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Liquid–Liquid Extraction of Alkali and Transition Metal Cations by Two Biscalix[4]arenes

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ABSTRACT

The synthesis and complexing abilities of the two biscalix[4]arenes with ligating ester and ketone groups in the cone conformation have been performed and determined by extraction and extraction constants measurements. The cations studied were the alkali (Li^+, Na^+, K^+, and Cs^+) and transition (Ag^+, Hg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}) metals. It has been observed that ester derivative **7** shows a higher affinity toward transition metals than the alkali metal cations. By contrast, ketone derivative **8** extracts both alkali and transition metal cations effectively. Both of compounds **7** and **8** are better extractants than their monomeric analog **1.**

Key Words. Solvent extraction; Biscalix[4]arenes; Alkali cations; Transition metal cations

INTRODUCTION

Calixarenes are a readily available and important class of macrocycles in supramolecular chemistry. Numerous potential applications of calixarene derivatives as specific ligands for cations, anions, and as hosts of neutral compounds have been reported (1–4).

Calixarenes bearing substituents attached at the phenolic oxygen atoms (i.e., functionalized at the lower rim) have been shown to exhibit interesting complexing, extraction, and transport properties toward a great variety of

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metal ions (5–15). In recent years, many neutral calix(4)arene-derived extractants containing functional groups, such as amides, esters, ketones, and ethers, have been synthesized and their ion binding properties investigated by solvent extraction, UV-Vis, and ^{1}H-NMR spectroscopy (16–20). Encapsulation of alkali metal cations involving the four pendant groups has been verified in several instances by NMR studies and x-ray analysis (21–27).

In this paper the synthesis of triester and triketone derivatives of biscalix[4]arenes was performed and their binding properties with alkali (Li^+, Na^+, K^+, and Cs^+) and selected transition metal cations (Ag^+, Hg^{2+}, Cu^{2+}, Co^{2+}, and Cd^{2+}) were examined.

EXPERIMENTAL

Reagents: Acetone, K_2CO_3, NaH (80% in paraffin oil), 1,8-diaminooctane, tetrahydrofuran, chloracetone (all Merck), pyridine (BDH), and ethyl bromoacetate (Fluka). Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck). Solvents were generally dried by storing them over molecular sieves (Aldrich; 4A°, 8–12 mesh). All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

Melting points were determined on a Gallenkamp apparatus. ^{1}H-NMR spectra were recorded on a Bruker 250 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-visible spectra were obtained on a Shimadzu 160 A UV-visible recording spectrophotometer.

Scheme 1 illustrates the formulas of the extractants used (**1, 7,** and **8**). 5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(benzoyloxy)-28-hydroxycalix(4)arene (**2**) (Fluka) and other reagents were used without further purification.

5,11,17,23-Tetra-*tert*-butyl-25,26,27-tris(benzoyloxy)-28-ethoxycarbonylmethoxycalix(4)arene (3)

A mixture of compound **2** (2.5 g, 2.6 mmol), potassium carbonate (0.92 g), and ethyl bromoacetate (0.55 mL) in dry acetone (50 mL) was stirred and heated under reflux for 15 hours. The cooled solution was filtered, the solid material was washed with acetone, and the filtrate and washing were combined. Most of the solvent was then evaporated and the residue was poured into 200 mL distilled water with vigorous stirring and neutralized by 0.1 M HCl. The solid was filtered off, washed thoroughly with distilled water, and dried under vacuum. Recrystallization of the crude product from ethanol–acetone furnished compound **3.** Yield 2.1 g (77%), mp 210°C. IR (KBr) 1733 cm^{-1} (C═O). ^{1}H-NMR ($CDCl_3$), δ 1.00 (s, 18H, Bu^t), 1.24 (s, 18H, Bu^t),

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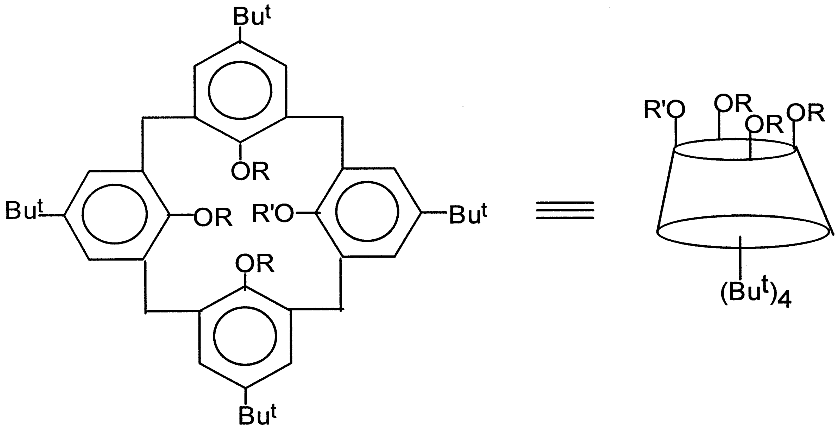
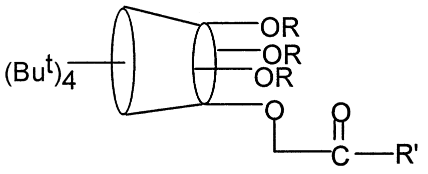


1 R = H R' = H

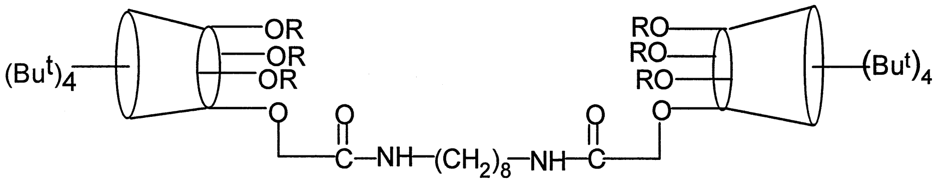
2 R = COC_6H_5 R' = H



3 R' = OCH_2CH_3 R = COC_6H_5

4 R' = OH R = H

5 R' = Cl R = H



6 R = H

7 R = $CH_2COOC_2H_5$

8 R = CH_2COCH_3

SCHEME 1

1.26 (t, 3H, CH_3), 3.60 (m, 6H, $ArCH_2Ar$, and CH_2O), 4.10 (m, 6H, $ArCH_2Ar$ and CH_2O), 7.35 (m, 23H, Ar—H). Analysis: Calculated for $C_{68}H_{74}O_9$: C, 78.9; H, 7.2. Found: C, 78.5; H, 7.1.

5,11,17,23-Tetra-*tert*-butyl-25-carboxymethoxy-26,27,28-trihydroxycalix(4)arene (4)

A mixture of compound **3** (1.00 g, 0.96 mmol) and 10 mL of 15% aqueous NaOH in 80 mL ethanol–THF (1:3) was stirred and refluxed for 24 hours after which most of the solvent was distilled off. The residue was diluted with hot water (200 mL) and neutralized by 0.1 M HCl. The solid material was then filtered and washed with hot distilled water. Recrystallization of the crude product from ethanol–acetone furnished **4.** Yield 0.45 g (53%), mp > 800°C. IR (KBr) 3225 cm^{-1} (O—H), 1737 cm^{-1} (C═O). ^1H NMR ($CDCl_3$), δ 0.95 (s, 18H, Bu^t), 1.20 (s, 18H, Bu^1), 3.45 (d, 4H, $ArCH_2Ar$), 4.10 (m, 6H, $ArCH_2Ar$ and CH_2O), 7.35 (m, 8H, Ar—H), 7.90 (br s, 4H, OH and CO_2H). Analysis: Calculated for $C_{46}H_{58}O_6 \cdot 2H_2O$: C, 74.4; H, 8.4. Found: C, 74.9; H, 8.7.

5,11,17,23-Tetra-*tert*-butyl-25-chloroformylmethoxy-26,27,28-trihydroxycalix(4)arene (5)

A solution of compound **4** (7.0 g, 9.92 mmol) in dry THF (150 mL) containing thionyl chloride (5 mL) was heated under reflux under nitrogen about 3.5 hours. Removal of the solvent and residual thionyl chloride under reduced pressure furnished the acyl chloride (**5**) in quantitative yield. The product was used in subsequent preparations without purification.

N,N′-Bis[carbonylmethoxy(5,11,17,23-tetra-*tert*-butyl-25,26,27-trihydroxycalix(4)-arenyl)] 1,8-diaminooctane (6)

Compound **5** obtained in the previous step was dissolved in dry THF (100 mL). A solution of 1,8-diaminooctane (2.8 g, 19.44 mmol) in THF (25 mL) was added dropwise in about 1 hour with continuous stirring at room temperature. The reaction mixture was then stirred further for 1 hour, after which most of the solvent was distilled off. The residue was diluted with water (200 mL) and neutralized by 0.1 M HCl. The solid material was then filtered and washed with distilled water. Recrystallization of residue from ethanol–THF furnished **6.** Yield 7.5 g (47%), mp > 300°C. IR (KBr) 3244 cm^{-1} (O—H), 1733 cm^{-1} (C═O). ^1H-NMR ($CDCl_3$), δ 1.10–1.25 (m, 72H, Bu^t), 1.30 (m, 8H, C—CH_2—C), 1.45 (m, 4H, N—C—CH_2—C), 3.45 (d, 8H, $J = 12.6$ Hz, Ar—CH_2—Ar), 3.80 (t, 4H, N—CH_2—C), 4.20 (s, 4H, O—CH_2—CO), 4.40 (d, 8H, $J = 12.6$ Hz, Ar—CH_2—Ar), 7.15–7.25 (m, 16H, Ar—H), 7.65 (s, 2H, N—H), 9.60 (s, 6H, OH). Analysis: Calculated for $C_{108}H_{132}N_2O_{10} \cdot 3H_2O$: C, 77.6; H, 8.3; N, 1.7. Found: C, 77.1; H, 8.2; N, 1.6.

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N,N'-Bis-[carbonylmethoxy(5,11,17,23-tetra-*tert*-butyl-25,26,27-triethoxycarbonylmethoxycalix(4)arenyl)] 1,8-Diaminooctane (7)

A mixture of compound **6** (1.5 g, 0.986 mmol), K_2CO_3 (4 g) ethyl bromoacetate (2 mL) in dry acetone (50 mL) was treated according to a previously described method (28). Yield 1.1 g (73%), mp 115°C. IR (KBr) 3447 cm^{-1} (N—H), 1732 cm^{-1} (C═O), 1693 cm^{-1} (N—C═O). ^{1}H-NMR ($CDCl_3$), δ 0.95–1.20 (m, 72H, Bu^t), 1.22–1.26 (m, 18H, CH_3), 1.30 (m, 8H, C—CH_2—C), 1.60 (m, 4H, N—C—CH_2—C), 3.45 (d, 8H, J = 12.6 Hz, Ar—CH_2—Ar), 3.85 (t, 4H, NCH_2—C), 4.00–4.25 (m, 28H, CH_2O), 4.40 (d, 8H, J = 12.6 Hz, Ar—CH_2—Ar), 6.75 (s, 2H, N—H), 6.95–7.25 (d, 16H, Ar—H). Analysis: Calculated for $C_{132}H_{168}N_2O_{20}\cdot 2C_2H_5OH$: C, 75.4; H, 8.4; N, 1.3. Found: C, 75.9; H, 8.9; N, 1.5.

N,N'-Bis-[carbonylmethoxy(5,11,17,23-tetra-*tert*-butyl-25,26,27-triacetonyloxy-calix(4)arenyl)] 1,8-Diaminooctane (8)

A mixture of compound **6** (1.5 g, 0.986 mmol), K_2CO_3 (4 g) Nal (3 g), and chloracetone (2 mL) in dry acetone (50 mL) was treated according to a previously described method (28). Yield 1.15 g (63%), mp 160°C. IR (KBr) 3424 cm^{-1} (N—H), 1739 cm^{-1} (C—O). ^{1}H-NMR ($CDCl_3$), δ 1.0–1.20 (m, 72H, Bu^t), 1.20–1.25 (m, 8H, C—CH_2—C), 1.60 (s, 18H, CH_3CO), 1.85 (m, 4H, N—C—CH_2—C), 3.45 (d, 8H, J = 13.2, Ar—CH_2—Ar), 3.85 (t, 4H, N—CH_2—C), 3.90–4.15 (s, 16H, CH_2O), 4.45 (d, 8H, J = 13.2, Ar—CH_2—Ar), 6.75 (s, 2H, N—H); 6.95–7.25 (m, 16H, Ar—H). Analysis: Calculated for $C_{126}H_{156}N_2O_{16}$: C, 76.0; H, 8.1; N, 1.4. Found: C, 76.5; H, 8.5; N, 1.7.

Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure (29). Ten milliliters of a 2.5 × 10^{-5} M aqueous picrate solution and 10 mL of a 1 × 10^{-3} M solution of calixarene in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 minutes, then magnetically stirred in a thermostated water-bath at 25°C for 1 hour, and finally left standing for an additional 30 minutes. The concentration of picrate ion remaining in the aqueous phase was then determined spectrophotometrically as previously described (13). Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described elsewhere (30) by stepwise addition of a 2.0 × 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 hours. Transition metal picrates were prepared by stepwise addition of a 1×10^{-2} M metal nitrate solution to a 2.5×10^{-5} M aqueous picric acid solution and shaken at 25°C for 1 hour.

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 given by Eq. (1):

$$M^{n+}_{(\mathrm{aq})} + n\mathrm{Pic}^{-}_{(\mathrm{aq})} + x[\mathrm{L}]_{(\mathrm{org})} \rightleftharpoons [\mathrm{M(Pic)}_n(\mathrm{L})_x]_{(\mathrm{org})} \qquad (1)$$

the overall extraction equilibrium constant is expressed as

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

and the distribution ratio *D* would be defined by

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

By introducing *D* into Eq. (2) and taking the log of both sides, one obtains

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

With these assumptions a plot of 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

We have extended our study of chemically modified calix[4]arenes to include derivatives with more than one type of functionality around the compound. Böhmer and coworkers (31) previously synthesized a few calix [4]arenes in which the upper edges confront each other. On the other hand, like Shinkai and coworkers (32), we were interested in the synthesis of biscalix[4]arenes in which the lower edges confront each other because the metal binding event in calix[4]arenes mostly occurs on the lower rim and it has been especially found that biscalix[4]arenes show ion selectivity in the two-phase solvent extraction systems of metal picrates. The present work is an extension of this strategy.

Compound **2** was treated with ethyl bromacetate in dry acetone in the presence of K_2CO_3 to obtained **3** in 77% yield. Hydrolysis of compound **3** with 15% aqueous NaOH in ethanol–THF removes the ester and benzoyl groups of

3, which was recognised by IR spectroscopy which shows disappearance of the carbonyl groups and appearance of a new band at 3225 cm^{-1} belonging to O—H groups. Compound **4** obtained after the hydrolysis, was then treated with thionyl chloride in dry THF under reflux and yielded the acid chloride in quantitative yield. The acid chloride **5** is useful synthetically in a number of ways. Simple replacement of chlorine can lead directly to other modifications. It has been demonstrated that it can be bridged across the lower rim. Treatment of **5** with 1,8-diaminooctane in THF furnished the biscalix[4]arene **6** in 47% yield.

We were interested in the synthesis of biscalix[4]arene and its derivatives to estimate their metal binding ability through the two-phase solvent extraction of metal picrates. Thus, compound **6** was converted to its ester derivative with ethyl bromoacetate in dry acetone in the presence of K_2CO_3. The ester derivative **7** was isolated in 73% yield.

Chloroacetone was used to synthesise the keto derivative. The reaction was facilitated by halogen exchange with NaI. Therefore, compound **6** was refluxed with chloroacetone in dry acetone in the presence of K_2CO_3 and NaI for 7 hours. The keto derivative **8** was obtained in 63% yield.

All new compounds were characterized by a combination of ^{1}H-NMR, IR, and elemental analysis. The ^{1}H-NMR data showed that these compounds (**6, 7** and **8**) have cone conformation (33), which was confirmed from the $ArCH_2Ar$ splitting pattern. The ^{1}H-NMR spectrum of these compounds (**6, 7,** and **8**) exhibited a single AB system for the bridging methylene groups at δ 3.45 and 4.40 ($J = 12.6$ Hz) for **6** and **7;** δ 3.45 and 4.45 ($J = 13.2$ Hz) for **8.**

Although numerous investigations have recently reported the extraction of alkali metals as well as lanthanides from an aqueous phase into an organic phase by calixarene (8, 20–27, 31), information regarding the extraction of transition metals is still limited (5, 6, 8, 12–15, 34).

Solvent extraction experiments were performed in this study to estimate the effectiveness of **7** and **8** in transferring such alkali cations as Li^+, Na^+, K^+, and Cs^+ and such transition metal cations as Co^{2+}, Cu^{2+}, Cd^{2+}, Ag^+, and Hg^{2+} from the aqueous shows into the organic phase (dichloromethane). The results are given in Table 1. These data were obtained by using a solution of the biscalixarenes to extract metal picrate from aqueous solution. The equilibrium concentration of picrates in the squeous phase was determined spectrophotometrically.

As shown in Table 1, the extraction results of **7** and **8** are not the same. Compound **7** extracted transition metal ions in high proportions but the alkali metals were not extracted effectively, whereas **8** shows high affinity for both alkali and transition metal cations. It was observed that both compounds **7** and **8** are effective extractants but not selective at extracting both alkali and transition metal cations. These results suggest that the ketonic groups are the efficient groups in this phase transferring.

TABLE 1
Extraction of Metal Picrates with Ligands[a]

	Picrate salt extracted (%)								
Ligand	Li^+	Na^+	K^+	Cs^+	Cu^{2+}	Co^{2+}	Cd^{2+}	Ag^+	Hg^{2+}
1	18.9	8.5	3.3	2.8	9.9	7.9	9.4	6.3	15.5
7	20.8	24.3	32.5	30.0	57.0	39.0	49.5	76.0	94.0
8	73.4	73.0	81.0	82.1	84.2	81.0	83.0	88.5	90.2

[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 hour.

In order to investigate whether these results were caused by the *p*-*tert*-butylcalix[4]arene itself, experiments were performed with *p*-*tert*-butylcalix[4] arene (**1**). Observations showed that when extraction was performed with unreacted *p*-*tert*-butylcalix[4]arene, the transfer of metal cations was very close to unity.

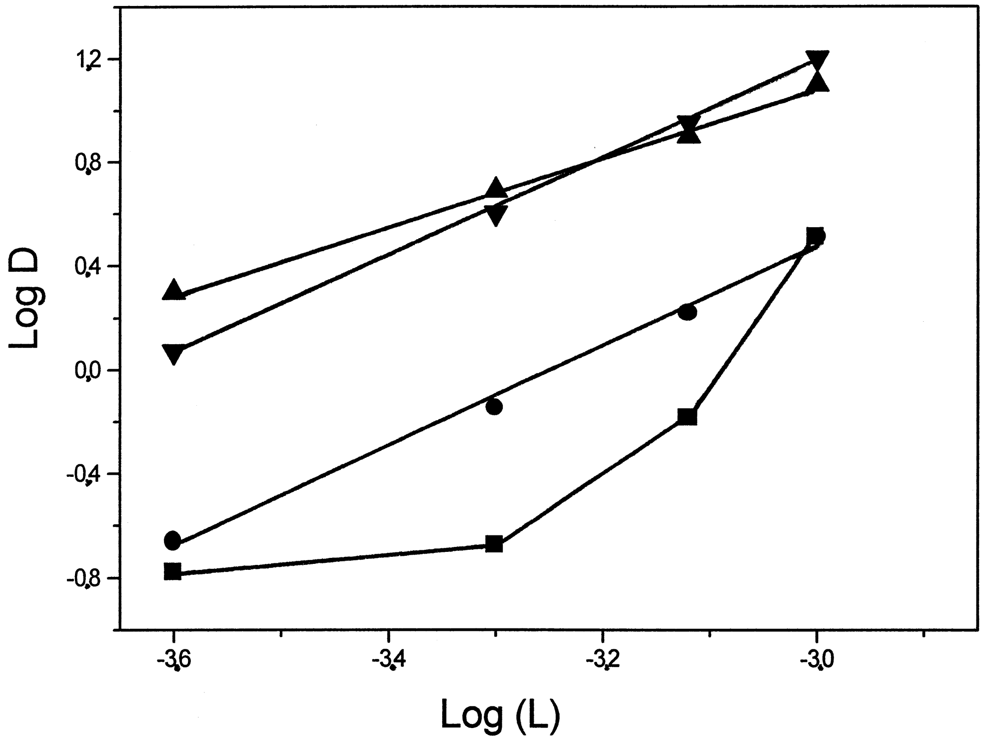

FIG. 1 Log *D* versus log[L] for the extraction of Hg-picrate by the ligands **7** (▼), and **8** (▲), and for the extraction of Ag-picrate by the ligand **7** (■) and **8** (●) from an aqueous phase into dichloromethane at 25°C.

Figure 1 shows the extraction into dichloromethane at different concentrations of **7** and **8** for Ag^+ and Hg^{2+}.

However, log-log plots for the extraction of Hg^{2+} by **7** and **8** have linear slope, with a 1:2 metal–ligand ratio for **7** and a 1:1 ratio for **8.** For the extraction of Ag^+ by these ligands, the results are a linear slope with **8** but is not with **7.** The observed metal–ligand ratio of Ag^+ with **8** is 1:2. As shown in Fig. 2, the log-log plots for the extraction of K^+ and Cu^{2+} by **7** and **8** are not linear, suggesting that the formation of at least two of the complexes are by different stoichiometries.

For this system the following logarithmic extraction constants corresponding to Eq. (1) were determined.

$$M^{n+}_{(aq)} + n\mathrm{Pic}^{-}_{(aq)} + x[L]_{(org)} \rightleftharpoons [M(\mathrm{Pic})_n(L)_x]_{(org)} \qquad (1)$$

$$\begin{aligned}\mathrm{Log}\, K_{ex} &= 12.41 \mp 4 \ (\text{for } Ag^+ \text{ with } \mathbf{8})\\ &= 15.19 \mp 2 \ (\text{for } Hg^{2+} \text{ with } \mathbf{8})\\ &= 20.86 \mp 3 \ (\text{for } Hg^{2+} \text{ with } \mathbf{7})\end{aligned}$$

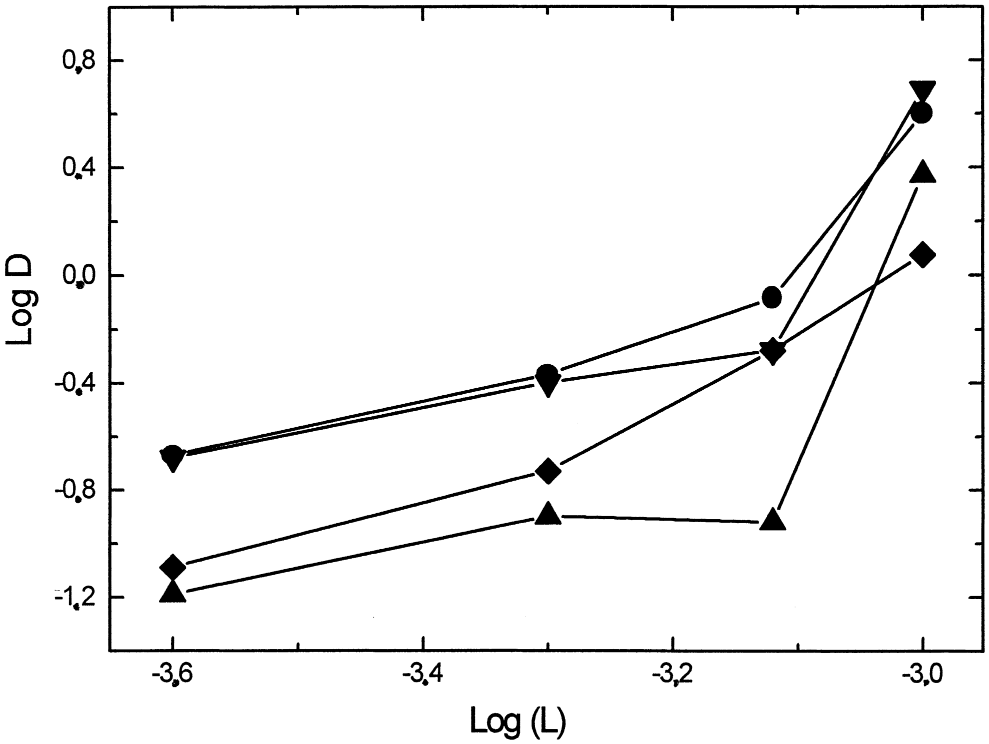

FIG. 2 Log *D* versus log[L] for the extraction of K-picrate by the ligands **7** (●) and **8** (▲), and for the extraction of Cu-picrate by the ligands **7** (◆) and **8** (▼) from an aqueous phase into dichloromethane at 25°C.

It is interesting to note, however, that the order of the extractability of metal cations by both ligands **7** and **8** decreases in the sequence $Hg^{2+} > Ag^{+} > Cu^{2+} > Cd^{2+} > Co^{2+} > K^{+} > Cs^{+} > Na^{+} > Li^{+}$.

CONCLUSION

The high complexation ability of chemically modified biscalix[4]arenes has been extended to include alkali and transition metal cations, using ester and ketones as the ligating functional groups in the cone conformation. The ketone derivatives of biscalix[4]arenes possess significant ionophoric properties.

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