Comparative studies on the solvent extraction of transition metal cations by calixarene, phenol and ester derivatives

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Abstract

The ionophore solvent extraction of various alkali metal and transition metal cations from the aqueous phase to the organic phase was carried out by using diazo-coupling calix[n]arenes [p-(4-phenylazophenylazo)calix[4]arene (**L1**) and p-phenylazocalix[6]arene (**L2**)], phenol derivatives [2,6-dimethyl-3-phenylazophenol (**L3**), 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol (**L4**), 2-chloro-4-nitro(phenylazo)-5-*sec*-butyl-2-phenol (**L5**) and 2-chloro-4-nitro(phenylazo)-5-*tert*-butyl-2-phenol (**L6**)], and ester derivatives [quinoline-8-benzoate (**L7**), phenyl-1,4-dibenzoate (**L8**), p-tolyltiobenzoate (**L9**)]. It was found that, all the compounds (**L1**–**L9**) examined showed selectivity for transition metal cations such as Ag^+, Hg^+ Hg^{2+}, and poor efficiency for alkali metal cations (Na^+ and K^+). The best extraction efficiency was obtained with **L1** and **L4**.
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1. Introduction

Calix[4]arenes and their derivatives have been attracting much attention as novel types of interesting host compounds [1–3]. Studies have been conducted on calixarene derivatives; their role as receptors for metal ions. As neutral ones, esters [4–8], ketones [6,7], amides [7,9,10] and so on were synthesized and their extraction properties for metal ions, such as alkali metal cations [11] and alkaline-earth metal cations were investigated.

Substituted azobenzene derivatives have been the most widely used class of dyes due to their versatile application in various fields, such as dyeing textile fiber, biomedical studies, advanced applications in organic synthesis and high-technology areas lasers, liquid crystalline displays, electro-optical devices and ink-jet printers [12]. However, many studies have been carried out on o,o'-dihydroxy, diamino and hydroxyamino compounds, and on their complexes with metals [13–16]. On the other hand, there has not been published on extraction from o-hydroxy diazo compounds.

Shinkai et al. have synthesized a new calix[4]arene-based, chromogenic ionophore through molecular design. This chromogenic calix[4]arene showed high Li^+ selectivity in solid–liquid two-phase solvent extraction [17]. A calix[6]arene derivative containing azo groups was synthesized by Nomura et al. [18]. The solvent extraction of metal picrates by this compound was selective for Ag^+, Hg^+ and Hg^{2+}.

In our recent works [19–32], the synthesis of new polymeric and monomeric calixarene derivatives were presented. These compounds were described, selective extraction of Fe^{3+} cations, solvent extraction and metal complexes.

In the present work, we investigated the extraction behaviour of diazo coupling derivatives of calixarenes, azo compounds containing various functional groups (phenols) and esters compounds have been used to investigate the solvent extraction of alkali metal (Na^+, K^+) and transition metal (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}) cations.
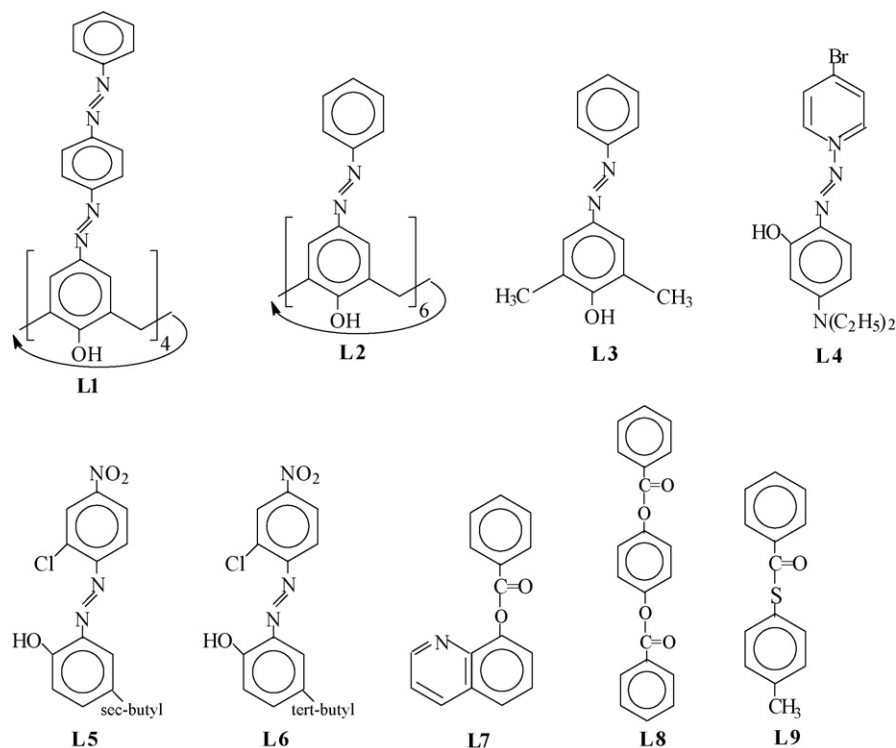
2. Experimental

2.1. Chemical and reagents

Scheme 1 illustrates the formulae of **L1**–**L9**. p-(4-Phenylazophenylazo)calix[4]arene (**L1**) and p-phenylazocalix[6]arene (**L2**) were synthesized according to the method described previously [13,20].

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Scheme 1. Extractants used in this work.

2,6-Dimethyl-3-phenylazophenol (**L3**), 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (**L4**) are commercially available (Aldrich-Chemie). 2-Chloro-4-nitro(phenylazo)-5-*sec*-butyl-2-phenol (**L5**) and 2-chloro-4-nitro(phenylazo)-5-*tert*-butyl-2-phenol (**L6**) were synthesized by diazo coupling reaction of 2-chloro-4-nitrophenyl diazonium chloride with 4-*sec*-butylphenol and 4-*tert*-butylphenol according to the general method [26]. Quinoline-8-benzoate (**L7**), phenyl-1,4-dibenzoate (**L8**), *p*-tolylthiobenzoate (**L9**) were synthesized by esterification reaction of benzoic acid with 8-hydroxy quinoline, 1,4-dihydroxy benzene and *p*-tolyl thiol. Metal hydroxide (Merck) for the 1A groups cations and metal nitrates (Merck) for the transition metal cations were used. All chemical used were of analytical grade purity and used without further purification.

2.2. Apparatus

Melting points were determined on an Electrothermal IA9100 digital melting point apparatus and they are uncorrected. UV–vis spectra were obtained on a Shimadzu 1601 UV–vis recording spectrophotometer.

2.3. Solvent extraction

A chloroform solution (10 mL) of ligand (1×10^{-3} M) and an aqueous solution (10 mL) containing 2×10^{-5} M picric acid and 1×10^{-2} M metal nitrate (metal hydroxide for group 1A metal cations) were shaken at 298 K for 1 h contact time. An aliquot of the aqueous solution was withdrawn, and the UV spectrum was recorded. A similar extraction was performed in the absence of picrate ion in the aqueous solutions. The extractability of the

metal cations is expressed by means of the following equation:

$$\text{extractability} (\%) = \left[\frac{(A_0 - A)}{A_0} \right] \times 100$$

where A_0 is the absorbency in the absence of ligand.

3. Results and discussion

Although numerous investigations have recently been reported regarding the extraction of alkali metal cations from aqueous phase into an organic phase by calix[*n*]arene [17,18,22,26] information regarding the extraction of transition metals is very limited. In this work, we have investigated the effectivenes of two diazo-coupling calix[*n*]arenes (**L1** and **L2**), four diazo compounds (phenol derivatives) (**L3–L6**), and three ester derivatives (**L7–L9**) in transferring the alkali metal cations (Na^+, K^+) and transition metal cations (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}) from the aqueous phase into the organic phase (Table 1).

Most of these ligands, which are very effective in transferring the transition elements, particularly Ag^+, Hg^+, Hg^{2+}, Cu^{2+} and Cr^{2+} do not extract the alkali metal cations to a significant extent as reported by Nomura et al. [18], who used *p*-phenylazocalix[6]arene(**L2**) as ligand. Since, **L1** and **L2** has different ring cavity their extraction efficiencies are different.

Because of the hyperacidity of **L1** and **L2**, and presence of intramolecular hydrogen bonding the alkali metal cations in acidic media were not extracted as expected. **L3–L6** contain hydroxy groups at the *para* or *ortho* position. The hydroxy groups at the *ortho* position is formed because of intramolecular hydrogen bonding and did not extract alkali metal cations in

Table 1
Extraction of metal picrates with ligands

Ligand	Picrate salt extracted (%)											
	Na^+	K^+	Ag^+	Hg^+	Hg^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}
L1 [26]	–	–	74.6	72.7	58.8	83.3	78.9	84.0	84.0	79.1	–	44.7
L2 [18]	–	–	22.0	8.0	18.0	–	–	–	–	–	–	–
L3 [18]	31.0	7.0	23.0	31.0	32.0	–	26.0	24.0	31.0	26.0	–	29.0
L4 [26]	–	3.5	89.1	72.2	84.2	42.6	77.3	59.6	5.9	11.8	–	14.1
L5 [26]	–	–	10.9	16.0	25.6	8.0	2.6	4.3	8.1	–	–	7.1
L6	–	–	11.2	16.5	12.5	2.0	4.2	–	8.7	–	–	7.4
L7	–	–	12.5	8.8	16.8	1.3	2.3	7.1	6.8	12.8	–	9.7
L8	–	–	8.1	11.9	18.8	1.4	2.6	1.9	8.1	7.2	–	9.1
L9	–	–	2.5	–	8.6	–	2.3	–	–	7.8	–	4.7

$H_2O/CHCl_3 = 10/10$ (v/v); [picric acid] $= 2 \times 10^{-5}$ M; [ligand] $= 1 \times 10^{-3}$ M; [metal nitrate] $= 1 \times 10^{-2}$ M [metal hydroxide for group 1A cations]; 298 K, 1 h contact time. Experimental error was $\pm 2\%$.

acidic media. However, **L3** extracted lower amounts of alkali metal cations by phenol groups at *para* positions. The ester compounds are not effective for extracting Na^+ and K^+ cations.

It was found that diazo coupling compounds **L1**–**L6** showed some selectivity towards Ag^+, Hg^+ and Hg^{2+}. This phenomenon plays an important role in the operation of selective extraction which has increasingly been applied in the quantitative determination of physiologycally essential cations, Ag^+, Hg^+, Hg^{2+}. As the calixarene and phenol diazo moiety can bind transition metal cations, all compounds acts as a host molecule with a hard–soft metal binding site.

There was obtained the best extraction efficiency with **L4** because of more soft ligands (with electron-donating $-N(C_2H_5)_2$). The extraction efficiency of **L5** and **L6** were similar because of their near structure. The extraction efficiency of **L3** and **L4** were highered effectively than **L5** and **L6**, which contain electron-withdrawing NO_2 groups (Fig. 1). These groups decreased electron density of diazo groups $(-N=N-)$ and lowered complexation capacity.

These phenomenons can be explained by the hard-soft acid-base (HSAB) principle as follows: $-N=N-$ is a soft base, hence has stronger affinity towards soft basic than hard metal cations. The participation of the $-N=N-$ group in complex formation was further confirmed by the results show for extraction experiments with **L1**–**L6**. Furthermore, **L7** and **L8** contain ester groups therefore their extraction efficiency was lowered effectively as

compared to calixarenes and diazo compounds, which was due to lower complexation capacity of ester groups. The extraction capacity of **L7** which contains pyridine ring was higher than that of the other ester compounds (**L8** and **L9**).

The chromophore indicator units are attached either to the end of diazo coupling linkage, or they are in conjugation through a phenolic hydroxy group with the cation coordination sphere. Direct participation of the chromophore unit in the complexation is also described [14].

The extraction efficiency of **L4** was highered effectively than the other compounds. Efficiency for **L4** which soft base increased in the order $Al^{3+} < Cr^{3+} < Co^{2+} < Zn^{2+} < Cu^{2+} < Hg^+ < Hg^{2+} < Ag^+$. In general, hard ligands (hard base) extracted hard cations, such as Al^{3+}, Cr^{3+}, Hg^{2+}, more effectively and similar soft ligands (soft base) extracted soft cations, such as Ag^+, Hg^+, Cd^{2+} (Fig. 2).

The ionophore solvent extraction studies proved **L1** to be an efficient extractant and a powerful ligand for alkali metal cations and transition metal cations. It is assumed that the double diazo-coupling calixarene (**L1**) delineating the upper rim of the cavity and the aromatic cavity act cooperatively by means of dipole and specific π-interactions for encapsulation for size adapted cationic species. Efficiency for **L1** increased in the order $Cr^{3+} < Hg^{2+} < Hg^+ < Ag^+ < Cu^{2+} < Al^{3+} < Co^{2+} < Zn^{2+}$, Cd^{2+} (Fig. 3).

The most interesting feature of cavitand **L1** is its potentiality to form complexes with cationic guests upon bonding to the $-N=N-$ diazo groups with possible participation of π–cation
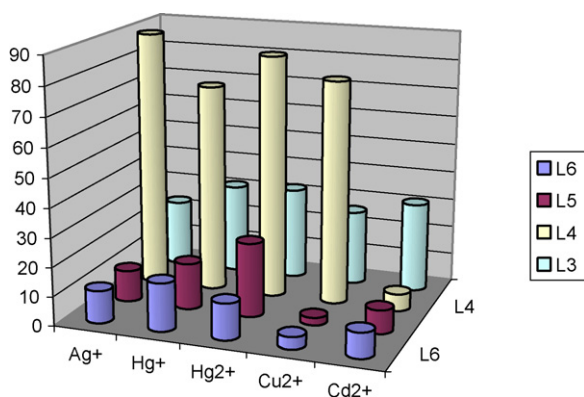

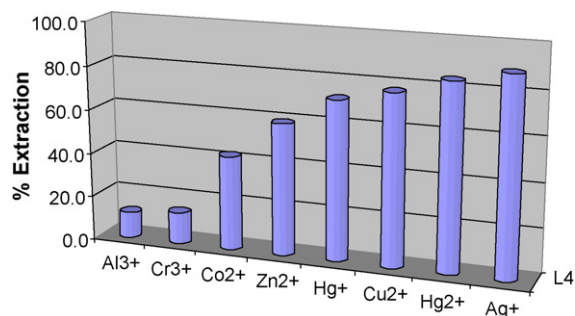Fig. 1. Extraction percentage of the metal picrates with **L3**–**L6** at 25 °C.

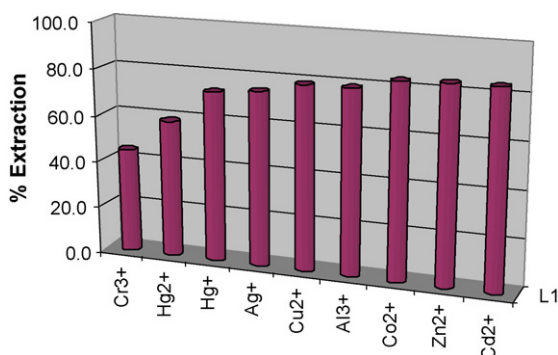Fig. 2. Efficiency for **L4** increased in the order.

Fig. 3. Efficiency for **L1** increased in the order.

interaction of intra-cavity complexation occurs. Strong evidence for complexation of alkali metal and transition metal cations was noted as these salts are readily dissolved in organic solutions of **L1**.

Binding constants of **L1** with transition metal cations reach a maximum with Zn^{2+} and Cd^{2+} ions. These cations fit perfectly the cavity of **L1** and it is tempting to suggest a strong participation of π—cation interactions in this complex with encapsulation of the cation into the host cavity. The origin of the relatively low selectivity observed for the transition metal cations complexation and the drop in the stability of the alkali metal complex are not clear.

The fact that all ligands failed to transfer Fe^{3+} ion from the aqueous into the organic phase was not unexpected, since, this ion prefers to bind with picric acid more than with the other ligands. This property is typical only of Fe^{3+} ion. Yet, our previous observations indicated that, when $Fe(NO_3)_3$ was used instead of the metal picrate, it was possible to efficiently extract Fe^{3+} into the organic phase by utilizing the same ligands [23,26].

Based on the above results, all the compounds (**L1–L9**) examined showed selectivity for Ag^+, Hg^+ and Hg^{2+}, and poor efficiency for Na^+ and K^+. The phase-transfer efficiency for Ag^+, Hg^+ and Hg^{2+} of diazo coupling compounds (**L1** and **L2**) and diazo compounds (**L3–L6**) are comparable to that of the corresponding ester derivatives (**L7–L9**) while the selectivity is somewhat lower.

4. Conclusion

From the obtained data it is concluded that:

- Liquid–liquid extraction of selected alkali and transition metals with the diazo-coupling calixarene and diazo compounds has been examined.
- Transport experiments for picrate salts have carried out with a H_2O–$CHCl_3$ phase-transfer system using these ligands as cation carriers.
- The ligand **L4** is rather selective for Ag^+, Hg^+, Hg^{2+} and Cu^{2+}.
- The ligand **L1** is an excellent extractant for all metals.
- The selectivity of calixarenes is the same as its monomeric compounds, but calixarenes shows different binding ability.

- The results of the cation transport experiments are in good agreement with those of the two-phase extraction measurements.
- In these phase-transfer experiments the effectiveness of diazo derivatives of calixarenes for transferring the metal cations is reflected by the soft π–donor systems and intra-cavity complexation.

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