Selective Extraction of Scandium from Other REEs Using Binary Extractant of PC-88A and Versatic 10 from Nitrate Media

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Comparative study for the extraction of rare earth metals was conducted using some binary extractant systems, in which PC-88A was used as the main extractant. The binary systems showed a different extraction behavior of synergism or antagonism depending on several factors such as the structure of extractant, the mechanism of extraction, interaction between the extractant and the coordinated ligand and others. Based on the results obtained, the binary system composed of PC-88A and Versatic 10 enables to achieve the selective extraction of Sc(III) from other rare earth metals and to enhance the stripping efficiency even with using a mild acidic solution, which was thought to be difficult from a solvent including PC-88A alone.

1. Introduction

The demand of scandium (Sc) has been increasing in high-technology industries [1], however its supply is not enough because Sc(III) is difficult to be purified and recovered. Organophosphorous extractants such as 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) have been commercially often used for the separation of rare earth metals, however it exhibits too high affinity towards the extraction of Sc(III), which results in difficulty in stripping operation with a mild acidic condition [2]. To control the extraction and separation efficiency, it is sometimes effective to use a binary extractant system, which shows a synergistic or an antagonistic effect between the two mixed extractants [3,4,5].

The extraction of metal cation M^{x+} by the acidic extractant HA could be expressed by the formation of the MA_x chelate in the organic phase. Combined synergistic behavior of two extractants (HA, Z) in the binary system will be appeared if the MA_xZ_n adduct is formed, which is extracted with a high efficiency rather than the acidic extractant alone. On the other hand, antagonistic behavior will be observed if HA and Z interacts among themselves, reducing the initial available amount of HA ready for complex formation [6].

In the present study, we investigated the extraction behavior of rare earth metals using several binary extractant systems composed mainly of PC-88A and another extractant with a different extraction mode such as solvation, chelation and an ionic interaction mechanism. Moreover, we will report the selective extraction and recovery of Sc(III) from other rare earth metals by using a mixture of PC-88A and an alkyl-monocarboxylic acid, Versatic 10.

2. Experimental

2.1 Reagents

Extractants PC-88A, Primene JM-T, TBP, Cyanex 272 and Versatic 10 were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and used without any purification. n-Dodecane, ammonium nitrate and nitric acid were supplied by Kishida Chemical Co., Ltd (Osaka, Japan). All the other chemicals were of analytical grade. The molecular structures of the extractants used in this study are shown in Figure 1.

2.2 Extraction experiments

Aqueous feed phases containing 0.1 mM of Sc ion and other rare earth metal ions (Y^{3+}, La^{3+}, Nd^{3+}, Eu^{3+} and Dy^{3+}) were prepared by dissolving the nitrate salts of the metals in 0.1 M HNO_3 and 0.1 M ammonium nitrate. The pH values in the aqueous phases were adjusted by mixing the two solutions. Extraction phases were prepared by dissolving a given amount of PC-88A and/other targeted extractant in the organic diluent (n-dodecane).

Equal volumes (2 ml) of the organic extraction phase and the feed aqueous phase were put into a sealed tube. The samples were mixed first for 1 min using a vibrating mixer then were shaken at 298 K for 1 h in a temperature-controlled bath to assure equilibrium. The equilibrium pH of the aqueous phase after extraction was measured by a pH meter (HM-60 G, DKK-TOA Co.). The stripping of metal ions from the extraction phase was achieved using an acid solution with the same procedure of extraction. Metal concentrations in the aqueous phases were estimated using an inductively coupled plasma (ICP)-atomic emission spectrometer (Optima 8300; Perkin Elmer Inc., MA, USA). The extraction ratio of the metal ions (E [-]) was calculated by Eq. (1):

$$E = \frac{[M]_{ex.eq}}{[M]_{aq.0}} = \frac{[M]_{aq.0} - [M]_{aq.eq}}{[M]_{aq.0}} \tag{1}$$

The distribution coefficient D [-] was defined as shown in Eq. (2):

$$D = \frac{[M]_{ex.eq}}{[M]_{aq.eq}} = \frac{[M]_{aq.0} - [M]_{aq.eq}}{[M]_{aq.eq}} \tag{2}$$

where [M] is the metal concentration, and subscripts aq and ex symbolize the feed aqueous and extraction phases, respectively. The subscripts 0 and eq denote the initial and the equilibrium state, respectively.

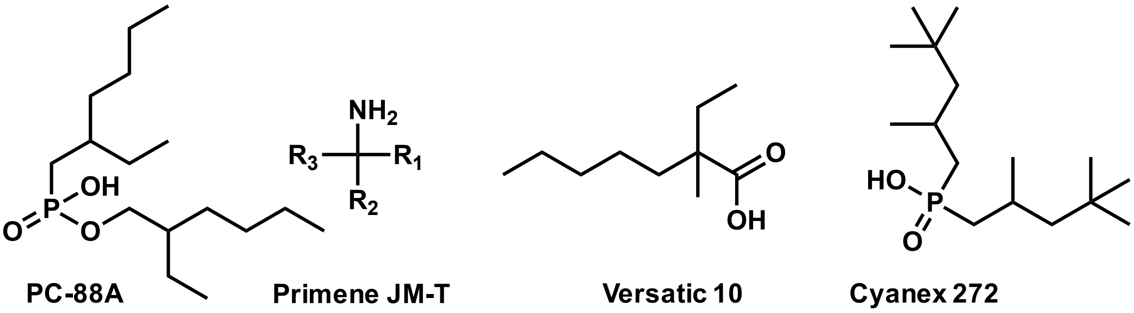

Figure 1. Molecular structures of extractants used in this study.

3. Results and Discussion

3.1 Extraction using individual PC-88A

The extraction ratio for the rare earth ions into the organic phase using 1 mM PC-88A alone is shown in Figure 2. Based on the results in Figure 2, PC-88A shows a high affinity towards Sc^{3+}; the extraction occurs from a high acidity (pH=zero), which is thought to be difficult to perform stripping operation from the Sc-loaded organic phase.

3.2 Extraction using different binary systems

Extraction isotherm equilibria using a binary mixture of PC-88A and TBP (solvating extractant) /or cyanex 272 (acidic chelating extractant) /or primene JM-T (basic extractant) are shown in Figure 3. Figure 3(a) shows the extraction behavior of 1 mM PC-88A and 5 mM primene JM-T, the addition of Primene JM-T delays the extraction of scandium, but on the other hand it enhances clearly the extraction of all Y, Dy and Eu ions, which is called the synergistic effect. We should notice that the extraction ratio of 5 mM Primene JM-T alone with the same concentration towards the rare earths ions is very low. Apparently, the last mentioned binary system decreases the selectivity towards Sc ion compared to that of PC-88A alone. While, the extraction ratio of Sc ion using the binary extractant of 1 mM PC-88A and 5 mM Cyanex 272 is obviously decreased indicating the strong antagonistic effect of adding Cyanex 272 to PC-88A for the extraction of Sc ion as shown in Figure 3(b). The addition of Cyanex 272 completely changes the extraction mode of PC-88A as the system becomes more selective to Y ion after pH 3 and enhances the extraction of other rare earths at the same time. The extraction using 5 mM Cyanex 272 alone shows very low extraction ability to rare earth ions, however, the addition of Cyanex 272 to PC-88A reduces the extraction ratio of Sc (antagonistic effect). The possible interaction between PC-88A and Cyanex 272 could be the reason for the antagonistic effect towards Sc ion but the extent of interaction had not been studied yet. The degree of interaction between the two extractants in the binary system can be deduced from the extent of the antagonistic effect, whereas in a synergistic effect, an additional extractant in return enhances the degree of extraction for some metal ions depending on the nature of extractant itself. Figure 3(c) demonstrates the effect of adding TBP (solvating agent) to PC-88A towards rare earth ions extraction. The results indicate the weak effect of adding TBP in the binary system that resembles the extraction by only PC-88A except for only Dy ion.

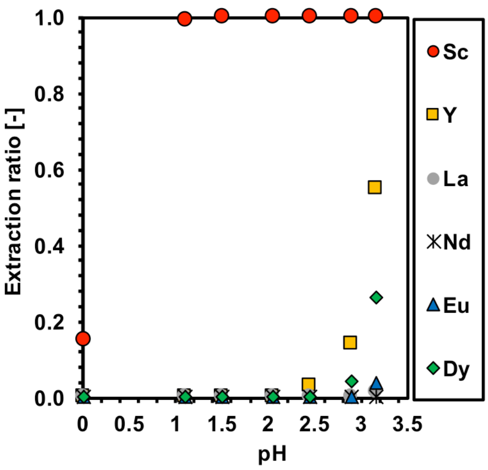

Figure 2. Extraction ratio of REE ions using 1 mM PC-88A alone, an aqueous phase: 0.1 mM M^{n+}.

Mixed extractant systems offer an interesting extraction behavior, which needs further investigation to elucidate the detailed reasons for the dissimilar features under set conditions. There are many factors, which will govern the extraction behavior such as the ligand effect, the mechanism of extraction, the structure of extractant, solubility parameters of metal chelate, a diluent effect, hydrogen bond formation in the extractant phase, a self adduct formation, miscellaneous combination when using a base extractant, coordination of two extractants to the metal ion and so on.

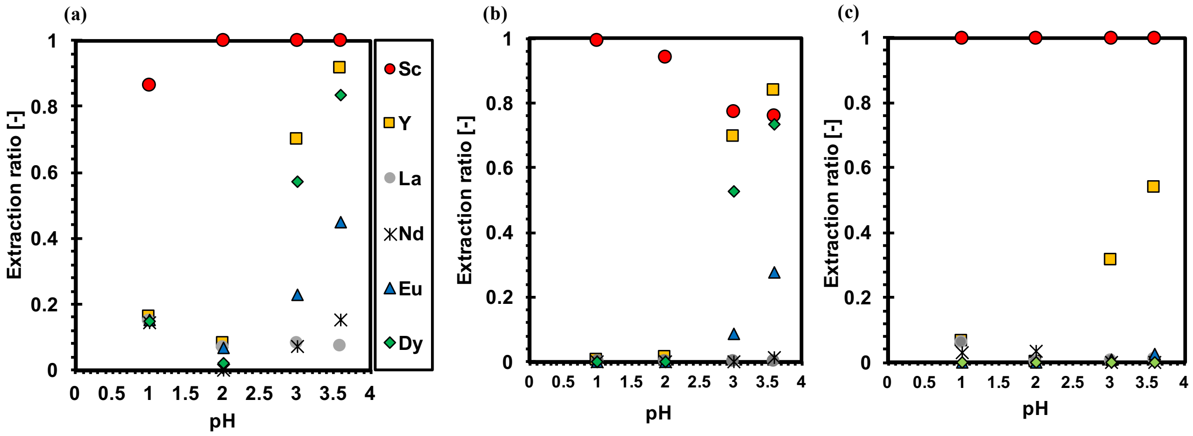

Figure 3. Extraction ratio of REE ions using (a) 1 mM PC-88A and 5 mM primene JM-T, (b) 1 mM PC-88A and 5 mM Cyanex 272 and (c) 1 mM PC-88A and 5 mM TBP in *n*-dodecane. Aqueous phase: 0.1 mM M^{n+}.

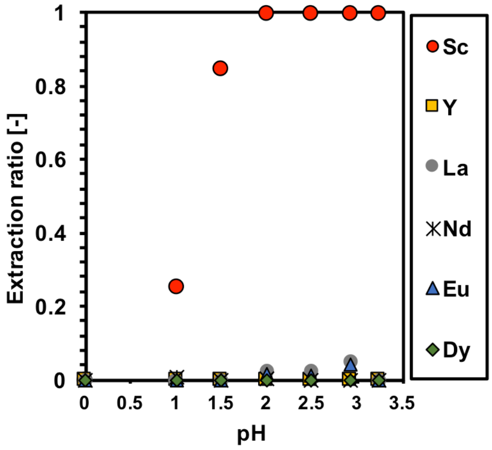

Figure 4. Extraction ratio of REE ions using 1 mM PC-88A+100 mM Versatic 10, an aqueous phase: 0.1 mM M^{n+}.

Interestingly, the binary system composed of 1 mM PC-88A and carboxylic acid extractant; 100 mM Versatic 10 delays the extraction of Sc ion more than the other binary systems used as shown in Figure 4. The addition of Versatic 10 to PC-88A causes the antagonistic effect i.e., the distribution coefficient of metal ions using the binary mixture is lower than the sum of that using the individual extractant. The extraction using only 100 mM Versatic 10 which attained less than 10 % extraction for Sc at pH 3.6. Shibata et al [7] reported the extraction of Sc using a high concentration of Versatic 10 (0.5 M) and quantitative extraction was achieved at high pH around 6. However, in the present study, we conducted extraction experiments in a low pH region to avoid the formation of Sc precipitation. It is proved in our study that the addition of Versatic 10 to PC-88A causes the antagonistic effect i.e., the distribution coefficient of metal ions using the binary mixture is lower than the sum of that using an individual extractant i.e ($D_{mix} < D_A+D_B$). We succeeded to carry out the selective extraction of Sc ion at an appropriate pH using the binary mixture 1 mM PC-88A+100 mM Versatic 10. Using the last binary system, we will overcome the problem of difficulty in the stripping process when using PC-88A alone as the extractant for Sc. In the case, a high acidic solution is required for both extraction and stripping processes and which also arises emulsification in the extraction operation [8]. After choosing the binary extractant; 1 mM PC-88A+100 mM Versatic 10 as the best combination to achieve the selective extraction of Sc at an appropriate pH. The stripping test was carried out from the Sc-loaded organic phases 1 mM PC-88A and the binary extractants with different nitric acid concentrations 0.5 M HNO_3, 0.75 M HNO_3, 1 M HNO_3 and 2 M HNO_3 at O/A=1, and at room temperature. Table 1 illustrates the stripping ratios after extraction. We found that 96% of scandium could be stripped from the binary mixture, whereas 49% of scandium was stripped from 1 mM PC-88A with 0.75 M HNO_3. The addition of Versatic 10 to PC-88A succeeded to achieve the complete scandium stripping with a mild acid consumption in one step, while 2 M nitric acid is required for achieving stripping of Sc from a 1 mM PC-88A solvent. Different acids were used to compare the stripping ability from the loaded organic phases and the stripping efficiency was increased in the order $HNO_3 \geq HCl > H_2SO_4$. It was confirmed that the stripping efficiency was improved using the last binary system rather than using PC-88A alone and the reason is the antagonistic effect, which could be due to the possible interaction between the two extractants in the organic phase that reduces available amount of free PC-88A ready for extraction.

Table 1. Stripping of Sc ion from the loaded organic phase .

Extraction systems (mM)	$[HNO_3]$(M)			
	0.5	0.75	1	2
[PC-88A] (1 mM)	30%	49%	60%	90%
[PC-88A] (1 mM) + [Versatic 10] (100 mM)	86%	96%	100%	100%

4. Conclusion

The extraction behavior of rare earth metal ions was investigated using several binary extractant systems composed mainly from PC-88A and another extractants, which follows a different mechanism for rare earth metals extraction. PC-88A is an acidic extractant, which interacts with a metal cation via a metal complex formation at very low pH. On the other hand, primene JM-T, TBP and Cyanex 272 are basic, solvating and acidic chelating agents, respectively. When mixing the two extractants, the new binary mixture could exhibit interesting behavior of synergism or antagonism towards the rare earth extraction as in case of adding primene JM-T, Cyanex 272 and Versatic 10 or shows no obvious change as for adding TBP. The addition of carboxylic acid type Versatic 10 to PC-88A causes the antagonistic effect that managed to achieve the selective extraction of scandium at anappropriate pH and improved stripping efficiency using a mild acid concentration overcoming the difficulties resultant from using PC-88A alone for extraction. In conclusion, among the studied binary combinations, PC-88A and Versatic 10 system is the best candidate to attain both high extraction and stripping under favorable conditions. The new binary system achieves high selectivity, high loading efficiency, and prevents crud formation at the interface, indicating its potential for economic industrial applications.

Acknowledgments

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