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Solvent Extraction of Fe^{3+} Cation by 25,26,27,28-Tetraisonitrosoaceto Calix[4]arene and Based Ligands

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ABSTRACT

25,26,27,28-Tetraisonitrosoaceto calix[4]arene [L_8] was synthesized by reacting 25,26,27,28-tetraacetyl calix[4]arene [L_7] with *n*-butyl nitrite. The synthesized compounds [L_7 , L_8] and based ligands {*p*-*tert*-butyl phenol [L_1], *p*-methoxy phenol [L_2], *p*-methyl aldoxime [L_3], *p*-methoxy glyoxime [L_4], *p*-*tert*-butyl calix[4]arene [L_5], and calix[4]arene [L_6] } were utilized for solvent extraction of Fe^{3+} cations from the aqueous phase to the organic phase. It was observed that the *p*-methoxy glyoxime [L_4] and oximated derivative of calix[4]arene are more efficient carriers of Fe^{3+} in the extraction process at pH 2.2.

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INTRODUCTION

Calixarenes, a class of polyphenolic macrocyclic ligands (1), are of great practical importance for their host–guest inclusion properties (2) and for solvent extraction and coordination of transition metal ions (3). They are relatively easy to prepare from other compounds (4).

The coordination chemistry of calixarenes has stimulated polymer chemists to design calixarenes as carriers in liquid membrane transport systems or hydrophobic membranes for an advanced level of performance (5, 6). Recently, calixarenes have gained attention for the transport of ions through hydrophobic membranes (7) and their potential for mediating shape-selective transformations (8). The fundamental understanding and technological improvement of calixarenes are major objectives in recent membrane science and coordination chemistry research programs.

It has been reported that *p*-*tert*-butyl calix[6]arene can extract Cu²⁺ ions from ammonia alkaline solution into an organic solvent (9). This observation is also reported by Shinkai et al. (10) who prepared a polymer which was bonded analog of a calixarene, synthesized through the reaction of *p*-(chlorosulphonyl)calix[6]arene with poly(ethyleneimine) (11). They used the polymer for selective adsorption of UO₂²⁺.

In our recent work (12–19) the preparation of two new polymeric calix[4]arenes were described. They were synthesized by reacting an oligomer or polyacryloylchloride with tetraethyl calix[4]arene tetraacetate. These polymers exhibited selectivity to Na⁺ similar to that of the parent calixarene (20).

In this work we discuss the synthesis and ion-binding properties of two phenols (L₁, L₂), two based oximes (L₃, L₄), two parent calixarenes (L₅, L₆), 25,26,27,28-tetraacetyl calix[4]arene [L₇], and 25,26,27,28-tetraisonitrosoaceto calix[4]arene [L₈], which were synthesized by reaction of 25,26,27,28-tetraacetyl calix[4]arene with *n*-butyl nitrite.

EXPERIMENTAL

p-*tert*-Butyl phenol [L₁] and *p*-methoxy phenol [L₂] were purchased from Merck (Germany) and are chemically pure. *p*-Methyl aldoxime [L₃] and *p*-methoxy glyoxime [L₄] were synthesized as described according to the method previously reported (17, 21). *p*-*tert*-Butyl calix[4]arene [L₅], calix[4]arene [L₆], and 25,26,27,28-tetraacetoxy calix[4]arene [L₇] were synthesized according to the reported procedures (4, 22, 23). 25,26,27,28-Tetraisonitrosoaceto calix[4]arene [L₈] was synthesized by treating [L₇] with *n*-butyl nitrite as described below. The solvent and reagents were purified by drying them over suitable dehydrating agents, followed by distillation.



^1H -NMR spectra were recorded on a Bruker 200 MHz spectrometer in CDCl_3 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 spectrophotometer. Melting points were determined on an Electrothermal IA 9100 digital melting point apparatus and are uncorrected. The elemental analyses were determined in the TUBITAK laboratory (Center of Science and Technology Research of Turkey).

Synthesis of 25,26,27,28-Tetraisonitrosoaceto Calix[4]arene [L_8]

A solution of 9.20 g (0.4 mol) of metallic Na in 100 mL of absolute ethanol was cooled to -5°C and treated dropwise with a solution of 0.4 mol *n*-butyl nitrite. The solution was stirred at the same temperature for 30 minute, and then 5.92 g (0.1 mol) 25,26,27,28-tetracetoxy calix[4]arene [L_7] in 100 mL methanol was added dropwise over a 20–30 minute period at the same temperature. The mixture was allowed to warm to room temperature, stirred for additional hours, and then allowed to stand until the following day. The solution was concentrated to a volume of 15–20 mL in vacuum and treated with dilute acetic acid. The resulting yellow powder was filtered, washed with water, recrystallized from CH_3OH and then from $\text{CH}_3\text{OH}-\text{CHCl}_3$ to give 4.20 g (60%) of an orange powder. M.p. 121–122°C. IR (KBr): $\nu_{\text{O}-\text{H}} = 3400\text{--}3300\text{ cm}^{-1}$, $\nu_{\text{C}=\text{N}} = 1630\text{ cm}^{-1}$, ^1H -NMR (CDCl_3): $\sigma = 2.88$ (4H, s, $=\text{C}-\text{H}$), 3.46–4.80 (8H, broad, ArCH_2Ar), 7.00–7.15 (12H, broad, ArH), 12.45 (4H, s, (N—OH). Found: C, 60.12; H, 4.21; N, 7.45. Calculated for $\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_{12}$. CH_3OH : C, 59.98; H, 4.36; N, 7.57.

Solvent Extraction

A 5-mL solution of chloroform containing [$\text{L}_1\text{--L}_8$] (5.3×10^{-4} M) and a 25-mL aqueous solution containing a metal salt (1.06×10^{-4} M) were placed in a flask. The aqueous solution was buffered to pH 2.2 (0.01 M $\text{NaNO}_3/\text{HNO}_3$, $\mu = 0.1$ with KCl), or to pH 3.8, 4.5 or 5.4 (0.01 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$, $\mu = 0.1$ with KCl). The mixture was shaken for 12 hours at room temperature. The extractability was not affected by further shaking, indicating that equilibrium was attained within 12 hours. The extractability (Ex %) was determined from the decrease in the metal concentration in the aqueous phase as follows:

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

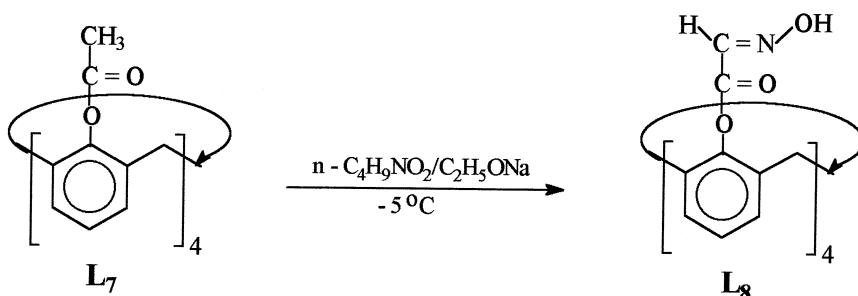
where $(\text{metal})_{\text{blank}}$ and $(\text{metal})_{\text{water}}$ denote the metal concentrations in the aqueous phase after extraction with a pure chloroform solution containing extractants.



RESULTS AND DISCUSSION

In recent years much work has been reported in the literature related to the functionalization of calixarenes. A number of the solid complexes containing oxime groups have been synthesized. As yet, reports on solvent extraction with the complexes of oxime compounds are scarce. Therefore, we have investigated the solvent extraction of Fe^{3+} through calixarene-based oxime compounds.

In this work, 25,26,27,28-tetraisonitrosoaceto calix[4]arene [L_8] was prepared from the reaction of *n*-butyl nitrite and 25,26,27,28-tetraacetyl calix[4]arene [L_7] in methanol at -5°C . The structure of the new compound was elucidated by $^1\text{H-NMR}$, IR, and elemental analyses. The general formulas of the compounds are shown in Scheme 1.



SCHEME 1

The chemical shift values of the $-\text{OH}$ protons of this compound are observed at 12.45 ppm in the $^1\text{H-NMR}$ spectra. The chemical shifts for the $-\text{OH}$ protons have a characteristic value for this type of mono-oximes (21). The IR spectrum of [L_8], $\text{C}=\text{N}$ band was observed at about 1630 cm^{-1} .

Figure 1 illustrates the formulas of the extractants used [L_1 – L_8] in this study. In order to compare the complexation characteristics of two phenols [L_1 , L_2], two based oximes [L_3 , L_4], two parent calix[4]arene [L_5 , L_6] and acetilated or oximated calix[4]arene [L_7 , L_8], the solvent extractions of Fe^{3+} cations with these ligands were carried out in a water/chloroform system at pH 2.2, 3.8, 4.5, and 5.4. The results of the extraction of Fe^{3+} cations with ligand are summarized in Table 1.

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 (12–19). In the present study we investigated the effect of varying pH upon extraction capability by using two phenols [L_1 , L_2], two based oximes [L_3 , L_4], two parent calix[4]arene [L_5 , L_6] and acetilated or oximated calix[4]arenes [L_7 , L_8]. The extraction of Fe^{3+} cations increases with increasing pH (Fig. 2).



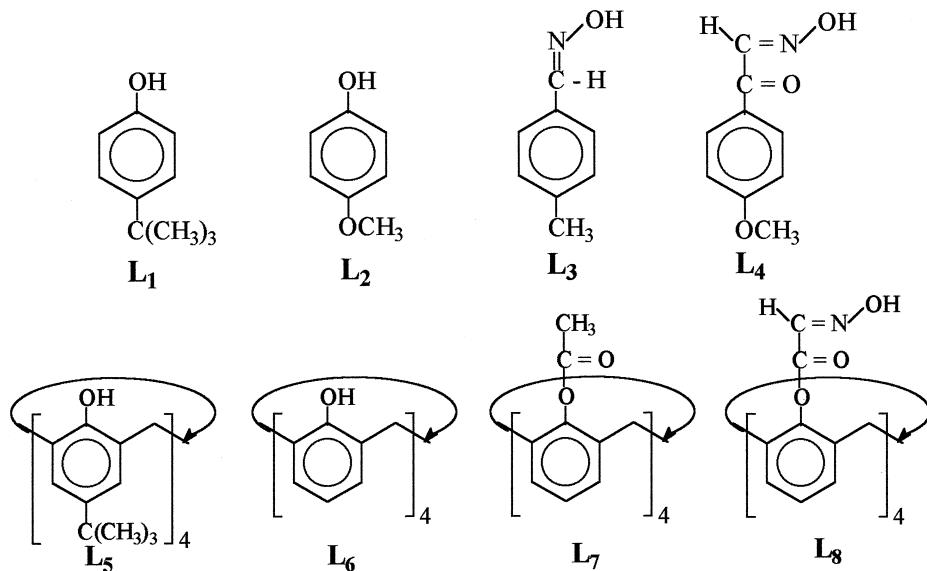


FIG. 1 Extractants used for this study.

When the extraction of L_1 containing the *tert*-butyl group and L_2 containing the $-\text{OCH}_3$ group are compared, extraction of Fe^{3+} by compound L_1 is higher than for the compound with the methoxy group. It has been found that the extraction of Fe^{3+} with L_4 is higher than that with L_3 , and the difference in the extraction process between ligands arises from the $-\text{C}=\text{O}$ group, which is an electron n-donor atom and may interact with the cation.

L_7 is capable of extracting Fe^{3+} even at lower pH ranges (67.1% at pH 2.2 and 86.0% at pH 5.4). This shows that the n electrons are effective in neutral media and that extraction depends on the hydrogen atoms in acidic media.

TABLE 1
Extraction of Fe^{3+} Cations with Ligands^a

Ligand	pH 2.2	pH 3.8	pH 4.5	pH 5.4
L_1	3.0	36.7	54.8	86.5
L_2	2.0	24.8	44.8	73.0
L_3	3.6	18.5	28.1	40.7
L_4	26.0	35.4	44.7	78.6
L_5	7.0	22.4	46.5	66.0
L_6	8.4	56.0	57.5	90.0
L_7	15.0	34.3	67.1	86.0
L_8	32.2	59.4	64.2	74.4

^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 $\text{NaNO}_3/\text{HNO}_3$, $\mu = 0.1$ with KCl), pH: 3.8, 4.5, and 5.4 (0.01 M $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$, $\mu = 0.1$ with KCl), at room temperature for 12 hours.



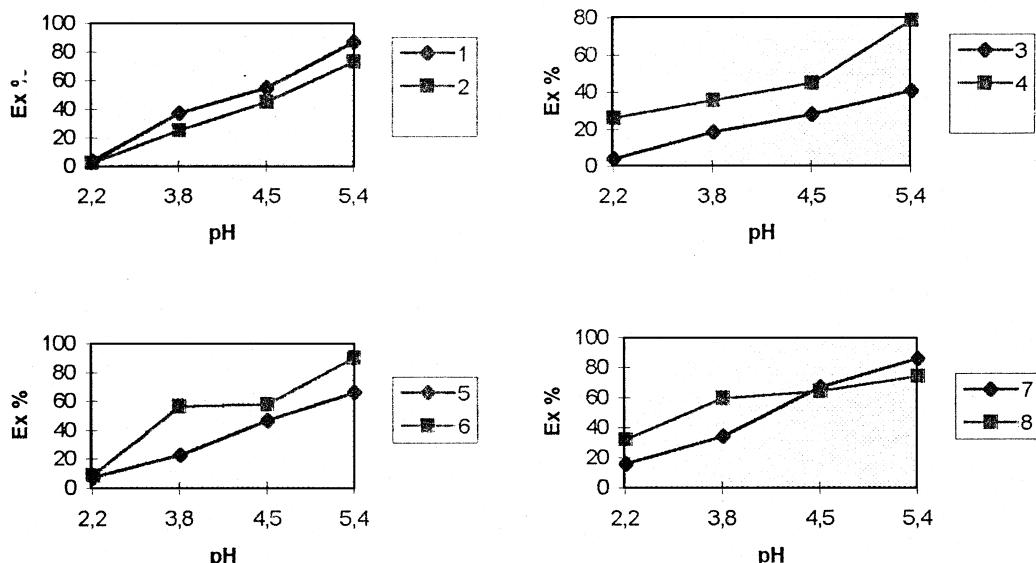


FIG. 2 pH dependence for Fe^{3+} extraction. Aqueous phase: [metal nitrate] = 1.06×10^{-4} M. Organic phase: [chloroform (ligand)] = 5.3×10^{-4} M, at room temperature for 12 hours.

Furthermore, the parent calix[4]arene L_5 and L_6 extracted about 90% of the Fe^{3+} , and this process is due the ease of ionization of L_6 . This ionization was also reported previously (12). L_3 and L_8 are extracted in lower pH, and the efficiency of the extraction process is affected by nitrogen atoms which plays a very important role in the extraction process (17, 18).

The above observations evidently indicate the important role of acidic hydrogen in the extraction procedure. Extraction experiments with L_4 and L_8 yielded results similar to those obtained with other compounds. The effect of pH on the extraction of L_4 and L_8 was small. Extractions of 26.0 and 32.2% of the Fe^{3+} for compounds L_4 and L_8 were accomplished even at pH 2.2. These results are due to the presence of four adjacent oxime groups ($-\text{C}=\text{N}-\text{OH}$) in compound L_8 . In extraction experiments performed with its monomer [L_3], the ratio was only 3.6% at pH 2.2. The above observations indicate that the cone conformation of the calixarene and the oxime groups plays an important role in the extraction process.

The extraction experiments were performed with L_8 in a water-chloroform system at pH 2.2, 3.8, 4.5, and 5.4. The results of the extraction of Fe^{3+} are summarized in Table 1, and the relationship between the equilibrium pH and the distribution coefficients are given in Fig. 3. L_8 showed the highest extraction for Fe^{3+} at pH 2.2 compared to the other compounds. The extraction of Fe^{3+} with L_8 increased with increasing pH, but the Fe^{3+} ratios at all pH values decrease more than those of other compounds. The results suggest that



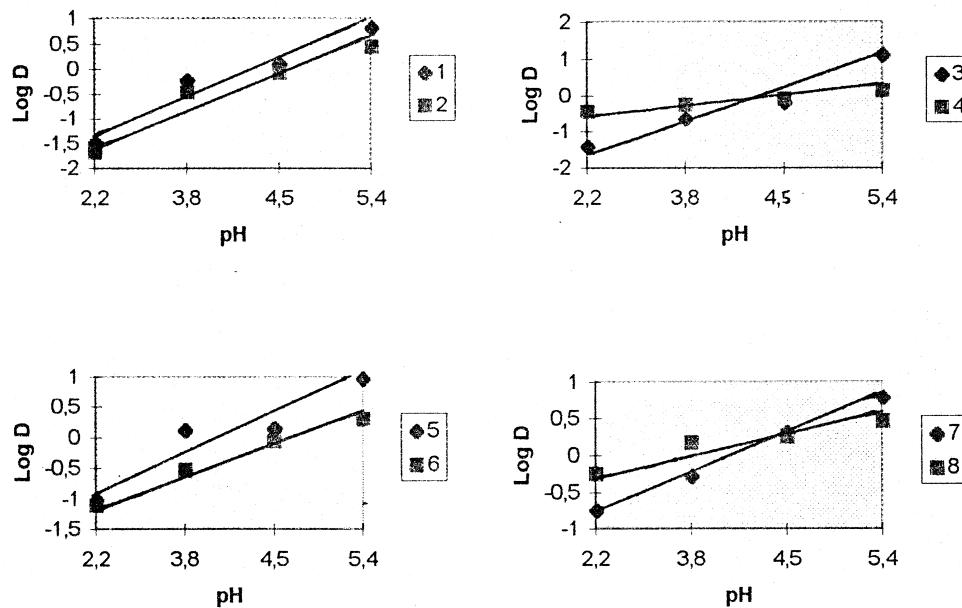
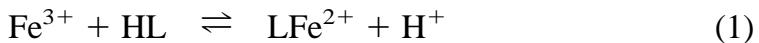


FIG. 3 Relations between pH and $\log D$ (correlation coefficients are 0.665 for L_2 ; 0.621 for L_4 ; 0.950 for L_6 ; 0.487 for L_8).

the conformation of L_8 and the $\text{C}=\text{O}$ groups in L_7 affect the extraction of Fe^{3+} .

The UV of L_6 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 turned brown and an absorption maximum appeared at 534 nm. The metal/ligand ratio (1:1) was determined at this wavelength by the Job method.

The extraction mechanism is described as follows: The increase of pH is due to the H^+ liberated (Eq. 1) after the complex was formed between L_6 and Fe^{3+} in DMF.



The extraction reaction of the present system can be expressed by



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

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

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

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



Equation (5) indicates that the slope n for the $\log D$ versus pH plot corresponds to the number of protons released upon extraction.

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

The detailed mechanism related to the extraction process was discussed in one of our earlier publications (12).

The primary observation of this study is that varying the pH in the organic phase can significantly impact the extraction of Fe^{3+} cation by calixarene-based oxime complexes. Even at lower pH, L_4 and L_8 are able to extract Fe^{3+} . This suggests environmental applications for mineral processing. Further studies are underway involving various oxime and functional groups of differing chelation strengths, selectivity, and extraction properties. From an applications viewpoint, the process is desirable for the selective extraction of Fe^{3+} .

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