Separation of Scandium from Yttrium in Aqueous Chloride Media 
by Solvent Extraction with an Acidic Phosphinate Extractant

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Separation of scandium (Sc) from yttrium (Y) in aqueous chloride media was investigated by solvent extraction with bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272). Conventional slope analysis method revealed the extraction equilibrium formulation of the metals. Sc is more strongly extracted than Y by Cyanex 272, and the separation factor of the metals is quite high at $2.82 \times 10^5$. Complete stripping of Sc from the loaded organic solution of Cyanex272 could not be achieved, even with a high concentration of hydrochloric acid. Addition of 1-octanol as a modifier to the organic phase decreased the extractability of Sc, leading to successful stripping of Sc from the loaded organic solution.

1. Introduction

Scandium (Sc) is a rare and expensive metal in high demand because of its excellent characteristics for various industrial applications, such as laser crystals, advanced ceramics, nuclear materials and catalysts for automobiles [1,2]. Although Sc is not particularly rare in its total crustal abundance, deposits of minerals with high scandium concentrations are scarce. Since Sc is similar to yttrium (Y) and the heavy lanthanides owing to its small ionic radius, it is commonly found together with Y and lanthanides. From the viewpoint of resource sustainability, development of a highly efficient separation process has thus gained considerable importance for most countries such as Japan, which has the second largest demand for Sc in the world and imports most of its Sc from China.

Solvent extraction is now widely used on an industrial scale for the separation and purification of metal ions such as vanadium, molybdenum, indium, and rare earth elements [3-7]. Solvent extraction has advantages such as simple processing, high speed, and ease of scale up, although it has disadvantages such as the need for large amounts of organic diluent. When considering the separation of rare earth elements, organophosphorus compounds are generally used as the extractant. There are some reports on the separation of Sc from Y with organophosphorus compounds, such as bis(2-ethylhexyl)phosphoric acid (D2EHPA) [8] or bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) [9]. In both cases, although Sc was selectively separated from Y and other lanthanides, stripping of the loaded Sc was difficult due to its high extractability. Among the organophosphorus compounds, stripping of the heavy rare earth elements from a loaded organic solution containing phosphinic acid extractants is even easier than those from loaded organic solutions containing phosphoric and phosphonic acid extractants, due to its low acidity. However, the highest stripping efficiency of Sc from a loaded organic solution containing a phosphinic acid extractant with sulfuric acid was reported to be no more than 80% [10-13].
Considerable enhancement in stripping efficiency could be attained in organophosphorus extractant systems by adding a modifier to the organic phase despite a small loss of loading capacity, since the modifier prevents the dimerization of the extractant and affects formation of the metal-extractant complexes [14,15]. To allow the stripping of Sc in a solvent extraction system, 1-octanol as a modifier was added to the organic phase to suppress Sc extraction as well as to enhance the stripping efficiency in a multistage process [16].

In the present study, therefore, extraction and stripping of Sc and Y by solvent extraction have been investigated, using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) as the extractant. The extraction and stripping behavior were first investigated in a conventional extraction system. Stripping enhancement was then investigated by adding 1-octanol as the modifier.

2. Experimental

2.1 Reagents

Cyanex 272 was supplied by Cytec Solvay Japan Co., Ltd (Tokyo, Japan). The extractant purity was measured by potentiometric titration with NaOH and was found to be 87.1 wt% with 12.9 wt% of phosphine oxide. Scandium oxide and yttrium oxide were supplied by Nippon Yttrium Co., Inc. (Fukuoka, Japan). IP Solvent 2835, a synthetic isoparaffinic hydrocarbon having 99.8 vol % or more iso-paraffin [17] was supplied by Idemitsu Kosan Co., Ltd (Tokyo, Japan). All other organic and inorganic reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) as analytical-grade reagents.

2.2 Extraction of Sc and Y

The aqueous rare earth chloride solutions were prepared by dissolving the oxides in 1 or 2 mol/L HCl solution, and then diluted with deionized water to obtain 1 mmol/L Sc or Y aqueous solutions. The pH of the aqueous solution was adjusted using HCl or NaOH. Organic solutions were prepared by diluting Cyanex 272, together with 1-octanol, in IP Solvent 2835. Concentrations of the extractant as a dimeric species base are shown in the figure captions. Extraction of Sc and Y was carried out by shaking the organic and aqueous solutions at a volume ratio of 1 : 1 at 25°C for more than 3 h. Concentrations of the metals in the resultant aqueous solutions were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000) and those in the organic solutions were calculated based on material balance. The pH was measured by a pH meter (Horiba F-74). The distribution ratio \(D\) was defined as:

\[
D = \frac{[M]}{[M]_i}
\]  

(1)

2.3 Stripping of Sc and Y from loaded organic solution

Stripping experiments were carried out using the metal loaded organic solution. In this case, the extraction was carried out in the same manner as described above, and the metal loaded organic solution was used in the stripping experiments. Stripping was performed by contacting the loaded organic solution with different concentrations of HCl (2 – 3 mol/L) at a volume ratio = 1 : 1, and the mixture was shaken at 25°C for more than 3 h. The concentrations of the metals in the resultant aqueous solutions were determined by ICP-AES and those in the organic solutions were calculated based on material balance.
3. Results and Discussion

3.1 Extraction of Sc and Y in the absence of 1-octanol

Figure 1 shows the effect of pH on the distribution ratio \( D \) of Sc and Y. A linear relationship between the pH and \( \log D \) was obtained for both metals with a slope of 3, indicating that the extraction is proceeded by cation exchange between the metal and three protons. Figure 2 shows the effect of the concentration of the dimerized extractant on the distribution ratio. The relationship between \( \log D[H^+]^3 \) and \( \log[(RH)_2]_{\text{feed}} \) for Sc and Y showed a dependency of slope 3, so that three dimeric extractants participate in the extraction of each metal ion. Based on the results of the slope analysis, the extraction equilibrium for Sc and Y is formulated as Eqs. (2) and (3).

\[
\text{Sc}^{3+} + 3(RH)_2 \leftrightarrow \text{ScR}_3(RH)_3 + 3H^+; \quad K_{\text{ex,Sc}} = 4.06 \times 10^4 \quad (2)
\]

\[
\text{Y}^{3+} + 3(RH)_2 \leftrightarrow \text{YR}_3(RH)_3 + 3H^+; \quad K_{\text{ex,Y}} = 1.44 \times 10^{-1} \quad (3)
\]

The \( K_{\text{ex}} \) value for Sc is extremely high, and thus the stripping of Sc is expected to be quite difficult. The separation factor \( S_{\text{Sc/Y}} \), defined as \( K_{\text{ex,Sc}}/K_{\text{ex,Y}} \), is \( 2.82 \times 10^5 \), indicating separation of the two metals is easily achieved.

\[\text{Figure 1. Effect of pH on the distribution ratios of Sc and Y. \([(RH)_2]_{\text{feed}} = 0.0354 \text{ mol/L, [Sc]}_{\text{feed}} = 1.00 \text{ mmol/L, and [Y]}_{\text{feed}} = 1.00 \text{ mmol/L.}\]}

\[\text{Figure 2. Effect of the concentration of dimeric extractants on the normalized distribution ratios of Sc and Y. \([\text{Sc}]_{\text{feed}} = 0.91 \text{ mmol/L, and [Y]}_{\text{feed}} = 1.05 \text{ mmol/L.}\]}

3.2 Stripping of Sc and Y in the absence of 1-octanol

Stripping of the loaded Sc and Y was then investigated. Table 1 lists the stripping yields of the metals from the loaded organic solutions containing Cyanex 272 alone with different concentrations of HCl. The stripping yield of Y was reasonably high and was little affected by the HCl concentration, while that of Sc was still low but did increase with increasing HCl concentration. Therefore, improvement of the stripping yield is required.
Table 1. Stripping yield of Sc and Y with HCl from loaded organic solutions containing Cyanex 272 alone.

| [HCl] (mol/L) | Sc     | Y      |
|---------------|--------|--------|
| 1.0           | 18.6%  | 91.1%  |
| 2.0           | 39.1%  | 91.9%  |
| 3.0           | 50.5%  | 85.9%  |

3.3 Effect of addition of 1-octanol on the extraction and stripping of Sc

The effect of the addition of 1-octanol to the organic phase was investigated. Figure 3 shows the effect of pH on the distribution ratio of Sc, in a single metal system, with an organic phase containing 1-octanol (molar ratio of [1-octanol]/[(RH)\textsubscript{2}] = 12). The distribution ratio of Sc in the absence of 1-octanol, shown in Figure 1, is also plotted in Figure 3 for comparison. The distribution ratio of Sc is dramatically decreased by the addition of 1-octanol to the organic phase. In addition, the slope of log D against pH is 3 even in the case of the 1-octanol/Cyanex 272 mixture, indicating that the extraction of Sc still occurred by a cation exchange mechanism. The effect of the addition of 1-octanol to the organic phase was finally investigated to try to improve the stripping of Sc. Figure 4 shows the effect of the molar ratio of [1-octanol]/[(RH)\textsubscript{2}] on the distribution ratio of Sc from aqueous solution at pH\textsubscript{feed} = 0.41. As the amount of 1-octanol added to the organic solution was increased, the distribution ratio of Sc decreased. This is likely because the 1-octanol causes dissociation of the dimeric species of the extractant in the organic phase due to its polar characteristics [15].

![Figure 3](image-url)  
Figure 3. Effect of pH on the distribution ratios of Sc. [1-octanol]/[(RH)\textsubscript{2}] = 12, [(RH)\textsubscript{2}]\textsubscript{feed} = 0.0355 mol/L, [Sc]\textsubscript{feed} = 1.00 mmol/L. Data without 1-octanol is from Figure 1.

![Figure 4](image-url)  
Figure 4. Effect of the molar ratio of [1-octanol]/[(RH)\textsubscript{2}] on the distribution ratio of Sc. [(RH)\textsubscript{2}]\textsubscript{feed} = 0.0340 mol/L, [Sc]\textsubscript{feed} = 0.97 mmol/L, pH\textsubscript{feed} = 0.41.
The effect of the molar ratio of \([1\text{-octanol}] / [(RH)_2]\) on the stripping yield of Sc was then investigated. In this case, the loaded organic solution was stripped 3 times with 2 mol/L HCl solution. Figure 5 shows the stripping yield of Sc. In the case a single strip, the stripping yield was increased with \([1\text{-octanol}] / [(RH)_2]\), as expected from the extraction results shown in Figure 3. After 3 stripping stages, almost complete stripping could be achieved at a molar ratio of more than 12, and a 99.8% stripping yield was obtained at a molar ratio of 24. Therefore, the addition of 1-octanol was shown to suppress the extractability thus improving the stripping ability of Sc.

4. Conclusion

Extraction and stripping of Sc and Y with Cyanex 272 was investigated with the following results. The extraction of Sc and Y proceeded by the conventional cation exchange mechanism and the separation factor for the two metals is extremely high at \(2.82 \times 10^5\). The stripping yield of Sc from Cyanex 272 in the absence of 1-octanol was quite low, even when using 3.0 mol/L HCl solution as the stripping reagent. The extraction of Sc was decreased by adding 1-octanol to the organic phase, and the stripping yield was improved. Almost complete stripping was achieved by the addition of \([1\text{-octanol}] / [(RH)_2]\) at a molar ratio more than 12.

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