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Shahabuddin Memon^a; Gülderen Uysal^a; Mustafa Yilmaz^a

^a Department of Chemistry, Selçuk University, Konya, Turkey

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SYNTHESIS AND COMPLEXATION STUDIES OF *p*-*TERT*-BUTYLCALIX[4]CROWN TELOMERS

Shahabuddin Memon, Gülderen Uysal, and Mustafa Yilmaz*

Selçuk University, Department of Chemistry, 42079, Konya, Turkey

ABSTRACT

Two calixcrown ionophores (3a and 3b) and their telomers (6a and 6b) were synthesized, and it has been found that the conformation of the monomeric calixcrowns was not maintained in the polymeric chain. The binding properties of the telomers toward alkali (Li^+ , Na^+ , K^+ , Cs^+) and selected transition metal cations (Ni^{+2} , Cu^{+2} , Co^{+2} , Cd^{+2} , Hg^{+2} , Pb^{+2}) was observed higher than those of monomeric analogs. It was suggested that this increased binding ability is due to the change of original cone conformation of the monomeric receptors into other various conformations in the polymeric skeleton.

Key Words: *p*-*tert*-Butylcalix[4]crown; Copolymer; Phase transfer; Alkali and transition metal.

INTRODUCTION

Calixarenes are supramolecular compounds that have a three-dimensional network of bridged phenolic units with varying annular space in which metals can be trapped due to the ionic interaction. The correct manipulation of the energetic and stereochemical features of the noncovalent, intermolecular forces within a defined molecular architecture should allow the design of artificial receptor molecules capable of binding substrate species strongly and selectively, forming supramolecular entities, so-called supermolecules, of well-defined structure and

*Corresponding author. E-mail: myilmaz@selcuk.edu.tr

function. Moreover, especially, calix[4]arenes are capable of binding neutral molecules inside the cavity or metal ions via the oxygen atoms at the lower rim (1–5).

Another family of macropolycyclic hosts is “calixcrowns” in which the cyclic structure of a calixarene is linked through a cyclic polyether moiety. Thus, referring to the communication by Alfieri *et al.* (6) reporting on the synthesis and complexing properties of *p*-tert-butylcalix[4]crown-5, a number of calix[4]arenes have been *O*-alkylated with polyethylene glycol ditosylates to produce globular ligands. In this connection various calix[4]crowns have been shown to possess good binding properties toward alkali-metal cations or alkyl ammonium ions (7–18).

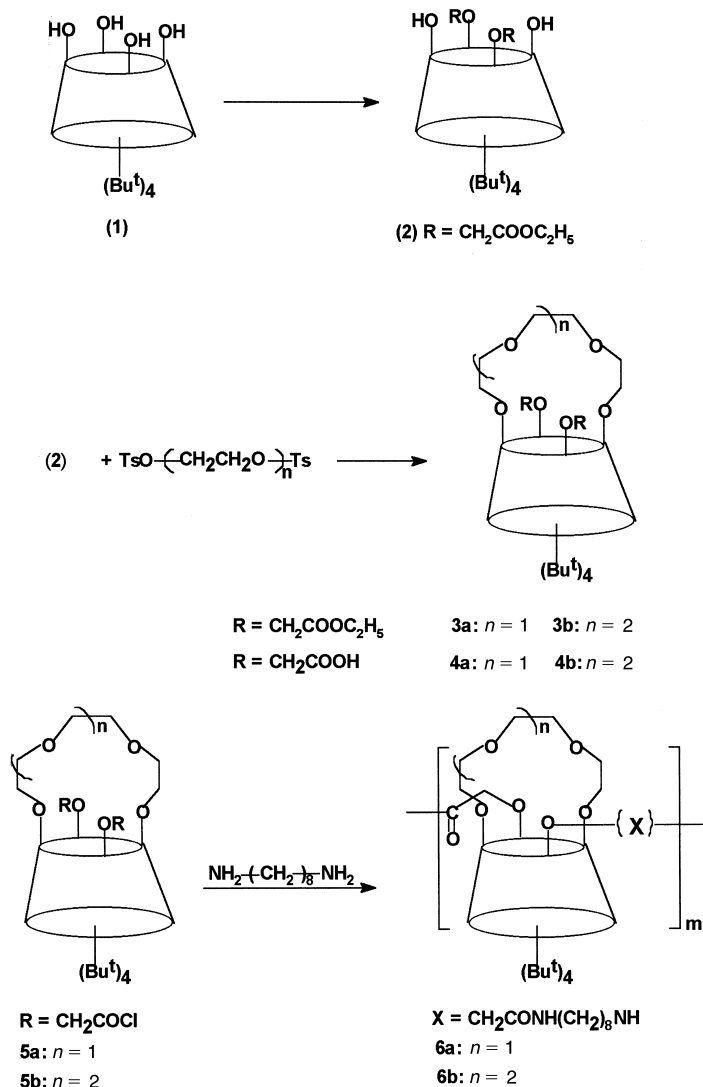
However, calixarene-based polymers have just begun to receive attention, and have been reported in the literature. Shinkai and coworkers (19) prepared a calix[6]arene fixed to polystyrene. Harris and coworkers (20) reported on the polymerization and Na⁺ complexation of calix[4]arene methacrylate. Gravett and Guillet (21) synthesized a water-soluble calixarene containing polymer and demonstrated its photo-physical properties. Zhong and coworkers (22) have reported synthesis and properties of calixcrown telomers. Recently, Ohto and coworkers (23) have presented a calix[4]arene carboxylate resin immobilized with polyallylamine. Blanda and Adou [24] prepared three vinyl copolymers containing pendant-calix[4]arene and reported that the copolymer were designed to take advantage of the well-established binding interactions of calixarenes with neutral molecules and ions.

Besides this, compared with calixcrown monomers, calixcrown polymers are a much more recent innovation. Only a few examples have been reported (19–24) in the literature. In our previous work (25–33), we synthesized a few polymeric calixarenes and have been investigated their ionophoric properties. Herein, we wish to report on the synthesis and binding properties of calix[4]crown telomers (**6a**, **6b**).

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker 250 MHz spectrometer in CDCl₃ with TMS as an internal standard. Infrared (IR) spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. Ultraviolet-visible (UV-vis) spectra were obtained on a Shimadzu 160A UV-visible recording spectrophotometer. Osmometric molecular weight determinations were carried out on a Kanauer vapor pressure osmometer at concentrations of ca. 10⁻³ mol/L in CHCl₃. Merck PF₂₅₄ silica gel was used for all forms of chromatography. The drying agent used was anhydrous sodium sulfate. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. The *p*-tert-butylcalix[4]arene **1** and its diester derivative **2**, were synthesized according to the

literature procedures (34,35). The other ionophores (3a-b, 4a-b, 5a-b, and 6a-b) used in this work, as illustrated in Scheme 1, have been synthesized as follows:



Scheme 1.

5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxycalix[4]arene crown-4 (3a)

Diester **2** (1.86 g; 2.27 mmol) was dissolved in THF (400 mL) and treated with NaH (1.0 g; 47 mmol). After the reaction mixture had been stirred for 10 min

at room temperature, it was treated with 1:1 equivalent of triethyleneglycol di-*p*-tosylate (1.04 g; 2.27 mmol) in THF (100 mL); added from a dropping funnel over 10 h at room temperature with continuous stirring in nitrogen atmosphere. The mixture was then refluxed for 6 h. Most of the solvent was evaporated at reduced pressure. The residue was acidified with 2 M aqueous HCl and extracted with CH₂Cl₂ (250 mL). The extract was washed with 2 M HCl and then brine, which was dried (Na₂SO₄), filtered and concentrated *in vacuo*. The product was purified by passage through a silica gel gravity column using 50% CH₂Cl₂ in *n*-hexane as eluent for **3a**. Yield was 0.99 g (47%), m.p. 103–104°C. Osmometric (CHCl₃, 37°C), 940 (Calculated: 935). IR (KBr) 1750 cm⁻¹ (C=O) and 1200 cm⁻¹ (C-O-). ¹H NMR (CDCl₃), δ 0.95 (s, 18H, Bu^t); 1.25 (m, 24H, Bu^t and CH₃ of Et); 3.45 (d, 4H, J=12.8, ArCH₂Ar); 3.50-4.00 (m, 16H, OCH₂CH₂O and CH₂ of Et); 4.15 (m, 8H, ArCH₂Ar, OCH₂CO); 6.50 (s, 4H, ArH); 7.15 (s, 4H, ArH); Calculated for (C₅₈H₇₈O₁₀) C, 74.49; H, 8.4. Found: C, 74.68; H, 8.8.

**5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxycalix[4]arene
Crown-5(3b)**

The reaction of diester **2** with tetraethylene glycol-di-*p*-tosylate was carried out under the above described procedure. The usual workup, followed by chromatography provided **3b**. Yield: (43%), m.p. 128-129°C. Osmometric Mn (CHCl₃, 37°C), 985; (calculated: 979). IR (KBr): 1753 cm⁻¹ (C=O) and 1205 cm⁻¹ (C-O-). ¹H NMR (CDCl₃): δ 0.90 (s, 18H, Bu^t); 1.20 (m, 24H, Bu^t and CH₃ of Et); 3.50 (d, 4H, J = 13 Hz, ArCH₂Ar); 3.60-4.10 (m, 20H, OCH₂CH₂O and CH₂ of Et); 4.25 (m, 8H, ArCH₂Ar, OCH₂CO); 6.45 (s, 4H, ArH); 7.10 (s, 4H, ArH). Calculated for (C₆₀H₈₂O₁₁) C, 73.59; H, 8.44. Found: C, 73.82. H, 8.50.

**5,11,17,23-Tetra-*tert*-butyl-25,27-diarboxymethoxycalix[4]arene
Crown-4 (4a)**

Compound **3a** (1.5 g; 1.606 mmol) was refluxed for 24 h in ethanol (90 mL) containing 10 mL of 15% aqueous NaOH. Most of ethanol was distilled off; the cooled mixture was acidified by 1 M HCl. The precipitates were filtered, washed with distilled water, and dried *in vacuo*. Recrystallization from ethanol-water furnished the compound **4a**. Yield: 0.90 g (63.8%) m.p. 155–157°C (decomp). Osmometric (CHCl₃, 37°C), 890, (Calculated: 879). IR (KBr): 3430 cm⁻¹ (O-H) and 1734 cm⁻¹ (C=O). ¹H NMR (CDCl₃): δ 1.00 (s, 18H, Bu^t); 1.20 (s, 18H, Bu^t); 3.35 (d, 4H, J = 13 Hz, ArCH₂Ar); 3.50-3.85 (m, 12H, OCH₂CH₂O); 4.25 (d, 4H, J = 13 Hz, ArCH₂Ar); 4.80 (s, 4H, OCH₂CO); 6.65 (s, 4H, ArH); 7.45 (s, 4H, ArH); 8.25 (s, 2H, COOH). Calculated for (C₅₄H₇₀O₁₀) C, 73.77; H, 8.02. Found: C, 73.45; H, 8.15.

**5,11,17,23-Tetra-*tert*-butyl-25,27-diarboxymethoxycalix[4]arene
Crown-5 (4b)**

The hydrolysis of the compound **3b** was carried out as described above, the usual work up afforded **4b**. Yield (55%), m.p. 148–149°C. Osmometric (CHCl₃, 37°C): 930 (calculated: 923). IR (KBr): 3440 cm⁻¹ br and 1740 cm⁻¹(C=O). ¹H NMR (CDCl₃): δ 0.95 (s, 18H, Bu^t); 1.25 (s, 18H, Bu^t); 3.50 (d, 4H, J = 13 Hz, ArCH₂Ar); 3.60–3.95 (m, 16H, OCH₂CH₂O); 4.15 (m, 8H, ArCH₂Ar OCH₂CO); 6.50 (s, 4H, ArH); 7.30 (s, 4H, ArH); 7.70 (s, 2H, COOH). Calculated for (C₅₆H₇₄O₁₁) C, 72.85; H, 8.08. Found: C, 72.65; H, 8.25.

**Reactions of Compounds 4a and 4b with Thionyl Chloride:
General Procedure**

The diacid **4a** (0.5 g; 0.569 mmol) was dissolved in THF (50 mL). Thionyl chloride (1.0 mL) in THF (10 mL) was added dropwise with stirring at room temperature. The mixture was then refluxed for ca. 3.5 h. Removal of the solvent and residual thionyl chloride under reduced pressure furnished the acyl chloride **5a** as a brownish solid in a quantitative yield. The product was used in subsequent preparation without purification.

Synthesis of Telomers 6a and 6b: General Procedure

The acyl chloride **5a** was dissolved into the minimum amount of dichloromethane (ca. 15 mL) and treated with a mixture of 1,8-diaminooctane (0.082 g; 0.569 mmol) and pyridine (6 mL) in dichloromethane (5 mL). The reaction mixture was stirred overnight at ambient temperature. The solvent was evaporated to dryness on a rotary evaporator and the residue was treated with 6 M HCl. The precipitates were filtered off, washed with water, then with ethanol, and finally with diethylether. Fine precipitates were dried *in vacuo*. Yield of **6a** (0.36 g; 64%), m.p. 250–251°C. Osmometric Mn (CHCl₃, 37°C): 6950; (calculated: 6910). IR(KBr): 3419 cm⁻¹ (N-H, NHCO), 1684 cm⁻¹ (C=O, NHCO). ¹H NMR (CDCl₃): δ 1.10 (s, 36H, Bu^t); 1.60–1.75 (m, 8H, -CH₂-C); 2.10–2.50 (m, 4H, N-C-CH₂-C); 3.30–3.60 (m, 16H, N-CH₂-C and OCH₂CH₂O); 3.70 (s, 8H, ArCH₂Ar); 4.95 (s, 4H, OCH₂CO); 7.25 (s, 8H, ArH); 7.65 (s, 2H, NH). Calculated for (C₆₂H₈₆N₂O₈)₇ C, 75.42; H, 8.78. Found: C, 75.55; H, 9.35.

Telomer 6b

Yield (70%); m.p. 155–158°C. Osmometric Mn (CHCl₃, 37 °C): 7250; (calculated: 7218). IR(KBr): 3419 cm⁻¹ (N-H, NHCO), 1675 cm⁻¹ (C=O, NHCO).

^1H NMR (CDCl_3): δ 0.85 (s, 36H, Bu^t); 1.10–1.25 (m, 8H, C- CH_2 -C); 2.25–2.50 (m, 4H, N-C- CH_2 -C); 2.95–3.55 (m, 20H, N- CH_2 -C and $\text{OCH}_2\text{CH}_2\text{O}$); 3.75 (s, 8H, ArCH_2Ar); 5.25 (s, 4H, OCH_2CO); 7.35 (s, 8H, ArH); 7.60 (brs, 2H, NH). Calculated for $(\text{C}_{64}\text{H}_{90}\text{N}_2\text{O}_9)_7$ C, 74.53; H, 8.79. Found: C, 74.75; H, 8.35.

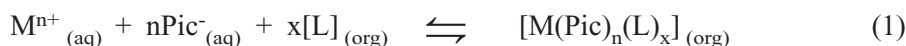
Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure (36). Ten mL of a 2.5×10^{-5} M aqueous picrate solution and 10 mL of 1×10^{-3} M solution of calixarene in CHCl_3 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water-bath at 25°C for 1 h, and finally left standing for an additional 30 min. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described (37). Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described elsewhere (38) by stepwise addition of a 2.5×10^{-2} M aqueous picric acid solution to a 0.14 M aqueous solution of metal hydroxide, until neutralization, which was checked by pH control with a glass electrode. They were then rapidly washed with ethanol and ether before being dried *in vacuo* for 24 h. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M of metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 h.

Log-Log Plot Analysis

To characterize the extraction ability, the dependence of the distribution coefficient D of the cation between the two phases upon the calixarene concentration was examined. If the general extraction equilibrium is assumed to be Equation 1 with M^{n+} metal ion, L neutral ligand and with the overlined species referring to species in the organic phase, the overall extraction equilibrium constant is given by Equation 2. If we introduce the distribution coefficient D , as given in Equation 3, and taking log of both sides, we obtain Equation 4.



$$K_{\text{ex}} = \frac{[\text{M}(\text{Pic})_n(\text{L})_x]}{[\text{M}^{n+}] [\text{Pic}^-]^n [\text{L}]^x} \quad (2)$$

$$D = \frac{[\text{M}(\text{Pic})_n(\text{L})_x]}{[\text{M}^{n+}]} \quad (3)$$

$$\log D = \log (K_{\text{ex}}[\text{Pic}^-]^n) + x \log [L] \quad (4)$$

With these assumptions a plot of the $\log D$ vs. $\log[L]$ should be linear and its slope should be equal to the number of ligand molecules per cation in the extraction species.

RESULTS AND DISCUSSION

Our previous study of chemically modified calix[4]arenes includes derivatives with more than one type of functionality around the calix moiety and recently we have demonstrated a few approaches to the synthesis and binding properties of calix[4]arene based telomers bearing different ligating functional groups (28). Here we report the synthesis and comparison between the complexing properties of two calixcrown telomers (6a and 6b) and their respective monomers (**3a** and **3b**).

The syntheses of compounds **1** and **2** were based on the previously published procedures (34,35), while reaction steps leading from **2** to **6b** are reported elsewhere. Refluxing a mixture of diester derivative of *p*-*tert*-butylcalix[4]arene **2** and polyethylene glycol ditosylate in THF in the presence of NaH afforded **3a** and **3b** in 47% and 43% yield. It has been recognized that both compounds (**3a** and **3b**) exist in cone conformation as inferred from the ^1H NMR spectra, which exhibit a characteristic pair of doublets for each compound (around 3,35-3,45 and 4,15-4,25 ppm) a single AB system for the bridging methylene groups of the calixarene moiety (1,2).

Hydrolysis of both these compounds (i.e., **3a** and **3b**) with 15% aqueous NaOH solution in ethanol removes ethyl groups of the compounds, which was recognized by the IR and ^1H NMR spectroscopy.

Synthetically, the usefulness of acid chloride is well known and has been demonstrated that it can be bridged across the lower rim. Thus, the compounds **4a** and **4b** were treated with thionyl chloride, in the presence of pyridine in THF, and provided the diacid chlorides **5a** and **5b** in a quantitative yield. No attempts were made to purify the crude product and it was used in subsequent preparation without purification. It was aimed to obtain under the copolymerization conditions telomers with moderate M_n values and good solubility in organic solvents such as CHCl_3 and CH_2Cl_2 at room temperature that could be used in host-guest studies. Therefore, the compounds **5a** and **5b** were treated with 1,8-diaminooctane in the presence of pyridine in a minimum amount of THF (ca. 15 mL) to give telomers **6a** and **6b** in 64 % and 70% yield, respectively, after purification by reprecipitation from a chloroform-methanol system. The average molecular weight of compound **6a** and **6b** was found 6950, 7250 (vapor phase osmometer), respectively, thus, copolymers contain ca. 7 calixarene units in the polymeric skeleton. The ^1H NMR spectra of the telomers (**6a**, **6b**) exhibit multiresonance peaks in the same spectral region, indicating that the symmetric cone conformation of the starting calix-

crown monomers (**3a**, **3b**) is no longer present in telomers. These observations suggest the existence of various conformations of macrocyclic molecule in the polymer chain, and are very likely due to structural variations of **3a** and **3b** under the polymerization conditions. In the literature similar, observations have been noted by Dondoni and coworkers in a modified interfacial polycondensation between bis-phenol-A and 1,3-dimethoxycalix[4]arene derivatives with dibromomethane (39).

In this study, our aim was to synthesize conformationally stable forms of the calixcrown telomers and compare their complexing abilities with the corresponding monomers. Results of the two-phase extraction measurements of the calixcrown monomers (**3a**, and **3b**) and their relative telomers (**6a**, and **6b**) with selected alkali and transition metal picrates are summarized in Table 1 and their graphic explanation is represented in Figure 1. These data were obtained by using dichloromethane solutions of the ligands to extract metal picrates from aqueous solution. The equilibrium concentration of picrate in aqueous phase was then determined spectrophotometrically.

From the extraction data shown in Table 1, neither alkali nor transition metal cations were significantly extracted by the starting material *p-tert*-butylcalix[4]arene(**1**) from aqueous to organic phase. By the introduction of esteric groups to 1,3-position of the lower rim changes the transferring characteristic of the compound **2**, especially for Cu^{+2} and Pb^{+2} , but the alkali metal cations could not be extracted significantly.

The extraction data of diester derivatives of calix[4]crown-4 (**3a**) and calix[4]crown-5 (**3b**), however, show no significant change in their extraction

Table 1. Extraction of Metal Picrates with Ligands

| Ligand | Picrate Salt extracted (%) | | | | | | | | | |
|----------------------|----------------------------|---------------|--------------|---------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | Li^+ | Na^+ | K^+ | Cs^+ | Hg^{2+} | Ni^{2+} | Cu^{2+} | Co^{2+} | Cd^{2+} | Pb^{2+} |
| 1 | 18.9 | 8.5 | 3.3 | 2.8 | 15.5 | 6.3 | 9.9 | 7.9 | 9.4 | - |
| 2^b | <1.0 | 16.3 | 4.3 | 2.2 | 33.3 | 37.4 | 51.2 | 25.4 | 23.6 | 82.0 |
| 3a | <1. | <1.0 | 1.9 | <1.0 | 48.7 | <1.0 | 7.8 | <1.0 | 7.03 | 57.0 |
| 3b | <1.0 | <1.0 | <1.0 | 15.0 | 90.0 | 21.0 | 43.0 | 20.0 | 44.4 | 95.0 |
| 6a | 88.0 | 92.0 | 91.3 | 86.7 | 91.8 | 24.0 | 87.0 | 31.6 | 66.0 | 92.7 |
| 6b | 90.0 | 93.5 | 92.0 | 91.4 | 93.0 | 91.5 | 92.0 | 92.8 | 99.6 | 94.3 |

^a Aqueous phase, [metal nitrate] = 1×10^{-2} M ; [picric acid] = 2.5×10^{-5} M ; organic phase, dichloromethane, [ligand] = 1×10^{-3} M ; at 25 °C, for 1 h.

^b Reference 29.

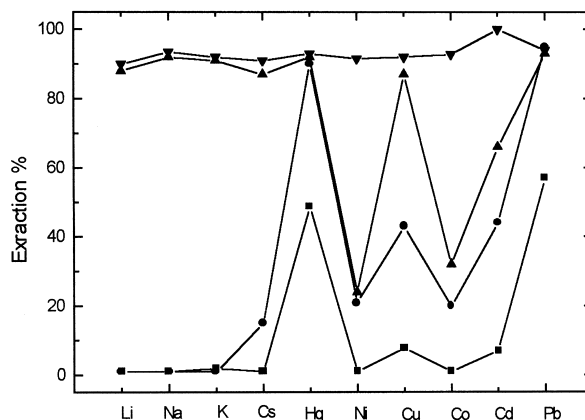


Figure 1. Extraction percentage of the alkali picrates with **2**-(■), **3b**-(●), **6a**-(▲), and **6b**-(▼) at 25°C. $[M^+Pic^-]_0 = 2.5 \times 10^{-5}$ M; $[Ligand]_0 = 1 \times 10^{-3}$ M. (For water to dichloromethane system).

behavior for alkali metal cations. The compound **3a** shows a slight decrease in extraction of transition metal cations except Hg^{+2} , whereas **3b** exhibits an increase in the extraction of Hg^{+2} , Cd^{+2} , and Pb^{+2} (Fig. 1). The low binding ability of these compounds (**3a** and **3b**) can be explained by the fact that the cone conformationally calixcrowns show little binding ability due to the steric reasons, generally exhibited by the two remaining bulky groups present on the lower rim of calixarene. Similar results were obtained by Casnati and coworkers (7), and they reported that cone isomers of dialkylated calix[4]crown-6 showed little ability for alkali metal cations. The effectiveness in transferring Hg^{+2} and Pb^{+2} , rather than the other cations by these monomeric compounds (**3a** and **3b**) indicate that, in this case, a cation- π interaction appeared to be operative, because the metal ion was bound between the two opposite carbonyl groups of the esteric ligating moieties of these compounds.

Very interesting results were observed in the case of telomers (**6a** and **6b**) in solvent extraction experiments. The extraction data showed a remarkable increase in binding ability of the telomers (**6a** and **6b**) for both alkali and transition metal cations (Fig.1). It can be suggested that calix[4]arene units in the polymeric materials exist in various conformations, very likely due to structural variations of monomers under the polymerization conditions. This conclusion is in agreement with that formulated above on the basis of the 1H NMR spectral data. In the event such a conformational preference may be used to explain the greater complexation ability of telomers (**6a** and **6b**) with respect to the calixcrowns (**3a** and **3b**) that exist in the less efficient cone conformation. There is full agreement between the extraction and the complexation data for the calixcrowns reported (7,17,39). A dramatic increase in the binding and extraction of metal cations is observed for all ligands in mixed conformations of the calix moieties in the polymeric skeleton.

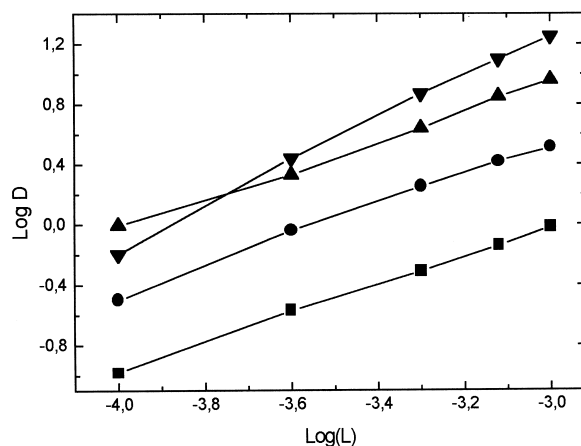


Figure 2. Log D versus log [L] for the extraction of Pb-pictrate by the ligands **2**-(●) and **3b**-(▼) and for the extraction of Hg-pictrate by the ligand **3b**-(▲) from an aqueous phase into dichloromethane at 25°C.

Figure 2 shows the extraction into dichloromethane at different concentrations of the ligands **2**, **3a** or **3b**, for Pb^{2+} and **3b** for Hg^{2+} .

A linear relationship between log D versus Log [L] is observed with the slope of lines for Pb^{2+} are roughly to 1.15, 0.95, and 1.45 by the ligands **2**, **3a**, and **3b**, respectively. The slope for Hg^{2+} by the ligand **3b** is equal to 0.96. These results suggest that except **3b** in case of Pb^{2+} , all the ligands bind to each metal ion in 1:1 manner under the experimental conditions (i.e., in the presence of an excess of ligands, according to Equation 1).

In this system, the following logarithmic extraction constants for Pb^{2+} and Hg^{2+} with the compounds **2**, **3a** and **3b**, corresponding to Equation 1, were determined.

$$\begin{aligned} \text{LogK}_{\text{ex}} &= 3.66 \text{ (for } \text{Pb}^{2+} \text{ with } \mathbf{2} \text{)} \\ &= 3.02 \text{ (for } \text{Pb}^{2+} \text{ with } \mathbf{3a} \text{)} \\ &= 3.90 \text{ (for } \text{Hg}^{2+} \text{ with } \mathbf{3b} \text{)} \end{aligned}$$

In the case of Pb^{2+} with **3b**, having a slope equal to 1.45, may be caused by a coextraction of 1:1 and 1:2 metal:reagent complex.

CONCLUSION

In conclusion, the synthesis and liquid-liquid extraction properties of calix-crown monomers (**3a** and **3b**) and their corresponding telomers (**6a** and **6b**) were studied. The macromolecular characterization showed that the original cone conformation of the calixcrown monomers was not maintained in the polymer, but a

mixture of various conformations of calixarene moieties was observed. It has been found that the telomers are better extractants, but not selective, compared with their respective monomers for the selected metal cations used in the phase transfer experiments, which enhances their utility in phase transfer reactions and as an adsorbent, etc.

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