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Synthesis of Oligomer and Styrene Polymer-supported Calix[4]arene Derivatives and Selective Extraction of Fe^{3+}

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Five new polymeric compounds containing more than one calix[4]arene have been synthesized by reacting an oligomer with 5,11,17,23-tetrakis[(diethylamino)-methyl]-25,26,27,28-tetrahydroxycalix[4]arene (L1), 25, 27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone (L2), and *p*-nitrocalix[4]arene (L3), and chloromethylated polystyrene with 25,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone (L4) and *p*-nitrocalix[4]arene (L5). These compounds were studied by the selective extraction of Fe^{3+} cation from the aqueous phase into the organic phase and was carried out by using compounds L1–L5. It was observed that the polymer support attached to the lower rim of *p*-nitrocalix[4]arene was the most efficient carrier of Fe^{3+} in the extraction process.

Keywords: Calixarene; Oligomer; Polystyrene; Solvent extraction; Fe^{3+} ion

INTRODUCTION

Calixarenes are cyclic phenol oligomers linked by methylene groups [1]. Over recent decades, the development of supramolecular chemistry has been largely dominated by the design and synthesis of macrocyclic compounds with potential receptor capabilities [2]. These compounds have been assuming an increasingly important role in host–guest chemistry, because they can provide a well-organized platform for the attachment of pendant functional groups [3].

Lower rim modifications of calixarenes through the phenolic oxygen atoms have been widely explored in the design and synthesis of these compounds; especially on calix[4]arene with lower rim carbonyl-containing substituents in the form of esters, ketones, amides, thioamides and carboxylic acids [4–10].

Over the past decade, several double or multiple calixarenes have been prepared as examples of higher-order molecular architectures with new high-level host properties, such as allosterism and cooperativity [11,12]. In these compounds, two or more calixarenes are linked at their upper or lower rims by one or more spacer elements [13,14].

In our previous work [15–21], we have reported the synthesis of two new polymeric calix[4]arenes by reacting an oligomer or poly(acryloyl chloride) with tetraethylcalix[4]arenetetraacetate [22,23]. These polymers exhibited selectivity for Na^+ similar to that of the parent calixarene [24,25].

Herein, five new polymeric calix[4]arenes are described, which were synthesized by reacting an oligomer with 5,11,17,23-tetrakis[(diethylamino)-methyl]-25,26,27,28-tetrahydroxycalix[4]arene (**L1**), 5,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]-arene diketone (**L2**) and *p*-nitrocalix[4]arene (**L3**), and chloromethylated polystyrene with 25,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone (**L4**) and *p*-nitrocalix[4]arene (**L5**). Their extraction capabilities were studied by the selective extraction of Fe^{3+} cation from the aqueous phase into the organic phase.

EXPERIMENTAL

Melting points were determined on an Electrothermal IA 9100 digital melting point apparatus in sealed capillaries and are uncorrected. ^1H NMR spectra

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were recorded on a Bruker 200 MHz spectrometer for samples in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on a Mattson 1000 FTIR spectrometer for KBr pellets. UV–VIS spectra were obtained on a Shimadzu 160A UV–VIS recording spectrophotometer. Elemental analyses were determined by the TUBITAK laboratory (Center of Science and Technology Research of Turkey). Osmometric molecular weight determination was carried out on a Knauer vapor pressure osmometer at concentrations of ca. 10^{-3} M in $CHCl_3$.

5,11,17,23-Tetrakis[(diethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene [26], 25,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone [27], *p*-nitrocalix[4]arene [28], the oligomer [22] and polystyrene [18] were synthesized as described in previously reported methods.

Attachment of the Oligomer Support onto the Lower Rim of 5,11,17,23-Tetrakis[(diethylamino) methyl]-25,26,27,28-tetrahydroxycalix[4]arene (L1)

A sample of 5,11,17,23-tetrakis[(diethylamino)-methyl]-25,26,27,28-tetrahydroxycalix[4]arene (1.40 g, 1.83 mmol) was dissolved in 10 ml THF and K_2CO_3 (7.00 g, 50.72 mmol) was added with stirring. The mixture was added to the oligomer (0.40 g, 0.37 mmol) in 10 ml THF at room temperature by means of a dropping funnel. This solution was heated at reflux temperature for 2 days under N_2 with stirring. At the end of refluxing period, the cooled solution was filtered and concentrated by removing part of the solvent (ca. 90%) under vacuum. The product was precipitated with methanol. The precipitate was filtered off, washed successively with very dilute HCl and water, and re-crystallized from THF–MeOH. The yield was 1.28 g (72.73%), mp 210°C. Osmometric M_n ($CHCl_3$, 37°C), 4703 (calculated: 4710.5). IR (KBr): $\nu_{O-H} = 3400-3300\ cm^{-1}$, $\nu_{C-O-C} = 1250-1170\ cm^{-1}$, $\nu_{C-N} = 1150-1120\ cm^{-1}$, $\nu_{C-Cl} = 760\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.10-1.30$ (s), 1.50–1.80 (br), 3.30–3.70 (q, AB), 6.82–7.70 (m), 9.80 (s). Anal. calcd. for ($C_{280}H_{397}O_{31}N_{20}Cl_5$): C, 71.33; H, 8.43; N, 5.94; Cl, 3.77. Found: C, 71.58; H, 8.61; N, 6.01; Cl, 3.62.

Attachment of the Oligomer Support onto the Lower Rim of 25,27-Dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene Diketone (L2)

A sample of 25,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone (1.40 g, 1.82 mmol) was dissolved in 10 ml THF and K_2CO_3 (7.00 g, 50.72 mmol) was added with stirring. The mixture was added to the oligomer (0.40 g, 0.37 mmol) in 10 ml THF. **L2** was obtained according to the procedure described for **L1**. The yield was 1.43 g (81.71%), mp 180°C. Osmometric M_n ($CHCl_3$, 37°C), 4678 (calculated: 4690.5). IR (KBr): $\nu_{O-H} = 3340\ cm^{-1}$, $\nu_{C-H} = 3030-3050\ cm^{-1}$, $\nu_{C=O} = 1720\ cm^{-1}$, $\nu_{C-O-C} = 1240-1190\ cm^{-1}$, $\nu_{C-Cl} = 755\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.10-1.25$ (s), 1.40–1.70 (br), 3.40–3.60 (q, AB), 6.85–7.73 (m), 9.28 (s). Anal. calcd. for ($C_{290}H_{377}O_{41}Cl_5$): C, 74.19; H, 8.04; N, 13.99; Cl, 3.78. Found: C, 74.36; H, 8.41; N, 13.72; Cl, 3.57.

Attachment of the Oligomer Support to the Lower Rim of *p*-Nitrocalix[4]arene (L3)

A sample of *p*-nitrocalix[4]arene (1.20 g, 1.99 mmol) was dissolved in 10 ml THF. To this K_2CO_3 (7.00 g, 50.72 mmol) was added with stirring. The mixture was added to the oligomer (0.40 g, 0.37 mmol) in 10 ml THF. **L3** was obtained according to the procedure described for **L1**. The yield was 1.34 g (91.78%), mp 248°C. Osmometric M_n ($CHCl_3$, 37°C), 3903 (calculated: 3910.5). IR (KBr): $\nu_{O-H} = 3400-3320\ cm^{-1}$, $\nu_{N-O} = 1560-1530\ cm^{-1}$, $\nu_{C-O-C} = 1230-1170\ cm^{-1}$, $\nu C-Cl = 760\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.20-1.40$ (s), 1.70–2.05 (br), 3.40–3.90 (q, AB), 6.75–7.90 (m), 10.98 (s). Anal. calcd. for ($C_{180}H_{157}O_{71}N_{20}Cl_5$): C, 55.24; H, 4.01; N, 7.16; Cl, 4.54. Found: C, 55.38; H, 4.23; N, 7.02; Cl, 4.62.

Attachment of Chloromethylated Polystyrene Support to the Lower Rim of 25,27-Dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene Diketone (L4)

A mixture containing 25,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone (3.42 g, 4.50 mmol), K_2CO_3 (7.00 g, 0.37 mmol) and chloromethylated polystyrene (2.79 mmol of chloromethyl groups per gram of polymer, 0.25 g 0.70 mmol) in 60 ml THF/acetone (2:1) was heated at the reflux temperature for 2 days under N_2. The solvent was removed under reduced pressure, and the residue was extracted with chloroform. The chloroform solution was washed with 1 M HCl and water and the product was dried *in vacuo*. The yield was 2.07 g (61.52%), mp 150–152°C. Osmometric M_n ($CHCl_3$, 37°C), 3438 (calculated: 3453). IR (KBr): $\nu_{O-H} = 3320\ cm^{-1}$, $\nu_{C=O} = 1730\ cm^{-1}$, $\nu_{C-O-C} = 1240-1180\ cm^{-1}$, $\nu_{C-Cl} = 760\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.10-1.30$ (s), 1.50–1.80 (br), 3.30–3.70 (q, AB), 6.80–7.75 (m), 10.92 (s). Anal. calcd. for ($C_{235}H_{274}O_{18}Cl_2$): C, 81.67; H, 7.94; Cl, 2.06. Found: C, 81.77; H, 8.05; Cl, 1.94.

Attachment of Chloromethylated Polystyrene Support to the Lower Rim of *p*-Nitrocalix[4]arene (L5)

A mixture containing *p*-nitrocalix[4]arene (2.54 g, 4.20 mmol), K_2CO_3 (7.00 g, 50.72 mmol), and chloromethylated polystyrene (2.79 mmol of chloromethyl groups per gram of polymer, 0.25 g, 0.70 mmol) in

60 ml THF/acetone (2:1) was heated at the reflux temperature for 2 days under N_2. **L5** was obtained according to the procedure described for **L4**. The yield was 2.51 g (87.15%), mp 266–269°C. Osmometric M_n ($CHCl_3$, 37°C), 2953 (calculated: 2961). IR (KBr): $\nu_{O-H} = 3400-3300\,cm^{-1}$, $\nu_{N-O} = 1560-1530\,cm^{-1}$, $\nu_{C-O-C} = 1230-1160\,cm^{-1}$, $\nu_{C-Cl} = 755\,cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.20-1.45$ (s), 1.60–1.90 (br), 3.40–3.80 (q, AB), 6.60–7.85 (m), 10.72 (s). Anal. calcd. for ($C_{169}H_{118}O_{36}N_{12}Cl_2$): C, 68.49; H, 3.99; N, 5.67; Cl, 2.40. Found: C, 68.67; H, 4.13; N, 5.74; Cl, 2.27.

Extraction of Fe^{3+} Cation

A 5 ml solution of chloroform containing **L1–L5** (5.3×10^{-4} M) and a 25 ml aqueous solution containing a metal salt (1.06×10^{-4} M) were placed in a flask. The aqueous solution was adjusted to pH 2.2 (0.01 M $NaNO_3/HNO_3$, $\mu = 0.1$ with KCl), or buffered to pH 3.8, 4.5 and 5.4 (0.01 M CH_3COONa/CH_3COOH, $\mu = 0.1$ with KCl). The reported pH values are those of corresponding buffers without individual pH measurement in equilibrated solutions. The mixture was shaken for 12 h at room temperature. The extraction was not affected by further shaking, indicating that the equilibrium had been attained within 12 h. The extractability (% Ex) was determined from the decrease in the metal concentration in the aqueous phase according to Eq. (1),

$$\%\,\mathrm{Ex} = \frac{[(\mathrm{metal})_{\mathrm{blank}} - (\mathrm{metal})_{\mathrm{water}}}{(\mathrm{metal})_{\mathrm{blank}}] \times 100} \qquad (1)$$

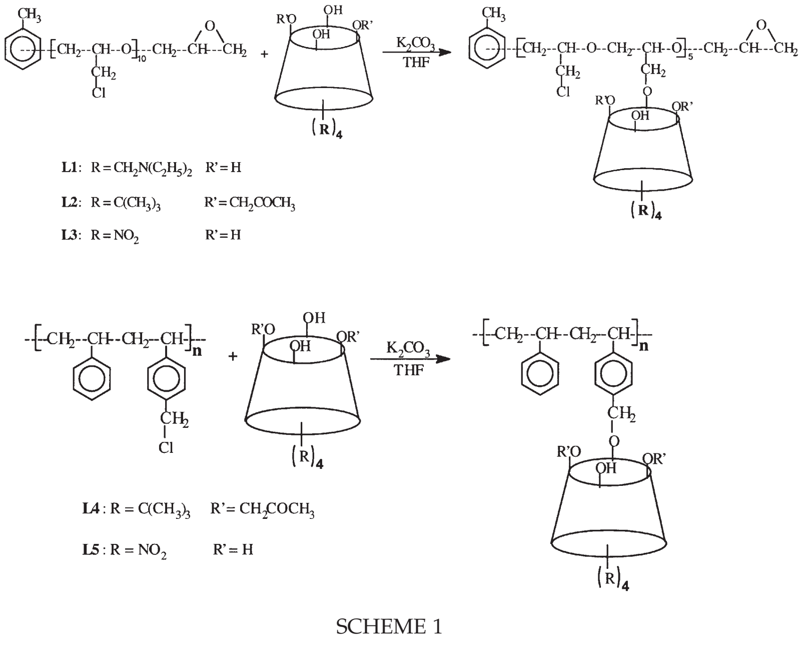
where $(\mathrm{metal})_{\mathrm{blank}}$ and $(\mathrm{metal})_{\mathrm{water}}$ denote the metal concentrations in the aqueous phase, after extraction with pure chloroform solution containing extractants.

RESULTS AND DISCUSSION

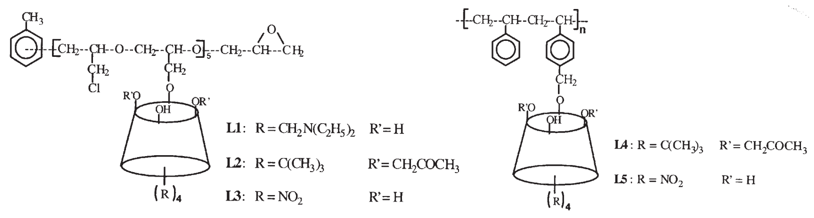
In our previous work, two-phase solvent extraction of Fe^{3+} cations from the aqueous phase into the organic phase was achieved with calix[4]arene and some of its derivatives [15]. In this work, we have synthesized new polymeric compounds containing more than one calix[4]arene, by reacting oligomer and styrene with some calixarene derivatives, and have investigated the extraction abilities of these polymeric calix[4]arenes in the water–chloroform system at various pH.

Polymeric calixarenes are potentially capable of forming stable complexes with many metal ions. On the basis of previous experience, oligomeric calix[4]arenes (**L1**, **L2**, and **L3**) and polystyrene calix[4]arenes (**L4** and **L5**) were constructed as shown in Scheme 1.

In recent years a large amount of work has been reported in the literature related to the functionalization of the calixarenes. However, investigations of polymeric macro structures containing more than one compound are quite limited. In the present work, synthesis of the polymeric calixarene (**L1**) was accomplished by reacting an oligomer with 5,11,17,23-tetrakis[(diethylamino)methyl]-25,26,27,28-tetrahydroxycalix[4]arene in the presence of K_2CO_3 in THF. In addition, the polymeric calixarenes **L2** and **L3** were synthesized by reacting the oligomer with 25,27-dimethyl-26,28-dihydroxy-*p-tert*-butylcalix[4]arene diketone (**L2**) and *p*-nitrocalix[4] arene (**L3**).



SCHEME 1



SCHEME 2

Based on the chlorine analysis performed at the end of the reaction, it was observed that the chlorine atoms of the compounds did not attach to each consecutive (CH_2Cl) group in a regular array. In the IR spectrum of these compounds, diethylamine group bands occurred at about 1150–1120 cm^{-1} for **L1**, carbonyl group bands occurred at about 1720 cm^{-1} for **L2**, and nitro group bands occurred at about 1560–1530 cm^{-1} for **L3**.

Examination of the ^1H NMR spectrum of **L2** revealed that this compound exists in a cone conformation, which was deduced from the presence of two characteristic AB systems at 3.40 and 3.90 ppm ($J_{AB} = 13.0$ Hz) for the bridging methylene protons.

The second polymeric calixarene (**L4**) was obtained by reacting chloromethylated polystyrene with 25,27-dimethyl-26,28-dihydroxy-*p*-*tert*-butylcalix[4]arene diketone in the presence of K_2CO_3 in THF. In addition, the polymeric calixarene **L5** was synthesized by reacting chloromethylated polystyrene with *p*-nitrocalix[4]arene.

The ^1H NMR spectrum of compound **L4** exhibits the same peaks in the same spectral region, indicating the symmetry of **L5**. These observations suggest the existence of various conformations of the macrocyclic molecules in the polymer chain very likely due to the structural variations under the reaction conditions. The IR spectra of **L4** and **L5** showed absorption bands at about 1730 cm^{-1} for the carbonyl groups and at about 1530–1560 cm^{-1} for the nitro groups, respectively.

TABLE I Percent (%) extraction of Fe^{3+} with ligands*

	pH			
Ligand	2.2	3.8	4.5	5.4
L1	34.5	57.5	67.0	89.0
L2	53.9	59.1	62.9	86.4
L3	44.0	65.0	94.0	96.5
L4	42.4	58.1	87.6	89.4
L5	44.7	79.5	88.6	90.2

*Aqueous phase [metal nitrate = 1.06×10^{-4} M]. Organic phase [chloroform (ligand)] = 5.3×10^{-4} M]. pH: 2.2 (0.01 M $NaNO_3/HNO_3$, $\mu = 0.1$ with KCl), pH: 3.8; 4.5, and 5.4 (0.01 M CH_3COONa/CH_3COOH, $\mu = 0.1$ with KCl), at room temperature for 12 h.

Two-phase Solvent Extraction

Polymeric calixarenes have been employed widely in the formation of metal complexes and in the study of inclusion phenomena due to their relatively easy preparation, remarkable stability and high versatility [29,30]. Thus, the present work was focused on determining the strategic requirements for the two-phase extraction measurements.

Ionophoric polymer-supported calixarenes in which the lower rims are linked via a single site on each calixarene were synthesized. The three synthesized oligomeric calixarenes (**L1**, **L2** and **L3**) and the chloromethylated styrene calixarenes (**L4** and **L5**) (Scheme 2) were subjected to comparative study. Results of the two-phase extraction measurements of **L1**–**L5** with Fe^{3+} cations in a water–chloroform system at pH 2.2, 3.8, 4.5, and 5.4 are summarized in Table I, and plotted in Fig. 1.

These data were obtained by using chloroform solutions of the ligands to extract metal ions from aqueous solution according to our previously described procedure [21]. The equilibrium concentration of Fe^{3+} in the aqueous phase was then determined spectrophotometrically. The extraction of Fe^{3+} increased with increasing pH (Fig. 1).

With all ligands substituted with more than one calix[4]arene 34.5–53.9% extraction was accomplished at pH 2.2. When the nitro-substituted

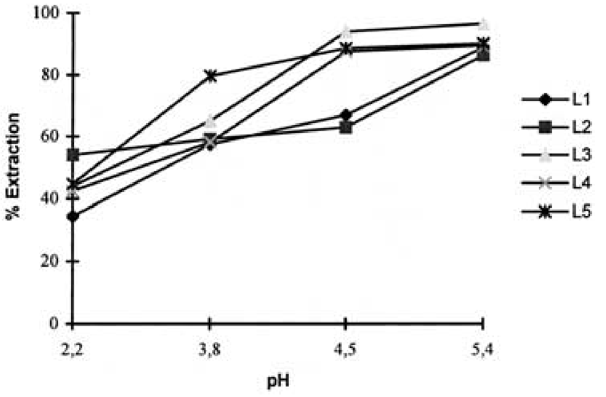


FIGURE 1 Effects of pH on Fe^{3+} extraction. Aqueous phase: [metal nitrate] = 1.06×10^{-4} M. Organic phase: [chloroform, (ligand)] = 5.3×10^{-4} M, at rt for 12 h.

compound **L3** was used, the extraction ratio was increased significantly (Table I).

These compounds are capable of extracting Fe^{3+} at even lower pH ranges. This shows that the *n* electrons are effective in neutral media and extraction depends on the hydrogen atom in acidic media. Furthermore, compound **L3** extracted about 96.5% of the Fe^{3+}, and this process is due to the easy separation of the hydrogen atom from compound **L3**. The hydrogen atom separation from this compound was also reported in a previously published paper [15].

The above observations clearly indicate the important role of the acidic hydrogen in the extraction procedure. Extraction experiments with compound **L3** yield results similar to those obtained for other compounds. The effect of pH on the extraction of all compounds was small. Extraction of 44.0 and 44.7% of the Fe^{3+} for compounds **L3** and **L5** was accomplished even at pH 2.2. These results are due to the presence of four adjacent nitro groups ($-NO_2$) in compound **L3**. In extraction experiments also performed with its monomer [20], the ratio was only 27.1% at pH 2.2. The above observations indicate that the polymeric compounds containing both more than one calix[4]arene and nitro groups plays an important role in the extraction process.

The calix[4]arene (**L4**), with the polystyrene attached to the lower rim (i.e. close to the OH side), can convert easily into the cone conformation, therefore, this position can easily transport the metal cations from the aqueous phase to the organic phase. However, those with the polystyrene attached to the upper rim (i.e. open *p*-position side) remain independent and do not convert into the cone conformation. Similar approaches and suggestions have also been reported in the literature [31,32].

The UV spectrum of the calix[4]arenes in DMF did not exhibit an absorption maximum above 300 nm. Complex formation was evident when the color of the solution turned brown and an absorption maximum appeared at 534 nm. The metal/ligand ratio (1:1) was determined at this wavelength by the Job method [21].

The increase of pH is due to liberated H^+, after the complex is formed between the calix[4]arene and Fe^{3+} in DMF. The extraction reaction of the present systems can be expressed by Eq. (2).

$$M^{n+}_{(aq)} + [LH_m]_{(org)} ===== [MLH_{m-n}]_{(org)} + nH^{+}_{(aq)} \quad (2)$$

If the logarithm of the ratio between Fe^{3+} content in the aqueous and organic phases is plotted as a function of pH, a linear relationship is obtained between pH 3.5 and 5.4, which deviates from linearity at lower pH values (2.2). The fact that the slopes of the curves were very close to unity indicates that only one proton is separated from the ligand. A detailed mechanism related to the extraction process has been discussed in our earlier publication [15,18,22].

Based on the above results, polymer-supported calix[4]arenes exhibit high levels of complexation ability. In addition, it was observed that nitro group substitution enabled extraction of Fe^{3+} under acidic conditions. Since calixarenes are not only easily available in large quantities but also suited to nearly unlimited chemical modification, it might be expected that even better extractants or ion carriers can be obtained. It is hoped that in this way the selectivity of certain ligands toward Fe^{3+} or other metal ions can also be improved.

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