A comparative study of the selective transport of Zn/Cd and Pt/Pd couples with activated composite membranes and hybrid membranes

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Abstract

Supported Liquid Membranes (SLMs) have demonstrated all along the years very high selectivity in facilitated transport of metal ions, however, they have some well known limitations, such as the gradual loss of the organic phase to the aqueous solutions. This paper describes two different types of novel membranes developed for the general purpose of separating and concentrating metal ions of interest in order to improve SLM physical and chemical characteristics. Both hybrid (organic-inorganic) membranes and activated composite membranes have been tested for the selective transport of Zn/Cd and Pt/Pd mixtures. For this purpose, different carriers have been used: 2-ethylhexyldithiophosphoric acid and 2-ethylhexylphosporic acid for the separation of Zn and Cd whereas Aliquat 336 for Pt/Pd mixtures. The choice of these metal couples is related to environmental detoxification and catalyst recovery respectively.

Keywords: Selective transport; Hybrid membranes; Activated composite membranes; Zn/Cd; Pt/Pd

1. Introduction

Selective metal ions recovery has attracted great interest of scientist and technologists in many different fields. For instance, it is necessary to recycle toxic metals ions such as zinc and cadmium ions from water streams of galvanic coating processes [1]. Moreover, Platinum Group Metals (PGM) based catalysts must be recovered due their high cost [2].

Among the existing separation technologies, Supported Liquid Membranes (SLMs) have demonstrated very high selectivity in facilitated transport of metal ions when they are found in low concentrations [3,4]. In SLMs, an organic liquid containing a solvent extraction reagent is held by capillary forces in the pores of a microporous film or support. This strategy allows the incorporation of expensive carriers due to the high performance of the membrane separation even when a low amount of these substances is incorporated into the membrane. Nevertheless, the main shortcoming of SLMs is the gradual loss of the organic phase to the aqueous feed and stripping solutions due to emulsification at the membrane/aqueous interfaces, and to the osmotic pressure difference across the membrane, among other causes [4]. Along the years, many attempts have been done to overcome SLMs limitations [5,6]. In this sense, two different types of novel membranes have been developed in our laboratory for the general purpose of separate and concentrate metal ions of interest. The main objective was to succeed in improving SLMs physical and chemical properties and overall performance.

On the one hand, Activated Composite Membranes (ACMs) consisting of a multilayer structure that includes a non-woven support, a macroporous layer of polysulfone and a thin dense layer of polyamide were prepared, it is to say, a common structure of membranes used for reverse osmosis [7]. Likewise to SLMs, a selective carrier agent was incorporated inside the polyamide layer of ACMs [8-10]. Usually, the carrier agent is selected from the well-known liquid-liquid extractants [11] and liquid membrane carriers what allows to take profit of SLMs previous experience [4,12,13]. Up to now, ACMs have been tested for the selective recovery of a wide range of cations [14-16] (including toxic ones such as mercury and rare earths) and aminoacids [17]. Depending on the species of interest to be separated, different carrier agents have been previously tested. In this case, di-(2-ethylhexyl)phosphoric acid (D2EHPA) and di-(2-ethylhexyl)dithiophosphoric acid (D2EHDTPA) were used for the selective separation of zinc and cadmium ions, whereas tricaprilylmethylammonium chloride (also known as Aliquat 336) was used in the case of platinum and palladium ions recovery in the ACM systems.

On the other hand, by using the same extracting agents in a cellulose triacetate matrix, new Hybrid Membranes (HMs) were also developed. These membranes are based in plasticized polymeric membranes [18,19] but modified by a sol–gel route that leads to the incorporation of inorganic moieties of polysiloxanes [20]. This strategy was firstly thought as a way to increase mechanical

strength of PIMs but, as it has been already demonstrated, the stability and transport properties of HMs are also enhanced by the presence of the inorganic material [21].

In this work we try to evaluate and compare the transport efficiency and the selectivity, among other characteristic parameters of both types of membranes considering the mentioned applications, the zinc recovery and the PGM ions separation.

2. Experimental

2.1. Reagents and solutions

Reagents used for the ACMs preparation were Ultrason S polysulfone from BASF (Germany), sodium dodecilsulfate, piperazine or 1,3-phenylenediamine, and benzenetricarbonyl trichloride. For HMs preparation, tetraethyl orthosilicate (TEOS) and dichlorodimethylsilane (DCDMS) from Merck (Germany) were used to obtain the silanes mixture. The plasticizers tested were 2-nitrophenyl octyl ether (NPOE) and Tris(2-butoxyethyl)phosphate (TBEP). Cellulose triacetate (CTA) was used to provide the polymeric mechanical strength. The carriers, D2EHPA, D2EHDTPA and Aliquat 336 were used as carriers for both types of membranes. Since D2EHDTPA is not a commercial compound, it was synthesized by the methodology described elsewhere [22].

Platinum (IV), palladium (II), zinc (II) and cadmium (II) 1000 mg L^{-1} stock solution in 0.1M HCl were prepared from platinum (IV) chloride, palladium (II) chloride, zinc (II) acetate hydrate (all from Merck, Germany), and cadmium (II) sulfate hydrate (Panreac, Spain), respectively. Also, zinc chloride, boric acid, sodium saccharine and sodium dodecyl sulfate were used to prepare a synthetic solution similar to that of exhausted galvanic coating liqueurs.

All the reagents were from Sigma-Aldrich (Germany) except the detailed ones; all them were analytical grade and used as received.

2.2. Activated Composite Membrane preparation

The preparation of ACMs was performed following a multi step route previously described [23]. Polysulfone (Ultrason S from BASF) casting solution was prepared by dissolving the polymer in dimethylformamide (DMF) by vigorous stirring. Then, a film was prepared onto a polyester non-woven support by phase inversion technique. The thin top layer of polyamide containing the carrier (DEHPA, D2EHDTPA or Aliquat 336) in a suitable concentration was obtained by interfacial polymerization of the diamine (piperazine or 1,3-phenylenediamine) and benzenetricarbonyl

trichloride both dissolved in water and hexane respectively [7,9]. The excess of solution was rinsed and finally dried in an oven at 60ºC during 1h.

2.3. Hybrid membranes preparation

To obtain the HMs casting solution, a dissolution was prepared by mixing together CTA, plasticizers NPOE and TBEP, and the suitable carrier [24] in chloroform. When the solution was homogeneous, a silanes mixture was added and, afterwards, everything was poured into a Petri dish to carry out the solvent evaporation [25,26]. This silanes mixture was prepared by mixing TEOS and DCDMS by following a multistage procedure developed in our laboratory [21,24]. The membranes were cured in an oven at 80 ºC during 20 h. The same procedure was followed for Polymeric Inclusion Membranes (PIMs) preparation but without the silanes mixture addition.

2.4. Carrier content

The amount of carrier in each HM was the entire carrier amount contained in the casting solution which was retained in the final membrane after solvent evaporation. Conversely, for ACMs it was necessary to determine the real carrier content after the membrane preparation, since only a part of the carrier used is retained during the interfacial polymerization procedure. For ACMs containing organophosphoric acids a calibration curve of phosphorous content was done by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) [27]. Contrary, for Aliquat 336 concentration determination, a weighted amount of ACMs was treated overnight with an extracting solution, consisting on a methanolic-aqueous solution of NaOH 0.001M. Then, the extracted chloride ion was quantified by using an ion selective electrode (ISE). The chloride anion content is directly related to the Aliquat 336 content on the membrane (the ratio between chloride anion and tricaprilylmethylammonium cation in the commercial salt is 1:1).

2.5 Membrane characterization

Synthesized membranes were characterised by some techniques to better understand their structure and morphology. In this sense, the inorganic part of HMs structure was analysed by Nuclear Magnetic Resonance (NMR) with a Bruker ASX300 300MHz high power dipolar decoupling-magic angle spinning (^{29}S HPDEC MAS NMR).

Moreover, Confocal Laser Microscopy (CLM) was used to identify both organic and inorganic parts of HMs. For that purpose a Leica TCS SP2 AOBS microscope was used. Scanning rate was 400 Hz and all the measurements were carried out with an argon laser ($\lambda = 488$ nm). Firstly, membrane samples were treated with a dye (acridine orange) which can adhere to the membrane matrix and which gives a fluorescent signal (between 505 and 568 nm) when the sample is irradiated. Contrary, the inorganic was observed by laser light reflection (between 479 and 498 nm) [28]. Both measures can be done simultaneously identifying and locating the different membrane components.

Besides, ACMs morphology was characterized by Scanning Electron Microscopy (SEM) images obtained with a Jeol JSM-840 instrument. Samples were frozen with liquid N_2 before cutting in order to avoid undesired deformations in the case of the cross-section images.

2.6. Transport experiments

Transport experiments were carried out by using a permeation cell with two compartments of 200 mL, which are separated by the membrane with an area of 12 cm^2 [8]. So, metal ions of interest diffused from a feed sodium chloride solution to a receiving phase which composition was varied depending on the studied system. Feed and stripping ionic strengths were equilibrated. However, a more complex artificial solution, similar to that used in galvanic coating industry, was also tested.

For sampling, 1 mL of feed and stripping solutions were withdrawn periodically and analysed by ICP-AES technique. Metal ion extraction (E) and recovery (R) percentages were calculated by considering the instantaneous ion concentration in feed ($C_{t,f}$) and stripping ($C_{t,s}$), as well as the initial feed concentration ($C_{0,f}$) as it is shown in Eqs. (1) and (2).

$$\%E = 100 \cdot \left(\frac{C_{0,f} - C_{t,f}}{C_{0,f}} \right) \qquad (1)$$

$$\%R = 100 \cdot \left(\frac{C_{t,s}}{C_{0,f}} \right) \qquad (2)$$

In order to consider the efficiency of metal selective separation, the ratio (r) of metal ions concentration in the feed phase ($C_{m1,f}$ and $C_{m2,f}$) was followed simultaneously along the time Eq. (3).

$$r = \frac{C_{m1,f}}{C_{m2,f}} \qquad (3)$$

3. Results

3.1. Membrane characterization

Along the years, different types of polyamides have been tested in our research group. Initially, 1,3-phenylenediamine, a very well-know precursor for preparing aromatic polyamides for reverse osmosis membranes, was used for ACM preparation (i.e. used in Zn(II) transport experiments [8,9]). However, for the transport of oxidant species such as Fe(III), Cr(VI) and Pt(IV) 1,3-phenylenediamine is not a suitable precursor for the polyamide layer because its oxidation induces the loss of membrane transport properties [9,10,29]. As a consequence, for this work piperazine was chosen to prepare ACMs for Pt(IV) recovery, since this heterocyclic amine has the advantage of being more stable towards oxidation [30]. The typical cross section of an Activated Composite Membrane containing Aliquat 336 observed by Scanning Electron Microscopy is shown in Fig. 1. Briefly, two different zones can be identified: on the bottom (Fig. 1(c)) there is an asymmetric microporous support containing macrovoids that corresponds to the polysulfone layer and, on the top, a thin layer of polyamide can be observed (more detailed in Fig. 1(a) and (b)). Note that although the SEM images in Fig. 1 correspond to an ACM prepared with piperazine based polyamide and Aliquat 336 as carrier agent, it is very similar to previous membranes obtained with 1,3-phenylendiamine and D2EHDTPA [31]. Furthermore, the thickness range was also comprised between 70 and 100 μm (without considering the non-woven support).
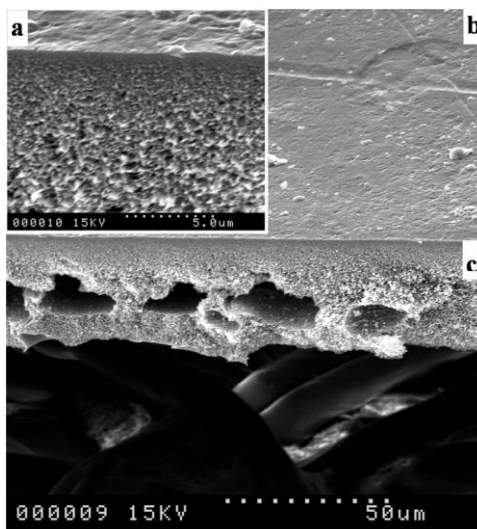
Figure 1: Different parts of an Aliquat 336-ACM can be observed by SEM: (a) interface between thin polyamide layer (made of piperazine) and porous polysulfone layer (prepared by phase inversion of a 15% casting solution) in the cross-section image, (b) thin polyamide layer surface image, and (c) polysulfone layer containing macrovoids.

On the other hand, since hybrid membranes can be considered as a plasticized polymeric membranes modified by the addition of an inorganic moiety, it is relevant to evaluate the effect of the variation of membrane components in the membrane structure. With this in mind, different types of HMs were prepared by varying the proportion of reagents in order to optimize the membrane formulation. Some membrane compositions are listed in Table 1 which also includes the carrier content.

Table 1: Weight percentages of HMs components calculated for a basis of 0.04 g of CTA, except for membrane HM-G (0.2g of CTA).

Membrane	%CTA	% NPOE	% TBEP	% silanes	carrier	% carrier	carrier (mg·cm^{-2})
HM-blank	36.0	18.0	16.2	29.7	none	0	0
HM-A	20.7	20.7	0	17.1	D2EHPA	41.5	2.8
HM-B	12.8	12.8	0	10.5	D2EHPA	63.9	7.1
HM-C	20.9	10.5	9.4	17.3	D2EHPA	41.9	2.8
HM-D	12.9	6.4	5.8	10.6	D2EHPA	64.3	7.1
HM-E	7.4	3.7	3.3	6.1	D2EHDTPA	79.5	15.2
HM-F	26.5	13.2	11.9	21.9	Aliquat 336	26.5	1.4
HM-G	18.2	9.5	0	1.0	D2EHPA	71.4	-

It is important to consider that, due to the different interactions of membrane components inside the final matrix, only some right combinations of components do form suitable membranes. For instance, either an excess or a shortage of plasticizers give as a result brittle or shrinking membranes, respectively, which can not be used as desired.

For all the suitable membranes, although their composition was quite different, the membrane thickness was always between 90-100 mμ because the CTA amount was kept constant, at 0.02g in all cases.

As stated before, laser confocal microscopy (LCM) allows us to identify organic and inorganic matrices that are present together in a composite material. As it can be seen in Fig. 2 (right images), although the membrane surface is properly dyed, the fluorescent dye only penetrates partially into the membrane matrix (less than 10 microns depth). Anyway, by this technique it is possible to observe the dense film of CTA in both HM and PIM. Simple examination demonstrates that both membranes have different morphologies: the CTA layer of PIM looks more homogeneous while the HM surface shows

a kind of porosity. At the same time, the inorganic part observed by light reflection of HMs (Fig. 2, left images) coincides with the gaps of the organic part, so it is possible to affirm that HMs are also dense membranes with separated domains. Moreover, it is important to notice that siloxanes derivatives are only located close to the membrane surface which was in contact with air during the solvent evaporation. This side is also the side of membrane which is in contact with the feed solution in transport experiments and, therefore, some interactions are expected.

In order to complete the information drawn from LCM observation, ^{29}Si NMR was used to characterise the coordination of the silicon atoms [32,33]. ^{29}Si NMR spectra showing signals in the -20 to -120 ppm range are represented in Fig. 3. As before [24**Error! No s'ha definit el marcador.**], it is possible to distinguish different coordination environments such as $[Si(OH)_{4-n}O_n]$ and $[O-Si(CH_2)_2-O]$ which clearly reveal that the inorganic part of HMs is not composed by SiO_2 which might have been produced by a complete hydrolysis of TEOS. The Q_3 signals corresponding to a $[Si(OH)_1O_3]$ coordination can be observed in some cases which indicate the presence of -OH groups. This free -OH groups might interact with the other components of the membrane by hydrogen bonding forces.

Summarizing, it is possible to affirm that the addition of inorganic components causes the formation of asymmetric membranes which may behave in a different way if compared with corresponding PIMs. The presence of the inorganic solid can affect the membrane transport in different ways. One the one hand, this presence can increase the free volume of the membrane resulting in an asymmetric membrane with higher porosity or, at least, a different structure. On the other hand, the OH groups corresponding to Q_3 units might provide the formation of hydrogen bonds between the inorganic and the organic components.
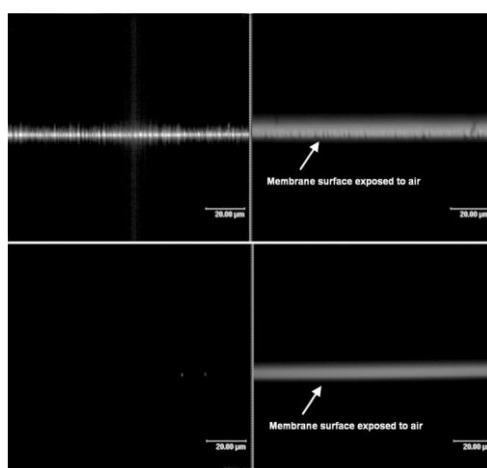
Figure 2: Confocal microscopy images of both HM-D (top) and PIM (bottom). Reflection images (left) and fluorescence images (right) permit to identify and locate the inorganic moieties in HM.
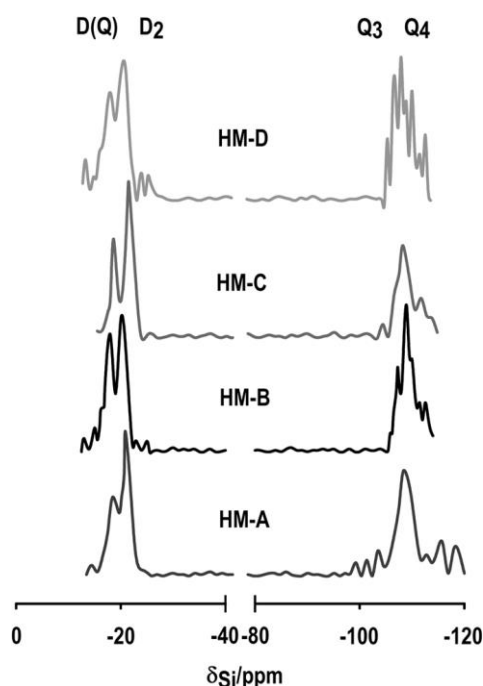
Figure 3: ^{29}Si NMR spectra corroborating the presence of the two types of silicon atoms into the hybrid membranes HM-A to HM-D.

## 3.2. Selective transport evaluation

The main purpose of the developed membranes is the facilitated transport of metal ions. The compositions of both feed and stripping solutions for each transport experiment are shown in Table 2. First, the results of zinc facilitated transport corresponding to two hybrid membranes (HM-A and HM-D) with very different amount of extracting agent are illustrated in Fig. 4. It can be seen that the higher the carrier amount the faster the transport and, consequently, higher recovery percentage after eight hours, despite the fact that they are not proportional. So, a high increase in carrier content does not improve transport so much while it could increase the membrane cost. To explain that fact, the saturation of the complexing sites which are close to the feed solution is predicted [8,14].

Fontàs et al. have recently stated a possible explanation for transport differences between with PIMs and SLMs postulating that the intern structure of PIMs varies in function of the transport agent concentration and that a carrier concentration threshold exists at which both types of membranes behave in the same way [19]. Taking into account that HMs are comparable to PIMs, it is possible to assume a similar situation and, therefore, a similar transport mechanism. However, our investigations prove that the morphology of HMs depends on its composition and they can only be prepared in a quite narrow range of formulations. Probably, the low increase in transport efficiency when using a

higher carrier concentration is related to the fact that the carrier content inside the membrane is already too high, and it is no longer the transport controlling factor. This fact implies that it is still necessary to find a minimal carrier concentration which provides acceptable transport efficiency and appropriate mechanical stability.

Table 2. Experimental conditions of selective transport experiments.

| Membrane type	Carrier	Feed composition	Stripping composition	Figure
HM-A	D2EHPA	50 ppm Zn, NaCl 0.5 M	HCl 0.5 M	4
HM-D	D2EHPA	50 ppm Zn, NaCl 0.5 M	HCl 0.5 M	4
ACM [8]	D2EHDTPA	50 ppm Zn, 86 ppm Cd, NaCl 2.2 M	HCl 2.2 M	5
HM-D [21]	D2EHPA	50 ppm Zn, 86 ppm Cd, NaCl 0.5 M	HCl 0.5 M	5
ACM	Aliquat 336	10 ppm Pt, 10 ppm Pd, NaCl 0.5 M	NaClO$_4$ 0.5 M	6
HM-F	Aliquat 336	10 ppm Pt, 10 ppm Pd, NaCl 0.5 M	NaClO$_4$ 0.5 M	6
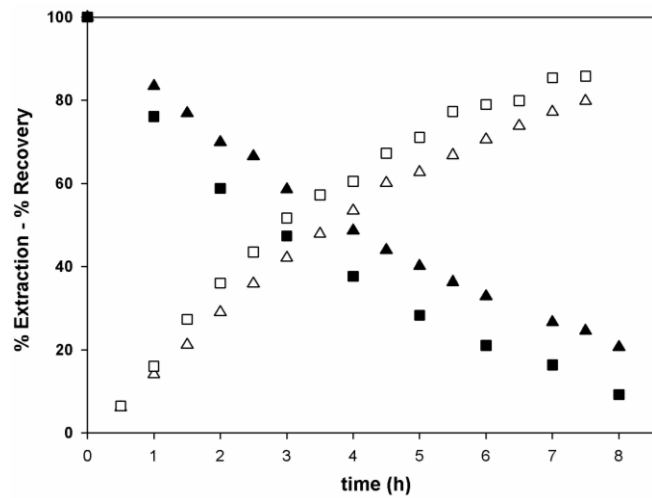
Figure 4: Zn^{2+} transport plots for the extraction and recovery of membranes HM-A and HM-D. The feed phase consisted of 50 ppm Zn^{2+} in 0.5 M NaCl and the stripping phase was 0.5 M HCl. (▲) %Zn extraction HM-A, (■) %Zn extraction HM-D, (△) %Zn recovery HM-A and (□) %Zn recovery HM-D.

Besides, in order to evaluate the degree of separation that can be achieved by the developed membranes it is possible to measure the variation of the metal ions ratio in the feed solution during a separation experiment. Considering the Zn/Cd system for the most performing membranes of both HMs and ACMs types, only little separation of Zn can be obtained when both metal ions are present in the feed initial solution at the same concentration (Fig. 5). Contrary, as it can be seen in the same

figure, the higher the difference between the species, the higher is the metal ion ratio that can be reached. Thus, for an initial ratio of 5:1 it is possible to get a 14:1 final solution. Again, a possible explanation could be the saturation of the active sites of the carrier which are close to the aqueous phase by Cd ions which are found in a relative too high concentration (Cd has a higher complexing equilibrium constant). On the opposite, with a lower concentration of cadmium, ions are not highly retained and they do preferably cross the membrane to the stripping phase liberating some active sites, increasing the separation factor.
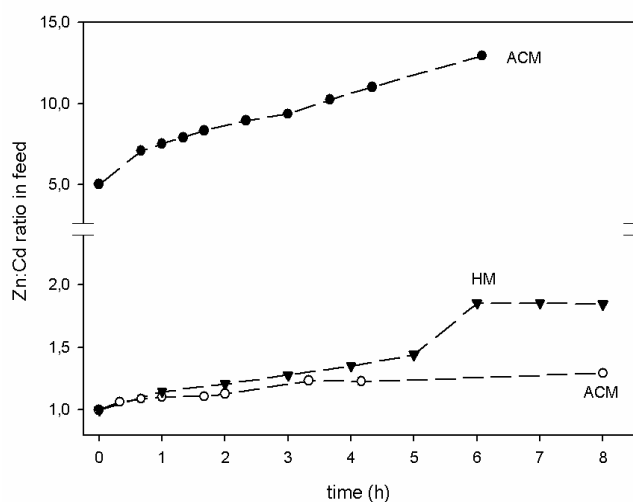
Figure 5: Evolution of Zn:Cd ratio in feed solution along the time for ACM and HM. For experimental conditions see Table 2.
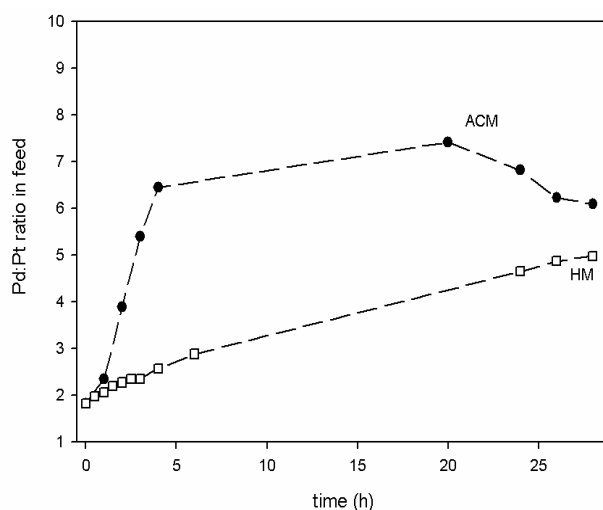
Figure 6: Evolution of Pd:Pt ratio in feed solution along the time for both ACMs and HMs. For experimental conditions see Table 2.

Different results can be found for ACMs and HMs when the system Pt/Pd is considered (Fig. 6). In this case, ACMs do purify Pd in the feed phase because Pt ions are transported rapidly to the stripping. Nevertheless, the separation efficiency is reduced along the time because Pd ions are also transported. So, for a practical application of this kind of membranes the separation system designed would be stopped at certain time when separation would reach the maximum separation performance. Conversely, for HMs, a constant rising in the metal ratio is found. This different behaviour can not be easily explained since the same extracting agent (Aliquat 336) is used for both ACMs and HMs. As before [34] the different membrane structure might be the main reason for these differences.

4. Conclusions

Summarizing, new developed membranes capable to separate metal ions with different efficiency have been prepared. From the obtained results, it is possible to say that the presented hybrid and ACMs can perform separations during several hours without losing their transport properties, which can be an advantage compared with traditional SLMs. A close relation between membrane morphology, membrane composition and transport efficiency is considered. Moreover, the following trends can be foreseen: transport selectivity depends on metal ion–carrier stability constants whereas separation performance mainly depends on metal ion initial ratio.

Acknowledgments

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