Original article

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Elaboration and characterization of multilayer polymeric membranes: effect of the chemical nature of polymers

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Abstract: The transport phenomena across polymeric membrane may be enhanced by applying various strengths inside or outside the system. Recently, polymer inclusion membrane (PIM) has been considered one of the most popular methods that acts as a sink for the contaminant and immobilizes it. In the literature, there is no report about how to achieve the synthesis of multi-layer PIMs. In this paper, an improvement of a novel category of membrane without carrier for performing ion separation is reported. Different membranes were elaborated from binary mixtures of polymers, cellulose triacetate (CTA), poly-methyl methacrylate (PMMA) and polyvinyl chloride (PVC) using 2-nitrophenyl octyle-ether (NPOE) as plasticizer and carrier in the same time, in order to increase specific interactions between the different polymers. The membranes (Polymer 1– NPOE – Polymer 2) were synthesized by phase inversion method modified by changing the procedure of a plasticizer/carrier addition and characterized by FTIR, TGA, SEM, zeta potential and contact angle. The CTA-based membranes exhibited well-defined pores partially filled with the second polymer and NPOE. Overall, our results

showed that the addition of NPOE resulted in homogeneous membranes with modified physical properties, such as thickness, and hydrophobicity. A study of transport of Pb(II) using the synthesized membranes was studied. Dialysis experiments of lead ions across a polymeric membrane have shown that (CTA + NPOE + PMMA) and (PMMA + NPOE + PVC) membranes proved a good performance in one stage by fixing 12.15 and 25.31% of lead, respectively, without any additionally added carrier and acids. These results confirm the affinity between a basic polymer (poly-methyl methacrylate) and the metallic ion (Pb^{2+}).

Keywords: heavy metals; multi-layer membranes; polymers; water purification.

1 Introduction

In recent years, there has been a substantial increase in the amount of industrial waste because of the thousands of different substances fashioned in the world which, in large part, have a damaging impact on the environment and public health. Heavy metals such as mercury, chromium, cadmium and lead are among the most dangerous pollutants from industrial waste, particularly the relative hazard of wastewater and water contamination.

Consequently, the past decade has seen a rapid development of new sample preparation techniques based on miniaturization of traditional methods such as liquid–liquid extraction and solid–liquid extraction. With a suitable combination of ring size, character and placement of donor atoms, macrocyclic multi-dentate ligands exhibit good extraction selectivity for preferred metallic ions [1–6]. Recently, a novel type of polymeric membranes called polymer inclusion membranes (PIMs) has been developed which provides metal ion transport with high selectivity, as well as easy setup and operation [7–17]. The selective separation of these membranes is accomplished commonly by the presence of selective compounds, called carriers, in

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the membrane phase. The carriers are responsible to facilitate the transport of the target component across the selective membrane. The carrier can be a complexing agent, a chelating agent or an ion exchanger. Transport of metallic ions obeys to a facilitated co-transport in the case of solvating-type carrier and counter-transport in the case of acid-type carrier.

Four types of PIM can be distinguished: (i) PIM containing polymer, plasticizer and a neutral carrier (active and selective co-transport) [18, 19], (ii) PIM consisting of a polymer, a plasticizer and an acid carrier (active and selective counter-transport) [20, 21], (iii) PIM synthesized using polymer, polyelectrolyte (charged) and plasticizer (without carrier) (passive and non-selective transport) [22, 23], (iv) PIM containing a mixture of polymers and a plasticizer which has high polarity and charges [24]. In this case, the plasticizer plays the role of the carrier by developing electrostatic and Van Der Waals interactions.

PIMs are useful tools for the liquid-phase extraction of various chemical species, including metal ions [25–29]. Polymeric membranes dominate the membrane separation industry market because they are very competitive in performance and cost [30–32]. Several polymers are available, but the selection of membrane polymer is not a trivial task. A polymer has to have appropriate characteristics for the intended application [33]. The polymer has to endure the cleaning conditions. It has to be compatible with selected membrane manufacture technology. The polymer has to be an appropriate membrane former in terms of chain rigidity, chain interactions, stereo-regularity, and polarity of its functional groups [34]. The most commonly used base polymer for PIM is cellulose triacetate (CTA), which has good film-forming properties. CTA is a polar polymer with a number of acetyl and hydroxyl moieties that are capable of forming highly orientated hydrogen bonding, giving CTA a crystalline structure [29]. However, CTA decomposes when used in strongly acidic or basic solutions. The concern of the long-term stability caused by CTA hydrolysis limits the practical application of PIM with CTA as the base polymer [35]. To resolve this problem, a typical approach is to use other base polymers for PIM [36]. Polymethyl methacrylate (PMMA) is an economical alternative to other polymers when flexural strength, transparency and polishability are more important than chemical resistance and heat resistance. It is often preferred because of its moderate properties, easy handling and processing and low cost. Poly(vinyl chloride) (PVC) exhibits time-dependent mechanical behaviour, as evidenced by rate-dependent elastic moduli and yield strength. Moreover, the PVC-based membranes are very stable in aggressive solutions (like acidic and basic solutions), and possess a remarkable mechanical strength

and flexibility. PVC is used as a polymer backbone in membranes because of its strength, inertness and compatibility with a variety of plasticizers [37]. The plasticizers used in the preparation of the polymeric membrane must be compatible with the polymer and also must be miscible with the solvent used in the membrane preparation. The plasticizers with high lipophilicity are preferred. 2-Nitrophenyl octyl ether (NPOE) is an organic solvent, which is mainly used as a plasticizer and a charge transferring liquid that can be used in electrochemical devices. It shows low solubility in water, low vapour pressure and is less toxic as compared to other organic solvents. NPOE can be used as a plasticizer or carrier in a polymeric inclusion membrane (PIM) that enhances the transport of metallic ions in the aqueous solution [38, 39].

In this paper, we have synthesized a new kind of PIM membranes considerably cheaper without any additionally added carrier and acids using binary mixtures of polymers (cellulose triacetate (CTA), polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC)) plasticized by 2-Nitrophenyl octyle-ether (NPOE). All synthesized membranes were characterized using several techniques, namely Fourier transform infrared (FTIR) spectroscopy, Thermogravimetric analysis (TGA), scanning electron microscopy (SEM), zeta potential, and contact angle. A comparative study of transport efficiency across synthesized membranes containing the same plasticizer (NPOE) in chloroform has been made.

2 Materials and methods

2.1 Chemicals

Cellulose triacetate (CTA pellets $M_w = 72000\text{--}74000$), polymethyl methacrylate (PMMA powder $M_w = 15000$) and polyvinyl chloride (PVC pellets $M_w = 43000$) were analytical grade reagents purchased from Fluka. 2-Nitrophenyl octylether (NPOE) (GC $\geq 99\%$) were product of Merck Company. All reagents were used as received without any supplementary purification. Aqueous solutions were prepared by dissolving the different reagents in deionized water (resistivity: $1\text{ M}\Omega\text{ cm}$).

2.2 Analysis

Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin-Elmer spectrometer (Spectrum One). All spectra were recorded at a resolution of 2 cm^{-1} and total of 32 scans were accumulated for each spectrum along with the background. TGA experiments were performed with a TA instrument thermogravimeter (Q500) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Scanning electron microscope (SEM) descriptions of the PIMs were obtained using a JOEL JSM 6360-LV microscope after gold coating and operating at 10 kV .

Membrane zeta potential was determined from streaming current measurements using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria) following the experimental protocol described elsewhere [40]. All electrokinetic measurements were performed in 1 mM KCl solutions. Contact angle measurements (sessile drop technique) were performed using a commercial contact angle device (DIGIDROP GBX DS model, GBX Company, France). Contact angles were determined from the average of at least 12 different measurements performed at different locations on the clean and dry membrane according to the experimental procedure described by Diagne et al. [41]. The surface tension components for the synthesized membranes can be determined through contact angle measurements of deionized water, formamide, and diiodomethane using the method proposed by Van Oss [42].

2.3 Membrane preparation

Membrane formation by immersion precipitation yield different morphologies depending on the choice of the components and their concentrations in polymer solution, temperature and plasticizer nature. During the development of multi-layer membranes, the plasticizer that improves the membrane mechanical properties is used in a mixture with different polymers or spread on the first film. These two methods affect the homogeneity, elasticity and mechanical characteristics of the elaborated membranes. For a two-layer membrane, the first case involves mixing the plasticizer with the second polymer before spreading the mixture on the first thin film containing only the first polymer. The second possibility is to spread the plasticizer very carefully on the first film. Then the second solution containing the second polymer is poured onto the first film. PIMs were prepared using the phase inversion method described by Sugiura et al. [43], but modified by changing the procedure of a plasticizer addition and using the rapid volatilization of solvent. Briefly, for example in the first case, 0.2 g of the first polymer was dissolved in 10 mL of chloroform (CHCl_3) and stirred for 4 h. The homogeneous solution was transferred in a circular glass container and let for a slow solvent evaporation during 24 h. After that, 0.2 g of the second polymer was dissolved in 10 mL of chloroform and stirred also for 4 h. Then 0.2 mL of 2-nitrophenyl octyle-ether (NPOE) was added and maintained for 2 h under vigorous stirring. The miscible solution (second polymer/NPOE) was poured onto the first film. The resulting membrane was extracted after evaporation of solvent by addition of water and dried at 40 °C.

2.4 Dialysis experiments

Transport experiments were carried out in a permeation cell made of Teflon in which the membrane film was tightly clamped between two cell compartments. Both the source and receiving aqueous phases (100 mL each) were stirred at 800 rpm using a multi-point magnetic stirrer (Wise-Stir MS-MP8 Model, made by DAIHAN Scientific Co. Ltd.). The metal concentrations were determined by samplings at different time interval aliquots (0.5 mL) from both the feed and strip solutions and analyzed using the atomic absorption spectroscopy technique (AAS) Perkin-Elmer Analyst 700 model. The membrane active surface S is a constant (9.61 cm^2). Three independent experiments were realized to determine the lead concentration. The experimental standard deviation was determined to be $\pm 5\%$.

3 Results and discussion

3.1 Characterization by FTIR

CTA, PMMA and PVC polymers, NPOE plasticizer and all synthesized membranes were characterized by FTIR using Perkin-Elmer spectrophotometer (Spectrum One model).

Figures 2 and 3 illustrate global FTIR spectra of pure components and synthesized membranes, respectively.

The FTIR spectrum of PVC showed a band at 622 cm^{-1} characterizing the presence of C–Cl bands. The presence of free carbonyl groups of the ester function ($\text{C}=\text{O}$) was evidenced by the existence of a pick located at around 1731 cm^{-1} for PMMA and 1729 cm^{-1} for CTA. The CTA spectrum exhibited another band at around 1758 cm^{-1} attributed to specific interactions of hydrogen bonding type between the carbonyl groups ($\text{C}=\text{O}$) of CTA and the hydroxyl ones ($\text{O}-\text{H}$) of the same polymer [44–46]. The presence of hydroxyl groups (OH) was confirmed by the band at 3445 cm^{-1} while acetate groups (COO^-) appeared at 1579 cm^{-1} and 1602 cm^{-1} in CTA. From Figure 1, we also noted that the CTA absorbed at around 1270 cm^{-1} and 1040 cm^{-1} characterizing the asymmetric and symmetric elongation vibrations of ($\text{C}-\text{O}-\text{C}$) groups. These bands appeared at 1242 cm^{-1} and 1064 cm^{-1} for PMMA and at 1282 cm^{-1} and 1037 cm^{-1} for NPOE plasticizer. The spectrum of the plasticizer also exhibited a band at 1603 cm^{-1} corresponding to the stretching modes of $\text{C}=\text{C}$ bonds and another one at 1522 cm^{-1} characteristic of the stretching modes of $-\text{NO}_2$ bonds. The FTIR spectra of the elaborated membranes (CTA/NPOE/PMMA), (CTA/NPOE/PVC) and (PMMA/NPOE/PVC) are illustrated in Figure 2.

As it can be seen from these figures, the coexistence of all the constituents of the elaborated membranes was

Figure 1: FTIR spectra of CTA, PMMA, PVC and NPOE plasticizer.

Figure 2: FTIR spectra of synthesized membranes.

Figure 3: FTIR spectra of membranes in the range 1650 cm^{-1} – 1480 cm^{-1} .

confirmed by the presence of the characteristic bands of the functional groups of each polymer and of NPOE plasticizer. From the global FTIR spectra of membranes, we noted the presence of CTA by the existence of bands in the carbonyl and hydroxyl regions while the presence of PMMA was evidenced by bands only in the carbonyl domain. The characteristic picks of C–Cl bands at 614 cm^{-1} also appeared in (CTA/NPOE/PVC) and (PMMA/NPOE/PVC) membranes.

Figure 3 presents the FTIR spectra of elaborated membranes in $1650\text{--}1480\text{ cm}^{-1}$ region.

The presence of the NPOE plasticizer within the three membranes was easily detected in Figure 3 by the existence

of the bands centered at 1607 cm^{-1} , relative to the stretching modes of C=C bonds, and at 1526 cm^{-1} , characteristic of the stretching modes of --NO_2 bonds of NPOE. It is noteworthy that these two picks did not appear in spectra of pure polymers. The shift of these bands to higher wavenumbers comparatively to those of the pure plasticizer which appear at 1603 cm^{-1} and 1522 cm^{-1} , respectively, confirmed the contribution of NPOE in the development of interactions with the other constituents of the elaborated membranes. This result was also evidenced by the appearance of a new band at 1580 cm^{-1} , initially absent in the pure components of the membranes, probably due the presence of specific interactions developed between the NPOE and the polymers in each membrane.

The existence of specific hydrogen bonding interactions within elaborated membranes is confirmed by the perturbation of some characteristic bands of the pure constituents essentially the widening and the shift of the characteristic band of the carbonyl groups located at 1729 cm^{-1} for the CTA and 1731 cm^{-1} for the PMMA, as shown in Figure 4.

From Figure 4, we can detect the presence of two bands in the CTA/NPOE/PMMA membrane in the carbonyl region. The first one located at 1732 cm^{-1} is characteristic of free carbonyl groups of CTA and/or PMAA which did not develop interactions. The second one, localized at 1752 cm^{-1} , is attributed to the presence of hydrogen bonding interactions between the hydroxyl groups of CTA and carbonyl ones of PMMA (inter-associations) or hydroxyl and carbonyl groups of CTA (self-associations). The CTA/NPOE/PVC membrane exhibited only one band

Figure 4: FTIR spectra of membranes in carbonyl region (1800 cm^{-1} – 1680 cm^{-1}).

localized at around 1751 cm^{-1} , confirming the consumption of all the free carbonyl groups of CTA (localized at 1729 cm^{-1} in the pure CTA) and the development of hydrogen bonding interactions between all the (C=O) groups of CTA and PVC. However, PMMA/NPOE/PVC membrane showed a broad band between 1726 cm^{-1} and 1736 cm^{-1} characterising the interactions between the (C=O) groups of PMMA and PVC.

3.2 Characterization by TGA

Thermal degradation study provides useful information for the optimization of the successive treatment of polymer materials in order to avoid or at least limit thermal degradation. The analysis of the degradation process becomes more and more important due to an increase in the range of temperatures for engineering applications. Weight loss thermograms, TGA, and the corresponding derivatives, d(TGA), curves of pure polymers CTA, PMMA and PVC, obtained by conventional TGA are shown in Figure 5.

As it can be seen from Figure 5, a significant weight loss of about 81% of the initial mass of CTA was observed from 297°C to 433°C . This step of degradation is attributed to the elimination of all the acetate substituents and the formation of pyranose ring in the polymer. The residue of this polymer at 580°C is about 13 wt %.

The thermal degradation behavior of PMMA is well known in the literature. This polymer degrades in three stages and the main product is the monomer, resulting from depolymerization [47–49]. A residual mass of 3 wt % was noted for this polymer at 580°C .

The dTG curves of PVC displayed two distinct degradation stages. The initial one between 151°C and 358°C was

attributed to the dehydrochlorination of the PVC matrix, resulting in the formation of the conjugated polyene sequences [50]. The Cl radicals and the H atoms from a repeating unit formed HCl which further catalyzes the degradation process, releasing more HCl, and leading to the formation of polyene [51]. The last stage of degradation of PVC, between 374°C and 550°C , was attributed to the thermal decomposition of the dehydrochlorinated PVC consisting mainly of conjugated double bonds [52].

Figure 6 shows the weight loss thermograms TGA and the corresponding derivatives d(TGA) curves of synthesized membranes (CTA + NPOE + PMMA), (CTA + NPOE + PVC) and (PMMA + NPOE + PVC).

As it can be seen from Figure 6 and based on the values of Tonset of elaborated membranes, all the membranes exhibited a thermal stability until 156°C (Tonset of (CTA + NPOE + PMMA) membrane = 156°C , Tonset of (CTA + NPOE + PVC) membrane = 170°C and Tonset of (PMMA + NPOE + PVC) membrane = 157°C).

The (CTA + NPOE + PMMA) membrane decomposed in two steps process while the two others degraded in three main stages. The first one occurring at 188°C for (CTA + NPOE + PMMA) membrane, 228°C for (CTA + NPOE + PVC) membrane and at 197°C for the last one represents the volatilization of plasticizer NPOE which have an ebullition temperature of 198°C . The other stages of degradation of the synthesized membranes are attributed to the main thermal degradation of the polymeric chains of polymers CTA, PMMA and PVC. Based on Figure 6, we confirmed that all the synthesized membranes exhibited a good thermal stability up to 156°C . This temperature is much higher than that required in the

Figure 5: Thermogravimetric analysis (TGA) and d(TGA) curves of CTA, PMMA and PVC polymers.

Figure 6: Thermogravimetric analysis (TGA) and d(TGA) curves of synthesized membranes.

membrane processes. We noted that the second membrane (CTA + NPOE + PVC) is the most stable one.

3.3 Characterization by SEM

It is important to mention that the study of the morphology of all the synthesized membranes by SEM analysis was carried out on the bottom side. The membrane constituted by only polymeric CTA (Figure 7a: view of surface) shows homogeneous porous structure, the distribution of the pores is nearly uniform (porosity = 50%) [18]. On the other hand, the (CTA + NPOE), (CTA + NPOE + PMMA), (CTA + NPOE + PVC) and (PMMA + NPOE + PVC) membranes (Figure 7b–e), respectively, present a dense structure where the pores of membrane have been filled by the plasticizer and the second polymer molecules yielding to a thicker and less porous membrane. We remark also that the polymeric membranes exhibited still homogeneous sponge microstructures. However, an obviously denser morphology of the hybrid membrane can be found with (CTA + NPOE + PVC) membrane. The SEM images of the cross-section for the synthesized membranes are shown in Figure 7f–h.

The cross-section of all membranes reveals homogeneous multi-layer structure. Moreover, a more compact morphology closer to the surface of the membrane than that of the inner can be observed if comparing the different

parts along the thickness of the polymeric membrane. We note also that the thicknesses of all synthesized membranes are very similar (< 30 μm).

3.4 Zeta potential

Table 1 shows the electrokinetic potential (zeta potential) of all synthesized membranes.

All membranes exhibit a positive charge density in the low pH range, pass through an isoelectric point (IEP, i.e. the pH at which the membrane net charge is 0) between pH 3.0 and 4.4 (Table 1), and then become negatively charged for pH higher than the IEP. In addition, membranes that are more negatively charged are found to have lower IEPs. More specifically, there is a shift of the membrane IEP after plasticizer addition to CTA. Indeed, according to IEP values given in Table 1, electrokinetic measurements performed along the membrane side that was not exposed directly to the plasticizer reveal a substantial modification of the IEP, namely 4.4 and 4.1 for the (CTA + NPOE) membrane (NPOE side) and (CTA + NPOE) membrane (CTA side), respectively. These results show that after spreading onto the polymer film the plasticizer does not remain on the surface but enters the polymer matrix. This is in agreement with SEM analysis (Figures 7a, b) which shows that CTA membranes become less porous after plasticizer spreading.

The negative charge of membrane shown over a wide range of pH might come from the deprotonation of functional groups with weak acid properties, most probably carboxylic acid groups present on the surface of CTA membranes. Indeed, in the case of the CTA, some authors revealed the existence of traces of acetic acid from the acetic anhydride used during acetylation [53].

Plasticizers used in this work contain ionizable groups ($-\text{N}^+\text{C}(=\text{O})\text{O}^-$). However, they can develop high electrostatic interactions and can interact also via hydrogen bonds with

Figure 7: Morphology of (a) (CTA), (b) (CTA + NPOE), (c) (CTA + NPOE + PMMA), (d) (CTA + NPOE + PVC) and (e) (PMMA + NPOE + PVC) membranes surfaces, (f) (CTA + NPOE + PMMA), (g) (CTA + NPOE + PVC) and (h) (PMMA + NPOE + PVC) cross section.

Table 1: Isoelectric point of the synthesized membranes.

Membrane	Isoelectric point (pH)
CTA	3.5
PMMA	3.5
PVC	3.0
CTA + NPOE (CTA side)	4.1
CTA + NPOE (NPOE side)	4.4
CTA + NPOE + PMMA (CTA side)	4.0
CTA + NPOE + PMMA (PMMA side)	3.3
CTA + NPOE + PVC (CTA side)	4.2
CTA + NPOE + PVC (PVC side)	3.9
PMMA + NPOE + PVC (PMMA side)	3.8

the CTA matrix. Consequently, the increase in the membrane IEP after addition of NPOE could result from the formation of hydrogen bonds between the oxygen atoms of the plasticizer and the hydrogen atoms of the carboxylic acid residues on the CTA matrix, which weakens the acid character of the carboxylic acid groups.

Zeta potential measurements carried out on both sides of the membranes show that, in both cases that the addition of the second polymer does not cause a significant change in the IEP of the CTA side of the active layer of the membrane while there is a substantial shift of the IEP on the plasticizer side after adding the second polymer. This result is due to the synthesis method of these membranes. Indeed, as mentioned in Section 2.3, polymer inclusion membranes were developed in two stages: first, the plasticizer was spread onto the first polymer film, then the second polymer was spread on the system polymer 1 and NPOE.

Therefore, the fact to spread the plasticizer on the first polymer reduces the action of the solvent during the addition of the second polymer which leads to a two-layer membrane.

Moreover, zeta potential measurements performed along the side on which the second polymer was added show that the IEP is shifted from 4.4 to 4.2 after PVC addition and from 4.4 to 3.3 after PMMA addition. In the latter case, the IEP is very close to that of PMMA which is 3.5. The slight IEP variation in the case of PVC addition is probably due to the better miscibility of PVC (compared with PMMA) into the matrix (CTA + NPOE). This hypothesis is confirmed by the previous SEM characterization which (Figure 7d) shows an obviously denser morphology of the (CTA + NPOE + PVC) membrane.

3.5 Contact angle

Contact angle measurements and the surface tension components were calculated according the Van Oss approach and are collected in Table 2. The surface energy

data show that all membranes have a dominant non-polar component (γ^{LW}). Moreover, the main contribution of the polar component comes from the electron donor component (γ^-) since very small electron acceptor components (γ^+) were determined for all membranes.

In addition to previous electrokinetic measurements, determining contact angles and surface tension components gives us a pretty clear picture of the surface features of the various membranes. Indeed, these latter provide valuable information on the hydrophobic/hydrophilic character of membrane surfaces as well as on the change in the polar/non-polar balance (which can be expressed by the ratio: $\gamma_M^{AB}/\gamma_M^{LW}$).

An increase in water contact angle is observed when adding a plasticizer to the CTA membranes, thus highlighting an increase in the surface hydrophobicity, which can be attributed to the presence of aromatic rings and alkyl chains in both plasticizers. Moreover, plasticizer addition changes the polar/non-polar balance by decreasing the polar character of both membrane surfaces (see $\gamma_M^{AB}/\gamma_M^{LW}$ values in Table 2). Regarding the addition of the second polymer on the first film, it is found that contact angles measured with different solvents as well as γ_M^{Tot} do not vary significantly (see Table 2). Notably, both γ_M^- and γ_M^+ remain almost constant when adding the second polymer. This confirms that the addition of the second polymer does not significantly alter the surface of the membrane because NPOE reduces the action of the solvent of the second polymer [54, 55].

3.6 Lead (II) transport experiments

It should be noted that the second method used to the development of multi-layer membranes yields more homogeneous membranes. This is probably due to the fact that the spreading of the plasticizer on the first layer provides the latter a high stability and substantially reduces the action of the solvent of the second polymer onto the

Table 2: Contact angle in water, formamide and diiodomethane and surface tension components of the synthesized membranes.

Membrane	θ_{wat} (°)	θ_{form} (°)	θ_{diiod} (°)	γ_M^{LW} (mN/m)	γ_M^+ (mN/m)	γ_M^- (mN/m)	γ_M^{AB} (mN/m)	γ_M^{Tot} (mN/m)	$\gamma_M^{AB}/\gamma_M^{LW}$ (%)
CTA	58.6	47.0	40.3	39.5	0.1	22.9	3.5	42.3	8.3
PMMA	70.0	50.0	32.8	43.0	0.1	11.2	1.7	44.8	3.8
PVC	84.3	61.1	30.5	44.0	0.0	3.2	0.0	44.0	0.0
CTA + NPOE	70.5	52.5	33.1	42.9	0.0	12.1	0.6	43.5	1.3
CTA + NPOE + PMMA	71.7	52.0	41.6	38.8	0.2	10.4	3.2	42.0	7.6
CTA + NPOE + PVC	71.7	56.1	40.0	39.6	0.0	12.8	0.5	40.1	1.3
PMMA + NPOE + PVC	77.60	64.40	37.20	40.99	0.18	10.61	2.74	43.73	2.76

Figure 8: Evolution of the concentration of lead in the strip (a) and in feed (b) compartments versus time.

first layer. This new method of preparation of multilayer membrane has virtually eliminated the possibility of chemical attack of the solvent of the second polymer solution on the first film. The most porous, homogeneous and mechanically resistant membranes were selected to use in the transport experiments: (CTA + NPOE + PMMA) and (PMMA + NPOE + PVC) membranes in comparison with (CTA + NPOE + PVC) dense membrane.

Figure 8a represents the evolution of the concentration of Pb^{2+} transferred to the strip phase as a function of time, the initial concentration of the metallic ion in the feed phase is fixed.

The obtained results show that the quantities of Pb^{2+} transferred to the reception phase are very low. A maximum of 4.97% yield was obtained with (CTA + NPOE + PVC) membrane.

Figure 8b shows the variation in the concentration of Pb^{2+} not transferred to the receiving phase versus time in order to determine the amounts retained in each membrane.

We clearly see that (CTA + NPOE + PMMA) and (PMMA + NPOE + PVC) membranes proved a good performance by fixing 12.15 and 25.31% of lead, respectively. These results confirm the affinity between poly-methyl methacrylate and the metallic ion (Pb^{2+}).

The results show that the transport of lead obtained using a three membranes without carrier are acceptable. The increase of the ions concentrations in the strip compartment toward PMMA + NPOE + PVC membrane shows that the combination (PMMA/PVC) facilitated the transport of lead ions. However, the study over time up to 24 h showed that the concentration of lead ions is saturated, suggesting that the transport is very low. These results confirm that the synthesized membranes are not appropriate for $Pb(II)$ transport in one stage, but, they show suitable thermal, structural and morphological properties and are probably appropriate for dye removal or for alcohol separation by using pervaporation process. These results are in accordance with the literature [24, 56]. The experimental results reported by Fontas et al. showed that after

300 min of experimentation, all the Cd initially present in the feed phase was transported to the stripping phase, whereas only 8.5% of Pb was transported [26].

It has been reported that the polymer inclusion membrane has low permeabilities relative to other membranes despite their significant stabilities. Several studies are conducted on the stability of this type of membranes, e.g., Tayeb et al. [57] have studied the influence of Lasalocid A on the stability of a membrane with CTA as a polymeric support and NPOE as plasticizer. Show et al. [58] have demonstrated that polymer inclusion membrane with CTA as a support and DC18C6 as a carrier, is stable for 100 days. Authors have got to develop a new type of membrane (the pore-filled membrane [PFM]) which can be stable over 3 months. This PIM system with complexing properties has been examined in previous work by Arous et al. [22] where the system operated continuously without any fault for 14 days. Other researchers reported that the lifetime of membrane including CTA/Aliquat 336/2-NPOE in PIM studies [29] reached 30 days.

4 Conclusion

In this work, a new kind of polymeric membranes using a mixture of polymers were prepared using the phase inversion method modified by changing the procedure of a plasticizer addition and using the rapid volatilization of solvent. All synthesized membranes were characterized by FTIR, TGA and SEM. The degradation of the membranes occurred via a two- or three-step process with the main loss starting at 150 °C due to the thermal degradation of NPOE. This result confirmed that all the synthesized membranes exhibited good thermal stability. The SEM observation of membranes revealed a homogeneous structure. Further analyses of membrane surface properties were performed by means of electrokinetic and contact angle measurements. We perceived that heating the film during synthesis did not modify the chemical composition of membrane surfaces. Finally, the results of

electrokinetic measurements on developed materials are confirmed by the SEM characterizations.

A study of the transport across a polymer inclusion membrane has shown that the lead transport efficiency was increased using PMMA as basic polymer. All synthesized membranes are probably appropriate for dye or surfactant removal or for alcohol/water separation by using pervaporation process. Further efforts will be directed to the determination of the nature of interactions between polymers and plasticizer/carrier by use of other materials and analysis as well.

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