

# Complexation and extraction behavior of trivalent indium with multiple proton ionizable *p*-*t*-butylcalix[5]arene pentacarboxylic acid derivative: a new efficient solvent extraction reagent for indium

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**Abstract** Complexation behavior of plural ion-exchangeable *p*-*t*-butylcalix[5]arene pentacarboxylic acid derivative towards trivalent indium has been investigated along with its monomeric analog from weakly acidic media into chloroform. The cyclic structure of calixarene ligand providing certain cavity and cooperativity of functional groups significantly affect the complexation behavior and calixarene derivative is an excellent extractant over monomeric analog. The extraction mechanism is ion exchange and carboxylic acid groups are adequate functional sites for extraction. Mononuclear and/or polynuclear species of indium and monomeric or bridged dimeric species of calixarene are involved in complexation and the composition of extracted complex varied with solution pH. One mole of calix[5]arene derivative tend to extract 3.5 mol of indium. The loaded indium was quantitatively back extracted with 1 mol dm<sup>-3</sup> hydrochloric acid solution.

**Keywords** Calix[5]arene pentacarboxylic acid · Solvent extraction · Indium · Ion exchange

## Introduction

Being a rare metal with high commercial uses, recovery of indium is of high interest and gets special attention. However, minerals containing indium as a major constituent are not known, but is usually recovered as a by-product from primary zinc and zinc-lead productions [1] and there is the need of renewed interest to develop

effective reagents for the selective recovery of indium. A number of research articles and review papers have been published which utilize the carboxylic acids for solvent extraction of indium (III) from an aqueous medium into organic phase [2–7]. Acidic organophosphorous compounds also enjoy the considerable reputation of being exploited for the solvent extraction separation of indium from the mixture of other ions [8–15]. In addition to carboxylic acids, organophosphoric and phosphinic acid reagents, and phosphine oxides have also proved their worth as efficient solvent extraction reagents for indium [16, 17]. The mixture of organophosphoric acid and carboxylic acid was also used for the solvent extraction separation of indium [18]. Besides these, the solvent extraction separation of indium has been investigated with some commercially available oximes [19] and pyridones having ionizable hydrogen [20]. All the extractants having ionizable hydrogen are reported to extract the trivalent indium and gallium ions with the aid of ion-exchange process inferring that the extractants having ionizable hydrogen are efficient solvent extraction reagents for such metal ions. However, indium is known to be strongly extracted with acidic organophosphorous reagent and excessive quantities of strong mineral acids such as 8–9 M (M = mol dm<sup>-3</sup>) HCl are needed for back extraction, which, in industrial scale, would pose serious problems in terms of safety, corrosion, and waste disposal [17].

In recent years, calixarenes [21] have been widely used as host molecules in diverse areas of supramolecular chemistry and are considered as the third generation of host compounds after cyclodextrins and crown ethers [22]. They are frequently used as molecular platforms for the construction of supramolecular receptors for the specific recognition of guests [21, 23, 24]. Though calixarenes have recently emerged as powerful extractants for many

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elements, the inclusion behavior of calixarenes with indium ion has been rarely reported, since ion-pair extraction with neutral calixarene ligands requires counter anions and is difficult particularly with trivalent metal ions. Zhou et al. reported the solvent extraction of indium with tetraester derivative of *p-t*-butylcalix[4]arene in presence of sodium bromide where indium was extracted by forming an ion-pair compound  $[\text{NaL}]^+ [\text{InBr}_4]^-$  (L is calixarene ligand)[25]. Later on, Gidwani et al. reported the synthesis and analytical application of chelating polycalixarenes having hydroxamate chelate group for the separation of gallium, indium, and thallium [26]. Kim et al., by fluorescent titration using indium perchlorate in acetonitrile, reported that calix[4]arene diamide linked to fluorescent pyrene unit is a highly In(III) selective fluoroionophore capable of binding indium in 1:2 (ligand: metal) ratio [27]. The lipophilic anions like perchlorate ion are easily and concomitantly transferred into organic phase along with metal ion to maintain the electroneutrality. However, most counter anions in real industrial waste solutions, such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , etc. are highly hydrophilic and are difficult to transfer into an organic phase from an aqueous phase which significantly reduces the extraction efficiency of non proton-ionizable solvent extraction reagents particularly for the extraction of polyvalent metal ions. Fortunately, proton-ionizable solvent extraction reagents incorporating acidic functionality act as cation exchange liquid and present a solution to this problem [28].

The survey of literature led us to anticipate that the extractants having preorganized geometry with well defined cavity such as calixarenes decorated with plural ion-exchangeable functional groups would be efficient extractants for separation of indium. Further, our results for recovery of some heavy metal ions with calixarene carboxylic acid derivative indicated that dilute HCl solutions were sufficient for back extraction [29, 30] and we predicted that the loaded indium could be back extracted with dilute acid solutions from indium-loaded calixarene carboxylate. It was reported by Bell et al. that penta *t*-butyl ketonic derivative of *p-t*-butylcalix[5]arene shows wide selectivity for alkali metal ions and the extracted sodium and rubidium ions are deeply encapsulated by the ethereal oxygen atoms [31]. Recently, we observed the size discriminating effect of *p-t*-butylcalix[5]arene pentacarboxylic acid derivative that Pb(II) ion is encapsulated by ethereal oxygen atoms and sit deeply inside the cavity but the smaller ions like Cu(II) and Zn(II) are just ion-exchanged with functional groups [32]. Thus, it became a matter of interest for us to evaluate the inclusion phenomena of calix[5]arene derivative towards In(III) which is smaller than sodium ion and slightly larger than Cu(II) and Zn(II) ions. Consequently, we report herein the complexation and extraction behavior of *p-t*-butylcalix[5]arene

pentacarboxylic acid derivatives and structure related acyclic monomeric compound (as a control compound) towards indium ion. The complexation behavior of cyclic pentamer is discussed in light of complexation stoichiometry, binding location and its analytical application for recovery of indium.

## Experimental

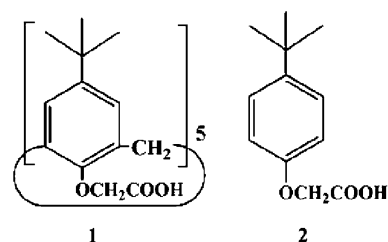
### Materials and methods

All reagents and solvents were of reagent grade and used without further purification unless mentioned otherwise. Analytical grade metal nitrate salts were used to prepare the stock solutions. Analytical TLC was performed on precoated silica gel plates ( $\text{SiO}_2$ , 60 F<sub>254</sub>). <sup>1</sup>H-NMR spectra were recorded by Jeol JNM-AL300 spectrophotometer in  $\text{CDCl}_3$  with TMS as an internal standard. IR spectra were recorded by JASCO FT-IR spectrophotometer. The solvent extraction reagents employed in the present study were synthesized by adopting the previously published procedure [30, 32] and analyzed for their purity by means of TLC and <sup>1</sup>H-NMR. Structures of the reagents employed in this study are shown in Fig. 1.

### The extraction experiments

#### General extraction

The percentage extraction of metal ions at different pH values was determined by conventional batch method. Aqueous metal solutions were prepared by dissolving analytical grade metal nitrate in 0.1 M  $\text{HNO}_3$  and 0.1 M HEPES buffer. Both the solutions were arbitrarily mixed to adjust pH. An organic solution was prepared by diluting the extractant into analytical grade chloroform to the desired concentration. Equal volumes of aqueous and organic solutions were mixed and the mixture was equilibrated by shaking. Metal concentration and pH of aqueous solutions before and after equilibrium were measured by atomic absorption spectrophotometer (AAS, Shimadzu AA 6500)



**Fig. 1** Structures of the reagents employed in the present study

and/or inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Shimadzu ICPS-8100) and pH meter (TOA DKK HM-30R), respectively.

#### Extraction as a function of extractant concentration

The distribution equilibria of indium as a function of extractant concentration were carried out by equilibrating the extractant solution varying in concentration from 0.5 to 2 mM with indium solution of 5 mM initial concentration. Aqueous solution was prepared by dissolving indium nitrate in 0.1 M HNO<sub>3</sub> and 0.1 M HEPES buffer and arbitrarily mixed to adjust the desired pH.

#### <sup>1</sup>H NMR titration

The host solution (2.5 mM) was prepared by diluting it in CDCl<sub>3</sub>/CD<sub>3</sub>CN (1/1) mixture. The titrant (50 mM) was prepared by dissolving In(ClO<sub>4</sub>)<sub>3</sub>·xH<sub>2</sub>O in the same solvent. To 1 cm<sup>3</sup> of host solution in NMR tube, the required volume of titrant was added ensuring both the solutions were mixed well and <sup>1</sup>H NMR was registered after each addition keeping the temperature of NMR probe constant at 27 °C.

#### Stripping test

Stripping test of the loaded indium was carried out by shaking the indium loaded extractant solution with acid solutions of various concentrations. The pH of aqueous solution was so adjusted that 100% of metal ion was extracted into the organic phase. For loading of indium, 50 cm<sup>3</sup> of 2.0 mM extractant solution in chloroform was equilibrated with the same volume of 5.2 mM indium solution. Five cubic centimeters of separated organic solutions were shaken with the same volumes of hydrochloric acid solutions of different concentrations for at least

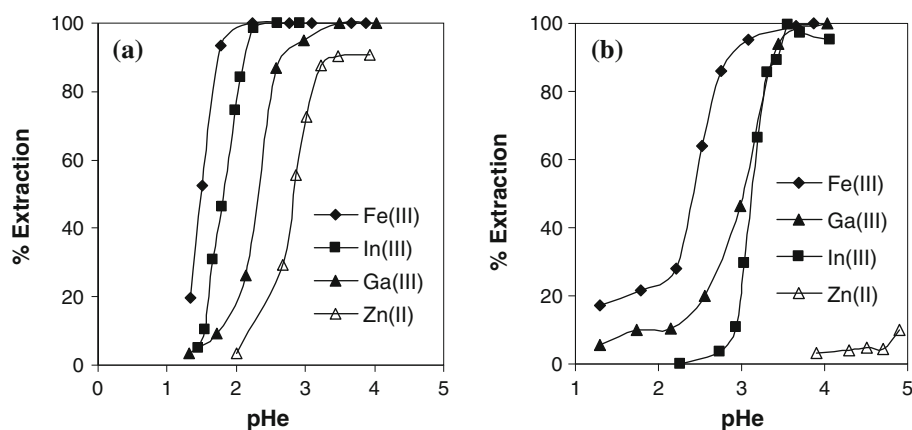
4 hours in order to strip the loaded metal ion. The concentration of metal ion in initial aqueous solution, the raffinate, and the stripped solutions were measured as mentioned above and stripped percentage of metal was calculated from the difference.

## Results and discussion

#### Effect of pH on percentage extraction of metal ions

The experimental results of single species extraction of some metal ions with **1** and **2** as a function of equilibrium pH are presented in Fig. 2a, b, respectively. These cations are chosen as the coexisting ions in by-product of primary metal refining from which indium is usually extracted. All the trivalent metal ions are classified into the same category in Pearson's classification of hard and soft acids and bases (HSAB) principle. The ionic radii of these trivalent metal ions follow the order Fe(III) < Ga(III) < In(III) and the reverse sequence of selectivity (Fe(III) > Ga(III) > In(III)) is expected in the pH of extraction based on the electrostatic effects that arises due to cation exchange during the course of extraction. The same is true for the monomeric extractant. However, the sequence of selectivity in the pH of extraction by calixarene derivative follows the order Fe(III) > In(III) > Ga(III) suggesting that the cyclic structure of calixarene derivative has significant contribution for indium selectivity. Further, the pH at which quantitative extraction of these metal ions takes place by **1** is shifted to lower value than in case of **2**, indicating that cooperativity effect of functional groups in **1** has considerable effect for extraction. As compared to control compound, the pH at which extraction of In(III) takes place by **1** is significantly shifted to lower value while the shift in pH of extraction is not so significant for Fe(III) and no shift in pH position takes place for the extraction of

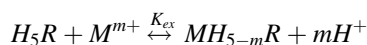
**Fig. 2** Effect of pH on percentage extraction of different metal ions. **a** [**1**] 2.4 mM, **b** [**2**] = 12.0 mM, [Metal ion] = 0.1 mM, shaking time = 10 h at 303 K, phase ratio = 1 (v/v), adjustment of pH = 0.1 M HNO<sub>3</sub>, 0.1 M HEPES buffer



Ga(III). Thus, it is not unreasonable to suppose that extraction of In(III) is greatly enhanced due to cooperativity effect of functional groups and structural contribution of **1**. The remarkably high Zn(II) extractability of **1** at relatively lower pH compared to control compound is attributable to cooperativity effect of functional groups. Nevertheless, the quantitative extraction of indium by **1** is achieved after pH 2.3 at which zinc is rarely extracted. The results suggest that **1** is applicable for analytical applications.

#### Extraction equilibrium

When the metal ion is assumed to be extracted with a single molecule of calix[5]arene carboxylic acid derivative ( $H_5R$ ) by the release of hydrogen ions equal to the valency of metal ion, the extraction reaction can simply be expressed as,



The extraction equilibrium constants in above reaction are expressed by the equation,

$$K_{ex} = \frac{[M^{m+}]_{org}[H^+]^m}{[M^{m+}]_{aq}[H_5R]} \quad (1)$$

The distribution ratio of metal ions between organic and aqueous phases is given by

$$D = \frac{[M^{m+}]_{org}}{[M^{m+}]_{aq}}$$

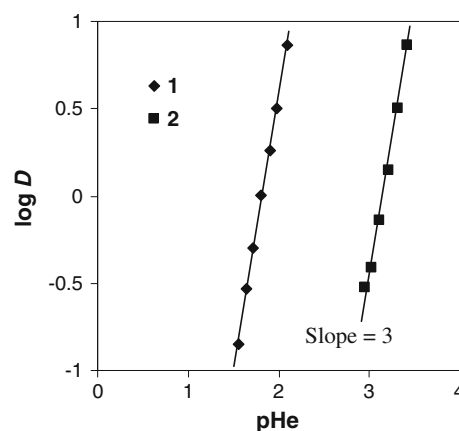
so that the equation becomes,

$$K_{ex,n} = D \frac{[H^+]^m}{[H_5R]}$$

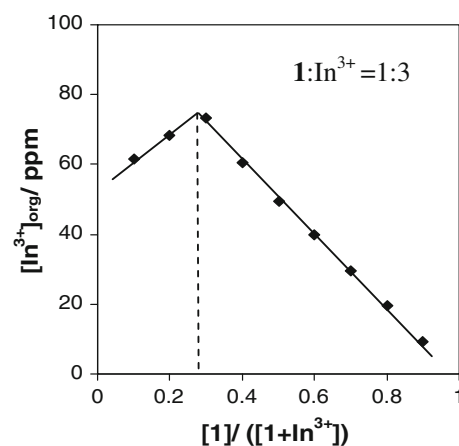
Taking logarithm and rearranging,

$$\begin{aligned} \log D &= \log K_{ex} + \log [H_5R] - m \log [H^+] \\ \log D &= m \text{pH} + (\log K_{ex} + \log [H_5R]) \end{aligned} \quad (2)$$

From the equilibrium equation (2), validity of the above equilibrium reaction can be checked by plotting  $\log D$  versus  $\text{pH}_e$ , where a straight line should be obtained with the slope of 3 for trivalent metal ions. The experimental data for the extraction of indium ion with different extractant are summarized in Fig. 3 by plotting the logarithm of distribution ratio against equilibrium pH. The distribution ratio of extraction increases along with pH and gives straight lines of the slope 3 at different position on the spectrum of pH. This suggests the complete neutralization of indium valency leading to the release of three protons as proposed in extraction reaction. The results support the extraction of indium with ion-exchange phenomenon under specified condition.



**Fig. 3** Effect of pH on distribution ratio of indium on different extractants.  $[In^{3+}] = 0.1$  mM,  $[1] = 2.4$  mM,  $[2] = 12.0$  mM shaking time = 10 h at 303 K, phase ratio = 1(v/v), adjustment of pH = 0.1 M  $HNO_3$ , 0.1 M HEPES buffer



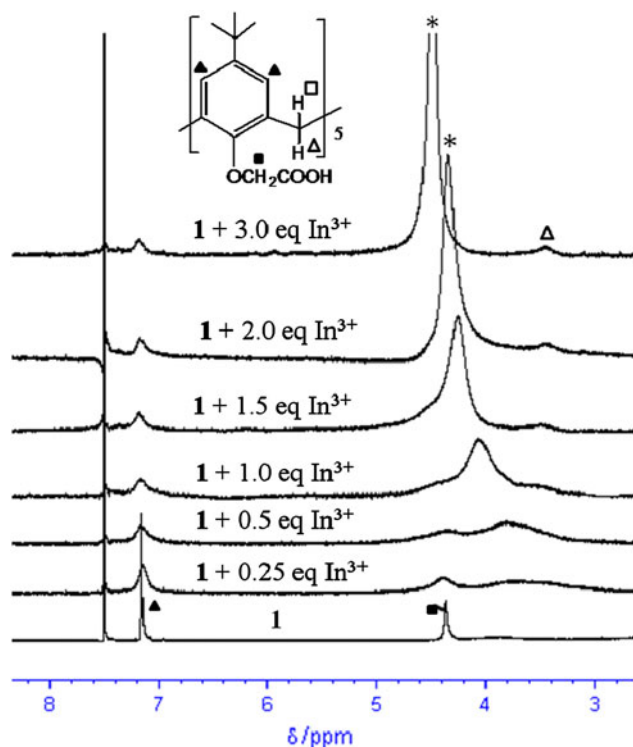
**Fig. 4** Typical Job's plot for extraction of indium with **1** at invariant total concentration of 1 mM. Initial pH = 3.2

#### Stoichiometry of complexation

In order to explore the host–guest binding ratio, complexation stoichiometry was investigated by using the method of continuous variation keeping the sum of concentration of host and guest species constant at 1 mM. Typical Job's plot for the extraction of In(III) with **1** is illustrated in Fig. 4. As indicated by the results, indium concentration in organic phase becomes maximum at the extractant mole fraction in between 0.2 and 0.3 and formation of 1:3 host–guest complexes is assigned.

#### Binding location

To have insight into the solution chemistry of the complex, binding location of indium within the host **1** and conformational reorganization of the host, if any,  $^1H$  NMR



**Fig. 5**  $^1\text{H}$  NMR titration of **1** (2.5 mM) with various equivalents  $\text{In}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$  in  $\text{CDCl}_3:\text{CD}_3\text{CN}$ ; 1:1. Residual solvent peak due to  $\text{CDCl}_3$  is at 7.49 ppm. \* = due to  $\text{H}_2\text{O}$  from  $\text{In}(\text{ClO}_4)_3 \cdot x\text{H}_2\text{O}$

titration experiment was carried out and characteristic peaks in the region of  $\delta$  8.0 to 3.0 ppm were considered for evaluation. The  $^1\text{H}$ -NMR spectrum of free host and in presence of various equivalents of indium is illustrated in Fig. 5. The free host displays two peaks, a singlet at  $\delta$  4.36 ppm for  $\text{ArOCH}_2$  protons and another singlet at  $\delta$  7.15 ppm for  $\text{ArH}$  protons. Due to the conformational freedom of the host under the investigated system, no sharp signals were observed for  $\text{ArCH}_2\text{Ar}$  resonances. In case of  $^1\text{H}$  NMR titration of **1** with  $\text{Pb}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$  in the same system reported earlier by the authors, new peaks were observed for  $\text{ArOCH}_2$  and  $\text{ArH}$  protons indicating the mixture of metal complexed and free host [32]. Further, the additional peaks were observed for  $\text{ArCH}_2\text{Ar}$  protons due to the conformational freezing of host induced by complementarity binding of lead ion inside the calix[5]arene cavity through the participation of  $\text{ArOCH}_2$  oxygen atoms [32]. However, in present case, new peaks were not observed for  $\text{ArOCH}_2$  and  $\text{ArH}$  protons upon the addition of indium to the solution of **1**, rather the peaks were broadened with incremental addition of metal ion solution. The results of  $^1\text{H}$  NMR titration of **1** with indium perchlorate suggests that the ionic size of indium, being smaller than that of lead, is not complementarity with the cavity size of calix[5]arene and  $\text{ArOCH}_2$  oxygen atoms have no significant contribution for the encapsulation of

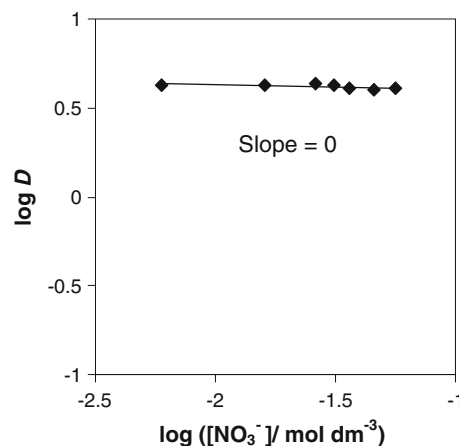
extracted indium. The appearance of a broad peak at  $\delta$  3.47 ppm for “exo-positioned”  $\text{ArCH}_2\text{Ar}$  proton implies that the conformational freedom entertained by the free host is restricted to some extent upon indium complexation. The piece of evidences from  $^1\text{H}$  NMR titration indicates that indium is extracted at aggregated carboxyl functional group site by ion exchange. During the course of NMR titration, broadening of the NMR line occurred because of insufficiently rapid exchange between the two species lying at the extremes of titration [33].

#### Composition of the extracted complex

The slope of lines in the plot of  $\log D$  against  $\text{pH}_e$  indicates the complete neutralization of indium valency by ion-exchange phenomenon. However, solely ion-exchange phenomenon cannot explain the multiple extraction of trivalent indium with single molecule of **1** as indicated by the results of Job's plot. It is thus necessary to look for the possibility of ion-pair extraction or the extraction of hydrolyzed species of indium so as to deduce the composition of the extracted complex in organic phase.

In order to evaluate the possibility of ion-pair extraction, nitrate dependency test on the distribution ratio of indium ion with **1** was carried out at initial pH 2.5 (maintained by very dilute solution of nitric acid) and the results are shown in Fig. 6 where the logarithm of indium distribution is plotted against the logarithm of nitrate concentration in solution. From the results of Fig. 6, it is evident that indium extraction with **1** is independent of nitrate concentration under the specified conditions.

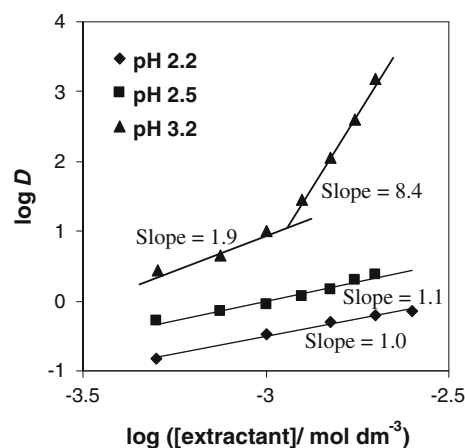
From the results of nitrate dependency test, the probable ion-pair complexation is ruled out. Nevertheless, the possibility of extraction of different species of indium cannot



**Fig. 6** Distribution of indium as a function of nitrate concentration with host **1**.  $[\mathbf{1}] = 2.0 \text{ mM}$ ,  $[\text{In}^{3+}]_{\text{initial}} = 2.0 \text{ mM}$ , volume ratio = 1/1, shaking time = 10 h, adjustment of nitrate concentration = 50 mM  $\text{LiNO}_3$  solution

be disregarded. Mononuclear hydroxide complexes of the types  $\text{In}(\text{OH})^{2+}$ ,  $\text{In}(\text{OH})_2^+$ ,  $\text{In}(\text{OH})_3$ , and  $\text{In}(\text{OH})_4^-$  have been discussed in numerous studies. It has been reported by Wood and Samson that the unhydrolysed  $\text{In}^{3+}$  ion is predominant at pH values up to 3 at 25 °C. It has also been depicted that the first mononuclear hydrolysis product,  $\text{In}(\text{OH})^{2+}$  as well as the second hydrolysis product of mononuclear species,  $\text{In}(\text{OH})_2^+$ , have relatively narrow field of predominance around pH 3.2 [34]. Thus, the possibility of extraction of hydrolysed species of indium under the specified condition is also negligible. However, it may be emphasized here that for  $[\text{In}(\text{III})] > 1 \text{ mM}$ , the predominant hydrolysis products are the polynuclear species [34]. While the existence of mononuclear hydrolysis species is negligible up to pH 5 at 25 °C in 10 mM indium solution, the existence of about 30% polynuclear species  $\text{In}_3(\text{OH})_4^{5+}$  is predicted in the pH range 3–5 [35]. In fact, a number of research articles have been well documented which describe the existence of some polynuclear indium hydroxide complexes such as  $\text{In}_2(\text{OH})_2^{4+}$ ,  $\text{In}_4(\text{OH})_6^{6+}$  [35, 36],  $\text{In}_4(\text{OH})_4^{8+}$ , or  $\text{In}_5(\text{OH})_5^{10+}$  [37]  $\text{In}_2(\text{OH})_3^{3+}$  and  $\text{In}_2(\text{OH})_4^{2+}$  [38],  $\text{In}_3(\text{OH})_4^{5+}$  [39, 40]. According to Han et al., the polynuclear species  $\text{In}_3(\text{OH})_4^{5+}$  exists from pH 2 to 6 [40]. Hence, in the present case also, the possibility of extraction of series of polynuclear species of indium along with  $\text{In}(\text{III})$  is not unreasonable. However, the question arises. Is the single host species capable of extracting the polynuclear species of indium? Consequently, there is the need to find out the number of host molecules exploited for the extraction of guest species.

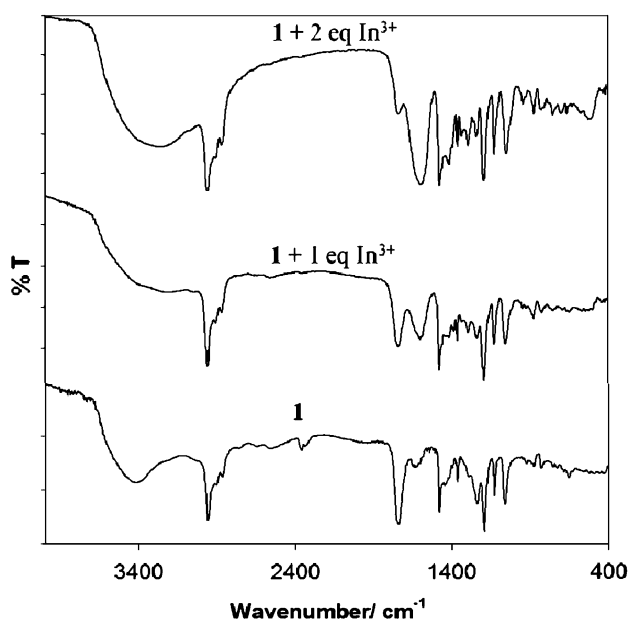
The most simple approach to determine the number of host molecules exploited for the extraction of guest species has been the use of log–log plot where the number of extractant molecules involved in the extracted species is found from the slope of the plot of  $\log D$  against  $\log[\text{extractant}]$  at constant initial concentration of guest. The experimental results obtained by plotting  $\log D$  versus  $\log[\text{extractant}]$  for indium with **1** at various initial pH values are presented in Fig. 7. As can be seen from the results of Fig. 7, the composition of extracted species varies with pH. At lower pH, the slope of line in the plot tends to be 1.0 which supports the formation of 1:1 host–guest complexes. However, as the pH increases, the slope also increases. At pH 3.2, the slope first tends to be 2 indicating that a dimeric species of extractant is involved in the extracted species. It is noteworthy, however, that the slope of the plot tends to be steeper with increasing indium concentration in the organic phase which is attributed either to the involvement of polymeric host species for indium extraction or polymerization of the extracted species. As metal ions can promote the formation of large polynuclear species by bridging functional groups of different extractant molecules, the extractants are expected to



**Fig. 7** Log [extractant] versus log  $D$  plot for extraction of  $\text{In}^{3+}$  with **1**.  $[\text{In}^{3+}]_{\text{initial}} = 5.0 \text{ mM}$ , shaking time = 12 h at 303 K, adjustment of pH = 0.1 M  $\text{HNO}_3$ , 0.1 M HEPES buffer

exhibit strong tendency to aggregate or polymerize under the influence of high metal concentrations [41]. Polymerization or self aggregation of the extracted metal complexes is also fairly common with carboxylic acid type of extractants [42]. According to Chiariza and Herlinger, when the concentrations of extracted metal approaches those corresponding to saturation of the extractant in organic phase, the discrete complexes familiar in solution co-ordination chemistry tend to disappear in favor of self-assembled structures, the driving force for the aggregation of the electroneutral metal–extractant complexes being provided by Van der Waals attraction between polar solutes in low polarity diluents [41]. In the present case also, it is evident from the results of Fig. 7 that the extracted species tend to self assemble and form the aggregated species in organic phase at high loading of indium. However, a monomeric host species is involved for the extraction of indium at low indium loading.

From the reported data, existence of a series of polynuclear hydroxide complexes of indium is obvious and one can infer the formation of polynuclear species of the extracted metal complexes from the results of log–log plot. Based on the above observations, it is not unreasonable to propose that composition of the extracted species varies according to the solution pH. At lower pH where indium loading on **1** is also low, a single host species extracts  $\text{In}(\text{III})$ . As the solution pH increases, however, a dimeric host species is involved for the extraction of  $\text{In}(\text{III})$  as well as the polynuclear hydroxide species of indium. Further, when the concentration of the extracted metal approaches corresponding to saturation of the extractant, the discrete complexes tend to self assemble and form the  $j$ -merized ( $j = 2, 3, \dots$ ) complex. Thus, it is very much difficult and unreasonable to predict the exact composition of extracted complex. Nevertheless, it is evident that the calix[5]arene



**Fig. 8** FT-IR spectra of free host **1**, **1** +  $\text{In}^{3+}$  and **1** +  $(\text{In}^{3+})_2$

pentacarboxylic acid derivative is capable of multiple extraction of indium.

#### FT-IR spectra of complexes

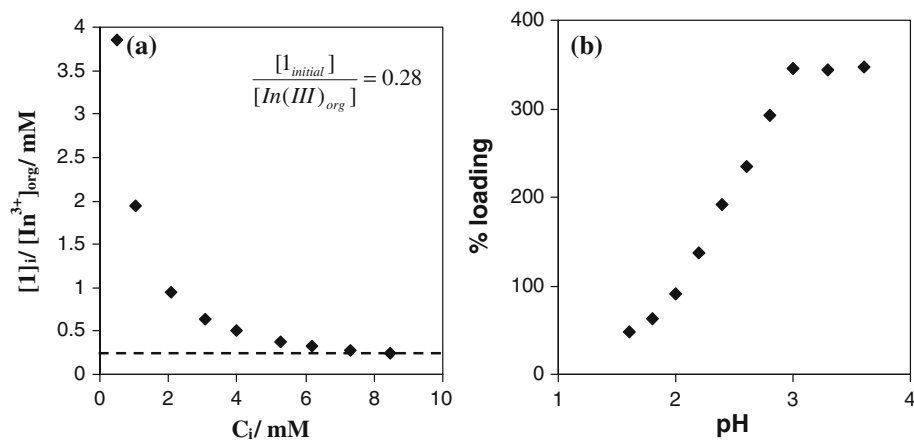
The multiple extraction of indium with **1** is also evident from the FT-IR spectra of indium complexed **1** compared to that of free host presented in Fig. 8. The free host **1** displays a sharp band at  $1741\text{ cm}^{-1}$  due to C=O stretching vibration. Upon complexation with one equivalent indium, intensity of the peak at  $1741\text{ cm}^{-1}$  decreased and new band was formed at  $1603\text{ cm}^{-1}$  which is attributed to C=O... $\text{In}^{3+}$  stretching. When indium concentration was two equivalent of host concentration, intensity of the peak at  $1604\text{ cm}^{-1}$  was further increased at the expense of intensity of the peak at  $1747\text{ cm}^{-1}$ . Since the C=O

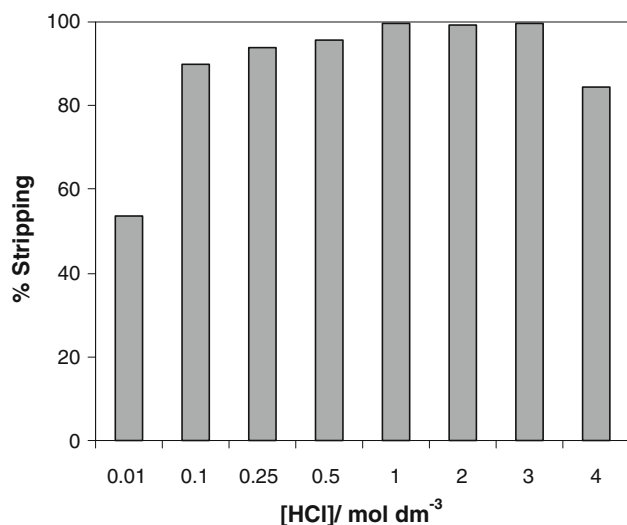
stretching of free host is still noticeable after loading of two equivalents of indium, one can infer that saturation with indium loading is still not achieved and **1** holds the capacity of binding more than two equivalents of indium.

#### Indium loading capacity of **1**

The results of Job's plot experiment and log–log plot to determine the stoichiometry of complexation and composition of extracted species did not give satisfactory result presumably due to the formation/extraction of multinuclear species. However, the results indicate that present extractant has high loading capacity for indium and holds promise in the sense that it is applicable for the preconcentration of indium. In order to investigate the loading capacity of **1**, loading test and percentage loading of indium were also carried out. In loading test, the ratio of initial extractant concentration to the loaded indium concentration is plotted against increasing initial concentrations of indium. As revealed by the Fig. 9a, the ratio of initial concentration of extractant to the indium concentration in organic phase gradually drops and becomes constant at around 0.28 with increasing initial indium concentration. This means the ratio of initial concentration of extractant to the loaded indium is roughly 1:3.5 which also support the possibility of formation of multinuclear complexes in organic phase. Fig 9b shows the results of percentage loading of lead on **1** at different pH. As indicated by the results, percentage loading of indium on **1** increase with increasing pH and becomes almost constant at around 350 beyond pH 3. The results of loading test and percentage loading concur with each other inferring that 1 mol of **1** tends to extract 3.5 mol of indium. From the piece of evidences of loading test and percentage loading of **1** towards indium, the results on host–guest complexation stoichiometry obtained by Job's plot can also be mentioned as 1:3.5. The maximum point at the extractant mole fraction between 0.2 and 0.3 in Job's plot, which is a

**Fig. 9 a** Loading test of In(III) on **1**.  $[\mathbf{1}] = 2.0\text{ mM}$ , shaking time = 12 h, initial pH = 3.2; **b** percentage loading of indium on **1** as a function of pH,  $[\mathbf{1}] = 3.0\text{ mM}$ ,  $[\text{In}^{3+}] = 5.0\text{ mM}$ , O/A = 1/2 (v/v), shaking time = 12 h, adjustment of pH = 0.1 M  $\text{HNO}_3$ , 0.1 M HEPES buffer





**Fig. 10** Relation between concentration of hydrochloric acid and stripping percentage of indium.  $[I] = 2.0$  mM, loaded indium =  $5.09$  mM, phase ratio = 1, shaking time = 6 h

little higher than that at the typical extractant mole fraction (0.22) for 1:3.5 stoichiometric complexes, is probably due to the extraction of different species of indium.

#### Stripping of loaded Indium

The remarkable indium selectivity over zinc and high indium loading capacity of **1** makes it a promising host compound for solvent extractive separation of indium from zinc. For potential analytical applications opening up the possibility of reusability of the extractant, stripping of loaded metal is crucially important. The relation between hydrochloric acid concentration and percentage elution of loaded indium is presented in Fig. 10. The results indicate that 1 M hydrochloric acid solution is enough for the back extraction of pre concentrated indium from organic phase into aqueous phase.

#### Conclusions

The carboxylic acid derivative of *p-t*-butylcalix[5]arene shows remarkable selectivity towards trivalent indium over divalent zinc ion. Though the extraction mechanism seems to be ion exchange, the composition of extracted complex varies according to solution pH. The extractant possesses high loading capacity towards indium around pH 3.2 at which zinc is rarely extracted. As we had anticipated, the loaded indium was extracted back using dilute hydrochloric acid solution. The extractant **1** is a promising reagent for solvent extraction of indium from Zinc refinery residues

because of high loading capacity and complete back extraction of loaded indium.

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