparent diffusion coefficient (D*) increases as the temperature increases against the association constant (K\textsubscript{ass}) decreases, which is explained by the fact that formation reaction of T-S complex is exothermic (∆H <0), hence increasing temperature decreases the association constant (K\textsubscript{ass}). It is well noted that these coefficients relative to uranyl ions are higher than sugars [42,43] which explained by the effect of the molecular size to be transported is important.

To confirm these results and to elucidate the nature of the mechanism that controls this facilitated extraction process, we have studied the evolution of the J\textsubscript{m} parameter with the temperature factor according to the empirical Arrhenius relationship, and so were able to determine the parameters activation for this process according to the activated complex theory (also known as Eyring theory). The graphs of Figure 10 show linear evolutions to the function Ln(J\textsubscript{moy}m) = f(1/T), confirming that mechanism is the same for this extraction process facilitated at all three temperatures investigated. The slopes and intercepts of straight lines obtained allow calculating of activation parameters \(E_a\) and \(\Delta H^*\) related to the transition state of the rate-determining step of facilitated process, and all values obtained are grouped in Table 5.

**Table 5: The activation parameters for the extraction facilitated U (VI) ions by the SLM membrane TOA**

| \(E_a\) (kJ/mole) | \(A_j\) (mole/m².s) | \(\Delta S^*\) (J/mole.K) | \(\Delta H^*\) (kJ/mole) |
|-------------------|---------------------|---------------------------|-------------------------|
| 27.35             | 5.64                | -239                      | 24.87                   |

Initially, for this extraction process for these cations with this type of SLM-TOA membrane, we remark that transition state of (r.d.s.) which correspond to diffusion of these ions through the membrane, requires an average energy \(E_a\) and \(\Delta H^*\). Therefore, it has a variable and negative value of activation entropy parameter \(\Delta S^*\) which indicate the transition state is early and depends on the nature of substrate (ion). In addition, at this stage of the diffusion of these ions through the membrane, this negative value of \(\Delta S^*\) parameter certainly confirms that their interactions between (substrate) and extractive agent (TOA). It means, they are reversible reactions (association / dissociation) between the substrate (ion) and the extractive agent, which are necessary for dissolution of these cations in membrane phase and its facilitated diffusion through this organic phase. On the other hand, the nature of the movement of these ions through the membrane is a successive jumps from one site to the other molecules of the mobile extractive agent in the organic phase, therefore a mechanism by jumps mobile sites characterized by high values of apparent diffusion coefficients D* and good performance of this type of SLM-TOA membrane [44,42].

**Figure 9: Evolution of K\textsubscript{ass} and D* parameters relating to facilitated extraction process of U (VI) ions through the membrane SLM-TOA**

**Figure 10: Verification of Arrhenius relationship Ln(J\textsubscript{moy}m) = f(1/T), for facilitated process of U (VI) ions by SLM-TOA**

**Figure 11: Mechanism by successive jumps on mobile sites for Facilitated extraction through SLM-TOA membrane.**
Conclusion

The metal ions (UO$_{2}^{2+}$) were transported by TOA and TBP as carriers, in same organic solvent (toluene) and with same polymer support (PVDF). The results conform well the proposed kinetic model, which allowed us to determine the macroscopic parameters (permeability $P$ and initial flux $J_0$) for ions studied. this results show SLM-TBP membrane is more efficient than SLM-TOA membrane which is also explained by the microscopic parameters ($D^{*}$ and $K_{a}$), we found that TOA carrier forms a stable complex with the ions uranium relative to TBP carrier, and therefore the uranyl ions diffuse less through SLM-TOA than SLM-TBP membrane, which is consistent with the macroscopic parameters ($P$ and $J_0$).

To better understand this phenomenon of facilitated transport through this latter type of liquid membranes, we have used the activated complex theory (or the theory of Eyring) to determine the activation parameters, we found that formation of relative complex to uranyl ions does not require much energy, so there are low interactions between these ions and the carrier used.

Finally all these results explain and confirm the performance of this type of membranes for this phenomenon of facilitated extraction of these cations and will elucidate the nature of the movement of these ions across the membrane phase, which is done by successive jumps and therefore according to a mechanism jumps on mobile sites. This type of SLM membrane may be applied to the extraction of uranyl and vanadate ions from acidic media and especially from phosphoric acid.

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Citation: Eljaddi T, Hor M, Benjjar A, Riri M, Mouadili H, et al. (2015) New Supported Liquid Membrane for Studying Facilitated Transport of U(VI) Ions Using Tributyl Phosphate (Tbp) and Tri-n-Octylamine (Toa) as Carriers from Acid Medium. BAOJ Chem 1: 003.

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