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Performance of Chelating Resins Containing Calixpyrroles in Sorption of Anions

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Abstract: Characteristics and sorptive properties of three series of chelating resins having incorporated calixpyrrole ligands within their structures is reported. Two sets of resins were obtained by immobilization of calix[4]pyrrole or calix[4]pyrrole[2]-thiophene on the beads of crosslinked (vinylbenzyl chloride)/divinylbenzene copolymer. The third series was synthesized by condensation of calix[4]pyrrole with formaldehyde. All resins displayed sorptive properties towards halide anions and cyanides in a non-aqueous medium (acetonitrile). The resins displayed superior selectivity for fluoride anions and the selectivity sequence for the uptake of other anions depended on their ionic radii. The bigger ligand, calix[4]pyrrole[2]thiophene, showed an enhanced affinity for bigger anions, including iodide, which was not observed in the case of calix[4]pyrroles. Thus, the resin containing the larger ligand complexes the whole range of anions, but with poorer selectivities.

Keywords: Chelating resins, sorption, calixpyrroles, anions

INTRODUCTION

Since the discovery of their binding potential in 1996 (1), calixpyrroles have become the object of intense research in the area of supramolecular chemistry. This porphyrinogen-like macrocycles are easy to synthesize, exhibiting high affinity towards simple anions in non-aqueous media, especially to fluoride

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anions e.g. calix[4]pyrrole **1**, where the binding constant to F^- anion (ca. 10^4 1/M in acetonitrile-d_3) is 1–2 orders of magnitude greater than for other simple anions (2). The selectivity of calixpyrroles for anions depends on the number of pyrrole units in the molecule as well as on the nature of other functional groups present in the macrocycle. Generally, calix[4]pyrroles have a noticeable preference for fluoride anions relative to other anionic guests, such as Cl^-, Br^- or $H_2PO_4^-$, whereas macrocycles of larger cavity show enhanced binding of larger anions. A variety of modifications of calixpyrrole structures were reported by different research groups. The modification resulted in the improved anion binding affinity as well as enhanced selectivity of the macrocycle for a desired guest anion (3–5).

Calixpyrroles have recently been studied as receptors for possible use in optical or electrochemical recognition of anions (6–8) and HPLC supports for the separation of anions and neutral substrates (9). Such macrocycles were also intensively studied as receptors for biologically important anions, such as phosphates, acetates, carboxylates, oxalates, or succinates (8, 10–12). So called "hybrid" calixpyrroles have also been reported in literature. These also incorporate other than pyrrole heterocyclic units in the macrocycle (10, 11, 13, 14). These structures are a new class of receptors with both anion and cation binding potential, due to the presence of the lone pair of donor electron in the structure (like thiophene or furan).

Synthetic ion-exchange/chelating resins are widely used in the industry as well as in analytical and synthetic chemistry as sorbents or catalysts (15). They are an alternative to the processes that involve the use of organic solvents (e.g. in liquid-liquid extraction). Since the molecule of an extractant or catalyst is attached to an insoluble polymeric resin, it is not lost during extraction and the resin can be used in continuous processes, regenerated and re-used. Industrially important processes like catalysis, as well as removal or preconcentration of ionic species involve mainly cations, so most of the known polymeric resins are cation-selective ion-exchangers or cation-containing catalysts. Anion-exchangers or chelating resins for anions have been explored to the lesser degree, although considerable efforts are currently being devoted to the development of receptors for anions (16, 17). This growth of interest in anion-selective receptors has been prompted by the importance of anions in biological processes as well as in the need to remove some toxic species, like chromium(VI), from the environment. For this initiative, materials that can selectively remove or detect anions are required, preferably in the form of insoluble, polymeric material. This can be achieved by incorporation of the selective anion-receptor on to or within the polymeric matrix by immobilization, polymerization, solvent impregnation procedure or other techniques.

In our recent papers (18, 19) we have shown that it is possible to obtain materials containing calixpyrrole units within the polymeric matrix by three methods—(a) immobilization of calix[4]pyrrole and calix[4]pyrrole[2]-thiophene receptors on the solid support (crosslinked polymeric resin) (b), condensation of an appropriate calixpyrrole molecule with formaldehyde, and (c) radical copolymerization of a calixpyrrole molecule containing double bonds with other monomers. Moreover, we have demonstrated that such materials exhibit sorption properties towards simple anions in acetonitrile, complexing fluorides, chlorides, and cyanides, and in some cases also bromides, though always with a preference for the fluoride anion. In the case of chelating resins with calix[4]pyrrole[2]thiophene we have also shown that it can, apart from the ability of the ligand to bind anions in non--aqueous systems, form complexes with cations of the precious metals, such as Au(III), Ag(I), Pt(IV) or Pd(II) in water (19). Thus, we have shown that it is possible to obtain sorbents of ions by incorporation of calixpyrrole macrocycles into a polymer network.

The reason that prompted us to undertake these studies was a need to find an efficient synthesis route to prepare chelating resins containing macrocycles, such as calixpyrroles. Since there is a demand for materials able to separate unwanted inorganic species, e.g. to remove heavy metal derivatives from fuels, we believe that our research may speed up the development of the anion-selective chelating resins, also working in the non-aqueous media, were they can be utilized as HPLC supports.

In this study we present the sorption properties of three types of chelating resins containing calixpyrroles, obtained either by immobilization of calix[4]-pyrrole **1** (series A) and calix[4]pyrrole[2]thiophene **2** (series B) on a polymeric support or by condensation of calix[4]pyrrole **1** molecule with formaldehyde (series C), which results in an insoluble material containing calixpyrroles distributed in the mass of the resin. The results of sorption studies including sorption isotherms, kinetics, and selectivities of the resins for simple anions in acetonitrile using batch sorption experiments are reported.

EXPERIMENTAL

Materials and Methods

Tetrabutylammonium salts were purchased from Sigma-Aldrich Co. and used as received. Dry acetonitrile (HPLC grade) was purchased from POCh Gliwice, Poland and used as received.

The nitrogen content in the resins was determined by the Kjeldahl method. Solvent regain (W) of the resins was measured by the centrifugation method in which ca. 1 g of swollen polymer was centrifuged for 5 min at 3000 rpm, weighted, dried at 100°C for 24 h and again weighted. $W = (m_w - m_d)/m_d$, where m_w is the weight of the swollen polymer after centrifugation and m_d is the weight of dry polymer.

The distribution coefficient K was calculated as the ratio of the amount of anion taken by 1 g of dry resin and the amount of the anion at equilibrium in 1 mL of solution.

The FTIR spectra of the chelating resins were recorded on a Perkin-Elmer System 2000 spectrometer. Bromide, iodide and cyanide ion-selective electrodes were purchased from Hydromet, Poland. Chloride and fluoride electrodes were purchased from Cole–Parmer.

Syntheses of the Chelating Resins

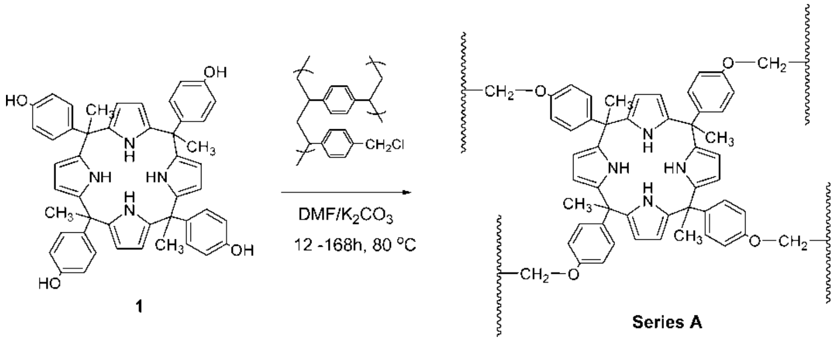
Resins of series A were synthesized *via* immobilization of tetra-(4-hydroxyphenyl)-tetramethylcalix[4]pyrrole **1** (20) on a (vinylbenzyl chloride)/divinylbenzene suspension copolymer (VBC/DVB) (gel type, containing 0.5% w/w of DVB) following the procedure described in Ref. (18) (Scheme 1).

Resins of series B were synthesized *via* immobilization of calix[4]pyrrole[2]thiophene **2** on the (vinylbenzyl chloride)/divinylbenzene suspension copolymer (VBC/DVB) (gel type, containing 0.5% w/w of DVB) following the procedure described in Ref. (19) (Scheme 2).

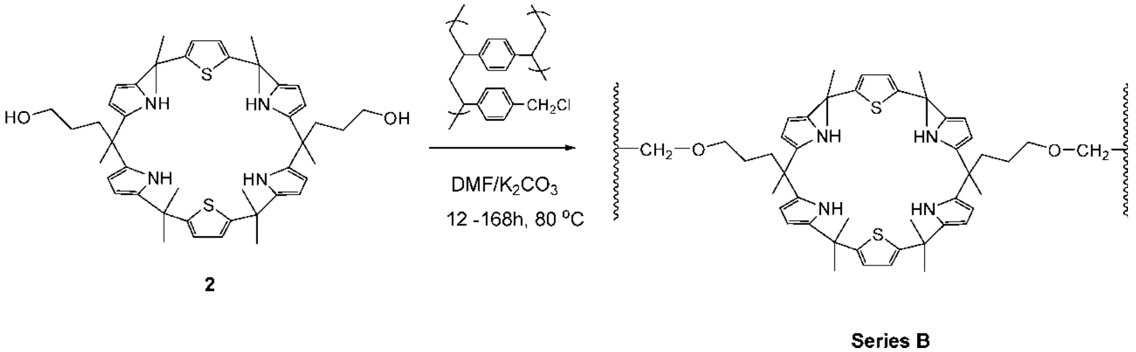
Resins of series C were obtained by condensation of tetra-(4-hydroxyphenyl)-tetramethylcalix[4]pyrrole **1** with formaldehyde in the presence of NaOH *via* reversed phase suspension polymerization in toluene as an inert continuous phase in which droplets of the pre-polymer containing calixpyrrole were dispersed. For details see Ref. (18).

Evaluation of the Sorption Properties

Batch-mode sorption studies were performed in dry acetonitrile. Resins were swollen in acetonitrile and then centrifuged at 3000 rpm for 5 min. Samples of swollen centrifuged resins containing a known amount of calixpyrrole were shaken for 24 h with 25 mL of 1 mM solution of tetrabutylammonium salt containing an appropriate anion in acetonitrile. At the end of each experiment resins were filtered off, a known amount of the solution (20 mL) was diluted



Scheme 1. Synthesis of resins of series A.



Scheme 2. Synthesis of resins of series B.

with deionized water to ensure conductance, and the concentrations of anions were measured using ion-selective electrodes.

For the determination of sorption isotherms for the best-performing resins the samples of resins containing 0.015 mmol of ligand swelled in acetonitrile were shaken with solutions containing $0.2 - 2 \times$ molar excess of an appropriate tetrabutylammonium salt in acetonitrile at $22 \pm 2^{\circ}C$ for 24 h.

For the kinetics of sorption identical samples of resin containing 0.015 mmol of ligand were shaken with a solution containing $2 \times$ molar excess of tetrabutylammonium fluoride in acetonitrile at $22 \pm 2^{\circ}C$. Samples were taken at different intervals of time, resin and solution separated and the concentration of anion measured by ion-selective electrode.

For the selectivity studies samples of the resin containing 0.015 mmol of ligand were shaken with 25 mL of solutions of a pair of anions (fluoride and another competing anion, 1 mM each) in acetonitrile at $22 \pm 2^{\circ}C$ for 24 h. The selectivity coefficient (S) was calculated as the quotient of distribution coefficients calculated for each anion.

RESULTS AND DISCUSSION

Characterization of the Resins

The resins studied in this work are divided into three series. Series A and B were obtained by immobilization of calixpyrroles **1** (18) and **2** (19) on the beads of gel-type, crosslinked copolymer ((vinylbenzyl chloride)/divinylbenzene, 0.5% of DVB) which is commonly used for such modifications, because the —CH_2Cl functionality reacts with nucleophilic functional groups and therefore various ligands can be easily attached to the polymer matrix. Resins of series C were obtained by condensation of calixpyrrole **1** with formaldehyde in the presence of 1 M NaOH (18). In this method, a pre-polymer of **1** and formaldehyde was initially prepared and then suspended in toluene and kept at an elevated temperature for different times (30 min–24 h) to harden. This process yielded beads (1–3 mm diameter) of chelating resins of different crosslinking degree.

All resins were characterized by their ligand content and swelling properties in acetonitrile, which was used as a non-aqueous medium for the sorption studies. Ligand content in the resins was calculated from the analysis of nitrogen (introduced to the polymers by calixpyrrole units). Four resins in series A and B and six resins in series C were obtained (refer to Table 1).

The immobilization reactions on VBC/DVB copolymer were performed in DMF in the presence of K_2CO_3 at 80°C for different periods of time to test how this influences the modification. It was found that extending the immobilization time improves the calixpyrroles capacity both in series A and B. Although the highest values were observed after 7 days of modification,

Table 1. Basic characteristics of the obtained series of chelating resins

	Resin no.	Modification time (h)	N (mmol/g)	Calixpyrroles content (mmol/g)	CH_3CN regain (g/g)
Series A	A1	12	0.65	0.16	0.37
	A2	24	1.25	0.31	0.46
	A3	72	2.17	0.54	0.55
	A4	168	2.43	0.61	0.54
Series B	B1	12	0.24	0.06	0.36
	B2	24	0.41	0.10	0.58
	B3	72	1.08	0.27	0.67
	B4	168	1.16	0.29	0.66
Series C	C1	0.5	4.12	1.03	5.43
	C2	1	4.14	1.04	4.04
	C3	2	4.01	1.00	1.75
	C4	5	4.37	1.09	1.30
	C5	20	3.90	0.97	1.02
	C6	24	4.40	1.10	0.80

3 days was enough to obtain satisfactory ligand content. In the case of series A and B a small increase of the acetonitrile regain is observed along with the ligand content increase. This may be a result of a slight change of solubility parameter of these resins connected with the introduction of calixpyrrole units to the polymer.

The modification of VBC/DVB copolymer can be followed by IR spectroscopy. Figure 1 shows the IR spectra of an unmodified VBC/DVB support and resins A1-A4. It can be seen that along with the increase of modification degree the C-Cl band at 1265 cm^{-1} disappears, band at 1175 cm^{-1} from pyrrole appears and the intensity of bands at 1610 cm^{-1} and 1010 cm^{-1} attributed to aromatic rings increases.

In contrast to A and B, resins in series C have similar ligand content (0.97–1.10 mmol/g) but they significantly differ in acetonitrile regain. This feature is attributed to the crosslinking degree of the resins, which was regulated by changing the hardening time during syntheses. Each molecule of calixpyrrole **1** has four p-hydroxyphenyl groups that undergo condensation reaction with formaldehyde. During the synthesis a viscous but soluble in 1 M NaOH prepolymer is first obtained, then suspended in toluene and heated. During heating further condensation reactions occur, which we believe are similar to what happens during the formation of phenol-formaldehyde resins that are heated—the prepolymer undergoes additional condensation that leads to an insoluble, crosslinked material (resite-type). Table 1 shows that the acetonitrile regain is higher when resin was shortly hardened (C1, 0.5 h, $W = 5.43$ g/g), but prolonged hardening makes the polymeric

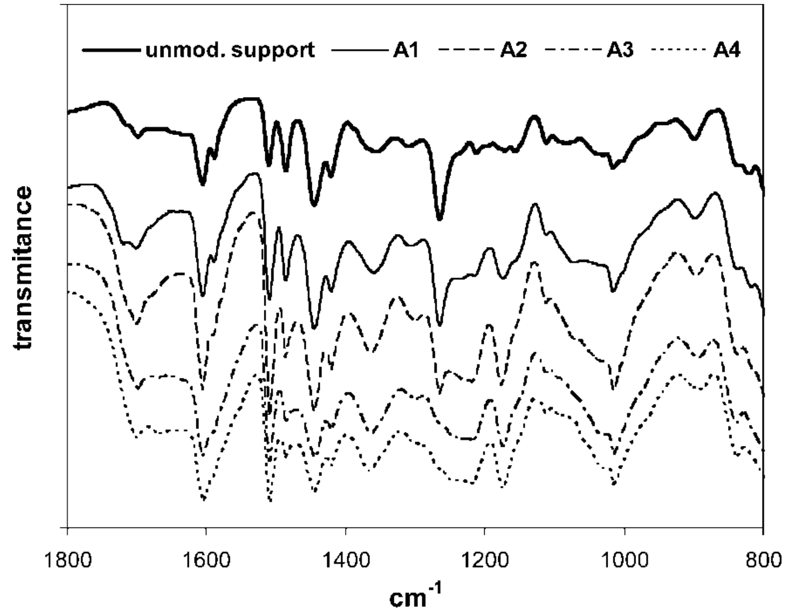
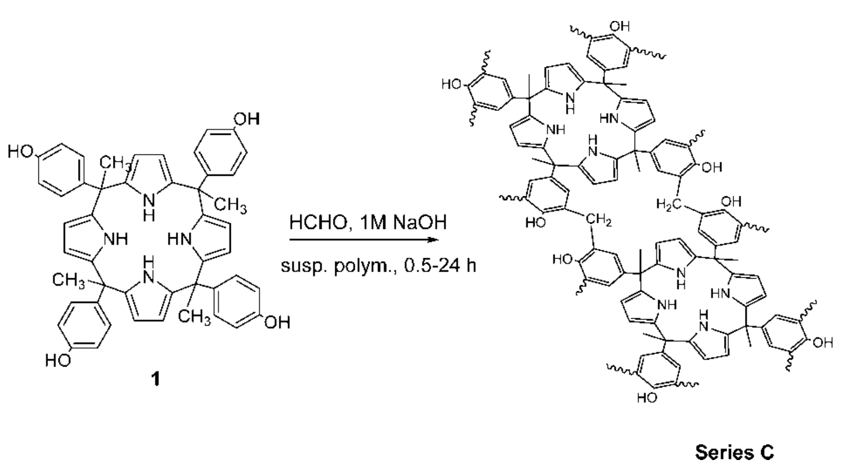


Figure 1. FTIR spectrum of unmodified VBC/DVB support and resins A1–A4.

network more rigid; crosslinking prevails due to the formation of further bridges between calixpyrroles. Therefore, the solvent poorly penetrates the resin, what results in low CH_3CN regain (C6, 24 h, W = 0.80 g/g). We suppose that resins of series C consists of linked calixpyrrole units (Scheme 3), with linkage through —CH_2— or —CH_2OCH_2— bridges



Scheme 3. Synthesis of resins of series C.

between calixpyrrole units. In the FTIR spectra of resins of series C (Fig. 2) dominating bands are: broad bands between 1700 and $1600\,cm^{-1}$, coming from aromatic rings; bands at $1475\,cm^{-1}$ and $1370\,cm^{-1}$ from methylene bridges and -CH_3 deformation vibrations, respectively, and broad bands at $1190\,cm^{-1}$ from pyrrole. This data indicate then the presence of —CH_2— linkage between calixpyrrole units, although the expected —CH_2OCH_2— bridges bands at about $1250\,cm^{-1}$ may overlap with the pyrrole band.

As a result of a different crosslinking degree, the resins in series C demonstrated a dependence of sorptive properties on the solvent regain. In Fig. 3 distribution coefficients (K) of resins of series C in sorption of fluorides, chlorides and bromides *versus* acetonitrile regain are plotted (batch sorption at 5 × excess of ligand relative to anions in solution). K values for all anions rises as solvent regain rises. This is due to the better accessibility of the binding place for anions when resin has high swelling. It can also be seen that bromides, which are bigger than fluorides and chlorides, are complexed only by the two resins of the highest swelling, which indicates that the better accessibility of the solvent in these resins enables bigger anions to penetrate the network and form complexes.

It is therefore seen that sorptive properties may not only be controlled by the content of the calixpyrroles in the resin but also by changing the crosslinking degree, thus enabling other anions to reach the ligand moiety and form complexes. Such dependence was not observed on the resins obtained

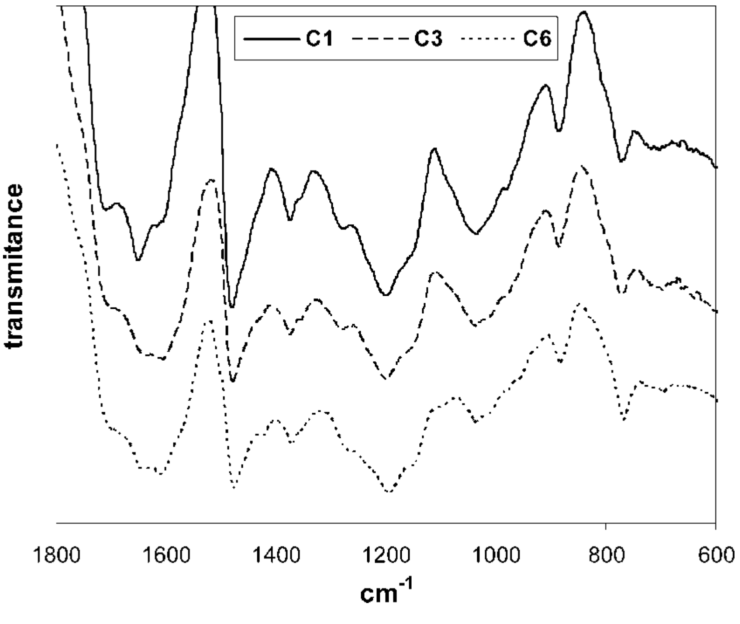


Figure 2. FTIR spectra of some resins of series C.

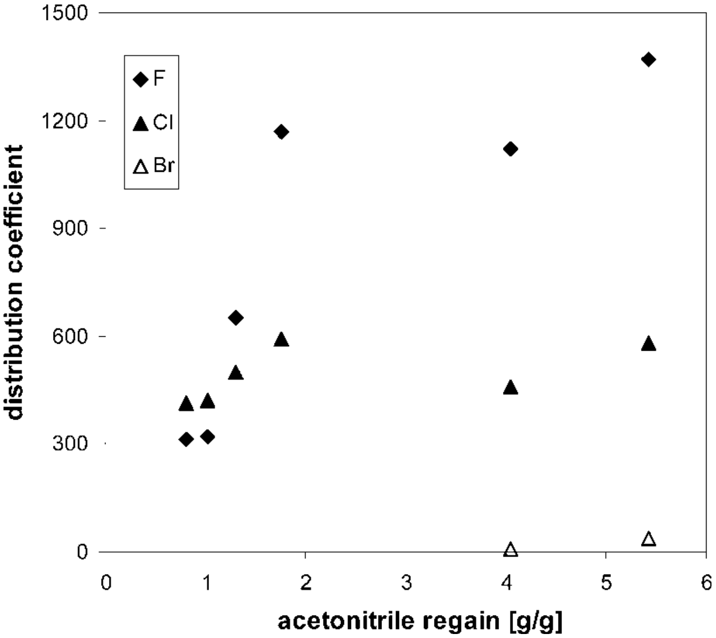


Figure 3. Distribution coefficients (K) of resins of series C in sorption of fluorides, chlorides and bromides as a function of acetonitrile regain of the resins (batch sorption at 5× excess of ligand relative to anions in solution).

by immobilization. This indicates that in this case calixpyrrole ligands are present on the outer surface of the beads.

Three resins: A4, B4, and C3 were chosen for further detailed studies on anion uptake, kinetics and selectivity. A4 and B4 showed the highest calixpyrroles content from their series and showed the best performance in preliminary studies. Resin C3 was used because of its high anion uptake, good swelling and mechanical properties.

Sorption Isotherms

Resins A4, B4, and C3 represent two types of materials obtained either by immobilization (A4 and B4) or condensation (C3), and they also represent two types of ligands incorporated into polymer: calix[4]pyrrole **1** in resins A4 and C3, and calix[4]pyrrole[2]thiophene **2** in resin B4. As a result, resins can be compared either with respect to their structure or the binding ability of the ligand. Sorption isotherms of resins A4, B4, and C3 determined for halide anions and cyanides in acetonitrile are presented in Figs. 4, 5, and 6, respectively.

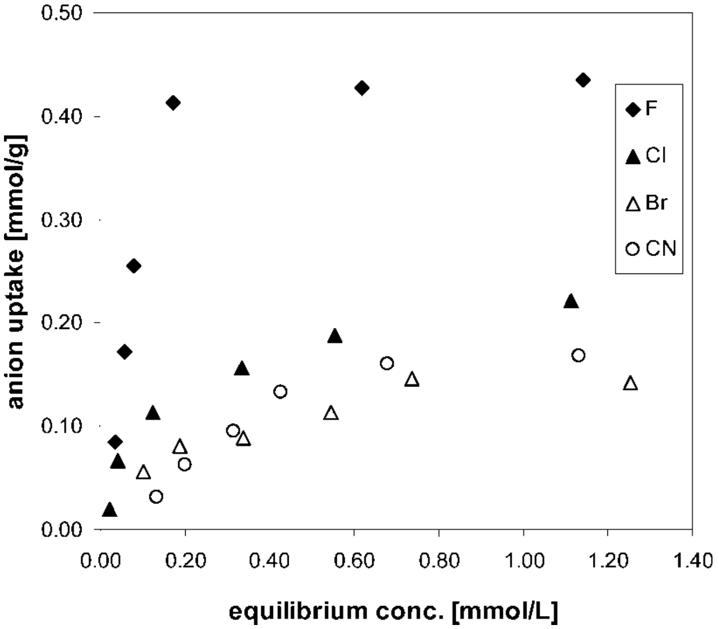


Figure 4. Isotherms of sorption of anions as their tetrabutylammonium salts in acetonitrile on resin A4 containing immobilized calix[4]pyrrole **1**.

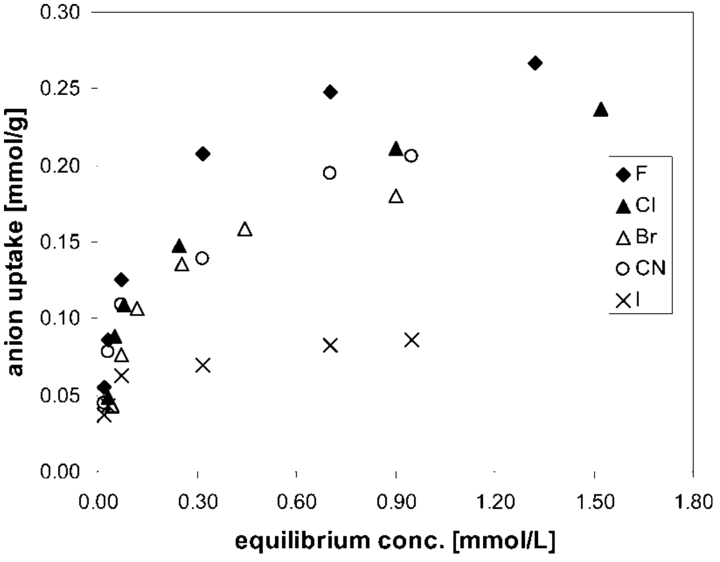


Figure 5. Isotherms of sorption of anions as their tetrabutylammonium salts in acetonitrile on resin B4 containing immobilized calix[4]pyrrole[2]thiophene **2**.

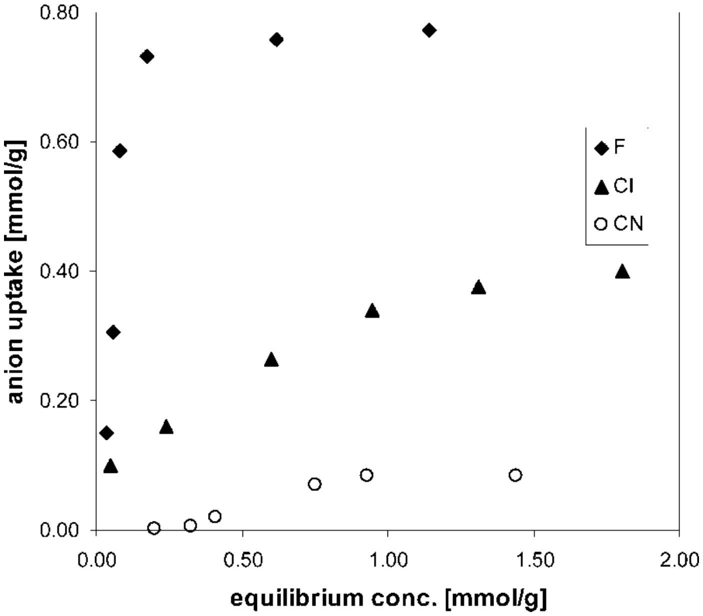


Figure 6. Isotherms of sorption of anions as their tetrabutylammonium salts in acetonitrile on resin C3 obtained by condensation of calix[4]pyrrole **1** with formaldehyde.

It can be seen that all resins show Langmuir-type isotherms and in all cases the best uptake is observed for fluorides. The maximum uptake of anions was calculated by fitting the sorption data to a modified Langmuir equation:

$$\frac{1}{q}=\frac{a}{q_{\max}c}+\frac{1}{q_{\max}}$$

where q is the uptake at equilibrum concentration (mmol/g_{resin}), $q_{\max}$ is the maximum uptake (mmol/g), c is the equilibrium concentration (mmol/mL), a is a constant (mmol/mL). The q_{max} values are given in Table 2.

The uptake of F^- by C3 is almost twice higher than for A4 and three times higher than for B4, which is the effect of the highest ligand content (1.00 mmol/g compared to 0.61 and 0.29 in A4 and B4, respectively). The other factor influencing the sorption here is the size of fluoride, which has the smallest ionic radius among the anions studied (1.33 Å) and bests fits the size of macrocyclic cavity. Such relationship is also observed for non-immobilized calixpyrroles (3).

A similar relation is observed for chlorides (1.81 Å), yet the uptake of larger anions, like bromides (1.96 Å) and iodides (2.20 Å) depends on the type of the material. Resins obtained by immobilization form complexes with bromides and cyanides but in case of C3 we could not calculate a clear

Table 2. Maximum anion capacity of the best-performing resins calculated by fitting the sorption data to Langmuir equation

Anion studied	Maximum anion capacity (mmol/g)		
	A4	B4	C3
F^-	0.436	0.279	0.774
Cl^-	0.223	0.256	0.420
Br^-	0.158	0.202	—
CN^-	0.180	0.213	0.085
I^-	—	0.083	—

uptake curve for bromides, because the sorption was minor. Also the uptake of CN^- (1.92 Å) on this resin was small. This may be a consequence of the structure of C3, which consists of linked calixpyrrole units distributed in the mass of polymer. Probably the high crosslinking degree in this resin causes a severe steric hindrance near the binding site of the ligand that influences the complexation, despite the relatively good swelling. As shown in Fig. 3, only resins of the highest swelling, and consequently having less rigid network, have shown some, although poor, sorption of bromides.

Interestingly, sorption of iodides was only observed for resin B4, which contains immobilized compound **2** (Scheme 2). This was achieved because calix[4]pyrrole[2]thiophene has an enlarged cavity, due to the presence of two thiophene units in the molecule, and therefore is capable of complexing bigger anions. Iodide, which has an anionic radius of 2.20 Å, cannot be bound by resins A4 and C3 that contain calix[4]pyrroles, because this macrocycle has a cavity too small for the iodide to form hydrogen bonds. The enlarged cavity of **2** is big enough to catch this anion, although at a moderate level (maximum uptake is *ca* 0.09 mmol/g). An increased uptake of cyanides is also observed in case of resin B4 (0.213 mmol/g) compared to A4 and C3, which is due to the formation of more stable complexes between CN^- and large cavity of calix[4]pyrrole[2]thiophene.

To sum up, the formation of chelating resins like C3, which consists of linked calixpyrroles, gives a material of good uptake of small anions, but low crosslinking degree is required to catch larger anionic guests like bromides. Immobilized calixpyrroles offer this possibility, but with limited uptake. On the other hand, changing the structure of the ligand to a spacious calix[4]pyrrole[2]thiophene **2** enables binding of bigger anions, like iodides.

Sorption Kinetics

The uptake of fluorides on resins A4, B4, and C3 as the function of time is shown in Fig. 7. It can be seen that the uptake is slow and reaches the

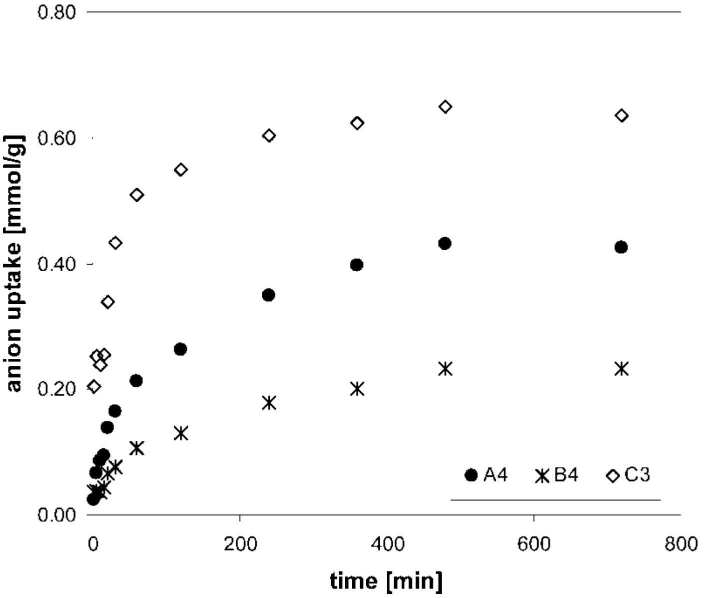


Figure 7. Kinetics of sorption of fluoride on resin A4, B4, and C3. Identical samples of resin containing 0.015 mmol of ligand were shaken with solution containing 2× molar excess of tetrabutylammonium fluoride in acetonitrile at 22 ± 2°C.

maximum value only after about 8 hours in all cases. The sorption does not seem to depend on the structure of the polymer or the type of calixpyrrole; it is probably driven only by the slow formation of equilibrium state between anions in solution and anion-macrocycle complexes on the polymer.

Selectivity Studies

Selectivity studies on resins A4, B4, and C3 were performed using binary mixtures containing fluoride and other anion in 1/1 concentration ratio in acetonitrile. After sorption, the selective measurement of concentrations of each anion was possible using anion-selective electrodes. Table 3 presents selectivity coefficients for the three types of resins studied, calculated as the quotient of distribution coefficients recorded for each anion. In all cases fluoride has a preference over other anions, which was expected from the above studies. Best selectivities are observed in the case of resins containing calix[4]pyrrole **1,** especially for bigger anions (Br^-, CN^-) and in the F^-/I^- pair a complete separation can be obtained, because iodides are not complexed. In contrast, resin B4 enables separation of fluorides and iodides in 12.8 ratio, due to the enlarged cavity of the ligand, but it shows rather poor selectivity coefficients for other anions. This is caused by the enhanced sorption of bigger anions on calix[4]pyrrole[2]thiophene **2**.

Table 3. Selectivity coefficients of resins A4, B4, and C3 in batch sorption from binary mixtures containing fluoride and other anion in acetonitrile. Samples of resins contained 0.015 mmol of ligand, the initial concentration of each anion was 1 mM

Anion pair	Selectivity coefficient A4	Selectivity coefficient B4	Selectivity coefficient C3
F^-/Cl^-	11.4	2.5	16.0
F^-/Br^-	31.0	3.7	90.9
F^-/CN^-	30.8	2.1	22.8
F^-/I^-	∞	12.8	∞

Regeneration of the Resins

During all presented studies special attention has been paid to the absence of water in the acetonitrile solutions of tetrabutylammonium salts. It is known from the literature (3, 6) that even a small amount of water in the solvent decreases the interaction strength between calixpyrroles and anions, due to competitive hydrogen bonding exhibited by water molecules. It is therefore possible to use this phenomenon to desorb anions from the resins using just water as eluent and regenerate these materials transferring them back to dry acetonitrile. Indeed, we have observed complete desorption of anions from all types of resins using water. Initial experiments on the durability of the resins containing calixpyrroles showed no change in anion capacity after several cycles of sorption and desorption. Detailed studies are in progress.

CONCLUSIONS

We have demonstrated sorptive properties of three types of resins incorporating calixpyrroles within the structure of polymer. Two series of resins were obtained by immobilization of the ligand on the crosslinked styrenic-type copolymers and the third series by condensation of calixpyrrole with formaldehyde. All resins have shown an ability to complex anions as their tetrabutylammonium salts from non-aqueous solutions, proving that the binding abilities described for native calixpyrroles (2) are also retained in case of such macrocycles in the polymeric matrix. The best uptake, as expected, was observed for fluorides and the bigger the anionic radius of the anionic guest was, the poorer sorption was observed. Best anion capacity was detected for resin C3 containing linked calixpyrrole units, but the structure of such resin was too rigid to let bigger anions penetrate the polymer. Such feature may be useful for selective sorption or separation of anions. The extension of the cavity of calixpyrrole in resin B4 resulted in an enhanced sorption of bigger anions, enabling even binding of iodides. This however, resulted in poorer selectivity coefficient of this type of resin.

In conclusion, we have shown that the binding ability of chelating resins containing calixpyrroles may be tuned either by changing the size of the macrocycle, which may be adjusted to the size of given anions, or by controlling the crosslinking of the polymeric material containing calixpyrroles, like in series C.

Although of limited applications, chelating resins complexing anions in non-aqueous systems may be implemented in different analytical techniques, e.g. HPLC. These materials can be also further developed to obtain sorbents of specific characteristics.

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REFERENCES

1. Gale, P.A., Sessler, J.L., Král, V., and Lynch, V. (1996) Calix[4]pyrroles: Old yet new anion-binding agents. *J. Am. Chem. Soc.*, 118: 5140.
2. Gale, P.A., Sessler, J.L., and Král, V. (1998) Calixpyrroles. *Chem. Commun.*, 1.
3. Gale, P.A., Anzenbacher Jr, P., and Sessler, J.L. (2001) Calixpyrroles II. *Coord. Chem. Rev.*, 222: 57.
4. Sessler, J.L., Anzenbacher Jr, P., Miyaji, H., Jursíková, K., Bleasdale, E.R., and Gale, P.A. (2000) Modified calix[4]pyrroles. *Ind. Eng. Chem. Res.*, 39: 3471.
5. Sessler, J.L., Camilo, S., and Gale, P.A. (2003) Pyrrolic and polypyrrolic anion binding agents. *Coord. Chem. Rev.*, 240: 17.
6. Miyaji, H., Sato, W., and Sessler, J.L. (2000) Naked-eye detection of anions in dichloromethane: Colorimetric anion sensors based on calix[4]pyrrole. *Angew. Chem. Int. Ed.*, 39: 1777.
7. Nielsen, K.A., Jeppesen, J.O., Levillain, E., and Becher, J. (2003) Mono-tetrathiafluvalene calix[4]pyrrole in the electrochemical sensing of anions. *Angew. Chem. Int. Ed.*, 42: 187.
8. Nishiyabu, R. and Anzenbacher, Jr, P., (2005) Sensing of antipyretic carboxylates by simple chromogenic calix[4]pyrroles. *J. Am. Chem. Soc.*, 127: 8270.
9. Sessler, J.L., Gale, P.A., and Genge, W. (1998) Calix[4]pyrroles: New solid-phase HPLC supports for the separation of anions. *Chem. Eur. J*, 4 (6): 1095.
10. Sessler, J.L., An, D., Cho, W.-S., and Lynch, V. (2003) Calix[2]bipyrrole[2]furan and calix[2]bipyrrole[2]thiopene: New pyrrolic receptors exhibiting a preference for carboxylate anions. *J. Am. Chem. Soc.*, 125: 13647.
11. Sessler, J.L., An, D., Cho, W.-S., Lynch, V., Yoon, D.-W., Hong, S.-J., and Lee, Ch.-H. (2005) Anion-binding behavior of hybrid calixpyrroles. *J. Org. Chem.*, 70: 1511.
12. Piątek, P., Lynch, V.M., and Sessler, J.L. (2004) Calix[4]pyrrole[2]carbazole: A new kind of expanded calixpyrrole. *J. Am. Chem. Soc.*, 126: 16073.

13. Cafeo, G., Kohnke, F.H., La Torre, G.L., White, A.J.P., and Williams, D. (2000) From large furan-based calixarenes to calixpyrroles and calix[n]furan[m]pyrroles: Syntheses and structures. *Angew. Chem. Int. Ed.*, 39: 1496.
14. Nagarajan, A., Ka, J.-W., and Lee, Ch.-H. (2001) Synthesis of expanded calix[n]-pyrroles and their furan or thiophene analogues. *Tetrahedron*, 57: 7323.
15. Dorfner, K. (ed.). (1991) *Ion Exchangers*; De Gruyter: Berlin.
16. Choi, K. and Hamilton, A.D. (2003) Macrocyclic anion receptors based on direct hydrogen bonding interactions. *Coord. Chem. Rev.*, 240: 101.
17. Beer, P.D. and Gale, P.A. (2001) Anion recognition and sensing: The state of the art and future perspectives. *Angew. Chem. Int. Ed.*, 40: 486.
18. Kałędkowski, A. and Trochimczuk, A.W. (2006) Novel chelating resins containing calix[4]pyrroles: Synthesis and sorptive properties. *React. Funct. Polym.*, 66: 740–746.
19. Kałędkowski, A. and Trochimczuk, A.W. (2006) Chelating resin containing hybrid calixpyrroles: New sorbent for noble metal cations. *React. Funct. Polym.*, 66: 957–966.
20. Anzenbacher Jr, P., Jursíková, K., Lynch, V.M., Gale, P.A., and Sessler, J.L. (1999) Calix[4]pyrroles containing deep cavities and fixed walls: Synthesis, structural studies and anion binding properties of the isomeric products derived from the condensation of p-hydroxyacetophenone and pyrrole. *J. Am. Chem. Soc.*, 121: 11020.