

SUPPORTED LIQUID MEMBRANE TRANSPORT OF U(VI) USING CALIX[n]ARENES AS CARRIERS

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ABSTRACT

The supported liquid membrane transport of U(VI) was investigated. Permeation behavior of U(VI) was performed by a PTFE microporous membrane using calix[n]arenes (n = 4, 6 and 8) in chloroform as a liquid phase. The transport driving force was the pH gradient between the feed and receiving phases. The transport rate was controlled by changing the pH of the solutions due to complexation process be governed by a proton-exchange mechanism. Different experimental variables, such as the pH, carriers, metal ion and stripping concentrations have been studied and evaluated to describe the process behavior. The experimental results obtained were analyzed and found that the transport rate through the membrane of U(VI) with calix[n]arenes was relatively slow and the results were discussed.

1. INTRODUCTION

The nuclear industry produces a great amount of radioactive liquid rejects and these rejects are continuously produced, varying considerably in volume, radioactivity, and chemical composition. Several treatment techniques have been used to treat them, however, these techniques are limited to remove all the contaminants.

Actually, the development of new chemical separation techniques as the supported liquid membranes (SLM) which associated to the new extractor agents synthesis for the separation of ionic and nonionic species is in ample expansion, therefore it presents characteristics in relation to the conventional separations processes like: energy saving, selectivity, the possibility of processing the thermolabile substances, it presents easiness of scale up, therefore it is modular and no extensive in workmanship (it can operate for years with a minimum of maintenance). This advance is not only connected to the necessities of the clean technology to preserve the environment and to optimize the industrial processes, but also to develop new materials, as extractor agents, exchangers, and adsorbents which are able to increase significantly the selectivity and the efficiency of a great number of separation techniques, appearing as a promising research field in the separation and nanoscience area [1].

Among those new molecules there are the calixarenes (Figure 1) as selective extractor agents for uranium extraction. The interest in these extractor agents is due to their versatility, because the starting compounds can be modified through the insertion of the function groups

in the calixarenes structure [2]. The calixarenes have been applied as catalyzers, sensors, and, mainly in separations and recuperations of metallic ions.

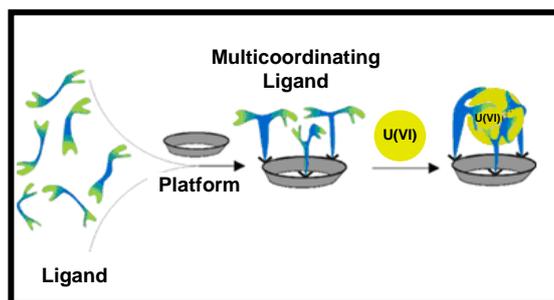
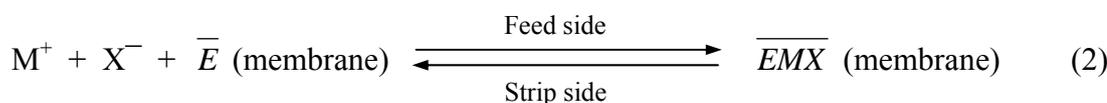
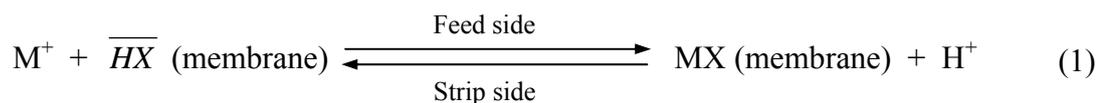


Figure 1. Metal separation using calixarene as platform of separation [3]

The supported liquid membranes consist in an organic solution containing the carrier or extractor agent dissolved in organic diluent which is impregnated in the porous of a hydrophobic polymeric support by van der Waals interaction.

When the simultaneous transport of the two different molecules occurs, but in opposite sides, it is defined as counter-transport. This phenomena happens when the extractor agent is acid (HX), and the transport rate is generally quantified by a pH gradient (Equation 1). However, when the simultaneous transport of the two different molecules occurs, in both sides, it is called as co-transport. This phenomena happens when the extractor agent is basic or neutral, and the transport rate is obtained through a concentration gradient of a counter ion which follows the metallic ion (Equation 2) [4].

The chemical reactions which are responsible for the transport can be schematized as:



The several stages, which characterize the transport of metallic ions through the membrane, can be described as:

1. The metallic species $[M^+]$, after diffusion to the interface feeding solution/SLM, react with the extractor agent. Simultaneously H^+ are liberated to the feeding solution (counter-transport, acid carrier) (Figure 2) or X^- ions follow the metallic ions to the inner membrane (co-transport, neutral or basic carrier) (Figure 3);

2. The complex metal-carrier spread out through the membrane by its concentration gradient that is negative;

- In the interface stripping solution/SLM the complex metal-carrier liberates the metallic ions to the stripping solution. H^+ ions substitute the metallic ions in the membrane (counter-transport) or the X^- ions are simultaneously substituted together with metallic ions to the stripping solution (co-transport);
- The regenerated carrier spread out to the inner membrane.

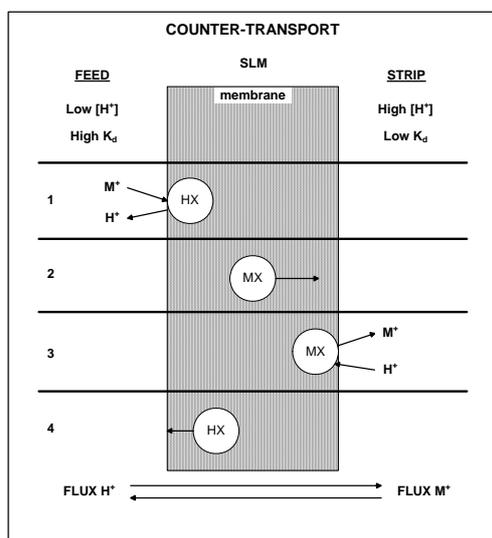


Figure 2. Schematic description of the counter-transport phenomena of a monovalent cation M^+ through a SLM. HX represents the carrier impregnated in the membrane porous [4].

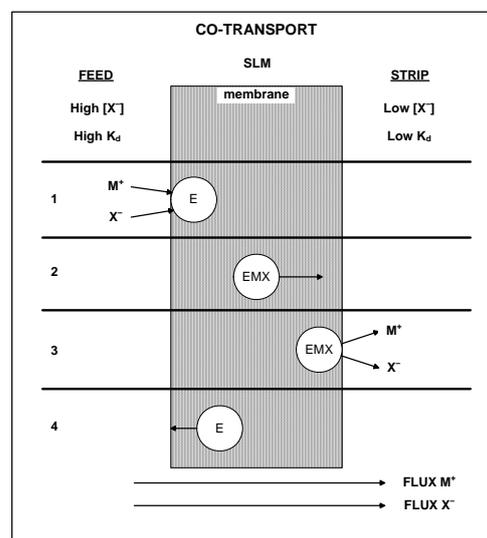


Figure 3. Schematic description of the co-transport phenomena of a monovalent cation M^+ through a SLM. E represents the carrier impregnated in the membrane porous and X^- a counter ion [4].

In this study the *p-tert-butylcalix[n]arenes* ($n = 4, 6$ and 8) dissolved in chloroform were used as liquid membrane.

2. EXPERIMENTAL

2.1 Reagents and Solutions

The chemical reagents $UO_2(NO_3)_2 \cdot 6H_2O$ and HNO_3 were used in the feeding solution. Calix[n]arenes ($n = 4, 6$ and 8) were used as carriers, and the diluent was chloroform. HNO_3 diluted was applied as a stripping solution. All chemicals were of analytical grade supplied by Merck and Sigma Aldrich.

2.2 Solvent Extraction Experiments

The U(VI) were made in batch, in 15 cm³ recipients, the U(VI) solution in HNO_3 media, and the calixarene in chloroform solution were shaken for 5 minutes ($V_{aq}:V_{org} = 2:1$). The concentration of U(VI) in the aqueous phase was determined by Arsenaze(III) method [5]. The absorbance was measured in a Shimadzu UV-Vis-1501 spectrophotometer using a 1cm optical path length cell. The pH was measured in a Quimis pH meter.

2.3 Apparatus and Measurements

The supported liquid membrane studies were carried out by using a methacrylate cell consisting of two compartments, viz, the feeding side of 15cm³ separated by a stripping side of 15cm³ capacity. Both compartments of methacrylate cell were jointed by flanges with SLM in between (Figure 4). The feeding and stripping solutions were mechanically stirred a 500 rpm using a magnetic stirrer at ambient temperature to suppress concentration polarization conditions at the membrane interfaces and in the bulk of the solutions. Assay of U(VI) in the feeding as well as the stripping side was done at different time intervals using the method described in 2.2.

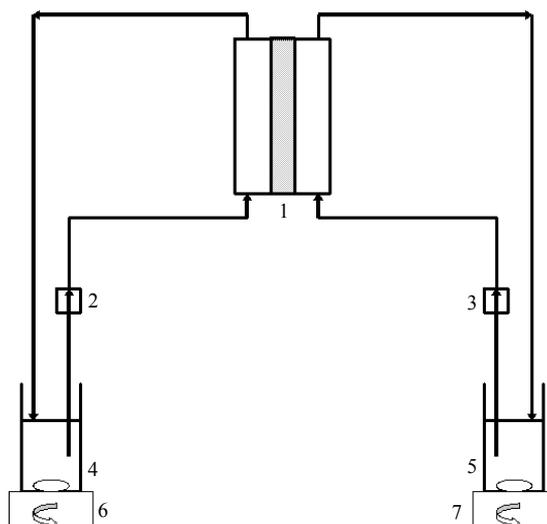


Figure 4. Schematic diagram of SLM: 1-supported liquid membrane; 2, 3-peristaltic pumps; 4-feeding solution; 5-stripping solution; 6, 7-magnetic stirrers

2.4 Supported Liquid Membrane

The polytetrafluoroethylene (PTFE) polymeric supports used in the present study were produced by Sartorius, Germany. The membranes were soaked in the carrier solution (calix[n]arenes in chloroform) overnight at about 18 hours prior to use. The effective membrane area with a 0.45 μm pore size was calculated to be 11.34 cm².

3. RESULTS AND DISCUSSION

3.1 Solvent extraction studies

Figure 5 shows the U(VI) extraction profiles of the systems using *p-tert*-butylcalix[n]arenes as extractor agents and chloroform as diluent. The results obtained in this work showed significant values of extraction for all the studied systems, with extraction percentage above 91% for all pH range studied with their maximum in pH 7, where the extraction percentage assumed values above 96% for all systems. This behavior is similar for the three *p-tert*-butylcalix[n]arenes studied.

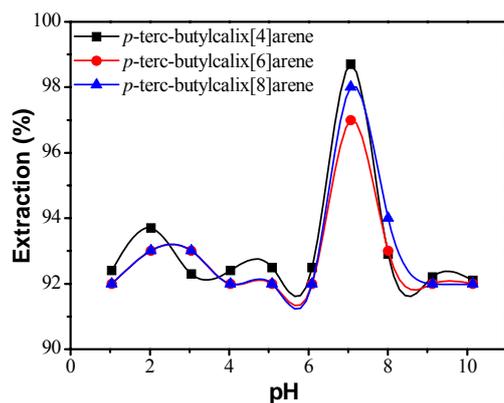


Figure 5. Effect of pH on the extraction of U(VI) (5×10^{-4} mol/L) using *p-tert*-butylcalix[n]arenes ($n=4, 6$ and 8) (5×10^{-3} mol/L) in chloroform

3.2 Membrane Studies

Figure 6 shows the U(VI) ion transport profile under the feeding solution pH influence in the studied systems. It can be observed in these results that the transport rate of the U(VI) increased with the increasing of the feeding solutions pH, it is according to the solvent extraction results and the process becomes faster with the increasing on the pH for all studied systems.

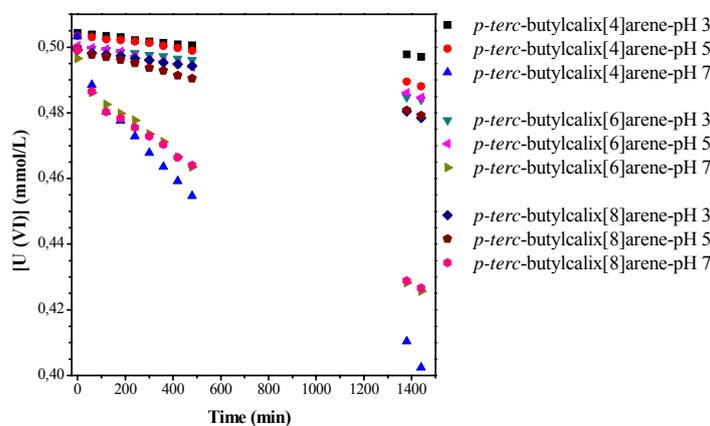


Figure 6: Feeding solution pH influence on the U(VI) transport rate

Feeding solution: 0,5 mM of U(VI); stripping solution: HNO₃ 2 M;

SLM: PTFE 0.45 μ m with 1 mM of *p-t*-butylcalix[n]arenes ($n=4, 6, 8$) in CHCl₃; flow rate: 5 mL/min

Figure 7 shows the U(VI) transport profile with the variation of the acidity stripping solution for the studied systems. It can be observed that, when the HNO₃ concentration decrease, occurs an increase in the metal transport, varying the transport rate with relation to the U (VI) in 40% when modified the concentration of HNO₃ from 2 mol/L to 0,001 mol/L in stripping solution. It was observed that the transport kinetic is slow to all studied systems.

The influence of U (VI) concentration was determined using its concentrations in the range of 0,1 mM to 7,5 mM in pH 7. In this study it was used the system *p-tert*-butylcalix[4]arene as a SLM in a PTFE film with 0.45 μ m porosity. The transport rate was calculated and the

influence of the metallic species concentration was analyzed in the first hour of permeation. Analyzing the curve profiler presented in figure 8, it was observed that when the U(VI) concentration increases in the feeding solution the transport rate increases considerably. On the other hand if the concentration is above 2 mM, flow rate trends to reduce. It is probably due to the concentration gradient in the feeding solution/SLM interfaces, therefore when U(VI) concentration is higher polarization in the interface could occur. This is attributed to the saturation of the membrane by complex formation in the interface, feeding solution/SLM.

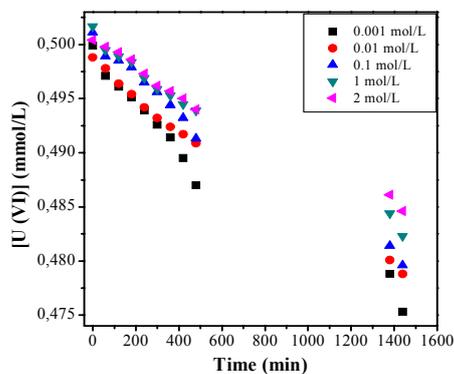


Figure 7: Effect of HNO₃ concentration of the strip solution

Feeding solution: 0,5 mM of U (VI) in pH 7;
stripping solution: HNO₃; SLM: PTFE 0.45 μ m
with 1 mM of
p-t-butylcalix[6]arene in CHCl₃; flow rate:
5 mL/min

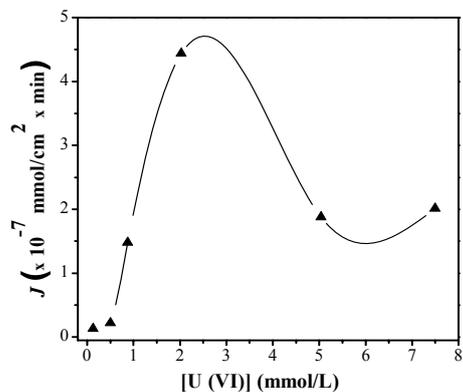


Figure 8: Effect of U (VI) concentration on initial permeability flux

Feeding solution: solution of U (VI) in pH 7; stripping
solution: HNO₃ 2 M; SLM: PTFE 0.45 μ m with
1 mM of *p-t*-butylcalix[4]arene in CHCl₃; flow rate:
5 mL/min

4. CONCLUSION

On the transport studies using the *p-tert*-butylcalix[n]arenes as carrier it was observed that the transport profiles were similar in all systems. The results showed that the pH of feeding solution influences in the U (VI) permeation and in pH 7 it was observed the better transport behavior.

The transport is also a function of the concentration of HNO₃ stripping solution. When the concentration of HNO₃ increase the transport rate of U(VI) decrease. The efficiency of the method depends of parameters as: feeding solution pH, stripping solution concentration, and carriers utilized as liquid membranes.

ACKNOWLEDGMENTS

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