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Research Article

Process of Facilitated Extraction of Vanadium Ions through Supported Liquid Membranes: Parameters and Mechanism

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To conduct experiments related to the facilitated extraction phenomenon of vanadium ions (VO_2^+), three supported liquid membranes (SLMs) were prepared, each containing 0.01 M of methyl cholate (MC), resorcinarene (RESO), or trioctylamine (TOA) as extractive agents. Kinetic and thermodynamic models were developed, based on the interaction of the substrate (VO_2^+) with the extractive agent T and the diffusion of the formed entity (TS) through the membrane. The experimental results verify the models, and to determine, macroscopic parameters, permeabilities (P) and initial fluxes (J_0), and microscopic parameters, association constants (K_{ass}) and apparent diffusion coefficients (D^*) related to formed entities (TS) and their diffusion through the membrane organic phase. The experimental results indicate that the mechanism on the migration of the VO_2^+ ions through the membrane organic phase is based on the successive jumps of substrate, from one site to another of the extractive agent. To explain these results and understand the mechanism, we studied influence of temperature factor, and we determined activation parameters (E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$). The results show that this extraction phenomenon is governed by a structural term. Therefore, the membrane performance changes according to nature and structure of the association site presented by each of extractive agents.

1. Introduction

Conventional industrial techniques of extraction and separation by distillation or crystallization have a high cost, since they require large amounts of energy and use polluting organic solvents. The technique of liquid-liquid extraction is cheaper, but it requires large amounts of volatile organic solvents, often considered pollutants to the environment, which limits its use. Membrane processes for separation and recovery are more economical because they can operate at standard temperature and pressure and with very small amounts of organic solvents [1, 2].

The supported liquid membranes (SLMs) are part of these membrane processes types; they have a major economic and environmental interest, since they are necessary for the treatment of liquid mediums, contaminated with metal ions or organic compounds. These membrane types (SLMs) are prepared from inert polymer support; in fact, an organic solution containing a hydrophobic extractive agent is incorporated usually by immersion of this polymeric support. Polypropylene remains a widely used polymer support, for its high porosity, which generates large fluxes of metal ions through these membrane types. The supported liquid membrane processes have several advantages compared to the liquid-liquid extraction phenomenon. In particular, a very low uses of organic solvents, which today an important criterion for the protection of the environment and the treatment of toxic effluents. These processes permit continuous operation in a single step, since the two steps extraction and reextraction are so coupled to the two interfaces. Indeed, the membranes are thin films that separate two fluids; an essential property of membranes is their permeability and therefore

their ability to allow the passage of only certain species from one environment to another, while acting as a barrier to other species.

Studies based on the use of supported liquid membranes for removing some toxic metal ions from concentrated acid solutions are very numerous; the interest in this study was focused on the phenomenon of facilitated transport and extraction of VO_2^+ ions. Indeed, vanadium is often present as an impurity during the process of manufacturing industrial phosphoric acid by the wet process, in which sulfuric acid is used to dissolve the phosphate ores. The obtained liquor is a complex solution composed of organic and inorganic impurities. Among these impurities, vanadium ions in high concentrations around 600 mg L^{-1}, this is a potential source of vanadium element [3].

In the present work, we try to use the SLMs technique for the facilitated extraction of vanadium ions (VO_2^+) from acid environments. This technique is based on work carried out by the principle of substrate transport by membrane processes, such as facilitated transport through liquid membranes. The used supported liquid membranes consist of a microporous inert polymeric support polyvinylidene difluoride (PVDF), a thickness of 100 μm, and a porosity of 60% with pores of 0.45 μm in diameter. For each of the prepared membranes, this support will be impregnated with organic solution toluene in 0.01 M concentration for each following carrier agents: methyl cholate (MC), resorcinarene (RESO), or trioctylamine (TOA). Kinetic and mechanistic models have been developed and tested to the facilitated extraction phenomenon of VO_2^+ ions from acid solutions. The macroscopic parameters, permeabilities P, and initial fluxes J_0 were determined and related to the microscopic parameters, the apparent diffusion coefficient D^* and the association constant K_{ass} characteristics of the formation of entity "Extractive agent-Substrate" (TS) and its diffusion across organic phase [4–7]. For a better understanding of this phenomenon, the explanation of the results and the identification of the mechanism for this process, we studied the temperature factor influence on the evolution of the parameters P, J_0, D^*, and K_{ass}, as well as the performance of adopted SLMs. Similarly, we determined the activation parameters, energy E_a, enthalpy $\Delta H^{\neq}$, and entropy $\Delta S^{\neq}$, in order to know the factor that governs the movement of VO_2^+ ions during their passage through the membrane organic phase.

2. Material and Methods

2.1. Description and Operating Principle of a SLM. The SLMs consist of an organic solvent immobilized by capillary forces in the pores of a polymeric support, separating the source and the receiving phases. The support of these membranes is generally an hydrophobic inert polymer which is characterized by a small thickness of 25 to 100 μm and pore diameters of 0.12 to 1 μm [3, 4]. The diffusion of chemical species through these membranes is an interfacial phenomenon; the use of a support having a high porosity is necessary to increase the contact area and the selectivity to the diffusion of species

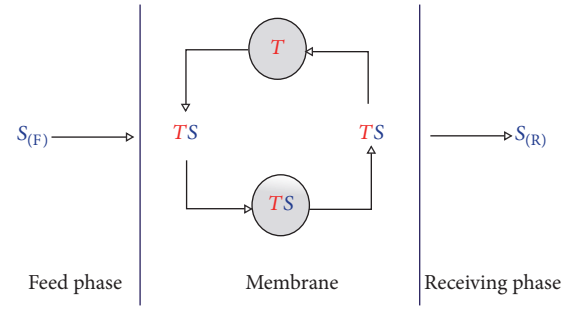


Figure 1: Facilitated transport and extraction mechanism through a SLM.

and very important to operate in the best conditions of extraction and separation through the SLMs [4]. To improve the separation process, the researchers added to the organic phases of SLMs mobile extractive agents, which accelerate and facilitate the extraction of species, while increasing the selectivity of these membrane types [8–11]. In addition, the technical SLM approach is widely used for the extraction and enrichment of metal ions and some organic compounds [12–14]. Indeed, this technique has been used to study the facilitated transport and apply it to the selective extraction and enrichment of varied organic compounds, such as amino acids [15, 16], amino-aromatic phosphates [17], sugars [18–20], herbicides [21, 22], and organic acids [23, 24].

This method, which is called facilitated transport or extraction through supported liquid membranes, is based on the recognition of a substrate (S) by a extractive agent molecule (T). This process involves the mobility within the membrane organic phase of a complex (ST) produced by a reversible forming reaction, between the agent (T) and the transported substrate (S), which takes place at membrane interfaces with the source and receiving phases. This facilitated extraction phenomenon through the SLMs is a cyclical process which is based on the five following successive steps:

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

(2) Formation of substrate-carrier complex (ST) at the interface source phase membrane

(3) Diffusion of entity (ST) through the membrane organic phase to the interface membrane-receiving phase

(4) Dissociation of entity (ST) at the interface membrane receiving phase

(5) Diffusion of free substrate (S) in the receiving phase and the extractive agent (T) in the membrane organic phase to perform a new cycle *(interaction-diffusion-dissociation)*

These five steps are represented by the diagram in Figure 1 and constitute the mechanism of facilitated extraction through a SLM, in which step (3) is the rate-determining step.

2.2. Cell for the Facilitated Extraction. Experiments on the transport of these ions were performed in the cell represented by the scheme in Figure 2. This cell consists of two glass

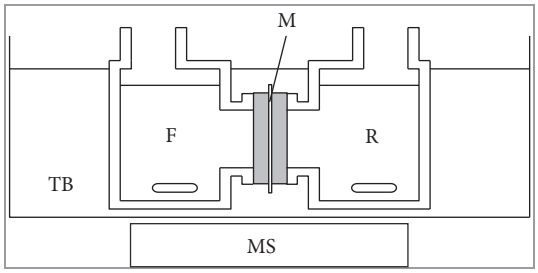


Figure 2: Scheme on the transport cell: M: SLM, F: feed source, R: receiving phase. TB: thermostated bath, and MS: multimagnetic stirrer.

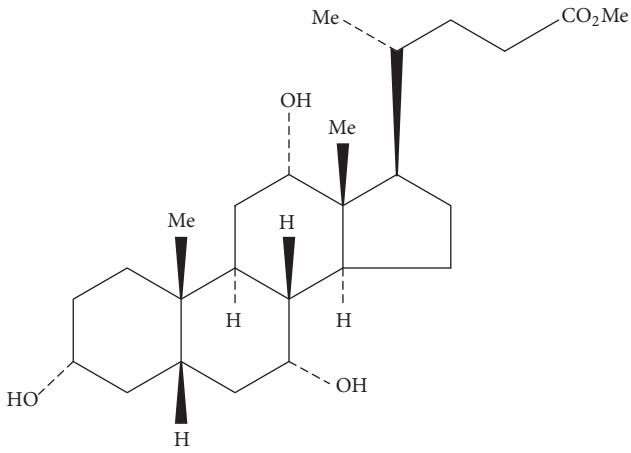


Figure 3: Methyl cholate structure (MC).

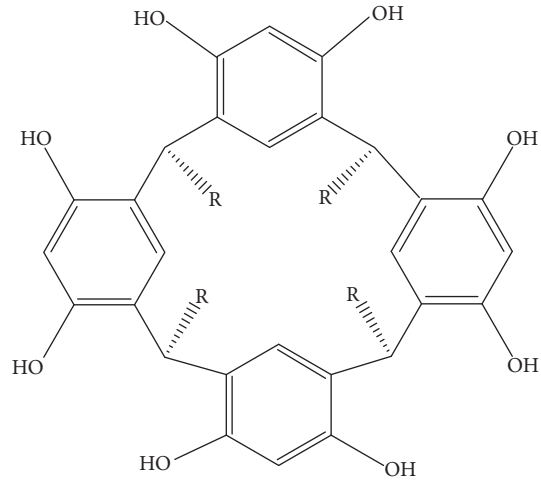


Figure 4: Resorcinarene structure (RESO).

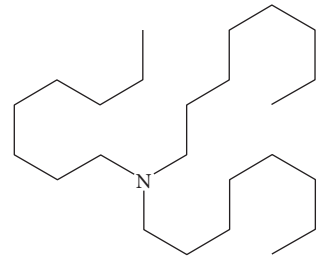


Figure 5: Tri-n-octylamine structure (TOA).

compartments of equal volumes (175 mL), separated by the microporous membrane (M). The cell is immersed in a water bath (TB), and a multiagitator allows continuous stirring solutions in both compartments.

2.3. Experimental Section. All chemicals, reagents, and solvents were pure commercial products (Aldrich, Fluka) of analytical grade. The used solutions of vanadium ions VO_2^+ are obtained by acid hydrolysis of ammonium metavanadate NH_4VO_3. The support is a microporous polymeric film of polyvinylidene difluoride (PVDF), a thickness of 100 μm, a porosity of 60%, and a pore diameter of 0.45 μm. Liquid solutions adopted for the SLM preparation consist of toluene organic phase containing 0.01 M of one of the following extractive agents: MC, RESO, or TOA (Figures 3, 4, and 5). The three used membranes were prepared by impregnation for a 5-to-6-hour period, each of three polymer supports by one of the previous organic phases. Acidic solutions (0.10 to 0.0125 M) of VO_2^+ ions are prepared in pure distilled water from stock solutions. Before being used, each of the prepared MLSs was treated in a conditioning step by pure water for 20 hours [6, 19], to remove a long induction period preceding the facilitated extraction process of a substrate by a SLM. Each used SLM was placed for a period of about 20 hours between the two compartments of the used cell for this facilitated transport process (Figure 2), filled with bidistilled pure water solution.

For experiments relating to the facilitated extraction of VO_2^+ ions, the feed phase is a fixed acidity solution of nitric acid containing a known concentration of VO_2^+ ions, and the receiving phase is a hydrochloric acid solution to same acidity. The two compartment solutions are maintained at the same agitation and kinetic study on the evolution of the VO_2^+ ions concentration C_r is done by regular sampling from the receiving phase at known time intervals. These samples were analyzed by UV-visible spectroscopy, and C_r concentration values in the receiving phase were calculated at the different time intervals as well as the term.

$\ln(C_0 - 2C_r)$ versus time. Table 1 includes an example of results for facilitated extraction of VO_2^+ ions from a concentrated acid medium.

3. Theoretical Models and Calculations

3.1. Kinetic Model and Calculation of Permeability (P) and Initial Flux (J_0). The membrane is placed between the two compartments; in source compartment, a known volume of the substrate solution (S) with C_0 concentration, is introduced, and the same volume of water is placed in the receiving compartment. We carry several samples from the receiving phase at known time intervals, we note C_r substrate concentration in this phase at time t, and the substrate

Table 1: Results for the facilitated extraction phenomenon of VO_2^+ ions by SLM containing resorcinarene extractive agent.

t (mn)	Absorbance	C_r (mol L^{-1})	$-\ln(C_0 - 2C_r)$
0	0.978	0	2.303
30	0.039	0.00398	2.386
60	0.052	0.00531	2.415
90	0.085	0.00869	2.494
120	0.114	0.01165	2.568

$C_0 = [VO_2^+]_0 = 0.1$ M, $[H_3O^+] = 1$ M, [RESO] = 0.01 M, and $T = 293$ K.

concentration in the source phase at this time is $C_s = C_0 - C_r$ (used support is very thin).

The equation that relates the flux J to the C_r concentration of the substrate S is given by the relationship:

$$\frac{dC_r}{dt} = J * \frac{S}{V}, \tag{1}$$

where S is membrane area in contact with the aqueous solutions and V is the receiving phase volume.

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

$$J = P * \frac{\Delta C}{l}, \tag{2}$$

where P is membrane permeability and l is the membrane thickness

Knowing that the membrane is very thin, then $C_s = C_0 - C_r$ and

$$\Delta C = C_s - C_r = C_0 - 2C_r. \tag{3}$$

Combining (1), (2), and (3), we have

$$P dt = \frac{(l * V/S)\, dC_r}{(C_0 - 2C_r)}. \tag{4}$$

After integration,

$$P(t - t_L) = \left(l * \frac{V}{2S}\right) \ln\left[\frac{C_0}{(C_0 - 2C_r)}\right]. \tag{5}$$

This equation shows that, after an induction period (t_L), which can reach several hours, the term $-\ln(C_0 - 2C_r)$ should be a linear function of time t.

The slope (a) of this line allows calculating the permeability, using

$$P = a \times \frac{Vl}{2S}. \tag{6}$$

The initial flux J_0 can be calculated from the permeability P according to the following:

$$J_0 = P \times \frac{C_0}{l}. \tag{7}$$

The experience end is achieved when a dynamic equilibrium is established between the two compartments, with $C_s = C_r = C_0/2$ and diffusion rates being equal in both directions.

3.2. Thermodynamic Model and Determination of Microscopic Parameters. Transport of a substrate S depends on the formation and dissociation of the complex carrier-substrate (TS) at solution-membrane interfaces. It should be noted that the carrier T is insoluble in aqueous phases and the substrate S is insoluble in the membrane organic phase. The formation-dissociation equilibrium of the complex (TS) is

$$T_{org} + S_{aq} \Longleftrightarrow TS_{org}, \tag{8}$$

where org and aq are, respectively, the membrane organic phase and the aqueous source and receiving phases. Concentration $[TS]_i$ of complex at the membrane interface is governed by the law of mass action according to the following:

$$[TS]_i = K_{ass}\,[T]_i\,[S]_i\,, \tag{9}$$

where K_{ass} is the association constant on the complex (TS) and is the equilibrium constant of this heterogeneous reaction at the interface feed phase-membrane; $[T]_i$ is the carrier concentration at the interface membrane-feed phase; and $[S]_i$ is the substrate concentration in the source phase at the membrane interface.

In the rate-determining step, the flux J is determined by (10), derived from Fick's first law, which assumes that the complex concentration $[ST]$ is almost zero at the interface membrane-receiving phase (dissociation of the complex):

$$J = \left(\frac{D^*}{l}\right) \times [TS]_i\,. \tag{10}$$

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

However, at the interface source phase-membrane, $[TS]_i \ll [S]_i$ (excess of substrate relative to the carrier) and the concentration $[S]_i$ is equal to the substrate concentration $[S]_t$ at time t and thus $[S]_i = [S]_t$. The total carrier concentration $[T]_0$ immobilized in the membrane is constant, and it is equal to the sum of the concentrations $[T]_i$ and $[TS]_i$.

$$\begin{aligned}[T]_0 &= [T]_i + [TS]_i \\ &= [TS]_i \cdot \left[\frac{(1 + K_{ass} \cdot [S]_i)}{K_{ass}} \cdot [S]_i\right],\end{aligned} \tag{11}$$

$$[TS]_i = [T]_0 \cdot K_{ass} \cdot \frac{[S]_i}{(1 + K_{ass} \cdot [S]_i)}. \tag{12}$$

But, in the initial conditions, we operate with an excess of substrate relative to the carrier and at the interface feed phase-membrane, $[S]_i = [S]_0 = C_0$. This allows to write the

expression for the initial flux J_0 according to $[T]_0$ and C_0 ((10) and (12)):

$$J = \left(\frac{D^*}{l}\right) \times \left([T]_0 \cdot K_{\text{ass}} \cdot \frac{[S]_i}{(1 + K_{\text{ass}} \cdot [S]_i)}\right). \quad (13)$$

or

$$J_0 = \left(\frac{D^*}{l}\right) \times \left([T]_0 \cdot K_{\text{ass}} \cdot \frac{C_0}{(1 + K_{\text{ass}} \cdot C_0)}\right) \quad (14)$$

This expression is used to calculate the membrane permeability P according to $[T]_0$, C_0, and constant K_{ass}:

$$P = J_0 \cdot \frac{l}{C_0} = (D^*) \times \left([T]_0 \cdot \frac{K_{\text{ass}}}{(1 + K_{\text{ass}} \cdot C_0)}\right). \quad (15)$$

These relationships indicate that the evolution of macroscopic parameters J_0 and P is proportional to the initial substrate concentration C_0 and it is of Michaelis-Menten type, since, at high substrate concentrations, these two parameters are the limit values by saturation phenomenon of the carrier.

To determine the microscopic parameters D^* and K_{ass}, we linearized the expression in (16) as Lineweaver-Burk straights $1/J_0 = f(1/C_0)$.

$$\frac{1}{J_0} = \left(\frac{l}{D^*}\right) \times \left[\left(\frac{1}{[T]_0} \cdot K_{\text{ass}}\right) \cdot \left(\frac{1}{C_0}\right) + \left(\frac{1}{[T]_0}\right)\right] \quad (16)$$

and therefore

$$K_{\text{ass}} = \frac{\text{intercept}\,(OO)}{\text{slope}\,(p)}, \qquad D^* = \left(\frac{l}{OO}\right) \cdot \left(\frac{1}{[T]_0}\right). \quad (17)$$

3.3. Determination of Activation Parameters. Studies relating to the facilitated extraction process of ions across membranes [25, 26] indicate that the initial flux is related to temperature factor by Arrhenius law, according to the following relationship:

$$J_i\,(T) = A_j \exp\left(-\frac{E_a}{RT}\right), \quad (18)$$

where R is the gas constant ($8.314\,\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), A_j is a constant (preexponential factor), and E_a is the transition state activation energy on the formation-dissociation reaction of entity (TS) 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 (TS). After linearization, we get

$$\ln J_i = \frac{-E_a}{R} \times \frac{1}{T} + \ln A_j. \quad (19)$$

Thus the terms of activation energy (E_a) and preexponential factor (A_j) are determined from the slope and intercept for the linear function $\ln(J_i)$ versus $(1/T)$. According to the activated complex theory (Eyring theory), we can calculate the activation parameters, enthalpy $\Delta H^{\neq}$, and entropy $\Delta S^{\neq}$, according to the expressions in

$$\Delta H^{\neq} = E_a - 2500\ \left(J \cdot \text{mol}^{-1}\right), \qquad \Delta S^{\neq} = R\left(\ln A_j - 30,46\right)\ \left(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\right) \quad (20)$$

at 298°K.

4. Results and Discussion

4.1. Macroscopic Parameters P and J_0. In the same experimental conditions, using each of the three prepared membranes (MLSs) with one of the agents MC, RESO, or TOA in the same concentration ($[T]_0 = 0.01$ M) facilitated extraction of VO_2^+ ions that was carried out for different initial concentrations C_0 (0.0125–0.100 M) at the same temperature 293 K. Proposed kinetic model for this phenomenon in which the diffusion of the complex carrier-substrate (TS) is considered the rate-determining step indicates that the evolution of the term $-\ln(C_0 - 2C_r)$ must be linear in function of time (see (5)). Indeed, the experimental results verify the model and allow obtaining the straight line segments shown by graphs of Figures 6 and 7.

The slopes calculated from these lines are used to determine the permeability values (P) of the used membranes with respect to VO_2^+ ions for different tested solutions (see (6)), while the initial flux values (J_0) of the substrate through the used SLMs are calculated using (7). Table 2 summarizes all results for the three membranes at temperature 293 K.

All these experimental results indicate that the permeability P of the used SLM varies inversely with the initial concentration C_0 of VO_2^+ ions, and an increase in substrate concentration results in a decrease in permeability. However, the initial flux values J_0 of these ions through each of studied SLMs increase as the initial concentration C_0 of the substrate [27–29]. On the other hand, we observe that the values of permeabilities P and initial fluxes J_0 relative facilitated extraction of VO_2^+ ions, using both SLMs containing, respectively, methyl cholate (MC) and resorcinarene (RESO) as extractive agents are slightly near, while the use of the SLM containing trioctylamine (TOA) as extractive agent provides relatively high values for these two parameters P and J_0, in the same experimental conditions and the same temperature.

4.2. Microscopic Parameters D^* and K_{ass}. To verify the proposed mechanism for this facilitated extraction phenomenon of the VO_2^+ ions by prepared SLMs and determine the *microscopic* parameters, apparent coefficients D^*, and association constants K_{ass}, we traced the Lineweaver-Burk lines ($1/J_0 = f(1/C_0)$) provided by (16), from the experimental results for the three used SLMs. The obtained line segments are shown by the graph in Figure 8.

The obtained straight lines clearly indicate that the proposed mechanism for this phenomenon is verified, and there is formation entity (ST) of composition (1/1), by association "substrate-extractive agent" in the organic phase of used SLM. The migration of this entity through this phase is the

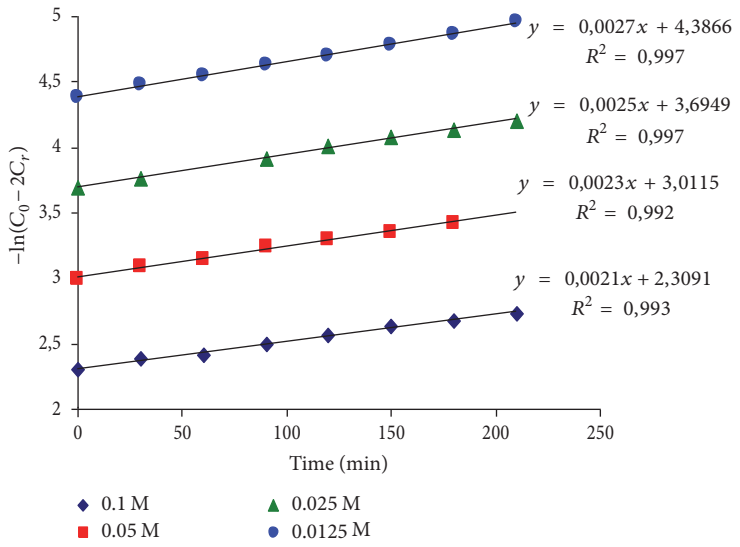


FIGURE 6: Evolution of the term $-\ln(C_0 - 2C_r)$ versus time for facilitated extraction of VO_2^+ ions by SLM containing extractive agent RESO. $[H_3O^+] = 1$ M, [RESO] = 10^{-2} M, and $T = 293$ K.

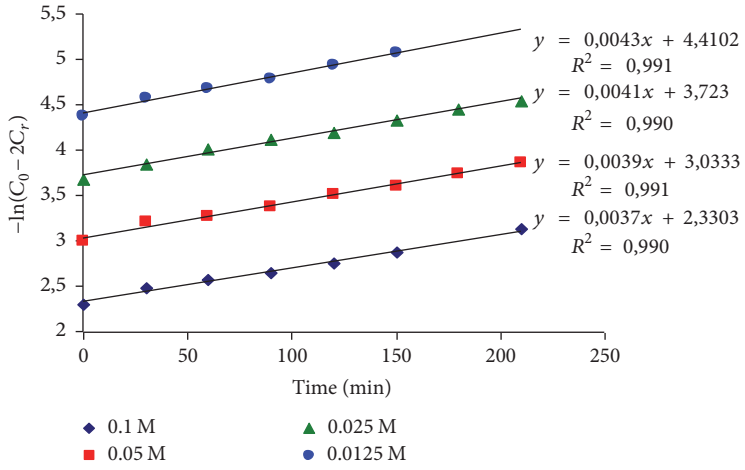


FIGURE 7: Evolution of the term $-\ln(C_0 - 2C_r)$ versus time for facilitated extraction of VO_2^+ ions by SLM containing extractive agent TOA. $[H_3O^+] = 1$ M, [TOA] = 10^{-2} M, and $T = 293$ K.

rate-determining step of the mechanism for the facilitated extraction of VO_2^+ ions. Slopes (p) and intercepts (OO) were calculated from these lines and using the expressions in (16); the apparent coefficients D^* and the association constants K_{ass} were determined. The obtained results for the used membranes are summarized in Table 3 and the histogram in Figure 9 shows that these two *microscopic* parameters vary inversely. This result indicates that a high stability of entity (ST) formed in the SLM organic phase results in a low diffusion of this entity and conversely.

The values of permeability P, initial flux J_0, (Table 2), association constant K_{ass}, and apparent diffusion coefficient D^* (Table 3), relating to this facilitated extraction phenomenon of VO_2^+ ions, clearly show that, for the same concentration of the extractive agent (0.01 M) and at the same temperature (293 K), the facilitated extraction of the substrate (VO_2^+) is more efficient through SLM containing trioctylamine (TOA) as extractive agent, compared with two other investigated membranes, containing, respectively, methyl cholate (MC) and resorcinarene (RESO). These results clearly show that the value of association constant K_{ass} depends on the nature of association site carried by each of the extractive agents, as well as the reverse evolution of K_{ass} and D^* parameters, indicates that the movement of VO_2^+ ions in the membrane organic phase cannot be a pure diffusion movement, but it takes place by successive jumps of the substrate (VO_2^+) from one site to another of the extractive agent in successive and reversible reactions (association/dissociation).

4.3. Influence of the Temperature Factor. Under the same experimental conditions and using membranes, respectively. MLS-RESO, SLM-MC, and SLM-TOA, we performed experiments to the facilitated extraction of VO_2^+ ions in solutions of C_0 concentrations ranging from 0.0125 to 0.1 M and at

Table 2: The values of macroscopic parameters (P and J_0) on the facilitated extraction of VO_2^+ ions by the three developed SLMs.

C_0 concentration (mol L^{-1})	Permeability P (10^7 cm^2 s^{-1})			Initial Flux J_0 (10^5 mmol s^{-1} cm^{-2})		
	RESO	MC	TOA	RESO	MC	TOA
0.1	13.37	17.28	23.56	1.33	1.72	2.35
0.05	14.64	18.22	24.84	0.73	0.91	1.24
0.025	15.92	20.27	26.11	0.39	0.50	0.65
0.0125	17.19	21.29	27.38	0.21	0.26	0.34

[RESO] = [MC] = [TOA] = 10^{-2} M $[H_3O^+]$ = 1 M, and T = 293 K.

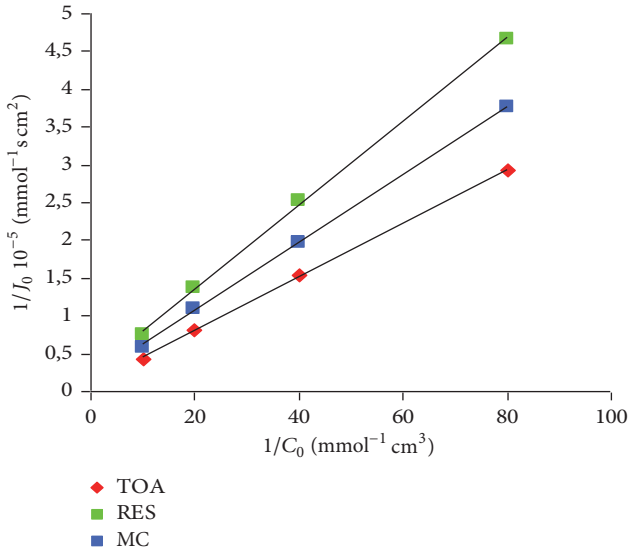


Figure 8: The Lineweaver-Burk representation $1/J_0 = f(1/C_0)$ for facilitated extraction of VO_2^+ ions by adopted SLMs. [RESO] = [MC] = [TOA] = 10^{-2} M, $[H_3O^+]$ = 1 M, and T = 293 K.

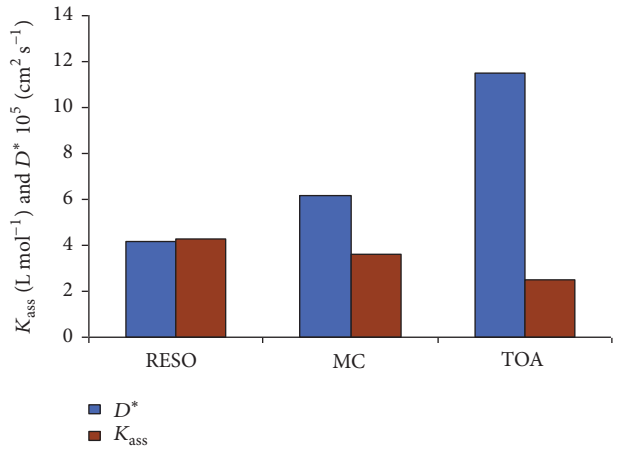


Figure 9: Microscopic parameters evolution for facilitated extraction phenomenon of VO_2^+ ions.

Table 3: Values of microscopic parameters (D^* and K_{ass}) for facilitated extraction of VO_2^+ ions.

Extractive agent	RESO	MC	TOA
D^* 10^5 ($cm^2 \cdot s^{-1}$)	4.19	6.15	11.50
K_{ass} (L· mol^{-1})	4.29	3.60	2.48

[RESO] = [MC] = [TOA] = 10^{-2} M, $[H_3O^+]$ = 1 M, and T = 293 K.

temperatures 293, 298, and 303°K. Graphs in Figures 10 and 11 represent the straight lines relating to the evolution of the term $-\ln(C_0 - 2C_r)$ with time provided by kinetic model, for different studied temperatures, at C_0 = 0.10 M, and for adopted membranes SLM-TOA and SLM-RESO.

The slopes calculated from obtained lines for the different experiments were used to calculate according to the expressions in (6) and (7), the values of permeabilities P, and initial fluxes J_0, relative to this facilitated extraction phenomenon of VO_2^+ ions through the adopted membranes. For the different studied temperatures, all obtained results are summarized in Table 4.

These results confirm that the permeability P and the initial flux J_0 parameters vary inversely and with the initial concentration C_0 of VO_2^+ ions [18, 19]. They indicate clear influence of temperature factor on the values of these parameters and therefore an increase in the membrane performances, with an excellent performance of SLM-TOA membrane relative to other adopted SLMs.

To confirm the previous results and to study temperature factor influence on the evolution of microscopic parameters D^* and K_{ass}, we traced the Lineweaver-Burk lines, $1/J_0 = f(1/C_0)$, and the obtained line segments are represented by the graphs in Figures 12 and 13, for two adopted membranes SLM-RESO and SLM-MC.

Slopes (p) and intercepts (oo) determined from different Lineweaver-Burk straight lines (Figures 12 and 13) were used to calculate the values of parameters D^* and K_{ass} according to the terms in (16). The obtained results are summarized in Table 5 and confirm the inverse evolution of these microscopic parameters, and the temperature factor influence, in fact, an increase in the temperature causes a decrease in the value of K_{ass} and increased the coefficient D^* and therefore an improvement of the adopted membrane performance.

For the three adopted membranes, the results indicate a clear influence of temperature factor on the evolution of K_{ass} and D^* parameters, and an increase in temperature results in a weak association of substrate (VO_2^+) with the extractive agent, so fast jumps of substrate from one site to another of extractive agent, and a good substrate diffusion through the membrane. These results also show that microscopic parameters K_{ass} and D^* are specific for the pair (substrate,

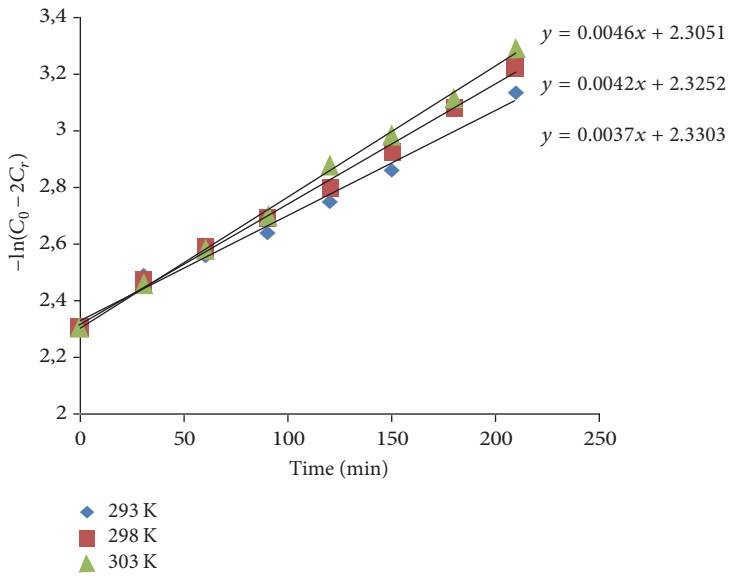


FIGURE 10: $-\ln(C_0 - 2C_r)$ term evolution versus temperature for the facilitated extraction of VO_2^+ ions through membrane SLM-TOA. $[H_3O^+] = 1$ M, $[TOA] = 10^{-2}$ M, $[VO_2^+] = 0.1$ M.

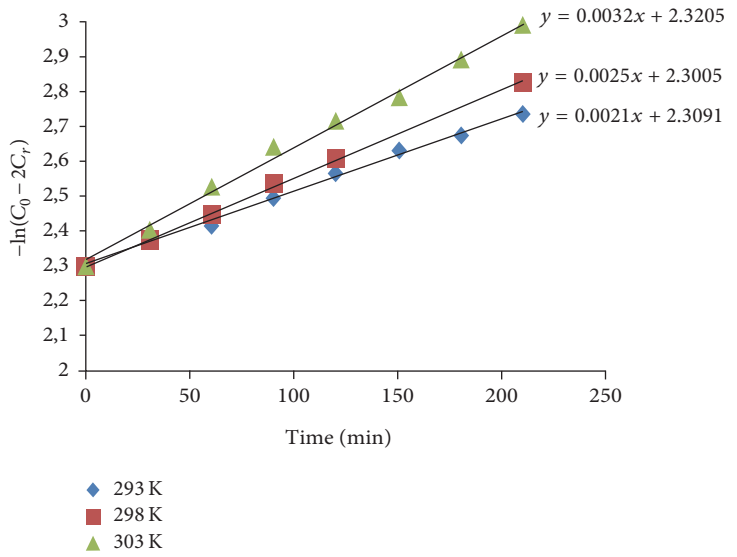


FIGURE 11: Temperature effect on $-\ln(C_0 - 2C_r)$ term evolution versus time, for the facilitated extraction of VO_2^+ ions by membrane SLM-RESO. $[H_3O^+] = 1$ M, $[RESO] = 10^{-2}$ M $[VO_2^+] = 0.1$ M.

extractive agent), and SLM-TOA membrane remains the most effective for this facilitated extraction process of VO_2^+ ions.

4.4. Activation Parameters E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$. To examine the influence of energetic and associative terms on the mechanism for the facilitated extraction process of VO_2^+ ions, we plotted the function $\ln(J_{0moy}) = f(1/T)$ provided by Arrhenius relationship (see (19)). For adopted SLMs, the line segments obtained at studied temperatures are represented by the graph in Figure 14.

The slopes (p) and intercepts (oo) calculated from straight lines represented by the graph in Figure 14 were used to determine according to the expressions in (20) and the values of activation parameters, energy E_a, enthalpy $\Delta H^{\neq}$, and entropy $\Delta S^{\neq}$, related to the transition states of association/dissociation reactions of substrate (VO_2^+) with each of extractive agents (TOA, MC, or RESO). All obtained results for these parameters are summarized in Table 6,

These results clearly indicate that the transition states related to association/dissociation reactions of substrate with the extractive agent are highly ordered states and require small amounts of energy. The analysis of the results shows that the facilitated extraction process VO_2^+ ions is a phenomenon governed by a structural term related to the nature and the structure of the interaction site of each extractive agents; then

Table 4: Temperature factor influence on the evolution of macroscopic parameters P and J_0.

Extractive agent	C_0 mol L^{-1}	$P \cdot 10^7$ cm^2 s^{-1}			$J_0 \cdot 10^5$ mmol s^{-1} cm^{-2}		
		293 K	298 K	303 K	293 K	298 K	303 K
RESO	**0.1**	**13.37**	**15.92**	**20.38**	**1.33**	**1.59**	**2.03**
	0.05	14.64	17.19	21.65	0.73	0.85	1.08
	0.025	15.92	18.47	22.92	0.39	0.46	0.57
	0.0125	17.19	19.74	24.20	0.21	0.24	0.30
		288 K	293 K	303 K	288 K	293 K	303 K
MC	**0.1**	**14.43**	**17.28**	**24.71**	**1.44**	**1.72**	**2.47**
	0.05	16.47	18.22	25.95	0.82	0.91	1.29
	0.025	17.57	20.27	28.43	0.43	0.50	0.71
	0.0125	18.66	21.29	29.89	0.23	0.26	0.37
		293 K	298 K	303 K	293 K	298 K	303 K
TOA	**0.1**	**23.56**	**26.75**	**29.30**	**2.35**	**2.67**	**2.92**
	0.05	24.84	28.02	30.57	1.24	1.40	1.52
	0.025	26.11	28.62	31.84	0.65	0.71	0.79
	0.0125	27.38	30.57	33.12	0.34	0.38	0.41

[RESO] = [MC] = [TOA] = 10^{-2} M.

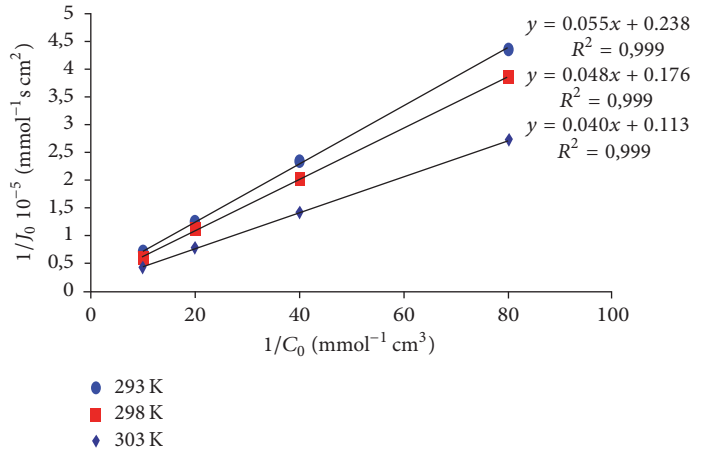


Figure 12: Lineweaver-Burk lines for the facilitated extraction of VO_2^+ ions by SLM-RESO membrane, for different values of temperature. [H_3O^+] = 1 M, [RESO] = 10^{-2} M.

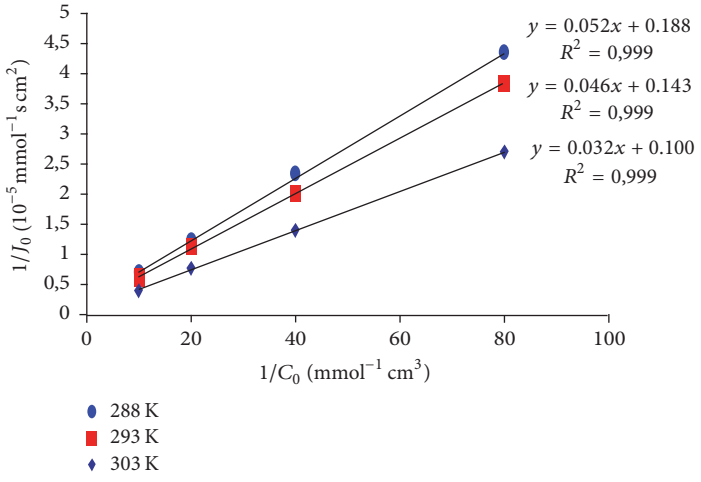


Figure 13: Lineweaver-Burk straight lines relating to the influence of temperature on the microscopic parameters for extracting VO_2^+ ions by SLM-MC membrane. [H_3O^+] = 1 M, [MC] = 10^{-2} M.

Table 5: Temperature factor influence on the values of K_{ass} and D^* for the facilitated extraction phenomenon of VO_2^+ ions.

Extractive agent	T (K)	$D^* \cdot 10^5$ ($cm^2 \cdot s^{-1}$)	K_{ass} ($L \cdot mol^{-1}$)
RESO	***293***	**4.19**	**4.29**
	298	5.67	3.61
	303	8.80	2.83
MC	***288***	5.19	3.75
	293	**6.15**	**3.60**
	303	9.42	3.29
TOA	***293***	**11.50**	**2.48**
	298	14.08	2.29
	303	17.24	1.97

[Extractive agent] = 0.01 M and $[H_3O^+]$ = 1 M.

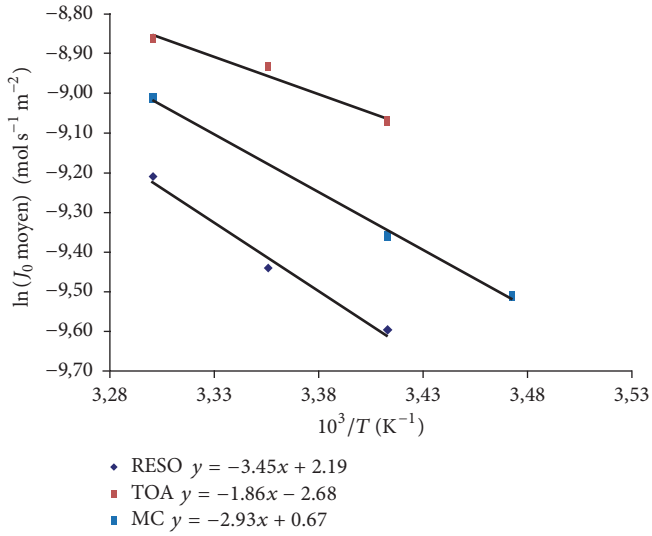


Figure 14: The representation of $\ln(J_{0moy}) = f(1/T)$ function on the facilitated extraction phenomenon of VO_2^+ ions by three membranes: SLM-RESO (-MC) and (-TOA).

the influence of energetic term is negligible. On the other hand, recent studies [5, 6, 30, 31] and this analysis confirm previous results which indicate that the substrate movement across each of the developed membranes cannot be a pure diffusion movement (*way A*), but it takes place by successive jumps of one site to an another of used extractive agent, via interaction reactions of VO_2^+ ions with the extractive agent according to *the way B* indicated by the diagram in Figure 15.

5. Conclusion

Three supported liquid membranes (SLMs) were prepared with same polymer support (PVDF), same organic phase (toluene), and three different extractive agents (TOA, MC, and RESO). These three SLMs were adopted for the facilitated extraction process of VO_2^+ ions from concentrated acidic environments. All experimental results verify the proposed kinetic model, which was used to determine the *macroscopic parameters* permeability P and initial flux J_0 relating to each adopted membranes. The obtained results show that prepared SLMs are highly permeable for the extraction process of VO_2^+ ions. To better understand this facilitated extraction phenomenon by this liquid membrane type, we developed a thermodynamic model based on the formation of an entity (ST) by association of substrate with the extractive agent at membrane interface and the migration of this formed entity through membrane organic phase. This model was verified by experimental results, which helped to determine the *microscopic parameters*, association constant K_{ass}, and apparent diffusion coefficient D^*, related to the formation of the entity (ST) and its diffusion through membrane organic phase. The low values of association constants K_{ass} and the high values of apparent coefficients D^* perfectly explain the large permeabilities and high fluxes obtained for this facilitated extraction process of VO_2^+ ions by prepared SLMs. Indeed, the parameters K_{ass} and D^* vary inversely, and the results indicate that very low values of constant K_{ass} result in higher values of apparent coefficients D^*; this important result shows that these high values of coefficients D^* certainly do not reflect a pure diffusion movement of the entity (ST) through adopted SLM organic phase. Some recent studies on the facilitated extraction process of metal ions or organic

Table 6: All values of microscopic parameters K_{ass} and D^* and activation parameters E_a, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ for facilitated extraction process of VO_2^+ ions.

Extractive agent	T (K)	$D^* \cdot 10^5$ ($cm^2 \cdot s^{-1}$)	K_{ass} ($L \cdot mol^{-1}$)	E_a ($J \cdot mol^{-1}$)	$\Delta H^{\neq}$ ($J \cdot mol^{-1}$)	$\Delta S^{\neq}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
RESO	**293**	4.19	4.29	28767.57	26291.19	**−232.85**
	298	5.67	3.61			
	303	8.80	2.83			
MC	**288**	5.19	3.75	24469.63	21969.63	**−235.84**
	293	6.15	3.60			
	303	9.42	3.29			
TOA	**293**	11.50	2.48	15531.39	13055.01	**−275.39**
	298	14.08	2.29			
	303	17.24	1.97			

[RESO] = [MC] = [TOA] = 10^{-2} M.

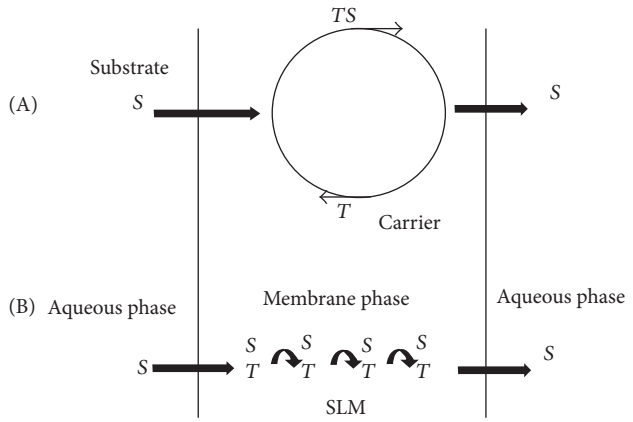


Figure 15: Possible movements of substrate across the organic phases of SLM membranes: (A) pure diffusion movement (low values of D^*), (B) movement in successive jumps (high values of D^*).

molecules by the same type of membranes clearly confirm the high values of the coefficients D^* and explain this result by the movement nature of the substrate S during its passage from the source aqueous phase to the receiving aqueous phase, through the membrane organic phase. Indeed, the results clearly show that the mechanism for this facilitated extraction process of VO_2^+ ions is a mechanism performed by successive jumps of substrate S from one site to another of extractive agent movable in the membrane organic phase. On the other hand, studies on the temperature factor influence indicated a clear evolution of all parameters for this phenomenon, and an increase in temperature results in a decrease in the association constant values (K_{ass}) and an increase in parameter values of D^*, P, and J_0 and improved performance of the adopted SLMs. The results confirmed the proposed mechanism for this facilitated extraction process, and an increase in the temperature factor disadvantage interactions between substrate S and the used extractive agent T (K_{ass} decreases) facilitates the phenomenon of substrate jumps from one site to another and therefore rapid passage (D^* increases) of VO_2^+ ions through the membrane organic phase.

Abbreviations

a: Slope of the plot $-\ln(C_0 - 2C_r) = f(t)$
C_0: Initial concentration of VO_2^+ ions in the feed phase ($mol \cdot L^{-1}$)
C_r: Concentration of VO_2^+ ions in the receiving phase ($mol \cdot L^{-1}$)
C_s: Concentration of VO_2^+ ions in the source phase ($mol \cdot L^{-1}$)
P: The membrane permeability ions ($cm^2 \cdot s^{-1}$)
J_0: Initial flux of VO_2^+ ions ($mmol \cdot cm^{-2} \cdot s^{-1}$)
D^*: Apparent diffusion coefficient of the complex (TS) ($cm^2 \cdot s^{-1}$)
K_{ass}: Association constant of the complex (TS) ($L \cdot mol^{-1}$)
l: The membrane thickness (mm or μm)
S: The membrane active area (cm^2)
$[T]_0$: Concentration of carrier in the membrane ($mol \cdot L^{-1}$)
$[TS]$: Concentration of the complex in the organic phase ($mol \cdot L^{-1}$)
T: Temperature (K)
t: Time (s)
V: Volume of the receiving compartment (cm^3).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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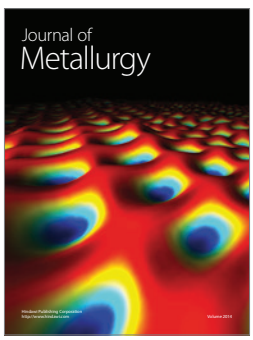




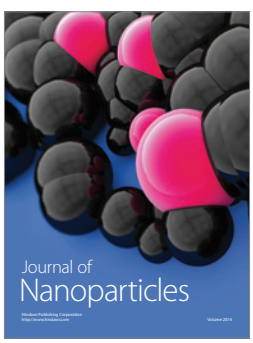


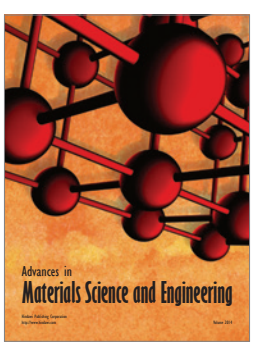


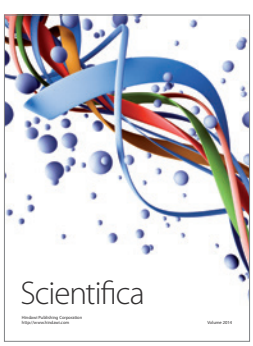


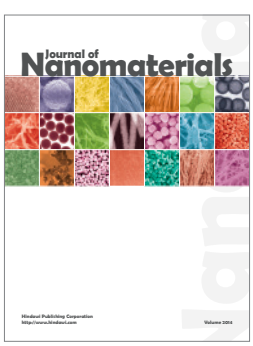






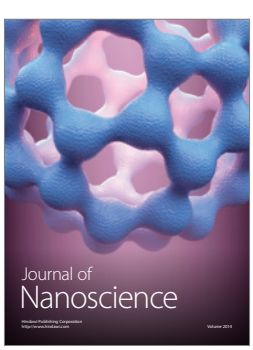




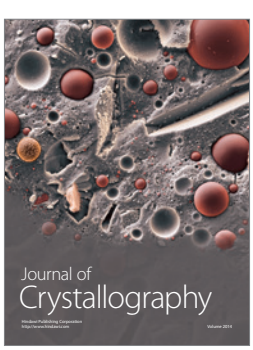




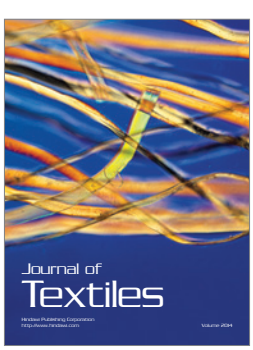












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