

# Studies on Ion Transport of Eu (III) and Gd (III) Through Supported Liquid Membranes Containing Di-(2-ethylhexyl) Phosphate, as a Carrier

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Recibido el 10 de enero de 2007; aceptado el 4 de mayo de 2007

**Abstract:** In this work, permeation of Eu (III) and Gd (III) between aqueous oxide solutions through supported membrane containing di-(2-ethylhexyl) phosphate as a carrier and kerosen has been studied. Mass transfer of these cations has been determined in terms of permeability coefficients (P) by measurement of metal concentrations in strip solution. The permeability coefficient increases with increase in pH acidity of feed solution ranged from pH 0.5 to 2.5 while that of strip solution was kept constant at 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>. Thus, the results obtained show that it is possible to get up to 93% of percentage of extraction.

**Keywords:** Europium, gadolinium. supported liquid membranes.

**Resumen:** En este trabajo, se estudió la permeación de Eu (III) y Gd (III) a partir de soluciones acuosas de óxidos, mediante una membrana líquida soportada conteniendo di-(2-etil hexil) fosfato como portador y queroseno. Se determinó la transferencia de masa de estos cationes en términos del coeficiente de permeabilidad (P) mediante la determinación de la concentración en la solución de despojo. Se observó que el coeficiente de permeabilidad incrementa con el incremento del pH ácido de la solución en un rango de pH de 0.5 a 2.5. La solución de despojo se mantuvo constante a 0.1 mol L<sup>-1</sup> de HNO<sub>3</sub>. Los resultados obtenidos mostraron que es posible obtener porcentajes de extracción del 93%.

**Palabras clave:** Europio, gadolinio, membranas líquidas soportadas.

## Introduction

Solvent extraction is widely used in the recovery and separation of metals from aqueous solutions [1]. A limitation in traditional solvent extraction is that a large inventory of solvent is required, especially when processing dilute solutions. Liquid membrane systems have now become an alternative separation technique for metals from dilute solutions as they offer advantages over conventional solvent extraction such as the use of minimal amounts of solvent and low capital cost [2].

The significant interesting aspects of SLM (supported liquid membranes) system are the continuous and simultaneous extraction and stripping of chemical species. The SLM system is interesting, attractive and effective because it can remove metal ions from dilute solutions with uphill ion transport mechanism [3]. The commercial extractants were PC - 88A, D2EHPA, Versatic 10, Naphthenic acid, Aliquat - 336, TOPO, TBP, etc. for the liquid-liquid extraction separation of metal ions. Although some investigations have been done on ion transport through liquid membrane by using different extractants as carriers [4, 5], the exploration of ion transport aspects of rare earth elements with solvating extractants are lacking. In order to consider its practical applications, SLM system consisting of two aqueous phases separated by a solid support was explored for the preconcentration of rare earth metal ions from low concentration aqueous solutions [6]. It is essential to have a suitable choice of carriers and porous supports with high stability. Although rare earth metals have attracted attention as magnetic, optical and superconducting materials, they have the inherent disadvantage that their mutual separation is very diffi-

cult because they have similar physical and chemical properties. However, their content in minerals such as monazite and xenotime are a trace levels [7]. Therefore, the developments of new efficient and effective separation and preconcentration methods are desirable. The selectivity can be achieved owing to the difference in the concentrations of the free rare earth metals brought about by the difference in the stability constants of their complexes, and also the difference in dissociation rates [8]. It is interesting to explore these aspects for the ion transport of rare earth elements in SLM system. The present paper deals with the effects of different experimental variables on the permeation of europium and gadolinium, in a SLM system, and to analyse the experimental results quantitatively in order to design the recuperation method.

## Experimental

### Reagents

The organic (membrane liquid) phase was prepared by diluting di-(2-ethylhexyl) phosphate acid (Fluka) in kerosene to the required concentration. The aqueous (feed) solutions were prepared by dissolving an appropriate quantity of Eu or Gd trioxides (BDH Chemicals) in HNO<sub>3</sub> (Aldrich). After evaporating excess acid, the solution was diluted with distilled water. Feed solutions of pH 0.5 to 2.5 (acidity adjusted with diluted nitric acid or sodium hydroxide) contained Eu (III) and Gd (III) at initial concentration of 5 µg mL<sup>-1</sup>. Their ionic strength was kept constant at 0.1 mol L<sup>-1</sup> (HNO<sub>3</sub>, NaNO<sub>3</sub>). As a strip solution, 0.1 mol L<sup>-1</sup> nitric acid was used. All other chemicals used

were of analytical grade. In the present investigation, the support Millipore Fluoropore FGLP 4700 was used.

### Membrane preparation

The microporous thin sheet membrane was impregnated with di-(2-ethylhexyl) phosphate dissolved in kerosene and excess extractant was removed with the help of filter paper. Membranes containing 30, 40 and 50 % di-(2-ethylhexyl) phosphate -kerosene were prepared. For a new experiment, the polymeric support was rinsed with water, dried with filter paper and shortly by air, washed in kerosene by using ultrasonic bath, dried and reimpregnated with di-(2-ethylhexyl) phosphate-kerosene solution. A given support was reused in up to 30 experiments with a good reproducibility of results.

### Membrane extraction

Membrane extraction studies were carried out in a two-compartment cell which was thermostated at 25 °C in a water bath (Fig. 1). Each compartment had a volume capacity of 60 mL. The membrane was sandwiched between the two compartments. Each compartment was stirred at a constant rate throughout the experiment. An aqueous solution of the same composition was placed in each compartment for the Gd (III) and Eu (III) extraction studies. The extraction of the metals was monitored by taking 1.0 mL aliquots from each compartment at regular time intervals for analysis by atomic absorption spectrometry. Solution removed was replaced each time with an equal volume of fresh metal solution.

## Results and discussion

The experimental data were expressed in terms of permeability coefficients  $P$ , determined from linear relationship derived by Danesi [9, 10]. Differences in the transport of Eu and Gd cations at carrier concentrations ranging from 0.01 to 1 mol L<sup>-1</sup> are demonstrated in Fig. 2. The runs were performed at pH values near to the position of maximal on  $P$  versus pH curves. The permeability is increasing rapidly with carrier concentration reaching maximal around 50 mmol L<sup>-1</sup> di-(2-ethylhexyl) phosphate for both metals studied. For Eu and Gd, the  $P$  values of these maximal decrease when increasing the atomic number and both, their shape and decrease of permeability at higher carrier concentrations are shaper.

The effect of feed solution pH on permeability was studied at 50 mmol L<sup>-1</sup> (Fig. 3) and at 500 mmol L<sup>-1</sup> di-(2-ethylhexyl) phosphate (Fig. 4) in the membrane. At lower carrier concentration, the  $P$  versus pH curves possess maximal situated at pH 1.9 for Eu and pH 1.6 for Gd. According to their maximum  $P$  values, the elements studied follow the same order as in Fig. 2. By increasing carrier concentration, the pH curves become broader and greater differences can be observed among values of permeability coefficients of both metals in Fig. 4. Maxima are shifted to lower pH values, i.e. to pH 1.7 for Eu and 1.4 for Gd.

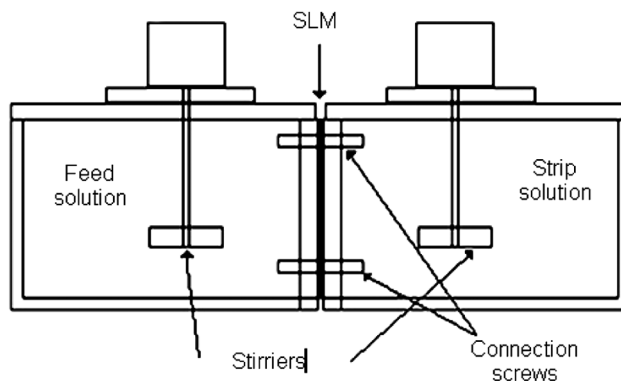


Fig. 1. Schematic presentation of SLM cell.

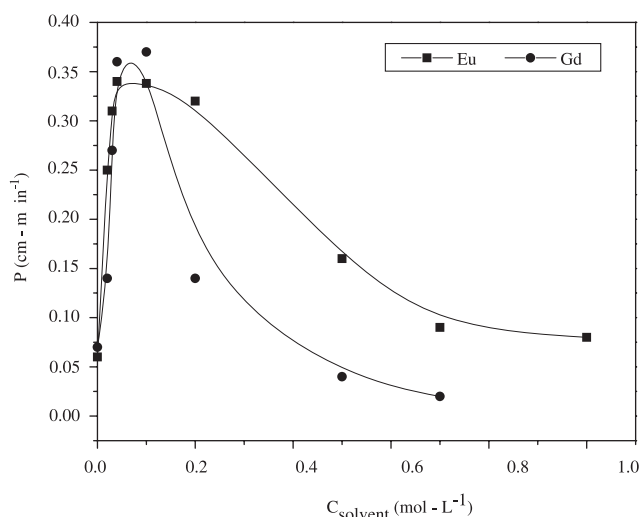


Fig. 2. Effect of carrier concentration, solvent: di - (2- ethylhexyl) phosphate in kerosene, Feed: Eu (III) and Gd (III): 5  $\mu\text{g mL}^{-1}$ . Strip: 0.1 mol L<sup>-1</sup> HNO<sub>3</sub>.

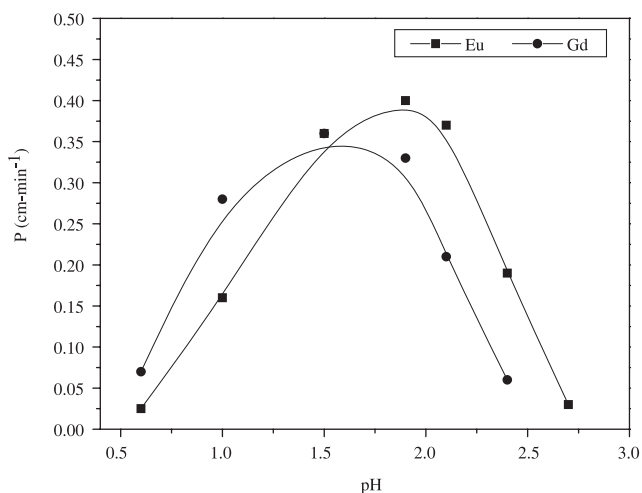
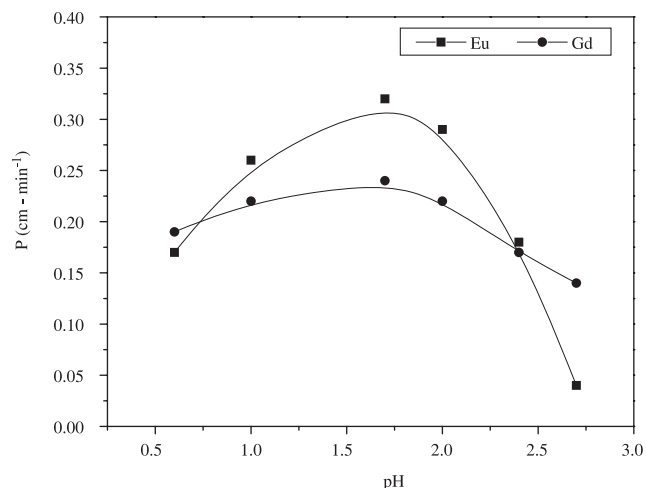
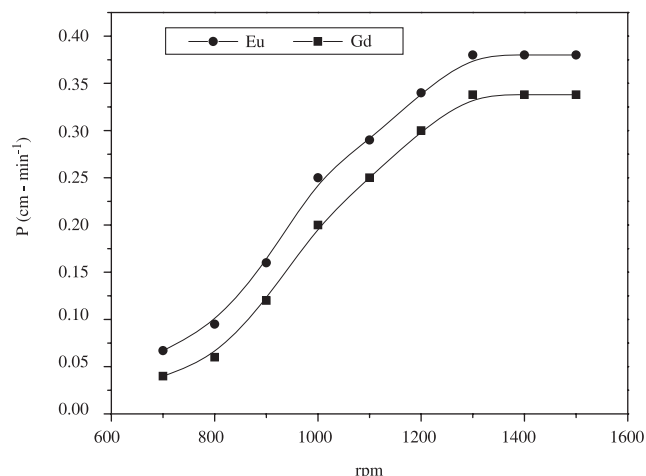


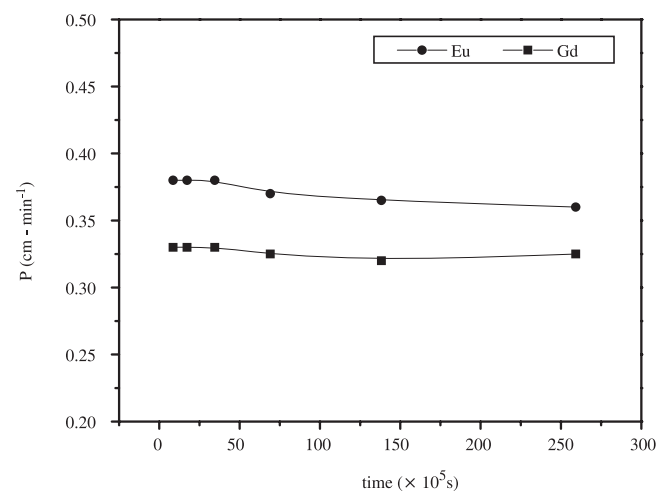
Fig. 3. Effect of feed solution pH at low carrier concentration. Feed and strip solutions as in Fig. 1. SLM: 50 mmol L<sup>-1</sup> di - (2- ethylhexyl) phosphate in kerosene.



**Fig. 4.** Effect of feed solution acidity at high carrier concentration. Feed and strip solutions as in Fig. 1. SLM: 500 mmol L<sup>-1</sup> di - (2- ethylhexyl) phosphate in kerosene.



**Fig. 5.** Dependency of permeability coefficient on rpm; pH 1.9, SLM: 50 mmol L<sup>-1</sup> di - (2- ethylhexyl) phosphate in kerosene.



**Fig. 6.** The stability of SLM system; pH 1.9 and rpm = 1300.

Varying the acidity of feed solution and the carrier concentration, the permeation of these elements through the membrane can be controlled and conditions for mutual separation can be established.

The decrease of permeation with increasing atomic number of lanthanide can be explained by the increase of the stability of complexes formed with di-(2- ethylhexyl) phosphate.

In order to achieve effective permeation of Eu y Gd in a SLM system, it is necessary to explore the effect of stirring speed on permeation coefficient. The stirring of the source and receiving phases were carried out from 700 a 1300 rpm (Fig. 5). It was observed that the permeability coefficient increases for both metals in the range from 750 to 1500 rpm. It indicates that permeation of these metals through SLM increases with increase in stirring speed. However, permeability coefficient remains constant in the range from 1100 to 1500 rpm for both cases.

The stability of SLM is other important factor. Basically, stability of SLM depends on the retention of concentration of immobilised carrier on porous support and stability of porous support during the operations. Fig. 6 shows the stability of SLM during continuous operation of SLM cell for 30 days. The results indicate that the porous support material is quite stable during the 30 days operation. However, the permeability coefficient, P, decreases. These results can be attributed towards the slow dissolution of organic solution in aqueous phases.

### Conclusions

Transport studies have shown that both Eu (III) and Gd (III) can be transported from a feed to a receiver phase separated by a di-(2-ethylhexyl) phosphate- kerosene/ FGLP membrane under a nitric acid concentration gradient.

Metal permeation is influenced by the stirring speed of the source phase and, especially the nitric acid concentration in this phase. Other variables which affect the transport are: carrier concentration, organic phase diluent, overall acidic concentration in the source phase and high Eu (III) and Gd (III) concentrations in the same phase, which decrease metal permeation probably due to membrane saturation.

The membrane lifetime was evaluated and a relative good performance in the metal transport was obtained after continuous usage (during 30 days) of the same membrane.

The similarities between the pattern of permeability coefficient versus pH and the distribution of the species versus pH may indicate that the thermodynamic parameters are responsible of the transport behavior of the related metal transport.

The differences among properties of various di-alkylphosphoric acids used as carriers becomes evident in different behavior of lanthanides at membrane transport and therefore, can be employed in separation of different groups of lanthanides and/ or in the mutual separation of adjacent elements. This membrane technique has the advantages such as energy saving, less amount of extractant required, no third phase formation, economic viability, etc.

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