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LIQUID–LIQUID EXTRACTION OF TRANSITION METAL CATIONS BY NINE NEW AZO DERIVATIVES CALIX[*n*]ARENE

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ABSTRACT

Liquid–liquid extraction of various alkali, alkaline-earth, and transition metal cations with *o*-(4-hydroxydiazophenyldiazophenyl)-*p*-*tert*-butylphenol (**L1**), bisdiazo (1-hydroxy-4-*tert*-butylphenyl)benzene (**L2**), *p*-(2-hydroxy-5-*tert*-butylphenylazophenylazo)calix[4]arene (**L3**), and *p*-(2-hydroxy-5-*tert*-butylphenylazophenylazo)calix[6]arene (**L4**), *p*-(4-butylphenylazo)calix[6]arene (**L5**), *p*-[4-(phenylazo)phenylazo]calix[6]arene (**L6**), *p*-(4-hydroxyphenylazo)calix[6]arene (**L7**), *p*-{4-[*N*-(thiazol-2-yl)sulfamoyl]phenylazo}calix[6]arene (**L8**), *p*-(4-acetamidophenylazo)calix[6]arene (**L9**), *p*-(thiazol-2-ylazo)calix[6]arene (**L10**), and *p*-(2-sulfanylphenylazo)calix[6]arene (**L11**) from the aqueous phase into the organic phase was carried out. For comparison, the corresponding azo calix[*n*]arene derivatives and two phenol derivatives were also examined. Since Ag^{+}, Hg^{+}, and Hg^{2+} cations form complexes with azo groups strongly, the extraction of these metals was found to be highly effective.

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INTRODUCTION

Over recent decades, the development of supramolecular chemistry has been dominated largely by the design and synthesis of macrocyclic compounds with potential receptor capabilities (1). Calix[*n*]arenes are a class of molecules with pronounced binding affinity to various ligands, which depends on the type of substituents on the upper and lower rims. A large number of substituted calix[*n*]arenes have already been synthesized with the aim of modifying these binding properties (2–6). Lower rim modifications throughout the phenolic oxygen atoms have been explored widely in the design and synthesis of receptors for metal cations (2).

Calixarenes play an increasingly important role in host–guest chemistry, largely because they can provide a well-organized platform for the attachment of pendant functional groups (3). Calixarene derivatives containing azo groups were synthesized by Nomura et al., Morita et al., Shinkai and coworkers, and Shimuzu et al. (7–10).

Much of our earlier work in this area concentrated on calix[*n*]arene with lower rim and upper rim in the form of mono oxime, *vic*-dioxime, polimeric, and diazo (11–15). Extraction, transport, and stability constant augmented by spectrophotometric studies have provided evidences that many of these lower rim derivatives have very significant ionophoric properties for cations, several with good selectivity within groups of metals (16–23).

We have been interested in synthesizing calix[*n*]arene derivatives containing azo groups because of their ability to serve as binding sites for complexation or as chromophores of dyes. We report here a comparison of the solvent extractions of metal ions (Na^+, K^+, Sr^{2+}, Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}) by the diazo coupling phenol derivatives [*o*-(4-hydroxydiazophenyldiazophenyl)-*p*-*tert*-butylphenol (**L1**), bisdiazo(1-hydroxy-4-*tert*-butylphenyl)benzene (**L2**)] and calix[*n*]arene derivatives [*p*-(2-hydroxy-5-*tert*-butylphenylazophenylazo)calix[4]arene (**L3**) *p*-(2-hydroxy-5-*tert*-butylphenylazophenylazo)calix[6]arene (**L4**), *p*-(4-*n*-butylphenylazo)calix[6]arene (**L5**), *p*-[4-(phenylazo)phenylazo]-calix[6]arene (**L6**), *p*-(4-hydroxyphenylazo)calix[6]arene (**L7**), *p*-{4-[*N*-(thiazol-2-yl)sulfamoyl]phenylazo}calix[6]arene (**L8**), *p*-(4-acetamidophenylazo)calix[6]-arene (**L9**), *p*-(thiazol-2-ylazo)calix[6]arene (**L10**) and *p*-(2-sulfanylphenylazo)-calix[6]arene (**L11**)].

EXPERIMENTAL

Figure 1 shows the formulae of **L1**–**L11**. *o*-(4-Hydroxydiazophenyldiazophenyl)-*p*-*tert*-butylphenol (**L1**), bisdiazo(1-hydroxy-4-*tert*-butylphenyl)-benzene (**L2**), *p*-(2-hydroxy-5-*tert*-butylphenylazophenylazo)calix[4]arene

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(**L3**), *p*-(2-hydroxy-5-*tert*-butylphenylazophenylazo)calix[6]arene (**L4**), *p*-(4-butylphenylazo)calix[6]arene (**L5**), *p*-[4-(phenylazo)phenylazo]calix[6]-arene (**L6**), *p*-(4-hydroxyphenylazo)calix[6]arene (**L7**), *p*-{4-[*N*-(thiazol-2-yl)sulfamoyl]phenylazocalix[6]arene (**L8**), *p*-(4-acetamidophenylazo)calix[6]-arene (**L9**), *p*-(thiazol-2-ylazo)calix[6]arene (**L10**), and *p*-(2-sulfanylphenylazo)calix[6]arene (**L11**) were synthesized according to the method described previously (24,25).

SOLVENT EXTRACTION

A chloroform solution (10 mL) of ligand ($1 \times 10^{-3} M$) and an aqueous solution (10 mL) containing $2 \times 10^{-5} M$ picric acid and $1 \times 10^{-2} M$ metal nitrate (metal hydroxide for group 1A metal cations) were shaken at 298K for 1 hr. An aliquot of the aqueous solution was taken and the ultraviolet spectrum was

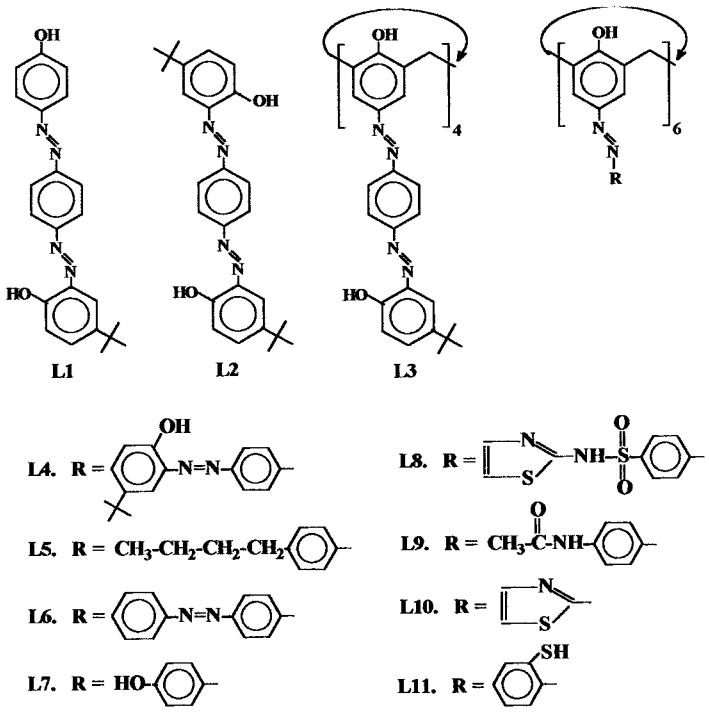

Figure 1. Extractants used in this work.

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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:

$$\text{Extractability}(\%) = [(A_0 - A)/A_0] \times 100$$

where A_0 and A are the absorbancies in the absence and presence of ligands, respectively.

RESULTS AND DISCUSSION

Although numerous investigations have been recently reported regarding the extraction of alkaline metals from aqueous phase into an organic phase by calix[*n*]arene (4,5,25–27), information concerning the extraction of transition metals is very limited. In this work, we have investigated the effectiveness of nine new diazo coupling calix[*n*]arenes (**L3**–**L11**) and two phenol derivatives (**L1** and **L2**) in transferring the alkaline metal cations (Na^+, K^+), alkaline-earth metal cation (Sr^{2+}), and transition metals (Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}) from the aqueous phase into the organic phase (Table 1).

From the data given in Table 1, it can be seen that ligands with diazo groups are not effective in extracting Na^+ and K^+ ions. This result is obtained by using 1A metal cations in the hydroxide form. When the metal nitrate is used, Sr^{2+} cation exhibits 80.2 and 45.0% extraction by ligands **L6** and **L5**, respectively. Use of metal cations in the hydroxide form causes a decline of metal cation extractability for pH values higher than 10. Ludwig et al. (26) observed that the solvent extraction of lanthanides is more effective in the pH range of 2.0–3.5.

Liquid–liquid extraction in which a metal ion is transferred as a complex from a polar aqueous phase to another immiscible phase is one of the particularly important processes in separation science. In the case of nuclear waste, the aqueous phase is frequently highly acidic and rich in sodium nitrate, both of which place severe limitations on the type of extractants that may be employed (8,9). Of the various extractants used in transition metal process chemistry as in nuclear waste treatments, neutral azo compounds are among the most useful. For example, the extracting ability of azo compound forms the basis of the azo process for separating Ag^+, Hg^+, and Hg^{2+} from aqueous solutions.

The compounds containing diazo groups are effective extractants towards transition metals. In our previous studies (20,21), we observed that they were also effective in the extraction of Fe^{3+} at low pH values. This observation was not new, however, and has been previously reported in the literature (17,18). Those ligands which are very effective in extracting the transition metal cations, particularly Ag^+, Hg^+, Hg^{2+}, Al^{3+}, and Cr^{3+}, do not extract the alkaline metal

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Table 1. Extraction of Metal Picrates with Ligands[a]

	Picrate Salt Extracted (%)													
Ligand	Na^{+}	K^{+}	Sr^{+2}	Ag^{+}	Hg^{+}	Hg^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Al^{3+}	Fe^{3+}	Cr^{3+}	La^{3+}
L1	—	—	2.2	1.2	26.9	36.3	—	10.3	2.5	2.4	1.2	—	3.4	1.1
L2	1.1	—	—	—	17.2	19.1	0.6	1.2	—	—	—	—	—	—
L3	—	—	3.5	1.9	43.7	45.1	—	6.1	2.4	—	4.7	—	5.1	3.5
L4	1.9	0.9	—	0.7	26.1	37.5	—	4.0	—	—	—	—	—	—
L5	—	—	45.0	47.1	71.4	74.6	5.2	—	10.5	—	17.8	—	29.1	22.1
L6	—	—	80.2	15.1	80.9	59.2	15.2	7.4	16.5	—	61.4	—	44.3	28.2
L7	—	—	18.3	2.5	72.7	74.2	1.8	2.6	1.8	—	2.7	—	5.1	2.3
L8	—	—	15.5	2.5	19.3	10.2	3.7	1.8	—	—	2.2	—	4.4	2.2
L9	—	—	0.6	3.6	8.2	12.8	—	—	18.5	2.8	3.0	—	1.2	1.1
L10	—	—	17.6	54.3	68.4	74.4	2.0	—	11.8	—	5.9	—	6.4	2.2
L11	—	—	16.8	12.8	50.6	72.5	9.9	11.5	12.6	—	35.0	—	47.7	6.9

[a] $H_2O/CHCl_3 = 10/10(v/v)$: [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]; 298K, 1 hr contact time. Experimental error was $\pm 2\%$.

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cations to any significant extent, as reported by Nomura et al. (7), who used *p*-phenylazo calix[6]arene as the ligand.

As compared to others, lower extractabilities observed with ligands **L1**–**L4** can be attributed to the formation of strong hydrogen bonds between –OH and –N = N– groups concealing metals for complexation. Slightly higher extractions observed with ligand **L1** than with **L2** could support this suggestion because in **L1** only one possible H-bond could form while two H-bonds could form for **L2**. Thus, intramolecular H-bonding may be one of the effective parameters in determining the extraction of metals with diazo groups containing ligands.

It was surprising that compound **L6** extracts all of the transition metal cations more effectively than the others. Similarly, in a previous study (21), these metals (except Na^+, K^+, and Fe^{3+}) were all effectively extracted by a ligand containing double diazo groups. It was observed that the double diazo coupling calix[6]arene (**L6**) was more effective than the other ligands in extracting Al^{3+} and Cr^{3+} metal cations.

The compounds **L5** and **L6** have a higher extraction yield with Ag^+, Hg^+, Hg^{2+}, Sr^{2+}, Al^{3+}, and Cr^{3+} metal cations than all other compounds. It was found that compounds **L5** and **L6** show some selectivity towards Ag^+, Hg^+, Hg^{2+}, and Sr^{2+}. The affinities of metals for ligand **L6** and **L5** in decreasing order is $Hg^+ = Sr^{2+} > Al^{3+} > Hg^{2+} > Cr^{3+}$, and $Hg^{+2} > Hg^+ > Ag^+ > Sr^{2+}$, respectively.

The compounds **L5** and **L6** show higher selectivity toward Hg^{2+} and Hg^+ than the other compounds. The above phenomena can be explained by the (hard–soft) acid–base principle as follows: the compounds **L5** and **L6** contain electron-donating and electron-withdrawing groups, respectively. Compound **L5** containing electron-donating group is a harder base and prefers the Hg^{2+} cation. Compound **L6** containing electron-withdrawing group is a softer base and prefers the Hg^+ cation. The hard-base properties of ligands for Hg^+, Hg^{2+}, and Cr^{3+} cations are as follows: for Hg^+ **L6** > **L7** > **L5** > **L10** > **L11**, for Hg^{2+} **L5**(**L10**(**L7** > **L11** > **L6** and for Cr^{3+} **L11** > **L6**.

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 (27). Yet, our previous observations indicated that, when $Fe(NO_3)_3$ was used instead of the metal picrate, it was possible to extract Fe^{3+} into the organic phase efficiently by utilizing the same ligands (17,22).

On the basis of the above results, we conclude that ligand groups circularly arranged on the upper rim of the calixarene cavity, construct novel cyclic metal receptors for selective extraction of transition metal cations. The results suggest that fine tuning in molecular design can be done by using functional groups arranged on the upper rim (open side of the calixarene cavity) rather than by using those arranged on the lower rim (closed side of the calixarene cavity).

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Furthermore, these synthesized compounds could be used for selective extraction of various metals from various sources.

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