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Gülderen Uysal Akkus[a]; Shahabuddin Memon[b]; Mehmet Sezgin[b]; Mustafa Yilmaz[b]
[a] Department of Chemistry, Afyon Kocatepe University, Afyon, Turkey [b] Department of Chemistry, Selçuk University, Konya, Turkey

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A Versatile Approach Toward Calix(aza)crown Oligomers: Synthesis and Metal Ion Extraction

Gülderen Uysal Akkus,[1] Shahabuddin Memon,[2] Mehmet Sezgin,[2] and Mustafa Yilmaz[2,*]

[1]Afyon Kocatepe University, Department of Chemistry, Afyon, Turkey
[2]Selçuk University, Department of Chemistry, Konya, Turkey

ABSTRACT

Four new calix(aza)crown oligomers (**5**–**8**) have been synthesized by reacting p-tert-butylcalix[4](aza)crowns (**3** and **4**) with triethylene glycol ditosylate or 1,5-dibromopentane. Their phase transfer studies were performed by using liquid–liquid extraction procedure. It has been deduced from the observations that, the oligomers **5** and **7** are good extractants, whereas, oligomers **6** and **8** show different extraction behavior toward selected alkali (Li^+, Na^+, K^+, Cs^+) and transition metal cations (Ni^{+2}, Cu^{+2}, Co^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}).

Key Words: Calix(aza)crown; Oligomers; Liquid–liquid extraction; Alkali; Transition metals.

INTRODUCTION

Calixarenes are a relatively new class of macrocyclic compounds whose conformational and chemical versatility has attracted chemists dealing with host–guest chemistry. Although a wide variety of calixarenes have been reported in the literature, a majority of those have been focused on tetramers called calix[4]arenes. Because, it is now

*Correspondence: Mustafa Yilmaz, Selçuk University, Department of Chemistry, 42031 Konya, Turkey; E-mail: myilmaz@selcuk.edu.tr.

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well established that the efficiency and selectivity in metal ion binding by calixarene ionophores depends not only on the ring size of calix but also on the nature of the binding groups attached and especially for calix[4]arene derivatives, on the conformations of the macrocycle (cone, partial cone, 1,3-alternate and 1,2-alternate).[1–3] It has been reported that, the introduction of more bulky groups at the lower rim of calix[4]arene could prevent the rapid inter-conversion of the different calix conformations and give stable isomers of the same compounds.[4–6] It was recently shown that a selectivity for different metal cations could be realized by using these conformational isomers. For example, they have been extensively used as selective ligands for a wide range of metal ions, such as, sodium,[7–10] lithium[11] calcium,[12,13] silver,[14] mercury,[15–17] cesium[18,19] or to a lesser extent anions[20–24] in extraction, transport and ion selective electrodes.

Besides this calix[4]arene-crowns are a family of macropolycyclic molecules in which the subunits of calixarene and crown ether are combined through the bridging of phenolic oxygen atoms of the calixarene moiety by polyoxyethylene chains.[2] An alternative strategy has been developed for the synthesis of calix(aza)crowns in which the distal positions on the lower rim of calix were linked with 1,3-diamide bridges.[25–27]

However, the synthesis of polymeric calixarene has drawn considerable attention from many workers,[28,29] because of the introduction of a chelating group between polymer and calixarene, which can be utilized in a column for metal separation. Shinkai and co-workers[30] prepared a calix[6]arene fixed to polystyrene as an extractant of UO_2^{+2} from seawater. Harris and co-workers[31,32] reported the silicon bound calixarene, which is attached via multiple ester functionalities between the polymer and calixarenes. They also synthesized a calixarene bearing single methacrylate functionality, which on homopolymerization yielded an oligomer with only six calixarene units on one chain. Gravett and Guillet[33] synthesized a water-soluble calixarene containing polymer and demonstrated its photo-physical properties. Zhong and co-workers[34] have reported synthesis and properties of calixcrown telomers. Recently Ohto and co-workers[35] have presented a calix[4]arene carboxylate resin immobilized with polyallylamine.

Blanda and Adou[36] 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. Munakata and coworkers[37] have studied reaction of open dimeric and capped polymeric calixarenes containing molecules with Ag^+ salt. Jain and coworkers[38] have synthesized a chelating resin by covalently linking calix[4]arene-semicarbazone derivative on chloromethylated polystyrene-divinyl benzene copolymer for separation of La^{3+}, Ce^{3+}, Th^{4+}, and U^{6+}. Trivedi and coworkers[39] reported a new polymer supported calix[6]arene hydroximic acid derivative for uranophile. In our previous work,[40–45] we have synthesized a few polymeric calixarenes and have been investigated their ionophoric properties. Herein we wish to report synthesis and binding properties of calix(aza)crown monomers and their oligomers (**3**–**8**).

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in

$CDCl_3$ with TMS as internal standard. IR spectra were recorded on a Perkin Elmer 1605 FTIR spectrometer as KBr pellets. 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 $CHCl_3$.

Analytical TLC performed on precoated silica gel plates (SiO_2, Merck PF_{254}), while silica gel 60 (Merck, particle size 0.040–0.063 mm, 230–240 mesh) was used for preparative column chromatography. NaH was used as an 80% dispersion in oil and washed twice with n-hexane before use. Generally, solvents were dried by storing them over molecular sieves (Aldrich; 4 Å, 8–12 mesh). Tetrahydrofuran and toluene (BDH) were dried by refluxing over sodium/benzophenone, then fractionally distilled and stored over molecular sieves. CH_2Cl_2 was distilled from $CaCl_2$, MeOH was distilled over Mg and stored over molecular sieves. The drying agent employed 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.[46,47] The other ionophores (**3**–**8**) employed in this work as illustrated in Scheme 1 have been synthesized as follows:

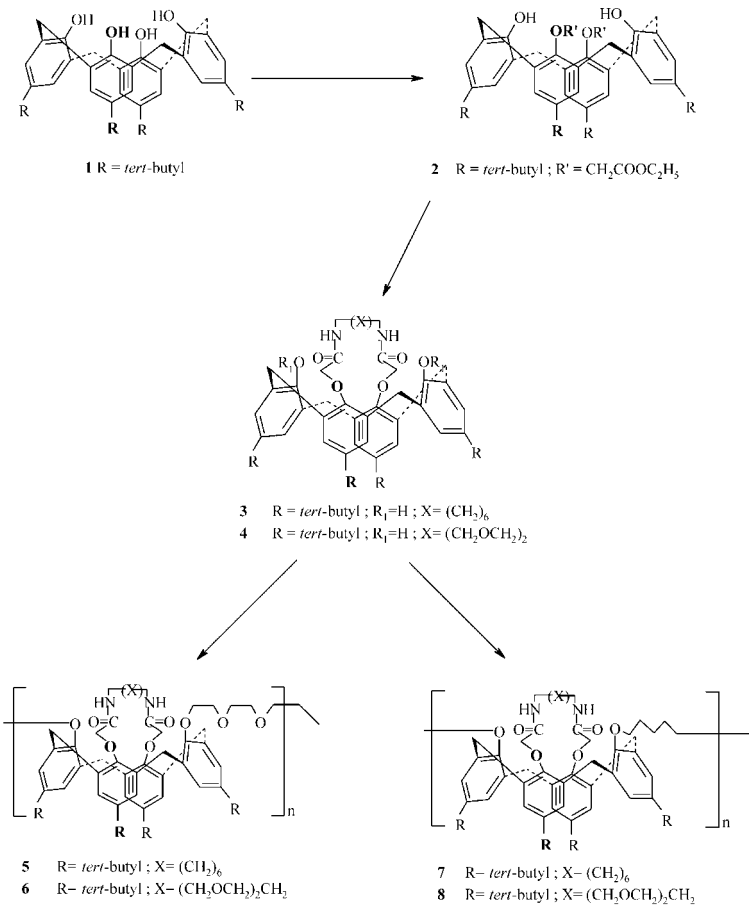
Treatment of 5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix-[4]arene 2 with 1,8-Diaminooctane (3)

A mixture of **2** (10.0 g, 12.19 mmol) and 1,8-diaminooctane (1.75 g, 12.19 mmol) in methanol/toluene (600 mL) was refluxed with continuous stirring for 38 h. Then another portion of 1,8-diaminooctane (1.75 g, 12.19 mmol) in methanol (15 mL) was added and the reaction mixture was further refluxed for 78 h. The reaction mixture was then cooled to room temperature, the solvent was removed under reduced pressure and a pure product of **3** was obtained by flash column chromatography using dichloromethane as eluent. Yield: 70%, m.p. 194–196°C.

IR (KBr) 3424 cm^{-1} (O—H), and 1648 cm^{-1}(C═O). ^1H NMR ($CDC1_3$), δ 1.0–2.1 (m, 48H, CH_2, Bu^t), 3.45 (d, 4H, J = 12.8, $ArCH_2Ar$), 4.10 (d, 4H, J = 12.8, $ArCH_2Ar$), 4.4–4.9 (m, 8H, NH—CH_2, OCH_2), 6.83 (brs, 2H, OH), 7.26–7.61 (m, 8H, ArH), 8.5 (brs, 2H, NH). Calculated for $C_{56}H_{76}N_2O_6$: C, 77.03; H, 8.77; N, 3.21. Found: C, 76.83., H, 8.32; N, 3.02.

Treatment of 5,11,17,23-Tetra-*tert*-butyl-25,27-diethoxycarbonylmethoxy-26,28-dihydroxycalix-[4]arene 2 with 1,8-Diamino-3,6-dioxaoctane (4)

A mixture of **2** (10.0 g, 12.19 mmol) and 1,8-diamino3,6-dixaoctane (1.8 g, 12.19 mmol) in methanol/toluene (600 mL) was refluxed with continuous stirring for 38 h. Then another portion of 1,8-diaminooctane (1.8 g, 12.19 mmol) in methanol (15 mL) was added and the reaction mixture was further refluxed for 78 h. The reaction mixture was then processed exactly as described above. Yield: 63%, m.p. 238–240°C.



Scheme 1.

IR (KBr) 3375 cm^{-1} (O—H), and 1670 cm^{-1} (C═O). ^{1}H NMR ($CDC1_3$), δ 1.15 (s, 36H, Bu^t), 3.35 (d, 4H, J = 12, $ArCH_2Ar$), 4.15 (d, 4H J = 12.8, $ArCH_2Ar$), 4.40 (brm, 16H, CH_2OCH_2), 6.75–7.25 (m, 10H, ArH, OH), 8.45 (brs, 2H, NH). Calculated for $C_{54}H_{72}N_2O_8$: C, 73.62; H, 8.51; N, 3.10. Found: C, 73.83., H, 8.32; N, 3.20.

A General Procedure for the Synthesis of Oligomers 5 and 6

A 1 mmol amount of each calixarene derivative was dissolved in minimum amount of THF (*ca*. 25 mL). To this solution 1 mmol (1:1 equivalent) of triethyleneglycol ditosylate was added. The addition of 80% NaH (1.0 g, 25.2 mmol) was carried out slowly with stirring at room temperature over a period of ~0.5 hours. The stirring was continued for a further 6 hours under a nitrogen atmosphere. Then the solvent was distilled off, then it was first washed with petroleum ether (15 mL) and then ethyl alcohol (15 mL) was added,

a portion of water was also added for complete precipitation. The solid material was filtered off, neutralized by 0.1 M HCl, washed with water and dried in oven. The crude product was dissolved in $CHCl_3$ and the insoluble material was filtered off, the clear filtrate was then concentrated to dryness. Finally, purified by reprecipitation from chloroform–methanol system. The following oligomers were thus obtained.

Oligomer 5 from 3 and Triethylene Glycol Ditosylate

Oligomer **5** was obtained in 66.3% yield, m.p. 206–208°C (decom.). Osmometric Mn ($CHCl_3$, 37°C) 6180, IR (KBr) 1650 cm^{-1} (C═O). ^1H NMR ($CDC1_3$), δ 0.85–1.90 (brs, 44H, C—CH_2, Bu^t), 2.50–4.80 (brm, 32H, $ArCH_2Ar$ and C—CH_2—NH, C—CH_2, OCH_2), 6.32–7.30 (brm, 10H, ArH, NH). Anal. Calcd. for $(C_{62}H_{86}N_2O_8)_n$: C, 75.42; H, 8.78; N, 2.84. Found: C, 74.92; H, 8.57; N, 3.02.

Oligomer 6 from 4 and Triethylene Glycol Ditosylate

Oligomer **6** was obtained in 63.7% yield, m.p. 250–253°C (decom.). Osmometric Mn ($CHCl_3$, 37°C) 4380, IR (KBr) 1655 cm^{-1} (C═O). ^1H NMR ($CDC1_3$), δ 0.85–1.48 (brs, 36H, Bu^t), 2.64–4.10 (brm, 36H, $ArCH_2Ar$, C—CH_2—NH, C—CH_2 and OCH_2), 6.37–7.20 (m, 10H, ArH, NH). Anal. Calcd. for $(C_{60}H_{82}N_2O_{10})_n$: C, 72.70; H, 8.34; N, 2.84. Found: C, 72.22; H, 8.86; N, 2.42.

A General Procedure for the Synthesis of Oligomers 7 and 8

3 mmol of each calixarene derivative (**3/4**) were dissolved into the minimum amount of THF (*ca.* 35 ml). The addition of 80% NaH (25 mmol) was made slowly. The mixture was stirred for 10 min at ambient temperature. To this solution 3 mmol (1:1 equivalent) 1,5-dibromopentane was added. The reaction mixture was refluxed and the stirring was continued for 6 h under nitrogen atmosphere. Then solvent was evaporated to dryness on a rotary evaporator, after that firstly washed with petrol–ether (30 mL) and then ethyl alcohol (30 mL) was added for complete precipitation. The solid material was filtered off, neutralized by 0.1 N HCl, washed with water and dried in oven. The crude product was dissolved in $CHCl_3$ and insoluble material was filtered off, the clear filtrate was then concentrated to dryness. Finally purified by reprecipitation from chloroform methanol system.

Oligomer 7 from 3 and 1,5-Dibromopentane

Oligomer **7** was obtained in 73% yield, m.p. 213–215°C (decom.). Osmometric Mn ($CHCl_3$, 37°C) 3290, IR (KBr) 1657 cm^{-1} (C═O). ^1H NMR ($CDC1_3$), δ 0.85–1.95 (brm, 50H, C—CH_2, Bu^t), 2.58–5.50 (brm, 24H, $ArCH_2Ar$ and C—CH_2—NH, C—CH_2, OCH_2),

6.40–7.30 (brm, 10H, ArH, NH). Anal. Calcd. for $(C_{61}H_{84}N_2O_6)_n$: C, 77.83; H, 8.99; N, 2.98. Found: C, 77.22; H, 8.36; N, 2.49.

Oligomer 8 from 4 and 1,5-Dibromopentane

Oligomer **8** was obtained in 77.7% yield, m.p. >300°C. Osmometric Mn ($CHCl_3$, 37°C) 2780, IR (KBr) 1660 cm^{-1} (C═O). ^1H NMR ($CDC1_3$), δ 0.99–1.51 (brs, 36H, Bu^t), 3.31–3.65 (m, 34H, $ArCH_2Ar$, C—CH_2—NH, and OCH_2), 6.53–7.25 (m, 10H, ArH, NH). Anal. Calcd. for $(C_{59}H_{80}N_2O_8)_n$: C, 74.97; H, 8.53; N, 2.96. Found: C, 74.82; H, 8.86; N, 2.78.

Liquid–Liquid Extraction

Picrate extraction experiments were performed following Pedersen's procedure.[48] 10 mL of a 2.5×10^{-5} M aqueous picrate solution and 10 mL of 1×10^{-3} M solution of calixarene (**3** and **4**) or a 1×10^{-3} M solution of calix[4]arene unit/g resin for oligomers (**5**–**8**) in CH_2Cl_2 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.[49] Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described[50] elsewhere 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.

$$M_{(aq)}^{n+} + n\,Pic_{(aq)}^{-} + x[L]_{(org)} \rightleftharpoons [M(Pic)_n(L)_x]_{(org)} \quad (1)$$

If the general extraction equilibrium is assumed to be given by Eq. (1) the overall extraction equilibrium constant is expressed as Eq. (2)

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

and the distribution ratio D would be defined by Eq. (3).

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

one obtains Eq. (4). By introduction it in Eq. (2) and taking log of both sides.

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

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

Several aspects of the ionophoric properties of calixarenes and their derivatives toward metal cations were probed experimentally. The objective of the present study was to investigate whether the complexing properties of monomeric *p-tert*-butylcalix[4]arene(aza)crown derivatives could be improved by converting them into their respective oligomers. Thus, synthesis of diester derivative of p-*tert*-butylcalix[4]arene **2** was based on previously published procedure.[47] The azacrown derivatives of p-*tert*-butylcalix[4]-arene (**3** and **4**) were synthesized by condensing compound **2** with 1,8-diaminooctane/1,2-diamino-3,6-dioxaoctane in toluene–methanol at reflux temperature. The IR spectra of compound **2** shows a carbonyl band at 1748 cm^{-1}, but this band was shifted to 1648 cm^{-1} and 1670 cm^{-1} for **3** and **4** respectively. Calix[4]arene can generally has four different conformations: cone, partial cone, 1,2-alternate, and 1,3-alternate.[1] The conformations of calixarenes can be determined by the splitting pattern of the bridging methylene protons ($ArCH_2Ar$) in the ^1H NMR spectra.[1–6] From the ^1H NMR spectra of the compounds **3** and **4**, it has been revealed that these compounds exist in cone conformation, which is deduced from the presence of two characteristic AB system (doublets at δ 3.45 and 4.10 ppm for 3, while doublets at δ 3.35 and 4.15 ppm for 4) for bridging methylene protons. The oligomers (**5**–**8**) were prepared by the treatment of **3** or **4** with triethylene glycol ditosylate/1,5-dibromopentane in the presence of NaH in a minimum amount of THF to give the corresponding oligomers in 66, 64, 73 and 78%, respectively. After purification by reprecipitation from a chloroform–methanol system. The average molecular weights of **5**–**8** oligomers were Mn = 6180, 4380, 3290 and 2780 g/mole (vapor phase osmometer), respectively. Thus, the average chain length of the oligomeric skeleton comprises *ca.* 5–6 calixarene units for oligomers **5** and **6**, while ca. 3–4 calixarene units for **7** and **8**. It is not a surprising result, because tosylate group is an easily leaving group as compared to the bromide groups in nucleophilic substitution reactions. It is in agreement with literature as Lhotak and Shinkai[51] and in our previous work[52] likewise results have been observed. The structures of the oligomers (**5**–**8**) were characterized by the combination of IR and ^1H NMR spectra. The IR spectra of the oligomers showed no absorption band at 3424–3375 cm^{-1} for phenolic hydroxyl groups. The ^1H NMR spectra of the oligomers exhibited mostly broad signals. Therefore, it was not possible to discern the conformation of the calixarene moieties in the polymeric skeleton.

Extraction Studies

Amide derivatives of calixarenes are potentially capable of forming complexes with many metal ions.[53] On the basis of previous experience, we were interested in synthesizing a type of ionophore that can selectively extract the metal cations from the aqueous to the organic phase. Thus, the present work was focused to elaborate the strategic requirements for the two phase extraction measurements. Therefore, solvent extraction experiments were performed to see the effectiveness of synthesized ionophores (**2**–**8**).

Results of the two-phase extraction measurements of (**2**–**7**) with selected alkali and transition metal picrates (such as, Li^+, Na^+, K^+, Cs^+, Ni^{+2}, Cu^{+2}, Co^{+2}, Cd^{+2}, Pb^{+2} and Hg^{+2}) are summarized in Table 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 given in Table 1, it was observed that, diester derivative of p-*tert*-butylcalix[4]arene **2** was a poor extractant for alkali metal cations but it showed a significant extraction ability towards transition metal cations. The conversion of compound **2** into calix(aza)crown derivatives (**3** and **4**) the extraction properties of this compound. The compounds **3** and **4** showed a remarkable extraction ability toward all of the metal cations used in the extraction studies. The effectiveness in transferring all metal cations by these compounds (**3** and **4**) indicate that, in this case, conformation of the calix, size of azacrown part, nature of the ligating groups and cation–π interactions may appeared to be operative in this case.

In order to see the extraction properties of more than one calixarene units together, four different oligomers (**5**–**8**) were synthesized. Observations show that the extraction ratio of metal cations with **5** and **7** remained same as compared to their monomer **3**, which indicates that both oligomers (**5** and **7**) have more or less protected their inherent extraction ability. Whereas, oligomer **6** and **8** showed a different extraction behavior as compared to their monomer **4**. Oligomers **6** and **8** are very poor extractants for alkali metal cations but they are good extractants for transition metal cations. This phenomenon can be explained by the fact

Table 1. Extraction of metal picrates with ligands[a].

	Picrate salt extracted (%)									
Ligand	Li^+	Na^+	K^+	Cs^+	Cu^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Hg^{2+}	Pb^{2+}
2[b]	< 1.0	16.3	4.3	2.2	51.2	25.4	23.6	37.4	33.3	82.0
3	98.1	97.2	97.3	95.9	91.5	96.7	94.8	94.3	98.9	97.1
4	60.2	62.7	62.4	57.6	90.0	89.0	88.2	84.3	92.2	91.5
5	98.4	97.2	96.9	96.5	97.2	97.1	96.6	96.8	96.7	97.1
6	12.2	3.6	5.4	1.5	95.9	97.4	95.9	95.8	98.2	98.1
7	95.8	96.9	97.9	98.1	98.2	98.1	97.7	95.8	97.8	96.4
8	8.25	7.8	8.7	6.5	98.5	95.0	96.3	93.0	98.9	97.8

[a]Aqueous phase, [metal nitrate] $= 1 \times 10^{-2}$ M; [picric acid] $= 2.5 \times 10^{-5}$ M; organic phase, dichloromethane, [ligand] $= 1 \times 10^{-3}$ M or a 1×10^{-3} M solution of calix[4]arene unit/g resin for oligomers at 25°C, for 1 h.
[b]Reference [44].

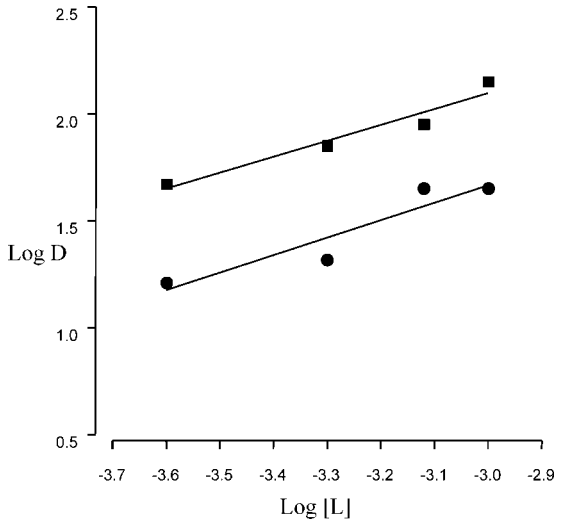


Figure 1. Log D versus log[L] for the extraction Cs^+ (•) and Hg^{2+} (■) picrates by the Ligand **3** from an aqueous phase into dichloromethane at 25°C.

that, during oligomerization process, the conformation of calix[4]azacrown may probably has been changed, which is well discussed in the literature.[18]

Figs. 1 and 2 show the extraction into dichloromethane at different concentrations of the ligand **3** and **4** for Cs^+ and Hg^{2+} respectively. A linear relationship between log D

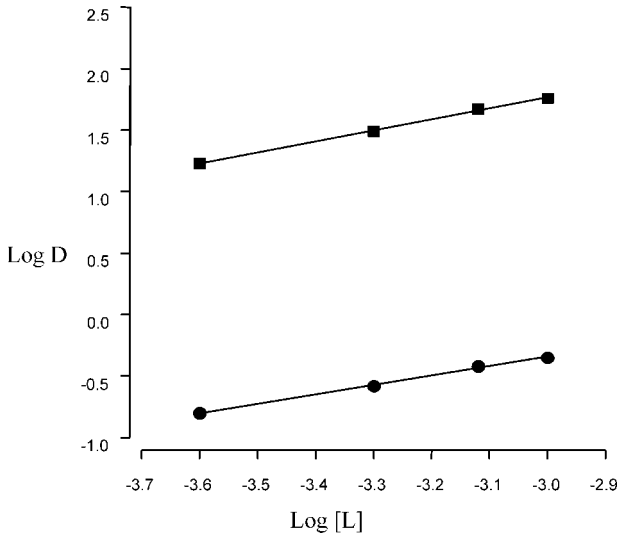


Figure 2. Log D versus log[L] for the extraction Cs^+ (•) and Hg^{2+} (■) picrates by the Ligand **4** from an aqueous phase into dichloromethane at 25°C.

versus-log[L] is observed with the slope of lines for $Cs^+$and Hg^{2+} by the ligand **3** and **4**, which are roughly equal to 0.82, 0.74, 0.76 and 0.90 respectively, suggesting that the ligand **3** and **4** forms a 1:1 complex with Cs^+ and Hg^{2+}. The analytical data of the **3** and **4** show that the complexation reactions take place according to the following equation.

$$M_{(aq)}^{n+} + nPic_{(aq)}^{-} + [L]_{(org)} \rightleftharpoons [M(Pic)_n(L)]_{(org)}$$

In this system the logarithmic extraction constants for Cs^+ and $Hg^{2+}$with the ligand **3** and **4** according to Eq. (1) were determined. The corresponding logarithmic extraction constants are 4.77 and 5.07 for Cs^+ and Hg^{2+} with **3** while 2.94 and 4.79 for Cs^+ and Hg^{2+} with **4**.

CONCLUSION

In this study, four new oligomers have been synthesized from p-tert-butylcalix[4]-arane-azacrowns by nucleophilic substitution reactions. The ion binding properties ability of the oligomers (**5**–**8**) was studied and it was observed that the oligomers **5** and **7** have protected their inherent extraction properties as compared to their monomer **3**. The oligomers **6** and **8**, however, showed a different extraction behavior as compared to their monomer **4**. The newly synthesized oligomers (**5**–**8**) show good potential for trace enrichment of initial ions as evident from extraction studies, which enhances their utility in phase transfer reactions, as adsorbents, or as potential candidate materials for fabricating sensors.

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