Uranium Adsorption by Chelating Resins Containing Amino Groups

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URANIUM ADSORPTION BY CHELATING RESINS CONTAINING AMINO GROUPS

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ABSTRACT

A series of porous polymers containing primary amino groups has been tested for their ability to complex the uranyl ion in aqueous solutions. The maximum capacity is obtained around pH 6, but that value is much lower than the theoretical value calculated on the basis of the loading in amino groups and the assumed stoichiometry of the metal ligand complex. Electron probe x-ray microanalysis demonstrated that the uranyl ion is chelated in a narrow surface layer, the thickness of which never exceed 250 μm, i.e., about 15% of the total diameter. On the other hand, copper can access all the chelating sites which are uniformly distributed inside the resins. This was explained by the formation of a precipitate of polyuranates in the first layer of the beads, preventing further penetration of the uranyl ion. This process is reversible, as shown by successive cycles of fixation and elution of the metal ion. The capacity of the resins toward uranium is not affected by the presence of an excess of calcium or magnesium or both.

INTRODUCTION

The selective extraction of uranium from seawater has been the subject of an increasing amount of work in recent years. Seawater contains only very small

amounts of uranyl ion UO_2^{2+} in the presence of large concentrations of alkaline and alkaline-earth ions. Therefore an efficient adsorbent for uranium should display high capacity and selectivity. Various organic adsorbents have been designed for this purpose with functional ligands more or less specific for uranium. Many of them are made of resins based on polyamines such as poly(ethyleneimine) [1–6] and poly(allylamine) [7]. Resins containing amidoxime groups were also extensively studied [8–12]. A calixarene moiety immobilized on a poly(ethyleneimine) support was recently prepared for selective uranium recovery [13]. In a previous paper we described the synthesis of porous polymers containing the vinyl amine function as the main component [14]. As they are chemically close to poly(ethyleneimine) or poly(allylamine) which exhibit good affinity for uranium, our polymers were tested for uranium recovery. Resins crosslinked with divinylbenzene (DVB) or ethylene glycol dimethacrylate (DMG) or mixtures of both were used to examine the influence of the matrix flexibility on the uptake of the metal.
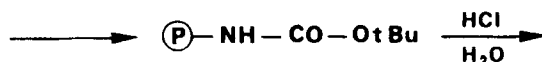
EXPERIMENTAL

Materials

Resins were prepared by suspension polymerization in the presence of heptane as a porogenic agent to obtain porous polymers. Details of the materials and the synthetic procedure have been described [4]. N-Vinyl t-butylcarbamate (NVTBC), precursor of vinylamine, was the main component of all the polymers. Styrene, methyl methacrylate, or methacrylic acid was the comonomer. The crosslinking agents were divinyl benzene (DVB), ethylene glycol dimethacrylate (DMG), or mixtures of both. The synthesis of the resins may be schematized as follows:

$$CH_2 = CH - NH - CO - OtBu \ + \ Comonomer \ + \ DVB \ or \ DMG$$

$$NVTBC$$

$$\longrightarrow \ \textcircled{P}\!\!-NH - CO - OtBu \xrightarrow[H_2O]{HCl}$$

$$\textcircled{P}\!\!-NH_3^+, Cl^- \ + \ CO_2 \ + \ tBuOH$$

The transformation of the carbamate groups is not complete [14], but this synthetic route ensures that no carboxyl groups are formed through sidechain reactions [15].

The following resins were prepared (see Table 1): Samples D60 to G70 contain styrene as comonomer. Samples D60 and D80 were crosslinked with DVB, Samples G6001 to G70 with DMG. GD70205 and GD701010 were crosslinked with a 20:5 or 10:10 mixture of DMG and DVB, respectively [14]. In the series G6001 to G6003 the amount of porogenic agent was decreased in order to change the overall porous volume of the samples (50, 40, 30, and 20%, respectively, of the total amount of monomers). G6004 and G6005 were crosslinked with 20 and 40% DMG, respec-

TABLE 1. Chemical and Physical Features of the Beads

Sample[a]	Contents of VA units, meq/g	Uptake of uranium, mmol/g	Porous volume, V_p, cm^3/g	Average pore radius, Å	Specific area, S_{sp}, m^2/g
D60	0.61	0.105	2.09	105	401
D80	1.95	0.100	2.14	200	216
GD70205	4.29	0.200	1.27	530	48
GD701010	2.35	0.210	1.67	205	163
G6001	2.75	0.150	1.67	1,590	21
G60	1.13	0.210	1.38	1,250	22
G6002	3.95	0.150	0.8	460	35
G6003	3.33	0.135	0.12	140	17
G6004	2.33	0.090	1.59	820	39
G6005	2.95	0.150	1.25	1,560	16
G70	3.58	0.130	1.32	1,650	16
GM40	1.53	0.180	1.38	13,800	2
GM60	2.80	0.200	1.71	2,010	17
GA40	0.12	0.145	1.92	6,400	6
GA60	0.17	0.105	2.05	5,860	7

[a]All samples have water contents ranging between 1 and 5%.

tively, instead of 30% as for the other G samples. Some samples were also synthesized with methyl methacrylate (GM) or methacrylic acid (GA) in place of styrene as comonomer.

Beads with diameters ranging from 1 to 2 mm were used in this study.

Linear poly(vinylamine) (PVA) was prepared by radical polymerization of the NVTBC monomer followed by hydrolysis with a large excess of hydrochloric acid, following the method of Hughes and St. Pierre [15, 16].

Uranyl acetate, $UO_2(CH_3COO)_2$ (Merck), was used as the metal ion source.

Methods

Loading of the Resins in VA Functions

After cleavage of the NVTBC function with HCl, the polymer is in the P—N-H_3^+,Cl$^-$ form. The amount of amino groups in the resins was determined from elemental analysis of nitrogen and chloride.

Texture Determination

The specific surface area S was obtained from nitrogen adsorption–desorption measurements following the BET method [17] (apparatus: Quantasorb Jr). Mercury porosimetry was used to determine the overall porous volume V_p and the pore size distribution (apparatus: Carlo Erba 800). The average pore radius was calculated from $r = 2V_p/S$.

Visible Absorption Measurements

This method was used for the determination of uranium in the solutions.

A metal solution (0.5 mL) was treated with 10 mL of 70% HClO$_4$, 1 mL of 10% hydroxylamine hydrochloride, and 2 mL of a 0.02% aqueous solution of Arsenazo III. Absorption of the mixture was recorded at 670 nm, and the concentration was determined from a calibration curve.

pH Measurements

pH measurements were carried out with a Radiometer pHM 65 pH meter equipped with a combination electrode.

Determination of the Chelating Capacities

The chelating capacities of the resins were determined by using the batch method. The resin (50 mg) was added to 25 mL of a 10^{-2} M solution of the metal ion. The formation of the complex between the metal ion and NH$_3^+$,Cl$^-$ liberates HCl, and the pH decreases according to the complexation reaction between one metal ion and three amino groups of the polymer:

$$3P-NH_3^+ + UO_2^{2+} \rightarrow [UO_2(NH_2)_3]^{2+} + 3H^+ \tag{1}$$
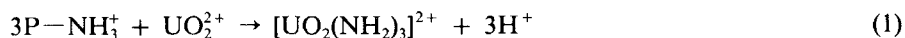
The pH was adjusted to the desired constant value with NaOH. Then the metal ion content of the supernatant was monitored by spectroscopy, and the amount of metal ion extracted was calculated by difference. The beads were filtered and washed many times with water, and the metal ion was stripped of the resin with 1 M HCl. The amount of metal ion in these solutions was also calculated. Capacities were determined at different pH values to obtain the capacity–pH profiles.

The capacities of the beads toward uranium in the presence of a large excess of calcium and magnesium ion were determined in the same way. Calcium and magnesium chloride were used as the metal ion source. A 100-fold excess of these metals was used on a molar basis.

Dialysis Experiments

For linear PVA, the binding of uranium was determined by dialysis equilibrium between PVA and uranium solutions. A dialysis bag (molecular weight limit of 12,000 g/mol) was loaded with 10 mL of a PVA aqueous solution at 1.2 g/L (0.15 mmol/L in NH$_2$ groups) and equilibrated with a volume V of an uranyl acetate solution (178 mg/L, i.e., 0.42 mmol/L). The volume V was adjusted to obtain NH$_2$/U ratios of 2, 3, and 4.

Electron Probe X-Ray Microanalysis

This technique was used to control the distribution of different atoms (Cl, Cu, U) inside the beads. Beads of polymer were first embedded in an araldite cold-setting resin. In most cases an epoxy resin was used because of its good physical properties. The pellets were then carefully polished so that a large number of transverse sections of beads appeared on the surface (final mechanical polish with 0.25 μm diamond paste). A 25-nm film of carbon was evaporated onto the surface of

these nonconductive samples. Electron probe x-ray microanalysis was carried out on a Camebax Micro. This fully automated electron microprobe is equipped with three wavelength-dispersive x-ray spectrometers with a take-off angle of 40°. Quantitative analysis was performed by using a ZAF correction program.

Batch Recycling of Resins

Resins were subjected to cyclic loading with metal ion and stripping with 1 M HCl under standard batch conditions. Four to five cycles were carried out for each resin.

RESULTS AND DISCUSSION

Figure 1 shows a typical curve capacity versus pH for one of the samples (G70). Complete coordination of the uranium ion is obtained at a pH between 6 and 7 in all cases. Beyond this value, precipitation of uranium as uranium hydroxide $UO_2(OH)_2$ and formation of polyuranates occurs in the aqueous solution.

Measurements at higher pH's would need the use of an appropriate buffer because of the competing complexing properties of uranium and to prevent its precipitation as hydroxides. This would have changed the conditions of interaction of the amino functions in the beads with aqueous uranium, and, for this reason, the pH range beyond 7 was not investigated.

Table 1 gives the chelating capacities of the different samples in this pH range. In the G series the maximum capacity is obtained for the following samples: GD701010 and GD70205 crosslinked with a mixture of DVB and DMG and with G60 crosslinked with DMG only. Thus, the use of DMG as a crosslinking agent
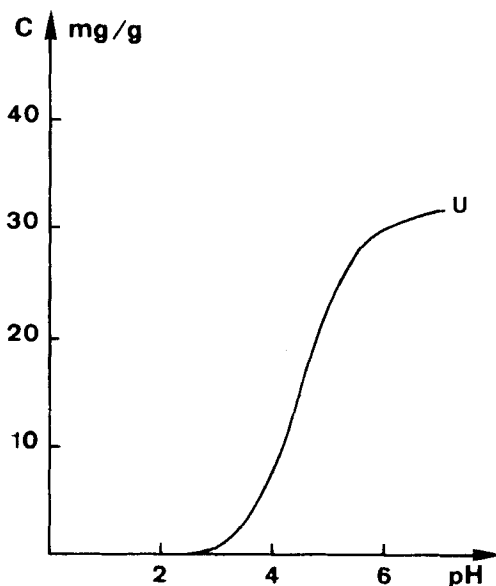

FIG. 1. Uranium capacity vs pH for resin G70.

seems favorable. This is in agreement with the results of Egawa et al. which have shown that higher capacities are obtained when using mixtures of DMG and DVB instead of pure DVB for the recovery of uranium with amidoxime resins [10].

No correlation exists between the capacity and the porous volume or capacity and specific area. For example, D samples have high porous volumes and specific areas but nearly the same capacity as G6003 which has a much lower porous volume. Samples GD701010 and G60 have similar capacities but very different surface areas. Samples GM, where the comonomer is methyl methacrylate instead of styrene, have rather good capacities with low surface areas.

The capacity is not directly related to the loading of the resin in amino groups. The average number R of metal atoms bound to one amino group range between 0.05 and 0.17 only for samples D60 to GM40 in Table 1. (This ratio is equal to 1.2 and 0.62 for GA40 and GA60, respectively, but this reflects the presence of the carboxyl groups of methacrylic acid, which are effective ligands for uranium.) Kobayashi et al. reported that the complexes of poly(allylamine) with the uranyl ion have a 3:1 stoichiometry [7], corresponding to a $R = 0.33$ value with a theoretical maximum capacity of 1.39 g of metal per gram of polymer. Figure 2 shows that the binding of uranium by linear poly(vinylamine) can reach about 600 mg/g, which is less than the theoretical value but much higher than the capacity of our resins.

Thus, it can be concluded that all the amino groups in the beads are not accessible to the metal ion. Electron probe x-ray microanalysis was carried out to obtain the distribution of the metal in the resins loaded with uranium. The metal is located in a very narrow surface layer, the thickness of which never exceeds 250 μm, i.e., 15% of the total diameter (Figs. 3 and 4).

There is no apparent correlation between the thickness of this layer and the overall capacity of the resin. Figure 5 shows that the distribution of the chloride ion
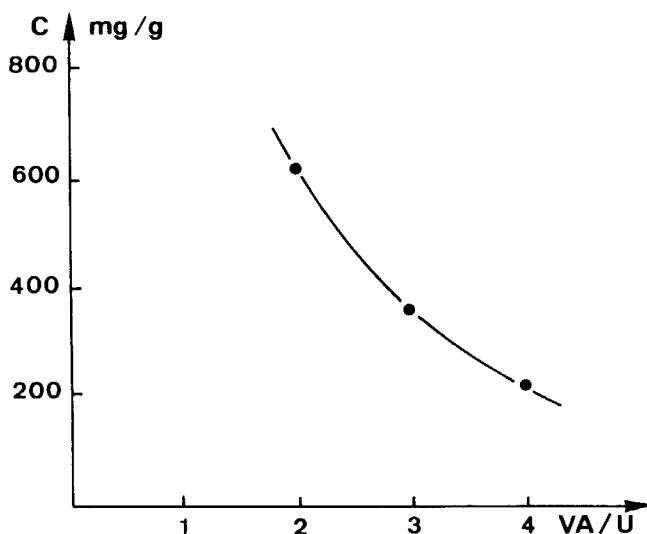

FIG. 2.   Variation of the capacity of linear polyvinylamine toward uranium at pH 5 versus the ligand/metal ratio.
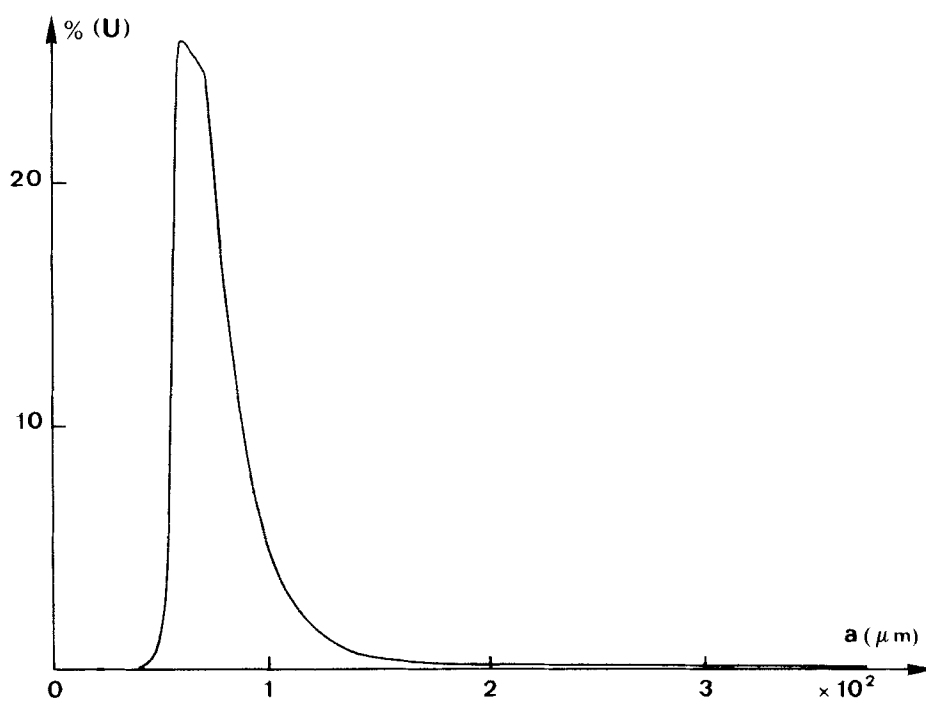
FIG. 3. Distribution of uranium in resin GD70205.

associated with the amino groups is uniform inside the resins, and that copper, contrary to uranium, can diffuse inside the beads to coordinate to all the chelating amino groups.

With copper, the value of R is close to 0.25, the theoretical value for a 4:1 complex stoichiometry. In the case of the Duolite ES 346 resin crosslinked with
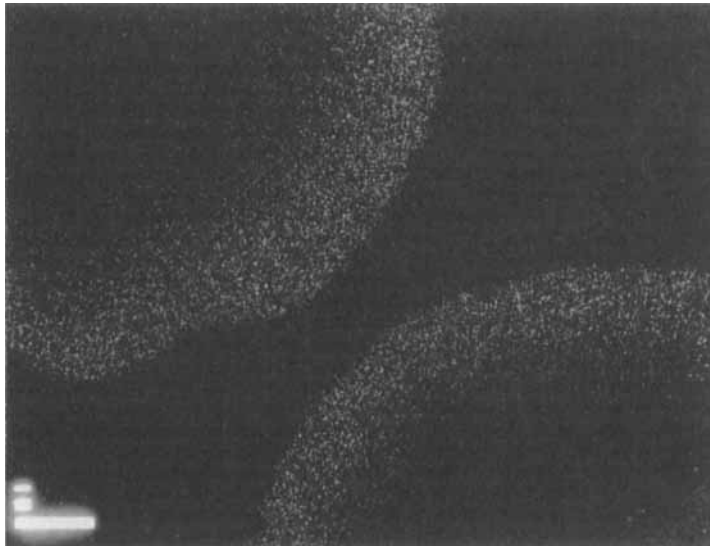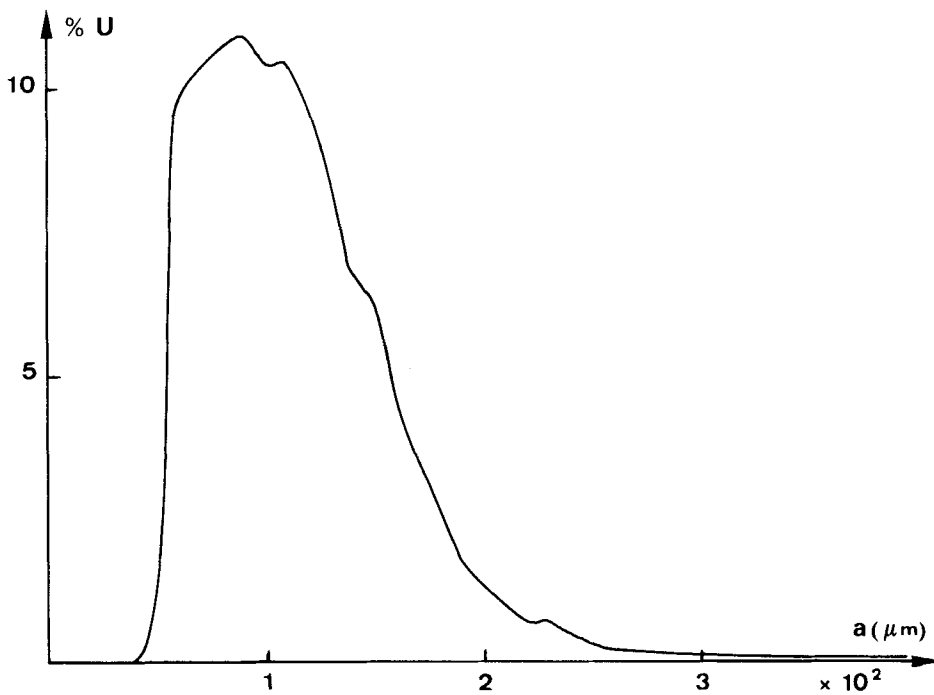
FIG. 4.   Distribution of uranium in resin D80.

DVB, Astheimer et al. [11] found that uranium accumulates in a narrow surface layer and that copper is uniformly distributed over the entire bead volume. They suggested that the uranyl ion was too large to easily diffuse inside the micropores and that the use of a more flexible matrix with other crosslinkers would facilitate its diffusion. Our results show that the use of DMG, which is much more flexible and
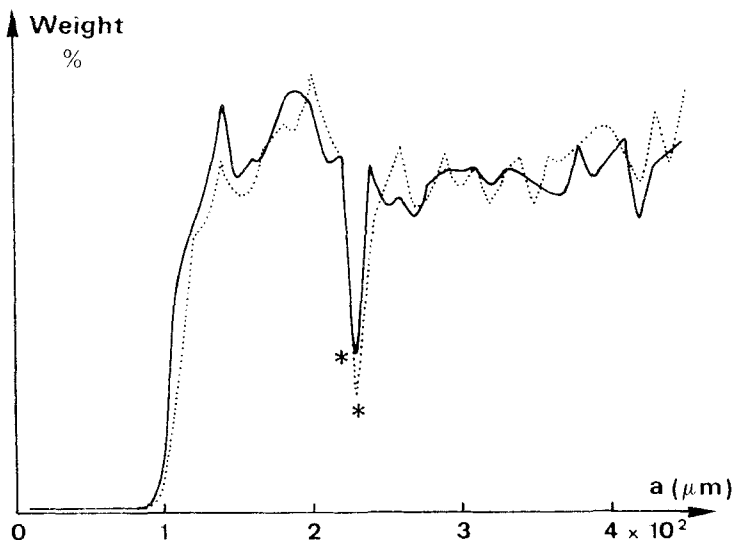
FIG. 5. Distribution of chloride (· · ·) and copper (——) in resin G70. The asterisks indicate a physical default in the bead.

hydrophilic than DVB, does not really enhance the diffusion. We suggest that the difficulty for the uranyl ion to penetrate deeply inside the bead is due to the formation of a precipitate of polyuranates. Polyuranates are known to form easily in this pH range, and they probably fill in the pores in the first surface layer, thus preventing further diffusion of the metal. The amino groups play no role in the formation of the polyuranates since it also occurs with polymers containing no amino groups [11].

Samples G6001 to G6003 differ only by the amount of porogen used during synthesis, and thus by their porous volume (Table 1). Figure 6 shows that the pH at which complexation between the charged amino groups and the uranyl ion begins depends on the porous volume and on the average pore radius.

A tentative explanation could be the following: The charged amino groups are much closer in small pores than in large pores. Thus, the deprotonation of the first amino group of the three which coordinate to uranium is easier due to the strong electrostatic repulsion between the proton liberated in Reaction (1) and the remaining NH_3^+ groups. In larger pores the electrostatic interactions are lower and the deprotonation of the amino groups occurs later. In other words, the NH_3^+ groups are more acidic in small pores.

This is the only direct relationship between the textural features of these resins and their complexing properties.

In order to see if the chelated metal ion can be readily and efficiently stripped off and the resin recycled many times, the beads of each series were submitted to four to five cycles of loading, stripping, and washing. These experiments were made at the pH of maximum capacity in each case. Figure 7 shows that in all cases the capacity is maintained and sometimes slightly increased with use. This indicates that the formation of the polyuranates suggested above is entirely reversible.
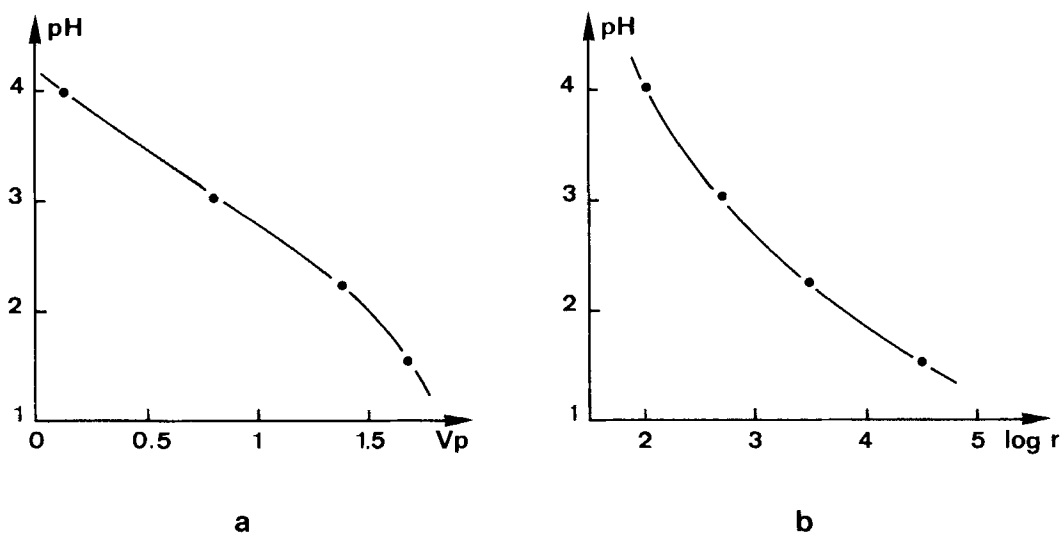
FIG. 6.   Variation of the pH of beginning complexation of uranium versus the porous volume (a) and the average pore radius (b) for resins G6001, G60, G6002, and G6003.

Finally, we evaluated the effect of competing alkaline earth cations. Adsorption of uranium was carried out in the presence of a 100-fold excess of calcium or magnesium or both (Table 2). The chelating ability of the G70 resin, as an example, is not affected by the presence of these metal ions.

The above results indicate that these resins could be considered as potential sorbents for the recovery of uranium in seawater. The most stable complex of uranium in seawater is the anionic complex $UO_2(CO_3)_3^{4-}$, which has a formation constant of about 10^3-10^4 [18]. On the other hand, the 1:3 $[UO_2(NH_2)_3]^{2+}$ complex,
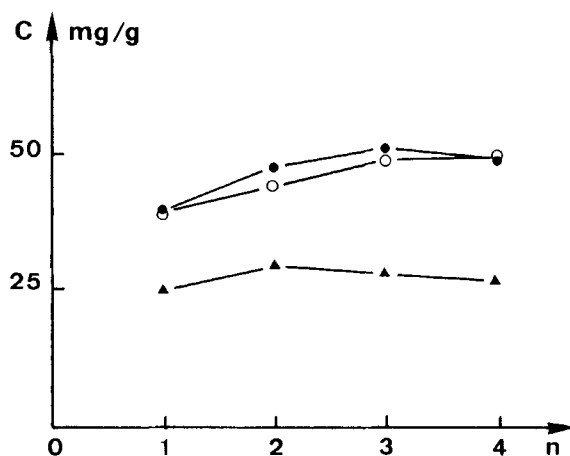
FIG. 7.   Variation of the capacity during cycles of chelation and elution of uranium: (●) G60; (○) G6002; (▲) GA60.

TABLE 2. Uptake of Uranium by the G70 Bead in the
Presence of an Excess of Calcium and Magnesium
(the ratios Ca/U and Mg/U are expressed on a molar basis)

	U	Ca	Mg	pH	Uptake of uranium, mmol/g
1st binding	1	100	0	5.1	0.16
	1	0	100	5.0	0.19
	1	100	100	5.6	0.21
2nd binding	1	100	0	4.4	0.19
	1	0	100	5.4	0.19
	1	100	100	5.6	0.20

which is formed by the interaction of uranium with the amino groups of the beads, has a formation constant of 10^{11} as shown by measurements on linear soluble poly-(allylamine) [7] or poly(vinylamine) [19]. Thus, the carbonato complex would be entirely displaced by the formation of the amino complex. In addition, poly(amines) do not bind the magnesium ion [20], and the binding of uranium is selective.

We have explained the limitation in capacity by the precipitation of polyuranates in the surface layer of the beads. This is probably a general problem encountered with porous polymers, which seems to have received little attention with few exceptions [11].

ACKNOWLEDGMENTS

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