Selective Solid–Liquid Extraction of Cations Using Solid-Phase Polyamides with Crown Ether Moieties as Cation Host Units

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ABSTRACT: This work describes the interaction of alkaline, alkaline earth, transition metal, heavy metal, and lanthanide cations from nitrate solutions with synthetic polyamides. The polyamides have pendant structures acting as cation host moieties. The host subgroups are benzo-12-crown-4, benzo-15-crown-5, benzo-18-crown-6, and the three dipodal counterparts of the three benzo-crown units. This interaction has been analyzed in terms of competitive polyamide solid-phase extraction of nitrate cations from aqueous or acetronitrile solutions. The solid-phase extraction of water or acetonitrile solutions of alkaline, alkaline earth, transition metal, heavy metal, and lanthanide ions using solid-phase polyamides is performed with a degree of selectivity. Higher selectivity is observable in the extraction of Pb(II) from a set of heavy metal ions in water and acetonitrile solutions, and the extraction of Cr(III) from a set of transition metals in acetonitrile solutions. It is a noteworthy result, which along with the reusability of the solid-phase polyamides points to potentially successful applications in the field of environmental chemistry: the decontamination and elimination of *poisoning* cations, the separation and modification of cation mixtures, and the development of fixed-site carrier membranes for selective transport or manufacture of cation-sensitive sensors. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2875–2884, 2007

Key words: polyamides; separation techniques; metal–polymer complexes; selective solid–liquid cation extraction

INTRODUCTION

Host–guest or supramolecular chemistry is based on the specificity of molecular interactions in which a *host* molecule interacts with a *target* or *guest* compound. If a feeble intermolecular interaction between the host and its guest is highly specific, the term recognition can be used, and the host can be employed in the development of technological devices based on its recognition properties and capabilities, as sensors, catalysts, or permselective membranes.[1–11]

The discovery of biological molecules that are able to bind porphyrin or valinomycin cations on a selective basis led researchers to try to mimic the recognition capabilities of some important natural products. This resulted in discovery of the selective interactions of macrocycle polyethers, or crown compounds, with cations through ion–dipole interactions, in which the positively charged cations interact with the lone pairs of the ether linkages.[12,13]

In previous studies, our research group has worked on the interactions of lanthanide(III) ions with methacrylic polymers bearing pendant crown ether moieties.[14,15] In this paper, we extend the study to selective extraction of cations from water or acetonitrile solutions containing cation nitrates using solid-phase polyamides. These are competitive solid–liquid extraction experiments that entailed keeping a mixture of cations of each cation series (alkaline, alkaline earth, transition metal, heavy metal, and lanthanide) in contact with each one of the six polyamides. The extraction of cations is carried out with a degree of selectivity, and the cation solvents played an important role in selectivity and in the extraction percentage of each cation. The aromatic polyamide has the peculiarity of bearing three host cation moieties—a benzo-12-crown-4, a benzo-15-crown-5, and a benzo-18-crown-6—in the pendant structure of each structural unit, as well as three dipodal counterparts of these tree crown subunits.[16–18]

We have chosen a polyamide backbone due to the outstanding thermal and mechanical stability of these polymers, but also due to their poor solubility

in common organic solvents,[16–24] which makes them especially useful as solid materials in molecular recognition, because they can be regenerated and reused by a simple procedure of filtration and washing.[25–30]

The results described in this article might potentially lead to practical applications for cation elimination, extraction and purification, and to selectivity tests for the study and the development of sensor membranes to be used as spectroscopic cation probes, ion-selective electrodes, and cation-selective transport membranes.

EXPERIMENTAL

Polyamides

The diacid monomers (Scheme 1) were prepared by previously described procedures.[16–18] The polyamides, depicted in Scheme 1, were prepared according to the general procedure[16–18]: in a 50-mL three-necked flask fitted with a mechanical stirring device, 10 mmol of diamine, 10 mmol of diacid, and 1.4 g of lithium chloride were dissolved in a mixture of 6 mL of pyridine, 22 mmol of TPP, and 20 mL of NMP. The solution was stirred and heated at 110°C in a dry nitrogen blanket for 4 h. The system was then cooled at room temperature and the solution precipitated in 300 mL of methanol, rendering a swollen fibrous precipitate. The polymer obtained herein was filtered off and washed with distilled water and acetone, and then extracted with acetone for 24 h in a Soxhlet, and dried in a vacuum oven at 80°C overnight. Yields were quantitative for all the polymers.
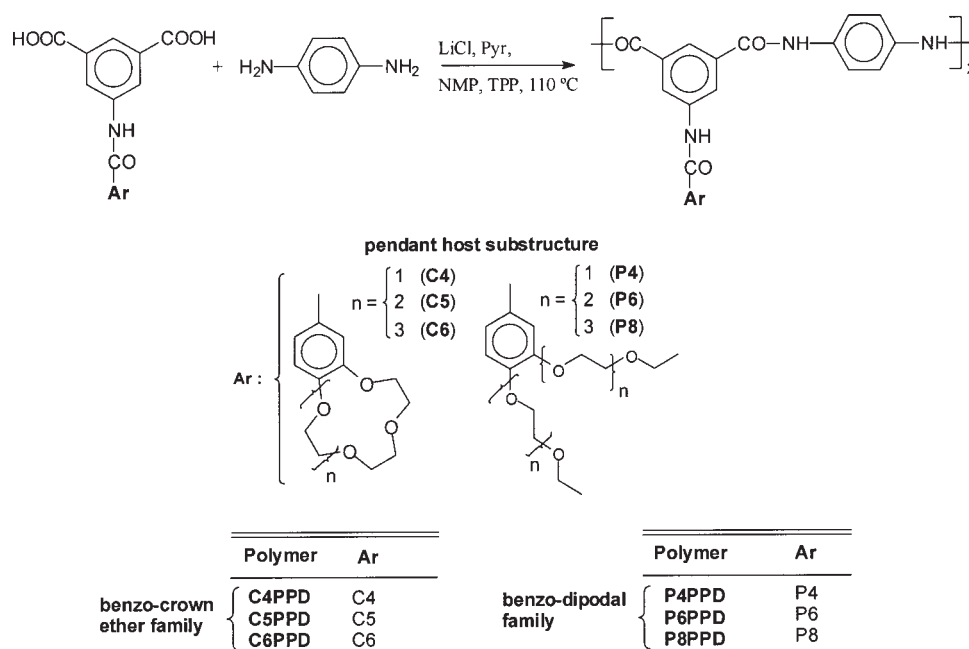
Measurements

Cation concentrations in the extraction studies were determined by inductively coupled plasma mass spectrometry (ICP, Agilent 7500 i). Consecutive dilutions of sample aliquots with ultrapure water/nitric acid (5% v/v) were made to reach concentrations in the range of the calibration curve, from 0 to 40 ppb.

Solid–liquid extraction

The competitive solid–liquid extraction of each cation series: alkaline [Li(I), Na(I), K(I), Rb(I), Cs(I)], alkaline earth [Mg(II), Ca(II), Sr(II), Ba(II)], transition metal [Cr(III), Mn(II), Co(III), Ni(II), Cu(II), Zn(II)], heavy metal [Ag(I), Cd(II), Hg(II), Pb(II)], and lanthanide ions [La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III)] was carried out as follows: ∼ 10 mg of the proper polymer was shaken with 1 mL of a water solution of the proper cation series for a week at 25°C (liquid phase) (from previous kinetic experiments on extraction, equilibrium can be said to be achieved in 3 days). The molar ratio of the overall cations in each cation series to crown subunits (polymeric structural units) was 1 : 1, and all the cations of a series were put at the same concentrations. After filtration, the concentration of the cations in the water solution phase was determined by ICP, and direct information of the selectivity of polyamides toward metal ions was obtained.

benzo-crown ether family	Polymer	Ar
	C4PPD	C4
	C5PPD	C5
	C6PPD	C6

benzo-dipodal family	Polymer	Ar
	P4PPD	P4
	P6PPD	P6
	P8PPD	P8

Scheme 1 Polyamide synthesis: Acronyms and structure.

RESULTS AND DISCUSSION

If a solution of different target or guest molecules is in contact with a solid phase that can interact selectively with the guest molecules, thus acting as solid host molecules, a solid–liquid extraction takes place. In our experiments, the crown ether moieties of the solid polyamides act as host molecules for cations dissolved in either water or acetonitrile. The selectivity and the effectiveness of the extraction can be studied in terms of extraction percentage (%E), distribution coefficient (Kd'), selectivity ($\alpha_{S,L}$), and cation crown occupation percentage (%O). The distribution coefficient is commonly defined as the concentration ratio of the cation in both phases, and is a measure of the capacity of the material to extract cations under competitive conditions, see eq. (1), where V is the solution volume in liters and m the polymer mass in kilograms.[31,32]

$$Kd = \left(\frac{\%E}{100 - \%E}\right)\left(\frac{V}{m}\right) \qquad (1)$$

In order to achieve better and more comparable results between different polymers, a modification in the distribution coefficient can be introduced. The molar amount of polymer structural units (n) instead of polymer mass can be employed, thus eq. (1) is transformed into eq. (2).

$$Kd' = \left(\frac{\%E}{100 - \%E}\right)\left(\frac{V}{n}\right) \qquad (2)$$

The solid–liquid extraction selectivity, $\alpha_{S,L}$, represents the ratio of two distribution coefficients [eq. (3)]. The cation with highest distribution coefficient (Kd'_{M2}) in each cation series is taken as the reference for the ion series.

$$\alpha_{S,L} = \frac{Kd_{M1}}{Kd_{M2}} = \frac{Kd'_{M1}}{Kd'_{M2}} \qquad (3)$$

Assuming an ideal interaction of one cation per polymer structural unit, the crown or podand occupation level percentage (%O) has also been calculated as shown in eq. (4), where S : cation represents the total moles of the {polymer structural unit : cation} complexes for each cation series, and S_0, the initial
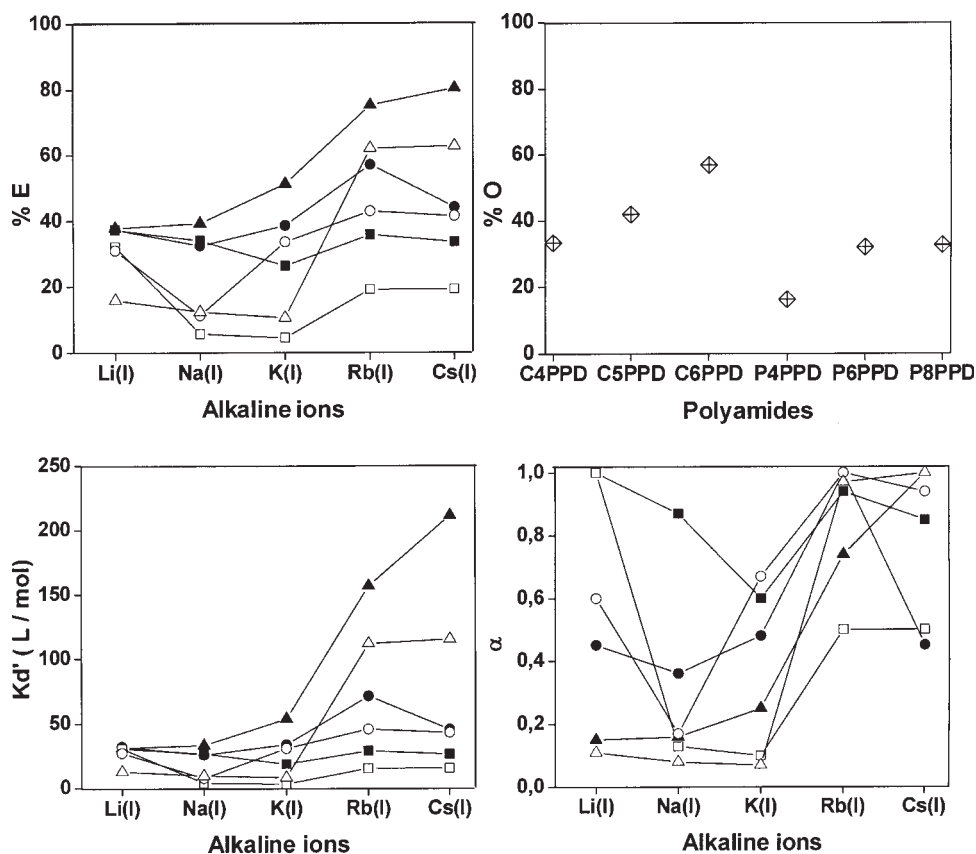

Figure 1 Solid–liquid extraction of alkaline ions in acetonitrile solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].
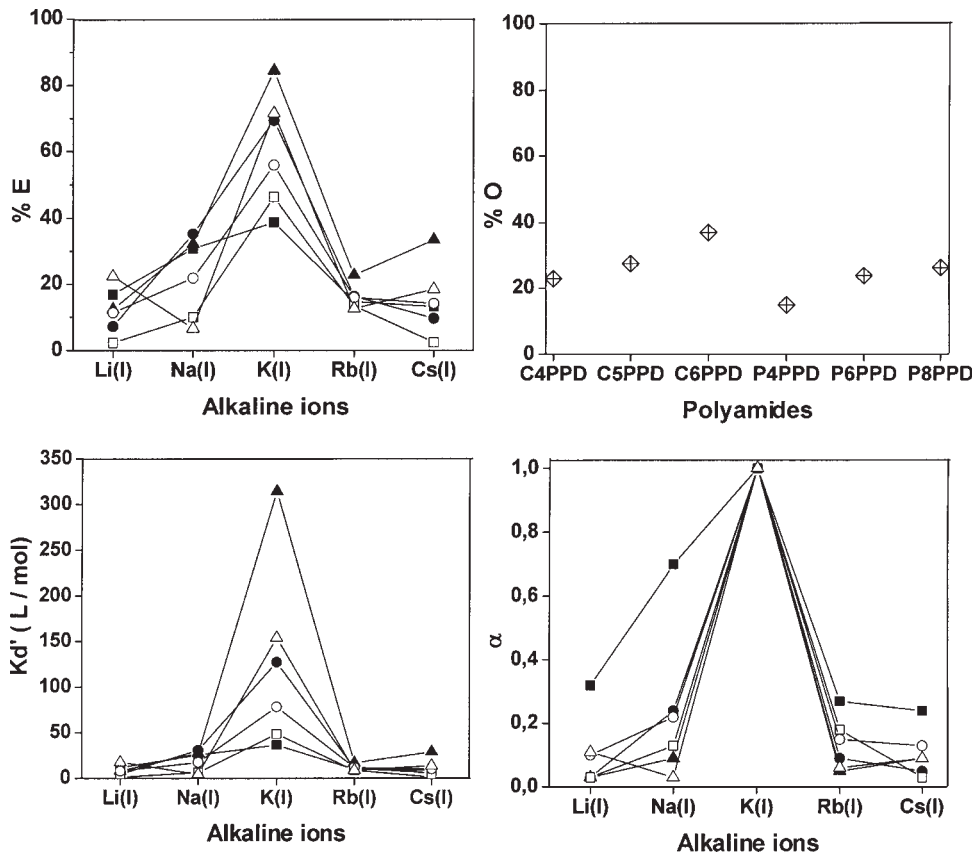
Figure 2 Solid–liquid extraction of alkaline ions in water solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].
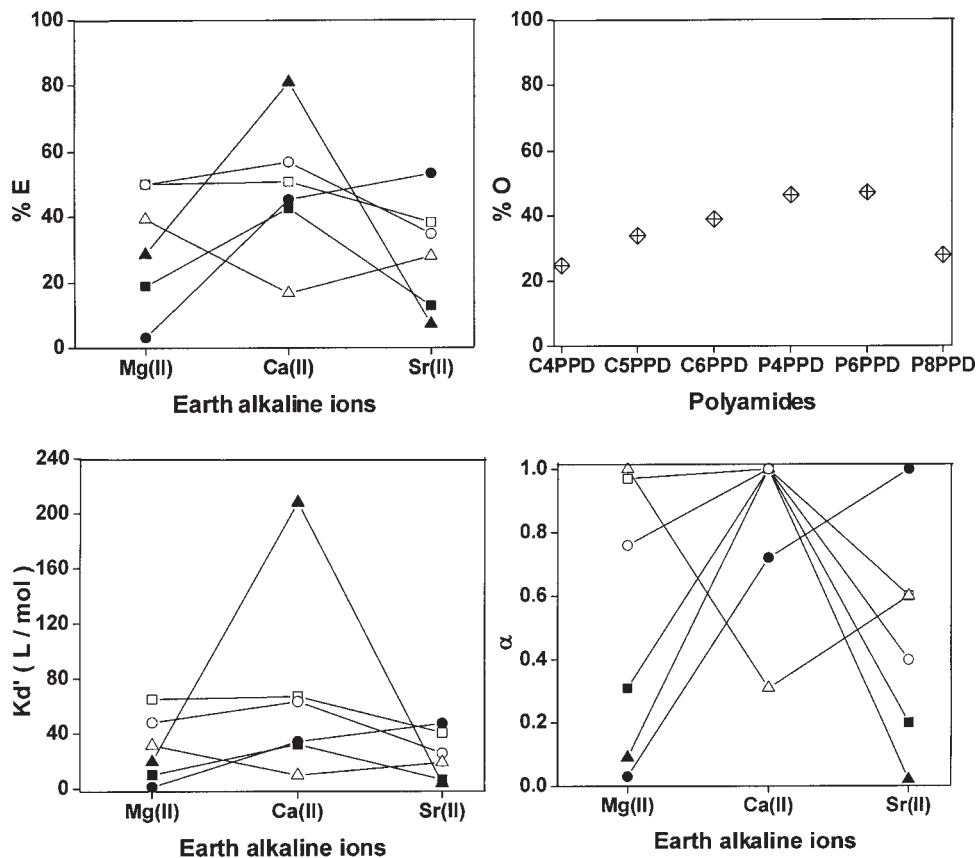
Figure 3 Solid–liquid extraction of alkaline earth ions in acetonitrile solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)]. The extraction of Ba(II) could not be studied because Ba(NO$_3$)$_2$ is insoluble in acetonitrile.

Figure 4 Solid–liquid extraction of alkaline earth ions in water solutions by solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].
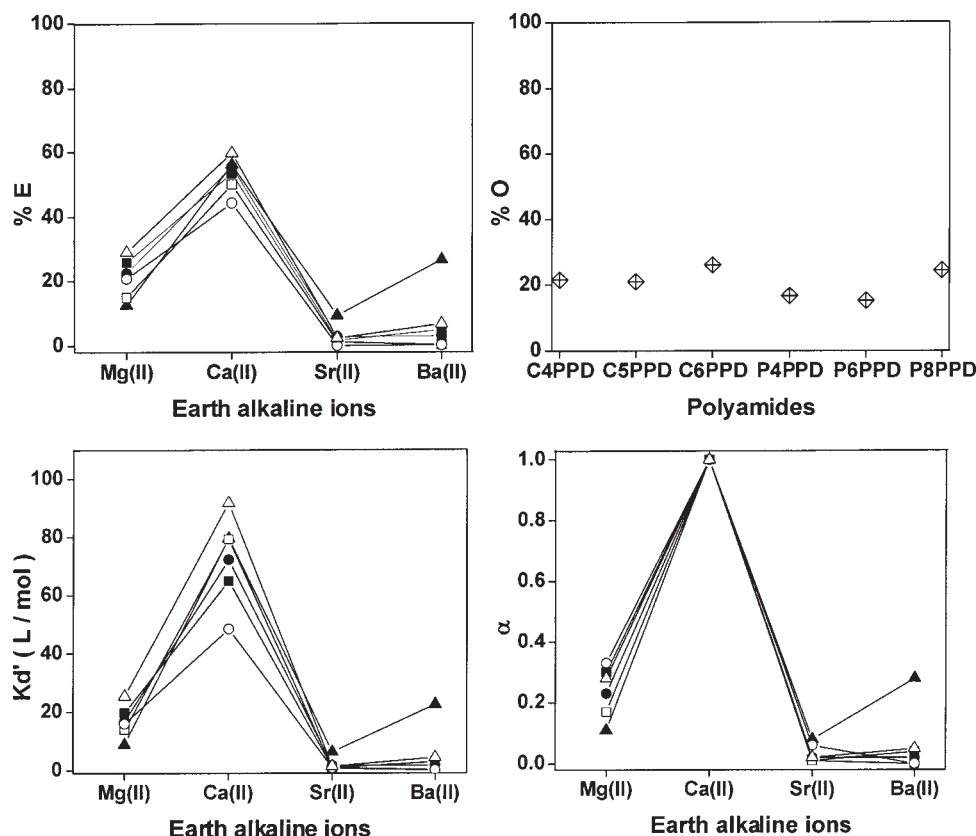
moles of the polymer structural units. Their ratio provides an approximate idea of the effectiveness of crown structures as ion extractants in solid–liquid extraction.

$$\%O = \frac{S : \text{cation}}{S_0} \quad (4)$$

Graphs showing data on the extraction percentage, distribution constant, selectivity, and occupation level for each alkaline, alkaline earth, transition metal, heavy metal, and lanthanide cation series are depicted in Figures 1–9.

The *a priori* analyses of the interactions involving the discrete crown ethers and a cation can be rationalized if we consider the cation radii and the cavity diameter of the crown. Thus, the better the fit of the cation radii to the cavity, the higher the stability constant of the crown–cation complex and, consequently, the higher extraction percentage and selectivity in solid–liquid extraction experiments. On the other hand, the comb-like structure of a polymer with pendant crown ether moieties could give rise to interaction between crown moieties and cations that could lead to the formation of sandwich structures of crown–cation–crown with the participation of the

crowns moieties of two vicinal structural units and one ion, or to more complex interactions between nonvicinal crown ether moieties and cations, such as zip structures.[5,33,34] The interaction of two or more crown moieties of the same or different polyamide chains could give rise to cavities of different radii, with the concomitant modification of the expected extraction selectivity.

Alkaline series [Li(I), Na(I), K(I), Rb(I), Cs(I)]

The extraction results of acetonitrile or water alkaline ion solutions by using solid-phase polyamides are shown in Figures 1 and 2. Cation extraction from the acetonitrile solution is selectivity performed if polyamides bearing the C6 or P8 moiety are employed, which are the higher cavity crown ethers and the dipodal moieties with the longer polyoxyethylene arms. This is in agreement with the facts showing that the higher ionic radii cations are by preference extracted [Rb(I) and Cs(I)]. Overall occupation percentages of ∼ 60 and 30% are, respectively, observed for polymers C6PPD and P8PPD.

Cation extraction from water occurs with high selectivity toward K(I) in nearly all the polyamides,
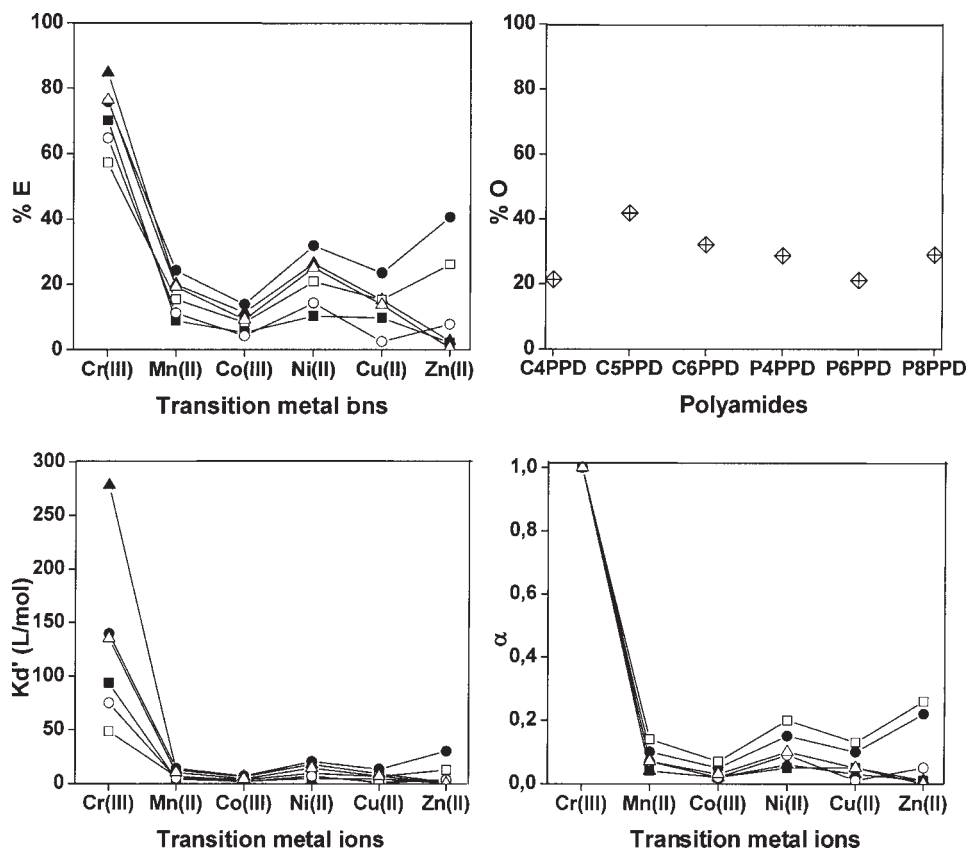
Figure 5 Solid–liquid extraction of transition metal ions in acetonitrile solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].

which evidences the important role played by the solvent in these experiments. The highly polar water molecules interact efficiently with cations, increasing the effective cation radii and hindering ion–dipole interaction between the ether linkages of the crown or dipodal moieties with cations. Thus, although the

K(I) is extracted in an almost quantitative manner with extremely high selectivity with C6PPD, the overall cation occupation percentages fall from 60% in the extraction of cations from acetonitrile solutions to 40% in the extraction of cations from water solutions.
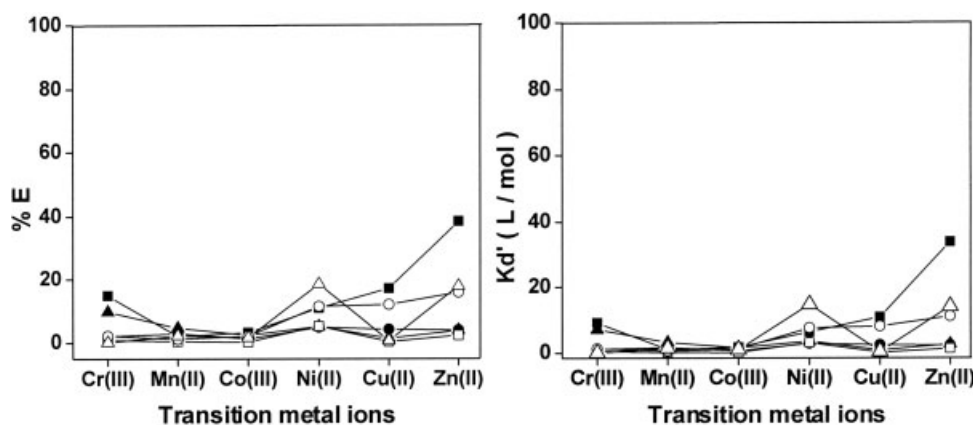

Figure 6 Solid–liquid extraction of alkaline earth ions in water solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].

Figure 7 Solid–liquid extraction of heavy metal ions in acetonitrile solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd′), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].
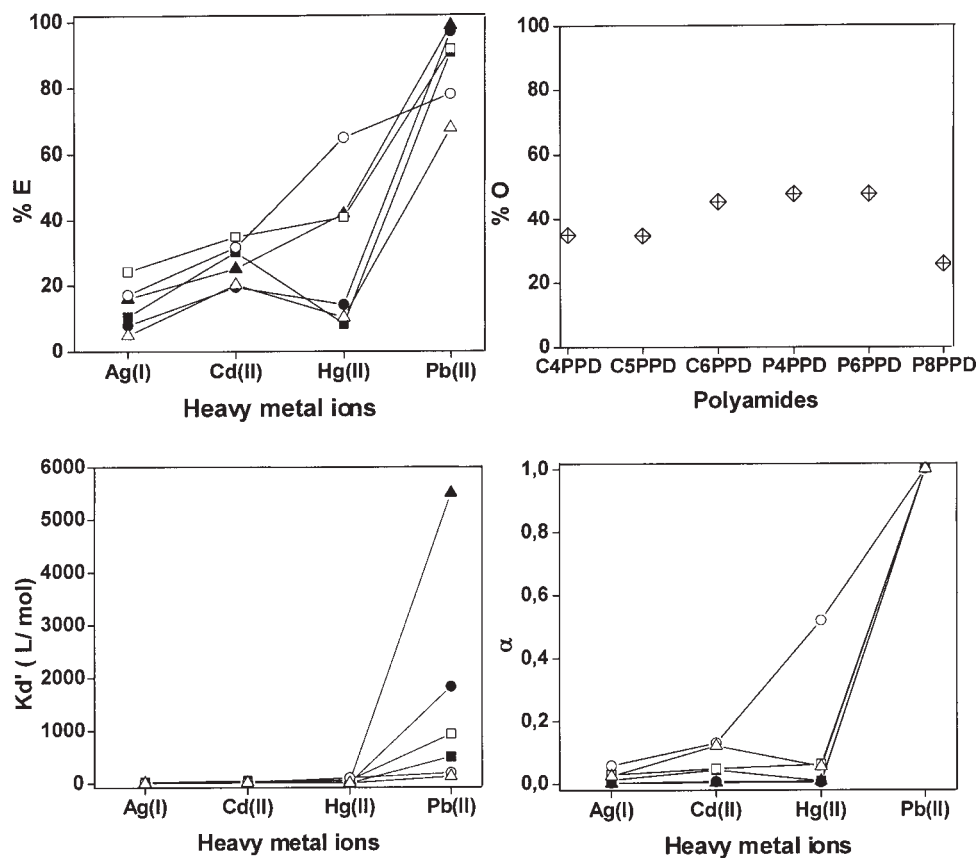
Alkaline earth series [Mg(II), Ca(II), Sr(II), Ba(II)]

The extraction of alkaline earth ions from acetonitrile or water solutions by means of the solid polyamides is shown in Figures 3 and 4. There is no selective extraction of cations from acetonitrile solutions using polyamides bearing dipodal moieties. In contrast, when polyamides with crown moieties are employed, good selectivity toward Ca(II) with C6PPD is observed, and toward Sr(II) when the extractant is C5PPD. The higher cavity radii of the C6 moiety double the extraction percentage of Ca(II) in comparison to C4PPD.

The cation extraction pattern of water cation solutions is very similar for all the polyamide phases, whose curves show good selectivity toward Ca(II) and extraction percentages in the region of 60%, the most interesting selectivity being obtained by C6PPD.

Transition metal series [Cr(III), Mn(II), Co(III), Ni(II), Cu(II), Zn(II)]

Figures 5 and 6 depict the extraction results of the transition metal ions in acetonitrile or water solutions using solid-phase polyamides. Cation extraction from acetonitrile solution with all the polyamides follows the same pattern, showing good

extraction percentages and excellent selectivity toward Cr(III), one of the most *poisoning* cations. The extraction with C6PPD is semiquantitative, while the extraction of other cations is almost negligible, which leads to a crown occupation level of 30%.

In contrast, the extraction of transition metal ions from water cation solutions using polyamides shows no selectivity; only Zn(II) is extracted preferably with solid-phase C4PPD. This is a drawback because environmental applications usually function in aqueous environments, although organic media are important in chemical ones.

Heavy metal series [Ag(I), Cd(II), Hg(II), Pb(II)]

The most promising result concerns the extraction of Pb(II) from a set of heavy metal ions in both acetonitrile and water solutions using solid-phase polyamides (Figs. 7 and 8). The extraction is quantitative and selective in both solvents with polyamide C6PPD. The extraction of Hg(II) is also noteworthy in both solvents employing C6PPD as an extractant. Both cations are important due to their environmentally poisoning nature and were a reusable plausible
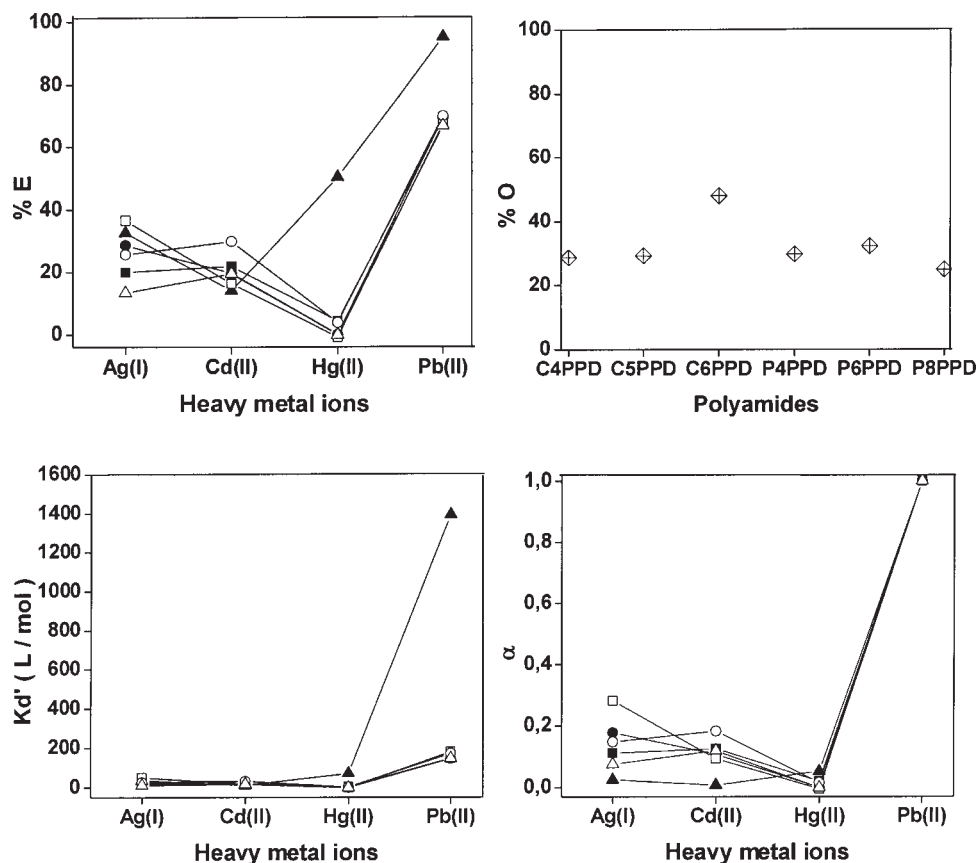
Figure 8 Solid–liquid extraction of heavy metal ions in water solutions using solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].

material ever able to eliminate them, then it would represent an important scientific achievement.

Lanthanide series [La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III)]

All lanthanide ions in oxidation state +3 are chemically and physically very similar, and it is therefore very difficult to separate and purify the cations from their mixture in solution.[35] Therefore, efforts intended to develop new separation techniques or procedures are always of interest. Concerning this point, the competitive extraction results of the set of lanthanide ions in acetonitrile solution with solid phases of the polyamides described in this work are shown in Figure 9. The extraction percentage of the lanthanide ions with C6PPD is related with the atomic radii of the cations, which descends from La(III) to Tb(III), in accordance with the decrease of the ionic radii. Although selectivity is not high, the extraction percentage of the lanthanide ions with higher ionic radii is noteworthy. In the case of C5PPD, a polyamide with a lower crown moiety cavity radii, the extraction percentage increased with the decrease in the cation radii, Tb(III) being

extracted in higher quantities than the other cations. The differences between extraction rates using C6PPD and C5PPD arises from the fact that La(III) and Tb(III) have ionic radii that fit better into C6 and in C5 cavities, respectively. The cation extraction selectivity employing C5PPD is much lower than the one obtained with C6PPD. The other polyamides give rise to unselective extraction.

The extraction of lanthanide ions from water solutions using solid-phase polyamides was negligible. In order to increase the overall cation extraction percentage, picric acid was added to the water phase, incrementing lanthanide extraction, but in the absence of selectivity. Thus, the crown occupation percentage rose to 30% for both C5PPD and P8PPD.

The extraction effectiveness of the different ions could not be correlated with the crown cavity to the effective cation ionic radii ratio. Although the cavity diameter of the crown compounds is well known (12-crown-4 has a cavity diameter of 1.2–1.5 Å; 15-crown-5 of 1.7–2.2 Å, and 18-crown-6 of 2.6–3.2 Å),[36] the cation ionic radii is not a straightforward matter. Thus, the ionic radii of a cation depends on its coordination number, i.e. radii of the K(I) varies between 1.38 and 1.64 (coordination number of 6 and 12,
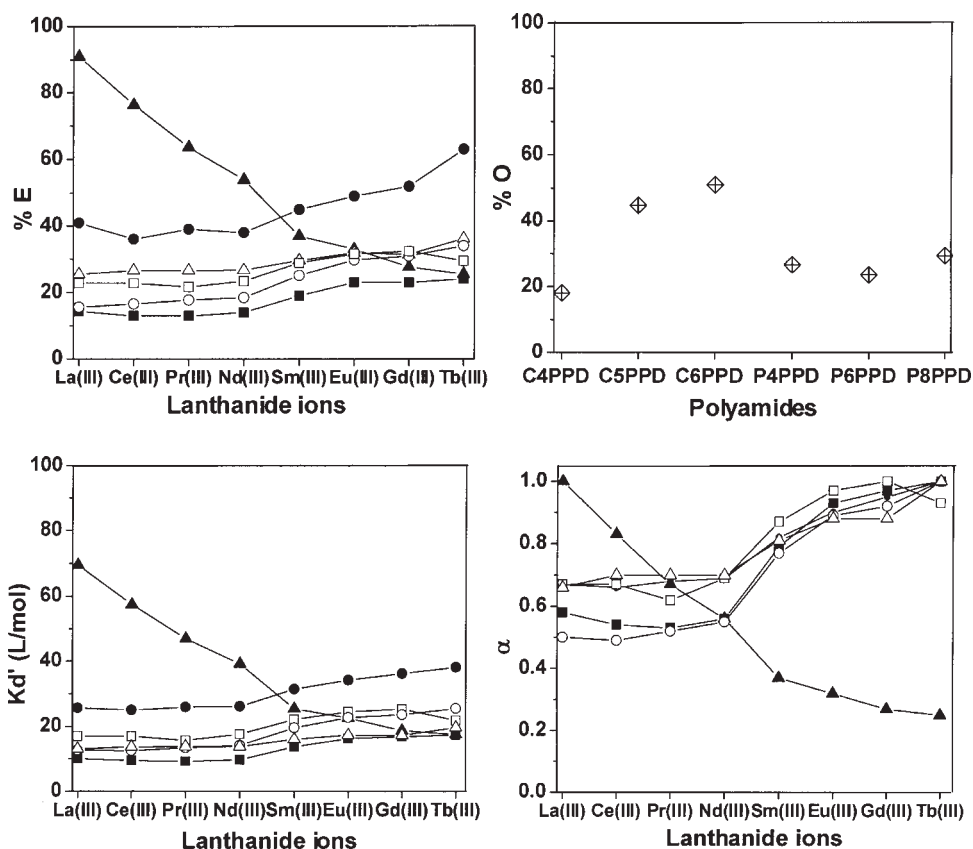
Figure 9 Solid–liquid extraction of acetonitrile-based lanthanide ions solution solid-phase polyamides. Extraction percentage (%E), cation crown occupation percentage (%O), distribution coefficient (Kd'), and selectivity (α). [C4PPD (■), C5PPD (●), C6PPD (▲), P4PPD (□), P6PPD (○), and P8PPD (△)].

respectively), and the radii of Pb(II) between 0.98 and 1.49 (coordination number of 4 and 12, respectively).[37] Hence, the solvent and the host–guest interaction can modify the coordination number and, thus, the effective ionic radii of the cations, hindering the interpretation of the cation selective extraction trends in terms of the ionic radii/crown cavity ratio. Moreover, and regarding the hosts, more complex zip or comb-like structures with higher cavity diameters could be proposed due to the plausible stacking of vicinal crown or podal moieties because of its periodical anchor to the main polymer chain according to the polymer structures (Scheme 1).

CONCLUSIONS

Metal ions interact selectively with polyamides bearing crown ether and oxyethylene dipodal arms as pendant structures. The specific interactions with some cations in alkaline, alkaline earth, transition metal, heavy metal, and lanthanide cation series lead to selective extraction in solid–liquid extraction experiments. In each cation series, and depending on the cation solvent, K(I), Ca(II), Cs(II), Cr(III), Hg(II) and, particularly, Pb(II) have all been selectively extracted by solid-phase polyamides. The most striking result is the noteworthy extraction percentage, nigh on 100%, of Pb(II) by polyamide bearing the benzo-18-crown-6 moiety (C6PPD) in both aqueous and organic media with a remarkable selectivity.

In summary and according to the results, C6PPD could be proposed for the extraction of: (a) Cs(I) and K(I) in acetonitrile and water solutions, respectively, from a mixture of alkaline ions; (b) Ca(II) from a mixture of alkaline earth ions in water and in acetonitrile solutions; (c) Cr(III) in acetonitrile solution; and (d) Pb(II) in water and acetonitrile media from a mixture of heavy metal ions. Otherwise C4PPD could be proposed for the extraction of Zn(II) in water solution from a mixture of transition metal ions.

These results confirm that polyamides are extremely useful materials in the preparation of tools for the extraction, purification, elimination or detection of cations, and particularly for the environmentally poisoning cations.

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