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Active Composite Polymeric Membranes for the Separation of Nd(III)

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ABSTRACT

Active composite polymeric membranes were prepared in order to improve the lifetime of supported liquid membranes (SLM) for the separation of Nd(III). The aim of the paper was to demonstrate the applicability of these type of composite membranes, based on two layer of polysulfone (PSf) and polyamide (PA), for metal transport. Thus, the membrane characterization, the influence of the carrier concentration in the transport, and the stability of the membranes have been studied. The results obtained are quite satisfactory, both from the standpoint of transport

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ability and stability. The need for an efficient carrier has been demonstrated and its influence reported. In addition, a preliminary investigation of the transport mechanism has been performed.

Key Words: Supported liquid membrane; Nd(III); Polysulfone; Separation.

INTRODUCTION

Liquid membranes have been shown to provide an effective separation technique for the selective recovery or concentration of different species, as they combine the process of extraction, diffusion, and stripping in a single step.[1,2] Their high selectivity, the possibility to concentrate ions, and their high diffusion rates make them very attractive. Supported liquid membranes (SLM) have been widely applied to studies of the transport of individual species as well as the separation of multicomponent mixtures.

Despite these advantages, they are not widely used for practical separation processes due to problems related to stability and lifetime, which are in general too low to assure good commercial applications. Membrane degradation is essentially caused by the loss of carrier by dissolution in the aqueous phases and by emulsion formation at the membrane interfaces.

A way to improve membrane stability is to chemically bind the mobile carrier within the membrane but, because the carrier reagent in this case has no mobility, the diffusion rates decrease to values close to those characteristic of solid systems.[3] In order to overcome these problems the strategy has been to prepare the membrane in the presence of the carrier using hydrophobic polymer.[4–6]

Composite membranes have great potential for the design of innovative membranes, which have not been fully explored for the selective separation of metals.

There are several methods to prepare composite membranes. Among the simplest are phase inversion or in-situ polymerization by interfacial reaction. These methods have been used in our group in order to prepare new membranes containing the carrier reagent.[7,8]

These membranes do not suffer from several of the disadvantages of conventional SLM and acceptable operational procedures are achieved.

Activated polymer membranes containing di(2-ethylhexyl) phosphoric acid (DEHPA) have been prepared and evaluated for Nd(III) separation.

DEHPA has been widely studied in the last two decades. It has been used for the extraction and/or separation of several metal ions and other species. Among metal ions, Cu(II),[9,10] Cd(II),[11] Zn(II),[12,13] lanthanides,[14,15] Pb(II),[16] and U(VI)[17] have been separated with membranes containing

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DEHPA. Selectivity studies for the separation of mixtures of lanthanides through the use of SLM have also been reported.[18]

EXPERIMENTAL

Reagents

Neodymium nitrate p.a. Fluka was used for the preparation of the samples.

The membranes were prepared in two stages. The ultrafiltration layer was prepared with Polysulfone U-3500, Union Carbide, and *N*,*N*-dimethylformamide (DMF, p.a. Fluka, Buchs, Switzerland). A non-woven fabric (Hollytex 3329, Lascaux, Brüttisellen, CH) was used as mechanical support. The top dense layer was prepared with 1,3-phenylendiamine (Merck, Darmstadt, Germany); 1,3,5-trichloride tricarbonylbenzene (Aldrich, Steinheim, Germany); DEHPA, 96%, PDH, England; and hexane (p.a. Carlo Erba, Milan, Italy).

Solutions of Arsenazo III (Fluka, Buchs, Switzerland) in 1.0–2.5 M NaCl and 2.0 M sodium formate (Fluka, Buchs, Switzerland) were used for the determination of Nd(III).

Apparatus

The experiments were carried out in a double-compartment cell connected by a circular window supporting the activated membrane. Feed and stripping solutions were placed in the compartments and stirred during experiments. The volume for feed and stripping solutions was always 200 mL.

The equipment for the preparation of the ultrafiltration membrane consisted of a mechanic stirring system (Heidolf, Germany) and a series of baths and casting bars of 150 and 200 microns of nominal thickness.

Samples were analyzed by ICP-AES Model 3410 with minitorch (Fisons ARL).

A flow injection analysis system was employed for the determination of neodymium (Fig. 1).[19]

Procedure

The membranes prepared were composite, therefore two different materials are present, one on top of the other. The first step is the preparation of an organic solution of polysulfone (PSF). For this purpose, a 15% w/w solution of PSf U-3500 in DMF was prepared and stirred during 12 hr, until complete dissolution. This solution was put on top of the non-woven support,

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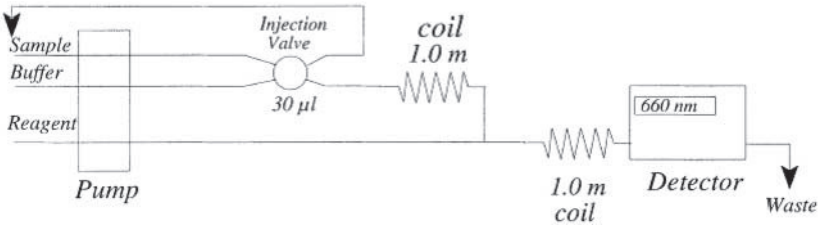

Figure 1. FIA manifold employed for the monitoring of Nd(III). The metal ion reacts with Arsenazo III and the absorption is detected with a spectrophotometer at 660 nm wavelength.

or directly on a casting glass support, and, using the casting bars (150–200 microns), a controlled size (60–80 microns) film was obtained.

The second polymer was obtained by in-situ polymerization on the porous PSf shell. This is a dense film that contains the selective carrier. For that, the PSf was soaked in an aqueous solution containing 3% w/w 1,3-phenylendiamine. After that, the organic solution (0.15% trichloride tricarbonylbenzene containing DEHPA) was added on top of the soaked PSf. A thin dense polymer, polyamide (PA), is then formed containing the selective carrier.

Several kinds of experiments were performed for the study of the transport of Nd(III) as well as for the SEM characterization of the membranes. The permeation was investigated with flat PSf membranes, reverse osmosis (RO) PSf/PA membrane and activated membranes (PSf/PA-DEHPA). A study on the permeation of water was performed with the activated membranes (PSf/PA-DEHPA) which happened to be denser as shown elsewhere.[20] Parameters affecting the transport such as the DEHPA concentration in the casting solution and the composition of the stripping solution were studied systematically (but not optimized). Finally, the stability and reuse of these membranes was demonstrated.

The permeability was calculated as in Eq. (1)[21]

$$P = \frac{-dC}{C}\frac{1}{\mathrm{d}t}\frac{V}{A} \tag{1}$$

or its integrated form

$$-\ln\frac{C_\mathrm{f}}{C_\mathrm{fo}} = \frac{A}{V}Pt \tag{2}$$

where f corresponds to feed solution, P is the permeability in cm min^{-1}, C are molar concentrations, A is the membrane area, V is the feed solution volume, and t is time in minutes.

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DEHPA is a strong complexing agent for several metal ions. The complexation reaction for lanthanide ions can be written as:[18]

$$Ln^{3+} + 3(HA)_{2org} \rightarrow Ln(A \cdot HA)_{3org} + 3H^{+} \quad (3)$$

Transport of lanthanide ions through the membranes containing DEHPA occurs through a counter-transport of protons with a 3 : 1 stoichiometry.

RESULTS AND DISCUSSION

Scanning Electron Microscopy Characterization

All prepared membranes are clearly asymmetric as can be observed in Fig. 2(a). There is a skin layer on top and a porous part underneath. The porous layer is in contact with the glass (or non-woven) support and the dense layer is in contact with the casting solution. Membranes prepared with DEHPA showed the same asymmetric structure [Fig. 2(b)]. This structure was obtained using a precipitation bath. In all cases we used distilled water that caused the presence of a skin layer.[22] Membranes prepared by using the 150 microns

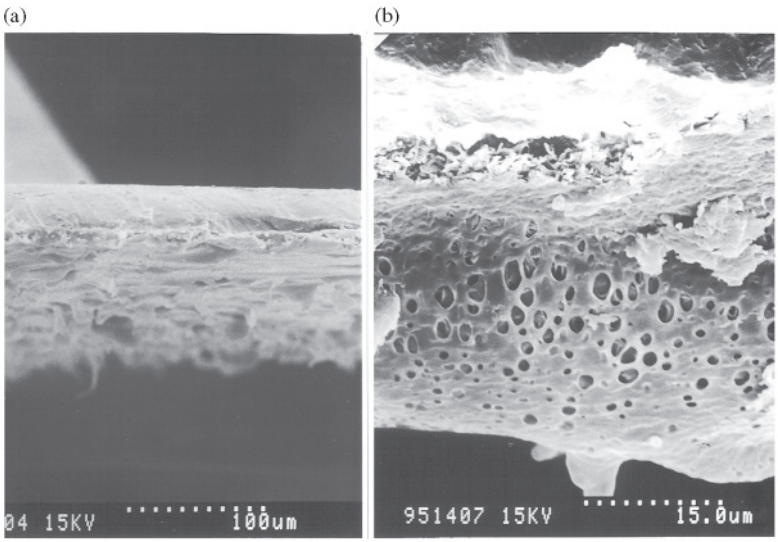

Figure 2. (a) SEM corresponding to a membrane prepared with a 150 microns casting bar, the real thickness was 60 microns. (b) SEM of a composite membrane where a skin dense layer and a porous face can be observed.

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casting bar showed a final thickness of 60 microns [Fig. 2(a)]. Membranes with 80 microns thickness were obtained when using the 200 micron bar.

Water Permeation Through Active Membranes

Experiments carried out with a difference in ionic strength between feed and stripping compartments of 4.4 M (NaCl) and a membrane of 4.4 cm effective diameter yielded a total transport in 24 hr of 17.0 mL of water. The initial volumes of the solutions were 200 mL. Therefore, the permeability was determined to be $7.76 \times 10^{-4}\,\mathrm{cm/min^{-1}}$. This difference in ionic strength would result in a theoretical osmotic pressure, calculated by Van't Hoff equation, applying an osmotic coefficient of 0.95 (maximum), equal to 102 atm ($298\,\mathrm{K} \times 4.4\,\mathrm{M} \times 0.082\,\mathrm{atm\,L\,mol^{-1}\,K^{-1}}$).

A much lower difference in ionic strength was used in the metal permeation experiments, where the maximum difference was 2.2 M. Therefore, the permeation of water in the experiments was lower. Also, Nd(III) transport experiments took 2–4 hr. Consequently, water permeation did not affect the determination of Nd(III).

Diffusion of Nd(III) Through Several Non-active Membranes

PS Membrane

In this case, the feed solution was a 5 ppm Nd(III) aqueous solution at pH 3.0 and the stripping one was 1.0 M nitric acid. The PS membrane was prepared by using a 150 microns bar. The results of the analyses for neodymium transport during 24 hr did not show any variation in the concentration of Nd(III) in the feed solution. The diffusion of the metal ion did not occur or was not detected within the time of the experiments.

RO PSf/PA Membranes

These membranes were prepared in the same manner as the activated ones, but in this case there was no addition of the selective carrier. These transport experiments were carried out in order to demonstrate the necessity of a carrier to have active transport between the two phases so that a diffusion mechanism could be excluded. Feed solution was 5 ppm Nd(III) at pH 3.2 and stripping was done with a 0.1 M nitric acid in water.

The analyses of Nd(III) performed during 24 hr did not show any decrease in the concentration of the metal ion in the feed solution. Therefore, we can

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conclude that there is no transport due to diffusion of Nd(III) in these membranes. Nevertheless, the pH in the feed solution was also monitored and a decrease observed (see Table 1). This means that protons can diffuse through these membranes.

Transport of Nd(III) by Active Composite Membranes PSf/PA-DEHPA

Effect of DEHPA Concentration

The effect of carrier concentration in one of the casting solutions was determined. The carrier was added to the hexane solution during the preparation of the dense top layer. Concentrations are referred to this precise solution and do not reflect the final concentration in the membrane. Nevertheless, the corresponding contents in the membrane were determined for several preparation conditions.

The concentrations used were 0, 25, 50, 100, 200, 400, and 700 mM. Two different sets of experiments were carried out by changing conditions in the feed and stripping solutions. For concentrations 0 up to 200 mM the feed solution was 5 ppm Nd(III) at pH 3.0 and stripping solution was 0.1 M HCl. For concentrations ranging from 200 to 700 mM, the feed solution was 10 ppm Nd(III) at pH 3.0 and stripping solution was an aqueous 2.2 M HCl solution. This difference was set in order to assure that the experiment would last a long enough period of time and osmotic effect was eliminated by adding NaCl in feed solution.

The results of these two sets of experiments are shown in Figs. 3 and 4.

Table 1. Time profile of neodymium and proton concentration in the feed solution.

Time (min)	Absorbance (Arsenazo III at 660 nm)	pH (feed)
0	0.058	3.19
3	0.056	3.19
18	0.057	3.14
60	0.058	3.13
120	0.057	3.11
150	0.057	3.10

Note: Initial feed conditions were 5 ppm Nd(III) at pH 3.2. The Nd(III) concentration did not change within the first 20 hr.

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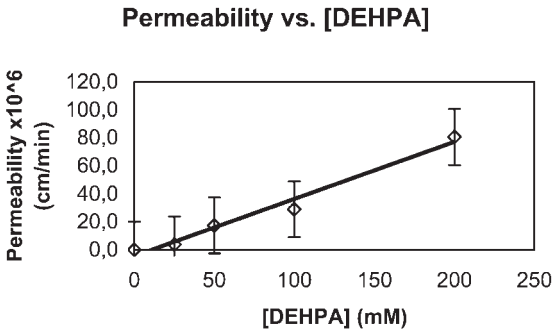

Figure 3. Influence of the concentration of DEHPA (0–200 mM) in the organic solution, precursor of the PA formation. Feed was a 5 ppm Nd(III) solution at pH 3.0 and stripping solution was 0.1 M nitric acid.

In Fig. 3 the permeability shows a linear dependence within the whole range of DEHPA concentrations. The influence is significant with regard to the values of the permeabilities. When no carrier was added, the permeability was zero. Adding DEHPA to a concentration 25 mM in hexane the membrane obtained showed a permeability of 3.8×10^{-6} cm min^{-1}. The highest concentration in this set of experiments yielded a permeability of 8.06×10^{-5} cm min^{-1}. The system did not reach a plateau. Therefore, a second set of experiments were performed under more extreme conditions, i.e., the DEHPA concentration was higher, the feed was more concentrated in Nd(III) and the receiving solution was more concentrated in hydrochloric acid (2.2 M). Under these conditions, the permeabilities ranged from 3.27×10^{-4} cm min^{-1} for 200 mM DEHPA

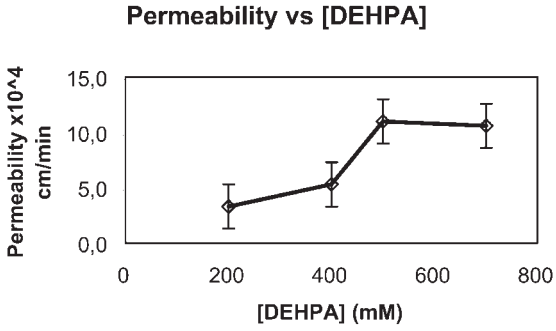

Figure 4. Influence of DEHPA concentration (200–700 mM) in the organic solution, precursor of the PA formation. Feed was 10 ppm Nd(III) solution at pH 3.0 and stripping was a 2.2 M hydrochloric acid.

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1.10×10^{-3} cm min^{-1} for 500 mM DEHPA. The 700 mM solution did not show any improvement (Fig. 4) as the permeability was determined to be 1.10×10^{-3} cm min^{-1}, and a plateau was reached under these conditions. Once the concentration of carrier in the membrane is high enough, other parameters, such as diffusion, are limiting the transport of the metal ions. Furthermore, as seen in the experiments when DEHPA was not present in the membrane, there is transport of protons, even when no carrier was present. This means that with a higher pH gradient, the protons are better transported from the receiving to the feed solution (counter-transport). The values for the SLM corresponding to optimum concentration of DEHPA found in the literature are 100 mM, much smaller than the ones obtained with ACM. Also, the values of permeabilities for neodymium are significantly smaller than those performed elsewhere by SLMs, 0.1–0.7 cm min^{-1}.[18] This result is due to the lack of mobility of the complex formed within the solid polymer. In the case of SLM the organic compound moves from side to side of the supported liquid organic phase. In the case of solid activated membranes the final mechanism is not so clear. Results of characterization of these kinds of membranes done by Ariza et al.[23] show two different possibilities of immobilization. Some of the carrier seems to be covalent bonded and some other would be just trapped within the polymeric structure. Therefore, two different behaviors could be present. One might be similar to SLM, the migration of the complex within the polymer due to the difference in chemical potential, but this is highly improbable. The other one, and most likely, would be due to the bonded phase. In this case a jumping mechanism would be activated. This second case would be strongly favored by the increase in carrier concentration, as it is observed in our case.

The final concentrations of feed and stripping solutions were also monitored at the end of each experiment in order to check the real transport and observe the quantity of metal ion retained within the membrane. It was done for the two sets of experiments. The results are shown in Table 2. We can observe that real significant transport occurred only when a sufficient concentration of DEHPA was present. In that sense, the results of final feed solution for 100 mM are not as good. On the other hand, for 200 mM DEHPA the remaining Nd(III) is of 0.52 ppm in the worse of the cases, starting with 5 ppm. The table shows results of reused membranes, but these will be commented afterwards.

The second set of experiments showed in all cases that the Nd(III) has been well removed from the feed solution. Nevertheless, examining the receiving aqueous solutions (for the two sets) not all the metal ion was recovered. When fresh membranes were used for the 200 mM DEHPA membrane in the first set of experiments, the receiving phase contained up to 3.41 ppm Nd(III). In the second set, for fresh membranes, the same amount was recovered. It is clear that the membrane retains part of the metal ion. On the other hand, it is

Table 2. Final concentrations in feed and stripping solutions.

Initial [Nd(III)] (ppm)	[DEHPA] (mM)	Final [Nd(III)] in feed (ppm)	Final [Nd(III)] in stripping (ppm)
5	100	4.91	0.00
5	200	0.21	3.41
5	200	0.52	9.96[a]
10	200	0.23	3.65
10	500	0.14	0.00
10	700	0.00	1.59
10	200	0.00	12.88[a]

Note: Feed was initially set at pH 3.0 and stripping was done by a 2.2 M hydrochloric acid solution.
[a]Experiments performed with reused membranes that may have some neodymium loaded prior second run.

interesting to observe what takes place when using a non-fresh membrane. The results of the stripping solutions are significant. In these cases, the amount of recovered Nd(III) is higher than the expected. Then, we can conclude that the best behavior of the membrane would be achieved by saturating the membranes with the ion and then performing the separation. With this procedure total recovery would be reached, as demonstrated in Table 2.

Transport Mechanism

A more precise analysis of the transport reported the existence of two behaviors depending on time. At short times, permeabilities of up to $5.50 \times 10^{-4}\,\mathrm{cm\,min^{-1}}$ are reached with 10 ppm at feed solution at pH 3.0 and 0.1 M nitric acid as stripping solution. The same experiment and longer time yielded permeabilities of $1.31 \times 10^{-4}\,\mathrm{cm\,min^{-1}}$ (Fig. 5). These results seem to confirm again the description of the transport done above. In a first part the membrane is loaded with the ion until a sufficient amount is retained. Then, the membrane starts releasing Nd(III) to the stripping solution, and loading it at the same time from the feed. It may mean that the loading kinetics is higher than the releasing one, or that the diffusion within the membrane would be the limiting step.

Effect of Stripping Solution Composition

Several compositions were assayed as receiving solutions. Two inorganic acids (0.1 M nitric acid and 2.2 M hydrochloric acid) and an organic acid

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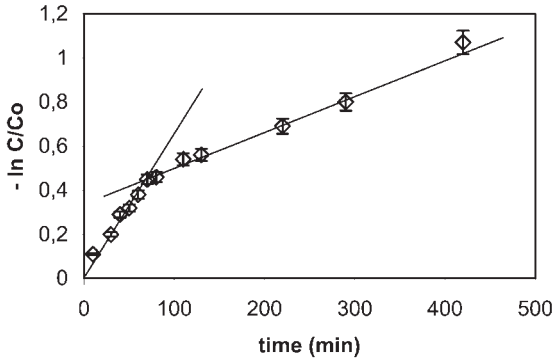

Figure 5. Example of the two different transports. Initial loading state (until 90 min) and final permeation that can be driven by the diffusion mechanism. Feed solution was a NaCl 2.2 M solution containing 10 ppm in Nd(III) at pH 3.0, membrane was prepared with 400 mM DEHPA and stripping solution was 2.2 M hydrochloric acid.

well known as lanthanide chelating agent α-hydroxy isobutiric acid (HIBA). The results are shown in Table 3. We can observe that for the initial part of the experiment, nitric acid causes the highest permeability. Nevertheless, the results corresponding to the effect of the stripping solution are those in the third column where the permeability is controlled by the stripping velocity or diffusion rate. In this case, nitric acid seems to be the best stripping solution, as far as low concentration is enough to equal hydrochloric acid and HIBA does not contribute to increase the permeability. Therefore, the exchange with protons seems to be more important than the chelation ability with HIBA. It means, the counter-transport has stronger effect than the complexation of the metal ion by the component in the stripping solution.

Table 3. Influence of receiving phase on the transport of Nd(III).

Stripping solution composition	Initial permeability ($cm\,min^{-1}$)	Final permeability ($cm\,min^{-1}$)
0.1 M HNO_3	0.00055	0.00013
0.1 M HIBA	0.00041	0.00009
2.2 M HCl	0.00039	0.00014

Note: Feed was 10 ppm Nd(III) solution at pH 3.0 and the membranes were prepared with 400 mM DEHPA.

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Membrane Stability

Two kinds of experiments were done with reused membranes after short or long period of storage time. In the first case the fresh membrane was used for a transport experiment and then the cells were emptied and refilled with fresh solutions, then a new experiment was performed. By this method, the membrane showed good stability as has been shown in Table 2. In the case of a permeability of 5.30×10^{-4} cm min^{-1} reached for a 400 mM fresh membrane, the second achieved a permeability of 4.02×10^{-4} cm min^{-1}. This result might be due to that the loading period is not present, or is less significant when reusing membranes and then the average permeability appears to be lower. In fact, the first mechanism reflected in Fig. 5 would not be present now, causing a decrease in the average permeability.

For long period stability, membranes were stored dry and without any special care for two months and later reused for new separation experiments. The results obtained were identical to those of membranes reused after a short period of time. This is a very remarkable result as far as the activated membranes were thought in order to solve the manifested instability of SLM.[19] In that sense, our membranes show great stability both during experiments and after a long storage time. This would be important from the point of view of a production plant and latter stock and commercialization processes.

Determination of Phosphorous

Several membranes containing DEHPA were submitted to liquid extraction with hexane for 24 hr of continuous shaking. After this time, the liquid part was analyzed by ICP and the percentage of phosphorous (w/w) determined. The results present in Table 4 show a direct relation but a little deviation. It seems that part of the DEHPA would not be covalent bonded and is therefore well extracted. Nevertheless, the rest of the compound

Table 4. Results of the phosphorous extraction from PSf/PA-DEHPA membranes with hexane after 24 hr of shaking.

DEHPA in casting solution (mM)	Extracted DEHPA (% w/w)
200	2.0
500	4.0
1,000	9.0

Note: Phosphorous was analyzed by ICP.

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could be chemically attached to the polymer. This is again in agreement with the results of Ariza et al.[23]

CONCLUSIONS

From the experimental data it is clear that the activated membranes prepared show ability for the transport of Nd(III), and for that, selective agent has to be present in the dense top layer. At the same time, these membranes show some proton and water permeation, even before activation under corresponding gradients.

Finally, the stability was accomplished, both in the short and in the long-term experiments. Therefore, these membranes solve the instability problem detected in SLM with the only drawback of a decrease in the permeability values for Nd(III) compared to SLM. In this work, despite the stripping phase was not optimized, the highest permeability for Nd(III) was in the range of $0.001\,\mathrm{cm\,min^{-1}}$. By optimization of the chemical conditions some improvement could be accomplished in order to come as close as possible to SLM results that range at about $0.1-0.7\,\mathrm{cm\,min^{-1}}$. Despite we used SLM optimal conditions as initial point, ACM have different transport mechanism and, therefore, new optimization for this system will have to be done once its ability for selective transport is demonstrated.

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REFERENCES

1. Bhandare, A.A.; Argekar, A.P. Separation and recovery of platinum and rhodium by supported liquid membranes using bis(2-ethylhexyl)phosphoric acid (HDEHP) as a mobile carrier. J. Chem. Technol. Biot. **2002**, *77* (7), 811–816.
2. Gherrou, A.; Kerdjoudj, H.; Molinari, R.; Drioli, E. Removal of silver and copper ions from acidic thiourea solutions with a supported liquid membrane containing D2EHPA as carrier. Sep. Purif. Technol. **2002**, *28* (3), 235–244.

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270 Madison Avenue, New York, New York 10016

3. Yahaya, G.O. Kinetic studies on organic acid extraction by a supported liquid membrane using functionalized polyorganosiloxanes as mobile and fixed-site carriers. Separ. Sci. Technol. **2001**, *36* (16), 3563–3584.
4. Campos, E.A.; Guishikem, Y. Composite membrane of niobium(V) oxide and cellulose acetate: preparation and characterization. J. Colloid. Interf. Sci. **1997**, *193* (1), 121–126.
5. Teramoto, M.; Sakaida, Y.; Fu, S.S.; Ohnishi, N.; Matsuyama, H.; Maki, T.; Fukui, T.; Arai, K. An attempt for the stabilization of supported liquid membrane. Sep. Purif. Technol. **2000**, *211* (2), 137–144.
6. Kemperman, A.J.B.; Rolevink, H.H.M.; Bargeman, D.; van den Boomgaard, Th.; Strathmann, H. Stabilization of supported liquid membranes by interfacial polymerization top layers. J. Membrane Sci. **1998**, *138* (1), 43–55.
7. Oleinikova, M.; Muñoz, M. Transport of rare earth metal ions through activated composite membranes containing DEHPA. Solv. Extr. Ion Exch. **2000**, *182*, 401.
8. Melita, L.; Oleinikova, M.; de Gyves, J.; Muñoz, M.; Meghea, A. Removal of Cu(II) and Zn(II) from waste waters using activated composite membranes. Science and Technology of Environmental Protection **2001**, *18* (2), 26–33.
9. Dai, L.M.; Minh, D.V.; Hai, P.V. Solvent extraction of lanthanides with triisoamylphosphate and di-(2-ethylhexyl)phosphoric acid from trichloroacetic acid and nitric acid solutions. J. Alloy Comp. **2000**, *311* (1,12), 46–52.
10. Cox, M.; Rus-Romero, J.R.; Sheriff, T.S. The application of montmorillonite clays impregnated with organic extractants for the removal of metals from aqueous solution: part I. The preparation of clays impregnated with di-(2-ethylhexyl) phosphoric acid and their use for the removal of copper(II). Chem. Eng. J. **2001**, *84* (2), 107–113.
11. Ortiz, I.; San Román, F.; Galán, B. Kinetics of the recovery of Cd from highly concentrated aqueous solutions by non-dispersive solvent extraction. Chem. Eng. J. **2001**, *81* (1–3), 129–136.
12. Serarols, J.; Poch, J.; Villaescusa, I. Expansion of adsorption isotherms into equilibrium surface: case 1: solvent impregnated resins (SIR). React. and Funct. Polym. **2001**, *48* (1–3), 37–51.
13. Juang, R.S.; Huang, H.C. Non-dispersive extraction separation of metals using hydrophilic microporous and cation exchange membranes. J. Membrane Sci. **1999**, *156* (2), 179–186.
14. Minh, D.L.; Vu, Minh Dang; Pham, Van Hai. Transport of zinc through a supported liquid membrane using di(2-ethylhexyl) phosphoric acid as a mobile carrier. J. Alloy Comp. **2000**, *311* (1), 46–52.

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15. Moreno, C.; Valiente, M. Studies on the mechanism of lanthanide ions through supported liquid membranes containing di(-2-ethylhexiyl) phosphoric acid (D2EHPA) as a carrier. J. Membrane Sci. **1999**, *155* (1), 155–162.
16. Gumí, T.; Oleinikova, M.; Palet, C.; Valiente, M.; Muñoz, M. Facilitated transport of lead(II) and cadmium(II) through novel activated composite membranes containing di(-2-ethyl-hexiyl) phosphoric acid as a carrier. Anal. Chim. Acta **2000**, *408*, 65–74.
17. Sun, X.B.; Du, H.F.; Yang, Z.X.; Zhou, Z.M. Extraction kinetics of uranium(VI) with di(2-ethylhexyl) phosphoric acid using a hollow fiber membrane extractor. J. Radioanal. Nucl. Ch. **2000**, *245* (2), 421–424.
18. Dolezal, J.; Moreno, C.; Hrdlicka, A.; Valiente, M. Selective transport of lanthanides through supported liquid membranes containing non-selective extractant, di(-2-ethylhexiyl) phosphoric acid, as a carrier. J. Membrane Sci. **2000**, *168* (1–2), 175–181.
19. Garcia-Valls, R.; Muñoz, M.; Valiente, M. Selective transport of lanthanides by supported liquid membranes containing cyanex 925 as a carrier. Anal. Chim. Acta **1999**, *387*, 77–84.
20. Garcia-Valls, R. New materials for lanthanides separation techniques. Activated polymeric membranes and inorganic materials for chromatography. Autonomous University of Barcelona, Ph.D. Thesis, 1995, ISBN 84-490-0500-0.
21. Danesi, P.R. Separation of metal species by supported liquid membranes. Separ. Sci. Technol. **1984–1985**, *19*, 857.
22. Mulder, M. *Basic Principals of Membrane Technology*; Kluwer: Dordrecht, 1992; ISBN 0-7923-4248-8(PB).
23. Ariza, M.J.; Rodríguez-Castellón, E.; Rico, R.; Benavente, J.; Muñoz, M.; Oleinikova, M. X-ray photoelectron spectroscopy analysis of di-(2-ethylhexyl) phosphoric acid activated membranes. J. Colloid. Interf. Sci. **2000**, *226* (1), 151–158.

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