Synergistic Extraction Studies of Thiocyanate Complexes of Gadolinium, Dysprosium and Erbium with Mixture of Tributyl Phosphate and Tricaprylmonomethylammonium Chloride

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The synergistic extraction behavior of thiocyanate complexes of gadolinium, dysprosium and erbium has been studied for a mixed system: M^{3+}/NH_4SCN /tributyl phosphate (TBP)+tricaprylmonomethylammonium chloride (Aliquat-336)+xylene. The percentage extraction and distribution ratios were measured as a function of the pH as well as the NH_4SCN , Aliquat-336 and TBP concentrations, respectively. The percentage extraction of gadolinium, dysprosium and erbium increases with increase in pH. It was significant in the pH range 4 to 6 in a thiocyanate media. The composition of a binary synergistic extracted complex of lanthanides into the organic phase is probably $M(SCN)_5 \cdot 2(L^+)_2 \cdot 2TBP$, under the conditions studied. The synergistic extraction sequence as a function of the atomic number of lanthanide elements is given.

Keywords Synergistic extraction, tributyl phosphate, tricaprylmonomethylammonium chloride, gadolinium, dysprosium, erbium, Aliquat-336

In a comparison with the extensive studies concerning the solvent extraction of lanthanides with their salts¹⁻⁴, little work has been carried out concerning synergistic extraction involving ion association and solvation systems. Recently published work on solvent extraction suggests that the solvation energy of anions and lanthanides in water and organic solvents could be one of the most important factors regarding the distribution of lanthanide salts and complexes between aqueous and organic phases. Because of the low hydration energy of the thiocyanate ion, the distribution of thiocyanate complexes of lanthanides between the organic and aqueous phases with a binary synergistic extraction system is extensively expected. Although the extraction behavior of lanthanides in a thiocyanate solution with a single extractant, tributyl phosphate (TBP) and tricaprylmonomethylammonium chloride (Aliquat-336), has been reported⁵⁻⁸, systematic studies on the synergistic extraction of gadolinium, dysprosium and erbium with a TBP+Aliquat-336+xylene system in thiocyanate solutions are lacking.

This paper describes the synergistic extraction of gadolinium, dysprosium and erbium with a binary synergistic extraction system of TBP+Aliquat-336+xylene from thiocyanate solution. The effect of such different factors as the pH, concentration of NH_4SCN , Aliquat-336 and TBP on the percentage extraction and distribution ratios is described. From binary synergistic extraction studies, the composition of extracted species is discussed.

Experimental

Reagents and apparatus

A digital pH meter type pH-120 (ELICO, India) with glass and calomel electrodes was used. A Hitachi-220 spectrophotometer was used for spectrophotometric determinations.

Stock solutions of gadolinium, dysprosium and erbium were prepared by dissolving appropriate amounts of rare earth trioxides (Indian Rare Earths Ltd., Alwaye) in hydrochloric acid; after evaporation of excess hydrochloric acid, the solutions were diluted with distilled water to 250 ml. They were standardized complexometrically.⁹ Working standard solutions were prepared by appropriate dilution of the stock standard solutions.

TBP and Aliquat-336 were obtained from Aldrich and FLUKA, respectively. Purification of TBP was carried out by washing with 2.5 M NaOH and water. All other materials used were of analytical grade and suitable purifications were carried out when necessary. The exchanger was converted into the thiocyanate form by shaking for 10 min with an equal volume of 1 M ammonium thiocyanate. A second equilibration with an additional 1 M ammonium thiocyanate gave no further exchange. The optimum concentration of ammonium thiocyanate used was 3.0 M.

Procedure

To an aliquot of sample solution containing up to

100 μg of lanthanide, add the required quantity of an ammonium thiocyanate solution, followed by a dilute ammonium hydroxide solution or hydrochloric acid to adjust the desired pH. Dilute the solution with water 10 ml. Transfer the solution into a separating funnel and equilibrate with 10 ml of xylene containing an appropriate amount of TBP and Aliquat-336 for 5 min. Allow the layers to separate and then discard the aqueous phase. Strip the metal ions from the organic phase with water. Add to the separated strippant 5 ml of a buffer solution, 2 ml of an Arsenazo-I solution, then adjust the pH to 7.50. Dilute the resulting solution to 25 ml. Measure the absorbance of complex at 585 nm against a reagent blank. Compute the metal ion concentration from a calibration graph¹⁰ constructed by taking 2 to 50 μg of metal ion per 25 ml of solution, developing the colored complex with Arsenazo-I and measuring absorbance at 585 nm.

Results and Discussion

Extraction equilibrium

The extraction of lanthanide ions M^{3+} with TBP alone can be represented by following reaction:^{6,11}

with

$$\log D_B = \log K_B + 3\log[\text{SCN}^-] + 3\log[\text{TBP}]_o \quad (2)$$

where the "o" subscript indicates the organic phase. D and K are the distribution ratio and equilibrium constant, respectively. The extraction of trivalent metal ion M^{3+} with Aliquat-336^{7,11} (L^+SCN^-) can be expressed as

with

$$\log D_A = \log K_A + 3\log[\text{SCN}^-] + 2\log[\text{L}^+\text{SCN}^-]_o \quad (4)$$

Assuming that a synergistic extracted complex exists in the form of $\text{M}(\text{SCN})_{3-l-m}(\text{L}^+)_m \cdot n\text{TBP}_o$ in the organic phase, the extraction equilibrium can be given by

with

$$\log D_{AB} = \log K_{AB} + l\log[\text{SCN}^-] + m\log[\text{L}^+\text{SCN}^-]_o + n\log[\text{TBP}]_o \quad (6)$$

For the extraction system of Gd, Dy and Er with

mixture of Aliquat-336 and TBP in thiocyanate media, the total distribution ratio D of these elements between organic and aqueous phases may be expressed as

$$D = \frac{[\text{M}(\text{SCN})_{3-l-m}(\text{L}^+)_m \cdot n\text{TBP}]_o + [\text{M}(\text{SCN})_3 \cdot 3\text{TBP}]_o + [\text{M}(\text{SCN})_5 \cdot 2(\text{L}^+)_2]_o}{[\text{M}^{3+}]} \quad (7)$$

Equation (7) can be written as

$$D = D_{AB} + D_A + D_B \quad (8)$$

where D_B and D_A are the distribution ratios of the extraction with a single extractant: TBP and Aliquat-336, respectively. D_{AB} is the distribution ratio of a binary synergistic system of TBP+Aliquat-336. The experimental concentrations of TBP and Aliquat-336 are fixed so that there is no considerable extraction of metal ion by a single extractant; total distribution ratio D can thus be set equal to D_{AB} .

Percentage extraction variation with pH

The results obtained for a binary synergistic extraction system for gadolinium, dysprosium and erbium at various pH values (but at constant Aliquat-336, TBP and NH_4SCN concentrations) are shown in Fig. 1. In these studies, aqueous phases containing 100 μg metal ion and NH_4SCN (3.0 M) were adjusted to various pH values by the addition of dilute HCl or a NH_4OH solution before extraction. As the pH value increased slightly after extraction, the points plotted in Fig. 1 were obtained just after an equilibrium of the two phases was attained. The percentage extraction increases with increasing pH value. The extraction was significant over the range of 4–6 pH. Further experiments were carried out at equilibrium pH 5.0.

Percentage extraction variation with ammonium thiocyanate concentration

As shown in Fig. 2, that the percentage extraction depends on the concentration of ammonium thiocyanate for complexation of lanthanides was confirmed by

Fig. 1 Percentage extraction dependency on pH, NH_4SCN 3 M, TBP 0.012 M+Aliquat-336 0.012 M.

Fig. 2 Percentage extraction vs. ammonium thiocyanate concentration. $M(\text{III})=100\text{ }\mu\text{g}$, $\text{TBP}=0.01\text{ M}$, $\text{Aliquat-336}=0.01\text{ M}$, $\text{pH}=5.0$.

extracting lanthanides with 0.01 M TBP and 0.01 M Aliquat-336 in xylene at various concentrations of ammonium thiocyanate (Fig. 2). Although the extraction commenced at 0.5 M , there was an increase in the extraction in two steps: first 0.5 to 2.0 M and second 2.0 to 5.0 M . However, further extraction studies were carried out in the concentration range of 2.5 to 4.0 M .

Type of extracted species

The nature of the extracted species was determined by extracting rare earth elements with a constant concentration of other two variables and changing one concentration variable at a time.

Thiocyanate concentration studies

To ascertain the participation of thiocyanate molecules in the extracted species, the ammonium thiocyanate concentration was varied from 2.5 to 4 M by keeping the TBP and Aliquat-336 concentrations constant. Plots of $\log D$ versus $\log(\text{thiocyanate concentration})$ at fixed concentration of TBP and Aliquat-336 are shown in Fig. 3. The slopes of the curves were found to be 2.8 , 3.10 and 2.9 for Er, Dy and Gd, respectively. This indicates that three molecules of thiocyanate take part in the extraction of solvated ion-pair complex into the organic phase.

TBP concentration studies

In this solvent extraction process, TBP plays a significant role in the solvation metal ions. It is important to determine the number of TBP molecules solvated to metal ions in the binary synergistic extraction process. Therefore, studies on the TBP concentration variation have been carried out by keeping the Aliquat-336 and ammonium thiocyanate concentration constant. The variation of the TBP concentration in these studies was investigated over the range from 0.005 to 0.02 M . Graphs were plotted for the $\log D$ versus $\log(\text{TBP concentration})$ at constant concentrations of Aliquat-336 and thiocyanate (Fig. 4). The slopes of the curves were observed to be 1.89 , 2.05 and 1.95 for Er, Dy and Gd, respectively. This

Fig. 3 Plots of $\log D$ vs. $\log[\text{NH}_4\text{SCN}]$. Aliquat-336 0.015 M + TBP 0.015 M .

Fig. 4 Plots of $\log D$ vs. $\log[\text{TBP}]$. Aliquat-336 0.02 M , $\text{NH}_4\text{SCN}\text{ }3\text{ M}$.

confirms that the solvation of lanthanide ions is achieved by TBP in this binary synergistic extraction system.

Aliquat-336 concentration studies

Aliquat-336 as a strong liquid anion exchanger competes with TBP in this binary synergistic extraction process. It extracts a negatively charged TBP solvated complex of lanthanide ions into the organic phase. To investigate the charge of the synergistic complex extracted into the organic phase, Aliquat-336 concentration variation studies were undertaken. The extractions were carried out with 0.02 M TBP in xylene and 3 M ammonium thiocyanate in the aqueous phase as fixed concentrations. Plots of the $\log D$ versus $\log(\text{Aliquat-336 concentration})$ are shown in Fig. 5. The slopes of the curves were found to be 1.96 , 2.10 and 1.88 for Er, Dy, and Gd, respectively.

From the above experimental results, it was observed that the values of l , m and n are 3 , 2 and 2 , respectively. It is thus confirmed that the $\text{M}(\text{SCN})_5^{2-}(\text{L}^+)_2 \cdot 2\text{TBP}$

Fig. 5 Plots of $\log D$ vs. $\log[\text{Aliquat-336}]_0$. TBP 0.02 M, NH_4SCN 3 M.

species of these elements are extracted in a binary synergistic extraction system. From these data, the stoichiometric relation for the extraction of these elements can be expressed by

The extraction equilibrium constants obtained were $\log K=5.68$, 5.40 and 5.18 for Er, Dy and Gd, respectively. The extraction for Er, Dy and Gd increases in the order $\text{Er} > \text{Dy} > \text{Gd}$.

Lanthanide extraction with mixture of TBP and Aliquat-336

The results of an extraction study for individual lanthanide ions with a constant concentration of a mixture of TBP, Aliquat-336, ammonium thiocyanate and at optimum pH are given in Fig. 6. Here, $\log D$ is plotted according to the increasing atomic number of elements. It can be observed from Fig. 6 that the heavy members of lanthanide ions, such as Yb^{3+} , Lu^{3+} , Er^{3+} and Ho^{3+} , could be extracted more easily with respect to rare earths than could the other rare earth elements. The yttrium extraction order with a mixture of TBP and Aliquat-336 in a thiocyanate media lies between holmium and erbium. The interaction between phosphate oxygen and metal ion could be strong, while competing with hydration water oxygen. The increasing D value with respect to an increase in the atomic number of rare earth elements, can be attributed to such a competition of water, TBP and metal ions as hard base and hard acid interactions. The synergistic extraction of lanthanide ions in a thiocyanate media follows a similar trend as in single TBP and Aliquat-336 extraction systems. The extraction of lanthanide elements with a mixture of TBP and Aliquat-336 in a thiocyanate media is enhanced by the formation of bulky ion pairs.

Extraction studies involving yttrium and lanthanides in nitrate and thiocyanate media are interesting. In

Fig. 6 $\log D$ as a function of atomic number of lanthanides. 0.011 M TBP+0.011 M Aliquat-336, NH_4SCN 3 M.

these media, yttrium behaves like a heavy rare earth in thiocyanate and nitrate systems ($\text{Tb} < \text{Y} < \text{Er}$) in extraction studies with TBP.¹² However, the behavior of yttrium¹² in extraction studies with Aliquat-336 in a nitrate media is like a heavy ($\text{Ho} < \text{Y} < \text{Lu}$) rare earth, whereas in thiocyanate media¹¹ it behaves like a lighter ($\text{Nd} < \text{Y} < \text{Gd}$) rare earth. Synergistic extraction studies of lanthanides and yttrium in thiocyanate and nitrate media with the mixture of TBP and Aliquat-336 show that the yttrium extraction sequence with respect to the lanthanides is shifted to a position in between dysprosium and erbium. A reversed sequence of the extraction of lanthanide in nitrate media was observed with the mixture of TBP and Aliquat-336, in comparison with that of a single extractant, Aliquat-336, in nitrate media.¹² The results show that coordinated water molecules and complexation with nitrate and thiocyanate play an important role in the behavior of the extraction of lanthanides and yttrium in mixed systems.

The formation of a bulky ion pair and the enhancement of extraction can be attributed towards the dehydration of metal ions and the extraction of a hydrophobic complex into the organic phase. This can be explained by following equation:

where x , y , z and z' denote the number of hydrated water molecules to metal ions, Aliquat-336, TBP and ion pair complexes, respectively. Since the coordination number of lanthanides varies from seven to nine, the number of water molecules released, $x+y+z-z'$, during the complexation process would also be large. The release of a large number of water molecules would be one of the causes for the enhancement of synergistic extraction.

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