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Exploration of Pb²⁺ Selective Behavior of Calix[6]arene Ester Derivative

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Dedicated to the honorable Professor Dr. Mustafa Yilmaz in recognition of his outstanding contributions to the area of calixarene chemistry.

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The selective behavior of calix[n]arene ester derivatives in two-phase extraction systems using polarographic technique has been investigated. Calix[4]arene tetraester derivative shows remarkable Na⁺ over Pb²⁺ selectivity; whereas calix[6]arene hexaester derivative shows Pb²⁺ over Na⁺ selectivity. The interference of some selected cations (Na⁺, K⁺, Cu²⁺ and Mg²⁺) were also examined and no significant effect on the selectivity behavior as well as extraction ability of these ionophores was found except Na⁺. The study reveals for the first time that the calix[6]arene hexaester derivative is highly Pb²⁺ selective ionophore and can be employed in the field of sensor as well as separation science and technology. The work also highlights the usefulness of polarographic technique in trace metal determination.

Keywords: Calix[n]arene, lead Selectivity, polarography, solvent extraction, toxicity

1. Introduction

The presence of a large amount of trace metals in the ground, as well as in river waters creates health hazards due to their toxicity to humans. Lead is a widespread constituent of the earth's crust, and its concentration in soil ranges from 2 to 200 mg kg⁻¹ (1). It is introduced into natural water sources in a variety of ways such as storage of batteries, lead smelting, tetraethyl lead manufacturing, mining, plating, ammunition, and the ceramic or glass industries (2). According to the WHO Guidelines, the proposed health-based value of lead is 0.01 mg L⁻¹ (3). In children, exposure to lead in drinking water above the action level results in delayed physical and mental development, along with slight deficits in attention span and learning abilities. In adults, it can cause increase in blood pressure (4).

There are several studies reported in the literature for the removal of lead (Pb²⁺) from aqueous environment. These include use of *Cassia grandis* seed gum-graft-poly (methylmethacrylate) (5), sorption from aqueous solution by non-living *Spirogyra neglecta* (6), effect of competitive interference on the biosorption of lead(II) by *Chlorella vulgaris*

(7), adsorption of lead onto formaldehyde or sulphuric acid treated acornwaste (8), adsorption onto manganese oxide-coated carbon nanotubes (9) and etc.

During last three decades, calixarenes a family of macrocyclic oligophenols have attracted much attention because of their unique molecular structure and simple one-pot operation. Indeed, calix[n]arenes have proved to be very important building blocks in supramolecular chemistry. In particular, cation complexing ligands containing calix[4]arene building block were synthesized to obtain more selective metal ion sensors. These molecules are generally *tetra-O*-substituted calix[4]arenes capable of alkali, alkaline earth and heavy metal ion recognition (10–14). It has been reported that ester function derived from calixarenes possess remarkable tendency to bind group IA cations with unique size-selectivity (15).

Remarkable and previously unknown selectivity based on a delicate balance of factors such as ring size and conformation have been found for calix[4]arene tetraester conformer which shows the highest Na⁺ over K⁺ selectivity (16–18), whereas the remaining three conformers show K⁺ selectivity (19). H. Deligöz and M. Yilmaz (20) have also demonstrated the selective complexation of Na⁺ by polymeric calix[4]arene tetraesters. Calix[6]arene hexaester extracts K⁺ better than Na⁺, whereas the octaester is the least effective ionophore (21). S-K. Chang (15) has evaluated the selectivities as the tetraester for Na⁺, hexaester for Cs⁺ and octaester for K⁺. Although several reports

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have appeared on the synthesis and complexation of alkali metal ions with calixarene based ester derivatives (15–24), relatively little work has been published about their complexation with transition metals (25,26).

However, in derivatives of calixarenes, other than esters Pb^{2+} over Na^+ selectivity is found for calix[4]arene triamide chromoionophore derivative fixed in cone conformation (27). Bonnamour and coworkers have also observed the Pb^{2+} selective behavior of β -ketoimine calix[4]arene (28). Yang et al. and coworkers have studied the adsorption selectivities of a series of novel calix[6]arene-based polymers towards Cu^{2+} , Co^{2+} and Ni^{2+} cations (29). Kim et al. reported the transition metal ion selective behavior of *ortho*-ester diazophenylcalix[4]arene (30). In our previous studies, we reported the synthesis of some calix[4]arene derivatives and their extraction properties toward alkali and transition metal cations (31–38); among them the nitrile derivatives of calix[4]arene have shown a remarkable selectivity towards Hg^{2+} (39,40). From these studies (25,26,40), it has been revealed that instead of using more complicated structures and expensive materials for the Pb^{2+} selective recognition; the use of a calix[6]arene ester derivative that can be prepared easily in bulk from cheaper raw materials and could be recharged effectively provide a better strategy. In the present work, the selective nature of calix[6]arene ester derivative for the extraction of Pb^{2+} is reported. The work efficiently imparts the importance, simplicity and usefulness of inexpensive polarographic technique for the determination of trace metals from the aqueous environment.

2. Experimental

2.1. Instrumentation

Melting points were determined on a Gallenkamp apparatus in a sealed capillary. IR spectra were recorded on a Thermo Nicolet 5700 FTIR spectrometer as KBr pellets. The pH measurements were made with pH meter (781-pH/Ion meter, Metrohm) with glass electrode and internal reference electrode. Voltammetric measurements were performed with Metrohm automatic 746-VA Trace Analyzer with Metrohm automatic 764-VA Trace analyzer equipped with 747-Va stand (Ω Metrohm Switzerland). The 747 stand includes a three electrode system, an Ag/AgCl (3MKCl), reference electrode, a platinum wire as an auxiliary electrode and hanging mercury drop electrode (HMDE) as working electrode.

2.2. Materials

Analytical TLC was performed on precoated silica gel plates (SiO_2 , Merck PF₂₅₄), 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 60% dispersion in oil and washed twice with n-hexane before

use. Dry THF was distilled from the ketyl prepared from sodium and benzophenone. Dichloromethane and acetone were distilled from CaCl_2 , and stored over molecular sieves. Anhydrous potassium carbonate, and ethyl bromoacetate, (all Merck) were used as supplied. Oxygen free nitrogen was purchased from British Oxygen Company (BOC) Karachi. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system.

2.3. Synthesis

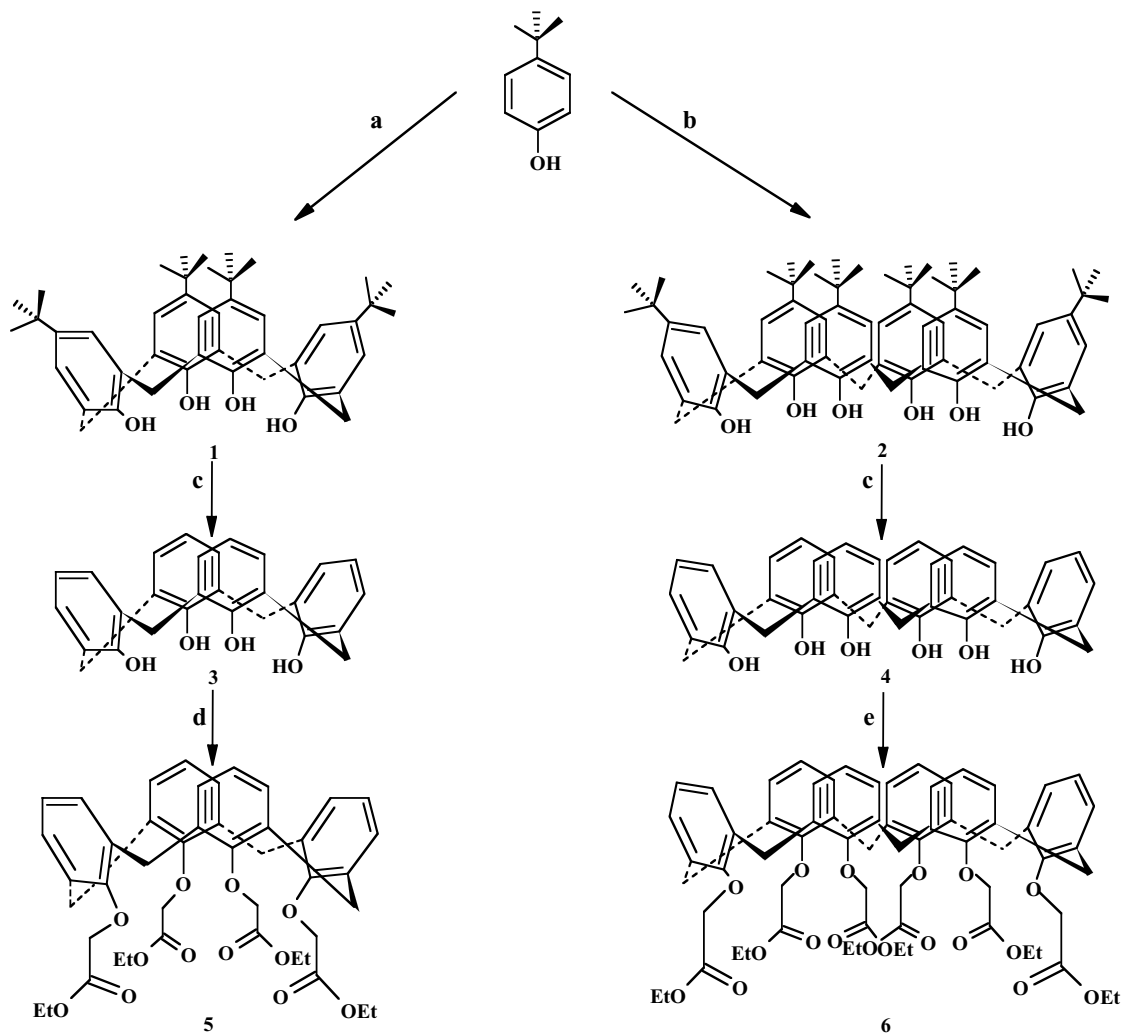
The ester derivatives of calix[n]arenes **5** and **6** ($n = 4/6$) from **3** and **4** as illustrated in Scheme 1 were synthesized according to the previously published procedures (20,21,41,42). Calix[n]arenes **3** and **4** were synthesized by phenol formaldehyde condensation reaction in the presence of an appropriate base (41) followed by dealkylation with reverse Fridel-Craft reaction in toluene as solvent in the presence of anhydrous aluminum chloride and phenol (42). Finally, the compounds **3** and **4** were converted into their tetra/hexaester derivatives **5** and **6** in the presence of $\text{NaH}/\text{K}_2\text{CO}_3$ in THF/acetone (20,21).

2.4. Analytical procedure

2.4.1. Procedure for the determination of Pb^{2+} by polarography

Solution of lead nitrate $5 \mu\text{g mL}^{-1}$ (20 mL) along with 1 mL of buffer (Acetic acid/potassium acetate $I = 0.2 \text{ M}$), 10 mL of ligand solution ($2.5 \times 10^{-3} \text{ M}$) was taken in a 50 mL flask and shaken well for 30 min. The layers were allowed to separate, and then the aqueous solution was withdrawn by pipette, taken in a small beaker and warmed at $75\text{--}80^\circ\text{C}$ to evaporate any residual chloroform. 10 mL of this extracted solution was taken in polarographic vessel; 0.5 mL of KCl (3 M) and 0.5 mL of HCl (0.2 M) were added. The sample was purged for 200 sec with oxygen free nitrogen. The preconcentration potential (-700 mV) measured against Ag/AgCl reference electrode were applied to the fresh mercury drop for 60 sec ($t_{\text{acc}} = 60 \text{ s}$) while the solution was stirred. The stirring was stopped for a period of 10 sec (equilibration time = 10 s). The voltammogram was then recorded by applying cathodic differential pulse scan with a plus amplitude of -50 mV ; the voltammogram were recorded in triplicate for each run automatically by instrument, the average peak height ($n = 3$) was assisted on the basis of the difference between peak height of the analyte and that of the base electrolyte alone recorded under the same conditions. The quantitation was carried out by calibration curve and standard addition method using $1 \text{ mg mL}^{-1} \text{ Pb}^{2+}$ solution as standard.

The concentration of metal ion remaining in the aqueous phase was determined polarographically as described above. Blank experiments showed that no metal extraction



Sch. 1. Structural representation of modified calix[n]arenes.

occurred in the absence of calixarene. The percent extraction ($E\%$) has been calculated as:

$$E\% = (C_0 - C)/C_0 \times 100$$

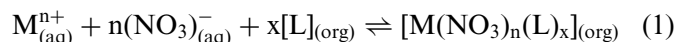
Where C_0 and C are initial and final concentrations of metal before and after the extraction, respectively.

2.4.2. Procedure to determine the interference of other metals

The interference of the selected cations (Na^+ , K^+ , Cu^{2+} and Mg^{2+}) on the extraction of Pb^{2+} by **5** and **6** has been determined by polarography according to the above general procedure by taking different ratios of binary solutions. For example; Pb^{2+} extraction was performed from the binary solutions of $\text{Pb}(\text{NO}_3)_2/\text{NaCl}$, $\text{Pb}(\text{NO}_3)_2/\text{KCl}$, $\text{Pb}(\text{NO}_3)_2/\text{CuSO}_4$ and $\text{Pb}(\text{NO}_3)_2/\text{MgSO}_4$ each in 5 different ratios (1:1, 1:2, 1:3, 1:4 and 1:5), respectively at pH 4.

2.4.3. 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 Equation 1,



the overall extraction equilibrium constant is expressed as Equation 2,

$$K_{\text{ex}} = \frac{[\text{M}(\text{NO}_3)_n(\text{L})_x]_{(\text{org})}}{[\text{M}^{n+}][\text{NO}_3^-]^n[\text{L}]^x} \quad (2)$$

and the distribution ratio D would be defined by Equation 3,

$$D = \frac{[\text{M}(\text{NO}_3)_n(\text{L})_x]_{(\text{org})}}{[\text{M}^{n+}]_{(\text{aq})}} \quad (3)$$

one obtains Equation 4 by introducing Equation 3 into Equation 2 and taking log of both sides.

$$\log D = \log(K_{\text{ex}}[\text{NO}_3^-]^n) + x \log [\text{L}]_{\text{org}} \quad (4)$$

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

3. 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 explore the complexing properties of 25,26,27,28-tetraethoxycarbonylmethoxycalix[4]arene and 36,37,38,39,40,41,42-hexaethoxycarbonylmethoxycalix[6]arene (**5** and **6**) at different pH. This would enable us to clarify the factors which control the extraction process by these ligands. Besides this, it helps to prove that the steric hindrance, effectiveness of donor sites, size of the calix macro ring, conformation of calixarene moiety and the nature of an ion are the clues in determining the selectivity of an ionophore toward metal cations and quantitatively evaluating the preorganization concept. Thus, solvent extraction experiments were performed to ascertain the effectiveness of **5** and **6** in transferring the Pb^{2+} from an aqueous phase into an organic phase. The results of two phase extraction experiments at different pH for the optimization of maximum Pb^{2+} extraction with **5** and **6** are shown in Figure 1. The interferences of other selected metal cations (Na^+ , K^+ , Cu^{2+} and Mg^{2+}) on the Pb^{2+} extraction ability of **5** and **6** were also studied and are summarized in Table 1. This data were obtained by using a chloroform solution of these ligands to extract Pb^{2+} ions from an aqueous phase. The equilibrium concentration of metal cations in the aqueous phase was determined by polarography. Moreover, for pH optimization buffer solutions of pH 1–3, 4–6, and 7 were used by mixing appropriate ratios of 0.2 mol L^{-1} HCl and KCl, 0.2 mol L^{-1} acetic acid and potassium acetate, and 0.5 mol L^{-1} ammonia and NH_4Cl solutions respectively. Among these buffer systems the range of acetic acid and potassium acetate was found the best and the whole work was performed using this buffer solution at $I = 0.2 \text{ M}$ throughout.

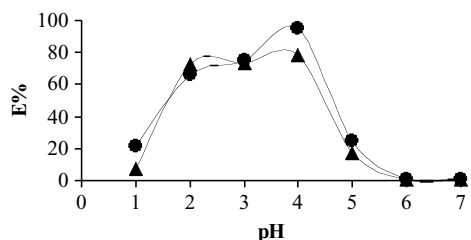


Fig. 1. Extraction of Pb^{2+} by **5** \blacktriangle and **6** \bullet from an aqueous (pH. 1–7) to organic phase.

Besides this, to check the accuracy of polarographic technique, the extraction results obtained were compared with those of atomic absorption spectroscopy (AAS), and it was found that there was only less than $\pm 3\%$ difference between them.

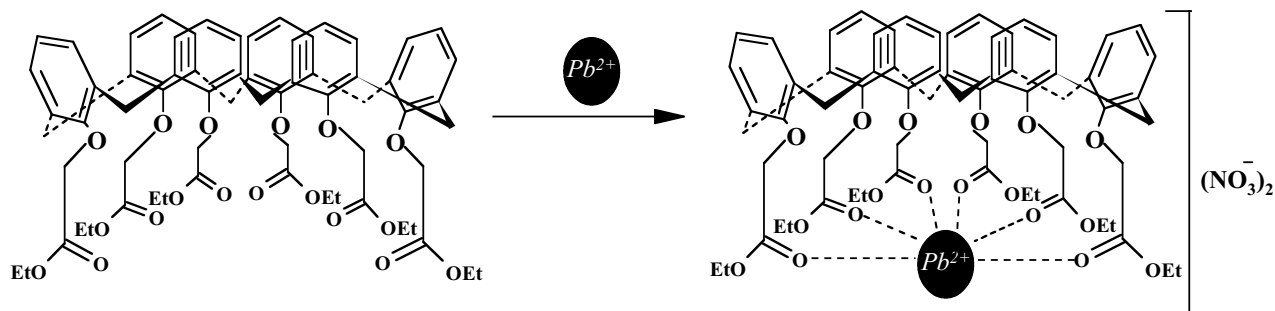
From the extraction data shown in Figure 1, it is observed that both of the ligands (**5** and **6**) show a relatively higher affinity towards Pb^{2+} . Observations show that the extraction ratio of Pb^{2+} with **5** and **6** increases as the pH increases from 2–4. The most significant difference was observed in the case of hexaester derivative **6**. It has shown maximum extraction i.e., 94.9% and high selectivity toward the Pb^{2+} at pH 4.

The studies regarding interferences of other selected metal cations (Na^+ , K^+ , Cu^{2+} and Mg^{2+}) on the extraction ability of these ligands **5** and **6** (Table 1) show that there is no significant effect of the other metal cations except Na^+ on the extraction ability of **5**. From these observations we conclude that the calix[4]arene ester derivative **5** is highly selective for Na^+ as it has been reported (15–17) may be due to the compatibility between the ionic radii of Na^+ and cavity size of **5**. In the case of **6**, the increased affinity for Pb^{2+} and less interference of Na^+ , as well as other metals can be explained by the same fact that the ionic radii of Pb^{2+} , size of the macrocycle and interaction of ester groups play an important role in complexation.

To understand the extraction phenomenon, experiments were carried out and observed that the calix[n]arene ligands **5** and **6** containing esteric binding sites possess the capability of capturing soft and hard metal ions. It can be speculated that ester derivatives **5** and **6** based on the electron donating nature of the O-containing carbonyl groups at their lower rim and the electron-accepting nature of metal ions, the ion exchange mechanism could be preferentially considered. For instance, a divalent heavy metal ion such as Pb^{2+} may attach itself to carbonyl groups which can donate pair of electrons to the metal ion, forming coordination bond between them. It is then readily understood that the equilibrium is quite dependent on pH of the aqueous solution. At lower pH, the H^+ ions compete with Pb^{2+} cations for

Table 1. Interference of Na^+ , K^+ , Cu^{2+} and Mg^{2+} on the extraction of Pb^{2+} with **5** and **6** at pH 4

Ligand	Ions	Extraction Percentage / $\text{Pb}^{2+} : \text{M}^{n+}$					
		1:0	1:1	1:2	1:3	1:4	1:5
5	$\text{Pb}^{2+} / \text{Na}^+$	78.5	<1.0	<1.0	<1.0	<1.0	<1.0
	$\text{Pb}^{2+} / \text{K}^+$	99.9	99.9	99.9	99.9	99.9	99.9
	$\text{Pb}^{2+} / \text{Cu}^{2+}$	99.9	99.9	99.9	99.9	99.9	99.9
	$\text{Pb}^{2+} / \text{Mg}^{2+}$	99.9	99.9	99.9	99.9	99.9	99.9
6	$\text{Pb}^{2+} / \text{Na}^+$	94.9	65.6	61.6	51.8	45.4	42.4
	$\text{Pb}^{2+} / \text{K}^+$	91.3	92.1	94.0	95.0	96.0	
	$\text{Pb}^{2+} / \text{Cu}^{2+}$	84.0	84.4	84.7	85.5	85.7	
	$\text{Pb}^{2+} / \text{Mg}^{2+}$	93.8	90.5	80.4	80.0	60.7	



Sch. 2. Representation of proposed interaction between ligand **6** and Pb^{2+} ion.

the exchange sites on the ligands **5** and **6**, thereby releasing the latter. The Pb^{2+} cations are completely released under circumstances of extreme acidic conditions. In this regard therefore, calixarene derivatives may be used as regenerable preconcentration agents. The chemical bonding results from the sharing of a free electron pair between the oxygen atom and metal atom or the formation of an $O-Pb^{2+}$ bond. Moreover, this phenomenon may reflect the ‘hard and soft acids and bases’ concept introduced by Pearson (43). As this environment exists due to the presence of π -bonds containing functionalities, where cation- π interactions favor the complexation with the more polarizable transition metal ions especially Pb^{2+} and which is known as intermediate soft and hard metal cation (25,40). The proposed interactions of the ligand **6** with Pb^{2+} are shown in Scheme 2.

Consequently, a plot of $\log D$ vs. $\log [L]$ leads to a straight line with a slope that admits for the determination of the stoichiometry of the extracted species at different concentrations, where $[L]$ is defined as the analytical concentration of the ligand in the organic phase.

Figures 2 and 3 depict the Pb^{2+} extraction into chloroform at different concentrations of ligands **5** and **6**, which exhibit almost a linear relationship between $\log D$ vs. $\log [L]$ with a slope roughly equal to 1.04 and 0.79. These results suggest that ligands **5** and **6** bind to Pb^{2+} in a 1:1 manner under the experimental conditions according to Equation 1. In these systems, the logarithmic extraction constants for Pb^{2+} with ligands **5** and **6** were determined.

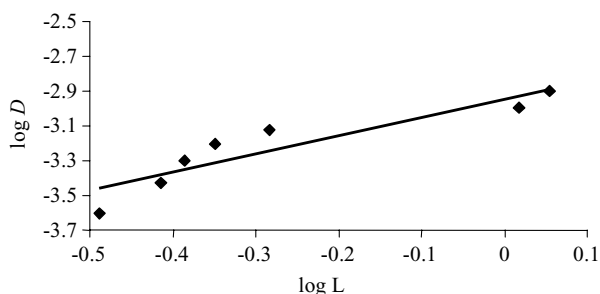


Fig. 2. $\log D$ Vs. $\log L$ for the extraction of Pb^{2+} by ligand **5** from an aqueous phase into chloroform at appropriate dilution to cover the range (2.5×10^{-4} – 1.25×10^{-3}) at pH 4.

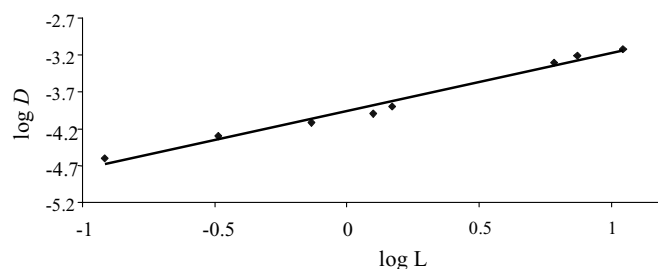


Fig. 3. $\log D$ vs. $\log L$ for the extraction of Pb^{2+} by ligand **6** from an aqueous phase into chloroform at appropriate dilution to cover the range (2.5×10^{-4} – 1.25×10^{-3}) at pH 4.

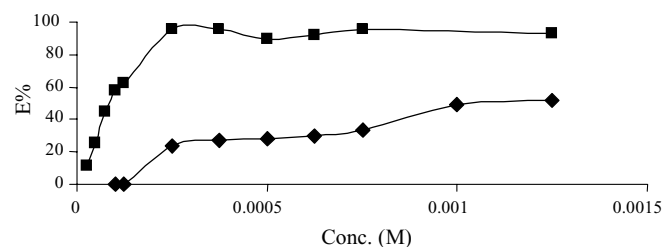


Fig. 4. The extraction efficiency of ligands **5** \blacklozenge and **6** \blacksquare for Pb^{2+} at pH 4.

The corresponding extraction constants are 7.83 ± 0.85 (for ligand **5**) and 9.88 ± 1.9 (for ligand **6**) calculated by using Eq. (2).

The extraction efficiency of the ligands **5** and **6** was evaluated by using their solutions of different concentration with the Pb^{2+} solution (pH 4) at the ambient temperature in solvent extraction experiments. The results (Fig. 4) show that the maximum extraction of Pb^{2+} may be obtained with 1.0×10^{-3} M and 2.5×10^{-4} M solutions of the ligands **5** and **6**, respectively. It reveals that ligand **6** is more efficient as compared to the ligand **5**.

4. Conclusions

The Pb^{2+} selective extraction behavior of ester derivatives of calix[n]arenes (**5** and **6**) suggest that the hexaester

derivative of calix[6]arene is more selective and efficient ionophore for the extraction of Pb^{2+} from aqueous to the organic phase at the given pH. It is suitable for the separation of Pb^{2+} from the solution containing other metals like Na^+ , K^+ , Cu^{2+} and Mg^{2+} . The study will find its applicability in various fields of material science.

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