

Synthesis and Transport Abilities of New Membrane Materials Incorporating Bipyrzolic Tripods

Fouad Malek, Abdelkrim Ramdani, Ismail Zidane, Smaail Radi

Département de chimie, Faculté des Sciences, Université Med I, Oujda Maroc

Received 18 October 2006; accepted 29 December 2006

DOI 10.1002/app.26211

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Membrane materials were obtained by photopolymerization reaction of formulation spread over a polyacrylonitrile (PAN) support. The formulation contains the active bipyrzolic tripods monomers, the styrene, and the photostart. The facilitated transport and the extraction power of Cd(II), Pb(II), and Hg(II) through the synthesized membranes were reported. We have deter-

mined both the diffusion flux F of different cations and the selectivity S of the prepared membranes towards each cations. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104, 3967–3972, 2007

Key words: photopolymerization; membrane; thin films; transition metals; diffusion

INTRODUCTION

The strong ability of pyrazole and its derivatives to act as ligands with sp^2 hybrid nitrogen donor have been the research subjects of many coordination chemists. This is evident from the large number of articles, several of them being reviews.^{1,2} Moreover, polydentate pyrazolic receptors are well known for their ability to complex not only alkali cations^{3–7} but also to form stable complexes with transition metal ions.^{8–11} These complexes are so stable that it is often difficult to obtain the free macrocycles from them.

In our recent works, a series of acyclic pyrazole compounds containing one, two, three, or four pyrazole rings were prepared and demonstrated to extract only the transition metal cations^{12–15} when the macrocyclic pyrazolic compounds expected to form stable complexes both with transition and alkali metals.^{16,17}

Major problems in using the solvent extraction method or liquid membrane systems are (a) maintaining the very expensive ligands in the organic phase (even a very slow loss of these materials from the organic layer of a liquid membrane or solvent extraction system often cannot be tolerated); (b) loss of extraction effectiveness when low concentrations of metal ions are involved; and (c) the relatively slow kinetics of extraction. One way to overcome these problems is the covalent attachment of the ligands to a solid support. The chemistry of the pyrazole compounds bonded to solid support has not

yet been developed, even though many studies have been reported in the literature.^{12,13,18–23}

This paper reports the photopolymerization of formulation that contain the bipyrzole active monomers **3** and **4** (Scheme 1) spread on a polyacrylonitrile (PAN) support. The resulting materials were used for the extraction and the facilitated transport of Cd(II), Pb(II), and Hg(II). The diffusion flux F of different cations and the selectivity S of the prepared membrane were also reported.

EXPERIMENTAL

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification except methacryloyl chloride, which was distilled before use. The proton NMR spectra were obtained on a Bruker AC 300 spectrometer. Elemental analyses were performed by Microanalysis Central Service (CNRS). Molecular weights were determined on a JEOL JMS DX-300 Mass Spectrometer. The synthesized membranes are observed with a Cambridge Stereoscan 100 microscope (SEM). Picrates absorbencies were measured with Philips PU 8620 Spectrophotometer. Concentrations of cations were determined by atomic absorption on Varian AA 400 Spectrophotometer and the conductometer used was a Tacussel CD6 with GMO1/G electrode. The chromatography columns were carried out with alumina 90 (70–230 mesh ASTM).

Syntheses of 3: To a cooled mixture (0°C) of 2×10^{-3} mol of **1** and 2×10^{-3} mol of triethylamine in 150 mL of CH_2Cl_2 was dropwisely added 2×10^{-3} mol of methacryloyl chloride. The mixture was

Correspondence to: Smaail Radi (radi_smaail@yahoo.fr).

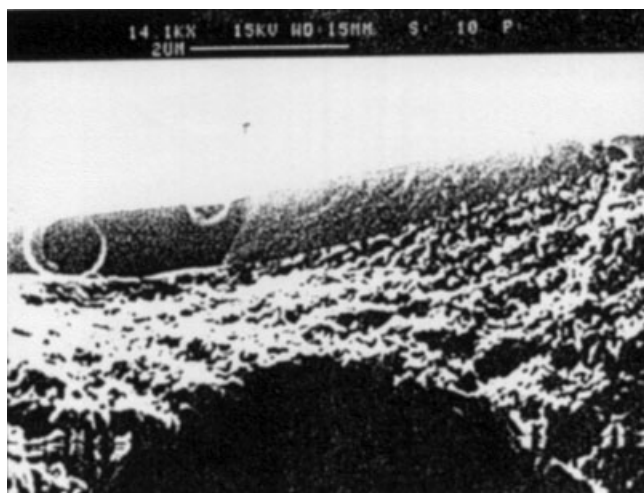


Figure 1 Morphology of the studied membrane.

Synthesis of membrane materials

The formulation was deposited on the PAN support and spread out to form membranes with a small thickness.

The components' flux F through a membrane is inversely proportional to membrane thickness. A small thickness will consequently optimize the flux. However, films having a small thickness are too fragile for being self-supported, it is therefore necessary to use a support, which will ensure the mechanic stability.

The PAN support has a low surface porosity which allows easy realization of the deposits and good mechanical resistance. It has very high total porosity with pores' diameter greater than $10\ \mu\text{m}$. It is also very permeable to ions and thus does not limit the transport. For example, the diffusion flux²⁴ F of KCl across this support is approximately $1\ \text{mol h}^{-1}\ \text{m}^{-2}$.

The formulation applied to the support is an equimolar mixture ($10^{-3}\ \text{mol}$) of active monomer and the styrene, which chosen as the thinner. The thinner was used to obtain formulations with compatible viscosity with the support. The photostart used is the 2,2-dimethoxy-2-phenylacetophenone because of its high absorption property in the near-UV^{25,26}; each formulation contains 3 wt % of photostart. The formulation is deposited on the PAN support and the whole is exposed to the UV radiation emitted by a mercury vapor lamp (250–440 nm).

The synthesized membranes are observed with a scanning electron microscope (SEM). We have characterized the surface aspect (porosity, presence of defects) and the layer interface deposited/support after having performed frank breaks of the samples in the liquid nitrogen in order to obtain net observation of the cuts. In the two cases, we have observed

dense surfaces free of microporosity, in contradiction to the PAN films where the pores presence is noticeable; thickness of films are between 4×10^{-6} and $6 \times 10^{-6}\ \text{m}$. Figure 1 shows the photo taken for the studied membrane, the topmost part corresponds to the polymeric layer, which constitutes the membrane, and the bottommost part corresponds to the porous support which ensures the mechanical rigidity of the membrane.

To be sure that the cations diffusion across the solid membranes prepared is only due to the ligands supported, Nishide et al.²⁷ recommend the preparation of a reference membrane from an equivalent molecule of the active monomer but without complexing properties. We have prepared the reference membrane from dimethacrylate ethylene glycol and styrene in the rates 50/50.

Study of the facilitated transport

The passage of cations into the reception phase is supervised by conductimetry. In this phase, samples are taken at regular intervals of time and are analyzed by atomic absorption spectrometry in order to determine the cation concentrations.

No metallic cation diffusion occurred when the reference membrane was used. In contrast, diffusion was observed with membranes M_I and M_{II} , as described below, revealing the essential role of the tripod ligands in the diffusion process.

Membrane M_I (incorporating tripod 3)

We have studied the individual and the competitive transport of the three cations Cd(II), Pb(II), and Hg(II) in *simple mode* (the reception phase contains only a pure deionized water), and the competitive transport *against the protons current* (the reception phase contains a nitrate acid solution 0.1M).

The study of the individual transport of the cations shows a remarkable diffusion across the membrane as well for Cd(II) as for Pb(II) (see Table I); the diffusion flux F is respectively 5.6×10^{-3} and $3.6 \times 10^{-3}\ \text{mol h}^{-1}\ \text{m}^{-2}$ (Fig. 2). The selectivity S ($F_{\text{Cd(II)}}/F_{\text{Pb(II)}}$) = 1.5 which means that Cd(II) is better transported by the membrane. This result is in good agreement with the concentrations of these cations in receiving phase (Fig. 3).

This observation was confirmed by the conductance and the concentration evolutions (Figs. 4 and 5) of the diffusion of these two cations simultaneously present at equal concentration ($5 \times 10^{-2}\ \text{M}$) in the source phase (competitive transport). The conductance of Cd(II) measured was a little improved compared to those measured in simple mode with concentration equal to $10^{-1}\ \text{M}$ in source phase (see Table I). We also noted a linear variation of the concentration

TABLE I
Values of Metal Cations Fluxes F ($10^{-3} \text{ mol h}^{-1} \text{ m}^{-2}$) and Selectivity S of Membranes M_I and M_{II}

	Individual transport (M_I/M_{II})	Competitive transport (M_I/M_{II})	Against protons current transport (M_I/M_{II})
F (Cd^{2+})	5.6/6.8	6/8.6	43/48
F (Pb^{2+})	3.6/5	1.5/4	6.5/13.3
S ($\text{Cd}^{2+}/\text{Pb}^{2+}$)	1.5/1.3	4/2	6.6/4

of Cd(II) in respect to time (Fig. 4) and a decrease of Pb(II) in the receiving phase. The diffusion flux F is respectively 6×10^{-3} and $1.5 \times 10^{-3} \text{ mol h}^{-1} \text{ m}^{-2}$; the selectivity $S = 4$ (see Table I), we can thus conclude that this membrane is selective with the transport of Cd(II).

The study against the protons current leads to an improvement of diffusion fluxes F (Fig. 5). The diffusion flux F of Cd(II) was multiplied by a factor of 7 ($F = 43 \times 10^{-3} \text{ mol h}^{-1} \text{ m}^{-2}$) and that of Pb(II) was multiplied by a factor of 4.4 ($F = 6.5 \times 10^{-3} \text{ mol h}^{-1} \text{ m}^{-2}$). In this case the selectivity S is 6.6 in favor of Cd(II). The comparison of the conductimetry measurements and the dosages of cations (Fig. 6) performed by atomic absorption show that the observed phenomenon is a crossed flux of cations and protons.

The study of the individual transport of Hg(II) shows a linear and weak variation of conductance in the receiving phase during the first hours of the experiments (Fig. 7). After 15 h of transport, a plateau was reached. However, we noted a reduction of its concentration in the source phase. This can be due only to the possible formation of stable complex in the membrane who prevents the passage of the Hg(II) in the receiving phase. In order to confirm this

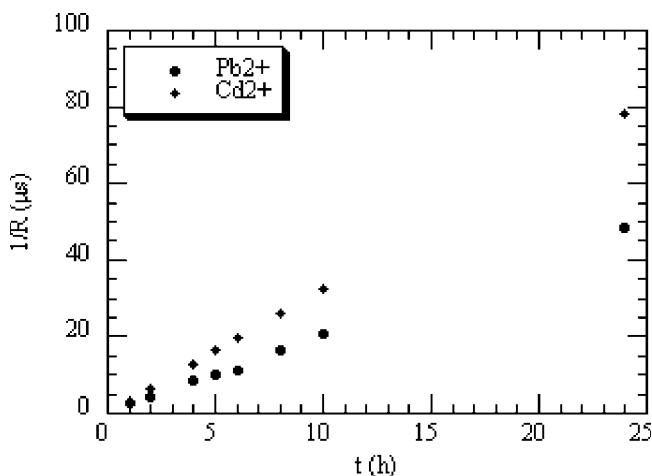


Figure 2 Individual transport of Cd^{2+} and Pb^{2+} across membrane M_I , evolution of conductance in reception phase.

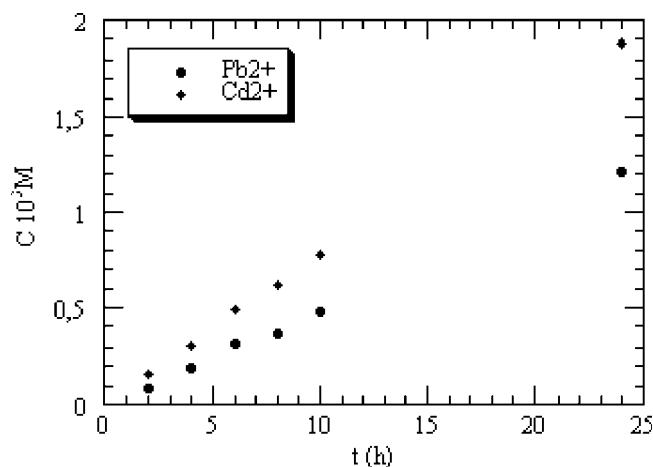


Figure 3 Individual transport of Cd^{2+} and Pb^{2+} across membrane M_I , evolution of concentration in reception phase.

supposition, we placed this complexed membrane which is beforehand washed with deionized water between the two halves of the measuring cell, the phase source is filled this time of a solution of HNO_3 (10^{-1} M) and the receiving phase contains pure water. After 2 h, we detected the presence in the receiving phase of the Hg(II) complexed by the membrane and which was salted out (decomplexed) in the presence of HNO_3 acid.

Membrane M_{II} (incorporating tripod 4)

Membranes M_I and M_{II} are different only by the side arm of tripods incorporated in each membrane. However, we noted a different values of diffusion fluxes F and of selectivity S with the various modes of diffusion used (simple mode or against the protons current). The results are given in Table I.

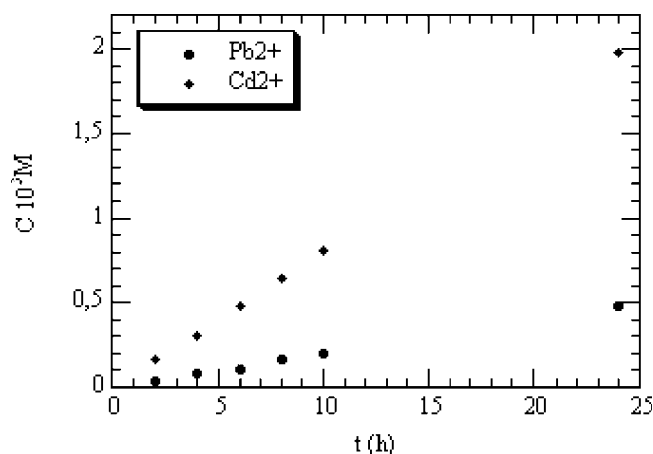


Figure 4 Competitive transport of Cd^{2+} and Pb^{2+} across membrane M_I , evolution of concentration in reception phase.

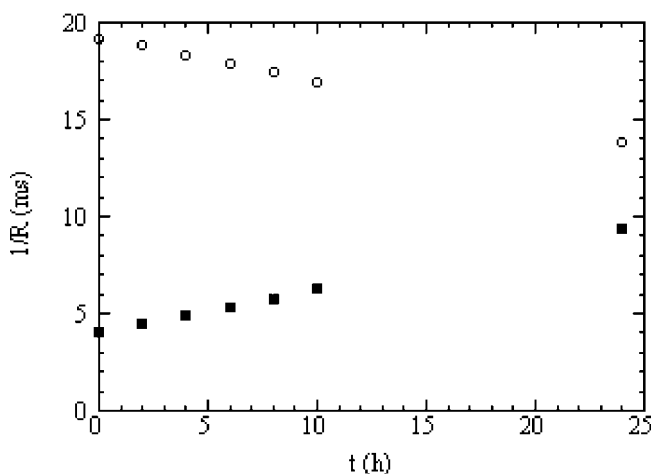


Figure 5 Competitive transport against the protons current across membrane M_I , evolution of conductance in reception phase (○) and in source phase (■).

The results in Table I show that the individual transport of the two cations Cd(II) and Pb(II) presents an improvement of diffusion fluxes F across M_{II} compared to M_I membrane. This simultaneous increase of transport of these two cations harmed the selectivity S .

In competitive transport, we also noted an increase of diffusion flux F of Cd(II) and a lower decrease of Pb(II) transport (see Table I) what means that Cd(II) is better transported by the membrane. However, the selectivity S in this case was equally lower compared to M_I .

The study against the protons current shows equally an improvement of diffusion fluxes F (see Table I) but the selectivity S is only 4 in favor of Cd(II).

We can thus say that the values of diffusion fluxes F are higher than in the case of the M_I membrane

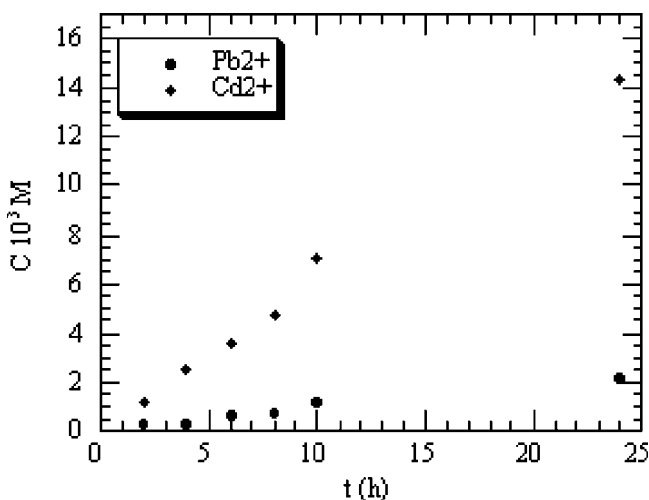


Figure 6 Competitive transport against the protons current, evolution of concentrations in reception phase.

with the three studied means of transport. This is probably due to the presence of the phenyl group on the side arm of the ligand incorporated on the membrane M_{II} , which presents a delocalization of π -electrons. Indeed the free electronic doublet of the sp^3 hybrid nitrogen donor which forms complexes with metals intervenes in mesomery with the phenyl group and consequently leaves the sp^3 nitrogen with a δ^+ character. This character confers to the formed complexes a lower stability compared to the sp^3 hybrid nitrogen donor (in the case of M_I), what increases the decomplexation of the trapped metals consequently their transport (high diffusion fluxes).

For the mercury which is well extracted by this free pyrazolic tripod,¹⁴ it blocks the membrane probably due to the possible formation of stable complex.

In all the cases we note that these two membranes present an interesting phenomenon of transport towards the transition metal cations compared to the membranes incorporating the monopyrazolic or the linear bipyrazolic units.²³ We recall here that the pyrazolic tripods present a higher complexation ability towards the transition metal cations compared to the mono- and the linear bipyrazolic compounds.^{13,14} We can thus say that the phenomenon of transport is governed by the complexation ability of ligands. In the same way, tetrapyrazolic macrocycles which are known for their affinity towards alkali cations present when incorporated to membranes materials an interesting phenomenon of transport.²²

CONCLUSION

In conclusion, we have prepared new membrane materials by photopolymerization of a formulation spread over a PAN support. The formulation contains the methacrylic monomer, the styrene, and the

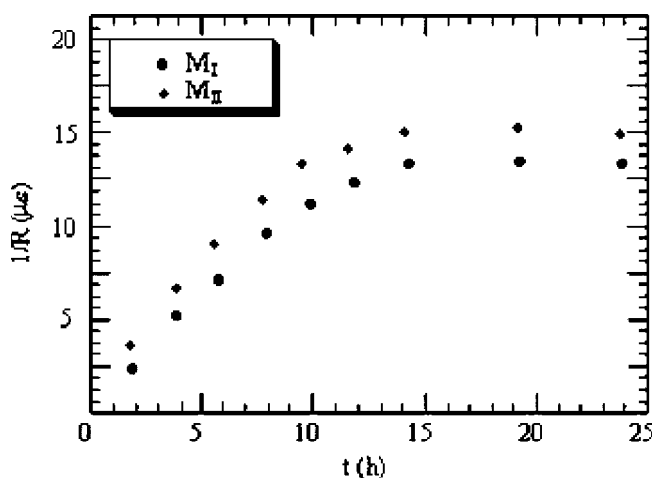


Figure 7 Individual transport of Hg^{2+} across membrane M_I and M_{II} , evolution of conductance in reception phase.

photostart. The monomer was obtained by esterification of hydroxypyrazoles with the methacryloyl chloride. Dense membranes were obtained by this method.

The study of the facilitated transport across these membranes show a selectivity for Cd(II). Speeds of transport are promising. Moreover, these speeds are improved when we operate against the protons current.

The free bipyrazolic tripods were demonstrated to extract mercury.¹⁴ These cations were not well transported by these membranes. This is probably due to the strong stability of the complex formed by this cation and the ligands used. These membranes would well be used as a selective electrode for entrapping mercury.

References

1. Trofimenko, S. *Chem Rev* 1972, 72, 497.
2. Trofimenko, S. *Prog Inorg Chem* 1986, 34, 115.
3. Lupo, B.; Tarrago, G. *Bull Soc Chim Fr* 1984, 2, 473.
4. Ramdani, A.; Tarrago, G. *Tetrahedron* 1981, 37, 987.
5. Gal, M.; Tarrago, G.; Steel, P.; Marzin, C. *New J Chem* 1985, 9, 617.
6. Boudouche, S.; Coquelet, C.; Jacquet, L.; Marzin, C.; Sandeaux, R.; Tarrago, G. *J Inclusion Phenom* 1993, 16, 69.
7. Tarrago, G.; Zidane, I.; Marzin, C.; Tep, A. *Tetrahedron* 1988, 44, 91.
8. Elguero, J.; Espada, M.; Ramdani, A.; Tarrago, G.; *J Heterocycl Chem* 1980, 17, 137.
9. Marzin, C.; Tarrago, G.; Gal, G.; Zidane, I.; Hours, T.; Lerner, D.; Andrieux, C.; Camp, H.; Saveant, J. M.; *Inorg Chem* 1986, 25, 1775.
10. Bol, J. E.; Mars, B.; Gonesh, G.; Driessen, W. L.; Goubitz, K.; Reedijk, J. *Heterocycles* 1997, 45, 1477.
11. Mary, F.; Marzin, C.; Salhi, S.; Tarrago, G. *Supramol Chem* 1993, 3, 57.
12. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Morcellet, J.; Janus, L. *Eur Polym J* 2000, 36, 1885.
13. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Janus, L.; Bacquet, M. *New J Chem* 2003, 27, 1224.
14. Malek, F.; Ramdani, A.; Radi, S. *J Chem Res* 2004, 9, 640.
15. Malek, F.; Ramdani, A.; Zidane, I.; Yahyi, A.; Radi, S. *Tetrahedron* 2005, 61, 2995.
16. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Janus, L. *J Chem Res* 2003, 11, 712.
17. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Janus, L. *Tetrahedron* 2004, 60, 939.
18. Ameduri, B.; Boutevin, B.; Malek, F. *J Polym Sci Part A: Polym Chem* 1994, 32, 729.
19. Boutevin, B.; Malek, F. *Eur Polym J* 1995, 12, 1279.
20. Boutevin, B.; Pietrasanta, F. G.; Malek, F. *Macromol Chem Phys* 1994, 195, 1121.
21. Radi, S.; Ramdani, A.; Lekchiri, Y.; Morcellet, M.; Crini, G.; Janus, L.; Martel, B. *J Appl Polym Sci* 2000, 78, 2495.
22. Malek, F.; Persin, M.; Ramdani, A.; Sarrazin, J.; Zidane, I. *New J Chem* 2002, 26, 876.
23. Malek, F.; Ramdani, A.; Zidane, I.; Radi, S. *Eur Polym J* 2005, 41, 817.
24. Lacan, P. Thèse de Doctorat d'Université, Montpellier, France, 1993.
25. Fizet, M.; Decker, C.; Faure, J. *Eur Polym J*, 1985, 21, 427.
26. Decker, C.; Bendaikha, T. *Eur Polym J* 1984, 20, 753.
27. Nishide, H.; Kawakami, H.; Kurimura, Y.; Tsuchida, E. *J Am Chem Soc* 1989, 111, 7175.