Selective Extraction of Ga(III) with \(p\)-t-Butylcalix[4]arene Tetrahydroxamic Acid

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(Received July 2, 2014; Accepted July 31, 2014)

Solvent extraction behavior of \(p\)-tert-butylcalix[4]arene tetrahydroxamic acid towards some trivalent as well as divalent cations was studied. The extraction selectivity of some cations followed the order Ga(III) > In(III) > Fe(III) > Cu(II) >> Zn(II), Ni(II). Since the extraction reagent exhibited high selectivity for Ga(III) and In(III), the detailed extraction behavior for Ga(III) and In(III) was investigated by slope analysis, the continuous variation method, and by loading tests. It was confirmed that both metals formed 1:1 complexes with the extraction reagent. Since the \(pK_a\) values for hydroxamic acids are 8-9, there was 6-7 units of pH shift in the metal extraction caused by the complexation of Ga(III) indicating that this ligand served as an excellent reagent for selective extraction of Ga(III). The coordination site of the ligand for both metals was qualitatively investigated by IR spectra before and after metal loading on the ligand. The loaded Ga(III) was quantitatively stripped by using dilute acidic solutions and the ligand was regenerated.

1. Introduction

Gallium and indium have emerged as important strategic metals as they are vital for the electronic industry. Gallium is essential as a doping material for semiconductors, and has been used to produce solid-state items like transistors, gallium arsenide laser diodes in the electronic industries, as an alloying component to substitute mercury, etc. On the other hand, indium and its compounds are used in electronic devices such as indium-phosphide semiconductors and indium-solar batteries, low melting alloys and corrosion resistant coatings, etc. Indium is also used in control rods in the field of nuclear energy. Consequently, the demands for gallium and indium have increased significantly in recent years. Unfortunately, these metals rarely form mineral compounds by themselves and are mainly found as minor components in the ores of other metals. One potential source for the two metals is zinc refinery residues in which both metals are contained as minor components [1]. Due to the various applications of these metals, it is necessary to develop separation reagents and methods for effective recovery of these metals from coexisting metals.

Solvent extraction is one of the widely applicable methods for recovery of gallium and indium from zinc refinery residues. Both Ga(III) and In(III) are typical metal ions which have strong tendencies to be extracted with chelating reagents coordinating through oxygen, nitrogen and phosphorus donor atoms. Among the various systems, the most often used are phosphorous-based extractants and resins [2-5]. Methyl isobutyl ketone (MIBK) [6], carboxylic acids [7,8], amines [9-11], quinolines [12] and \(\beta\)-diketones [13] have also been applied for this goal. In addition to these compounds, hydroxamic acids [14] are a class
of versatile extractants which have significant importance as analytical tools for the separation and quantitative determination of a large number of metal ions [15,16].

Calixarene derivatives, which are easily synthesized from $p$-substituted phenol and formaldehyde [17] and functionalized in various ways [18], have been noted as useful extractants for a variety of metal ions [17-22]. Suitably functionalized calixarenes can selectively host a target metal ion due to the effect of the cavity size of the cyclic molecule together with the chelating and cooperating effect of multifunctional groups [17-22]. Therefore, functionalized calixarenes are most promising candidates as highly selective and efficient solvent extraction reagents towards the target species. In our earlier reports, the solvent extraction behavior of calix[4]-, [5]- and [6]arene derivatives containing carboxylic acid groups was described [23,24]. These ligands selectively and very effectively extracted the trivalent metal cations Fe(III), In(III) and Ga(III) over the divalent cation Zn(II) as a function of pH. However, separation of Ga(III) and In(III) over Fe(III) as well as the separation of Ga(III) from In(III) with calixarene carboxylic acid ligands as a function of pH led to a problem as these ligands exhibited very little discrimination behavior towards Ga(III) and In(III). In 1979, Agrawal gave a generalization that the stability constants of the metal complexes of hydroxamic acids increased with increasing ionic potential [25]. In accordance with this generalization, Evers et al. found that the formation constant of negative hydroxamate oxygen donors with Ga(III) was higher than that with In(III) [26]. Alakhras et al. later found that the metal uptake capacity of hydroxamic acid functionalized sorbents increased with decreasing ionic radii of the trivalent rare earth cations [27]. In our preliminary investigations, a very simple screening of extraction percentages of hydroxamic acid ligands towards a series of cations between pH 2.5 and 4.5 was conducted. The hydroxamate derivatives of calix[4]- and [6]arenes were more effective for the extraction of some trivalent cations over divalent cations. However, the extraction stoichiometry and metal selectivity for the hydroxamate derivative of calix[4] arene with high Ga(III) selectivity were not investigated in detail [28].

In the present study, we have prepared a tetrahydroxamic acid derivative of $p$-tert-butylicalix[4]arene 4 (Scheme 1) and have explored the solvent extraction behavior of this ligand towards some trivalent and divalent cations. The selectivity behavior of the ligand towards Ga(III) and In(III) over Fe(III) and some other base metal cations has been investigated. Extraction stoichiometries of the selectively extracted Ga(III) and In(III) were determined by slope analysis, the continuous variation method, and loading tests. The coordination site of the ligand for both metals was qualitatively determined by IR spectra before and after metal loading. Stripping of the loaded Ga(III) was also investigated.

2. Experimental

2.1 Instrumentation

$^1$H NMR spectra were recorded with a nuclear magnetic resonance spectrophotometer (NMR, Jeol JNM-AL300) in deuterated solvent(s) with TMS as an internal standard. FT IR spectra were recorded using a fourier transform infrared spectrophotometer (FT IR, JASCO FT IR 410) by KBr pellet method. Metal ion concentrations in aqueous solutions were measured using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Shimadzu ICPS-8100). The pH of the solution was measured by a pH meter (TOA DKK HM-30R).

2.2 Reagents

All reagents were of reagent grade and used without further purification unless mentioned otherwise.
Generally, solvents were dried by storing them over Linde type 3A or 4A molecular sieves. Analytical grade metal nitrate salts purchased from Wako Chemical Company, Japan were used to prepare the stock solutions (10 mM; M = mol dm$^{-3}$) in 0.1 M HNO$_3$, and the stock solutions were then diluted to the desired concentration either with 0.1 M HNO$_3$ or with 0.1 M HEPES [2-{4-(2-hydroxyethyl)-1-piperazinyl} ethanesulphonic acid] buffer.

2.3 Synthesis

The compound $p$-tert-butylcalix[4]arene 1 was synthesized by adopting the procedure available elsewhere in the literature [29]. Chemical modification of 1 with hydroxylamine functional groups was accomplished by following the reaction sequence shown in Scheme 1. Reaction of 1 with ethyl bromoacetate in the presence of a base [30] in a manner similar to Williamson’s ether synthesis afforded an ester 2 in good yield. Alkaline hydrolysis of 2 followed by acidification [24] gave an acid 3 in near quantitative yield. Treatment of 3 with thionyl chloride yielded an acid chloride in quantitative yield, which was then reacted with hydroxylamine hydrochloride in the presence of a base to get the desired compound in a good yield [28]. Identification of the synthesized compounds was achieved by means of TLC, IR and $^1$H NMR spectra. The synthesis and structure of the extractants employed in the present study are shown in Scheme 1.

![Scheme 1. Synthesis and structure of the extractants employed in the present study.](image)


White solid obtained in 75 % yield from 1. $^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 1.22 (s, 36H, $^t$Bu), 1.38 (t, J = 9.0 Hz, 12H, COOCH$_2$CH$_3$), 3.41 (d, J = 9 Hz, 4H, ArCH$_2$Ar, exo), 4.20 (d, J = 9 Hz, 4H, ArCH$_2$Ar, endo), 4.37 (q, J = 7.5 Hz, 8H, COOCH$_2$CH$_3$), 4.45 (s, 8H, ArOCH$_2$), 7.11 (s, 8H, ArH).


White solid obtained in near quantitative yield from 2. $^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$ 1.07 (s, 36H, $^t$Bu), 3.41 (d, J = 15.6 Hz, 4H, ArOCH$_2$CH$_3$), 4.18 (bs, 8H, ArOCH$_2$), 4.49 (d, J = 15.9 Hz, 4H, ArCH$_2$Ar, endo), 6.94 (s, 8H, ArH).


White solid obtained in 71% yield from 3. $^1$H NMR (300 MHz, DMSO-d6, TMS) $\delta$ 1.06 (s, 36H, $^t$Bu), 3.18
(d, J = 12.6 Hz, 4H, ArCH2Ar, exo), 3.36 (s, 8H, ArOCH2), 4.78 (d, J = 12.6 Hz, ArCH2Ar, endo), 6.92 (s, 8H, ArH).

2.4 Extraction experiments

2.4.1 General extraction

The percentage extraction of metal ions at different pH values was determined by the conventional batch wise method. An organic solution was prepared by diluting the extractant into analytical grade chloroform to the desired concentration. The metal ion solutions prepared separately in 0.1 M HNO3 and 0.1 M HEPES buffer were arbitrarily mixed to adjust the pH. Equal volumes of aqueous and organic solutions were mixed and the mixture was shaken for a defined time in a thermostatic incubator maintained at 303 K. After phase separation, the equilibrium pH and the metal concentrations in the aqueous phase were measured by pH meter and ICP-AES, respectively. From the initial and equilibrium metal concentrations so obtained, the percentage of each metal ion extracted into the organic phase was calculated from eq. (1),

\[ \%E = \frac{C_i - C_e}{C_i} \times 100 \]  

(1),

where \( C_i \) and \( C_e \) are the initial and the equilibrium concentrations of the metal ions in aqueous solution, respectively. The distribution ratio of the metal ions between the two phases was calculated from eq. (2),

\[ D = \frac{C_i - C_e}{C_e} \]  

(2).

2.4.2 Job's plot analysis

The continuous variation method to determine complexation stoichiometry was used. Nine different solutions of \( \mathbf{4} \) ranging from 0.1 to 0.9 mM concentration were prepared by diluting the stock solution (1.0 mM) with chloroform. Aqueous solutions of Ga(III) and In(III) were prepared similarly by diluting their stock solutions. The stock solution of Ga(III) was prepared at pH 3.00 and that of In(III) was prepared at pH 3.20 and were diluted with blank solution having the same pH adjusted by arbitrarily mixing 0.1 M HNO3 and 0.1 M HEPES buffer solutions. Equal volumes of the aqueous and the organic phases were mixed so that the total concentration was 1.0 mM. The biphasic mixtures were then shaken for a certain time. After phase separation, the metal concentrations were determined by ICP-AES. The results obtained were plotted as the amount of metal extracted into the organic phase against the mole fractions of the extractant.

2.4.3 Loading test

The loaded metal amounts on ligand \( \mathbf{4} \) for Ga(III) and In(III) were determined according to the following procedure: 3 cm\(^3\) organic solutions (5.0 mM) were mixed with 3 cm\(^3\) solutions of an aqueous phase containing increasing amounts of M(III) ions (0.5 to 7.0 mM) and the biphasic mixtures were shaken for 10 h. After phase separation, the residual concentrations of M(III) in the aqueous phase were determined by ICP-AES. The obtained results were plotted as the ratio of initial extractant concentration to the extracted metal concentration in the organic phase against the increasing initial concentration of M(III) in the aqueous phase.

2.5 FT IR experiments

The \( \mathbf{4} \)-Ga(III) and \( \mathbf{4} \)-In(III) complexes for FT IR spectra analysis were obtained by equilibrating equal volumes of equimolar solutions of the ligand and the metal nitrate at pH 3.00 in the case of the Ga(III)
complex and 3.20 in the case of the In(III) complex. After phase separation, the organic phase was dried and FT IR experiments were conducted by the KBr pellet method for the complexes as well as the acid ligand 4.

2.6 Stripping tests
Stripping of the loaded Ga(III) was carried out by shaking the organic phase containing the Ga(III) loaded extractant with HCl and HNO$_3$ solutions of various concentrations. The pH of the aqueous solution in the forward extraction prior to back extraction was adjusted to 3.00 so that quantitative extraction of metal ions in organic phase was achieved. For Ga(III) loading, 50 cm$^3$ of a 5 mM extractant solution in chloroform was equilibrated with the same volume of a 0.1 mM Ga(III) solution. Five cubic centimeters of the separated organic solution were then shaken with the same volumes of hydrochloric and nitric acid of different concentrations for 4 h in order to strip the loaded metal ion. The concentration of metal ion in the initial aqueous solution, the raffinates and the stripped solutions were determined as described above and the stripped percentage of metal was calculated from the differences.

3. Results and Discussion
3.1 Extraction selectivity
The effects of pH on percentage extraction of metal ions with the ligands 4 and 3 in the competitive system are shown in Figures 1(a) and (b), respectively. These cations were chosen as the most common coexisting ions as by-products of primary metal refining from which Ga(III) and In(III) are usually recovered. The extraction selectivity for the metal ions as a function of pH for ligand 4 followed the order Ga(III) > In(III) > Fe(III) > Cu(II) >> Zn(III), Ni(II). It is worth mentioning that ligand 4 exhibited apparent Ga(III) selectivity over In(III) compared with ligand 3. Extraction of Fe(III) at low pH values was strange (it seemed to take place not by simple exchange but by specific interaction with the oxygen atoms of calixarene) The results indicated that ligand 4 is a promising ion receptor for effective separation of Ga(III) and In(III) from the highly interfering cation Fe(III) and some other common base metals such as Cu(II) and Zn(II). It was further indicated that this ligand is also effective in achieving mutual separation of Ga(III) and In(III) by properly adjusting the pH of the extraction system.

The formation constants of negative hydroxamate oxygen donors of with some metal ions were found to follow the order: Fe(III) > Ga(III) > In(III) > Cu(II) > Ni(II) > Zn(II) [26]. The preferred selectivity and extractability exhibited by ligand 4 towards Ga(III) over In(III), Fe(III), Cu(II) and Zn(II) were in accordance with the stability constants of their hydroxamic acid metal complexes. Significant Ga(III) selectivity over In(III) was also observed in the case of sorption of Ga(III) and In(III) on a chelating resin with hydroxamate groups [31]. Our earlier results indicated that extraction of these trivalent cations with calix[n]arene carboxylic acids took place mainly due to the effect of the functional groups appended on the calix[4]arene platform rather than the macrocyclic effect, and the calix[n]arene carboxylic acids were more selective for Fe(III) compared to In(III) and Ga(III) [24]. While the carboxylate ligands were more selective towards Fe(III), a hexadentate triazamacrocyclic ligand 1,4,7-triazacyclonane- N,N',N"-triacetic acid (NOTA), which provides an adequate coordination site for Ga(III) and nitrogen donor atoms with a hard-borderline nature (relatively soft compared with oxygen atoms) based on HSAB theory, had a higher stability constant towards Ga(III) over Fe(III) and In(III) [32]. Due to the nature of the ligating atom, hydroxamic acid may exhibit Ga(III) selectivity over other ions. Calix[4]arene hydroxamic acid 4 can
provide a relatively narrow coordination site compared with the acetic acid derivative 3. That is, the oxygen atoms of the hydroxamic acid are located at a farther position compared with those of the carboxylic acid and consequently the coordination site of the hydroxamic acid derivative becomes narrower than that of the carboxylic acid site, because the calixarene has a cone-shaped bottom. The high selectivity for Ga(III) is attributed to such a size-fitting effect together with the effect of the hydroxamic acid functionality. The results qualitatively corresponded with the extraction behavior of $p$-tert-octylcalix[4]arene tetrahydroxamic acid towards some trivalent cations [28].

Figure 1. Effect of pH on the percentage extraction of different metals with (a)4 and (b)3 in a competitive system. [Extractant] = 5 mM, [metal ion] = 0.1 mM each, shaking time = 12 h at 303 K, phase ratio = 1 (v/v), 0.1 M HNO$_3$ - 0.1 M HEPES buffer.

The remarkable Ga(III) selectivity exhibited by ligand 4 at pH values around 2.00 - 2.50 is worth considering and these results were compared with the extraction results for the tetracarboxylic acid ligand 3 towards Fe(III), Ga(III) and In(III) shown in Figure 1(b) [24]. Ligand 3 exhibited metal selectivity in the order Fe(III) > In(III) > Ga(III) > Zn(II) with very little discrimination. The $pK_a$ of phenoxyacetic acid in water is 3.12 [33], and this pH dependence of the extraction in the case of the carboxylic acid ligand 3 is apparently correlated with the dissociation of the carboxyl groups. Since the carboxylic acid groups in 3, arranged on the lower rim of the calix[4]arene ring, would form intramolecular hydrogen bonds resulting in a lowering of the $pK_a$ of the acetic acid groups of 3 [33], this pH shift in the extraction profile by 0.5 to 1.0 of a pH unit is partly attributed to the effect of hydrogen bond formation and partly to the cooperating effect of carboxyl groups facilitating the uptake of metal ions by providing proper coordination. As in the case of 3, the possibility of intramolecular hydrogen bonding in 4 would also significantly lower the $pK_a$ of the hydroxamic acid groups [33]. The $pK_a$ values for hydroxamic acids are 8-9, but the percentage extraction of these cations with 4 appears to fall in an unusually low pH region. The pH drop in the extraction of Ga(III) and In(III) with 4 was 6 to 7 pH units, which is very significant compared to the case of extraction of these cations with 3. It has been revealed by spectrophotometric studies that in the binding of Ga(III) and In(III) with hydroxamic acids only the chelate ML forms, and the concentration of the undissociated species, MHL, is negligible [34]. Thus, it is not unreasonable to argue that the interaction of
Ga(III) and In(III) cations with the hydroxamic acid ligand 4 is very special and facilitated the dissociation of the ligand in a fairly acidic region than would be expected from the pKₐ value of the ligand. The chelate forming ability of the hydroxamate group was certainly advantageous for this.

3.2 Stoichiometry of the extracted complexes

3.2.1 pH dependency

The effect of the pH on the distribution ratio of Ga(III) and In(III) with 4 is shown in Figure 2. Both plots lie on straight lines with a slope of three. The results suggest that the extraction of the trivalent cations proceeded simply via a proton-exchange reaction.

3.2.2 Job’s method

The complexation stoichiometry for binding of Ga(III) and In(III) with 4 was investigated by using the continuous variation method keeping the invariant summed concentrations of the ligand and the metal to be 1 mM. Job’s plots for the extraction of Ga(III) and In(III) with 4 are shown in Figures 3(a) and (b), respectively. In both cases, the concentrations of the extracted species in the organic phase approached a maximum when the mole fractions of the extractant was approximately 0.5. These results suggested that the metals and the ligand formed 1:1 complexes, respectively.

![Figure 2. Effect of pH on the distribution ratio of Ga(III) and In(III) with 4.][2]

![Figure 3. Typical Job’s plots for the extraction of (a) Ga(III) and (b) In(III) with 4.][3]

3.2.3 Loading tests

Loading tests were performed in order to reconfirm the observed complexation stoichiometry from the
Job’s plot experiments. The results are shown in Figures 4(a) and (b). As shown in Figure 4(a), the ratio of the initial concentration of the extractant to the loaded Ga(III) concentration gradually dropped with increasing concentration of Ga(III) in the aqueous phase and approached a plateau at 1 at higher Ga(III) concentrations. This means the ratio of the initial concentration of the extractant to the loaded Ga(III) is 1:1, which supports the formation of 1:1 metal: ligand complexes as obtained from the results of the Job’s plot. Similar results were obtained in the case of the In(III) loading test shown in Figure 4(b) indicating the formation of 1:1 metal: ligand complexes.

![Figure 4. Loading tests for (a) Ga(III) and (b) In(III) on extractant 4. [4] = 5.0 mM, shaking time = 12 h, initial pH = 3.0 for Ga(III) and 3.2 for In(III), pH adjusted by 0.1 M HNO₃ and 0.1 M HEPES buffer.](image)

### 3.2.4 Extraction reactions, extraction equilibrium constants and separation factors

Having determined that the non-hydrolyzed species of the trivalent cations, Ga(III) and In(III), form 1:1 host-guest complexes with the ion-exchangable ligand 4 and the electroneutrality of the complex in the organic phase was maintained by the release of an equivalent number of protons into the aqueous solution, the extraction equilibrium reaction for the extraction of Ga(III) and In(III) ions with the acid ligand 4 (designated as H₄R) is expressed by eq.(3),

\[
M^{3+} \text{aq} + H_4R_{\text{org}} \rightleftharpoons MHR_{\text{org}} + 3H^{+} \text{aq}
\]  (3)

where M represents Ga and In and H₄R represents ligand 4.

The extraction equilibrium constant \(K_{ex}\) for the above equilibrium reaction is given by eq.(4),

\[
K_{ex} = \frac{[MHR_{\text{org}}][H^+]^3}{[M^{3+} \text{aq}][H_4R_{\text{org}}]}
\]  (4)

The distribution ratio of the M(III) ions between the organic and the aqueous phases is given by eq.(2). From eqs. (4) and (2), eq.(5) is obtained as,

\[
K_{ex} = D \frac{[H^+]^3}{[H_4R_{\text{org}}]}
\]  (5)

Taking logarithms and rearranging, eq.(6) is obtained as,

\[
\log D = 3pH + \log[H_4R_{\text{org}}] + \log K_{ex}
\]  (6)
The obtained straight lines with the slope of 3 shown in Figure 2 are in accordance with the equilibrium eq. (5). It indicates the validity of the extraction reaction.

The extraction equilibrium constants ($K_{ex}$) for Ga(III) and In(III) were estimated from the equation for the straight lines in Figure 2 and using the relationship given by eq.(6). The values are summarized in Table 1, together with the separation factors for Ga(III) over In(III), $\beta_{Ga(III):In(III)}$ for 4. For comparison of the extraction ability and separation efficiency of ligands 3 and 4, half pH values and half pH value differences for Ga(III) and In(III) with ligand 3 [35] and 4 are also listed. The results indicate that ligand 4 is a candidate to selectively extract Ga(III) over In(III).

### 3.3 Determination of the coordination site

In order to understand the binding mode of 4 with Ga(III) and In(III), the FT-IR spectra of 4 as well as 4-Ga(III) and 4-In(III) complexes were studied. The FT-IR spectra of the free ligand and metal complexes are shown in Figure 5. The free ligand 4 showed a characteristic absorption band at 1737 cm$^{-1}$ corresponding to the C=O stretching vibration of the hydroxamate group. Appearance of a sharp absorption band at 1479 cm$^{-1}$ along with some weak bands in the region of 1380-1230 cm$^{-1}$ is attributable to the bending and stretching vibrations of the C-N and N-H bonds of the C-N-H hydroxamate. The absorption bands at 1192 and 1126 cm$^{-1}$ correspond to C-O stretching vibrations from the OCH$_2$ group and another band at 1051 cm$^{-1}$ is attributable to N-O bond vibrations. After complexation with Ga(III) and In(III), a new band appeared at 1591 cm$^{-1}$ in the case of the Ga(III) complex and at 1583 cm$^{-1}$ in the case of the In(III) complex. These new, relatively broad bands appearing with a concomitant decrease in intensity of the free carbonyl stretching band but at lower frequencies compared to that of the free ligand are due to the stretching vibrations of the carbonyl groups.

<table>
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<tr>
<th>Ligands</th>
<th>$K_{ex}$ [mol$^2$ dm$^{-3}$]</th>
<th>$\beta$</th>
<th>pH$_{1/2}$</th>
<th>$\Delta$pH$_{1/2}$</th>
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<td>Ga(III)</td>
<td>7.96x10^{-4}</td>
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<td>0.57</td>
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<tr>
<td>In(III)</td>
<td>1.55x10^{-5}</td>
<td></td>
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Table 1. Extraction equilibrium constants, separation factors, half pH values and half pH value differences for Ga and In with 3 and 4.
coordinated with metal ion [C=O⋯⋯M(III)]. Though not significant, some changes were also observed in the 1480-1240 cm\(^{-1}\) region of the spectra indicating the formation of chelate complexes of 4 with Ga(III) and In(III).

3.4 Stripping of the loaded Ga(III)

For complete recovery of the loaded metal ion and regeneration of the extraction reagent, stripping of Ga(III) from the loaded organic phase was examined using various concentrations of aqueous HCl and HNO\(_3\) solutions. The relation between the hydrochloric and nitric acid concentration and the percentage elution of the loaded Ga(III) is shown in Figure 6. The results indicate that 0.05 M HCl and HNO\(_3\) were enough for the back extraction of the loaded Ga(III) from the organic phase into the aqueous phase. However, the stripping percentage decreased with an increase in the acidic concentration. At high acidity, hydroxamic and acetic acids can be dissociated. However, after metal loading, it remained highly acidic, because the carbonyl oxygen atoms contribute to hold the metal ions by coordination, not by ion-exchange. At high acidity, a significant amount of anions also contributes to load metal ions by coordination as counteranions. Thus, dilute acidic solutions are suitable for complete stripping.

![Figure 6. Stripping of the loaded Ga(III) ions with HCl and HNO\(_3\) solutions of different concentrations.](image)

4. Conclusion

The present study has shown that the hydroxamic acid derivative of \(p\)-tert-butylcalix[4]arene is a promising reagent for selective extraction of Ga(III) and In(III) from a mixture of coexisting metal ions. The tetrahydroxamate ligand demonstrated strong affinity towards Ga(III) and In(III) with pH dependency. The slope analysis indicated that the extraction took place by a simple ion-exchange process. The strong affinity of the hydroxamate group for chelate formation coupled with the structural contribution of calix[4]arene providing proper coordination from ligating arms has a beneficial effect in achieving the Ga(III) selectivity of the ligand over the most interfering Fe(III) ion. Moreover, effective mutual separation of Ga(III) and In(III) can also be achieved by control of the pH. Job’s plots and loading tests unequivocally confirmed the formation of 1:1 host-guest complexes of both metals with ligand 4. The IR spectra of the metal loaded ligand confirmed the participation of the hydroxamic acid groups of the ligand in coordination with the loaded cation. Back extraction of the extracted Ga(III) from the organic phase was easily achieved using very dilute acidic solutions.

References