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Strontium Extraction with a Polymer-Bound 18-Crown-6 Polyether

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ABSTRACT

A 18-C-6 crown ether-functionalized polystyrene network (2.04 mmol 18-C-6/g, noted R-18C6) has been synthesized by reaction of hydroxymethyl-18-crown-6 with the related chloromethylated polymer (5.6 mmol Cl/g, 6.5% crosslinked with divinylbenzene). The extraction of strontium from 1 M $LiNO_3$–LiCl aqueous solutions with R-18C6 has been studied. The experimental data agree with the sorption equilibrium

$$Sr^{2+} + 2NO_3^- + *18C6 \rightleftharpoons *18C6,Sr(NO_3)_2$$

($\log K_{25°C} = 2.52$, and the superscript asterisk denotes a polymer bound species). $Sr(NO_3)_2$ is selectively extracted with R-18C6 from aqueous nitrate solutions containing trivalent lanthanum and europium. Replacing $LiNO_3$ with HNO_3 does not alter the extraction yield. The stripping of $Sr(NO_3)_2$ from the polymer network is complete at 60°C in distilled water but, owing to poor water swelling of the resin, the kinetics of extraction and stripping are rather slow.

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INTRODUCTION

Liquid–liquid extraction is certainly a very useful method for selectively separating and concentrating metal ions from complex aqueous solutions because a great number of selective ligands are available which can be used as metal extractants. However, these ligands are often quite expensive and their application on a large scale remains limited. Metal transport through supported liquid membranes is another interesting possibility owing to the rather small quantities of ligand (carrier) immobilized in the membrane. But in both cases, it is difficult to avoid loss of the ligand in the aqueous phase due to its distribution. Long hydrocarbon chains increase the ligand lipophilicity, but the loss can remain too great owing to the high aqueous/organic volume ratios involved in detoxication or decontamination processes. Binding the extracting ligand on a network polymer appears to be a good alternative to eliminate this difficulty.

Although liquid–liquid extraction of alkali metals with crown ethers or their sorption on polymer-bound crown ether have often been reported in the literature, papers about alkaline earth metals are less numerous (1–3). Moreover, most sorption studies have been performed in organic diluents (THF, dioxane), seldom in water. This paper deals with the synthesis of a crosslinked polystyrene containing 18-crown-6 polyether and the study of strontium extraction from aqueous nitrate medium. In addition, preliminary results concerning its possible application to strontium extraction from concentrated lanthanide solutions, an important industrial problem, are presented.

EXPERIMENTAL

Hydroxymethyl-1,4,7,10,13,16-hexaoxa-cyclooctadecane or Hydroxymethyl-18-crown-6: Preparation

Hydroxymethyl-18-crown-6 was synthesized following a slightly modified Czech method (4): 3-benzyloxy-1,2-propanediol was prepared according to Ref. 5 and added (0.1 mol) to a solution of LiOBu (0.2 mol) in *t*-BuOH (0.5 L). After a 20 minutes reflux, pentaethylene glycol ditosylate (0.1 mol) (6) and KF (0.5 mol) were added, and the mixture was stirred for 2 days. After the usual work-up, a pure colorless oil was obtained in 83% yield. The benzyl group was removed by hydrogenolysis on Pd/C (5%) catalyst in anhydrous dioxane in the presence of *p*-toluenesulfonic acid, affording a pasty hydroxymethyl-18-crown-6 in 90% yield. Further purification by formation of a crystalline complex with KBF_4 in CH_2Cl_2 lead to the pure ligand as confirmed by H-NMR and elemental analysis.

Crown-Ether-Containing Polymer Network: Preparation and Analysis

Polymer Network. The chosen chloromethylated, crosslinked polystyrene was a macroporous Duolite resin "LES 3780 Cl" (beads of 0.5–1 mm, 6.5% crosslinked, 5.64 mmol Cl/g).

Hydroxymethyl-18-crown-6 Polymer Network or R-18C6. R-18C6 was prepared according to the alkylation procedure (7). To a slurry of NaH (50% oil dispersion) in anhydrous THF was added an equimolecular amount of hydroxymethyl-18-crown-6. After 4 hours of refluxing, the chloromethylated, crosslinked polystyrene, swollen with THF, was added with a crown ether/chlorine ratio of 2.6/1. After 120 hours of refluxing, the resin was filtered and washed continuously with H_2O/THF solutions of increasing H_2O concentration. The resin was dried in vacuo. A very poor binding yield was achieved, which could be explained by the hygroscopic character of hydroxymethyl-18-crown-6. Then, in order to avoid this failure, the less hygroscopic hydroxymethyl-18-crown-6,KBF_4 complex was prepared by reaction in CH_2Cl_2, and it was successfully bound on the resin. The weight increase of the resin and its elemental analysis agreed with 2.04 mmol crown ether/g and a chlorine-crown ether exchange yield of 74%.

Metal Extraction Procedure

50 mg of dry R-18C6 (0.102 mmol 18C6) was swollen during 10 hours in 0.5 mL methanol, separated, and introduced into a thermostated tube (25.0 ± 0.2°C) containing 10 mL of an aqueous strontium solution of 1 M ionic strength ([LiCl] + [$LiNO_3$] = 1 M) at pH 3. The resin beads were suspended in a small cotton gauze bag to avoid breakage during stirring. Aliquots of strontium solution were withdrawn and analyzed, after suitable dilution, by atomic emission using a 2380 Perkin-Elmer spectrophotometer. When necessary, the strontium mass balance was checked: the resin beads were dried on absorbent paper and mineralized before analysis. The absence of rare earths in network polymers was verified by Energy Dispersive X-Ray Fluorescence (EXDRF) (Siemens prototype).

RESULTS AND DISCUSSION

Choice and Characteristics of the Crown Ether Network Polymer

A 18-crown-6 crown ether was chosen because of the good compatibility between its cavity radius (1.3–1.6 Å) (8) and the crystal ionic radius of

Sr (1.13 Å) (9) which leads to a 18-C-6–Sr^{2+} complex formation constant in water at 25°C of 525 M^{-1} (10). This formation constant is only 90 M^{-1} (10) with 15-crown-5 ether of cavity radius 0.85–1.1 Å (8). Although it is perhaps easier to synthesize 4′-hydroxymethylbenzo-18-crown-6, the hydroxymethyl-18-crown-6 was preferred because of its

Better complexing properties: for example, the dibenzo-18-crown-6–Sr^{2+} complex formation constant in water is 50 times smaller than the 18-crown-6 one (10)

Less hydrophobic character due to the absence of the benzo group

Better flexibility and smaller size of the unsubstituted 18-crown-6 which allows higher ligand concentrations in the resulting crown ether-functionalized polymer network: the maximum possible concentrations of 4′-hydroxymethylbenzo-18-crown-6 and hydroxymethyl-18-crown-6 bound to polystyrene are 2.18 and 2.43 mmol/g, respectively. In the present work, 2.04 mmol/g was achieved with the latter (see the Experimental Section), but only 1.30 mmol/g was found with the former (11).

Among the possible matrices, we used a poly(styrene–divinylbenzene) copolymer. This commercially available matrix is the one most commonly used due to its excellent physical strength and remarkable resistance to temperature degradation and oxidation.

Strontium Behavior in Liquid–Liquid Medium: Interesting Equilibria

The interactions between Sr^{2+} and NO_3^- in aqueous medium have been quantitatively studied by Fedorov et al. (12). They are described by Equilibria (1) and (2):

$$Sr^{2+} + NO_3^- \overset{\beta_1}{\rightleftharpoons} SrNO_3^+ \quad (1)$$

$$Sr^{2+} + 2NO_3^- \overset{\beta_2}{\rightleftharpoons} Sr(NO_3)_2 \quad (2)$$

Constants $\beta_1 = 1.12\ M^{-1}$ and $\beta_2 = 0.50\ M^{-2}$ (ionic strength 1 M, 25°C).

The complex formation between Sr^{2+} and crown ethers (E) in water is described by

$$Sr^{2+} + E \overset{K_C}{\rightleftharpoons} ESr^{2+} \quad (3)$$

Constants log K_C = 2.72, 3.24, and 2.64 for E = 18-C-6, DC-18-C-6 A, and DC-18-C-6 B, respectively, at 25°C (by calorimetry) (13) (DC-18-C-6 A and B are the *cis-syn-cis* and *cis-anti-cis* isomers of dicyclohexano-18-

crown-6). The complex formation constant of 18-C-6,Li^+ is largely lower since log $K_C = 0$ (by NMR) (13).

The Sr^{2+} extraction from 1 M Li(Cl,NO_3), pH 5, aqueous solutions with DC-18-C-6 A and B in chloroform was studied by Delloye et al. (14). Only $Sr(NO_3)_2$ was extracted by Equilibrium (4):

$$Sr^{2+} + \text{DC-18-C-6}_{org} + 2NO_3^- \overset{K_{ex}}{\rightleftharpoons} \text{DC-18-C-6,Sr}(NO_3)_{2,org} \qquad (4)$$

with log $K_{ex} = 3.22$ and 2.77 at 25°C for the A and B isomers, respectively.

According to the low formation constant of 18-C-6,Li^+ type complexes (13), neither $LiNO_3$ nor LiCl was extracted. The strong hydration of chloride anions together with the weak interactions between Sr^{2+} and Cl^- are certainly responsible for the rather poor liquid–liquid extraction of $SrCl_2$. These previous results led to the choice of the current experimental conditions.

Extraction of Strontium Nitrate with R-18C6 Polymer Network

Strontium Extraction Kinetics. Typical sorption curves of R vs time (R = number of Sr bound to the polymer network/total number of 18C6) performed at constant [$LiNO_3$] = 1 M, at a constant total number of 18C6 and a variable strontium concentration, are shown in Fig. 1. Although rather long times are necessary to attain saturation, the equilibrium half-time is of the order of 20 minutes at a higher strontium concentration. Such a time period is currently observed with polystyrene resins containing nonionic ligands. In particular, the same type of kinetics was recently obtained by using the same polystyrene matrix grafted with linear polyethyleneoxides (7). It is now well established that the exchange reaction is controlled by the diffusion process through the particle in this type of matrix (15). In these conditions the kinetics strongly depend on the concentration gradient between the bulk and the polymer phase and on the size of the particles. Both dependences are observed with the R-18C6 resin. Whereas concentration dependence is confirmed in Fig. 1, preliminary results obtained by using polystyrene matrices of 50 and 10 μm average diameters show an acceleration of the kinetics by a factor of 3 and 6, respectively (11). Moreover, and in spite of the hydrophilic character of the ligand, resin swelling in water is poor (2.8% in volume). It is clear that crowding inside the resin and the hydrophobic character of the polystyrene matrix limit the water diffusion and the accessibility and mobility of the rather large crown ether ligand (7, 15). This is particularly important for the part of the ligand grafted inside the walls of the macroporous

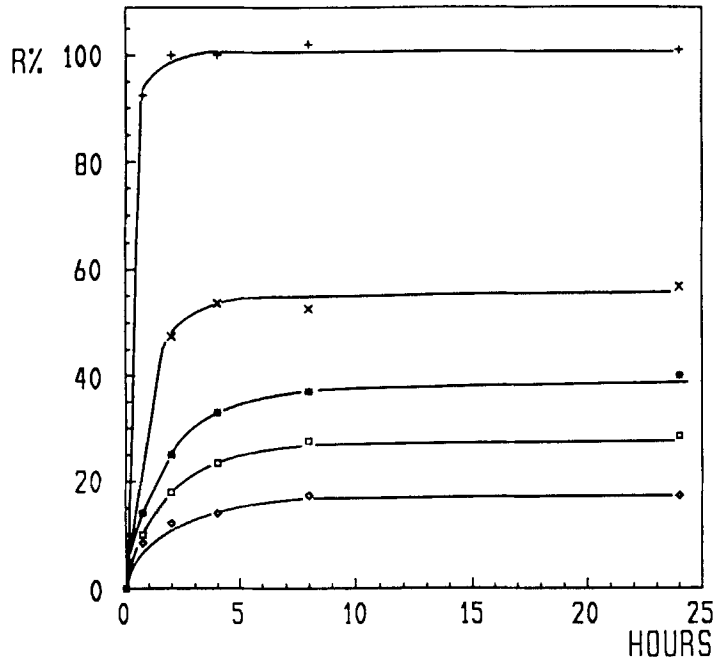

FIG. 1 Sorption of strontium from 1 M $LiNO_3$, pH 3, aqueous solutions (10 mL) at 25°C on R-18C6 polymer network (10^{-4} mol 18C6): from bottom to top, 10^2[Sr] = 0.18, 0.31, 0.73, 1.70, 5.06 M.

structure. Obviously, this may explain the slow process observed after the first hour while saturation is attained.

Strontium Extraction Equilibrium. In Fig. 1 it is shown that R increases with increasing [Sr] and reaches a maximum value of 1 when the total number of moles of Sr is at least 5 times that of 18C6. These results indicate that the Sr–18C6 complex stoichiometry in the network polymer is 1:1, but its formation is not quantitative.

If it is assumed that all of the 18C6 attached to the polymer network is statistically equivalent with respect to the Sr^{2+} binding (which implies that electrostatic repulsions between the bound Sr^{2+} are negligible), and that each Sr^{2+} is bound to only one 18C6 (which corresponds to the usual stoichiometry of 18C6 crown ether–Sr^{2+} complexes), strontium extraction with the hydrophobic R-18C6 polymer network can be described by Equilibrium (5), close to Equilibrium (4) which describes the $Sr(NO_3)_2$ liquid–liquid extraction.

$$Sr^{2+} + *18C6 + 2NO_3^- \overset{K_1}{\rightleftharpoons} *18C6,Sr(NO_3)_2 \quad (5)$$

(The asterisk refers to network-bound species.)

$$K_1 = [*Sr]/[*18C6][Sr^{2+}][NO_3^-]^2 \quad (6)$$

where [*Sr] and [*18C6] are the Sr and uncomplexed 18C6 concentrations in the polymer phase, respectively. Denoting $[*18C6]_0$ as the total 18C6 concentration in the polymer phase, it follows from Eq. (6) that

$$1/R = [*18C6]_0/[*Sr] = 1 + 1/K_1A \quad (7)$$

where $A = [Sr^{2+}][NO_3^-]^2 = [Sr(NO_3)_2]/\beta_2$.

Equation (7) is a particular form of

$$1/R = 1/n + 1/nK_NA \quad (8)$$

proposed by Smid et al. (16), as a rearranged form of the Langmuir adsorption isotherm used to describe the cation binding of alkali picrates (M^+Pic^-) to crown ether–polymer networks in dioxane: $1/R$ = total number of crown units in the polymer network/number of (M^+Pic^-) bound to the polymer network, $1/n$ = number of crown units per bound (M^+Pic^-), A = free (M^+Pic^-) concentration, K_N = the intrinsic binding constant.

The binding constant K_1 of Equilibrium (5) can be calculated by plotting $1/R$ vs $1/A$. Calculating $[Sr^{2+}]$ from

$$[Sr] = [Sr^{2+}](1 + \beta_1[NO_3^-] + \beta_2[NO_3^-]^2)$$

where [Sr] is the analytical Sr concentration in the aqueous solution at equilibrium. Plotting the experimental data obtained with constant $[LiNO_3] = 1$ M, a straight line of equation

$$1/R = 1.14 + 0.00297(1/A)$$

is obtained whereas a straight line of equation

$$1/R = 0.85 + 0.00303(1/A)$$

is achieved by varying $[NO_3^-]$ from 0 to 1 M. Plotting all the experimental data together (Fig. 2) leads to the linear equation

$$1/R = 0.98 + 0.003(1/A)$$

with a correlation coefficient of 0.997. These results are in agreement with the formation of $*18C6,Sr(NO_3)_2$ complexes of stoichiometry 1:1 ($1/n = 1$) and $\log K_1 = 2.52$.

The lower [Sr-bound 18C6/free 18C6] ratio found in the polymer phase compared to that in the DC-16-C-6/chloroform phase (liquid–liquid extrac-

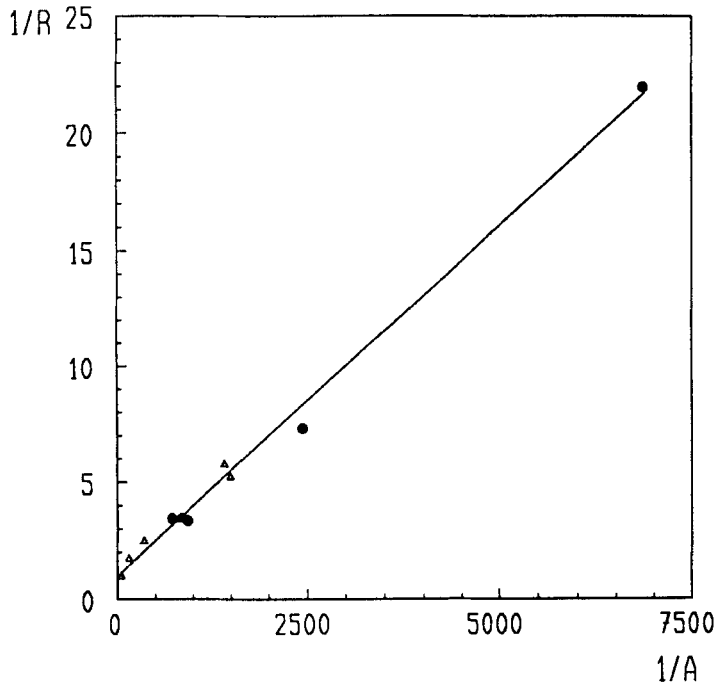

FIG. 2 Sorption of strontium from 1 M LiCl–$LiNO_3$, pH 3, aqueous solutions (10 mL) at 25°C on R-18C6 polymer network (10^{-4} mol 18C6): $1/R$ vs $1/A$ plot at various [Sr] and [NO_3^-] (●: [NO_3^-] varying from 0.1 to 0.4 M; △: [NO_3^-] = 1 M).

tion), which is expressed by $K_1 < K_{ex}$ (both in M^{-3}), can be explained by a loss of flexibility and accessibility of the 18C6 moieties bound to the polymer network.

The sorption of Sr^{2+} on the R-18C6 polymer from a 1 M LiCl nitrate free aqueous solution was found to be negligible as was its liquid–liquid extraction with DC-18-C-6 crown ethers (14).

Temperature Effect and Strontium Stripping. The temperature effect on the R-18C6,$Sr(NO_3)_2$ complexation is shown in Fig. 3. Increasing the temperature clearly induces a decrease in bound 18C6/Sr^{2+} in the polymer network, confirming the results of Warshawsky et al. (17). Because of this, stripping experiments were performed by equilibrating 50 mg resin initially saturated with $Sr(NO_3)_2$ into 10 mL distilled water. After 1 hour at 60°C, 70% of the strontium was released compared to only 35% at 25°C. A complete release was achieved after more than 5 hours, allowing new sorption–desorption cycles without any noticeable alteration.

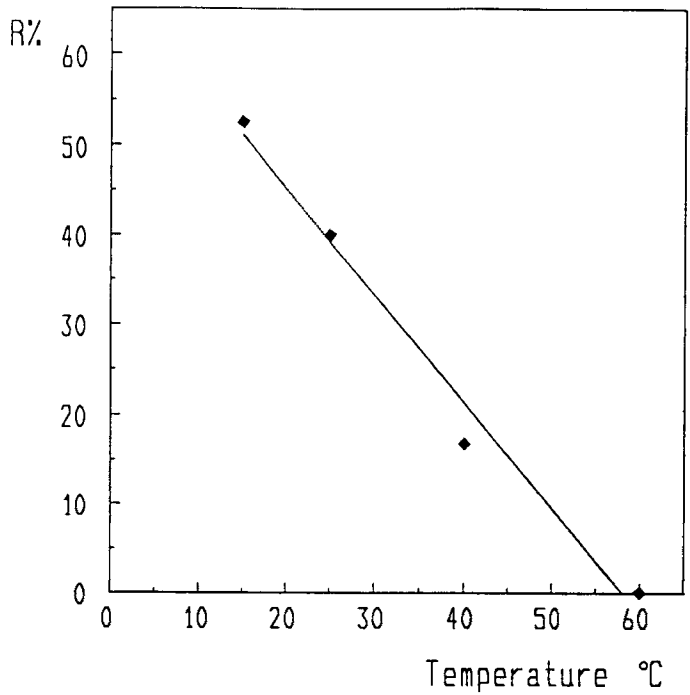

FIG. 3 Sorption of strontium from 1 M $LiNO_3$, pH 3, aqueous solutions (10 mL) on R-18C6 network polymer (10^{-4} mol): temperature effect (total initial strontium concentrations ≈ 1.1–$1.5\ 10^{-2}$ M).

Acidity Effect. In order to check the possibility of strontium extraction with R-18C6 from acidic nuclear wastes, complexation experiments were carried out in 1 M HNO_3. No noticeable difference was observed for strontium extraction compared with the $LiNO_3$ medium. This behavior differs from the results obtained for liquid–liquid extraction using DC-18-C-6 in chloroform (14). In this case, competitive extraction of HNO_3 was observed, which was very likely due to the solvating power of chloroform.

Strontium Extraction in the Presence of Rare Earths. The reactions of lanthanide cations with macrocycles have received little attention. The stabilities of 18-crown-6 complexes formed in methanol were studied by Izatt et al. (18). They show that the binding constant for lanthanum is about 1000 times lower than that for strontium. In order to check the possible usefulness of R-18C6 resin for the extraction of strontium from concentrated aqueous rare earth water solutions, two types of experiments were performed. In the first series, the extraction of lanthanum

nitrate at pH 3 in 1 M $LiNO_3$ solution was studied using equimolecular concentrations of lanthanum and ligand; no extraction of lanthanum was observed. In the second series, extractions of mixtures of strontium and lanthanum or europium were realized. The concentrations of strontium and the ligand were kept constant (10 mM), whereas the rare earth concentrations were varied as 2, 5, and 10 mM. The results showed that strontium extraction is unaffected and that no lanthanum or europium is present in the resin.

The good selectivity of the resin observed for strontium and expected for barium, which is also well complexed by the crown ether, make the use of such a resin very attractive for trace extraction of these elements. However, further experiments are needed to complete this study.

CONCLUSIONS

A 18-C-6 crown ether-containing polystyrene network, crosslinked with 6.5% divinylbenzene and with a capacity of 2.04 mmol ligand/g, was prepared. It extracts $Sr(NO_3)_2$ selectively from 1 M LiCl–$LiNO_3$ aqueous solutions containing La^{3+} or Eu^{3+} ions with the formation of 1:1 complexes [18C6,$Sr(NO_3)_2$]. The replacement of 1 M $LiNO_3$ with 1 M HNO_3 does not significantly modify strontium extraction. Complete stripping of strontium can be performed in distilled water at 60°C. These properties make the use of such a bound ligand very attractive in rare earth elements purification as well as in the separation of strontium from nuclear wastes. However, the kinetics of strontium uptake and release are rather slow because of the hydrophobic character of the polystyrene matrix. An increase in water swelling of the resin through the use of a more hydrophilic matrix without a loss of the exceptional mechanical properties and stability of the polystyrene matrix is needed.

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REFERENCES

1. Y. Takeda, *Top. Curr. Chem.*, *121*, 1 (1984).
2. S. K. Sahni and J. Reedijk, *Coord. Chem. Rev.*, *59*, 1 (1984).
3. J. Smid and R. Sinta, *Top. Curr. Chem.*, *121*, 105 (1984).
4. B. Czech, *Tetrahedron Lett.*, *21*, 4197 (1980).
5. J. Howe and T. Malkin, *J. Chem. Soc.*, p. 2663 (1951).
6. J. Dale and P. O. Kristiansen, *Acta Chem. Scand.*, *26*, 1471 (1972).

7. M. Lauth, Y. Frère, B. Meurer, and Ph. Gramain, *Reactive Polym.*, *12*, 155 (1990).
8. R. M. Izatt and J. J. Christensen (Eds.), *Synthetic Multidentate Macrocyclic Compounds*, Academic Press, New York, 1978.
9. L. Pauling (Ed.), *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960.
10. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, *98*, 7620 (1976).
11. Present authors, Unpublished Results.
12. V. A. Fedorov, A. M. Robov, I. I. Shmyd'ko, N. A. Vorontsova, and V. E. Mironov, *Russ. J. Inorg. Chem.*, *19*, 950 (1974).
13. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, and J. J. Christensen, *Chem. Rev.*, *85*, 271 (1985).
14. T. Delloye, M. Burgard, and M. J. F. Leroy, *New J. Chem.*, *13*, 139 (1989). T. Delloye, Dissertation Thesis, U.L.P., F-Strasbourg, 1985.
15. Ph. Gramain, in *Recent Developments in Ion Exchange* (P. A. Williams and M. J. Hudson, Eds.), Elsevier Applied Science, London, 1987, p. 300.
16. R. Sinta and J. Smid, *J. Am. Chem. Soc.*, *103*, 6962 (1981).
17. A. Warshawsky and N. Kahana, *Reactive Polym.*, *4*, 27 (1985).
18. R. M. Izatt, J. D. Lamb, J. J. Christensen, and B. L. Haymore, *J. Am. Chem. Soc.*, *97*, 8344 (1977).

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