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Selective Extraction of Fe^{3+} Cation by Calixarene-Based Cyclic Ligands

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ABSTRACT

The selective liquid-liquid extraction of Fe^{3+} cation from the aqueous phase to the organic phase was carried out by using *p-tert*-butylcalix[4]arene [L_1], calix[4]arene [L_2], *p*-nitro-calix[4]arene [L_3], calix[4]arene *p*-sulfonic acid [L_4], *p*-(diethylamino)methylcalix[4]arene [L_5], tetramethyl-*p-tert*-butylcalix[4]arene tetraketone [L_6], 25,27-dimethyl-26,28-dihydroxy-*p-tert*-butylcalix[4]arene diketone [L_7], calix[4]arene-bearing dioxime group on the lower rim [L_8], and a monooxime [L_9]. The effect of varying pH upon the extraction ability of calixarenes substituted with electron-donating and electron-withdrawing groups at their *p*-position was examined. Observed results were compared with those found for unsubstituted calix[4]arene.

INTRODUCTION

Calixarenes, which are accessible from the base-catalyzed condensation of para-substituted phenols with formaldehyde, are now well-known compounds (1). These compounds have lately attracted considerable attention because their potential as enzyme mimics has been suggested (2).

In spite of their attractive architecture, studies of host–guest chemistry related to calixarenes are limited (3). This is in sharp contrast to cyclodextrins and crown ethers, which can form a variety of host–guest-type solution complexes. Recently, several groups have succeeded in demonstrating that calixarenes serve as an excellent platform to design the receptor site for the specific binding of guest atoms and molecules (3–6). For example, Gutsche (7) and Shinkai (8–10) found that water-soluble calixarenes

can form a variety of host–guest-type complexes with organic guests in water, and Ungaro (11), McKervey (12), Chang (13), Casnati (14), and Arnaud-Neu (15) found that calixaryl esters show high alkali metal ion affinity.

In our previous work (16–18) we examined the selective extraction of Fe^{3+} ion from the aqueous phase into the organic phase of *p-tert*-butylcalix[4]arene, calix[4]arene, tetramethyl-*p-tert*-butylcalix[4]arene tetraketone, tetraethyl-*p-tert*-butylcalix[4]arene tetraacetate, and a polymeric calix[4]arene.

Herein we have studied the selective extraction of Fe^{3+} from the aqueous phase into the organic phase by using various calixarenes.

EXPERIMENTAL

Figure 1 illustrates the formulas of the extractants used (L_1–L_9). *p-tert*-Butylcalix[4]arene [L_1], calix[4]arene [L_2], *p*-nitro-calix[4]arene [L_3], calix[4]arene *p*-sulfonic acid [L_4], *p*-(diethylamino)methylcalix[4]arene [L_5], tetramethyl-*p-tert*-butylcalix[4]arene tetraketone [L_6], and 25,27-dimethyl-26,28-dihydroxy-*p-tert*-butylcalix[4]arene diketone [L_7] were synthesized according to the method described previously (12, 19–23).

L_8 was synthesized by treating L_7 with hydroxyl amine hydrochloride as follows: A solution containing 2.00 g (0.0026 mol) of L_7 in 25 mL THF was mixed with a solution containing 1.50 g (0.0220 mol) $HONH_2 \cdot HCl$ in 15 mL THF. To this mixture, 1.0 mL pyridine and (2.50 g) powdered K_2CO_3 were added. This mixture was then refluxed for 12 hours under a nitrogen stream. The solvent was evaporated in vacuo, and the residue was treated with dilute HCl. The precipitate formed was dissolved in chloroform. The solution was washed with distilled water and left for phase separation. The separated chloroform layer was concentrated in vacuo. The oily residue was then crystallized in methanol; mp 240°C, yield 1.26 g (61%). IR(KBr):, υ_{H-O} = 3420 cm^{-1}, $\upsilon_{C=N}$ = 1630 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ = 0.95 and 1.30 (s; —$C(CH_3)_3$), 2.13 (s; —CH_3), 3.55–4.18 (broad, d; —CH_2—Ar), 4.53 (s; OCH_2C), 6.9–7.12 (s; Ar—H and OH). Found: C, 75.15; H, 8.22; N, 3.18. Calculated for $C_{50}H_{66}N_2O_6 \cdot CH_3OH$: C, 74.42; H, 8.57; N, 3.40.

Solvent Extraction

A 5-mL solution of chloroform containing 5.3×10^{-4} M ligand and a 25-mL aqueous solution containing 1.06×10^{-4} M metal salt were placed in a flask. The aqueous solution was buffered to pH 2.2 (0.01 M $NaNO_3$/HNO_3, μ = 0.1 with KCl), or to pH 3.8, 4.5, and 5.4 (0.01 M CH_3COONa/

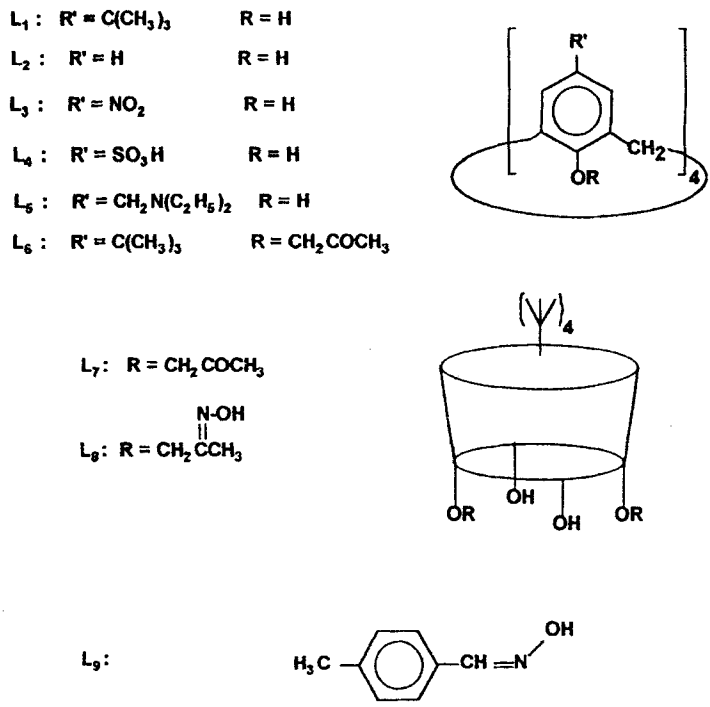

FIG. 1 Extractants used for this study.

CH_3COOH, $\mu = 0.1$ with KCl). The mixture was shaken for 12 hours at 25°C. The extractability was not affected by further shaking, indicating that equilibrium had been attained within 12 hours. The extractability (Ex %) was determined from the decrease in the metal concentration in the aqueous phase:

$$\text{Ex } \% = [(\text{metal})_{\text{blank}} - (\text{metal})_{\text{water}}/(\text{metal})_{\text{blank}}] \times 100$$

where $(\text{metal})_{\text{blank}}$ and $(\text{metal})_{\text{water}}$ denote the metal concentrations in the aqueous phase after extraction with a pure chloroform solution containing extractants.

RESULTS AND DISCUSSION

Extraction of Fe^{3+} from the aqueous phase into the organic phase with *p-tert*-butyl calix[4]arene and calix[4]arene was reported in our previous work (16, 17). In the present study we investigated the effect of varying pH

upon extraction capability by using calixarenes substituted with electron-donating and electron-withdrawing groups at their *p*-position. The observed results were compared with those found for unsubstituted calix[4]arene. Compounds L_3 and L_4 were used as electron-withdrawing and, L_1 and L_5 as electron-donating calixarenes (Table 1). The results of the extraction experiments indicated that the nature of the *p*-substituted group did not significantly affect the extraction process.

The extraction of Fe^{3+} ions was increased by increasing pH, but exhibited a decrease at pH 2.2 (Fig. 2). Extraction of 51.0% was accomplished at pH 5.4 with L_6 in which all phenolic groups were substituted. When compound L_7, in which two phenolic groups were substituted, was used, the extraction ratio increased significantly (Table 1). The above observations evidently indicate the important role of phenolic oxygen in this procedure. Extraction experiments with compound L_8 yielded results similar to those obtained with other compounds. The effect of pH on the extraction of L_8 was smaller. Extraction of 62.8% was accomplished even at pH 2.2. This result is due to the presence of two adjacent oxime groups (—C=N—OH) in compound L_8. In extraction experiments performed with its monomer [L_9], the ratio was only 3.6% at pH 2.2. The above observations indicate that with the cone conformation of calixarene, the oxime groups also play an important role in the extraction process.

The UV spectrum of compound L_2 in DMF did not exhibit an absorption maximum above 300 nm. The formation of such a complex was evident when the color of the solution changed brown and an absorption maximum appeared at 534 nm. The metal/ligand ratio determined at this wavelength by the Job method was 1:1.

The extraction reaction of the present systems can be expressed by

$$M^{n+}_{(aq)} + [LH_m]_{(org)} = [MLH_{m-n}]_{(org)} + nH^{+}_{(aq)} \quad (1)$$

TABLE 1
Extraction of Fe^{3+} Cation with Ligand (%)[a]

pH	L_1	L_2	L_3	L_4	L_5	L_6	L_7	L_8	L_9
2.2	7.0	8.4	27.1	15.7	22.0	12.0	20.7	62.8	3.6
3.8	22.4	56.0	42.1	28.2	40.5	18.5	48.3	72.0	18.5
4.5	46.5	57.5	77.0	65.0	72.0	20.4	87.8	88.6	28.1
5.4	66.0	90.0	77.1	77.8	84.5	51.0	92.1	89.4	40.7

[a] Aqueous phase [metal nitrate = 1.06×10^{-4} M]. Organic phase [chloroform (ligand) = 5.3×10^{-4} M]. pH 2.2 (0.01 M $NaNO_3/HNO_3$, μ = 0.1 with KCl). pH 3.8, 4.5, and 5.4 (0.01 M CH_3COONa/CH_3COOH, μ = 0.1 with KCl). 25°C for 12 hours.

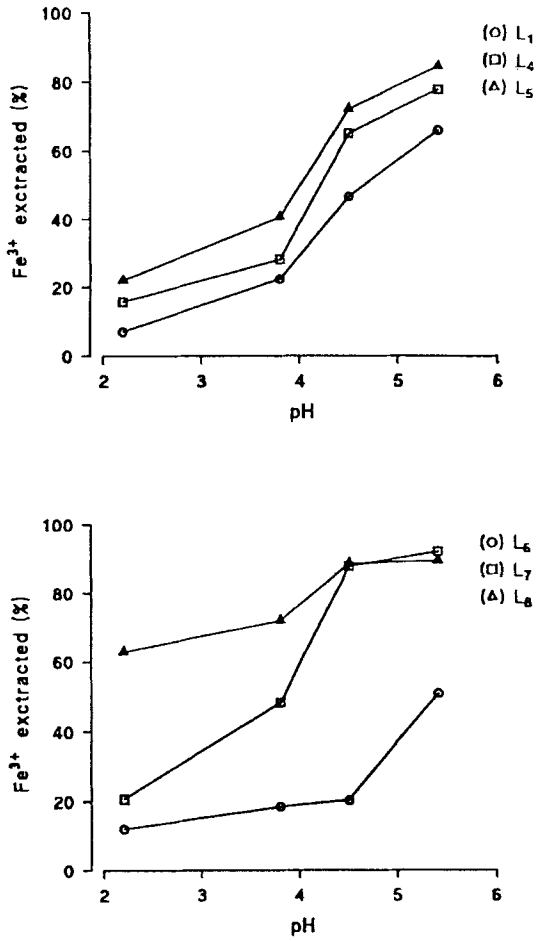

FIG. 2 pH dependence for the Fe^{3+} extraction. Aqueous phase: [metal nitrate] = 1.06×10^{-4} M. Organic phase: [chloroform, (ligand)] = 5.3×10^{-4} M. 25°C for 12 hours.

(where aq and org denote the species in the aqueous and the organic phase).

$$D = [MLH_{m-n}]_{org}/[M^{n+}]_{aq} \tag{2}$$

The extraction equilibrium constant (K_{ex}) is given by

$$K_{ex} = \frac{[MLH_{m-n}]_{org}[H^+]^n_{aq}}{[M^{n+}]_{aq}[LH_m]_{org}} \tag{3}$$

$$\log D = n\text{pH} + \log K_{ex} + \log[LH_m]_{org} \quad (4)$$

Equation (4) indicates that the slope n for the log D versus pH plot corresponds to the number of protons released upon extraction.

If the logarithm of the ratio between Fe^{3+} content in the aqueous and organic phases is plotted as a function of pH, a linear relation is obtained between pH 3.5 and 5.4, which deviates from linearity at lower pH values (2.2). The fact that the slopes of the curves were very close to unity indicates that only one proton has separated from the ligand (Eq. 5):

$$Fe^{3+} + HL \rightleftharpoons LFe^{2+} + H^+ \quad (5)$$

Since a one-proton separation will hardly occur at pH 2.2, extraction ratios of Fe^{3+} with compounds L_1–L_7 are quite low. Yet compound L_8, which carries oxime groups, was capable of extracting a considerable amount of Fe^{3+} at pH 2.2.

The logarithmic extraction constants log K_{ex} (K_{ex} in mol/L) corresponding to Eq. (4) are as follows:

$$\log K_{ex} = 1.79 \pm 0.15 \ (L_1)$$

$$\log K_{ex} = 1.50 \pm 0.15 \ (L_4)$$

$$\log K_{ex} = 3.40 \pm 0.10 \ (L_5)$$

$$\log K_{ex} = 1.80 \pm 0.10 \ (L_7)$$

The solvent extraction mechanism with L_1–L_5, L_7, and L_8 is different from L_6 since L_6 is a remarkably good ion extracting compound for Na^+ ions [12]. The two-phase solvent extraction of Fe^{3+} from the organic phase into the aqueous phase with L_6 can be explained in terms of the exchange of Fe^{3+} ions by the Na^+ ions in the organic phase. The extraction processes are shown in Fig. 3. In order to ascertain that the Na^+ salt

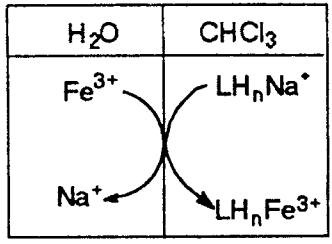

FIG. 3 Extraction mechanism proposed for L_6.

of L_6 really exists in the chloroform phase, we shook an aqueous solution (25 mL) containing 0.01 M CH_3COOH/CH_3COONa buffer (pH 4.5) and a chloroform solution (5 mL) containing 5.3×10^{-4} M L_6. After 12 hours at 25°C, the chloroform phase was separated and extracted with 0.1 M HCl solution. Flame photometric analysis of this solution established that 70% of L_6 is dissociated as the Na^+ salt.

Based on the above results, we conclude that ligand groups circularly arranged on the lower 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 lower rim (closed side of the calixarene cavity) rather than by using those arranged on the upper rim (open side of the calixarene cavity).

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