

Transport Abilities of New Synthesised Membrane Materials Incorporating Tetrapyrazolic Tripods

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ABSTRACT: The synthesis of new membrane materials was carried out by photopolymerisation of formulation that contain the active tetrapyrazolic tripods monomers spread on a polyacrylonitrile support. The obtained membrane films were applied for their facilitated transport and extraction power towards Cd(II), Pb(II), and Hg(II). We have determined both the diffusion flux F of different

cations and the selectivity S of the prepared membranes towards each cations. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 57–62, 2009

Key words: photopolymerisation; membrane; thin films; heavy metals; diffusion

INTRODUCTION

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 heavy metal cations,^{1–6} when the macrocyclic pyrazolic compounds expected to form stable complexes both with heavy and alkali metals.^{7–9}

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. In this context, we recently^{10–12} developed some solid membranes incorporating a pyrazole, a linear bipyrazole and a bipyrazolic tripodal ligands. These membrane films were revealed to be good candidates for the extraction and the facilitated transport of some heavy metals.

Following our research program, the present investigation reports the synthesis of new solid membrane films using the photopolymerisation of formulation that contain the tetrapyrazole active monomers (3–4) (Scheme 1) spread on a polyacrylonitrile 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.

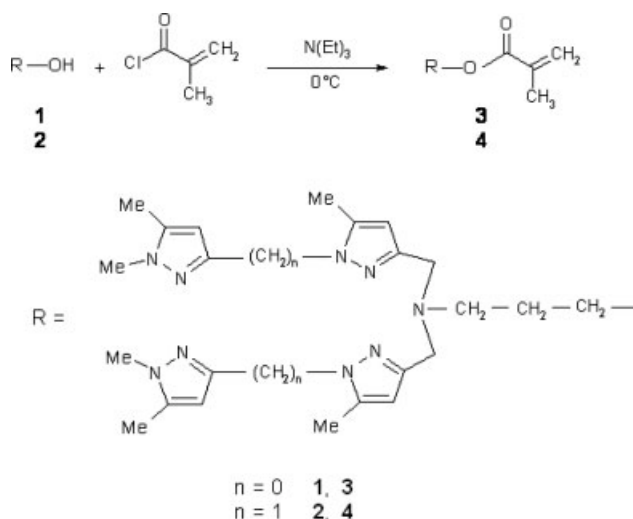
EXPERIMENTAL

All solvents and other chemicals, obtained from usual commercial sources, were of analytical grade and used without further purification except methacryloyl chloride that was distillate before each utilization. The proton NMR spectra were obtained with a Bruker AC 300 spectrometer. Elemental analyses were performed by Microanalysis Central Service. 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 AA¹³ on Varian AA 400 Spectrophotometer and the conductimeter used was a Tacussel CD6 with GMO1/G electrode.

Synthesis of 3

To a cooled mixture (0°C) of (2×10^{-3} mole) of 1 and (2×10^{-3} mole) of triethylamine in 150 mL of CH₂Cl₂ was added dropwise (2×10^{-3} mole) of methacryloyl chloride. The mixture was stirred at ambient temperature for 4 h. The mixture was filtered, evaporated less than 40°C and the residue was separated on alumina using CH₂Cl₂/EtOH (99/1) as eluant to give a 85% yield of active monomer 3 (colorless liquid).

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Scheme 1. Synthesized tetrapyrazolic monomers.

$^1\text{H NMR}$ (CDCl_3) δ : 1.90 (s, 3H); 2.15 (m, 2H); 2.30 (s, 6H); 2.40 (s, 6H); 2.60 (bs, 2H); 3.75 (s, 10H); 4.15 (t, 2H); 5.45 (s, 1H); 5.95 (s, 1H); 6.12 (s, 4H); Anal. Calc. for $\text{C}_{27}\text{H}_{37}\text{N}_9\text{O}_2$: C 62.42, H 7.12, N 24.27, Found: C 62.40, H 7.18, N 24.31; m/z : 520 ($\text{M}+\text{H}$) $^+$.

Synthesis of 4

Under similar procedure, an equimolar (2×10^{-3} mole) cooled mixture (0°C) of **2** and triethylamine in 150 mL of CH_2Cl_2 was added dropwise (2×10^{-3} mole) of methacryloyl chloride. After 4 h of stirring at ambient temperature, the resulting mixture was purified on alumina using $\text{CH}_2\text{Cl}_2/\text{EtOH}$ (98/2) as eluant to give a 80% of active monomer **4** (yellow oil).

$^1\text{H NMR}$ (CDCl_3) δ : 1.82 (bs, 2H); 1.95 (s, 3H); 2.18 (s, 6H); 2.25 (s, 6H); 2.85 (t, 2H); 3.72 (m, 12H); 5.18 (s, 4H); 5.45 (s, 1H); 5.85 (s, 4H); 5.95 (s, 1H); Anal. Calc. for $\text{C}_{29}\text{H}_{41}\text{N}_9\text{O}_2$: C 63.61, H 7.49, N 23.03, Found: C 63.57, H 7.52, N 23.07; m/z : 548 ($\text{M}+\text{H}$) $^+$.

Synthesis of membrane materials

Into a test tube, we introduce 10^{-3} mole of monomer (**3** or **4**), 0.1 g (10^{-3} mole) of styrene and 0.024 g (10^{-4} mole) of 2,2-dimethoxy-2-phenylacetophenone. The mixture was stirred at ambient temperature for 5 min. The formulation was then deposited on the polyacrylonitrile (PAN) support, cut out in square with 6 cm of side and we spread out with a threaded rod "hand-coater" to form uniform layer with 6 μm of thickness. The whole was exposed to the UV radiation emitted by a mercury vapor lamp (250–440 nm) at ambient temperature for 20 s.

Procedure of the facilitated transport

Transport experiments have been conducted by means of a system containing two half-cells of a volume of 90 cm^3 , which constitute the source and reception phases. Two joints of a hollow Teflon are applied to the membrane which separates the two phases. The airtightness of the system is ensured by means of strap and fixing screws. The two aqueous phases are agitated by magnetic bars, and the surface of the membrane in contact with the two aqueous phases is $12.56 \times 10^{-4} \text{ m}^2$. The transport experiments were performed on a source solution of metallic nitrate 0.1M. The reception phase contains initially pure deionized water (18 $\text{M}\Omega \text{ cm}$) (simple mode). Against the protons current, the reception phase contains a nitrate acid solution 0.1M. The variable duration of the experiment depends on the speed of the *trans*-membrane transport. We have terminated the experiments after approximately 24 h, which is considered to be sufficient time for calculating the diffusion flux F and the selectivity S . The temperature is maintained constant at 25°C during all the experiments. Formulates used for calculating the diffusion flux F and the selectivity S are given below:

$$F = pV/s; S = F_{\text{M}^+}/F_{\text{M}^+}$$

where, F is the diffusion flux ($\text{mol h}^{-1} \text{ m}^{-2}$), S is the selectivity, p is the slope of curve: $\text{C}_{\text{M}^+} = f(t)$, ($\text{mol L}^{-1} \text{ h}^{-1}$), V is the volume of the two half-cells ($90 \times 10^{-3} \text{ L}$) and s is the surface of the membrane in contact with the two aqueous phases ($s = \pi \cdot r^2 = 12.56 \times 10^{-4} \text{ m}^2$).

The membrane in contact with the half-cells has a radius of 2 cm.

RESULTS AND DISCUSSION

Synthesis of monomers

Compounds (**1–2**) were prepared as described in a previous work.⁴

The new acrylic monomers (**3–4**) were obtained using the literature procedure^{10–12} by direct esterification of tetrapyrazolic alcohol (**1–2**) with acryloyl chloride. The addition was performed at 0°C in the presence of the triethylamine to trap the HCl formed which was transformed into triethylammonium salt. The purity of the resulting active monomers (**3–4**) (Scheme 1) was controlled by HPLC to be higher than 98% yield and the products were identified by $^1\text{H NMR}$, mass spectrometry, and elemental analysis data.

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

	Individual transport (M_I/M_{II})	Competitive transport (M_I/M_{II})	Competitive transport against protons current (M_I/M_{II})
F (Pb^{2+})	14.6/9.7	5.8/5	54/50
F (Cd^{2+})	9.2/4.6	1.8/1.7	5.3/4
S ($\text{Pb}^{2+}/\text{Cd}^{2+}$)	1.5/2.1	3/3	10/12.5

Synthesis of membrane materials

Obtaining membranes with a small thickness is a need, knowing that the components' flux F through a membrane is inversely proportional to membrane thickness. However, films having a small thickness are too fragile for being auto supported, it is then 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 higher than 10 μm . It is also very permeable to ions and thus does not limit the transport. For example, the diffusion flux F^{14} of KCl across this support is approximately 1 mol h^{-1} m^{-2} .

The formulation applied to the support is an equimolar mixture (10^{-3} mol) of tetrapyrazolic active monomer, and styrene chosen as the thinner. The thinner was used to obtain formulations with compatible viscosity with the support. The photo-start used is the 2,2-dimethoxy-2-phenylacetophenone because of its high absorption property in the near UV^{15,16}; each formulation contains 3% in weights of photo-start. 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 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 and 6 $\times 10^{-6}$ m.

To be sure that the cations diffusion across the solid membranes prepared is only due to the ligands supported, Nishide et al.¹⁷ recommend the preparation of a reference membrane from an equivalent molecule of the active monomer but without com-

plexing 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 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 tetrapyrazolic 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 *against the protons current* (the reception phase contains a nitrate acid solution 0.1M).

The study of the individual transport of the cations shows an effective capacity of the membrane to transport Pb(II) and Cd(II) (see Table I). The curves of Figure 1 present a linear and fast increase of conductance during the first 10 h as well for Pb(II) as for Cd(II). After 15 h of transport, a plateau was reached. The diffusion flux F is respectively, 14.6×10^{-3} and 9.2×10^{-3} mole h^{-1} m^{-2} (Fig. 1). The selectivity S ($F_{\text{Pb(II)}}/F_{\text{Cd(II)}} = 1.5$, which means that Pb(II) is better transported by the membrane. This result is

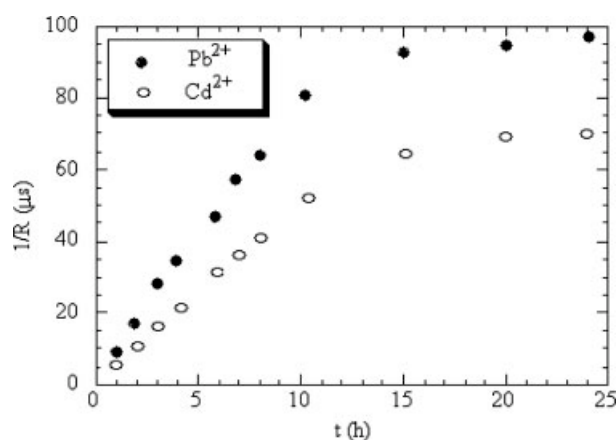


Figure 1 Individual transport of Cd^{2+} and Pb^{2+} across membrane M_I , evolution of conductance in reception phase.

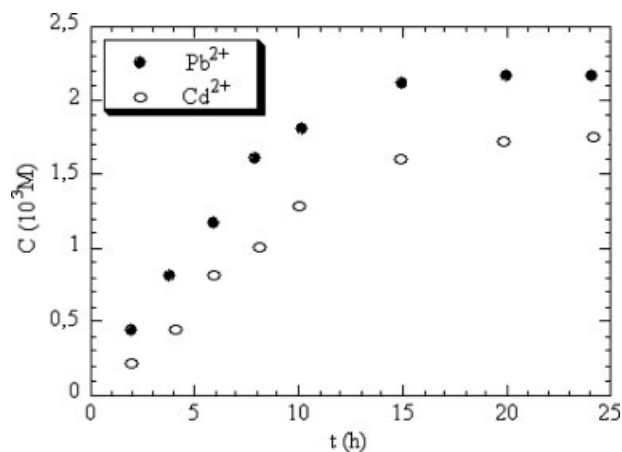


Figure 2 Individual transport of Cd^{2+} and Pb^{2+} across membrane M_I , evolution of concentration in reception phase.

in perfect agreement with measurements of concentrations of these cations in receiving phase (Fig. 2).

This observation was confirmed by the concentration evolutions of the diffusion of these two cations simultaneously present at equal concentration (5×10^{-2} M) in the source phase (competitive transport) (Fig. 3). We noted a linear variation of the concentration of Pb (II) in respect to time and a decrease of Cd(II) in the receiving phase. The diffusion flux F is respectively, 5.8×10^{-3} and 1.8×10^{-3} mole $\text{h}^{-1} \text{m}^{-2}$; the selectivity $S = 3$ (see Table I), we can thus conclude that this membrane is selective for the transport of Pb(II).

The study of the individual transport *against the protons current* shows for Pb(II) (Fig. 4) a linear and fast variation of conductance in opposed directions in the two compartments because of a cross flux of H^+ and Pb(II). These variations reach a threshold after 10 h of transport; we can thus suggest that equilibrium in metal concentration was established

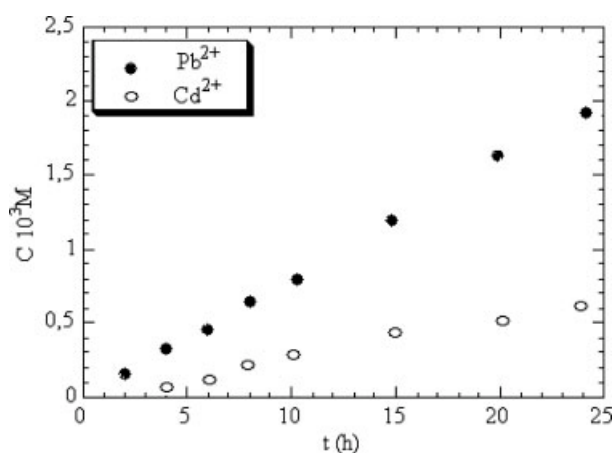


Figure 3 Competitive transport of Cd^{2+} and Pb^{2+} across membrane M_I , evolution of concentration in reception phase.

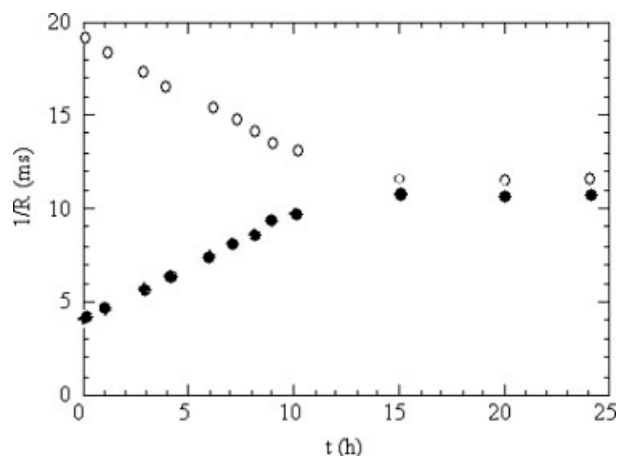


Figure 4 Individual transport of Pb^{2+} against the protons current across membrane M_I , evolution of conductance in reception phase \circ and in source phase \bullet .

between the upstream and the downstream. We also followed the evolution of the conductance *against the protons current* for Cd(II) (Fig. 5); we also noted here a cross flux of H^+ and Cd(II) but slower than that of Pb(II), which is in perfect agreement with the results of the individual transport *in simple mode*.

The study of the competitive transport *against the protons current* leads to an improvement of diffusion fluxes F (Fig. 6). The diffusion flux of Pb(II) was multiplied by a factor of 9.4 ($F = 54 \times 10^{-3}$ mole $\text{h}^{-1} \text{m}^{-2}$) and that of Cd(II) was multiplied by a factor of 3 ($F = 5.3 \times 10^{-3}$ mole $\text{h}^{-1} \text{m}^{-2}$). In this case, the selectivity S is 10 in favor of Pb(II). The comparison of the conductimetry measurements and the analysis of cations (Fig. 7) 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

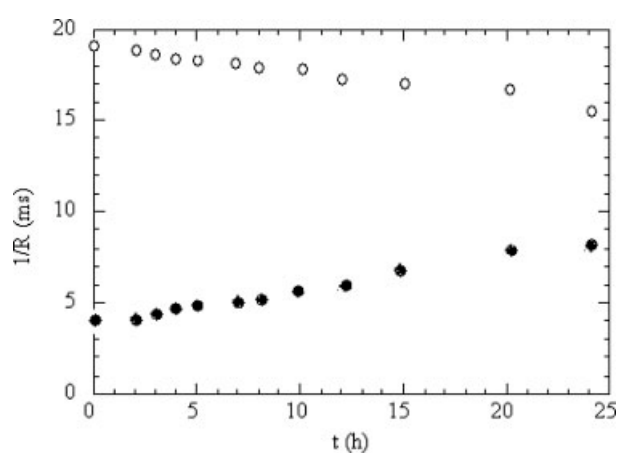


Figure 5 Individual transport of Cd^{2+} against the protons current across membrane M_I , evolution of conductance in reception phase \circ and in source phase \bullet .

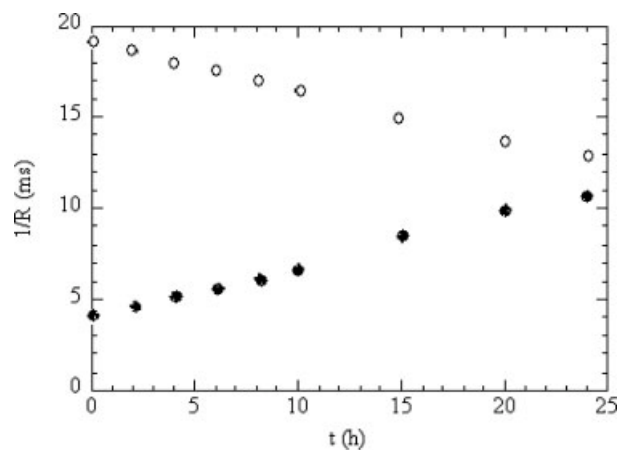


Figure 6 Competitive transport against the protons current across membrane M_I , evolution of conductance in reception phase \circ and in source phase \bullet .

the receiving phase (Fig. 8). In spite of the remarkable reduction of the concentration of $Hg(II)$ in the source phase indicating a transport to the receiving phase, we noted only a weak concentration in the receiving phase. This can be only due to the possible formation of stable complex in the membrane, which prevents the passage of the $Hg(II)$ in the receiving phase. To confirm this supposition, we placed this complexed membrane which was beforehand washed with deionized water between the two halves of the measuring cell, the phase source is filled this time with a solution of HNO_3 (10^{-1} M) and the receiving phase contains pure water at pH 7. 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.

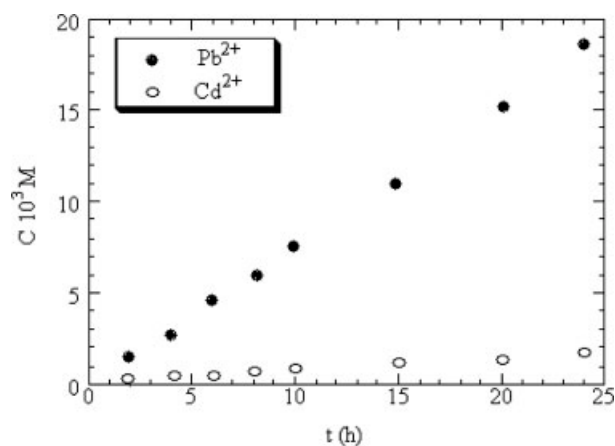


Figure 7 Competitive transport against the protons current, evolution of concentrations in reception phase.

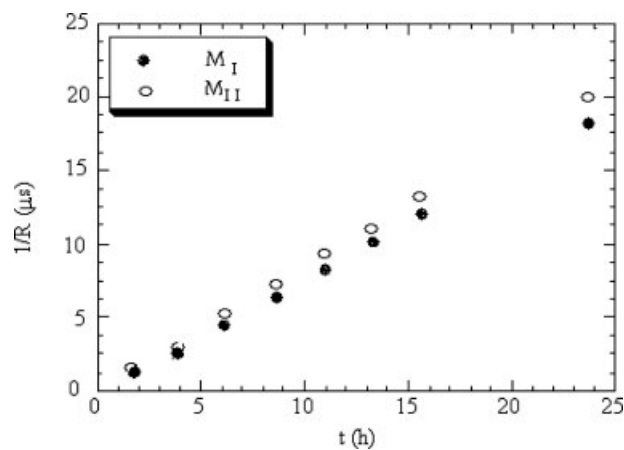


Figure 8 Individual transport of Hg^{2+} across membranes M_I and M_{II} , evolution of conductance in reception phase.

Membrane M_{II} (incorporating tripod 4)

Membranes M_I and M_{II} are different only by the CH_2 junctions between pyrazole units 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.

The results in Table I show that the individual transport of the two cations $Cd(II)$, $Pb(II)$ presents a reduction of diffusion fluxes F across M_{II} compared to M_I membrane (see Table I). This result is in perfect agreement with the free tetrapyrazolic ligands in which we noted an increase in complexation ability towards Cd^{2+} and Pb^{2+} when going from compound 2 with two CH_2 junctions to compound 1 without a CH_2 junction because of the chelating effect. Indeed, in most cases, bipyrazole groups act as convergent chelating bidentate donors. The term convergent refers to the nitrogen donor atoms coordinating to the same metal center. The CH_2 junctions form a six-membered ring with the complexed metal cation, whereas absence of the CH_2 junction leads to a five-membered ring, which is thus part of several such rings when the whole ligand is considered. It is well known¹⁸ that five-membered ring chelates are more stable than six-membered and four-membered ones. Thus, $N-C-C-N$ arrangements are preferable to the homologous $N-C-C-C-N$ and $N-C-N$ ones.

In competitive transport, we found that the diffusion flux F for $Pb(II)$ and $Cd(II)$ is respectively, 5×10^{-3} and 1.7×10^{-3} mole $h^{-1} m^{-2}$. The selectivity S ($F_{Pb(II)}/F_{Cd(II)}$) = 3, which means that $Pb(II)$ is equally better transported by this membrane (M_{II}).

Against the protons current, we notice that this mode accelerates the diffusion of $Pb(II)$ more than $Cd(II)$. The diffusion flux F of $Pb(II)$ was multiplied by a factor of 10 ($F = 50 \times 10^{-3}$ mole $h^{-1} m^{-2}$) and

that of Cd(II) was multiplied by a factor of 2.35 ($F = 4 \times 10^{-3} \text{ mole h}^{-1} \text{ m}^{-2}$). In this case, the selectivity S is 12.5 in favor of Pb(II).

We can thus say that in spite of the higher values of diffusion fluxes F in the case of the M_I membrane with the three studied means of transport, the selectivity S is higher in the case of the M_{II} membrane.

For mercury, which is well extracted by the free tetrapyrazolic tripodal ligand **2**,⁴ its transport by the membrane incorporating this ligand shows a blocking of the membrane probably because of 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 with the previous membranes¹⁰⁻¹² incorporating the mono-pyrazolic, the linear bi-pyrazolic units and the bipyrazolic tripods. We recall here that the tetrapyrazolic tripods present higher complexation ability towards the transition metal cations compared with the mono- and bi-pyrazolic ligands.⁴⁻⁶ 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 an interesting phenomenon of transport of alkali cations when incorporated to membranes materials.¹²

We recall that the membranes incorporating pyrazolic macrocycles are selective toward alkali cations¹² and the membranes incorporating mono- and bi-pyrazole units are selective toward Cd(II)^{10,11}; we underline here the selectivity of these membranes containing tetrapyrazolic units toward Pb(II).

CONCLUSION

In conclusion, we have prepared new membrane materials by photopolymerisation of a formulation spread over a PAN support. The formulation contains the methacrylic monomer, the styrene, and the photostart. The monomer was obtained by esterification of acyclic hydroxy-tetrapyrazoles with the methacryloyl chloride. Dense membranes were obtained by this method.

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

The free tetrapyrazolic tripods were demonstrated to extract mercury.⁴ This cation was not well transported by these membranes. This is probably because of 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.

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