



## Research Paper

## A Study on Neodymium Recovery from Aqueous Solutions for Designing a New Generation of Sandwich Liquid Membrane

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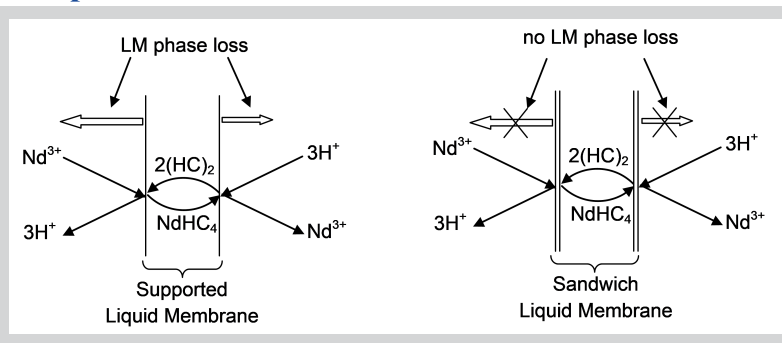
## Highlights

- Liquid Membranes LMs are a powerful process to recovery chemicals from dilute streams
- Studies on Supported Liquid Membrane (SLM) are useful to design a 2<sup>nd</sup> generation SwLM
- TOC measurements showed that carrier release is the main cause of SLM destabilization
- 2<sup>nd</sup> generation of Sandwich Liquid Membranes (SwLMs) could solve the stability problem
- A high concentration ratio (114) of Nd in the strip phase was obtained using the SLM

## Abstract

Liquid Membrane (LM) based processes, as Supported Liquid Membranes (SLMs), have been proposed, for over 30 years, as effective methods for the selective separation of inorganic/organic species from different water streams. The industrial use of SLMs has been limited mainly by their insufficient stability. To investigate on the main cause of system destabilization and the optimal conditions for mass transport, a good reference system is the traditional SLM. To this aim the recovery of neodymium (Nd) from acidic media by a traditional SLM has been studied, giving particular attention to permeation and stability. The results clearly evidenced that system stability was strongly influenced by the solubilization of the carrier in the aqueous phases. The consideration and the experimental results reported in this work give useful information to shift the next research step versus the development of a 2<sup>nd</sup> generation of SwLM able to give satisfactory system performance in view of industrial application, such as Nd as well as rare earth elements or salt recovery from aqueous media.

## Graphical abstract



## 1. Introduction

Transport of organic and inorganic compounds across a liquid membrane (LM) and, in particular, through a supported liquid membrane (SLM), is a powerful technology incorporating solvent extraction (SX) and stripping in a one-step continuously operating system [1, 2]. In many cases, such as the recovery of inorganic metallic ions from aqueous media, LM based systems are competitive with solvent extraction (SX), which is generally accepted as the most appropriate commercial technology due to its fast kinetics and high efficiencies [3, 4]. However, SX has many operational drawbacks including the large inventory of extracting agents, the possible third phase formation, the involvement of aggressive chemicals that may degrade the organic solvent and extracting agent during prolonged contact, and the necessity of scrub stages to increase the purity of the final product. Furthermore, the employed solvents have usually adverse environmental impact [5].

SLMs generally are prepared with of an organic solvent (the LM phase) contained into the pores of a hydrophobic microfiltration membrane and kept

there by capillary forces [6, 7]. This LM phase may also contain an extracting agent (carrier), which binds one or more components in the donor feed phase, transporting it (or them) to the strip phase across the membrane, resulting in the so called facilitated transport [8]. This approach responds to the process intensification strategy thanks to the benefit arising from the coupling of a chemical reaction and a mass transfer phenomenon [9].

SLMs have been tested in the separation and recovery of various metal ions [8, 10-12], anions [13], molecules of biological interest and organics [14, 15] from different aqueous media. For example SLMs have been proposed for rare earth recovery from wastewaters coming from the treatment of Waste of Electrical and Electronic Equipment (WEEE) [16-19] and for the desalination of saline water [20-22]. Recently SLMs have been also tested for the separation of Cd and Ag from high saline waters [23, 24].

SLM based processes have many interesting features compared to conventional separation processes [10, 25, 26]. The effective contact area is

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known, constant and independent from the flow rates of the fluid phases. A very small volume of organic solvent is required due to the smaller organic phase volume existing in the membrane pores. A small amount of extracting agent, owing to its cyclical use, is required. A non-dispersive contact between the feed, organic and strip phases is achieved avoiding additional separation stages and the formation of emulsions. Moreover, since the extracted component is continuously released in the strip phase, SLMs are not equilibrium limited. Therefore, a high driving force is maintained for prolonged periods of time, giving the intensification of the extraction and stripping stages.

Despite the basic chemistry of SX and LM is similar, enhanced process selectivity can be obtained by using the LM. The overall selectivity of the LM process can be ascribed to two consecutive factors called thermodynamic and kinetic selectivity, respectively [8, 17]. The first one, common to both LM and SX processes, is related to the equilibrium of the extraction reaction at the interface. Thus, a component (A), contained in the feed phase at lower concentration than another one (B), can be present at higher concentration into the organic phase thanks to its higher extraction degree. The second factor, typical of LM, is related to the kinetics of the permeation across the membrane which is related to the concentrations at the interfaces. Thus the component A, presenting a higher concentration gradient between the two sides of the membrane, can diffuse faster across the LM giving an overall selectivity higher than the thermodynamic selectivity. On these bases Kim et al. [17], starting from a feed solution containing both Nd and Fe ions at concentrations of 1550 and 1950 ppm, respectively, and using a carrier which extracted both ions, recovered only Nd in the strip phase. Then a well optimized LM process does not require scrubbing stages to obtain a highly selective separation.

Despite the above mentioned advantages and the encouraging results obtained by using SLM in the separation and recovery of different solutes from aqueous media, the low system stability largely hinders the commercialization of SLMs [27, 28].

Among the inorganic ions which can be recovered by LM based systems, rare earth elements (REEs) play an important role in developing green and energy efficient technologies and high-tech industries [29-33]. Based on the fast growing of technological application of REEs, it is very important their selective recovery from aqueous media (e.g. acidic leaching solutions coming from hydrometallurgical treatment of waste electrical and electronic equipment) and enrich them [18, 34].

In the present work, to investigate deeply the cause of system destabilization and to find the optimal conditions for mass transport, Nd recovery by using a traditional SLM has been studied as reference system. Some chemical aspects for the application of a LM have been investigated by carrying out L-L extraction tests. The optimal operating conditions for Nd extraction and transport across LM and stoichiometry and equilibrium constant of the extraction reactions have been determined. Mass transport tests of Nd in the SLM system were carried out by determining the permeability and the stability of the LM system. The results clearly evidenced that system stability was strongly influenced by carrier solubilization in the aqueous phases giving useful information to shift the next research step versus the development of a 2<sup>nd</sup> generation of SwLM able to give satisfactory system performance in view of industrial application (e.g. Nd recovery from aqueous media).

## 2. Materials and methods

### 2.1. Reagents

Neodymium (III) chloride hexahydrate  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  (MW = 358.69 g  $\text{mol}^{-1}$ , purity 99.9%) from Sigma Aldrich was used to prepare neodymium aqueous solutions.

Octane  $\text{C}_8\text{H}_{18}$  (MW = 114.23, purity 98%,  $d^{20} = 0.703$  g  $\text{mL}^{-1}$ ,  $T_{\text{cb}} = 125.52$  °C) and n-decane  $\text{C}_{10}\text{H}_{22}$  (MW = 142.29  $\text{g mol}^{-1}$ , purity > 99%,  $d^{20} = 0.73$  g  $\text{mL}^{-1}$ ,  $T_{\text{cb}} = 174.1$  °C) from Sigma Aldrich were used as the organic solvents.

Two cationic extracting agents were tested in the L-L extraction tests to evaluate the best one to use as carrier in the SLM transport: i) D2EHPA (di-(2-ethylhexyl) phosphoric acid, MW = 322.4 g  $\text{mol}^{-1}$ , purity = 97%,  $d^{20} = 0.965$  g  $\text{mL}^{-1}$ ) from Sigma Aldrich; ii) CYANEX® 272 (Bis(2,4,4-trimethylpentyl) phosphinic acid, MW = 290.4 g  $\text{mol}^{-1}$ ,  $d^{20} = 0.94$  g  $\text{mL}^{-1}$ ) from Cytec.

Hydrochloric acid HCl (MW = 36.45 g  $\text{mol}^{-1}$ , 37% w/w in water) and sodium hydroxide NaOH in pellets (MW = 40 g  $\text{mol}^{-1}$ , purity = 98%) from Sigma-Aldrich were used to correct the pH of the aqueous phases.

Flat sheet microfiltration hydrophobic membranes of polypropylene (PP Accurel by Membrana, thickness 142  $\mu\text{m}$ ; pore size 0.2  $\mu\text{m}$ ; porosity 70%)

were employed as the supports to prepare the SLM.

### 2.2. Analytical methods

Neodymium concentrations in the aqueous phases were determined by using an ELAN® 9000 ICP-MS from Perkin Elmer. Reproducibility of the analyses was within 5%. Nd concentration in the organic phase was calculated by a mass balance.

A TOC-V<sub>CSN</sub> from Shimadzu was used for determining the total organic carbon (TOC) of the aqueous phases.

The pH of the aqueous phases was determined by using a pH meter (WTW Inolab Terminal Level 3) equipped with a glass pH electrode SenTix 81 (WTW).

### 2.3. L-L extraction tests

Each extraction step was carried out as reported in our previous works [2, 6, 8, 35]. 5 mL of aqueous Nd solution ( $[\text{Nd}]_{\text{in}} = 100$  mg  $\text{L}^{-1} = 0.69 \times 10^{-3}$  mol  $\text{L}^{-1}$ ) at different initial pH were contacted with 5 mL of organic phase in a test tube ( $T = 25$  °C). The organic phase was prepared by adding the carrier to the organic solvent at different concentrations: 0.1, 0.3 and 0.5 M (3.33, 10.02 and 16.67 % v/v, respectively).

The experiments were repeated two or more times evidencing a satisfactory reproducibility (standard deviation around 5%).

### 2.4. SLM preparation and experimental set up used for accomplishment of permeation tests

SLMs were prepared by immersing the polymeric support into the organic phase (20 mL) for about 24 h. The excess of the organic phase was removed by drying the surface of the impregnated membrane with a soft paper sheet. The so obtained SLMs were then placed in the permeation module.

Permeation tests were carried out in the experimental set-up described in our previous works [2, 6, 8, 35]. At established time intervals feed and strip samples were withdrawn and Nd concentrations were measured.

Permeation tests using two feed/strip solution couples were carried out to measure Nd permeability across the LM. Feed and strip phases were changed with “fresh” ones when quite complete Nd transport from feed to strip was obtained (after 210 minutes). When a permeation run was finished, the TOC of feed and strip phases were measured thus quantifying the loss of the organic phase from the LM systems. The experiments were repeated two or more times, finding an agreement of the data within 5–8%.

Stability tests were also carried out replacing feed and strip phases with fresh ones till to system destabilization. The latter was evidenced by passage of aqueous phase across the membrane and/or decrease of membrane permeability below 50% of the initial value.

### 2.5. Theory

The key concepts useful for understanding the present work are reported in this section.

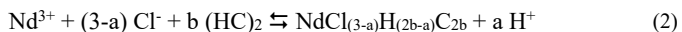
#### 2.5.1. Theory and modeling of the L-L extraction tests

A key parameter in the L-L extraction process is the extraction percentage  $E\%$ , defined as follows:

$$E\% = \frac{n_{A,org}}{n_{A,in}} \times 100 = \frac{n_{A,org}}{n_{A,org} + n_{A,aq}} \times 100 \quad (1)$$

where A is the component to extract (Nd in this work),  $n_A$  represents the amount (moles) of A, and the subscripts “org”, “aq” and “in” means organic, aqueous and initial feed phase, respectively.

The real stoichiometry of the extraction reaction has been evaluated considering that in general the extraction of Nd(III) by using an acidic carrier as D2EHPA or Cyanex 272 can be expressed as follows [11, 12]:



where  $a$  and  $b$  are two positive real numbers and  $(\text{HC})_2$  represents the dimeric form of the carrier into the organic phase.

From reaction (2), it can be observed that the extraction process is strongly pH dependent.

The equilibrium constant of reaction (2) can be written as:

$$K_{eq} = K_d \frac{[H^+]^a}{[Cl^-]^{3-a} [(HC)_2]^b} \quad (3)$$

where  $K_d = [Nd]_{org} / [Nd]_{aq}$  = distribution factor.

To evaluate the stoichiometry of the reaction (2) and the equilibrium constant,  $a$  and  $b$  parameters have been determined by using the slope analysis method based on the following equation (4), obtained by taking the logarithm of equation (3) and rearranging:

$$\log K_d = \log K_{eq} + (3-a) \log [Cl^-] + b \log [(HC)_2] + a \text{ pH} \quad (4)$$

The value of the parameter  $a$  was estimated by plotting the  $\log K_d$  vs. the equilibrium pH at fixed carrier concentration and temperature. To estimate the value of the parameter  $b$ , the  $\log K_d$  was plotted as function of  $\log[(HC)_2]$  at fixed equilibrium pH and at the three tested carrier concentrations (0.1, 0.3 and 0.5 M).

### 2.5.2. Theory of the SLM transport

In the case of metal ions permeation ( $Nd^{3+}$  in this study) through the SLM with an acidic carrier HC, the transport mechanism is the so-called facilitated coupled counter transport [26]. As deduced from eq. (2), the metal ion  $Nd^{3+}$  is transported from feed to strip, while the  $H^+$  ion is transported in opposite direction (counter transport). The effective driving force of the permeation process is represented by the difference of  $H^+$  concentration between the feed and the strip, quantified in terms of pH ( $pH_{feed} > pH_{strip}$ ).

The permeation flux has been calculated by using the following equation:

$$J_A = -\frac{V_F}{S_{exp} \cdot \varepsilon_m} \times \left( \frac{d[A]}{dt} \right) \quad (5)$$

where  $A$  represents the target species to be transported ( $Nd^{2+}$  in this study),  $V_F$  is the volume of the feed phase,  $S_{exp}$  is the exposed membrane surface (5.76  $cm^2$  in this study) and  $\varepsilon_m$  is the porosity of the membrane.

Another important parameter used to evaluate the LM performance is the permeability ( $P$ ) [13], which takes into account the overall transport across the LM. Considering neodymium fluxes: i) across the boundary layer feed-side, ii) across the interface between the feed phase - membrane and iii) through the membrane, and operating under efficient stripping conditions ( $[A]_{Fi} \gg [A]_{Si}$  where "Fi" and "Si" mean feed and strip interfaces, respectively) the permeability can be expressed by the following equation [36]:

$$P = \frac{K_d}{K_d \frac{\delta}{D_{bl}} + \frac{l}{D_m}} = \frac{J_F}{[A]_F} \quad (6)$$

where  $K_d$  is the distribution factor,  $\delta$  is the boundary layer thickness,  $l$  is membrane thickness and  $D_{bl}$  and  $D_m$  represent neodymium diffusivity in the boundary layer and in the membrane, respectively. Eq. (6) also evidences that the permeation flux and the permeability are related by the Fick's law of diffusion: the flux is the concentration of the solute in the feed times the permeability.

The permeability values have been graphically estimated by combining Eqs. (5) and (6) and integrating with the boundary conditions  $[A]_F = [A]_{F0}$  at  $t = 0$  min (initial feed concentration) and  $[A]_F = [A]_F$  at time  $t = t$ , thus the following equation is obtained:

$$\ln \frac{[A]_F}{[A]_{F0}} = -\frac{S_{eff}}{V_F} \times P \times t \quad (7)$$

Equation (7) permits to graphically evaluate the permeability  $P$  of the SLM system by plotting the experimental data of  $\ln([A]_F/[A]_{F0})$  versus the time. A straight line should be obtained, whose slope is related to the permeability  $P$ .

Another parameter, in view of operating the SLM system in practical applications, is the concentration ratio (CR) of the target component defined as:

$$CR = \frac{[A]_{SE}}{[A]_{FE}} \quad (8)$$

where  $[A]_{SE}$  and  $[A]_{FE}$  represent the concentrations of the target species ( $Nd^{3+}$ )

in the strip and feed phases at the end of each permeation run, respectively. The value of this ratio also indicates how much the strip coming out from a continuous LM system can be more concentrated than the outgoing feed.

## 3. Results and discussion

In the following subsections the results obtained in the extraction and permeation of Nd across a traditional flat sheet SLM system are reported to find the optimal chemical conditions for mass transport and to investigate the main causes of system destabilization.

### 3.1. Study of the chemistry of the extraction process

L-L extraction tests were carried out for determining the chemical conditions (organic solvent/carrier combination, carrier concentration in the LM phase, extraction and stripping pH) to be employed in the SLM tests.

The stoichiometry and the equilibrium constants involved in the extraction process were also evaluated, evidencing their effects on the extraction conditions.

#### 3.1.1. L-L extraction tests with D2EHPA in octane

The results obtained by using octane as the organic solvent and D2EHPA as the carrier, summarized in Figure 1, clearly evidence that Nd ion is complexed by the D2EHPA carrier (E% = 0 without the carrier), giving a quantitative extraction from the aqueous phase at pH higher than 1. The stripping condition is obtained at  $pH \approx 0$ , meaning 1.0 M HCl concentration. The extraction percentage vs. the equilibrium pH follows the typical sigmoid trend. Because of carrier acidity and according to the extraction reaction (Eq. 2), E% decreases by decreasing the equilibrium pH while the sigmoid shifts to left by increasing the carrier concentration. As a consequence, for a fixed pH the E% increases with carrier concentration.

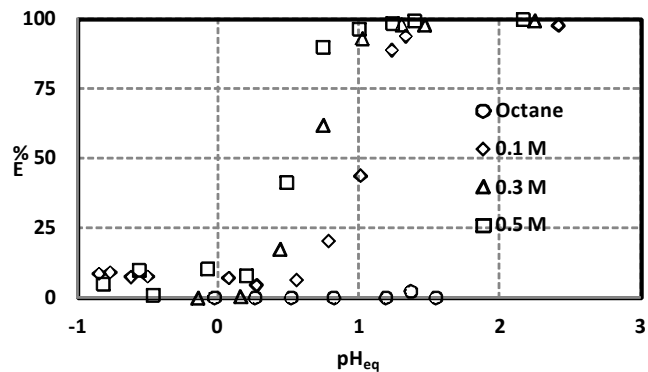


Fig. 1. Extraction percentage vs. the equilibrium pH in L-L extraction tests with D2EHPA at different concentration in octane ( $V_{aq} = V_{org} = 5$  mL;  $[Nd]_{aq,in} = 100$  mg  $L^{-1}$ ,  $T = 25^\circ C$ ).

TOC concentrations in the aqueous phase at equilibrium give important information about the determination of the main cause of SLM stabilization, which is a fundamental step in view of developing a 2<sup>nd</sup> generation of SwLM able to give satisfactory performance. The measured TOC were negligible when only the solvent was present (see Figure 2). This result clearly indicates that the TOC released in the aqueous phases was mainly due to the carrier, whose increase of concentration in the organic phase is caused by its solubilization through the solvation (hydration) of the dissociated polar groups. For this reason, the TOC increases by increasing carrier concentration and decreases by decreasing the pH. The latter can be explained by considering that a  $[H^+]$  increase in the aqueous phase shifts the acid dissociation in the side of the non-dissociated form of the carrier and thus its solubility in water is lower.

The estimated  $a$  and  $b$  values of complexation stoichiometry (Eq. (2)) were:  $a = 3$  and  $b = 2$ . This means no effect of  $Cl^-$  anion on Nd extraction using D2EHPA. Satisfactory fit of the experimental data with the employed complexation model was obtained ( $R^2 \geq 0.98$ ), thus confirming its validity under the considered operating conditions.

Substituting the estimated  $a$  and  $b$  values in eq. (2), the extraction reaction becomes:



and the equilibrium constant, from eq. (3), becomes:

$$K_{eq} = K_d \frac{[\text{H}^+]^3}{[(\text{HC})_2]^2} \quad (10)$$

From eq. (10) a  $K_{eq}$  equal to  $4.93 \times 10^{-1} \pm 6.38 \times 10^{-2}$  was numerically estimated and this value was practically equal to that one graphically evaluated (see Table 1).

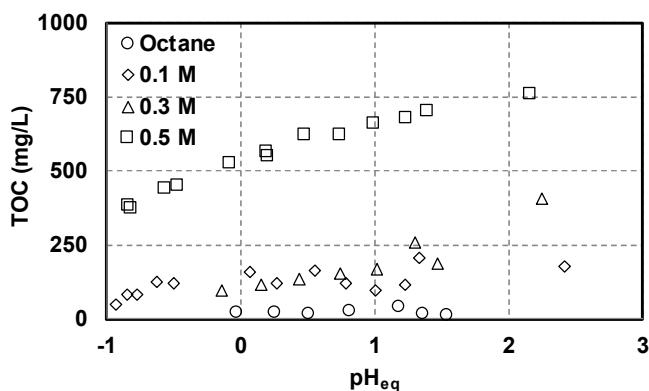


Fig. 2. TOC in the aqueous phase vs. the equilibrium pH in L-L extraction tests with D2EHPA at different concentration in octane ( $V_{\text{aq}} = V_{\text{org}} = 5 \text{ mL}$ ;  $[\text{Nd}]_{\text{aq, in}} = 100 \text{ mg L}^{-1}$ ,  $T = 25^\circ\text{C}$ ).

Table 1

$K_{eq}$  estimation for Nd extraction with D2EHPA in octane ( $V_{\text{aq}} = V_{\text{org}} = 5 \text{ mL}$ ;  $[\text{Nd}]_{\text{aq, in}} = 100 \text{ mg L}^{-1}$ ,  $T = 25^\circ\text{C}$ ).

Carrier concentration (M)	$K_{eq, \text{numerical}}$	$K_{eq, \text{graphical}}$
0.1	$5.66 \times 10^{-1}$	$5.84 \times 10^{-1}$
0.3	$4.63 \times 10^{-1}$	$4.83 \times 10^{-1}$
0.5	$4.50 \times 10^{-1}$	$3.93 \times 10^{-1}$
average	$4.93 \times 10^{-1}$	$4.87 \times 10^{-1}$
standard deviation	$6.38 \times 10^{-2}$	$9.59 \times 10^{-2}$

### 3.1.2. Other L-L extraction tests: comparison of the results and choice of the LM phase

Other sets of L-L extraction tests were carried out by using D2EHPA in *n*-decane as the organic solvent, thus evaluating the influence of the type of organic solvent on system performance. CYANEX 272 both in octane and in *n*-decane was also tested, determining its ability to extract Nd and comparing its performance with that one of D2EHPA. The overall results are summarized in Table 2 for the four couples's carrier-organic solvent.

Concerning the influence of the organic solvent on the extraction performance, in the case of the D2EHPA carrier it can be observed that a perfect matching between the E% vs. pH curves with the two organic solvents (Figure 3) is obtained. Identical considerations can be done by considering CYANEX 272 as the carrier. As a consequence, both the extraction and the stripping pHs did not change by changing the organic solvent (see the 3<sup>rd</sup> and 4<sup>th</sup> columns of Table 2). Thus it can be concluded that the two considered organic solvents do not affect the extraction ability of the D2EHPA and CYANEX 272.

An important operational advantage of D2EHPA with respect to

CYANEX 272 is its ability to work at lower pHs. Indeed, both the extraction and release of Nd using CYANEX 272 occur at higher equilibrium pHs (see 3<sup>rd</sup> and 4<sup>th</sup> columns of Table 2), i.e. the E% vs. pH sigmoid is shifted to right, compared to D2EHPA, because of lower carrier acidity (see Figure 4). This is an advantage because REEs are usually dissolved in very acidic aqueous systems as consequence of their hydrometallurgical recovery both from natural minerals and WEEEs.

Table 2

Comparison of L-L extraction tests for the four couples's carrier/organic solvent.

Carrier	Organic solvent	Extraction pH (E% = 100)	Stripping pH (E% = 0)	a	b	$K_{eq, \text{numerical}}$
D2EHPA	Octane	$\approx 2.0$	$\approx 0$	3	2	$4.93 \times 10^{-1} \pm 6.38 \times 10^{-2}$
D2EHPA	<i>n</i> -decane	$\approx 2.0$	$\approx 0$	3	2	$5.90 \times 10^{-1} \pm 1.72 \times 10^{-1}$
CYANEX® 272	Octane	$\geq 2.5$	$\approx 1$	2	1	$4.42 \times 10^{-2} \pm 1.45 \times 10^{-2}$
CYANEX® 272	<i>n</i> -decane	$\geq 2.5$	$\approx 1$	2	1	$4.38 \times 10^{-2} \pm 7.62 \times 10^{-3}$

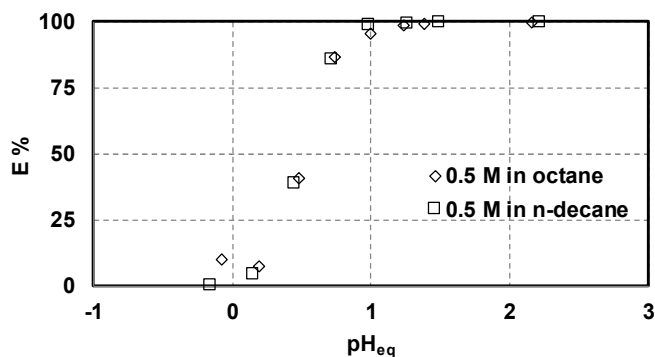


Fig. 3. Comparison of Extraction percentage vs. the equilibrium pH in L-L extraction tests with D2EHPA 0.5 M in octane and *n*-decane ( $V_{\text{aq}} = V_{\text{org}} = 5 \text{ mL}$ ;  $[\text{Nd}]_{\text{aq, in}} = 100 \text{ mg L}^{-1}$ ,  $T = 25^\circ\text{C}$ ).

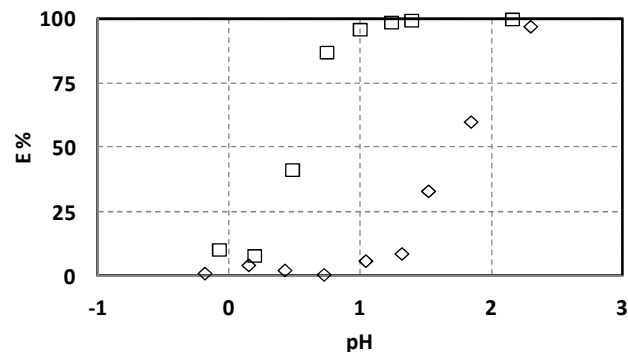


Fig. 4. Extraction percentage vs. the equilibrium pH in L-L extraction tests with CYANEX® 272 and D2EHPA in octane at 0.5 M carrier concentration ( $\diamond$ : CYANEX 272;  $\square$ : D2EHPA;  $V_{\text{aq}} = V_{\text{org}} = 5 \text{ mL}$ ;  $[\text{Nd}]_{\text{aq, in}} = 100 \text{ mg L}^{-1}$ ,  $T = 25^\circ\text{C}$ ).

The influence of the type of organic solvent can be evidenced by comparing the TOC trends at the same extracting agent concentration, as reported in Figure 5 for D2EHPA. A higher TOC concentration in the aqueous phase was obtained in the case of octane. Since TOC detected into the aqueous phase was caused by the carrier solubilization and not by the solvent, as previously observed, these results evidence that *n*-decane possess a higher ability to solubilize D2EHPA, thus decreasing its release into the aqueous phase. This behavior is very interesting in view of LM application

(SLM or SwLM), because the carrier (i.e. the extracting agent) release into the feed and strip aqueous phases has to be minimized, having it a key role on permeation flux and system stability.

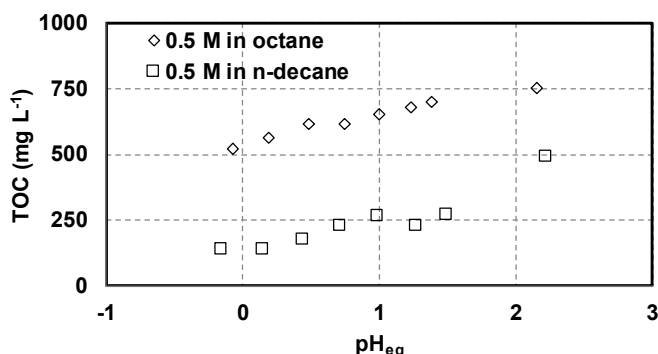


Fig. 5. Comparison of TOC vs. the equilibrium pH in L-L extraction tests with D2EHPA 0.5 M in octane and n-decane ( $V_{aq} = V_{org} = 5$  mL;  $[Nd]_{aq,in} = 100$  mg L<sup>-1</sup>, T = 25°C).

Both the decrease of dissolved organic carbon by decreasing the pH and the increase of TOC concentration by increasing carrier concentration were confirmed by using the CIANEX 272 as carrier (see Figure 6). Besides, it was confirmed that released organic content in the aqueous phases was mainly due to the carrier. Indeed TOC values, obtained without the carrier, were negligible compared to those obtained with the carrier. TOC values obtained with CYANEX 272 were comparable to those obtained with D2EHPA, evidencing that both carriers have similar affinity with the same solvent.

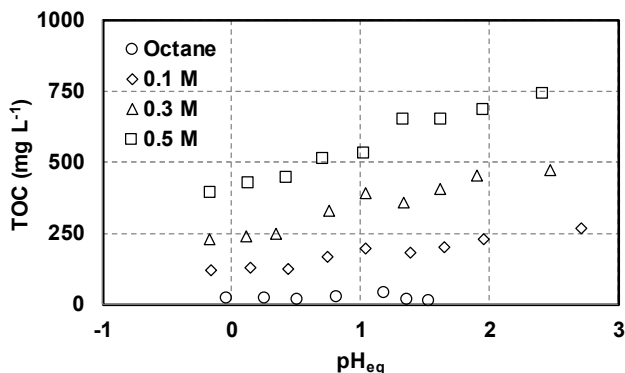
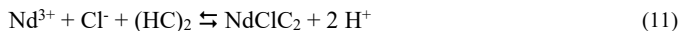


Fig. 6. TOC in the aqueous phase vs. the equilibrium pH in L-L extraction tests with CYANEX<sup>®</sup> 272 at different concentration in octane ( $V_{aq} = V_{org} = 5$  mL;  $[Nd]_{aq,in} = 100$  mg L<sup>-1</sup>, T = 25°C).

Looking at the stoichiometry of the extraction reaction, the no effect of the employed organic solvent on the extraction ability of both the carriers was confirmed. Indeed, the values of the parameters *a* and *b* (see 5<sup>th</sup> on 6<sup>th</sup> columns of Table 2) did not change by changing the organic solvent. The previous evidenced benefit in using D2EHPA, which permits to operate at lower pHs, is also confirmed by the estimated *a* and *b* values. These parameters, giving indication about the stoichiometry of the complexation reaction (2) and permitting to determine its equilibrium constant (3), influence the operating conditions to be employed in the LM system. Considering equation (4), the highest *a* value obtained in the case of D2EHPA indicates a more rapid increase of log *K*<sub>d</sub>, and then E%, by increasing the pH (see Figure 4). Thus, at a fixed pH, D2EHPA extract a higher amount of Nd ions with respect to CYANEX 272, justifying the lower extraction pH reported in Table

2.

The estimated *a* and *b* values for CYANEX 272 (*a* = 2 and *b* = 1) show that presence of the chloride ion is necessary to form the complex. By substituting these values in eq. (2), the extraction reaction becomes:



and the equilibrium constant (from eq. 3) is:

$$K_{eq} = K_d \frac{[H^+]^2}{[Cl^-][HC]_2} \quad (12)$$

The highest values of *K*<sub>eq</sub> estimated in the case of D2EHPA (Table 2, 7<sup>th</sup> column), indicate that this carrier has a higher tendency to extract the Nd ion with respect to CYANEX 272.

On the basis of previous considerations D2EHPA, which permits to operate at lower pH and shows a little higher tendency to extract Nd, was chosen as the carrier to perform the successive SLM permeation tests.

Regarding the organic solvent, n-decane gave a lower TOC release into the aqueous phase, evidencing it as better solvent for D2EHPA. However, the successive SLM tests were performed by using both octane and n-decane as the organic solvent because transport properties within the LM could be different.

### 3.2. Permeation of Nd across the SLM system

#### 3.2.1. Permeation tests using D2EHPA in octane

A first set of permeation tests was carried out by using the following conditions:

- LM phase: D2EHPA 0.1 M in octane
- Feed phase:  $[Nd]_{F0} = 100$  mg L<sup>-1</sup> Nd(III), pH ≥ 2
- Strip phase:  $[Nd]_{S0} = 0$  mg L<sup>-1</sup>,  $[HCl] = 1.0$  M, pH ≈ 0
- T = 25 °C

where  $[Nd]_{F0}$  and  $[Nd]_{S0}$  represent the initial Nd concentration in the feed and in the strip phases, respectively.

Obtained results, reported in Figure 7, show that Nd concentration in the feed phase ( $[Nd]_F$ ) decreases following an exponential decay for both feed/strip couples injected sequentially in the experimental plant. A clear mass transport slowdown with the 2<sup>nd</sup> feed/strip couple was evidenced by the lower coefficient in the exponential term (0.011 vs. 0.018), the higher counter transport time (CTT, 60 min vs. 45 min, which is the time needed to start Nd transport against the concentration gradient) and the highest final concentration in the strip  $[Nd]_{FE}$  (9.38 mg L<sup>-1</sup> vs. 2.52 mg L<sup>-1</sup>). This trend, in accordance with the pertinent literature [6, 8, 37], was due to the progressive release of the LM phase (mainly the carrier as observed in the L-L extraction tests) in the aqueous feed and strip phases, as confirmed also by TOC measurements (see Table 3). TOC values in both the feed phases were higher than that in the respective strip phases. In particular, the mass of LM phase released in the feed phases represents about 85% of the total. This trend can be explained considering that  $pH_{feed} > pH_{strip}$ . According to the consideration made analyzing the results of the L-L extraction tests, higher carrier ionization and then its solubilization happens in the feed side.

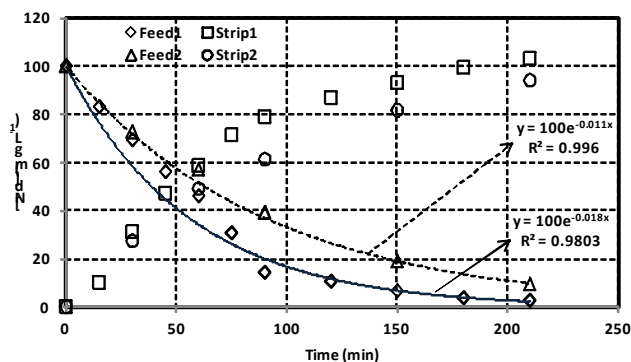


Fig. 7. Neodymium concentration versus time for two feed-strip couples sequentially injected in the SLM system (feed phase:  $[Nd]_{F0} = 100$  mg L<sup>-1</sup>, V = 75 mL, pH ≥ 2; strip phase:  $[Nd]_{S0} = 0$  mg L<sup>-1</sup>, V = 75 mL, pH ≈ 0; organic phase: D2EHPA 0.1 M in octane, T = 25 °C).

The parameter which quantifies the observed system slowdown is the permeability  $P$ . System permeability, estimated for the first and second feed/strip couples according to eq. 7, was:  $P_1 = 0.335 \text{ cm min}^{-1}$  for the 1<sup>st</sup> couple and  $P_2 = 0.205 \text{ cm min}^{-1}$  for the 2<sup>nd</sup> couple. This important diminution of permeability (39%) can be strictly related to the significant TOC release (mainly carrier) observed during the L-L extraction tests with octane as the organic solvent (see Figure 5). On the basis of this, the use of an organic solvent as *n*-decane which give a lower carrier solubilization in the adjacent aqueous phases should be suggested.

### 3.2.2. Permeation tests using D2EHPA in *n*-decane

Using a 0.1 M D2EHPA concentration in *n*-decane, which was the same employed in octane, a very low Nd flux across the membrane was evidenced. The reason of this behavior will be explained in Appendix A. Then the permeation tests continued using 0.5 M D2EHPA.

Obtained results (see Figure 8) showed that the trends of Nd concentration both in the feed ( $[\text{Nd}]_F$ ) and in the strip ( $[\text{Nd}]_S$ ) for the 1<sup>st</sup> and the 2<sup>nd</sup> couple were practically coincident, evidencing no system slowdown.

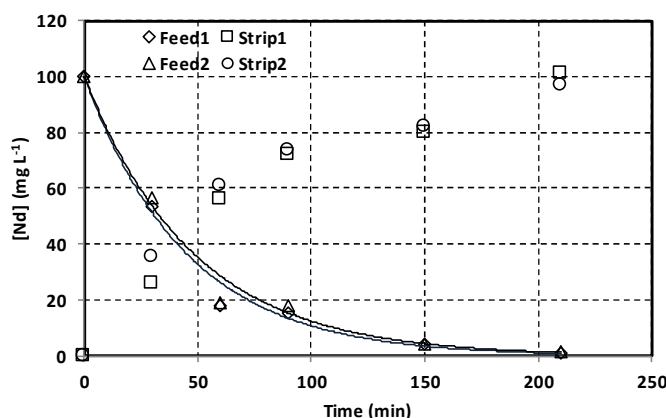


Fig. 8. Neodymium concentration versus time for two feed-strip couples sequentially injected in the SLM system (feed phase:  $[\text{Nd}]_{F0} = 100 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \geq 2$ ; strip phase:  $[\text{Nd}]_{S0} = 0 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \approx 0$ ; organic phase: D2EHPA 0.5 M in *n*-decane,  $T = 25 \text{ }^\circ\text{C}$ ).

TOC measurements (see Table 4) confirmed the improved system performance. TOC release in the feed/strip couples was lower (about 50% in total) with respect to that obtained by using octane as organic solvent (see Table 3). The release was a little higher in the feed as already explained by the pH effect.

About the same permeability values ( $P_1 = 0.385 \text{ cm min}^{-1}$  and  $P_2 = 0.372$

$\text{cm min}^{-1}$ ) were estimated for the 1<sup>st</sup> and the 2<sup>nd</sup> couple, showing a quite stable SLM. Then, *n*-decane as the organic solvent was better than octane, since it is a better solvent for maintaining the carrier in the LM phase as confirmed by the lower TOC values in the aqueous phases. The poor diminution of permeability can be ascribed to the progressive release of the carrier into the aqueous phase, thus decreasing its concentration in the LM phase.

The observation of the lower LM release from the membrane phase to the adjacent aqueous phase's results in improved system performances, as it was confirmed by the permeability values, and strictly relates to the system stability. The limitation/avoidance of this release, which is the main cause of system destabilization, is the key step in view of applying LM based processes on large scale applications.

Considering the concentration ratio CR defined by eq. (8), it can be observed that the SLM system utilized in the present work, operated in semi-continuous mode, permitted to obtain a treated strip 114 times more concentrated than the treated feed (99.14 vs.  $0.867 \text{ mg L}^{-1}$ ). On the basis of this it can be hypothesized that by operating in a continuous system, consisting of several SLM modules in series to obtain an overall contact time between the feed and strip phases of 210 minutes (which is the duration of an experiment), a final strip 114 times more concentrated than the treated feed (retentate) can be obtained. This very high enrichment ratio confirms that a well operated LM: i) permits to obtain uphill separation and concentration of the transported component, and ii) possesses the ability to separate and recovering species from diluted solutions.

### 3.3. Stability tests and perspectives to improve the LM stability

Stability tests were carried out with the best SLM system (0.5 M D2EHPA in *n*-decane). Complete Nd transport from feed to strip phase was obtained for six consecutive permeation runs despite a progressive diminution of membrane permeability was observed (see Figure 9). As previously reported, this progressive mass transport slowdown was caused by the progressive release of the LM phase (mainly the carrier) out of the pores of the support into the adjacent aqueous phases. The permeability of the SLM obtained with the 7<sup>th</sup> feed/strip couple injected in the system after 46 hours of continuous operation was about 47% than the initial one. This was the first evidence of system destabilization. After 48.5 hours (at the 150<sup>th</sup> minute of the 7<sup>th</sup> permeation run), the destabilization of the SLM system was observed. Indeed a passage of the aqueous phase from feed to strip phase, across the membrane, took place. This passage was caused by the progressive substitution of the LM phase with the aqueous solutions which creates some water channels through the membrane which influence both the flux and the selectivity. Thus the transport test was stopped, despite Nd concentration in the feed and strip phases were 27.99 and  $67.52 \text{ mg L}^{-1}$  with the SLM which was still working against Nd concentration gradient.

The obtained stability was comparable with that one obtained in our previous work [8] by studying Cu(II) transport across a traditional SLM with 30% v/v (ca. 0.9 M) D2EHPA in *n*-decane.

TOC measurements confirmed the progressive release of the LM phase into the aqueous phase (see Table 5) with values decreasing from the 1<sup>st</sup> to last couple. All the efforts to avoid and/or control this drawback of intrinsic chemical nature could shift the LM from the laboratory to industrial application.

Table 3

Total TOC release for the two feed-strip couples sequentially injected in the SLM system (feed phase:  $[\text{Nd}]_{F0} = 100 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \geq 2$ ; strip phase:  $[\text{Nd}]_{S0} = 0 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \approx 0$ ; organic phase: D2EHPA 0.1 M in octane,  $T = 25 \text{ }^\circ\text{C}$ ).

	TOC (mg)
Feed 1	0.254
Strip 1	0.048
Feed 2	0.160
Strip 2	0.027

Table 4

Total TOC release for the two feed-strip couples sequentially injected in the SLM system (feed phase:  $[\text{Nd}]_{F0} = 100 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \geq 2$ ; strip phase:  $[\text{Nd}]_{S0} = 0 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \approx 0$ ; organic phase: D2EHPA 0.5 M in *n*-decane,  $T = 25 \text{ }^\circ\text{C}$ ).

	TOC (mg)
Feed 1	0.122
Strip 1	0.063
Feed 2	0.053
Strip 2	0.019

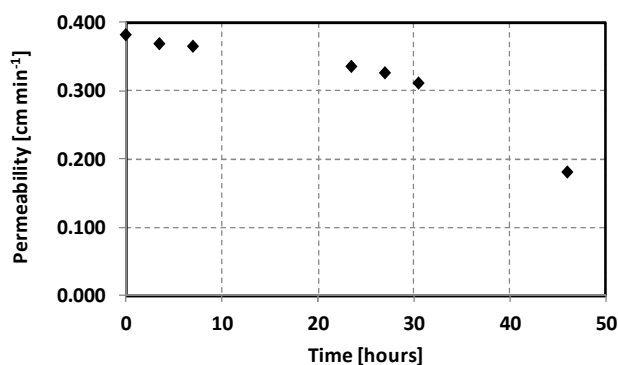


Fig. 9. SLM permeability versus time for seven feed-strip couples sequentially injected in the SLM system till to system destabilization (feed phase:  $[\text{Nd}]_{\text{f}0} = 100 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \geq 2$ ; strip phase:  $[\text{Nd}]_{\text{s}0} = 0 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \approx 0$ ; organic phase: D2EHPA 0.5 M in n-decane,  $T = 25 \text{ }^\circ\text{C}$ ).

Table 5

TOC release for the seven feed-strip couples sequentially injected in the SLM system (feed phase:  $[\text{Nd}]_{\text{f}0} = 100 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \geq 2$ ; strip phase:  $[\text{Nd}]_{\text{s}0} = 0 \text{ mg L}^{-1}$ ,  $V = 75 \text{ mL}$ ,  $\text{pH} \approx 0$ ; organic phase: D2EHPA 0.5 M in n-decane,  $T = 25 \text{ }^\circ\text{C}$ ).

	TOC (mg)	
	Feed	Strip
1 <sup>st</sup> couple	0.116	0.072
2 <sup>nd</sup> couple	0.054	0.033
3 <sup>rd</sup> couple	0.042	0.021
4 <sup>th</sup> couple	0.035	0.011
5 <sup>th</sup> couple	0.026	0.007
6 <sup>th</sup> couple	0.020	0.009
7 <sup>th</sup> couple	0.023	0.005

#### 4. Literature survey on methods to improve system stability

Despite the encouraging results obtained by using SLMs in the separation and recovery of different solutes from aqueous media, the low system stability hinders the large scale application of SLMs [27, 28]. As experimentally emphasized in the present work, the main cause of SLM instability is the gradual loss of the LM phase out the pores of the support. The lost LM phase is substituted by the aqueous solutions, thus creating water tunnels influencing both the flux and the selectivity [38, 39].

Different approaches have been suggested into the pertinent literature to enhance SLM stability. A simple strategy consists in the continuous regeneration of the LM [40] by reimpregnation of SLM when system performance degrades. Rehn et al. [41], testing the use of a hollow fiber SLM to separate chiral amines produced by a biocatalytic synthesis, detected a system destabilization after 36 h of operation. To maintain the performance of the system, the hollow fiber SLM was regenerated by reimpregnation at 22–24 h intervals. The results showed that continuous regeneration of LM was efficient in restoring the SLM performance. Despite this achievement, the release of LM phase in the adjacent feed and/or strip solutions was not avoided. Thus the aqueous feed and/or strip phases were polluted with the LM phase [42].

Another approach tested for stabilizing a SLM consists in the use of the so called feed and/or strip dispersion phases [18, 43-45]. A mixture of the organic LM and feed and/or strip phase, stirred to contain uniformly dispersed organic droplets, was circulated feed and/or strip side of the SLM. Operating in this way, some organic dispersed droplets continuously renew the LM, thus promoting long term stability of the SLM. The use of this technique is limited by two main reasons: i) the volume of the liquid membrane phase is not minimized; ii) the loss of the LM phase is not blocked, and the aqueous phases are contaminated with the organic LM phase.

The stability of the SLM can be also enhanced by creating a protective layer to limit the loss of the LM phase from the pores of the membrane e.g. by interfacial polymerization or plasma polymerization surface coating [46-48]. Unfortunately the use of this approach is limited by the not strong adhesion of the layer deposited on the membrane support, giving a poor mechanical stability. Besides, the coating layer could represent an additional mass transfer resistance [42], also considering the reduction of the pore size on the membrane surface caused by surface coating. The increased mass transfer resistance could result in a lower mass transfer of SLM system [7]. Besides, the coating layer can undergo degradation when contacted with aggressive aqueous solutions.

Total or partial gelation of the LM phase to stabilize SLMs gave encouraging results [49, 50]. By using this approach a specific dispersion (gel) may fulfill the function of blocking the LM phase into the support pores, thus improving the SLM stability. In 1990, for the first time, Neplenbroek et al. [38] proposed a polyvinyl chloride gelled SLM. The results evidenced that SLM gelation effectively suppressed destabilization and did not negatively affected the permeation flux. Using this approach, Ren et al. [51] recently prepared, via gelation technique, an extraction gel membrane (EGM), in which an extraction gel layer was formed on the shell side of PVDF ultrafiltration hollow fibers. Obtained results evidenced that the proposed EGM, avoiding the loss of the carrier (D2EHPA), permitted to obtain both good permeability across the thin extraction gel layer and increased system stability. Despite these encouraging results, the reproducibility of membrane preparation and the suitability of membrane coating with a thin extraction gel layer for practical purpose have to be evaluated. Furthermore, precise control of the interface between the aqueous phases and LM is required, which is technically difficult.

The use of ionic liquids (ILs) as a LM phase could overcome the inconvenience of SLM instability thanks to their characteristics such as: i) very low volatility; ii) high viscosity ( $> 500 \text{ cP}$ ); iii) possibility of minimizing their solubility in the surrounding aqueous phases by adequately selecting their constituents (cation and anion). ILs are organic salts remaining in the liquid state under ambient temperatures [52]. The possibility of designing suitable ILs for specific separation problems has also opened up new potential applications of Supported Ionic Liquid Membranes (SILMs) [21, 22].

The high viscosity of LM could significantly slow down the permeation flux when ILs are used, because of the increased mass transport resistance. Besides, simple impregnation is inadequate to prepare a SILM. The IL phase must be forced into the membrane pores by pressure or vacuum [53]. Moreover, despite ILs are considered as “environmental friendly” because of their negligible vapor pressure, a better understanding of toxicity and potential environmental impact is needed. Various studies conducted in recent years showed a not negligible toxicity of the ILs [54-56], making their application in SILMs not very eco-friendly. In this context, the decomposition of the IL in acidic media has to be taken into account [57].

More interesting approaches to stabilize a SLM are based on the development of appropriate SLM configurations, designed to avoid/minimize the release of the LM phase in the adjacent aqueous phases. In particular, membrane contactor systems seem to be a promising approach to overcome system destabilization. In these systems the contact between the organic and the aqueous feed and strip phases is mediated by a solid membrane. Zhu and Li [58] and Kislik and Eyal [59], proposed the use of a LM system, denoted as Hybrid Liquid Membrane (HLM). In this system, the LM phase flows in a chamber limited by two solid membranes. The solid membranes, permeable to solutes, avoid the loss of the LM phase into the feed or into the strip solutions. If the membrane material is hydrophilic, it is wetted by the aqueous phases. The aqueous/organic interface is located at the membrane/LM phase surface of the porous membrane. To maintain a stable aqueous/organic interface the pressure inside the chamber is higher than that of the aqueous phases, but lower than that required to displace the aqueous phase from the pores. If the membrane material is hydrophobic, the organic LM phase wets the solid membranes and the aqueous/organic interface is located at the membrane/aqueous phase interface of the porous solid membranes. To maintain a stable interface, the pressure of the aqueous phase is higher than that inside the chamber. A significant stability enhancement was obtained by operating with the HLM configuration. Despite this important achievement, lower fluxes were obtained respect to the traditional SLM configuration, because of the higher transport resistance.

Composite membrane supports, prepared by dip-coating ion exchange layer (sulfonated poly ether ether ketone (SPEEK)) on hydrophobic porous support (e.g. PP support), possess the capacity to completely block the loss of LM phase. By using these supports in membrane contactor systems, stable operation for 75 days was achieved [60]. Despite these encouraging results, chemical degradation of the membrane supports was observed [61]. This degradation was ascribed to the wetting of the membrane with the LM

organic phase. To avoid this problem, hydrophilic supports (e.g. made in polyethersulfone (PES)) can be coated with SPEEK [62-64]. By using SPEEK/PES hydrophilic ion exchange composite membranes, the organic LM phase did not wet the porous support, thus avoiding membrane degradation. These membranes were recently tested in the selective separation of copper and nickel [65]. The results evidenced that the membrane contactor made by using the PES/SPEEK membrane supports permitted to prevent the loss of the organic LM phase. One drawback of this approach is the presence of an additional mass transfer resistance due to the nanoporous membrane supports, which require further developments to improve the membrane morphology and/or membrane module design.

A conceptually similar approach, indicated as hollow fiber non dispersive solvent extraction and stripping, was recently considered by some research groups [66-69]. In this configuration, the organic LM phase is continuously circulated across two hollow fiber modules, which operated as membrane contactors. The main limitation of this approach consists in the high volume of organic phase involved. Besides the circulation flow rate of the LM phase between the two modules strongly influences transport kinetics.

#### 4.1. From 1<sup>st</sup> to 2<sup>nd</sup> generation of Sandwich Liquid Membranes

Based on the limits of HLMs, in our previous works [2, 6, 8, 26, 35] we proposed the use of a Stagnant Sandwich Liquid Membrane (SSwLM). In this system, a stagnant (not circulating) very thin liquid film of LM phase was sandwiched between two hydrophilic membrane supports. This system was developed with the aim of: i) increasing system stability, since the two hydrophilic membrane supports should avoid the loss of the organic LM phase; ii) increasing system permeability, since the transport takes place in a thin layer of free organic phase. The SSwLM system was tested in the separation of inorganic metal ions ( $\text{Cu}^{2+}$ ) and organic species (Gemfibrozil). Obtained results, summarized in Table 6, show that the SSwLM achieved both higher flux and higher stability compared to the traditional SLM configuration.

**Table 6**  
Comparison of flux and stability between SSwLM and SLM configurations.

	Copper [8]		Gemfibrozil [3]	
	SLM	SSwLM	SLM	SSwLM
Flux ( $\text{mol m}^{-2} \text{s}^{-1}$ )	$1.18 \times 10^{-5}$	$1.52 \times 10^{-5}$	$1.05 \times 10^{-7}$	$2.39 \times 10^{-7}$
Stability* (h)	49.2	183	23.5	336

\*Stability is measured as the time to reduce 50% of the initial flux

On the basis of these results, the sandwich seems a promising LM configuration in view of large scale applications. An important drawback observed by operating with this system was the LM phase stratification of water droplets entered across the hydrophilic support. This phenomenon decreased system performance [26]. By taking advantage of the previous experience on the SSwLM and the results described in the present work, a new generation (2<sup>nd</sup> generation) of sandwich LM can be designed and tested to solve the problem of stability caused by carrier solubilization in the aqueous phase and/or carrier hydration by water. The 2<sup>nd</sup> generation of SwLM should be not stagnant but dynamic. Operating in this way, the water entered in the organic LM because of the hydration of the hydrophilic head of the carrier molecules can be easily removed.

#### 4. Conclusions

- The recovery and concentration of Nd ion from acidic media by extraction and transport across a traditional SLM has been investigated.
- L-L extraction tests were carried out to study the chemistry of the LM process.
- D2EHPA with respect to CYANEX® 272 permits to operate at lower pHs both the extraction and the stripping operations. This is an important feature in view of processing very acidic aqueous leaching solutions coming from hydrometallurgical recovery of REEs from natural minerals and/or WEEEs.
- Permeation tests across the SLM were carried out determining the best

LM phase (0.5 M D2EHPA in n-decane) in terms of membrane permeability ( $0.381 \text{ cm min}^{-1}$ ), Nd recovery (99.14%) and concentration ratio feed/strip (114).

- Despite these achievements, system destabilization was observed after 48.5 hours of continuous operation.
- The development of appropriate LM configurations (e.g. the SwLM), designed to minimize/avoid the release of the LM phase in the adjacent aqueous phases, seems to be the most promising approach in view of SLM stabilization.
- Combining the know-how on the SSwLM with the results obtained in the present work, a new generation of sandwich LM can be designed to overcome carrier hydration and solubilization.

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#### Appendix A

The very low Nd flux across the liquid membrane, at 0.1 M carrier concentration, using n-decane instead of octane, can be explained considering that solvent evaporation happened probably during the assembling of the SLM in the permeation module. Octane is more volatile than n-decane ( $t_{\text{cb}} = 125.52 \text{ }^\circ\text{C}$  vs.  $174.1 \text{ }^\circ\text{C}$ ), and this difference can have a significant effect on “real” carrier concentration in the LM phase. To investigate on this aspect, evaporation tests were performed by impregnating twin pieces of PP support with 0.1 M D2EHPA in octane and 0.1 M D2EHPA in decane, and leaving them to evaporate at  $25^\circ\text{C}$ . Obtained results, reported in Table A1, evidenced significant higher evaporation rate by using octane. This faster evaporation can affect also system stability. Indeed, a lower solvent amount in the LM phase increases carrier solubilization in the aqueous phase because of the lower solvating power of the LM phase.

**Table A1**  
Percentage of LM phase, impregnated in the PP support, evaporated vs. the time during the evaporation tests (0.1 M D2EHPA concentration in octane and in n-decane).

Time (min)	Evaporated LM phase (%)	
	Octane	Decane
5	16.97	2.13
10	34.32	4.74
20	59.80	8.12
30	79.08	11.01

Consequently, the “real” initial carrier concentration in the permeation test by using octane was higher than the nominal 0.1 M. From this observation, permeation tests using n-decane as the solvent were carried out at 0.5 M D2EHPA concentration.

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