Poly(vinyl chloride) functionalization by aliphatic and aromatic amines: application to the extraction of some metal cations

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Abstract: The aim of this study was to evaluate the efficiency of 3 new polymers obtained by functionalization of a commercial poly(vinyl chloride) by grafting amino-alkyl and amino-aryl groups to extract some metal cations from aqueous solutions.

The percentage of extraction was determined by comparing the initial electrical conductivity of the aqueous solution containing the studied metal and that of the aqueous solution at the extraction equilibrium. One of the obtained polymers gave an extraction ratio of $Sn^{2+} = 87.1\%$, which highlight the importance of the substitution of chlorine atoms by diethylenetriamine groups. These results were compared with those obtained by atomic absorption spectrometry.

A kinetic study of the extraction shows that the optimal duration of extraction was obtained with the polymer that has more chlorine atoms substituted by diethylenetriamine groups. The influence of metal extraction on the infrared spectra, differential scanning calorimetry diagrams, and X-ray diffraction of metal-loaded polymers was also studied.

Key words: Poly(vinyl chloride) (PVC), functionalization, metal cation, extraction

1. Introduction

Pollution of the aquatic environment by heavy metals from industrial and consumer waste is considered a major threat to aquatic organisms including fish and thus to human health.

Heavy metals are of serious concern due to their persistence in the environment and carcinogenicity to human beings. They cannot be destroyed biologically but are only transformed from one oxidation state or organic complex to another. Thus, it would be interesting to develop new materials for removing heavy metals from natural waters.

From PVC and to extract metal cations several products based on polymers have been synthesized. Shortly after the work by Frye and Horst on PVC and their theory of mechanism of reversible blocking,[1] several studies were dedicated to illustrate the presence of the unstable atoms of chlorine by undertaking chemical modifications on commercial PVC (i.e. plasticized PVC) as well as samples prepared in laboratories.

Several chemical reactions were applied such as substitution, elimination, reduction, and degradation. By far, nucleophilic substitution was the reaction studied most. However, when the basicity of the nucleophile exceeds its nucleophilic power, the elimination of HCl can occur with substitution. Kameda et al.[2] conducted substitution of chlorine in PVC by I^-, SCN^-, OH^-, and N_3^- in a solution of DMF or ethylene glycol. He et

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al.[3] realized highly efficient dechlorination of PVC by using 1-butyl-3-methylimidazoliumhydroxyde at 180 °C and at atmospheric pressure. Navarro et al.[4] realized the modification of PVC with several aromatic thiols (4-fluorothiophenol, 4-chlorothiophenol, 4-bromothiophenol, 3,4-di-fluorothiophenol, pentafluorothiophenol, and pentachlorothiophenol) by using cyclohexane as solvent. Moulay[5] presented many chemical modifications of PVC based on reports over the last decade, along with related applications; these modifications are presented according to the bond formed, C_{PVC}-X, between the PVC carbon C_{PVC} and atom X (X = N, O, S, Hal) of the modifying molecule.

Several extraction tests of metal cations have been carried out. In fact, Bagheri et al.[6] studied efficient removal of Cr^{3+}, Pb^{2+}, and Hg^{2+} ions from industrial effluents by hydrolyzed/thioamidated polyacrylonitrile fibers. Arsalani et al.[7] studied removal of Ni(II) from synthetic solutions using new amine-containing resins based on polyacrylonitrile. Maksin et al.[8] studied the kinetics of Cr(VI) sorption by methacrylate-based copolymers grafted on diethylene triamine. Esengül et al.[9] used poly(2-chloroaniline)/polyvinylidenefluoride cation-exchange membranes for the removal of chromium(III) and copper(II) ions from aqueous solution with Donnan dialysis.

In the present work, we synthesized new products by grafting amino-alkyl and amino-aryl groups on PVC for use in the extraction of a series of metal cations such as lead, magnesium, tin, and cadmium, which are widespread in the environment and known to be harmful to human health.

2. Results and discussion

2.1. Analysis of synthesized polymers

2.1.1. DSC analysis

The DSC diagram (Figure 1) of the commercial PVC has a melting point of 279 °C with the absence of an exothermic peak up to 500 °C; it also has a glass transition around 80 °C. That of the polymer P_0 presents 3 endothermic transformations at 204, 341, and 418 °C with the absence of an exothermic peak up to 500 °C. In the case of polymer P_1 we note the presence of 2 endothermic transformations at 120 and 324 °C and an exothermic peak at 178 °C. Finally the diagram of the polymer P_2 exhibits an exothermic peak at 177 °C and 2 endothermic transformations at 185 and 367 °C.
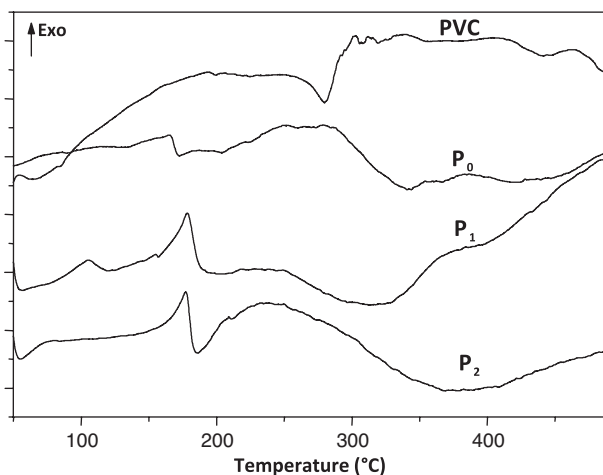

Figure 1. DSC diagrams of commercial PVC, polymers P_0, P_1, and P_2.

2.1.2. Analysis by XRD

The X-ray (Figure 2) tells us about the amorphous nature of the commercial PVC and the 3 synthesized materials P_0, P_1, and P_2.

2.1.3. IR spectroscopy

Figure 3 shows the IR spectra of the powder form of the studied polymers. On the commercial PVC spectrum, we notice a high intensity band assigned to the stretching vibration ν_{C-Cl} at 690 cm^{-1}. The spectrum of P_0 shows 2 broad peaks around 3382.97 and 3309.42 cm^{-1} attributed to the stretching vibration of NH primary amines. In the case of P_1 we observe that the band ν_{C-Cl} at 690 cm^{-1} becomes very low compared to that corresponding to P_0 as a consequence of the realization of the high-temperature reaction inducing an increase in the number of chlorine atoms substituted by diethylenetriamine groups.
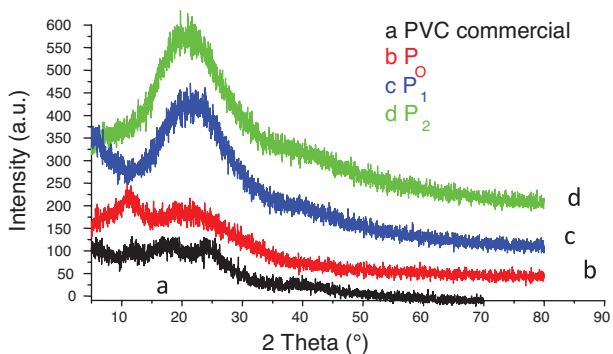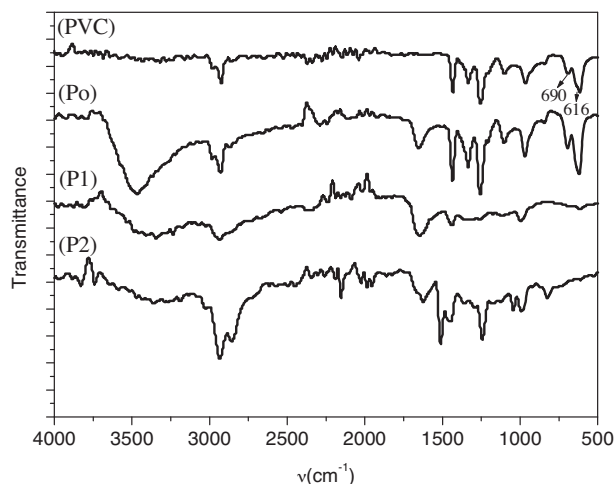

Figure 2. XRD of commercial PVC, P_0, P_1, and P_2.

Figure 3. IR spectra of PVC, P_0, P_1, and P_2.

The IR spectrum of P_2 shows some bands of stretching vibration $\nu_{C=C(arom)}$ at 1617, 1513, and 1437 cm^{-1}, ν_{C-O} at 1244, and bending vibration bands $\delta_{\text{tetrahedral carbon}-H\,(Me)}$ at 1332 and $\delta_{\text{trigonal carbon}-H\,(para-substituted aromatic)}$ at 828 cm^{-1}.

2.1.4. Proposed structures

Based on the analytical results obtained by different physicochemical analyses (absorption IR, DSC, and X-ray diffraction), we propose the following structures for the 3 materials P_0, P_1, and P_2 in Scheme 1.

The structure proposed in Scheme 1c is based on the IR spectrum of the polymer P_2, which shows that the chlorine atoms have not all been substituted.

2.2. Study of extraction

2.2.1. Percent removal

The extraction percentage of metal cations with the polymers was calculated as follows:

$$\%E = (C_0 - C_f)/C_0 \times 100 = (\sigma_0 - \sigma_f)/\sigma_0 \times 100$$
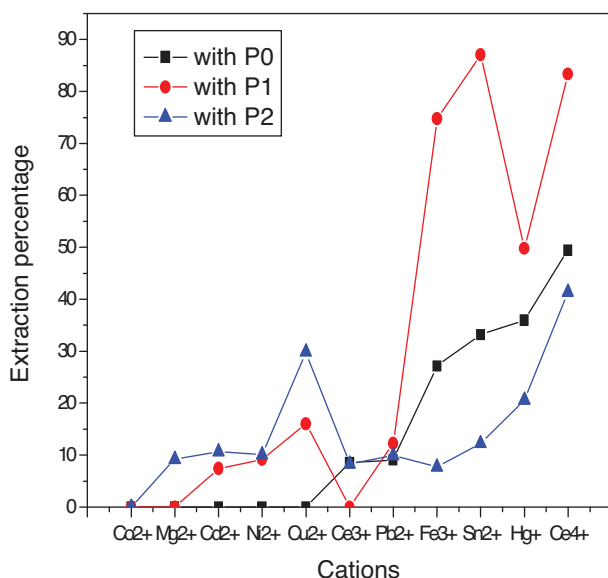
diethylenetriamine, KI

PVC $\xrightarrow{\hspace{3cm}}$ (P$_0$)

dioxane, 48h, 80°C

Diethylene triamine, KI

PVC $\xrightarrow{\hspace{3cm}}$ (P$_1$)

THF, 3h, 160°C

(a)

(b)

4-methoxyaniline, KI

(P$_1$) $\xrightarrow{\hspace{3cm}}$ (P$_2$)

THF, 3h, 150°C

(c)

Scheme 1. Scheme of synthesis of (a) amino-PVC P$_0$, (b) amino-PVC P$_1$, and (c) amino-p-anisidine-PVC P$_2$.

σ_0 (μS/cm): initial electrical conductivity of the aqueous solution containing the metal.

σ_f (μS/cm): electrical conductivity of the aqueous solution at the extraction equilibrium.

C$_0$ (mol/cm^3): initial concentration of metals in aqueous solution.

C$_f$ (mol/cm^3): final concentration of the metal in the aqueous solution at the extraction equilibrium.

2.2.2. Interpretation

Figure 4 shows the curves representing the percentage of metal cation removal with the studied materials P$_0$, P$_1$, and P$_2$. These results are the average of 3 experiments for each studied metal.

These results show that the material P$_1$ gives the best extraction percentages with the cations Fe^{3+}, Hg$_2^{2+}$, Ce^{4+}, and Sn^{2+}. Sn^{2+} is extracted with a percentage of 87.1%. This confirms the proposed structures in Scheme 1 since the material P$_1$ corresponds to a greater number of chlorine atoms substituted compared to P$_0$.

The material P$_2$ is a poorer extractant than P$_0$ for cations Fe^{3+}, Sn^{2+}, Hg$_2^{2+}$, and Ce^{4+} probably due to the presence of aromatic amine groups in P$_2$, which makes it less accessible. The material P$_2$ gives

Figure 4. Compared extraction percentage of metal cations with P_0, P_1, and P_2.

extraction percentages for cations Mg^{2+}, Cd^{2+}, Ni^{2+}, and Cu^{2+} slightly better than those obtained by P_0 and P_1. A priori the presence of oxygen atoms due to the introduction of groups in the structure of anisidine (P_2) confirmed by IR analysis promotes the extraction of these metal cations.

2.3. Atomic absorption spectrometry (AAS)

2.3.1. Method of analysis

In this work, flame atomic absorption spectrometry was used to assay the metals using a PinAAcle 900 T spectrometer.

The calibration of the spectrometer was performed using standard solutions for each metal. The calibration range was between 0.2 and 2 ppm.

2.3.2. Interpretation

The extraction was performed using the technique described in section 3.4. Table 1 shows the extraction percentages obtained by conductivity measurements and by AAS for the studied metals.

Table 1. Extraction percentages obtained with conductivity and atomic absorption spectrometry (AAS).

Metal cation		Ce^{3+} *	Ce^{4+} *	Hg_2^{2+}	Sn^{2+}	Pb^{2+}	Fe^{3+}	Cd^{2+}	Ni^{2+}	Cu^{2+}	Mg^{2+}
Percentage of	Conductivity	8.5	49.4	36	33.2	9.1	27.1	0	0	0	0
extraction with P_0	AAS	-	-	44.2	41.1	17.0	35.1	11.7	7.9	10.8	9.3
Percentage of	Conductivity	0	83.4	49.8	87.1	12.2	74.8	7.4	9.1	16	0
extraction with P_1	AAS	-	-	57.7	94.9	20.3	82.6	19.5	17.2	27.1	8.8
Percentage of	Conductivity	8.3	41.4	20.6	12.2	9.9	7.7	10.6	10	29.8	9.2
extraction with P_2	AAS	-	-	28.9	20.5	18.1	15.9	22.6	18.3	40.8	18.2

*Ce^{3+} and Ce^{4+} studied only by conductivity.

Except for Ce^{3+} and Ce^{4+}, which were studied only by conductivity, the results show that the atomic absorption method gives higher extraction percentages than those found with conductivity. The differences between the extraction percentages obtained by the 2 methods varied between 8% and 12%.

2.4. Kinetic study

2.4.1. Curves $\sigma = f(t)$

Figure 5 shows the variation in the conductivity σ (μS/cm) of different aqueous solutions over time with respectively P_0, P_1, and P_2.
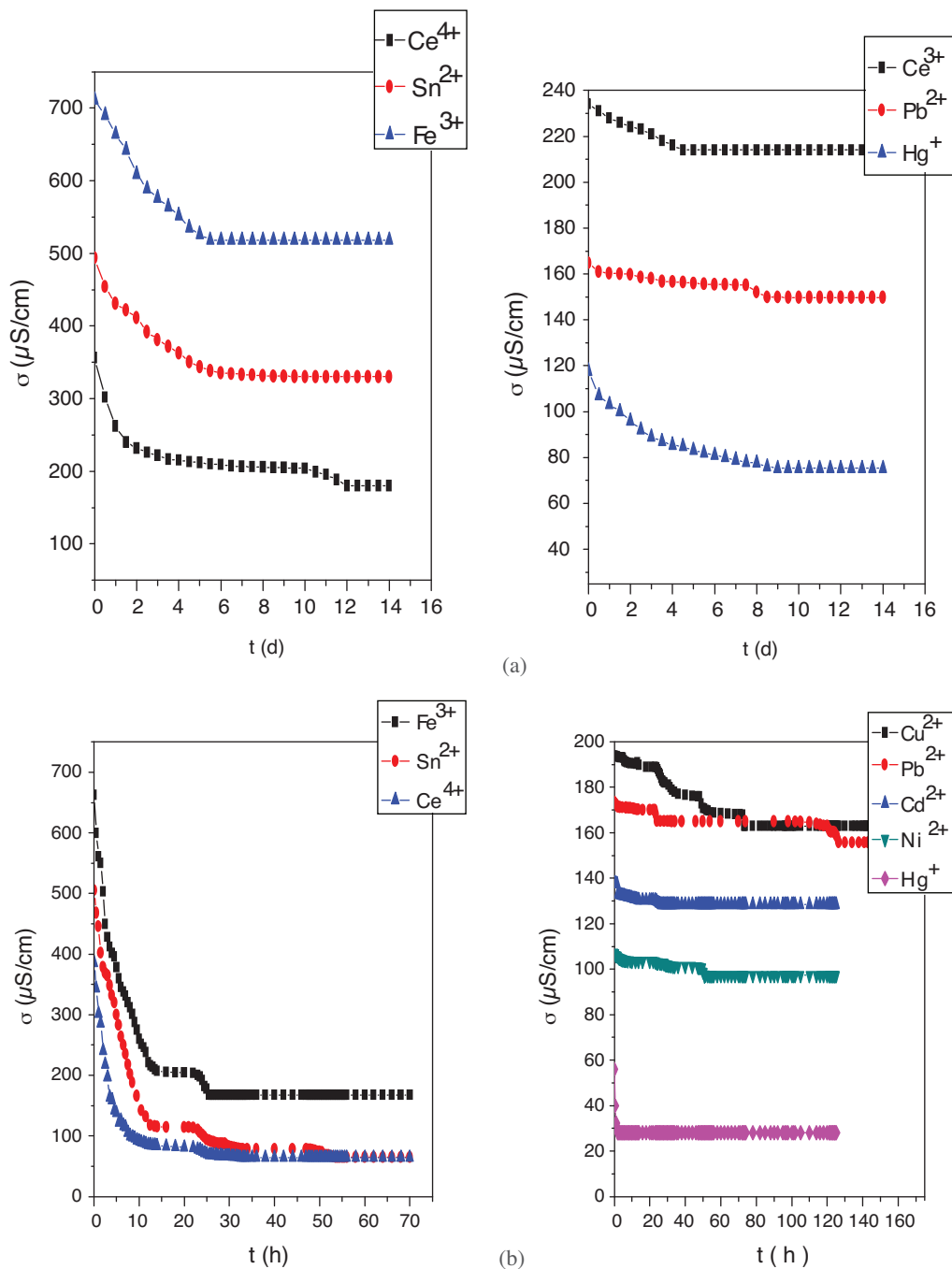

Figure 5. Curves of variation of conductivity with time for some cations (a) in contact with P_0, (b) in contact with P_1.
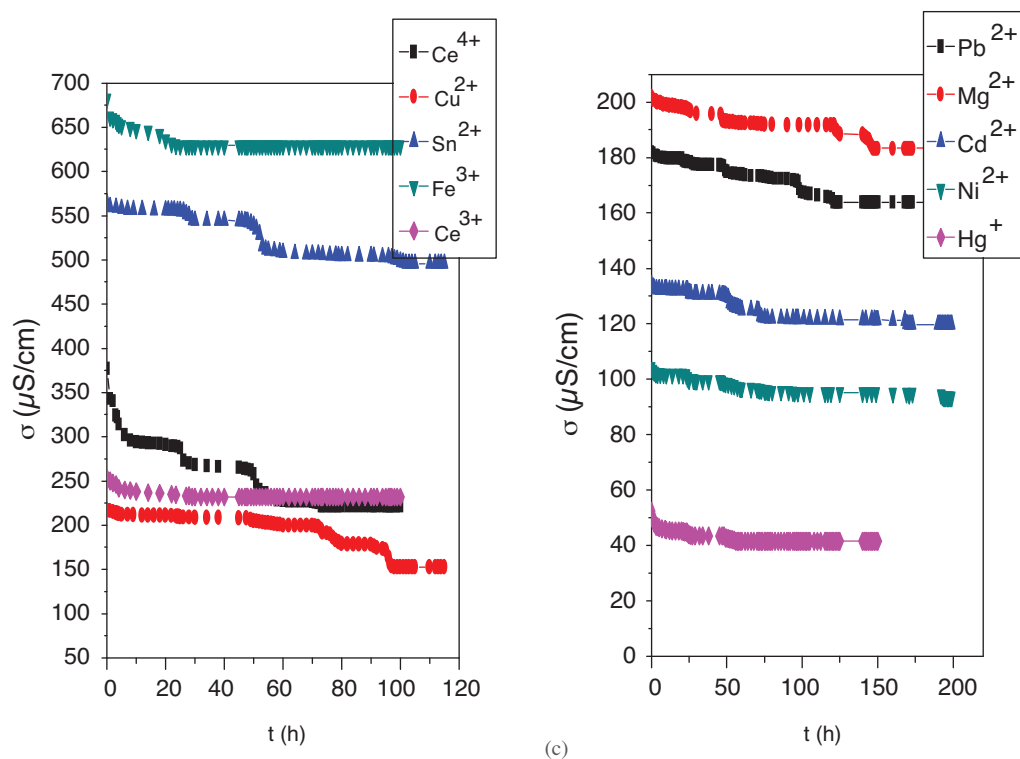
Figure 5. Curves of variation of conductivity with time for some cations (c) in contact with P_2.

2.4.2. Interpretation

The curves representing the change in conductivity σ in different aqueous solutions with time show that σ decreases and then after a period Δt remains constant. Δt represents the optimal duration of extraction (Table 2).

Table 2. Optimal duration of extraction with polymers P_0, P_1, and P_2.

Metal cation	Ce^{3+}	Fe^{3+}	Hg_2^{2+}	Sn^{2+}	Pb^{2+}	Ce^{4+}	Cd^{2+}	Ni^{2+}	Cu^{2+}	Mg^{2+}
Duration of extraction (days) with P_0	4	5.5	9	10	11	12	-	-	-	-
Duration of extraction (h) with P_1	-	25.5	2	53.5	150.5	32.5	26	53.5	73	-
Duration of extraction (h) with P_2	29	27	56	102	121	73	170	194	98	147

These results show that P_2, which has more chlorine atoms substituted by diethylenetriamine groups, gives better results (shorter extraction durations) than P_0. However, due to the introduction of the aromatic amine groups in this polymer (P_2) the extraction durations were extended compared to P_1. Thus, P_1 gives the optimal extraction durations.

2.5. Influence of extracted metals on some physical characteristics of new materials

2.5.1. Influence on the IR spectra

The IR absorption spectra of the studied complexes (Figure 6) indicate that the influence of free polymers and their complexes on IR spectra is not very significant. This could be due to the counter-anions of metal cations because of the use of these salts: $Ce(NO_3)_3, 6H_2O$; $Ce(SO_4)_2, 4H_2O$; $CuSO_4, 5H_2O$; $Pb(NO_3)_2$; $CdCl_2, H_2O$; $SnCl_2, 2H_2O$; and $MgSO_4, 7H_2O$. Apparently, the anions SO_4^{2-} and NO_3^- easily fix water molecules via hydrogen bonds, which makes the drying of new materials difficult.
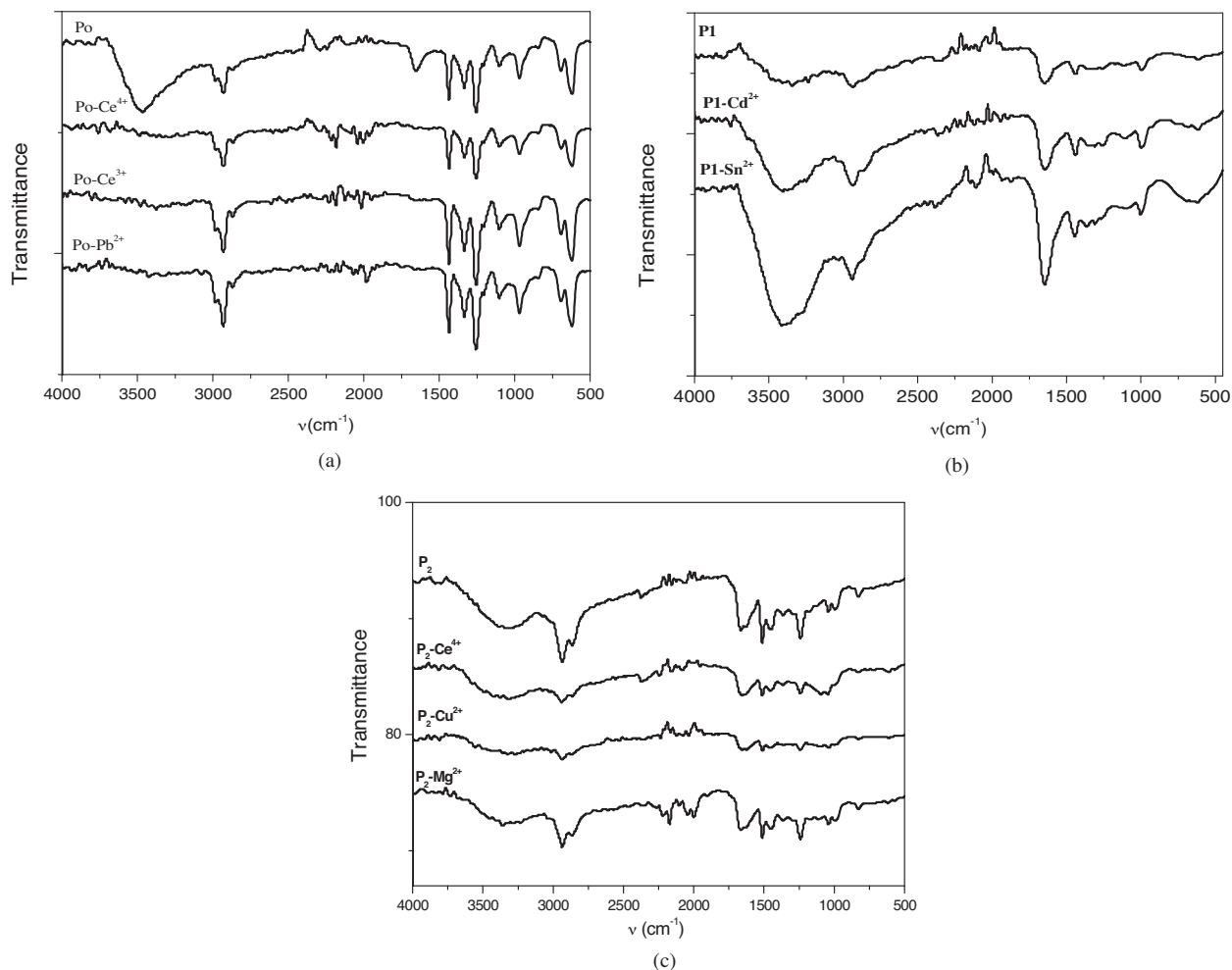
Figure 6. IR spectra of (a) polymer P_0 and complex P_0-Ce^{4+}, P_0-Ce^{3+}, and P_0-Pb^{2+}; (b) polymer P_1 and complex P_1-Cd^{2+}, P_1-Sn^{2+}; and (c) polymer P_2 and complex P_2-Ce^{4+}, P_2-Cu^{2+}, and P_2-Mg^{2+}.

2.5.2. Influence on DSC diagrams

DSC complex diagrams for P_0-Ce^{4+}, P_1-Sn^{2+}, and P_2-Ce^{4+} are shown in Figure 7.

The DSC diagrams show a difference in endothermic transformations, which occur at 204, 341, and 418 °C for P_0 and at 121 and 219 °C for the complex P_0-Ce^{4+}. The complex P_0-Ce^{4+} also presents an exothermic peak at 242 °C, which was not present in the case of P_0.

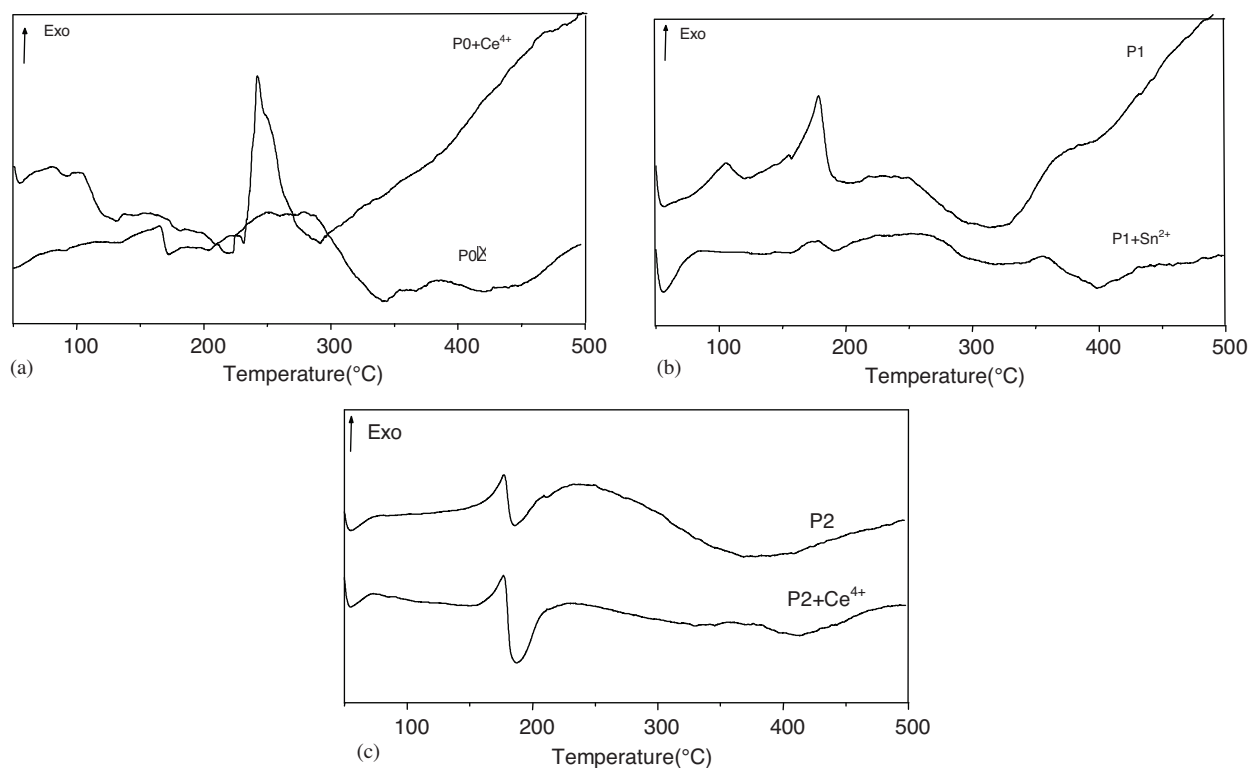**Figure 7.** DSC diagrams of (a) P_0 and complex P_0-Ce^{4+}, (b) P_1 and complex P_1-Sn^{2+}, and (c) P_2 and complex P_2-Ce^{4+}.

The DSC diagrams confirm the complexation of P_1, which has 2 endothermic transformations at 120 and 324 °C and an exothermic peak at 178 °C, while that of the complex P_1-Sn^{2+} has 3 endothermic transformations at 190, 323, and 398 °C with the absence of an exothermic peak up to 500 °C.

In the case of P_2 and complex P_2-Ce^{4+}, there is a difference starting from 350 °C since the DSC diagram of free polymer presents 2 endothermic transformations at 185 and 367 °C, while that of the complex has 2 endothermic transformations at 187 and 413 °C.

2.5.3. Influence on XR diffractograms

The X-ray diffractograms of the complexes P_0-Ce^{4+}, P_1-Sn^{2+}, and P_2-Ce^{4+} recorded for 2θ between 0° and 90° are shown in Figure 8.

In the X-ray diffractograms of P_0 and P_0-Ce^{4+}, we notice a shift of bands $2\theta = 11°$ and 21.5° to $2\theta = 12°$ and 22° and higher intensities indicate the insertion of Ce^{4+} cation in the network of P_0, which results in a change in the observed diffraction.

The offset of the strip $2\theta = 20.9°$ to $2\theta = 22°$ and the reduction in its intensity confirm the insertion of Sn^{2+} cation in the network of P_1. The emergence of a new band at $2\theta = 12.5°$ suggests chelation of Sn^{2+} in P_1.

In this case, the X-ray diffractograms of P_2 and P_2-Ce^{4+} show a shift of the band towards low angles from $2\theta = 22.3°$ to $2\theta = 20.34°$ with an increase in intensity, which proves the insertion of Ce^{4+} cation in the network of P_2. The emergence of a new band at $2\theta = 11.5°$ suggests the presence of 2 types of insertion sites.
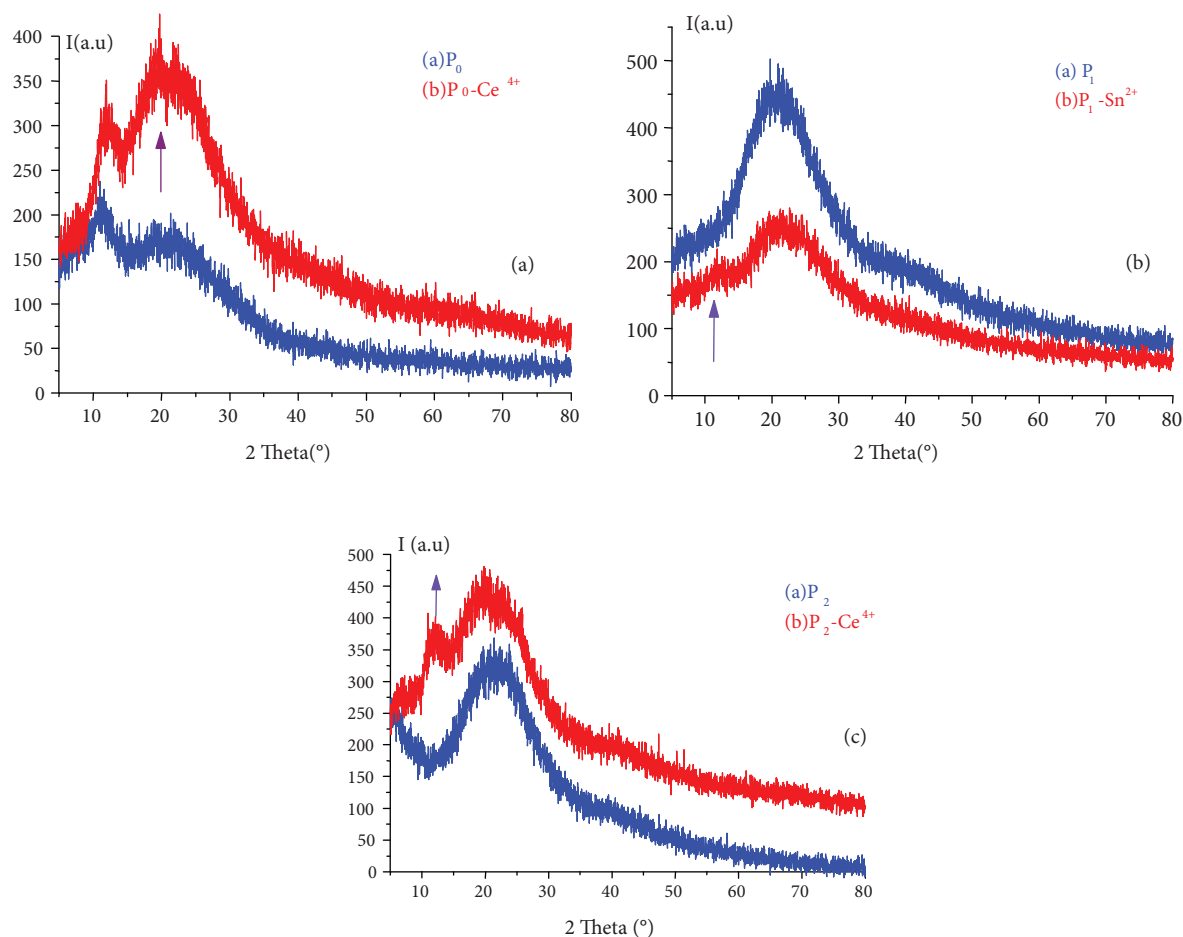
Figure 8. XRD of amino-PVC P_0 and complex P_0-Ce^{4+} % E = 49.4%, (b) amino-PVC P_1 and complex P_1-Sn^{2+} % E = 87.1%, and (c) amino-p-anisidine-PVC P_2 and complex P_2-Ce^{4+} % E = 41.4%.

3. Experimental

3.1. Chemicals

The commercial PVC, Mw = 48,000 (packed in Switzerland), was purchased from Fluka, diethylenetriamine and 4-methoxyaniline were purchased from Aldrich (Germany), dioxane and THF were purchased from Prolabo (Groups Rône Poulenc), and chemicals including $Ce(NO_3)_3$,$6H_2O$; $Ce(SO_4)_2$,$4H_2O$; $CuSO_4$,$5H_2O$; $Pb(NO_3)_2$; $CdCl_2$,H_2O; $SnCl_2$,$2H_2O$; and $MgSO_4$,$7H_2O$ were obtained from Germany.

3.2. Instrumentation

IR: Thermo Scientific Nicolet IR 2000 (Madison, WI, USA), DSC: Setaram DSC 131 (Caluire, France), XR: X'Pert Pro. dar Panalytical min voltage 40 kV, current 30 mA (Karlsruhe Germany), Conductivity: Consort C861 (RS Components, Beauvais Cedex), AAS: PinAAcle 900 T Atomic absorption spectrometer/PerkinElmer (Waltham, MA, USA).

3.3. Synthesized polymers

3.3.1. Synthesis

In order to make the polymer more reactive, we performed the Conant–Finkelstein reaction[10] to replace some chlorine atoms of the original PVC with atoms of iodine through a nucleophilic substitution mechanism.

Aromatic amines, less reactive than aliphatic ones, do not react with PVC at temperatures above 100 °C, since the lone pair of nitrogen is involved in the conjugation with the benzene ring.

3.3.2. Preparation of amino-PVC (P_0)

First, 4.8 g of commercial PVC, 1.2 g of diethylenetriamine, and 1 g of potassium iodide were mixed in 60 mL of dioxane. Stirring was maintained for 48 h at 80 °C. At the end of the reaction the obtained product was washed with distilled water and with diethyl ether and finally dried in an oven at 65 °C to obtain a yellow solid (P_0) of mass m = 7.46 g. The obtained yellow solid was then crushed and washed several times with distilled water until the wash water no longer drained any salt (verification of the electrical conductivity of the wash water).

3.3.3. Preparation of amino-PVC (P_1)

In a hydrogenating bomb 4.8 g of commercial PVC, 8 g of diethylenetriamine, and 1 g of potassium iodide were mixed in 70 mL of THF. After stirring for 3 h at 160 °C we obtained a paste, which was washed several times with distilled water to obtain a brown powder that was crushed and then washed several times with distilled water and with diethyl ether and finally dried in an oven at 65 °C to obtain a mass m = 10.48 g (P_1).

3.3.4. Preparation of amino-p-anisidine-PVC (P_2)

In a hydrogenating bomb 11 g of amino-PVC (P_1), 11 g of 4-methoxyaniline, and 3 g of potassium iodide were mixed in 70 mL of THF. After stirring for 3 h at 150 °C a paste was obtained. Washed several times with distilled water it turns into powder, which was crushed and washed several times with distilled water and with diethyl ether and finally dried in an oven at 65 °C to get a yellow-brown powder (P_2) of mass m = 7.27 g.

3.4. Technique of extraction by AAS

In a 30-mL vial, 20 mL of aqueous solution of metal salt (5×10^{-4} M) was mixed with 100 mg of each polymer (P_0, P_1, or P_2). At the extraction equilibrium and after filtration, each sample was diluted with distilled water and assayed to determine the final concentration of metal remaining at the extraction equilibrium.

The extraction percentage of the metal is given by the following relationship:

$$\%E = (C_0 - Cf)/C_0 \times 100$$

C_0: initial concentration of the metal in the aqueous solution.
C_f: final concentration of the metal in the aqueous solution at the extraction equilibrium.

3.5. Kinetic study

In a 30-mL vial, 20 mL of aqueous solution of metal salt (5×10^{-4} M) was mixed with 100 mg of each polymer (P_0, P_1, or P_2 carefully ground powders in an Agathe mortar). The mixture was stirred and the

initial conductivity was measured, σ_0. The conductivity of the mixture was then monitored over time. The experiment was performed with Sn^{2+}, Pb^{2+}, Ce^{4+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Co^{2+}, Hg_2^{2+}, $Fe^{3,+}$ and Ce^{3+}.

4. Conclusions

This work enabled us to obtain 3 new materials by functionalization of a PVC (Mw = 48,000) namely amino-PVC (P_0 and P_1), and amino-p-anisidine-PVC (P_2). The metal cations extraction was performed with P_0, P_1, and P_2. The first polymer (P_0) is selective for Sn^{2+}, Hg_2^{2+}, and Ce^{4+} cations. The second one (P_1) is selective for Hg_2^{2+}, Fe^{3+}, Ce^{4+}, and Sn^{2+} cations. The third polymer (P_2) is cation-selective for Hg_2^{2+}, Cu^{2+}, and Ce^{4+}.

This study also showed that increasing the number of substituents in diethylenetriamine P_1 compared to P_0 improves the properties of functionalized PVC as extractant. In contrast, the introduction of aromatic amine groups in P_2 decreased these extractant properties. In fact, P_2 becomes a less good extractant than P_0 and P_1, which is probably due to the high congestion near the functionalized polymer complexing sites. However, P_2 gives shorter durations of extraction than P_0 does.

These results show that the polymers P_0, P_1, and P_2 may be useful in the purification of polluted waters.

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