

Solvent Extraction of Scandium and Yttrium Using Carboxylic Acid

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Abstract Separation of scandium (Sc) from yttrium (Y) in aqueous chloride media by solvent extraction using Versatic acid 10 was investigated. Conventional slope analysis method revealed the extraction equilibrium formulation of the metals. Sc is more strongly extracted than Y by Versatic acid 10, and the separation factor of the metals is quite high at 1.93×10^4 . Complete stripping of Sc from the loaded organic solution of Versatic acid 10 was achieved by 3M HCl solution. Then Versatic acid 10 was applied to solvent impregnated resin (SIR), separation of Sc was progressed via Langmuir adsorption model.

1 Introduction

Scandium (Sc) is one of the rare earth metals in high demand, providing excellent characteristics for various industrial applications (USGS, 2018; Paulick and Machacek, 2017). Although Sc is not particularly rare in the overall crustal abundance, there is little reserves of scandium-rich minerals. 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 heavy lanthanides. Thus, from the perspective of resource sustainability, the development of high-efficiency separation processes has become very important in most countries such as Japan, which has the second largest scandium in the world, relies on imports from China for most of its demand. Thus, separation of Sc from yttrium (Y) and other rare earths is required.

Separation of rare earth metals is generally performed hydrometallurgical processes. Solvent extraction is one of the most widely used hydrometallurgical processes for the separation and purification of rare earth elements (Wang and Li, 1995; Wang *et al.*, 2002; Jia *et al.*, 2009). Solvent extraction is carried out using functional groups of particular interest, taking into account such disadvantages as use of large amounts of organic solvents with the advantages of high selectivity and ease of scale-up. Therefore, solvent impregnated resin (SIR) is getting attention which is environmentally friendly, possessing high selectivity by integrating the unique features and process advantages of solvent extraction and ion exchange. The major disadvantage of SIRs is loss of extractant due to solubility in the aqueous phase, which can be minimized by coating with polymers and chemical crosslinking (Trochimzuk *et al.*, 2004).

When considering the separation of rare earth elements, organophosphorus compounds such as bis (2-

ethylhexyl)phosphoric acid (D2EHPA) (Ochsenkuhn-Petropupu *et al.*, 1995) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) (Lee *et al.*, 2005) are generally used. Although Sc could be extracted separately from other rare earths, it is difficult to strip the rare earth elements from the loaded organic solution due to high extractability. Thus, in this work, carboxylic acid, such as naphthenic acid and Versatic acid (Zheng *et al.*, 1991), which are widely used for extracting scandium, is applied. When naphthenic acid in kerosene was used as the organic phase and hydrochloric acid was used as the stripping solution, the separation factor of Sc over all rare earth elements was very high and the order of separation of Sc was far ahead of Y (Liao *et al.*, 2001). Although Sc³⁺ was extracted separately at pH 3 to 5 from other rare earth metal ions, extraction mechanism by Versatic acid 10 was not demonstrated (Baba *et al.*, 2014).

In the present study, therefore, separation and recovery of Sc and Y using Versatic acid 10 have been investigated. The extraction and stripping behavior of solvent extraction were first investigated in a conventional extraction system. Conventional slope analysis method revealed the extraction equilibrium formulation of the metals. Versatic acid 10 impregnated SIR was finally employed in batchwise adsorption.

2 Experimental

2.1. Reagents

Versatic acid 10 was supplied by HEXION Specialty Chemicals Co., Ltd (Tokyo, Japan), 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 isoparaffin was supplied by Idemitsu Kosan Co., Ltd (Tokyo,

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Japan). Diaion HP2MG, a methacrylic ester copolymer containing no functional group, was supplied by Nippon Rensui 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

Aqueous rare earth chloride solutions were prepared by dissolving each oxide 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 Versatic acid 10 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 298K for more than 6 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:

$$D = [\bar{M}]/[M] \quad (1),$$

where $[\bar{M}]$ and $[M]$ are concentrations of metals in the organic phase and aqueous phase, respectively.

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 298K 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.

2.3 Preparation and coating of SIR

The SIR was prepared by the following method (Kabay *et al.*, 2010; Nishihama *et al.*, 2013). HP2MG was washed with methanol and dried in vacuo. Washed HP2MG (2.5 g) was then immersed overnight in a 0.2 mol/L Versatic acid 10–toluene solution (50 mL). The toluene was then removed by evaporation, and the resin dried in vacuo for 24 h. The amount of Versatic acid 10 impregnated in the resin was 8.23 mmol/g. Coating of SIRs were conducted using PVA, of polymerization degree ca. 2000, crosslinked by glutaraldehyde (GA). The prepared SIR (3 g) was immersed in an aqueous solution (50 mL) containing 3 wt% PVA and 1 wt% acetamide and the mixture was shaken for 17 h. The resultant suspension was then mixed with 1 mol/L KCl aqueous solution (10 mL) and the mixture was shaken for 24 h. The pre-treated SIR was filtered and resuspended in a 0.32 mol/L H₂SO₄ solution (10 mL) for 1 h. 0.32 mol/L GA aqueous solution

(10 mL) was then added, followed by shaking the mixture for 24 h, to complete crosslinking. The coated SIR obtained was filtered, washed with deionized water, and then dried. Hereafter, SIR used in the present study was all coated SIR.

2.4 Adsorption of Sc with SIR

Aqueous rare earth chloride solutions were prepared by dissolving each oxide in 1 or 2 mol/L HCl solution, and then diluted with deionized water to obtain 1 mmol/L Sc and Y aqueous solutions. The pH of the aqueous solution was adjusted using HCl or NaOH. The SIR (20 mg) was added to 20 mL of aqueous solution, and the suspended mixture was shaken at 298 K for 24 h. The concentrations of the metal ions were determined, after filtration of the resin, with an ICP-AES. The amount of adsorbed metal ion, q (mmol/g), is defined as:

$$q = ([M]_{\text{ini}} - [M]_{\text{eq}}) \times V / W \quad (2),$$

where $[M]_{\text{ini}}$ and $[M]_{\text{eq}}$ are initial and equilibrium concentrations of metals in the solution (mmol/L), respectively, V is the volume of the solution (L), and W is the weight of the resin (g).

Elution experiments were carried out using the metal loaded SIR. In this case, the adsorption was carried out in the same manner as described above, and the metal loaded SIR was used. Elution was performed by adding 10 mg of metal adsorbed SIR to 10mL of different concentrations of HCl (1 – 3 mol/L), and the mixture was shaken at 298K for more than 24 h. The concentrations of the metal ions were determined with ICP-AES. The elution rate was calculated by material balance.

3 Results and Discussion

3.1. Extraction of Sc

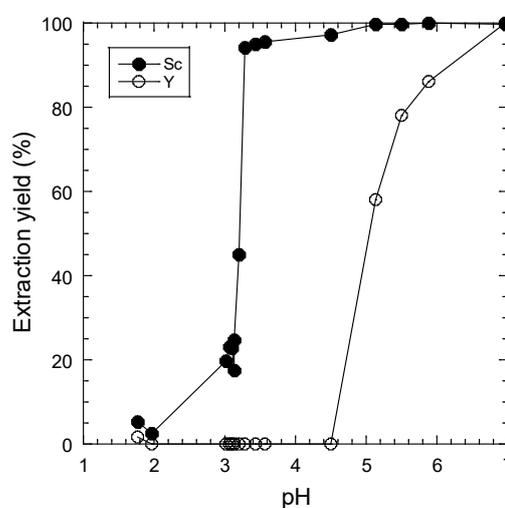


Figure 1. Effect of pH on the extraction yield

Figure 1 shows the effect of pH on the extraction yield of Sc and Y. Extraction of Sc proceeds at pH 3–4, while extraction of Y proceeds at pH > 4.5. Thus, separation of Sc from Y is expected to be achieved at pH 3–4.

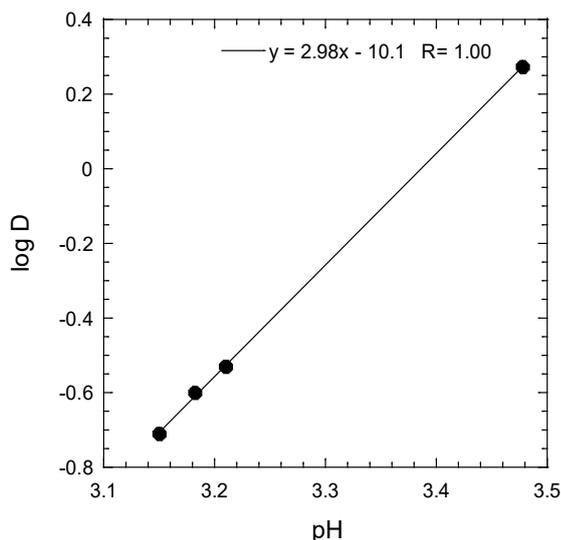


Figure 2. Effect of pH on the distribution ratios of Sc. $[(RH)_2]_{feed} = 0.0354$ mol/L, $[Sc]_{feed} = 1.00$ mmol/L

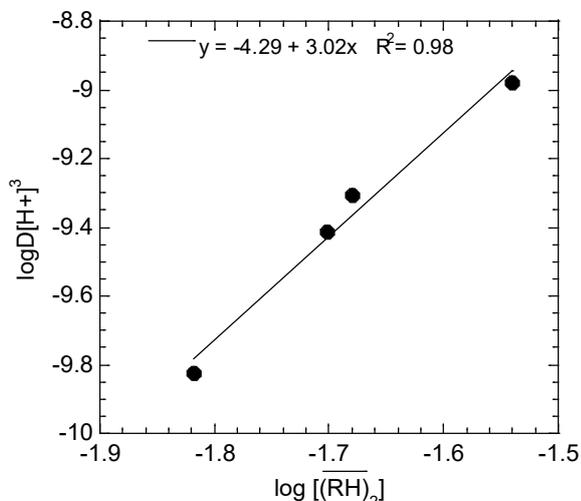
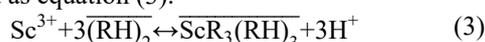


Figure 3. Effect of concentration of dimeric extractants on the normalized distribution ratios of Sc. $[(RH)_2]_{feed} = 0.0354$ mol/L, $[Sc]_{feed} = 1.00$ mmol/L

Figure 2 shows the effect of pH on the distribution ratio of Sc from pH 3.1 to 3.5 where extraction of Y hardly occurs. For Sc, a linear relationship with a slope of 3 between pH and $\log D$ was obtained, indicating that the extraction proceeds by cation exchange between scandium and the three protons. Figure 3 shows the effect of the concentration of the dimerized extractant on the distribution ratio. The relationship between $\log D[H^+]^3$ and $\log[(RH)_2]_{feed}$ for Sc 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 is formulated as equation (3).



K_{ex} value for Sc is 1.93×10^4 which is quite high, and it implies the stripping of Sc is expected to be difficult.

Stripping of the loaded Sc was then investigated. Table 1 lists the stripping yields of Sc from the loaded

organic solutions containing Versatic acid 10 with different concentrations of HCl. The stripping yield of Sc reached 100 % by 3 mol/L HCl.

Table 1. Stripping rate of Sc using different concentrations of hydrochloric acid

HCl (mol/L)	Stripping rate (%)
1	49.2
2	87.7
3	100

3.2. Adsorption of Sc and Y with SIR

Figure 4 shows the effect of pH on the adsorption of Sc and Y with Versatic acid 10 SIR in the binary solution. From pH 1.5 to 3.5 Sc and Y are adsorbed and Sc was maximum at pH 2.5, while Y was also maximum at pH 2.7.

Adsorption isotherm of Sc in pH 2.8 with Versatic acid 10 is shown in Figure 5. Assuming that the adsorption is of Langmuir mechanism, as shown in equation (4),

$$q = \frac{q_0 K[M]}{1 + K[M]} \quad (4)$$

where q_0 is the maximum adsorption amount (mmol/g) and K is the adsorption equilibrium constant (L/mmol). From the linear relationship of the Langmuir mechanism, Figure 5 (b), the adsorption of Sc with the Versatic acid 10 SIR is of Langmuir mechanism. The maximum adsorption amounts of Sc calculated was 1.31 mmol/g, and the adsorption equilibrium constant was 0.664 L/mmol, respectively.

Elution of adsorbed Sc was then investigated. Table 2 lists the elution yields of Sc from the adsorbed resin with different concentrations of HCl. The stripping yield of Sc reached only 52.2 % by 3M HCl.

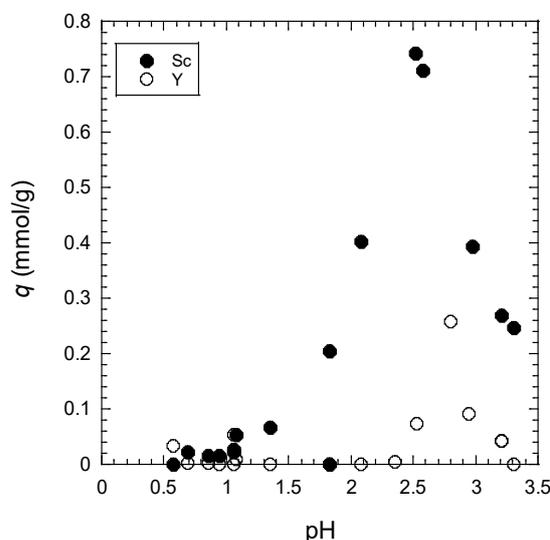


Figure 4. Effect of pH on amount of adsorption of Sc and Y with Versatic acid 10 SIR

Table 2. Elution yield of Sc using different concentrations of hydrochloric acid

HCl (mol/L)	Stripping rate (%)
1	25.4
2	31.0
3	52.2

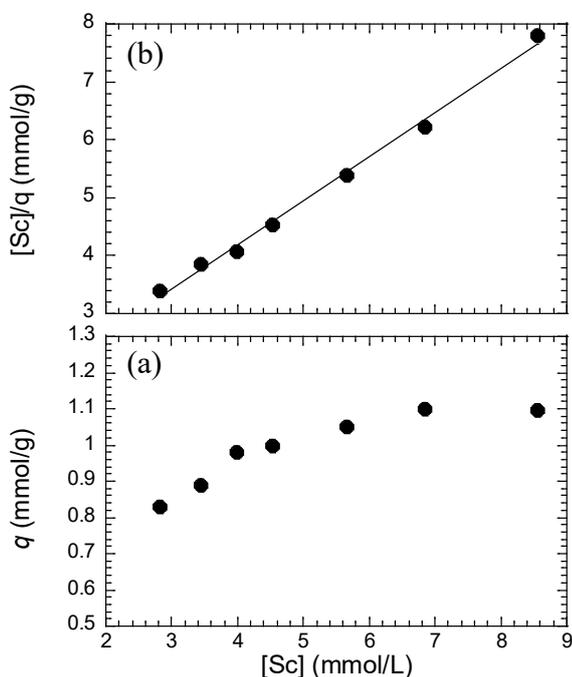


Figure 5. Adsorption isotherm and linearized relationship Langmuir mechanism of Sc with Versatic acid 10 SIR. $y = 0.760x + 1.15$, $r^2 = 0.99$

4 Conclusion

Extraction and stripping of Sc with Versatic acid 10 and adsorption using Versatic acid 10 SIR were investigated with the following results.

1. The extraction of Sc was proceeded by the conventional cation exchange mechanism and equilibrium constant was quite high at 1.93×10^4 .
2. The stripping yield of Sc from Versatic acid 10 reached 100% using 3.0 mol/L HCl solution as the stripping reagent.
3. Versatic acid 10 SIR can adsorbs Sc under specific pH region. Adsorption of Sc by Versatic acid 10 follows the Langmuir adsorption model and the maximum adsorption amounts of Pt was 1.31 mmol/g, and the adsorption equilibrium constant K was 0.664 L/mmol, respectively.

References

Baba, Y., A. Fukami, F. Kubota, N. Kamiya, and M. Goto; "Selective Extraction of Scandium from Yttrium and Lanthanides with Amic Acid-Type Extractant Containing Alkylamide and Glycine Moieties," *RSC*

Adv., **4**, 50726–50730 (2014)

Jia, Q., S. Tong, Z. Li, W. Zhou, H. Li, and S. Meng; "Solvent Extraction of Rare Earth Elements with Mixtures of Sec-Octylphenoxy Acetic Acid and bis(2,4,4-trimethylpentyl) Dithiophosphinic Acid," *Sep. Purif. Technol.*, **64**, 345–350 (2009)

Kabay, N., J. Cortina, A. Trochimczuk, and S. Streat; "Solvent-Impregnated Resins (SIRs) – Methods of Preparation and Their Applications," *React. Funct. Polym.*, **70**, 484–496 (2010)

Lee, M. S., J. Y. Lee, J. S. Kim, and G. S. Lee; "Solvent Extraction of Neodymium Ions from Hydrochloric Acid Solution Using PC88A and Saponified PC88A," *Sep. Purif. Technol.*, **46**, 72–78 (2005)

Liao, C., J. Jia, G. Xu, C. Yan, B. Li, and G. Xu; "Extraction of Scandium from Ion-Adsorptive Rare Earth Deposit by Naphthenic Acid," *Alloys. Compd.*, **323–324**, 833–837 (2001)

Nishihama, S., K. Kohata, and K. Yoshizuka; "Separation of Lanthanum and Cerium Using a Coated Solvent Impregnated Resin," *Sep. Purif. Technol.*, **118**, 511–518 (2013)

Ochsenkuhn-Petropupu, M., T. Lyberopulu, and G. Parissakis; "Selective Separation and Determination of Scandium from Yttrium and Lanthanides in Red Mud by a Combined ion Exchange/Solvent Extraction Method," *Anal. Chem. Acta*, **315**, 231–237 (1995)

Paulick, H. and E. Machacek; "The Global Rare Earth Element Exploration Boom: An Analysis of Resources Outside of China and Discussion of Development Perspectives," *Resources Policy*, **52**, 134–153 (2017)

Trochimczuk, A., N. Kabay, M. Arda, and M. Streat; "Stabilization of Solvent Impregnated Resins (SIRs) by Coating with Water Soluble Polymers and Chemical Crosslinking," *React. Funct. Polym.*, **59**, 1–7 (2004)

USGS; Mineral Commodity Summaries 2018, pp. 132-133, U.S. Geological Survey, Reston, USA (2018)

Wang, C. and D. Q. Li; "Solvent Extraction of Sc(III), Zr(IV), Th(IV), Fe(III), and Lu(III) with Thiosubstituted Organophosphinic Acid Extractants," *Solvent Extr. Ion Exch.*, **13**, 503–523 (1995)

Wang, Y. G., S. T. Yue, D. Q. Li, M. J. Jin, and C. Z. Li; "Solvent Extraction of Scandium(III), Yttrium(III), Lanthanides(III), and Divalent Metal Ions with Sec-Nonylphenoxyacetic Acid," *Solvent Extr. Ion Exch.*, **20**, 701–716 (2002)

Zheng, D., N. B. Gray, and G. W. Stevens;

“Comparison of Naphtenic Acid, Versatic Acid and D2EHPA for the Separation of Rare Earths,” *Solvent Extr. Ion Exch.*, **1**, 85–102 (1991)