

# Solvent Extraction of Fe<sup>3+</sup> Cation by Diazo-Coupling Calix[4]arenes

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The solvent extraction of Fe<sup>3+</sup> cations from the aqueous to the organic (chloroform) phase was carried out using p-tert-butyl calix[4]arene(**1**), calix[4]arene(**2**), diazo-coupling calix[4]arenes [p-(4-n-butylphenylazo)calix[4]arene (**3**), p-(4-phenylazophenylazo)calix[4]arene(**4**), p-(4-acetanilidazo)calix[4]arene(**5**), p-(N'-2-thiazol-2-ylsulphonylazo)calix[4]arene(**6**) and p-(2-thiazolazo)calix[4]arene(**8**) and the derivatives of phenol [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol(**8**) (Bromo-PADAP) and 2-hydroxy-5-methylphenylazonaphthol(**9**) (HMPAN)]. It was found that the compounds (**1-9**) showed the highest extractability toward Fe<sup>3+</sup> at pH 4.5-5.4 Compound **5** shows strong binding ability to Fe<sup>3+</sup> ion. Based on the method of continuous variation, calixarene **5** formed a 1:1 complex with Fe<sup>3+</sup> ion.

## 1. Introduction

Calix[4]arenes, a class of polyphenolic macrocycles<sup>1</sup>, are receiving increased attention since they are relatively easy to prepare<sup>2</sup>, have host-guest inclusion properties<sup>3,4</sup>, and coordinate to transition metal ions<sup>5,6</sup>. Absent from this list of known transition metal calix[4]arene complexes are those having multiple metal-metal bonds, although the calixarenes represent good ligand candidates since many members of this class have been prepared with alkoxide and aryloxide donor ligands<sup>7</sup>.

The coordination chemistry of calixarenes is a field of investigation that is attracting growing interest, partly owing to the ability of calixarenes to transport ions through hydrophobic members, and also because of their potential for mediatic shape-selective transformations<sup>8-10</sup>.

Although there are numerous reports on the binding of alkali metal ions, reports on the binding of transition metal ions are limited<sup>1</sup>. Yoshida<sup>11</sup> reported that the p-tert-butyl-calix[6]arene can extract Cu<sup>2+</sup> from the ammonia-alkaline solution to the organic solvent. Shinkai<sup>12</sup> has reported the synthesis of water-soluble calixarenes and the selective extraction of UO<sub>2</sub><sup>2+</sup> ion from aqueous phase into the organic phase. Shinkai et al.<sup>13</sup> reported the synthesis of a polymer-bound analog of calixarene which was prepared by reacting p-(chlorosulphonyl)calix[6]arene with poly(ethyleneimine), and used the polymer for selective absorption of UO<sub>2</sub><sup>2+</sup>.

In our recent work<sup>14–19</sup>, preparation of the new polymeric calix[4]arenes was described, which were synthesized by reacting an oligomer or polyacryloylchloride with tetraethyl calix[4]arene tetraacetate. These polymers exhibited selectivity to Na<sup>+</sup> similar to the parent calixarene<sup>20</sup>.

Fe<sup>3+</sup> solution is used as an indicator of phenolic compounds in organic chemistry. In addition to our previous studies, we have attempted to extract Fe<sup>3+</sup> by the use of five new calixarene and two diazo compounds. Previous studies have confirmed that in the presence of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> ions, Fe<sup>3+</sup> can be extracted selectively by the use of calix[4]arenes.

## 2. Experimental

<sup>1</sup>H-NMR spectra were recorded on a Bruker 200 MHz spectrometer in CDCl<sub>3</sub> with TMS as the 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 recording spectrophotometer.

p-Tert-butyl-calix[4]arene(**1**)<sup>2</sup>, calix[4]arene(**2**)<sup>21</sup>, p-(4-n-butyl-phenylazo)calix[4]arene(**3**), p-(4-n-butyl-phenylazo)calix[4]arene(**4**), p-(4-n-butyl-phenylazo)calix[4]arene(**5**), p-(N'-2-thiazol-2ylsulphanylazo)calix[4]arene(**6**), and p-(2-thiazolazo)calix[4]arene(**7**) and the derivatives of phenol [2-(5-bromo-2-pyridylazo)-5-diethylaminophenol(**8**)<sup>22</sup> and 2-hydroxy-5-methylphenylazonaphthol(**9**)<sup>23</sup> (HMPAN)] were synthesized according to the method described previously<sup>24</sup>.

A 5 ml solution of chloroform containing (**1**)-(9) (5.3.10<sup>-4</sup> M) and 25 ml aqueous solution containing metal salt (1.06.10<sup>-4</sup> M) were placed in a flask. The aqueous solution was buffered to pH 2.2 (0.01 M NaNO<sub>3</sub>/HNO<sub>3</sub>, μ=0.1 with KCl), or to pH 3.8, 4.5 and 5.4 (0.01 M CH<sub>3</sub>COONa/CH<sub>3</sub>COOH, μ=0.1 with KCl). The reported pH values are those of corresponding buffers without individual pH measurement in equilibrated solutions. The mixture was shaken for 12 hours at 25°C. The extraction was not affected by further shaking, indicating that the equilibrium was attained within 12 hours. The extractability (Ex %) was determined from the decrease in the metal concentration in the aqueous phase by the following equation.

$$Ex\% = [(metal)_{initial} - (metal)_{final} / (metal)_{initial}] \times 100$$

Where  $(metal)_{initial}$  and  $(metal)_{final}$  are metal concentrations before and after the extraction in the aqueous phase, respectively.

## 3. Results and Discussion

Figure 1 illustrates the formulas of the extractants used (**1**)-(9). In order to compare the complexation characteristics of the calix[4]arenes(**1**)-(2), the diazo coupling calix[4]arenes(**3**)-(7) and two phenol derivatives(**8**)-(9), the solvent extraction of the Fe<sup>3+</sup> cation with these ligands was carried out in a water/chloroform system at pH 2.2, 3.8, 4.5 and 5.4.

The Table 1 and Figure 2 illustrate the effect of pH and ligand type on the extraction of the Fe<sup>3+</sup> cation. The lower extraction recovery of compound (**1**) containing the electron-donating tert-butyl group compared with compound (**2**) which does not contain this group can be explained by the difficult in removing the -OH proton of compound (**1**). Compounds (**3**), (**4**), (**5**), (**6**) and (**7**) include both coupled diazo (-N=N-) groups and calix[4]arene. Due to the positive effect of this group on complex formation, higher extraction

yields were observed especially at lower pH values. Compounds (8) and (9) were similar to each other in structure because of the presence of -OH groups in ortho position. The higher extraction yields were obtained with compound (9) than with compound (8), however because of the presence of two -OH groups in ortho position. Decrease in extraction yield can be explained by the presence of resonance among the three nitrogen atoms in compound 8 thus lowering the electron donating capacity of diazo groups. It can be concluded that the extraction yields of diazo coupled calix[4]arenes increased with respect to their monomers.

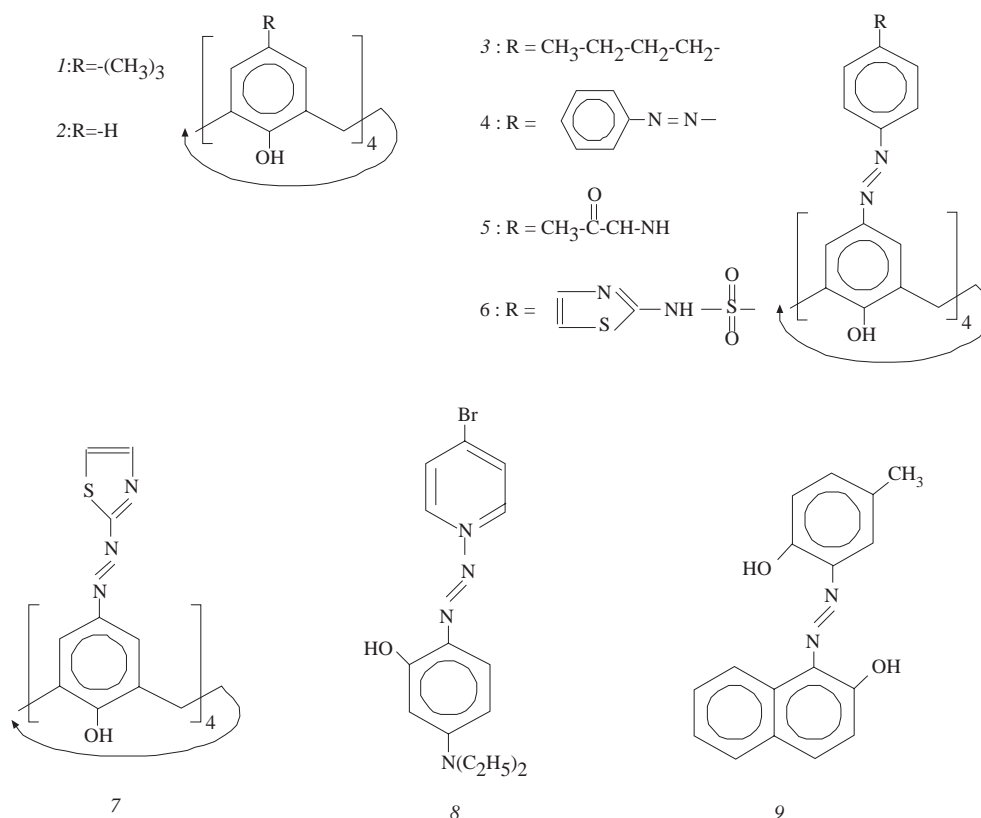


Figure 1. Extractants used for study

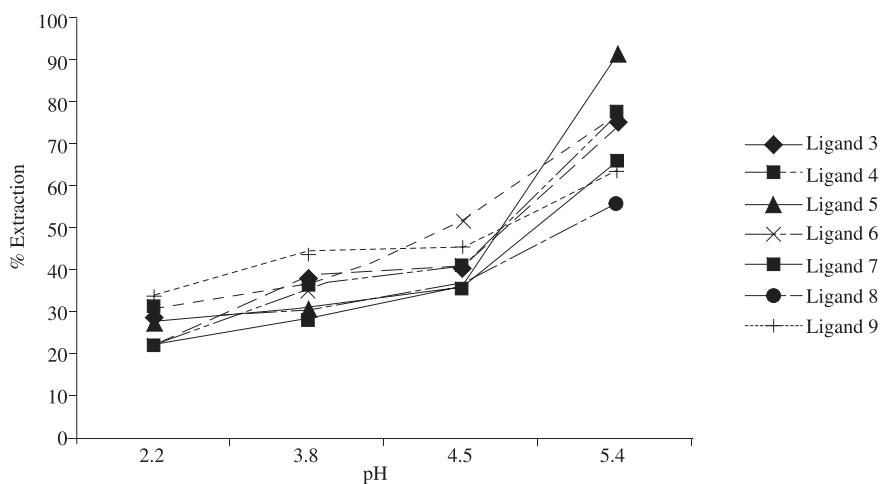


Figure 2. pH dependence for the  $\text{Fe}^{3+}$  extraction. Aqueous phase:  $[\text{metal nitrate}] = 1.06 \cdot 10^{-4}$  M. Organic phase:  $[\text{chloroform}, (\text{ligand})] = 5.3 \cdot 10^{-4}$  M.  $25^\circ\text{C}$  for 12 hours.

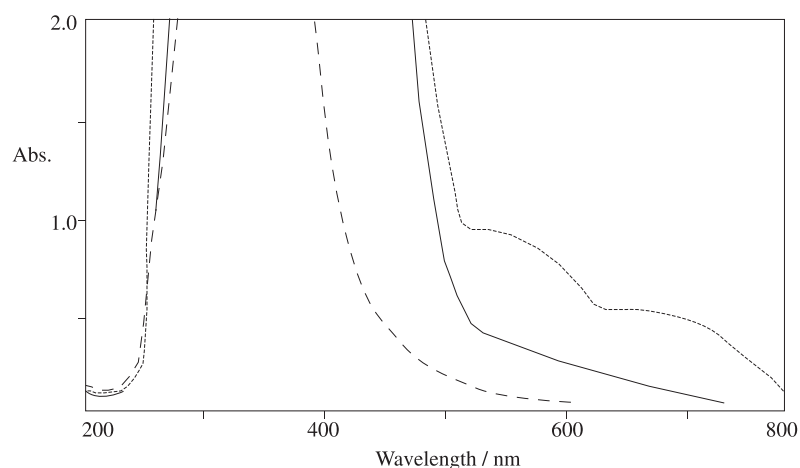
**Table 1.** Extraction of metal cations with ligands(\*)

Ligand	Percent Recovery			
	pH 2.2	pH 3.8	pH 4.5	pH 5.4
<b>1</b>	7.0	22.4	46.5	66.0
<b>2</b>	8.4	56.0	57.5	90.0
<b>3</b>	21.7	38.8	40.9	76.1
<b>4</b>	31.1	36.9	41.7	78.6
<b>5</b>	28.3	31.3	36.9	92.4
<b>6</b>	22.8	35.9	52.5	77.5
<b>7</b>	22.4	28.9	36.6	66.9
<b>8</b>	28.2	30.4	36.5	56.8
<b>9</b>	34.1	44.6	46.0	64.5

(\*) Aqueous phase [metal nitrate=1.06.10<sup>-4</sup> M]. Organic phase [chloroform (ligand)=5.3.10<sup>-4</sup> m]. pH: 2.2 (0.01 M NaNO<sub>3</sub>/HNO<sub>3</sub>,  $\mu$ =0.1 with KCl), pH: 3.8; 4.5, and 5.4 (0.01 M CH<sub>3</sub>COONa/CH<sub>3</sub>COOH,  $\mu$ =0.1 with KCl), at 25°C for 12h.

The extraction of Fe<sup>3+</sup> ions increased with increasing pH but exhibited a decrease at pH 2.2. The maximum extraction was observed at pH 5.4 for all compounds (64.5-92.0) **5** (92.4 %). Extraction recovery levels of **1** and **2** (not containing nitrogen) were much lower than those of the other ligands at pH 2.2. This is presumably because diazo groups increase the complexation of Fe<sup>3+</sup> cations. The extraction yields at pH 2.2 of the compounds (**3-9**) containing nitrogen are similar to those reported in recent work [e.g., recovery of p-(diethylamino)methylcalix[4]arene and p-nitrocalix[4]arene, 22.0 and 27.1, respectively]<sup>19</sup>.

The UV spectra of compound **5** and Fe<sup>3+</sup> at the same concentrations (1.10<sup>-3</sup> M), individually or in combination were taken in DMF (Figure 3). The formation of a complex was evident when the color of the mixture solution changed from light brown to dark brown and an absorption inflection appeared at 586 nm. The molar ratio of **5** to Fe<sup>3+</sup> ion in the complex was determined by the continuous variation plots (Job's Method)<sup>25</sup>. The compound **5** and Fe<sup>3+</sup> has its maximum absorbance at [FeCl<sub>3</sub>/calix+FeCl<sub>3</sub>]=0.50. The results indicate that **5** forms a 1:1 complex Fe<sup>3+</sup> in solution.



**Figure 3.** The UV-visible absorption of **5** and Fe<sup>3+</sup> ion and complex [----- 1.10<sup>-2</sup> M of **5** in DMF, —:1.10<sup>-2</sup> M of FeCl<sub>3</sub> in DMF, ..... a mixture of **5**(1.10<sup>-2</sup> M) and FeCl<sub>3</sub>(1.10<sup>-2</sup> M) in DMF.

It was concluded that the solvent (DMF) has a very important role in the formation of the complex with Fe<sup>3+</sup>, since 5 cannot complex with Fe<sup>3+</sup> in chloroform. This can be interpreted by the higher Lewis basicity of DMF, complexing the octahedral coordinating of iron(III) in the complex.

The pH of the 10<sup>-2</sup> M p-(4-acetanilidazo)calix[4]arene in DMF is 3.95 and the pH of the 10<sup>-2</sup> M Fe<sup>3+</sup> in DMF is 2.65. After the complexation, the pH decreased to 2.48. The decrease in pH is due to the H<sup>+</sup> liberated (Eq.1.), after the complex was formed between 5 and Fe<sup>3+</sup> in DMF.



The extraction reaction of the present system can be expressed by Eq.2.,



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

$$D = [MLH_{m-n}]_{(org)} / [M^{n+}]_{aq} \quad (3)$$

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

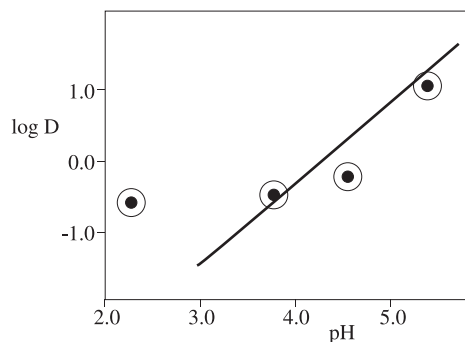
$$K_{ex} = \frac{[MLH_{m-n}]_{org} \cdot [H^+]_{aq}^n}{[M^{n+}]_{aq} \cdot [LH_m]_{org}} \quad (4)$$

$$\log D = npH + \log K_{ex} + \log [LH_m]_{org} \quad (5)$$

Eq.5 indicates that the slope n for the log D versus pH plot corresponds to the number of protons released upon extraction.

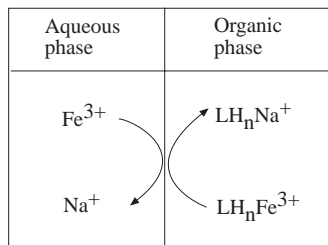
Figure 4 shows the pH versus Log D plot of compound 5 results in a slope of 0.89. The deviation from linearity observed especially at low pH values may be due to the different complexing effects of the side groups, e.g., H<sub>3</sub>C-CO-NH<sub>2</sub>-, -N=N-, resulting in different stoichiometries. The results indicate that in the two-phase solvent extraction with 5 the dissociation of one proton (i.e., an exchange between Fe<sup>3+</sup> and Na<sup>+</sup> or H<sup>+</sup>) take place at the water-chloroform interface. Similar results can be seen in literature references 13, 19, 20 and 26. The logarithmic extraction constant, log  $K_{ex}$ , for the Fe(III)- compound 5 complex corresponding to Eq. 5 is as follows:

$$\log K_{ex} = 1.74 \pm 0.15$$



**Figure 4.** Relation between pH and log D for compounds 5 (in chloroform)

The solvent extraction processes with 1-9 are similar. In our recent work<sup>19</sup>, it was shown that the solvent extraction mechanism is the same when calixarenes were used, containing different functional groups. The solvent extraction mechanism with the calixarenes and the phenols are shown in Figure 5.



**Figure 5.** Extraction mechanism proposed for 5

In conclusion, the new diazo coupling calix[4]arene compounds can be successfully used for the extraction of the Fe<sup>3+</sup> cation. The percent recovery of Fe<sup>3+</sup> increased with increasing pH, and the highest recovery of Fe<sup>3+</sup> was observed at pH 5.4 within the range studied for all the ligands.

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