

SUPPORTED LIQUID MEMBRANES (SLM) UTILIZED TO SEPARATION OF ELEMENTS 4f AND URANIUM

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ABSTRACT

Liquid membranes have been an emerging technique used as an alternative for the separation and pre-concentration of several metallic species. It has been applied as one alternative technique in the separation of metallic ions originating from several areas of industry like the hydrometallurgical, gases separation, biotechnology, treatment of nuclear and non-nuclear waste. The recovery of those metals through that technique has good potential to reduce, in very low levels, pollutants in processes.

The liquid membrane is a solution, which is an organic solvent, water immiscible and with low dielectric constant, that is used as a diluent for an extractor agent, also called the sequestering agent, loader or metal transporter, which is absorbed in the microporous of a polymeric film and actuates as solid support of the liquid membrane. The extractor agent gets the metallic ion from the feed solution liberating it on the other side of the membrane, through stripping solution. Then, the extraction and stripping of the metallic species are carried out in a single step in the process, and has this advantage in relation to the liquid-liquid extraction that requests a large number of stages to obtain products with high purity. Besides, the technique of SLM needs low capital and operational cost, low energy consumption and use of little amount of extractor agent, making possible the use of expensive extractor agents.

The main objective of this research is to investigate the influence of several parameters in the process of extraction of lanthanide metals and uranium originating from a simulated radioactive waste using as polymeric support membranes, PTFE and as loader calixarenes. The calixarenes are part of a very versatile class of macrocyclic compounds that can be functionalized, being obtained like this a great variety of multifunctional receptors.

1. INTRODUCTION

Rare earth metals possess very unique and superior physical and chemical properties that are suited to the creation of advanced material components for high-technological devices [1]. Some rare earth metals are reclaimed from secondary waste materials along with other alloying elements into solution. Furthermore, high-purity products of rare earth metals are required.

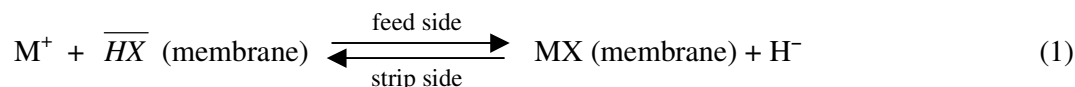
Although the solvent extraction technique has been used to purify rare earth metals from dilute impure solutions, it needs of a large number of stages for effective separation. The supported liquid membrane (SLM) system containing carriers has been studied for several metal ions as a new separation and preconcentration technique [2-4]. The development of this technology has been established as very effective and commercially attractive options for separation and purification processes [5-8]. Membrane separation process are used now in numerous industrial application processes with the following advantages: requires lower initial capital costs and lower operating costs, capability of

treating variety of elements and compounds in industrial settings at greater speed and with a high degree of effectiveness, with varying contaminant concentrations and volume requirements, environmentally safe technology, possibility of total recovery of products, no sludge production, no post-treatment costs and improves process quality.

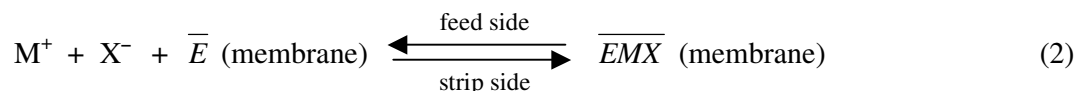
The membrane can be defined essentially as a barrier, which separates two phases and restricts the transport of various chemicals in a selective manner. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient. The membrane thickness may vary from as small as 0.02 μm to several millimeters [4].

The SLM process involves the permeation of metal species through SLMs as the simultaneous combination in a single stage of an extraction and a stripping operation, occurring in no equilibrium conditions.

The SLM consists of a solution, in a water immiscible low dielectric constant organic diluent, of an extracting reagent (a metal carrier) absorbed on a microporous polymeric film, which acts as solid support of the liquid membrane. Polymeric materials, for instance, polysulfone, polypropylene, nylon 6, polytetrafluoroethylene (PTFE), PVC, acrylic copolymer, etc. have been used successfully as membranes. The SLM is interposed between two aqueous solutions. The aqueous solution, initially containing all the metal ions, which can permeate the SLM, is referred to as the feed solution. The distribution ratio between the organic phase absorbed in the membrane pores and the aqueous feed solution of metal species permeating the SLM, K_d , is here high enough to favor metal extraction into the membrane phase. The aqueous solution present on the opposite side of the membrane, which is initially free from the permeable metal ions, is referred to as the strip solution. In this case the distribution ratio K_d is accepted to be as low as possible in order to favor complete back extraction of the metal species from the liquid membrane. If the metal carrier is an acidic extractant, HX, the difference between K_d of feed and strip sides of the SLM is generally achieved due a pH gradient. In this case we deal with a counter-transport phenomenon (Fig. 1a) and the chemical reaction, which is responsible for the coupled transport, can be schematized as [4]:



If the metal carrier is a neutral or a basic extractant, E, the difference in K_d between feed and strip is generally obtained by a concentration gradient of the counter ion, X^- , which follows the metal cation into the membrane. In this case we deal with a co-transport phenomenon (Fig. 1b) and the chemical reaction, which is responsible for the coupled transport, can be schematized as [4]:



The pH and counter ion concentration gradients are most often used as driving forces. However, any other expedient, which assures a large chemical potential gradient between the

two opposite sides of the membrane, can be used as long as coupled transport of metal ions and some other chemical species occurs through the SLM [4].

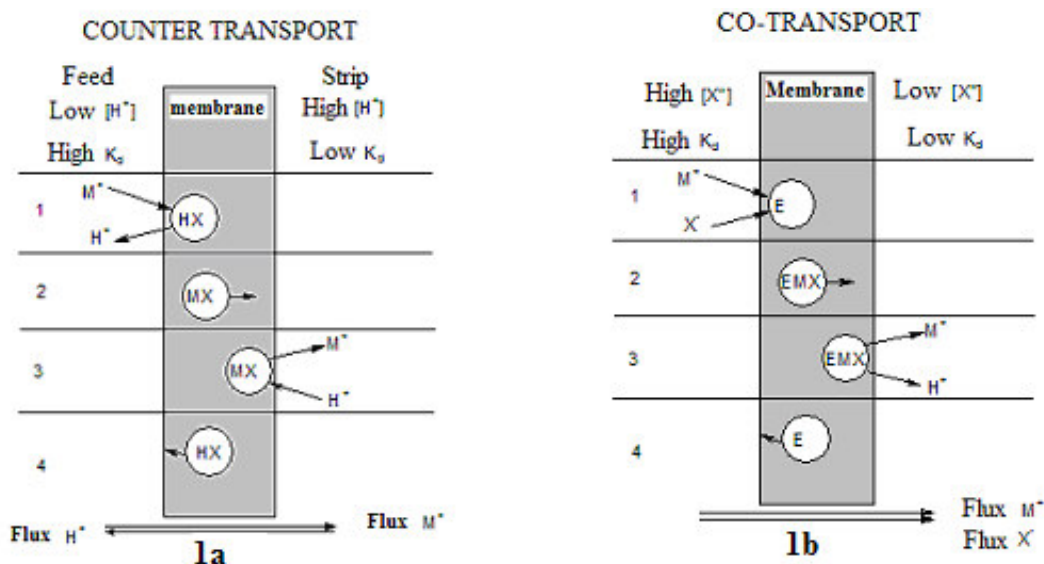


Figure 1 – Schematic description of transport of a metal through a SLM

The various steps that characterize the transport of metal species through SLMs can be described on the Fig. 1 [2, 4].

1-The metal species after diffusing to the feed solution-SLM interface react with the metal carrier. H^+ ions are simultaneously released into the feed solution (counter transport) or X^- ions accompany the metal ions into the membrane (co-transport);

2-The metal-carrier complex diffuses across the membrane accounted for by the fact that its concentration gradient is negative;

3-At the SLM-strip interface solution, the metal-carrier complex releases metal ions into the aqueous phase. H^+ ions are replaced simultaneously together with released M^+ ions into the strip solution (co-transport);

4-The uncomplexed carrier diffuses back across the membrane.

The selective liquid membrane system can be designed through molecular architecture of specific chemical carriers. One of the most promising carrier synthesized is so-called calixarene family. The calix[n]arenes, macrocyclic compounds composed of n phenols units alternatively combined with methylene groups, are known due their molecular cavity size-related selectivity in the binding of the cation. Because the cavity size can be adjusted with a number of phenols and various functional groups introduced easily to the upper and lower rims of the molecule, various calyx[n]arenes having desirable properties as metal ligands have been prepared [5].

The object of this study was to investigate the applicability of this technique for recovery of the rare earths for production technology.

2. RESULTS AND DISCUSSION

An extensive study on separation and recovery of rare earth and uranium using supported liquid membrane technique is presented [6-10].

Yaftian et al. [6] studied the transport of rare earth metal ions through a supported liquid membrane mediated by 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diphenylphosphino)ethoxy)calix[4]arene on *o*-nitrophenyl hexyl ether (NPHE). The effect of the initial metal concentration, salting-out agent concentration in the feed phase and temperature as well as the carrier concentration on the flux was studied. The extractability of the carrier was tested for the separation of a mixture of rare earth metal ions La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Y. The flux depends on the salting-out agent and varies according to order: $\text{Al}(\text{NO}_3)_3 > \text{NaNO}_3 > \text{HNO}_3$. The maximum flux was found for Pr and Nd in each case.

Kakoi et al.[8, 9] studied the extraction behavior of Ho, Er and Y using a calixarene carboxyl derivative, as a mobile carrier and the effect of sodium ions on extraction of rare earth metals by liquid surfactant membranes. The calixarene carboxyl derivative showed a high extractability for all rare earth metal ions when compared with their analog monomer compound. The extractability for the rare earth metals was found to increase in the following order: monomer < tetramer < hexamer. However, the extraction rate of the tetramer was higher than that of the hexamer. The addition of a small amount of sodium ion into the aqueous solution drastically accelerated the permeation rate and also enhanced the selectivity between heavy rare earths (Er and Ho) and Y. The experimental results obtained under a variety of conditions were analyzed by a diffusion model which combined with the complexation reaction at the aqueous-organic interface, taking into account the velocity distribution of aqueous and organic solutions through the feed and strip sides, respectively, of the hollow-fiber membrane extractor.

Kondo et al. [10] studied the transport of uranyl ions through a liquid membrane containing a lipophilic ion-associate of methyltrioctylammonium and hydroxycalix[*n*]arene-*p*-sulfonates as metal carriers. Uranyl ion in an aqueous sodium hydrogen carbonate solution of pH 4-8 (feed solution) was simultaneously and selectively transported into a dilute sulfuric acid solution (strip solution) through a membrane (chloroform) containing the carrier. The rate of transport increased with the increase of UO_2^{2+} concentration in the feed solution, the concentration of the carrier in the membrane, the increase of system temperature and with increase of pH in feed solution. The presence of large amounts of sodium hydrogen carbonate and sodium chloride in the feed solution interfered with the transport by causing a delay in the start of transport.

The results of these papers showed that the studies of these parameters (pH, ion concentration, carrier concentration, etc.) are important for to explore the effectiveness and

efficiency of transport of metal ions on the diffusion process, their chemical reactions as well as their permeation fluxes on the transport of ions.

3. CONCLUSIONS

These studies indicate that is possible the calixarenes matrix acts as a template increasing and do the selectivity of the recovery of metal ions and that new host compound calixarene derivative is very effective as a mobile carrier for rare earth metal extraction using supported liquid membrane technique.

The suggestions for future works are: to synthesize calixarenes functionalized with β -diketones for separation and recovery of rare earths and uranium and explore some separation parameters utilizing SLM technique.

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