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ABSORPTIVE IONOPHORES FOR Fe³ CATION BY PARENT CALIX[n]ARENES

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NOTE

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ABSTRACT

The absorption of Fe^{3+} ion from the aqueous phase to the solid phase was carried out by using p-tert-butyl calix[6]arene (L_1), calix[6]arene (L_2), p-tert-butyl calix[8]arene (L_3), and calix[8]arene (L_4). The effect of varying pH upon the absorption capability of parent calixarenes was examined. It was found that the compounds (L_1, L_2, L_3, and L_4) showed the highest extractability toward Fe^{3+} ion at 4.5-5.4. The calixarene L_2 shows a strong binding ability to Fe^{3+} ion. Based on the continuous variation method, calixarene L_2 formed 1:1 complex with Fe^{3+} ion.

INTRODUCTION

Calixarenes, which are accessible from the base-catalyzed condensation of para-substituted phenols with formaldehyde, are now well-known compounds [1, 2]. Chemically modified calixarenes have been widely used as extractants

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for metal ions. Calixarenes are three-dimensional molecules that can be used as hosts for metal ions and for small organic guest molecules [3, 4]. By far the largest amount of work using calixarenes as extractants has been focused on the alkali and alkaline earth metals, but recent efforts have begun to be targeted towards a broader range of metals [5-7].

The calixarenes are particularly attractive as metal extractants because they have two chemically distinct rims that can each be selectively modified to incorporate any desired properties. One of the rims can specifically coordinate with the chosen metal ions, and the order rim can be used to bind functional groups that will impart any desired solubility characteristics. These complementary properties make the calixarenes a very attractive choice for use as complexants for metals. Calixarenes are host molecules that are particularly effective as extractants for transferring metal ions from aqueous solution into an organic phase. This property results from the chemical structure of calixarenes where the upper rim with tertiary butyl substituents has hydrophobic character, and the lower rim has hydrophilic character [6-10].

Yoshida *et al*. [11] found that the p-tert-butyl calix[6]arene can extract Cu^{2+} from the ammonia-alkaline solution to the organic solvent. Shinkai *et al*. have synthesized polymeric and water soluble calixarenes and they have shown that they can be used for selective extraction of UO_2^{2+} ion from aqueous phase into the organic phase [12, 13].

In our recent work, [14-19] we examined the selective extraction of Fe^{3+} ion from the aqueous phase into the organic phase with p-tert-butyl calix[4]arene, calix[4]arene, tetramethyl-p-tert-butyl calix[4]arene tetra ketone, tetraethyl-p-tert-butyl calix[4]arene tetraacetate, and a polymeric calix[4]arene. New polymeric calix[4]arenes have been synthesized by reacting an oligomer or poly-acryloylchloride with tetraethyl calix[4]arene tetraacetate. These polymers exhibited selectivity to Na^+ similar to that parent calixarene [20].

In a previous paper, we examined the selective extraction of Fe^{3+} ion from the aqueous phase into the organic phase by using diazo-coupled calix[4]arenes and the phenol derivatives [21-23].

L_1 : R = -(CH$_3$)$_3$	n = 6
L_2 : R = - H	n = 6
L_3 : R = -(CH$_3$)$_3$	n = 8
L_4 : R = - H	n = 8
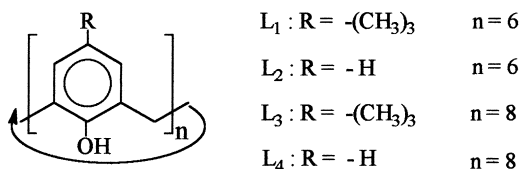
Figure 1.   Extractants used for this study.

In our previous studies, we reported the extraction of Fe^{3+} with parent calix[4]arenes [14] and with polymeric calix[4]arenes [15]. In this work, we have studied the adsorption of Fe^{3+} ion from the aqueous phase into the solid phase by using parent calix[n]arenes.

EXPERIMENTAL

Materials

^{1}H-NMR spectra were recorded on a Bruker 200 MHz spectrometer in CDCl$_3$ with TMS as internal standard. IR spectra were recorded on a Mattson 1000 FTIR Spectrometer as KBr pellets. UV-visible spectra were recorded on a Shimadzu UV-1601 UV-visible spectrophotometer. Melting points were determined on a Electrothermal IA 9100 digital melting point apparatus and are uncorrected.

p-tert-Butyl calix[6]arene (**L₁**), calix[6]arene (**L₂**), p-tert-butyl calix[8]arene (**L₃**), calix[8]arene (**L₄**) were synthesized according to the method described previously [24, 25].

Metal Cation Adsorption

A 1 mL solution of ethanol containing **L₁** (0.103 g/L), **L₂** (0.067 g/L), **L₃** (0.137 g/L) and **L₄** (0.090 g/L) and 25 mL aqueous solution containing metal nitrate (1.06.10^{-4} M) were placed in a flask. The pH of aqueous solution was adjusted 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$_3$COONa/ CH$_3$COOH, μ = 0.1 with KCl). The mixture was shaken for 1, 4, and 24 hours, at room temperature. The adsorptibility (Ad %) was determined from the decrease in the metal cation concentration in the aqueous phase:

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

where (metal)$_{blank}$ and (metal)$_{water}$ denote the metal concentrations in the aqueous phase, after this was also proved by regeneration of Fe^{3+} ion from the solid phase.

RESULTS AND DISCUSSION

Selective extraction of Fe^{3+} ion from the aqueous phase into the organic phase with p-tert-butyl calix[4]arene and calix[4]arene were reported in our previous work [14, 15, 19]. In this study, we investigated the effect of pH on adsorp-

tion capacity by using parent calix[n]arenes. Due to high molecular weight (636-1296 g/mol), parent calix[n]arenes are not soluble in major solvent systems which are immiscible with aqueous phase. Therefore, parent calix[n]arenes were used as solids and ethyl alcohol was added to overcome surface tension of the aqueous phase.

The results of the adsorption of Fe^{3+} ion with four different ligands from aqueous phase to organic phase at the different pH and for different adsorption time are summarized in Table 1.

The adsorption of Fe^{3+} ion was increased by increasing pH. The maximum adsorption was carried out at pH 5.4 for compound L_2 (87.7 %). The percent adsorption of metal cation from the aqueous solution to the solid phase have been effected the kind of ligand, the solution pH and the adsorption times as showing the Table 1.

The cavity size of ligands L_2 and L_4 are larger than the cavity size of L_1 and L_3. Thus, higher adsorption of the Fe^{3+} ion was observed with ligands L_2 and L_4. In addition, cavity size and the electron-donating capability of t-butyl groups

TABLE 1. Adsorption Percent of Fe^{3+} ion with Ligands (%)[a]

Calix[n]arene	Extraction time (h)	pH			
		2.2	3.8	4.5	5.4
L_1	1	24.0	44.0	45.8	68.5
	4	29.6	63.1	78.2	81.5
	24	54.9	62.0	67.0	76.9
L_2	1	9.6	14.3	46.8	58.4
	4	34.8	56.4	58.1	87.7
	24	29.6	43.3	71.8	77.2
L_3	1	23.7	36.0	43.2	45.2
	4	34.6	54.8	63.1	83.8
	24	32.7	55.3	67.0	74.7
L_4	1	20.0	26.9	51.8	56.0
	4	42.1	56.3	60.0	70.2
	24	34.6	44.2	44.7	53.7

[a] Aqueous phase [metal nitrate = $1.06.10^{-4}$ M and 1 ml ethanol]. Solid phase [(ligand)= L_1 (0.103 g/L), L_2 (0.067 g/L), L_3 (0.137 g/L) and L_4 (0.090 g/L)]. pH: 2.2 (0.01 M $NaNO_3$/ HNO_3, $\mu = 0.1$ with KCl), pH: 3.8; 4.5, and 5.4 (0.01 M CH_3COONa/CH_3COOH, $\mu = 0.1$ with KCl), at room temperature.

present on ligands L_1 and L_3 may be involved in the lower absorption capacities observed with these two ligands as opposed to ligands L_2 and L_4, which do not have t-butyl groups. Similar results were reported in the literature [14, 18, 19].

The higher absorption efficiencies of L_1 and L_2 than L_3 and L_4 result from having a smaller cavity size than L_3 and L_4 since one proton is released when Fe^{3+} ions bind. Therefore, Fe^{3+} ion coordinates with order hydroxyl groups and this coordination is favored if these hydroxyl groups are closer to each other. The hydroxyl groups on calix[8]arene is farther apart from each other than the groups on calix[6]arene. Over 90% extraction efficiencies observed with calix[4]arene strongly support this idea [18]. We determined that the times of four hours was enough for this adsorption process.

The UV spectrum was taken respectively of ligand (L_2), $FeCl_3$, and mixture of this solution at the same concentration in the DMF. Although the solution of ligand in DMF did not exhibit any absorption above 295 nm, the mixture of solutions of ligand and Fe^{3+} cation was exhibited at 542 Nm. The mixture has an absorption at 542 Nm and the color of the mixture was different from the solution color of the ligand and metal cations.

This indicates the formation of a complex between the ligand and the metal cation as shown in Figure 2.

This is interpreted to indicate that L_2 and Fe^{3+} ion formed a complex in solution. We determined the ratio of L_2 and Fe^{3+} ion in the complex by the continuous variation plots method. The complex of L_2 and Fe^{3+} ion has maximum
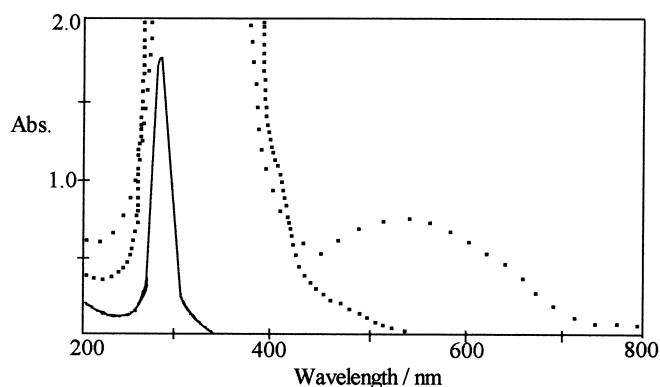
Figure 2. The UV-visible spectrums of L_2, Fe^{3+} ion and their mixture. —— : 1.10^{-3} M of L_2 in DMF. . . . . . : 1.10^{-3} M of $FeCl_3$ in DMF. . . . . : a mixture of L_2 (1.10^{-3} M) and $FeCl_3$ (1.10^{-3} M) in DMF.

absorbance in ratio mole ($FeCl_3$/calix + $FeCl_3$) = 0.50. The results show that the complex is formed between ligand and metal cation in ratio mole 1:1.

It was concluded that the solvent has a very important role in the formation of complex with Fe^{3+} ion since L_2 compound formed complex with Fe^{3+} ion in DMF but no complex was detected in $CHCl_3$. This night be attributed to the presence of free electrons present on the DMF which could coordinate with the ligands that is not possible for $CHCl_3$.

Although the pH of ligand L_2 and $FeCl_3$ solutions (1.10^{-3} M) in DMF were 3.80 and 2.63, respectively, the pH of complex solution in the same solvent was 2.53. It was shown that the decrease of pH is due to H^+ liberated (Equation 1.) after the complex was formed between L_2 and Fe^{3+} in DMF.

$$Fe^{3+} + H_6L \rightleftharpoons [H_5LFe]^{2+} + H^+ \tag{1}$$

The adsorption equilibrium of the present system can be expressed by Equation 2,

$$M^{n+}_{(aq)} + [LH_m]_{(org)} \rightleftharpoons [MLH_{m-n}]_{(org)} + nH^+_{(aq)} \tag{2}$$
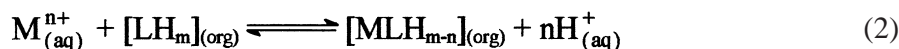
(where aq and org denote the species in the aqueous and the organic phase).

The ratio of metal ions in the organic phase to aqueous phase (D) can be expressed by the following Equation 3,
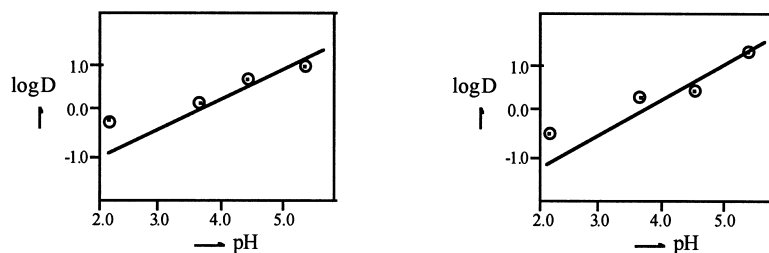
$$D = [MLH_{m-n}]_{(org)} / [M^{n+}]_{aq} \tag{3}$$

The adsorption equilibrium constant (K_{ad}) is given by,

$$K_{ad} = \frac{[MLH_{m-n}]_{org} \cdot [H^+]^n_{aq}}{[M^{n+}]_{aq} \cdot [LH_m]_{org}} \tag{4}$$

$$\log D = n\, pH + \log K_{ad} + \log [LH_m]_{org} \tag{5}$$

Equation 5 indicates that the slope is value of n, of plot for the log D versus pH corresponds to the number of protons released upon adsorption.

Figure 3. Relation between pH and log D for ligands of L_1 and L_2 (t = 4 hours).
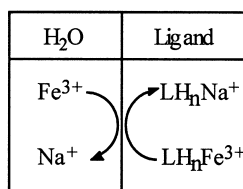
Figure 4. Adsorption mechanism proposed for ligands.

Though the slope of the plots are 0.35 and 0.45 respectively for adsorption of the ligands L_1 and L_2 for one hour, the slopes are 0.6 and 0.7 respectively for adsorption of the same ligands for four hours (Figure 3). These results show that at least four hours, instead of 1 hour are needed in order to reach adsorption equilibrium. The results indicate that in two-phase adsorption with L_2, the dissociation of one proton (i.e., an exchange between Fe^{3+} and H^+) takes place at water-solid interface. The logarithmic adsorption constants log K_{ad} (K_{ad} in mol/L) corresponding to Equation 5 are as follows:

$$\log K_{ad} = 2.26 \pm 0.15 \ (L_2)$$

The adsorption processes with L_1-L_4 are similar. In our recent work [14], it was shown that the solvent extraction mechanism is the same when used with calixarenes containing different functional groups. The adsorption mechanism with the calixarenes are shown in Figure 4.

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