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SYNTHESIS AND COMPARATIVE COMPLEXATION STUDIES OF SCHIFF BASE DERIVATIVES OF *p*-TERT BUTYLCALIX[4]ARENE COPOLYMERS

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Key Words: *p*-tert-butylcalix[4]arene, Copolymer, Schiff Base, Phase Transfer, Alkali, and Transition Metal

ABSTRACT

Two different Schiff base derivatives of *p*-tert butylcalix[4]arene **3**, **6** in which one of them carrying two oxime groups, while the other has a 1,8-oxylenediimino bridge, are synthesized. Treatment of these monomers with triethylene ditosylate provided corresponding copolymers **5**, **7**. Their complexing properties with selected alkali and transition metals are reported here. It has been concluded that the binding ability of Schiff base-calixarene derivatives in transferring the metal cations is due to the presence of soft π -donor systems in the macrocyclic structure.

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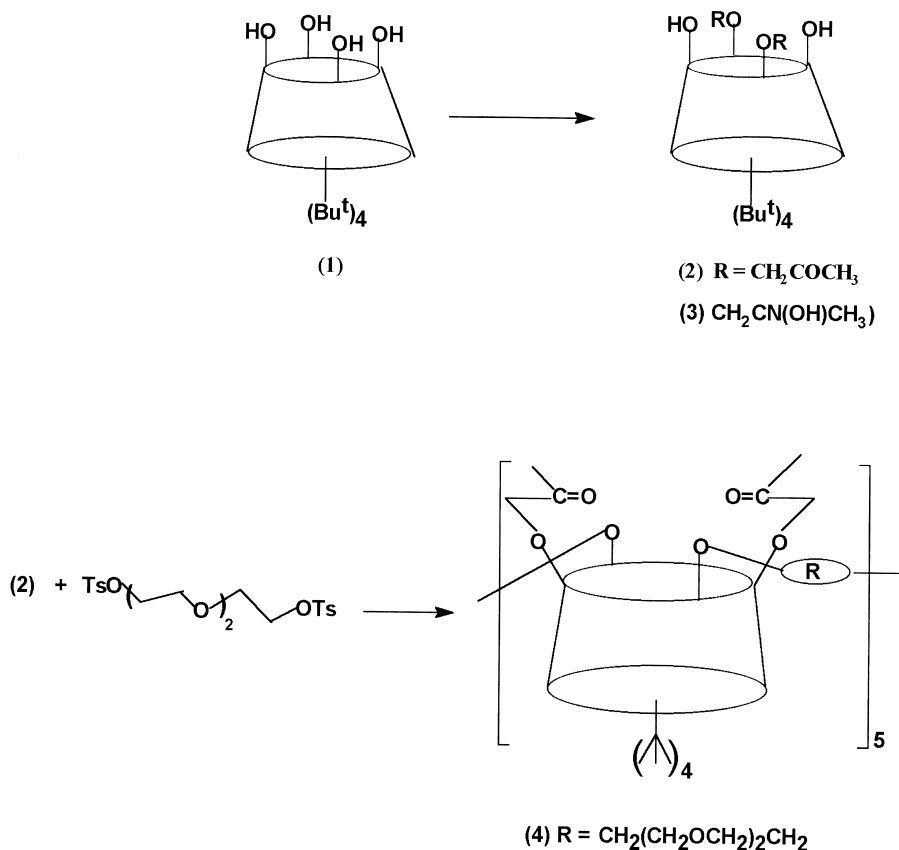
INTRODUCTION

Calixarenes are metacyclophanes comprising phenolic and methylene units. They are very well known as attractive and excellent ionophores because they provide a platform for the attachment of convergent binding groups either at to create host molecules mainly for the attraction of simple cations, anions, and small molecules. Lower rim modifications on calixarenes through the phenolic oxygen atoms have been widely explored in the design and synthesis; especially on calix[4]arene with lower rim carbonyl containing substituents in the form of esters, ketones, amides, thioamides and carboxylic acids [1-10]. The complexation of alkali and transition metals has been the focus of much interest for an extended period of time. Generally, the complexation processes are used for the selective extraction of metals for purification purposes. To achieve the required goal, different procedures were developed and used to investigate the complexation behavior of ligands [11-28].

However, one option to use the calixarene derivatives as effective ionophores with high recognition ability is to immobilize them on some polymer matrices and later on to investigate their binding properties in two phase extraction systems. A few papers have been reported in this regard [29-35]. We undertook the present study in accordance with our previous experience [36-41], in order to gain information on the structural requirements necessary for selective metal ion complexation with Schiff base *p-tert*-butylcalix[4]arene copolymers (5, 8, and 7) along with their analogs (3 and 6). Their syntheses and comparative complexing abilities toward selected alkali and transition metals are reported here.

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus in a sealed capillary and are uncorrected. ^1H 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-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 . Merck PF_{254} silica gel was used for all forms of chromatography. The drying agent employed was anhydrous sodium sulfate. All aqueous solutions were pre-



Scheme 1.

pared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

The compounds 1, 2 and, 4 were synthesized according to previously published methods [40, 43-45]. The other ligands [3, 5, 6, and 7] synthesized are described as follows.

Treatment of Diketone 2 with Hydroxylamine Hydrochloride (3)

In a mixture of diketone 2 (3.04 g; 4.0 mmol) pyridine (2 mL) and K_2CO_3 (14.0 g) in THF (30 mL) was added hydroxylamine hydrochloride (1.688 g; 24.0 mmol) in THF (30 mL) with the help of a dropping funnel at room tem-

perature. The mixture was then heated under reflux about 12 hours with continuous stirring. After that, the cooled contents were filtered and washed with THF, the filtrate and washings were combined and subjected to the rotary evaporator where most of the solvent (ca. 90%) was evaporated. The remaining contents were poured in a beaker containing distilled water (300 mL) with vigorous stirring with the help of a glass rod. The precipitates were filtered off, washed first with very dilute HCl, finally with water, and recrystallized from THF-MeOH. Yield 2.4 g (66.6%), m.p. 170-172°C. IR (KBr): 3400 cm^{-1} brd. (O-H) and 1620 cm^{-1} (C=N). ^1H NMR (CDCl_3) δ 0.90 (s, 18H, Bu^t); 1.20 (s, 18H, Bu^t); 1.55 (s, 6H, C- CH_3); 3.35 (d, 4H, $J=12.8$ Hz, ArCH_2Ar); 3.55 (s, 4H, $\text{OCH}_2\text{-C}$); 4.25 (d, 4H, $J=12.8$ Hz, ArCH_2Ar); 7.00 (s, 4H, ArH); 7.10 (s, 4H, ArH); 7.25 (s, 2H, ArOH); 9.75 (s, 2H, N-OH). Anal. Calcd. for $\text{C}_{50}\text{H}_{66}\text{N}_2\text{O}_6$; C, 75.91; H, 8.41; N, 3.54; Found: C, 75.95; H, 8.61; N, 3.74.

Compound 5 from Diketone Copolymer 4 and Hydroxylamine Hydrochloride

The reaction of diketone copolymer 4 with hydroxylamine hydrochloride was carried out under the above described procedure. Usual workup provided 5. Yield (77%), m.p. 187-189°C. Osmometric M_n (CHCl_3 , 37°C), 4500 (calculated: 4520). IR (KBr): 3430 cm^{-1} brd. (N-OH); 1620 cm^{-1} (C=N). ^1H NMR (CDCl_3): δ 0.90-1.35 (m, 36H, Bu^t); 1.45 (s, 6H, C- CH_3); 3.45-4.05 (m, 12H, ArCH_2Ar and ArOCH_2); 4.25 (t, 12H, $\text{OH}_2\text{CCH}_2\text{-O}$); 6.90 (m, 4H, ArH); 7.30 (d, 2H, ArH); 7.80 (d, 2H, ArH); 9.70 (s, 2H, N-OH). Anal. Calcd. for $(\text{C}_{56}\text{H}_{76}\text{N}_2\text{O}_8)_5$ C, 74.30; H, 8.46; N, 3.09; Found: C, 74.60; H, 8.75; N, 3.29.

Treatment of Diketone 2 with 1,8-Diaminooctane (6)

The reaction of diketone 2 with 1,8-diaminooctane was carried out as described previously [44]. The usual work up afforded 6. Yield (74.5%), m.p. 250-252°C. IR (KBr): 3410 cm^{-1} brd (OH); 1635 cm^{-1} (C=N). ^1H NMR (CDCl_3): δ 0.85 (s, 18H, Bu^t); 1.10 (s, 18H, Bu^t); 1.30 (m, 8H, C- $\text{CH}_2\text{-C}$); 1.45 (s, 6H, C- CH_3); 2.60 (m, 4H, N-C- $\text{CH}_2\text{-C}$); 3.30 (t, 4H, N- $\text{CH}_2\text{-C}$); 3.45 (d, $J=13$ Hz, 4H, ArCH_2Ar); 4.15 (s, 4H, CH_2O); 4.30 (d, $J=13$ Hz, 4H, ArCH_2Ar); 6.95-7.15 (m, 8H, ArH); 7.20 (s, 2H, OH). Anal. Calcd. for $\text{C}_{58}\text{H}_{80}\text{N}_2\text{O}_4$; C, 80.13; H, 9.27; N, 3.22. Found: C, 80.45; H, 9.45; N, 3.28.

Copolymer 7 from 6 and Triethylene Glycol-Ditosylate

The reaction of **6** with triethylene glycol-di-*p*-tosylate was carried out as described previously [41]. The usual work up resulted in **7**. Yield (76.5%), m.p. 188-190°C. Osmometric Mn (CHCl₃, 37°C), 4900 (calculated: 4910). IR(KBr): 1635 cm⁻¹ (C=N). ¹H NMR (CDCl₃): δ 0.85 (m, 36H, Bu¹); 1.30 (m, 8H, C-CH₂-C); 1.75 (s, 3H, C-CH₃); 2.00 (s, 3H, C-CH₃); 2.65(m, 4H, N-C-CH₂-C); 3.00 (t, 4H, N-CH₂-C); 3.15-3.65 (m, 24H, ArCH₂Ar, ArOCH₂, OCH₂CH₂O); 6.45 (d, 1H, ArH); 6.50 (d, 2H, ArH); 6.8 (dd, 1H, ArH); 7.15 (d, 2H, ArH); 7.25 (s, 2H, ArH). Anal. Calcd. for (C₆₄H₉₀N₂O₆)₅; C, 78.16; H, 9.22; N, 2.85; Found: C, 78.45; H, 9.55; N, 2.38.

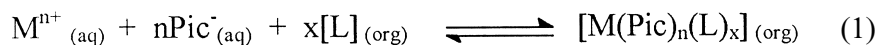
Solvent Extraction

Picrate extraction experiments were performed following Pedersen's procedure [46]. 10 mL of a 2.5x10⁻⁵ M aqueous picrate solution and 10 mL of 1x10⁻³ M solution of calixarene in CHCl₃ 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 [47]. Blank experiments showed that no picrate extraction occurred in the absence of calixarene.

The alkali picrates were prepared as described elsewhere [48] by stepwise addition of a 2.5 x10⁻² 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 1x10⁻² M of metal nitrate solution to a 2.5x10⁻⁵ M aqueous picric acid solution and shaken at 25°C for 1 hour.

Log-Log Plot Analysis

In order 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 Mⁿ⁺ metal ion, L neutral ligand and 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.



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

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

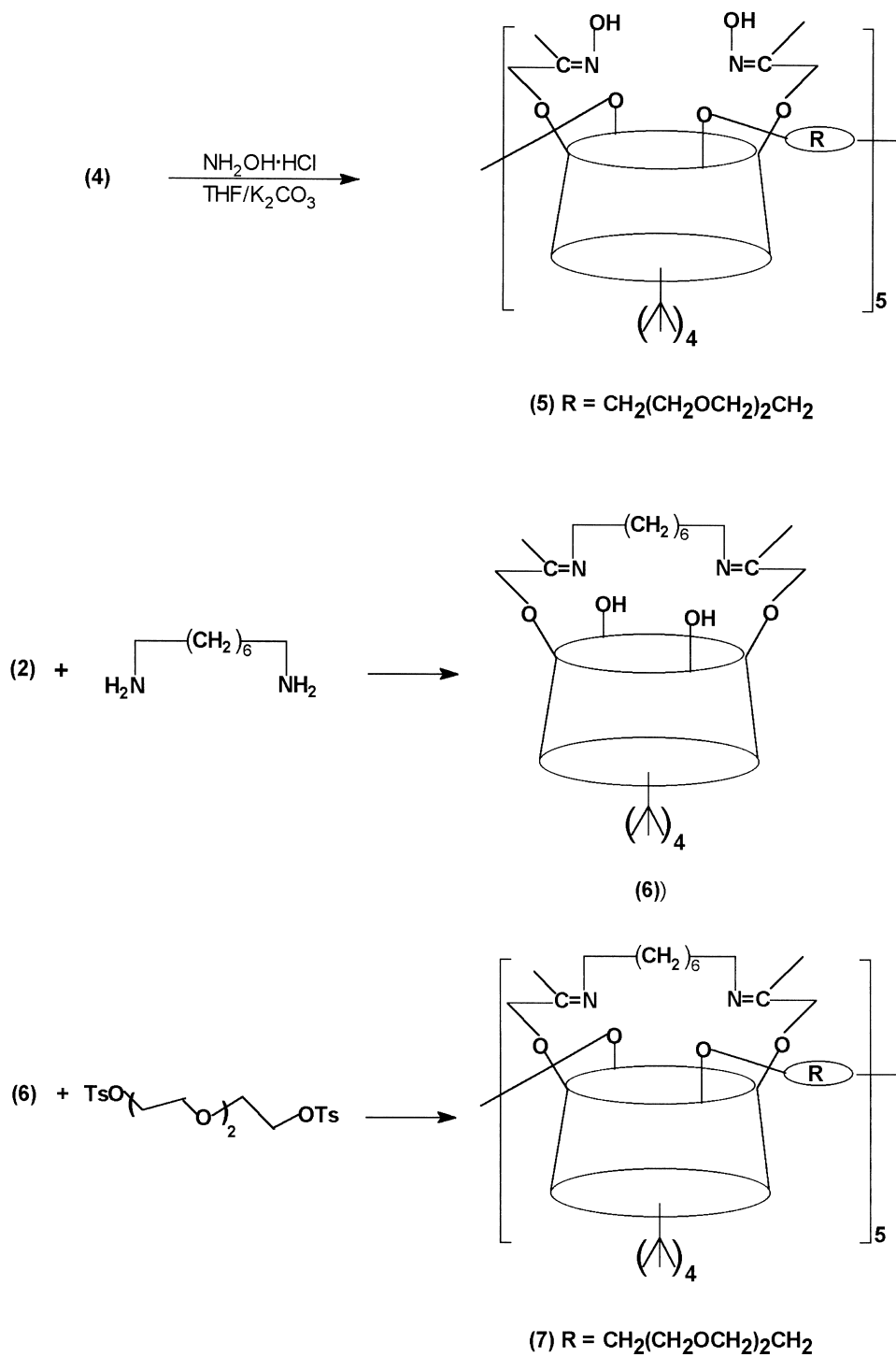
$$\log D = \log (K_{ex}[Pic^{-}]^n) + x \log [L] \quad (4)$$

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

Schiff bases are potentially capable of forming stable complexes with many metal ions. On the basis of previous experience, Schiff base *p-tert*-butylcalix[4]arenes (**3** and **6**) and their respective copolymers (**5** and **7**) were constructed as shown in Schemes 1 and 2. The cone-1,3-diketone **2** was synthesized according to the literature [45]. The dioxime derivative of *p-tert*-butylcalix[4]arene (**3**) was synthesized by condensing compound **2** with excess of $NH_2OH \cdot HCl$ in the presence of pyridine/ K_2CO_3 in THF at room temperature. The IR spectrum of compound **3** shows the absence of carbonyl band at 1720 cm^{-1} but shows the appearance of a new band at 1620 cm^{-1} for C=N.

Examination of 1H NMR spectrum of **3** revealed that this compound exists in a cone conformation, which was deduced from the presence of two characteristic AB systems at 3.35 and 4.25 ppm ($J = 12.8\text{ Hz}$) for the bridging methylene protons. The other monomer **6** was obtained by the treatment of **2** with 1,8-diaminooctane as described in the literature [44] in 74% yield. The reaction was completed when no carbonyl band (1720 cm^{-1}) was detected in the product. The cone conformation of compound **6** was also deduced from 1H NMR



Scheme 2.

spectra, which showed two AB system signals at 3.45 and 4.30 ppm ($J = 13.0$ Hz) for the bridging methylene protons.

Copolymer **4** was prepared as reported method [41] and was reacted with an excess of $\text{NH}_2\text{OH}\cdot\text{HCl}$ in the pyridine/ K_2CO_3 in THF to obtain dioxime derivative **5** in 77% yield. The completion of this reaction was followed by IR spectroscopic method. The most significant difference in the IR spectrum was the absence of a carbonyl band at 1720 cm^{-1} and appearance of new bands at 3430 cm^{-1} (N-OH) and 1620 cm^{-1} (C=N). The average molecular weight calculated (vapor phase osmometer) was $M_n = 4500\text{ g/mole}$. Thus, the copolymer contains ca. 5 calixarene units in the polymeric skeleton.

The ^1H NMR spectrum of compound **5** exhibits multi-resonance peaks in the same spectral region, indicating that the symmetric cone conformation of the starting copolymer **4** was no longer present in polymer **5**. These observations suggest the existence of various conformations of macrocyclic molecules in the polymer chain very likely due to the structural variations under the reaction condition.

Copolymer **7** was synthesized by the method reported previously [41]. The compound **6** was treated with triethyleneglycol ditosylate (1:1 equivalent) in the presence of NaH in a minimum amount of THF to give the corresponding copolymer in 76.5% yield, after purification by reprecipitation from a chloroform-methanol system. The average molecular weight was $M_n = 4900\text{ g/mol}$ (vapor phase osmometer). Thus, in this case, also ca. 5 calixarene units are present in the polymeric skeleton.

The structure of compound **7** was characterized by the combination of IR and ^1H NMR spectra. The IR spectrum of **7** showed no absorption band at 3410 cm^{-1} for phenolic hydroxyl groups. The ^1H NMR spectrum of **7** exhibited rather broad signals for all protons, with a multiplet for *tert*-butyl groups (δ , 0.85), a multiplet for bridging methylene (ArCH_2Ar) protons (δ , 3.15-3.65) and a singlet, three doublets, and a doublet of doublet for non-equivalent protons of aromatic rings (δ , 6.45-7.25). From these observations, we can deduce that the calixarene units in the copolymer **7** mostly exist in partial-cone conformation.

Two-Phase Solvent Extraction

Schiff bases 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 [44, 49, 50]. Thus, the present work was focused to elaborate the strategic requirements for the two-phase extraction measurements. Two recently synthesized Schiff base mono-meric lig-

ands (**3** and **6**) and their copolymers (**5** and **7**) have been comparatively studied. 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} , and Hg^{+2}) are summarized in Table 1, and their graphic explanation is represented in Figures 2 and 3.

These data were obtained by using dichloromethane solutions of the ligands to extract metal picrates from aqueous solution according to the Pedersen's procedure [46]. The equilibrium concentration of picrate in aqueous phase was then determined spectrophotometrically.

From the extraction data shown in Table 1, it was observed that neither alkali nor transition metal cations except Hg^{2+} and Pb^{2+} were significantly extracted by the diketone derivative of *p*-*tert*-butylcalix[4]arene (**2**). The introduction of oxime groups to 1,3-position of the lower rim, changes the transferring characteristic of compound **3**; especially in the case of Cu^{2+} , Hg^{2+} and Pb^{2+} , but the alkali metal cations could not be extracted remarkably (Figure 1). The effectiveness in transferring Hg^{2+} , Cu^{2+} and Pb^{2+} rather than the other cations by these monomeric compounds (**2** and **3**) indicate that, in this case a cation- π interaction appeared to be operative, since the metal ion was bound between the two opposite C=O or C=N ligating moieties of these compounds. Similar results were obtained by Vicens and co-workers [49] who had studied various Schiff base derivatives of calix[4]arene. The slight increase in extraction ability of **3** is due to the presence of soft donor nitrogen groups in its molecule.

A very pronounced increase in extractability was observed with the macrocyclic Schiff base **6** for both alkali and transition metal cations; could be a result of stronger bonding by the nitrogen donor groups in **6** due to its cyclic structure and relatively fixed stereochemistry compared with the more flexible molecule of the ligand **3**.

In order to see the extraction properties of more than one Schiff base derivatized calixarene units together, their corresponding copolymers (**5** and **7**) were synthesized. The extraction data of **5** shows no significant change for alkali metal cations, but shows a slight increase in the extraction behavior for Cu^{2+} , Hg^{2+} , and Pb^{2+} as compared to its analog **3**. This is in agreement with previous results the ethyleneglycol bridges of copolymer here play an important role at the water dichloromethane interface [39, 41]. However, in the case of **7** the situation is quiet different, and shows a remarkable decrease in extraction of alkali metal cations; while the extraction behavior for transition metals is not regular. Observations show that the extraction ratio of Cd^{2+} , Co^{2+} , and Ni^{2+} was increased to some extent, whereas the extraction ratio of Cu^{2+} , Hg^{2+} , and Pb^{2+} was

TABLE 1. Extraction of Metal Picrates with Ligands^(a)

Ligand	Picrate Salt extracted (%)									
	Li ⁺	Na ⁺	K ⁺	Cs ⁺	Ni ²⁺	Cu ²⁺	Co ²⁺	Cd ²⁺	Hg ²⁺	Pb ²⁺
2 ^b	<1.0	<1.0	<1.0	<1.0	3.7	<1.0	<1.0	<1.0	29.4	10.6
3	<1.0	<1.0	<1.0	<1.0	<1.0	20.6	<1.0	<1.0	60.6	27.7
4 ^b	<1.0	<1.0	<1.0	<1.0	3.4	8.6	5.6	8.0	47.5	46.0
5	<1.0	<1.0	<1.0	<1.0	4.4	18.2	7.5	7.9	78.4	57.9
6	30.3	35.6	38.7	78.9	59.1	80.0	59.0	60.2	95.0	69.0
7	5.2	9.8	3.9	6.0	68.9	72.4	63.8	74.6	77.6	59.2

(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 1h.

(b) Reference [41]

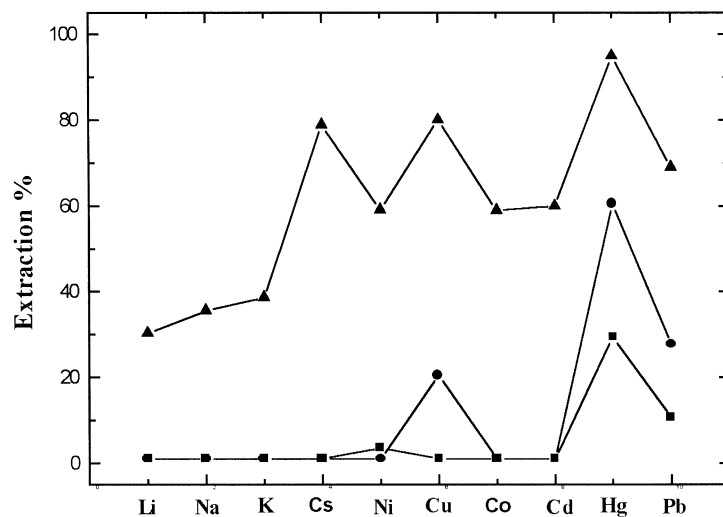


Figure 1. Extraction percentage of the alkali picrates with 2-(■), 3-(●) and 6-(▲) at 25°C. $[M^+Pic]_0 = 2.5 \times 10^{-5}$ M; $[Ligand]_0 = 1 \times 10^{-3}$ M (for water to dichloromethane system).

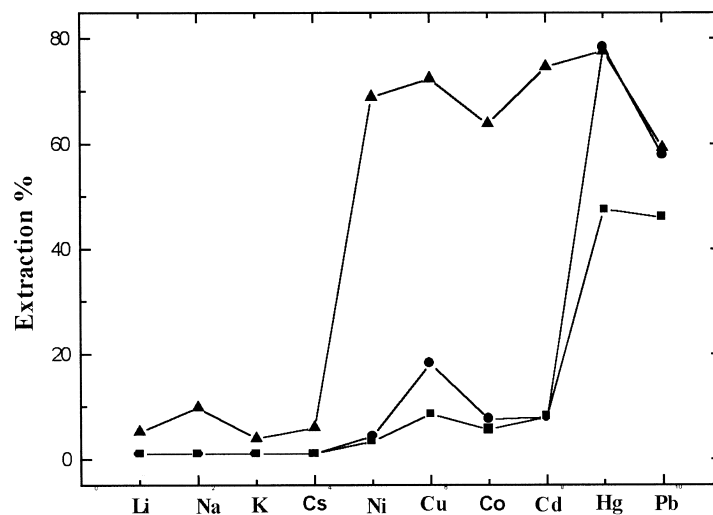


Figure 2. Extraction percentage of the alkali picrates with 4-(■), 5-(●) and 7-(▲) at 25°C. $[M^+Pic]_0 = 2.5 \times 10^{-5}$ M; $[Ligand]_0 = 1 \times 10^{-3}$ M (for water to dichloromethane system).

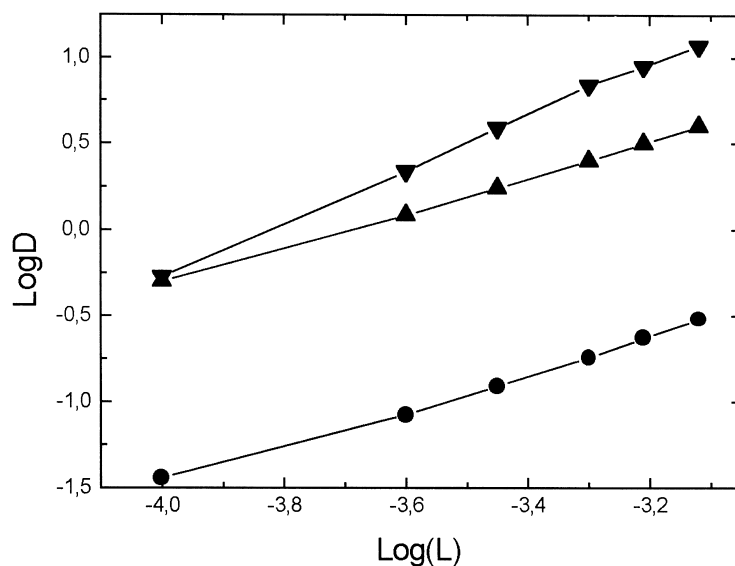


Figure 3. Log D versus log [L] for the extraction Pb-(●) and Hg-(▲) picrates by the ligand **3** and for the extraction of Cu-(▼) picrate by the ligand **6**-from an aqueous phase into dichloromethane at 25°C.

decreased as compared to its parent monomer **6**. Besides this, the extraction behavior of Schiff base calix-copolymers (**5** and **7**) was compared to 1,3-diketone calix-copolymer (**4**) as shown in Figure 2. It has been observed that the Schiff base calix copolymers (**5** and **7**) are better extractants than diketone calix-copolymer (**4**). It is not a surprising result, because the affinity of C=O group toward metal cations is less as compared to C=N group, especially for transition metal cations [44].

Figure 3 shows the extraction into dichloromethane at different concentrations of the ligand **3** for Pb²⁺ and Hg²⁺ and ligand **6** for Cu²⁺. A linear relationship between log D versus-log[L] is observed with the slope of lines for Pb²⁺ and Hg²⁺ by the ligand **3** which is roughly equal to 1.01 and 1.02 respectively, suggesting that the ligand **3** forms a 1:1 complex with Pb²⁺ and Hg²⁺. Another slope for Cu²⁺ has been observed with the ligand **6** which is equal to 1.54 suggesting that, it may be caused by co-extraction of 1:1 and 1:2 metal reagent complex.

CONCLUSION

In the present study liquid-liquid extraction of selected alkali and transition metals with Schiff base-calixarenes has been examined. The ligand **3** is rather selective for Cu^{2+} , Hg^{2+} , and Pb^{2+} , but the ligand **6** is an excellent extractant for all metals. Moreover, the selectivity of copolymer **5** is the same as its monomer **3**, but the copolymer **7** shows different binding ability.

As a result, we can say that in these phase transfer experiments the effectiveness of Schiff-base derivative of calixarenes for transferring the metal cations is reflected by the soft π -donor systems and the stereochemistry of the compounds.

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