Binary extractant system for the recovery of rare earths and the application to environmentally-friendly separation processes

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In the name of Allah, the beneficent, the Merciful

{Say work soon will Allah observe your work and His Messenger and the believers}

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Chapter 1

Introduction

1.1 Rare earth elements

Rare earth elements (REEs), are a group of 17 elements, (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) as well as yttrium and scandium as shown in Table 1.1. These elements are existed in same ores, and have similar chemical properties.[1-2] Currently, they have been increasingly applied in many industrial applications such as magnets, batteries, alloys, electronic materials, nuclear materials and so on.[3-6] They have become important in green technologies including hybrid cars and wind turbines.[7] The name 'rare earth' is unsuitable as some of them are abundant in earth crust falling between copper and gold. However, still they are not concentrated enough in ores to allow a processing method and so the extraction of rare earth is typically challenging task. It is worthy to mention that the rare earths usage had been increased recently, where five of the elements were listed as critical to the clean energy economy.[8] Usually, the industrial applications of REEs require one or two elements, therefore, it is necessity to separate some of the targeted metal ions individually from others. Due to their chemical similarity during REEs, it is a notoriously difficult mission. For example, dysprosium was named after the greek word dysprositos, means hard to get.[9] The REEs are dominated the trivalent oxidization state in the aqueous solution except for Ce, Pr and Tb can be tetravalent (IV) where, Eu, Sm, and Yb are divalent (II).

The phenomena of lanthanide contraction, the ionic radius gets smaller moving across the periodic table from light to heavy elements, if applied in separation techniques could progressively separate REEs from each other.[10] The heavy elements are hard Lewis acids and strongly interact with hard Lewis base extractants. Nowadays, Organophosphorus extractants such as EHEHPA commercially known as PC-88A (2-ethylhexyl phosphonic acid, mono-2-ethylhexyl ester) is widely used in solvent extraction (SX) techniques for the recovery of various metal ions.[11] Thus, the development of an efficient extraction system of REEs is crucial

to sustain the continuous demand. Notably, China is the leader in providing the REEs till 2010,[12] but because of the high prices and increased applications, the world is focusing on new strategies for the recovery from effluents and industrial wastes that often contains several contaminants.

Table 1.1 The periodic table.

1 H 1.007																	2 He 4.0
3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.0	8 O 15.99	9 F 18.99	10 Ne 20.17
11 Na 22.98	12 Mg 24.30											13 Al 26.98	14 Si 28.08	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.98
19 K 39.0983	20 Ca 40.078	21 Sc 44.95591	22 Ti 47.86	23 V 50.94	24 Cr 51.99	25 Mn 54.93	26 Fe 55.84	27 Co 58.93	28 Ni 58.69	29 Cu 63.54	30 Zn 65.40	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 78.9	35 Br 79.9	36 Kr 83.79
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.94	43 Tc [98]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.8	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.7	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.90	56 Ba 137.327	71 Lu 174.96	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	103 Lr [262]	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [269]	109 Mt [268]	110 Ds [271]	111 Rg [272]	112 Uub [285]		114 Uuq [289]				

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 151.9	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.93	68 Er 167.3	69 Tm 168.9	70 Yb 173.1
89 Ac [227]	90 Th 232.03	91 Pa 231.03	92 U 238.02	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]

Scandium (Sc), is a silvery- white metallic rare earth element with the atomic number 21. It is a rare element, and is very expensive metal because of its scarcity and the complicated purification and recovery processes. The hydrated ions of Sc are Pearson hard acids that prefers hard ligands such as phosphates, sulfates, hydroxides and fluorides for complexation. It is ranking as the 31st most abundant element in the earth's crust, with 22 ppm as a crustal abundance.[15] It was discovered in 1879 from gadolinite and euxenite minerals of Scandinavia. [16] Sc presents as trace element in minerals in small quantities to allow scandium recovery for

production process, therefore, the supply of Sc is very limited. Currently, Sc is recovered as a by-product from many processing tailing wastes for example, uranium leach liquors, dusts in chlorinating magnetovanailmenite, titanium pigment production waste liquors, red mud, tungsten refinery residues, etc. Nonetheless, Sc is widely applied in many industrial applications, for example, aluminium–scandium alloys, high-intensity metal halide lamps, electronic components, solid oxide fuel cells, analytical standards, oil well tracer, fuel cells, and lasers.[17] Recent applications of scandium, especially in laser research, inaugurated much interest in the production of high-purity product and improving the current recovery methods.

1.2 Hydrometallurgical separation methods

As mentioned above, the increased number of application of rare earth metals inaugurated the development of new techniques for their recovery from the alternative sources (mainly industrial wastes). There are various methods that can be applied for this purpose, for instance, the pyro metallurgical and mechanical methods have high costs due to energy consuming. In addition, additional stages are required for cleaning gas system and dust collection where it is less versatile comparing to the hydrometallurgical processes. On the other hand, the hydrometallurgical separation processes are consisted of many steps; leaching (dissolve in acid/ or base), purification and recovery of the targeted metal ions from the leach liquor. For the purification step of the hydrometallurgical method, precipitation, solvent extraction known as (liquid – liquid extraction) and ion exchange are used in the mining industries nowadays. Whereas, an electrolysis and precipitation methods are widely used for the final metal recovery after purification step. The common methods used for metal extraction from aqueous solutions will be summarized briefly in this chapter.

1.2.1 Precipitation

Far before 1947, both the reduction and oxidation with the fractional precipitation technique were the available methods for separating the rare earth metals. The precipitation method in general is based on the formation of insoluble salts with a particular anion, such as Cl^-, CO_3^-, SO_4^{-2}, Thus, one metal can be separated from others by precipitation. There are no

specific differentiation categories between insoluble salts, sparingly soluble, and soluble salts, but concentrations of their saturated solutions are small, medium, and large. However, solubility products are known for insoluble and sparingly soluble salts, but they are not listed for soluble salts as it is bigger.

The commercial separation of rare earths in 1950, made use of precipitation along with solvent extraction and ion exchange as precipitation method alone proved to be inefficient and laborious.[13] Now, the precipitation is also involved commercially to precipitate the stripped rare earth ions. The dissolved REEs in the stripped aqueous phases are stripped with inorganic salts, followed by precipitation as oxalates or carbonates. Worthy to say that stripping and precipitation are accompanied to solvent extraction till now.[14] However, precipitation method alone is not enough to attain highly purity product, and further processing is needed.

1.2.2 Solvent extraction

In a solvent extraction technique, the metal ion solution is mixed with an organic phase represented in Figure 1.1. The extractant used in the organic phase is responsible for the transfer of metal ions or targeted metal ion to the organic phase. Therefore, the choice of extractant is the key for successful extraction for a specific metal ion. It is widely applied for the industrial applications. One of the earliest studies to separate REEs by solvent extraction was performed by Gupta, 1992.[13] The method is continued till now for the REEs separation. However, the individual separation between REEs is still difficult by solvent extraction as this method depending on the complex formation affinity between a metal and an extractants, and most REEs are similar in chemical behavior.[18]It is better to apply a chemical reaction e.g. a redox reaction during the extraction process of REEs to improve their separation abilities. Nishihama et al, studied the separation between Eu from Sm/Eu/Gd using EDTA (ethylenediaminetetraacetic acid) as a complexing agent while applying a photochemical redox reaction that instantly improve the extraction process.[18] There are many important factors governing the performance of solvent extraction process such as pH, solvent, temperature,

contact time and extractant choice. Among them, extractant is very important therefore, we will explain in details latter.

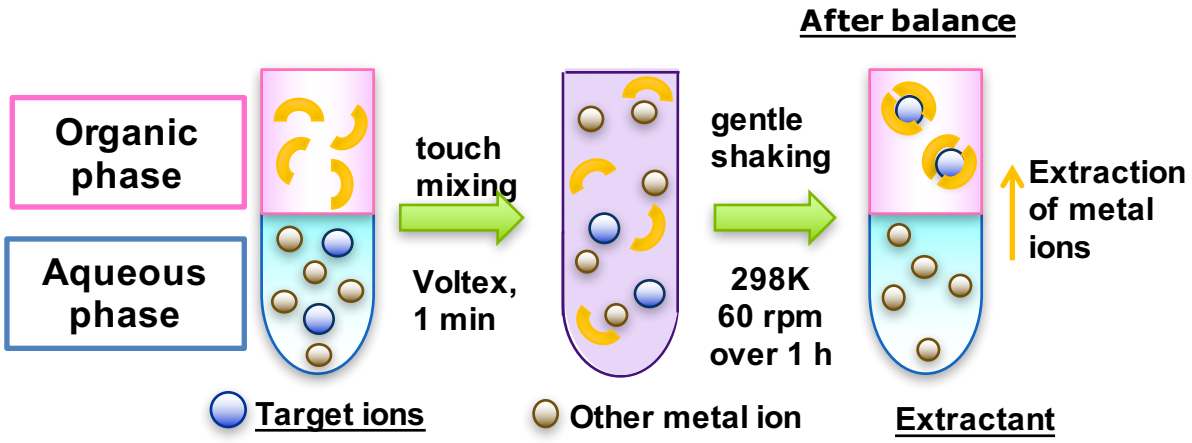

Figure 1. 1 A representative scheme for the solvent extraction technique.

1.2.2.1. Extractant

The extraction ability is dependent on the structure and properties of extractant. The extractant can be acidic, basic, solvating, chelating and synergistic system. Many extractants were employed in the recovery of REEs and other metal ions as will be briefly reviewed.

1.2.2.1.1. Acidic extractants

A review of the solvent extraction of the rare earth elements was recently reported by Xie et al. (2014).[19] The review demonstrated that PC-88A (EHEHPA or 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) is most widely used as the extractant, which is a cation exchange reagent. The extraction mechanism is shown in (Eq. 1.1):

$$RE^{3+} + 3\,(HA)_2 \rightleftharpoons RE(HA_2)_3 + 3H^+ \qquad \textbf{(1.1)}$$

Generally, sodium hydroxide or ammonia is used to drive the equilibrium in Eq. 1.1 to the right, and extract the heavier element(s). Scrubbing is usually accomplished using either a portion of the loaded strip, or an acid. In the stripping operation, the acidity is increased to shift the equilibrium back to the left, causing the heavier elements to be recovered to an aqueous solution.

In fact, there are two important drawbacks and shortcoming for the based processes using PC88A. The first is the high acidity required for the stripping of heavier elements ~ 5M

HCl or more[20], which increases the cost and environmental hazards of the separation. In addition, the separation factors of PC88A, while greater than for most rare earth extractants, are considerably smaller compared with most commercially viable processes. For example, the separation factor for uranium from iron(III) using a tertiary amine is in excess of 9000. [21]The separation of cobalt and nickel was historically difficult, however a separation factor of approximately 7000 can be achieved using Cyanex 272.[22] By contrast, the average separation factor for a pair of adjacent lanthanides is 3.6, and is as low as 1.6 for the Nd/Pr separation. [23] This means that many equilibrium stages must be used to achieve a good degree of separation, and a large amount of rare earths are recycled through the scrubbing section.

Despite these issues and concerns, PC88A remains the solvent of choice for rare earth extraction processes. In China, the separation plants are basically consisted of 50 stages for the 15 REEs separation with hundred mixer settlers [24] and about 1000 stages in total.[25] Clearly, both the CAPEX and OPEX would be reduced if an extra work is done to enhance the separation factor during the REEs. On the other hand, the stripping acidity will also be reduced alternatively, resulting in a saving in the OPEX. An alternative commonly used solvent in the in separation circuits in China is naphthenic acid.[20] The main advantage of this extractant compared with the organophosphorus extractants is the selective extraction of yttrium, often more concentrated than the other heavy rare earths, is shifted from Ho/Er toward the lighter rare earths.[26-27] This enables the selective extraction of Y ions from the other heavy rare earths. Scandium has a different coordination number and complex formation with PC88A rather than other rare earth elements. Sc(III) is selectively extracted than lanthanides, cerium and thorium by PC88A in 1-5 M acidic solutions of both hydrochloric and nitric acids along with iron extraction. It is worthy to illustrate that the stripping from PC88A is easier than that of D2HEPA (di-2-ethylhexylphosphoric acid). Striping with 5 M H_2SO_4 achieved 20% and 5% stripping percentage from PC88A and D2HEPA, respectively. Regardless the high affinity of acidic phosphorus extractants from acidic solutions towards Sc, Iron is also selectively extracted. As both iron(III) and Sc are similar in their Lewis acid hardness.[38] Moreover, many ions interfere

with Sc separation such as zirconium, titanium, thorium, yttrium, and lanthanides. The larger impurities co-extraction induces a difficulty in stripping while emulsion formation limited the potential application in industry.[38] Table 1.2 summarized the extraction behavior of Sc along with other elements by different extractants. The results confirm that despite scandium extraction efficiencies with HDEHP and PC88A are high, scandium stripping efficiencies are very low.[38]

Table 1.2 Extraction of Sc and other metals by acidic organophosphorus extractants.

Extractant	pKa	Organic Solution	Aqueous feed Solution	Selectivity	Ref.
PC88A	3.36	0.2 M Ionquest 801 and 1% TBP	pH 1–5.5 H_2SO_4	$Sc^{3+} > Zn^{2+} > Al^{3+} > Mn^{2+} \sim Cr^{3+} \sim Ca^{2+} \sim Mg^{2+} > Ni^{2+} \sim Si$	31
		0.1 M PC-88A in toluene	0.01–1 M $HClO_4$	$Sc^{3+} > Fe^{3+} > Al^{3+} > Mg^{2+}$	32
		EHEHPA and Cyanex 272	1.0 M ionic strength (NaCl / HCl)	(Ce~ Pr ~Nd ~ Sm~ Tb~ Dy~ Ho~ Er ~ Yb~ Lu ~Y)	33
HDEHP	2.16	20% HDEHP, 15% TBP and in kerosene	2.5 g L−1 Sc, 25 g L−1 Mg, Al and Fe and 0.5 M HCl	$Sc^{3+} > Fe^{3+} > Al^{3+}, Mg^{2+}$	34
		0.2 M D2EHPA and 1% TBP in Escaid 110	pH 1.5–3.5 H_2SO_4	$Sc^{3+} \sim Zn^{2+} > Ca^{2+} \sim Al^{3+} > Mn^{2+} > Cr^{3+} \sim Mg^{2+} \sim Ni^{2+} \sim Si$	31
		Purified HDEHP in n-octane	pH 3–10 M HCl	$Sc^{3+} >> Fe^{3+} > Lu^{3+} > Yb^{3+} > Er^{3+} > Y^{3+} > Ho^{3+}$	29
		0.75 M HDEHP in n-heptane or cyclohexane	1–11 M HCl, $HClO_4$ or HNO_3	$Sc^{3+} \sim Ti^{4+,} Zr^{4+}$, Hf $^{4+} > Y^{3+} > La^{3+} > Mn^{2+}$	30
Cyanex 272	5.32	4.8 × 10−2 M Cyanex 272 in n-hexane	2 × 10−4 − 6 × 10−4 M metals, pH 3–10 M H_2SO_4	$Sc^{3+} \sim Th4^{+} > Fe^{3+} > Lu^{3+}$	35
		0.1 M Cyanex 272 and 5% TBP	pH ~1 H_2SO_4	$Sc^{3+} >> Al^{3+} > Ni^{2+} > Si > Mn^{2+} \sim Mg^{2+} \sim Ca^{2+} > Cr^{3+}$	31
Cyanex 302	4.32	4.8 × 10−2 M Cyanex 302 in n-hexane	2 × 10−4 − 6 × 10−4 M metals, pH 3–10 M H_2SO_4	$Zr^{4+} > Sc^{3+} > Th^{4+} > Fe^{3+} > Lu$	36
Cyanex 301	3.86	4.8 × 10−2 M Cyanex 301 in n-hexane	2 × 10−4 − 6 × 10−4 M metals, pH 3–10 M H_2SO_4	$Zr^{4+} > Sc^{3+} \sim Fe^{3+} \sim Th^{4+} > Lu^{3+}$	36

Based on Shan et al [37] and Wang and Cheng [38]

The table also shows the study of extraction behavior of Sc ion in presence of Zr(IV), Th(IV), Fe(III) and Lu(III) using bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301).[31, 36, 37] The experiments conducted in sulfate media with the last mentioned three extractants showed metal selectivity's in the order Zr(IV) > Sc(III) > Fe(III) > Lu(III) at low acidities.[38] Their extractabilities were lower than that of HDEHP, due to the higher values of pKa. Correspondingly, the stripping of Sc(III) from Cyanex 272, Cyanex 302 and Cyanex 301 was much easier than that from HDEHP and PC88A.[35,36] Haslam and Arnall[31]studied the separation of Sc(III) from a laterite waste solution using D2EHPA, Ionquest 801 and Cyanex 272.[38] Their stripping results agree with that of Wang and Li.[36] that stripping of scandium from Cyanex 272 was achievable using 300–400 g/L sulfuuric acid (90% stripped), while stripping of scandium from D2EHPA and Ionquest 801 (PC-88A) with sulfuric acid was difficult.[38]

Alkyl-monocarboxylic acids such as naphthenic acids and Versatic acids (e.g. Versatic 9, Versatic 10 and Versatic 911) are commercially used.[38] Naphthenic acids are widely used for rare earth extraction. Some researchers investigated the extraction of scandium from iron using 5–10% carboxylic acid where the stripping was achieved with a high concentrated hydrochloric acid.[38-49] However, there are some problems associated with carboxylic acid such as the high affinity to iron at pH around 3 and an emulsion formation resulting in slow phase separation. [50] Thus, preliminary removing of iron is required prior to the extraction with naphthenic acid. Aluminium was another co-extracted element that must also be removed before the extraction process of rare earths as it was completely extracted at pH 4.

1.2.2.1.2 Basic extractants

Basic extractants are mainly amines including primary amines (RNH_2), secondary amines (R_2NH), tertiary amines (R_3N), and quaternary ammonium salts ($R_3N^+CH_3X^-$). These extractants had affinity to the anionic species of metal ions in the aqueous phase, therefore, the

metal could be extracted via an anion exchange mechanism.[39] Primary amines such as Primene JMT and N1923 (RNH_2) were studied for the extraction behavior of Sc and REEs from wastes.[30-31] Primene JMT was found to be effective for the recovery of Sc from an uranium mill waste in a pilot scale. In the plant operation, 2.5% Priemene JMT in kerosene was applied as the extractant with the aqueous to the organic ratio 50:1 for the extraction process. Scandium could be extracted contaminated with ferric ions that could be selectively separated by selective stripping by 2M NaCl acidified to pH 1. Whereas, R_2NH was applied to a solution constitution of Sc (III), Ga, Tl(III), Bi, Sb(III), Cr(III), Cu(II), Fe(III), U(VI), Ce, Zr, In, Th and Ti). Primene JMT, tri-iso-octylamine, tributylamine and tribenzylamine were also examined, but found to be unsatisfactory for several reasons. Kovalancik et al, studied the separation of both La and Sm by benzyldibutylamine (BDBA) from 6 M $NaNO_3$ and 0.5 M HNO_3. The separation was weak and improved by the addition of a complexing agent, 2-hydroxyethylethylenediaminetriacetic acid (HEDTA).[42] The basic extractant is less powerful comparing to that of the acidic extractant.

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1.2.2.1.3. Solvating extractants

Solvating extractants are those extractants that contain either C=O or P=O groups like ketones, ethers and phosphate. They participate in the metal extraction process through the the neutral inorganic molecules solvation in the organic phase or by complexation with the electron-donor-groups in the extractants.[39] For instance, the selective extraction of Sc(III) from Fe(III), Mo(VI), V(V), Cr(VI), Ti(IV), Bi(III), Zr(IV), Ln(III) and Th(IV) was carried out using mesityl oxide (4-methyl-3-pentene-2-one, MeO) as the extractant from the sodium salicylate ($C_6H_4(OH)COONa$) solution at specific pH.[43] Neutral organo-phosphorus compounds are commonly used, which are four kinds of trialkylphosphate $(RO)_3P\ O$, dialkyl-alkylphosphonate $(RO)_2RP\ O$, dialkyl-alkylphosphinate $(RO)R_2P\ O$, trialkylphosphine oxide $R_3P\ O$. In which the electron density of the phosphoxyl group decreases in the order phosphates > phosphonates > phosphinates > phosphine oxides.[44] Whenever, tri-butyl phosphate (TBP) is commonly used for the recovery and separation of rare earth elements including scandium. However, there are some

problems for the extraction process such as the high acidity range, high co-extraction of zirconium especially with Sc. These disadvantages result in the impractical usage of TBP, for example, complete extraction of Sc(III) can be attained only using higher than 8 M HCl, whereas iron was also completely extracted, suggesting the difficulty in Fe/ Sc separation.[45]

1.2.2.1.4. Chelating extractants

Chelating extractants contain coordination functional groups such as CO, N-, and N- or acidic functional groups such as –OH, NOH, and –SH. Several literatures reported the recovery of yttrium, lanthanides, scandium, and transition metals by acidic β-diketone type extractants, such as thenoyltrifluoroacetone (HTTA) and 1-phenyl3-methyl-4-benzoyl-pyrazolone-5 (1-phenyl-3-methyl-4-benzoyl5-pyrazolone, 4-benzoyl-3-methyl-1-phenyl-2- pyrazolin-5-one, HPMBP).[46,47] The extraction occurs with chelating mechanisms. In addition, the aqueous anions can participate in the extracted complex is done with a mechanism as solvating mechanism. For the recovery of scandium from manganese and iron, reduction of iron is preliminary required. Then quantitative extraction of scandium by HTTA in the pH range 1.8–2.0 was achieved. [48]

1.2.2.1.5. Synergistic extractants

A synergistic solvent can be defined as a mixture of two reagents in the same diluent. Upon mixing these two different extractants, two possible results are assumed. First, an increase in the distribution ratio of the mixture compared with the sum of the individual contribution of the extractants.[51] The second is called the antagonistic effect, the distribution ratio of the mixture is less than the sum of the separate extractants.[52] In general, the synergistic mixture is applied to bind to a specific element to enhance the poor extrability. Strong extractants for rare earth metals are already commercially available such as (EHEHPA or PC-88A: 2-ethylhexyl phosphonic acid, mono-2-ethylhexyl ester) at very low pH. However, if synergism or antagonism themselves would represent significant enhancement in the separation factors or result into more facile stripping, then the continuous circuit of rare earths would be smaller and

cheaper. The synergism phenomenon has been studied since the 1950s. DEHPA (di-2-ethylhexyl phosphoric acid)/TOPO (tri-n-octyl phosphine oxide) mixture is industrially applied for the uranium separation as a part of DAPEX process.[53] Whilst, the synergism for lanthanide extraction was reported by Cunning- ham et al. in 1954,[54] since that plentiful combinations; binary extractants have been examined.

It is well known that the extraction strength of rare earth is increased from light to heavy elements due to the steady increase in the ionic radius through the same period. This phenomenon is called lanthanide contraction, that makes them harder moving to the right and strongly interacted. This is noticeable for organophosphorus acids extractants that heavier elements are strongly interacted with the oxygen donors of the extractant, and caused difficulty in rare earth separation from each other. Lanthanides are hard Lewis acids and therefore interact with hard bases such as those containing oxygen donors. Further, Yttrium has an ionic radius between that of Ho and Er, and acts as heavier elements in its chemistry.[51] The reverse is observed with the carboxylic acids such as naphthenic acid, where the extraction strength increases from the light to the heavy rare earth elements.[55]

Likely, there have been numerous studies about the binary systems for the lanthanides extraction. More than 184 papers (roughly) could be found that used different types of extractant mixture. It will be difficult to present all, still some prominent combinations will be discussed in this work. One of the remarkable review of the chemistry of lanthanide/actinide separations was carried out by Nash in 1993.[56] Despite the target of this review was for separating transplutonium actinides from lanthanide fission products for nuclear fuel reprocessing, it examined the intra-lanthanide separation techniques focusing on synergism. The review literally stated that synergism "rarely achieves much enhancement in selectivity for a given group or in the mutual separation of members of the groups".[56] The review by Lumetta et al. (2010) on using acidic and neutral reagents for lanthanide/actinide separation tackled the research papers only for lanthanide/actinide separation.[57] Therefore, it gave less insights on

lanthanide/lanthanide or lanthanide/ contaminants separations.

Li et al, 2013. reviewed the work done in rare earth separation in one of his conference papers.[58] He and his group at the state key lab of rare earth resource utilization, Changchun, China, are working on the synergistic systems for rare earth separation. Mainly, they are using three sets of binary mixtures; a mixture containing a phosphinic acid (Cyanex 272) and a phenoxyacetic acid (CA-12), a mixture of two organophosphorus acids, and a mixture of a cation exchanger with an alcohol modifier. They also applied the bifunctional ionic liquids for the rare earth recovery.[59] This group is examining the most relevant synergistic systems for the industrial application of rare earth separation.

As I stated, many mixtures have been applied for rare earth separations such as mixtures of cation-exchange/neutral extractants, mixtures of cation-exchange/cation-exchange extractants, mixtures of cation-exchange/anion exchange extractants, mixtures of neutral/neutral or neutral/anion exchange extractants. We summarize the solvent combinations that had been previously studied focusing only on the mixtures that one of them is organophosphorus acid based on their importance as strong extractants, commercial, and industrial application for rare earth elements. In this regard some points are very critical such as:

- Identifying the solvent combinations for rare earth and determining the combinations that have not yet been examined.
- Comparing the separation factors between rare earths and other contaminants.
- Figuring out the mechanism of extraction and the chemistry of separation
- Studying the experimental techniques.

Mixture of DEHPA and Cyanex 923 (a liquid alkylphosphine oxide mixture) showed synergistic effect for Ce (IV) extraction from sulfate media at a 4:1 ratio of Cyanex 923: DEHPA.[60] The same extractant when mixed with PC-88A with a 1:2 ratio was used to recover cerium (IV) from other rare earths in sulphuric acid leach solutions.[61] Whereas, stripping of Ce

was difficult that was run in two times and using H_2O_2 for reduction, followed by sulphuric acid. The famously DEHPA-TOPO system was applied to extract rare earths from phosphoric acid solutions along with uranium.[62] Alternatively, when TOPO was added to PC-88A instead of DEHPA, an antagonistic for yttrium was observed.[63] Sun and Meng investigated the extraction of La, Nd, Gd, Y and Yb, and noted both synergism and antagonism effect depending on the pH in the extraction process.[64] Recently a new combination of PC-88A and isooctanol was applied for heavy REEs, that enhanced the stripping behavior and the separation factors between Er, Tm and Yb.[58] Actually, this improvement in stripping ability is related to the antagonistic effect, where the mechanism of antagonism was deduced as the formation of hydrogen bonding between the alcohol and phosphonic acid in the binary extractant system.

Additionally, the Cyanex 923 and Cyanex 272 mixture was tested o improve the selectivity for heavy rare earths over yttrium in nitrate media.[65] However, the separation factors were relatively small for the mixture comparing to that of the solely Cyanex 272 and couldn't be used for this target. Similarly, adding Cyanex 923 to Cyanex 301 (dithio-substituted analogue of Cyanex 272) was tried for the same aspect.[66] Whereas, the combination of TOPO to Cyanex 272 enhanced lanthanum extraction from nitrate solution. [67] Ramakul et al. (2009) applied the combination TBP (tributylphosphate) and Cyanex 272 for rare earth separation but the study didn't discuss the separation factors among them.[68] On contrary to other research, these mixture system was found to be selective for yttrium rather than the others. Eu extraction was enhanced with the synergistic system composed of TBP and Cyanex 301.[69] Meanwhile, a mixture of bis(chlorophenyl)dithiophosphinic acid (a deriva- tive of Cyanex 301) and tris(2-ethylhexyl) phosphate preferred for the light over middle and heavy REE elements.[70] Adding TBP to bis(chlorophenyl)dithiophosphinic was investigated for lanthanide/actinide separation. Banda et al. (2012) examined mixtures of Cyanex 272 with neutral (TBP, TOPO, dioctyl sulphide), cation-exchange (Cyanex 301, Versatic 10 (neodecanoic acid)) and anion- exchange (Alamine 336, Alamine 308 (trioctyl/decylamine)) extractants for the separation of Pr and Nd from La.[71] They had not studied the extraction mechanism while the pH was not controlled.

Even, the separation factor wasn't determined for the studied elements. However, adding Versatic 10 seems to increase the distribution ratio. Mixtures of Cyanex 272, EHEHPA and DEHPA with Cyanex 923, Alamine 336 and Aliquat 336 were examined by Kim et al. (2012).[72] They reported that the binary mixture didn't increase the separation abilities between heavy and middle rare earths, and they used the combined separation factor not the individual so, we can't judge the whole process. Panda et al. (2013) studied a mixture composed of Cyanex 272 and TOPO/Cyanex 923, however, the slope analysis was different than that of other research works with the same extractants.[73]

Sudersanan[74] reported the synergistic extraction of scandium with HTTA and HDEHP, on contrary to Hirashima et al., who examined the antagonistic effect for the HTTA and TBP system.[75] Despite, the several literature reports for the extraction of lanthanides with different kinds of extractant, until now, only limited information has been reported for scandium. Due to the chemical similarities between scandium(III) and lanthanides(III), it is reasonable to postulate that mixture solvent systems should also demonstrate synergism/antagonism for the extraction of scandium or at least express new characteristics. Therefore, the solvent extraction of scandium with binary system is a possible direction to be studied in the future. Some synergistic systems for scandium(III) and lanthanides(III), based on literature are summarized in Table 1.3.

Table 1.3 Some synergistic systems for scandium(III) and lanthanides(III), based on literature are summarized.

		Cation Exchangers							Neutral extractants					Anion exchangers		
		DEHPA	*EHEHPA*	*Cyanex 272*	*Cyanex 301/302*	*β-diketones*	*Carboxylic/ Phenoxyacet*	*Other*	*Phosphine Oxides*	*TBP*	*Phen/Bipy*	*Crown Ethers*	*Others*	*Amines*	*Quaternary Ammonium*	*Others*
Cation Exchangers	*DEHPA*		76	78	79		80	81	62	82	83	84	72	85	94	86
	EHEHPA			72	87		88	89	61					72	59, 95	
	Cyanex 272		33		71, 77		90	78	73,67, 72,73	68				71, 72	91, 95	92, 93
	Cyanex 301/302						96	97	66	98	69		70	99	100	
	β-diketones						101		54	102	103	86	101	105	105	106
	Carboxylic/ Phenoxyacetic							107	108	109	110		111	85	112	113
	Others							114	115		116	117	118	119	120	
Neutral Extractants	*Phosphine Oxides*									121						122
	TBP									123						
	Phen/bipy															
	Crown ethers												124			
	Calixarenes															
	Others														125	

Based on the results in Table 1.3 we found the following points; the majority of the binary systems in the literature review is composed mainly of at least one cation exchanger, and either neutral, anion or cation exchange extractants. The synergism is decreased along the period in the periodic table using the neutral oxygen donor extractants. This could be due to the steric hindrance and the higher hydration energies, that lowers the separation factors gradually and makes it very difficult to separate the REEs apart. However, the synergism is increased with increasing the basicity of the oxygen donor. The antagonism was reported for some nitrogen donors extractants. In addition, the mixtures of phosphonic and phosphinic acids have been reported by Quinn et al, 2017, predominantly due to a reduction in stripping acidity compared with EHEHPA. At the same time, some authors asserted that the mixture has synergistic effect, which appears to be contradictory. The mixture system was studied for the rare earth separation and hadn't shown the desired separation factors. Ionic liquids composed of a quaternary ammonium cation/deprotonated acid anion have received some attention in recent years. It could slightly increase the separation factor between Nd/Pr, and ease the stripping to some extent. A binary system composed of carboxylic acid extractants such as sec-octylphenoxyacetic acid sec-nonylphenoxyacetic acid showed new characteristics in light and heavy rare earth elements separation. Upon mixing these extractants with Cyanex 272 (organophosphorus acids), dominated the separation of yttrium from heavy rare earths. The combination of a phenoxyacetic acid and TOPO improved the separation of LRE over HRE. From the above summary, we found the promising synergistic system. The mixture used is a mixture of Phosphonic acid and Versatic 10 that caused reduction in stripping acidity compared with PC-88A. Antagonism is noted for RE extraction rather than synergism.

Our main target in this study is to examine the effectiveness of the mixture system towards the industrial applications for Sc recovery. Despite the literature review displayed numerous research work in lanthanide extraction, the experimental work did not focus on effective stripping of Sc. Furthermore, they focused on the synergism phenomena itself as new trend rather than the overall improvement of the process conditions. Therefore, the subsequent

experimental studies in this work focused mainly upon investigating systems that haven't been proposed before, and could be industrially applied to overcome the stripping difficulties. Three classes of techniques were examined, as will be presented in Chapter 2,3 and 4 namely solvent extraction, polymer inclusion membrane and extractant impregnated resin.

On the other hand, there are some literature gaps and uncertainties that need further investigation. Antagonism should result in a decrease in stripping acidity, not an increase – why is this the case? What is the performance of individual extractant at process relevant and metal concentrations? How does the mixed extractant compare with that of PC-88A alone in Sc/ REEs separation process? Why does a binary mixture exhibit different characteristics? These questions will be answered in this work.

1.2.3 Liquid membranes

The many limitations in the traditional solvent extraction process such as consuming highly amounts of organic solvents, highly acidic concentrations, emulsion formation or third phase, and so on inaugurated the application of new strategies for metal processing.

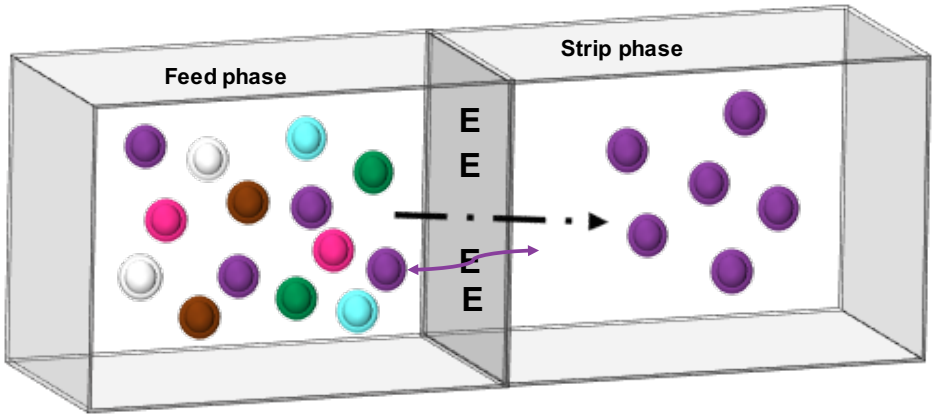

Figure 1.2. Schematic diagram of selective transport of metal ion through a liquid membrane.

In recent years, the membrane technology gained a big attention in separation and recovery of metal ions from aqueous solutions[126] because of its energy efficiency, flexibility, low cost, environmental regulations and controlled permeability. Liquid membrane extraction (LME) is a technique for the separation of metals (solutes) in double-system as represented in

Figure 1.2. There are many kinds of liquid extracting membranes, such as supported (SLM), emulsion (ELM), bulk (BLM), polymer inclusion membrane (PIM) and hollow fiber liquid membranes (HFSLMs). BLMs based on putting immiscible membrane (usually an organic solvent) between two phases (aqueous solutions), but it had small exposed surface area that limits their wide applications .[127] SLMs resemble BLMs but the organic phase is incorporated into a macroporous polymer and are considered an effective method for extraction and pre-concentration of metal ions. The main disadvantages of SLMs are the low stability and the potential release of the impregnated organic solvent to the enclosing solution due to many reasons like emulsion formation, solubility and others. HFSLMs are more favorable technique that are selective, have a larger surface area compared with that of SLMs, low extractant consumptions and one step process.[128]Although HFSLMs acquire good qualities, they exhibit deficient stability[129] that limits their industrial applications. ELMs are considered energy saving technique that provide high surface area for extraction, one step process, high speed, efficiency and large scale application, only have a disadvantage in maintenance due to the high volume ratios.[130]

There are many reports on the application of hollow fiber liquid membrane towards the extraction of some rare earths. For example, Liang et al [131] studied the transport of Dy^{3+} from HCl solution using PC-88A as a carrier, Prakorn et al [132] used the same mass transport theory of Liang et al to separate La^{3+} and Ce^{3+} using D2EHPA as an extractant. Whenever, Jingui et al [133] also used D2EHPA to transport Ce^{3+} from sulfuric acid media using emulsion liquid membrane. Recently, ELMs were also used to transport Dy^{3+} [134] and other mixed REEs [135] under different conditions of a carrier and an aqueous feed. An experience acquired until now in the use of SLMs in the separation of REEs; however, research papers on scandium transport is very limited. Many papers manipulate the transport of yttrium metal ion through a supported liquid membrane using TOPO [136], EHPA [137] and PC-88A [138]. Liang et al [139] conducted the transport of Tm^{3+} with PC-88A using a dispersion supported liquid membrane at slightly high pH. SLMs were also used to investigate the transport of other rare metal ions such as neodymium [140],

dysprosium [141], praseodymium [142] and europium [143]. The fluxes of some rare earth metal ions (Sc^{3+}, Y^{3+}, La^{3+}, Sm^{3+} and Lu^{3+}) has been supplied using different carriers to study the ions' permeation through SLM between two compartments, one contained 1 mM rare earth nitrate and 0.1 mM sodium acetate buffer, and the second contained 1 mM rare earth nitrate and 0.05 M sulfuric acid. [144] The main aim of that study was to study the permeation efficiency in respect of carrier composition rather than transport experiment because both sides contained the same metal ions concentration. Meanwhile, the transport of Sc^{3+}, Sm^{3+}, Gd^{3+} and Al^{3+} had been reported by Cherkasov et al [145] using SLM with aminophosphoryl and diphosphinylpiperazine carriers. The results showed the transport of scandium when changing the diffusion parameters of feed phase, but indicated the incomplete extraction and transport of scandium ion.

The major drawbacks reviewed above associated with liquid membranes, rendered the impractical applications in the large scale. For this regard, PIMs are considered a promising separation method with high stability, selectivity, efficiency and durability. [146]

PIMs are prepared by casting a solution containing an extractant, plasticizer and a base polymer such as cellulose triacetate (CTA) or poly(vinyl chloride) (PVC) to form a flexible and stable film of membrane. Then, the resultant membrane can be applied to separate the solutes of interest in a similar way of SLMs. The lowe diffusion rate of diffusion coefficients can be overcome by preparing thinner PIMs in comparison to the traditional supported liquid membranes. Additionally, it is possible to prepare a negligible carrier loss PIM that is very difficult in the traditional liquid membrane method. Where, the amount of carrier can be obviously reduced that reduced the overall costs of used extractants, that will no doubt provide a wider range of applications for PIMs. Consequently, this will enable the PIM based systems to exhibit incredible advantages such as ease of operation, flexibility in membrane composition and minimum use of hazardous chemicals as well as separation efficiency. The outstanding performance of PIMs in comparison to other kinds of membranes, promotes increasingly number of research to be industrially applied in the near future. It is reflected by the increased

research using PIM reported over the last decades. Given the advantages of PIMs compared to other kinds of liquid membranes, they are good candidates for industrial applications.

The facilitated transport of some rare earths [147] was studied using PIM, where extractants such as ß-diketones, hinokitiol (HIPT) and flavonol, polyoxyethylene n-alkyl ethers (POEs), N,N,N`,N`-tetraoctyl-3- oxapentanediamide (TODGA), octyl(phenyl)- N,N-diisobutylcar-bamoylmethylphosphine oxide (CMPO), and D2HEPA were examined towards the recovery of some rare earth elements. Few studies have been conducted on the use of PIMs for rare earth metal ions separations. PIMs were also applied for the transport of actinides [148] and other heavy metals [149] There is no published research about the transport of Sc using PIM till now. Therefore, it is important to carry on extra research work on the transport of rare earth metal ions for more efficient PIMs applications.

Even though, the research done to investigate the extraction behavior of Sc by other kinds of membranes is very limited. The recovery of Sc^{3+} from Fe^{3+} was achieved using emulsion liquid membranes containing bis (2,4,4-trimethylpentyl) phosphinic acid and a polyamine surfactant N205 in n-heptane.[150] In this case, the concentration is very low compared with that of other ions, thus, the membrane technology could attain higher capacity for recovery, higher yields, suitability for Sc- pre-concentration. However, the disadvantages of LME such as the emulsion instability resulting in mixing both the feed and the receiving phases. The use of a hollow-fiber contactor avoids the re-mixing problems and attain fast extraction, but large capital costs and fouling are still existing problems.

On the other hand, for the extraction of scandium using strong extractants that are known with high affinity such as HDEHP, PC-88A and HTTA as liquid membrane carriers, the carriers are poisoned with time because of the accumulation of metal ions in the membrane, which cannot be stripped at the interior interface of the membrane.[151] Therefore, these extractants can't be beneficial in applications for the recovery of scandium due to stripping obstacle, and only used in a conventional solvent extraction process with the previous

mentioned disadvantages. The need for developing membraned with good stripping ability is crucial for the industrial applications.

1.2.4. Ion exchange

The separation using ion exchange resin is another environmentally-friendly method like membrane techniques because organic solvent is not used in the process. As with solvent extraction, the functional group of the resin that binds to the metal ion is the key to the efficient separation and recovery of target ions. However, there are not so many types of commercial resin, and the conventional ionic exchange technique sometimes suffers from several disadvantages such as incomplete elution, slow exchange rate, and poor recyclability of ion exchange resins. The long time consuming due to the slow rate of exchange as well as the high operation costs are also problems for industrial applications. Separation and recovery of scandium from red mud, which contains the high concentration of other metal ions, is the typical case. The reason that the resin loses its selectivity due to the accumulation of the large amounts of contaminants and consequently the resin effectiveness is reduced significantly. [152] All these reasons deemed the technique inefficient for the effluent treatment containing high metals concentration.

Recently, impregnated resins have been widely studied for the recovery of rare earths. [153,154] The impregnated resin technology could overcome the subsequent problems of using solvent extraction such as emulsion formation, extractant loss, and many complicated cycles. There are two methods for the preparation of the impregnated resins either by the polymerization of styrene and divinylbenzene in the presence of the extractant [155,] or directly the extractant is adsorbed onto the polymer support, formulating the solvent-impregnated resins.[156] The commonly used extractants for this purpose are organophosphorus and alkyl phosphoric acid, with a simple mechanism of adsorption for the targeted metal ion, as shown in Figure 1.3.

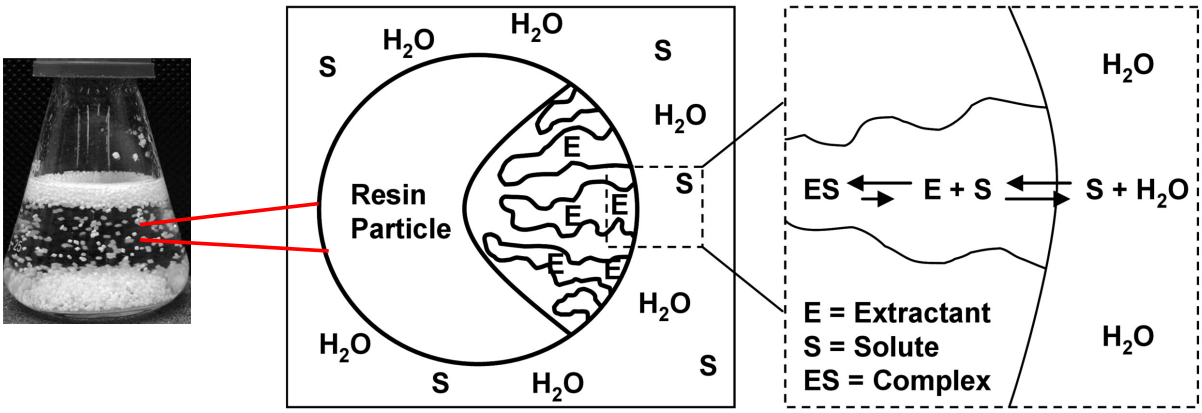

Figure 1.3. Simple representation for the resin mechanistic adsorption of solute from aqueous solutions.

The adsorption and desorption of some rare earths were examined in many research papers, where the elution was also possible under mild acidic conditions. On contrary, Sc recovery is still a challenging task to be achieved due to the very stable complexes between Sc and acidic organophosphorus extractants that is difficult to be stripped within the elution step. A D2HEPA (Lewatit VP OC 1026) impregnated resin was applied for the recovery of Sc from iron manganese. Scandium was selectively extracted from a wolframite leach liquor with a PC88A-impregnated resin with Amberite XAD resin beads.[157] The study reported the separation factors between scandium and other common metal ions including calcium, aluminium, manganese, yttrium, antimony, and iron. However, the Sc-HEHEHP could not be eluded except with 4-methyl-2-pentanone/ then precipitated with 10 equimolar amounts of oxalic acid in ethanol. Korovin et al [153] reported the adsorption of scandium with a high capacity TVEX resins containing TBP or di-isooctyl methyl phosphonate (DIOMP) supported on a porous matrix. The resin showed higher capacity due to the extraction of scandium in multiple complexes. The co-extraction of uranium with scandium occurred upon using the nitrogen–phosphoruscontaining ampholite resins.[154] Scandium could be only eluted with 150 g L^{-1} Na_2CO_3 followed by precipitation with an excess concentration of 20–30 g L−1 NaOH solution.

On the other hand, the PC88A impregnated resin was applied for the separation of Tb, Dy, Ho, Y, Er, Tm and Yb from the heavier rare earth residue.[158] The study investigated the individual separation of targeted REEs using column method with impregnated PC88A into the

macro porous resin, Amberlite XAD-7. The extraction occurred at very low pH due to the high affinity of PC88A, which means the difficulty of elution. However, the elution of individual rare earth metal ions was successful with changing the pH and concentration of the elution reagent. The solvent impregnated resin was also applied for the extraction of Lithium ion, [159] heavy metals and alkaline earth metals.[160]

As mentioned, the impregnated resins are suitable for extraction from tailing wastes, red mud and ore pulps. Therefore, more applications for scandium extraction could be possible if we able to enhance the elution, which are usually difficult for direct application of conventional solvent extraction techniques.

1.3 Research aim and thesis organization

The aim of this thesis is to develop a binary extractant system to enable the separation and recovery of scandium as the model case of metals which are difficult to recover, and to applied the extractant system to the environmentally-friendly membrane separation and ion exchange systems. The present graduation thesis is composed of 5 chapters, which are the general introduction in Chapter 1, and the research achievements in Chapter 2, Chapter 3 and Chapter 4 and the general conclusion in Chapter 5, together with references and acknowledgement.

Chapter 1 is a general description on the rare earths and the hydrometallurgical separation techniques, such as solvent extraction including the binary extractant systems, the membrane separation and ion exchange separation systems.

In Chapter 2, combinations of the strong extractant PC-88A with other extractants were screened and separation and recovery of scandium were examined using the selected binary extractant PC-88A and Versatic 10.

Chapter 3 describes the application of the binary extractant system to a polymer inclusion membrane (PIM) and the separation of rare earth metals including scandium was examined.

In Chapter 4, impregnated resin with the selected binary extractant was prepared and applied to the separation and recovery of rare earth metals including scandium.

Chapter 5 describes the overall conclusion based on the research results presented in Chapters 2, 3 and 4.

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Chapter 2

Selective extraction of scandium by a long alkyl chain carboxylic acid/organophosphonic ester binary extractant

2.1. Introduction

Scandium (Sc) is a rare earth element (REE) and it is found in the same ore as lanthanides. Compared with lanthanides, Sc has a smaller ionic radius and forms more stable complexes.[1] Sc has important uses in high-technology industries. For example, it is used in alloys [2] and metal halide lamps. Sc occurs in low concentrations in deposits, although it is produced as a by-product in many effluents from tailing and industrial processes. The applications of Sc are increasing, requiring alternative techniques for Sc separation to fulfill the demand.

In hydrometallurgy, solvent extraction is a useful technique to separate metal ions from metal leaching solutions. The extractant used in the solvent extraction process is the key for efficient separation of metal ions. Organophosphorus extractants, such as di-(2-ethyl hexyl) phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (commercial names PC88A and IONQUEST 801), and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), are widely used for separation of REEs. [3–6] The studies reported that D2EHPA is not only selective for Sc and quantitative extraction of other metals occurred under the same experimental conditions, which could interfere with Sc separation. A binary extractant system of D2EHPA and TBP (Tributyl phosphate) has also been used to recover Sc from HCl media.[7] It achieved quantitative extraction of Sc, but unfortunately stripping of Sc was not successful for any concentration of hydrochloric acid. The difficulty in stripping, co-extraction, and emulsion formation has limited the use of D2HEPA in industrial applications. Extraction of Sc and other REEs has also been investigated using Cyanex 272 and its thiosubstituted analogues bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) and bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301).[8–11] The extraction efficiencies with the aforementioned extractants are lower than that of D2EHPA, but the stripping efficiencies are

higher. The maximum stripping efficiencies of Sc^{3+} after one time contact with Cyanex 272, Cyanex 302, and Cyanex 301 are around 82%, 78%, and 75% with 1.5 M, 3.5 M and 5.8 M sulfuric acid, respectively.[9,10] Complete stripping of Sc from a Cyanex 302 organic loaded phase can be achieved using 5 M nitric acid,[12] which is a high acid concentration for the stripping process. PC88A exhibits high versatility, chemical stability, and offers a high separation factor similar to D2HEPA, while lower stripping acidity is required than for D2HEPA.[13] Extraction of Sc can be performed with 1–5 M acids (HCl, H_2SO_4, and HNO_3) and Sc can be quantitatively extracted with PC88A. The stripping efficiency from the PC88A solvent using mineral acids is higher than that from D2EHPA: 20% of loaded Sc can be stripped from the PC88A solvent by 5 M H_2SO_4 compared with only 5% from the D2EHPA solvent.

As described above, the scandium extraction efficiency with PC88A is sufficiently high but the efficiency of scandium stripping is quite low. In such a case, antagonistic extraction is considered to be effective. Combining two different extractants sometimes shows different characteristics than the original extractants alone as simplified in figure 2.1. If the combination enhances the extraction behavior it is called synergism,[14] where the distribution coefficient of the extractant mixture is higher than the sum of those of the individual extractants. The opposite phenomenon is called antagonism that could lower the overall metal loading.[15] In our preliminary study[16] the different types of reagents such as Versatic 10, Cyanex 272, TBP and an alkyl primary amine (Primene JM-T), were examined as antagonists to PC88A, and Versatic 10 was found to be effective for the recovery of scandium, that is, the combination is appropriately delayed the pH of extraction.

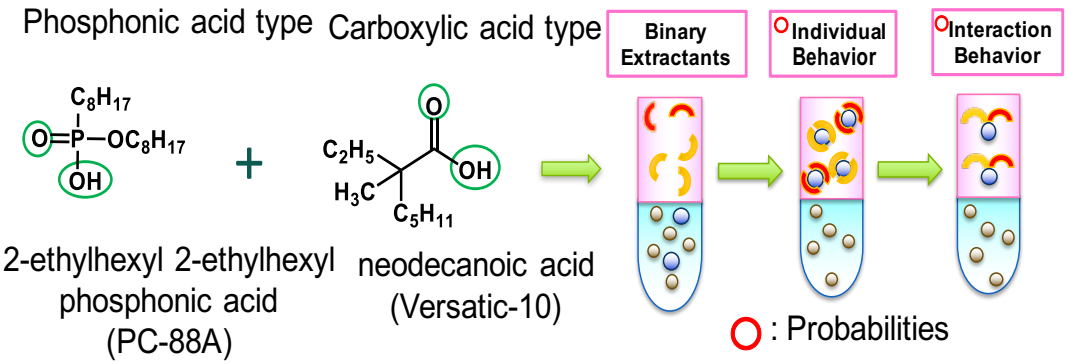


Figure 2.1. A simplified representation of possible behavior of binary extractant mixture.

In this study, the antagonistic effect of a binary combination of PC88A and Versatic 10 was investigated for the selective extraction of scandium from other REEs in nitrate media. The extraction mechanism was investigated for scandium in the mixture extractant system to clarify the cause of the antagonistic effect. Another important factor is the potential stripping efficiency using a low acidity solution, which is generally difficult for the PC88A system. The effect of adding Versatic 10 on the stripping efficiency was also examined. The results provide a reference data for the addition of carboxylic acids to organophosphonic esters. In the future, the data could be used to develop methods for REE extraction to completely overcome the crud formation appeared using PC88A alone.

2.2. Experimental

2.2.1 Materials and reagents

PC88A and Versatic 10 were supplied by Daihachi Chemical Co., Ltd. (Osaka, Japan) and Japan Epoxy Resin (Tokyo, Japan) (currently Mitsubishi Chemical Corporation), respectively, and used without further purification. C_6D_6 and the nitrate salt of the REEs were provided by Sigma-Aldrich Co,. LLC. *n*-Dodecane, nitric acid, and ammonium nitrate were purchased from Kishida Chemical Co. Ltd (Osaka, Japan). All of the other chemicals were of analytical grade.

2.2.2. Extraction experiments

The extraction experiments were performed with aqueous solutions containing 0.1 mM of each REE ion (Sc^{3+}, Y^{3+}, La^{3+}, Nd^{3+}, Eu^{3+}, and Dy^{3+}), Or Sc and some common metals (Fe^{3+}, Mn^{2+}, Co^{2+}, and Ni^{2+}). The aqueous phases were prepared by dissolving 0.1 mM of each metal salt in 0.1 M HNO_3 and 0.1 M NH_4NO_3, adjusting the pH by mixing the two solutions and/or by adding 1 M HNO_3. The organic phases were prepared by dissolving a given amount of PC88A and/or Versatic 10 in *n*-dodecane as a diluent. All of the extraction experiments were performed with a 1:1 organic to aqueous ratio, 1 h shaking at 160 rpm in a thermostatic shaker at 25 ℃ to attain equilibrium, and centrifuging for 5 min to assure phase separation. The equilibrium pH was measured using a pH meter (H-M-60 G, DKK-TOA Co.). The metal ion concentrations in the aqueous solution were determined by an inductively coupled plasma (ICP)-atomic emission spectrometry (Optima 8300, Perkin Elmer Inc., MA, USA). The extraction ratio (E [-]) and distribution coefficient (D [-]) of the metal ions were calculated by

$$\boldsymbol{E} = \frac{C_{\mathrm{M,ex,eq}}}{C_{\mathrm{M,aq,init}}} = \frac{C_{\mathrm{M,aq,init}} - C_{\mathrm{M,aq,eq}}}{C_{\mathrm{M,aq,init}}} \quad (\mathbf{2.1})$$

$$\boldsymbol{D} = \frac{C_{\mathrm{M,ex,eq}}}{C_{\mathrm{M,aq,eq}}} \quad (\mathbf{2.2})$$

where C_M is the metal concentration. The subscripts ex and aq represent the organic extraction and the aqueous phase, and init and eq represent the initial and equilibrium states, respectively.

The stripping experiments of the metal-loaded phase were performed in the same way as extraction with acid solution, and the degree of stripping was calculated from the ratio of the ion concentration stripped to the initial metal concentration in the organic phase.

2.2.3. NMR analysis

To investigate the interaction between PC88A and Versatic 10, ^{1}H NMR measurements were carried out for the organic phases prior to any extraction process using Bruker VA300 at 300

MHz. The spectra were internally standardized to trimethylphospite. C_6D_6 was added to the organic samples prior to NMR analysis with a percent (90:10 sample/C_6D_6) for locking. Then, ^1H NMR was recorded for the individual and binary extractants dissolved in n-hexane as diluent.

2.2.4. FT-IR analysis

To investigate the interaction between PC88A and Versatic 10, FT-IR measurements were performed using a Spectrum 65 FT-IR spectrometer (PerkinElmer Co., MA, USA) for the organic phases in carbon tetrachloride as a diluent before extraction. The spectra were obtained using thirty-two scans from 400–3500 cm^{-1} with a resolution of 4 cm^{-1}. The spectra were recorded for the individual extractants and binary mixtures. All of the scans were performed using a KBr cell to discuss the changes in the hydrogen bonding.

2.3. Results and discussion

2.3.1 Investigation of various binary systems

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 extraction as explained before.

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 (Figure 2.2), to confirm whenever the selective extraction and recovery of Sc(III) from other

rare earth metals can be achieved by using other mixtures rather than the previous reported mixture of PC-88A and an alkyl-monocarboxylic acid, Versatic 10.

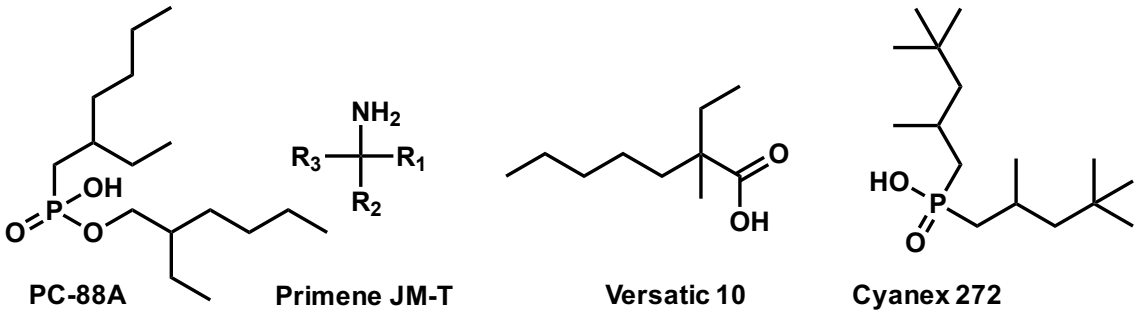
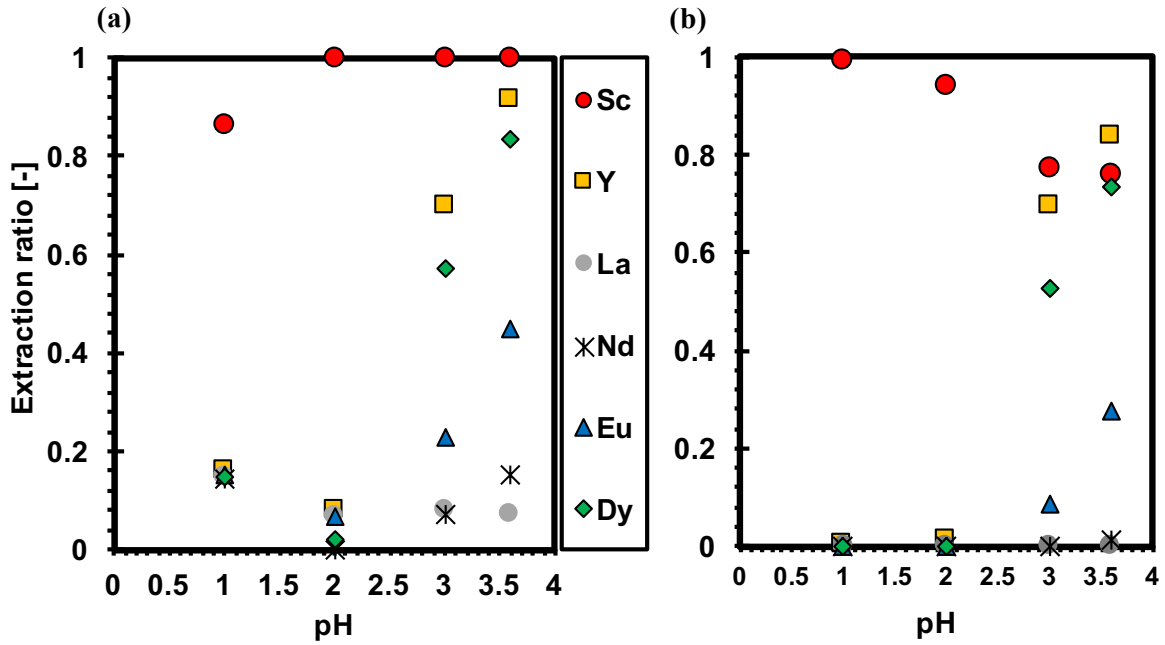


Figure 2.2. Molecular structures of extractants used in this study.

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 2.3. Figure 2.3 (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 (antagonism) 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 2.3 (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 however, 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 2.3 (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.

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



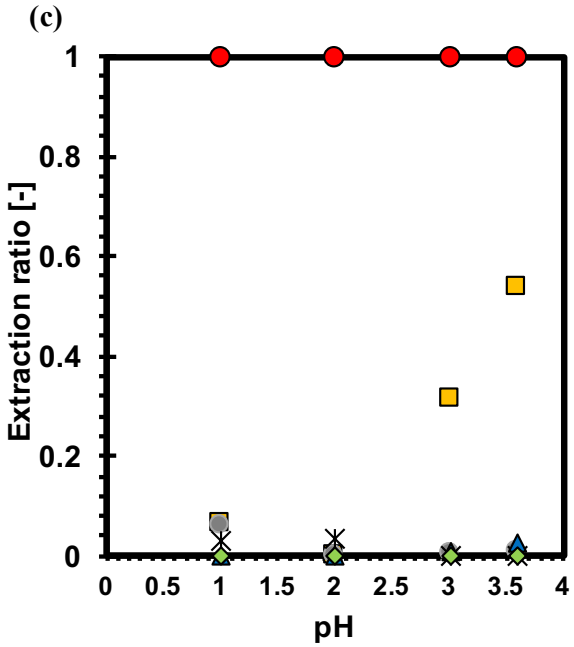


Figure 2.3. Extraction ratio of REE ions using (a) 1 mM PC-88A and 5 mM primene JM-T, (b) 1 mM PC-88A and 5 mM Cyanex 272 and (c) 1 mM PC-88A and 5 mM TBP in n-dodecane. Aqueous phase: 0.1 mM Mn+.

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 2.5. The extraction was performed using only 100 mM Versatic 10 which attained only 8.8% extraction for Sc at pH 3.6. Shibata et al [25] reported the extraction of Sc using a high concentration of Versatic 10; 0.5 M but the quantitative extraction was obtained at high pH value equal to 6 which is not favored condition due to the potential precipitation of Sc in the aqueous phase over pH 4. It is proved in our study that the addition of Versatic 10 to PC-88A causes the antagonistic effect i.e., the distribution ratio of metal ions using the binary mixture is lower than the sum of that using an individual extractant i.e ($D_{mix} < D_A+D_B$). However, 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, which is considered to be adequate. Using the last binary system, we will overcome the problem of difficulty in the stripping process using PC-88A alone as an extractant. In the case, a high acid solution is

required for both extraction and stripping processes and which also arises emulsification in the operation. 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.

2.3.2. pH isotherms for the individual extractants

The extraction behavior of the individual extractants was investigated for 0.1 mM REE/0.1 M HNO_3 solutions. Using only the PC88A extractant, Sc was quantitatively extracted with 5 mM PC88A, and around 20% was even extracted using 1 mM PC88A at pH = 0 under the same conditions, as shown in Figure 2.4 (a) and (b). Quantitative extraction of Sc^{3+} at high acidity is considered to be an obstacle for performing the stripping operation because it generally requires a high acid concentration. Extraction of the other REEs was promoted with both increasing pH and increasing PC88A concentration. The experimental data show that PC88A extracts more Sc than the other REE ions, which could be because of its much smaller ionic radius and coordination number compared with that of the other REE ions. Thus, PC88A forms a stable, coordinately saturated, and hydrophobic complex with Sc that is selectively transferred into the organic phase.

Figure 2.4 (c) and (d) show the extraction ratios of REEs from the same aqueous feed solution using 100 mM and 0.5 M Versatic 10, respectively. High-efficiency extraction of Sc (92%) is achieved using 0.5 M Versatic 10 at around pH 3.5. Figure 2.4(c) shows that the extraction efficiency of Versatic 10 is poor at low Versatic 10 concentration. PC88A has a low pK_a value (3.36),[17] which is responsible for effective extraction at low pH. In contrast, Versatic 10 has a high pK_a value (7.33),[17] which enables extraction in the high pH region, although Versatic 10 is highly selective for Sc^{3+} over the other REEs.

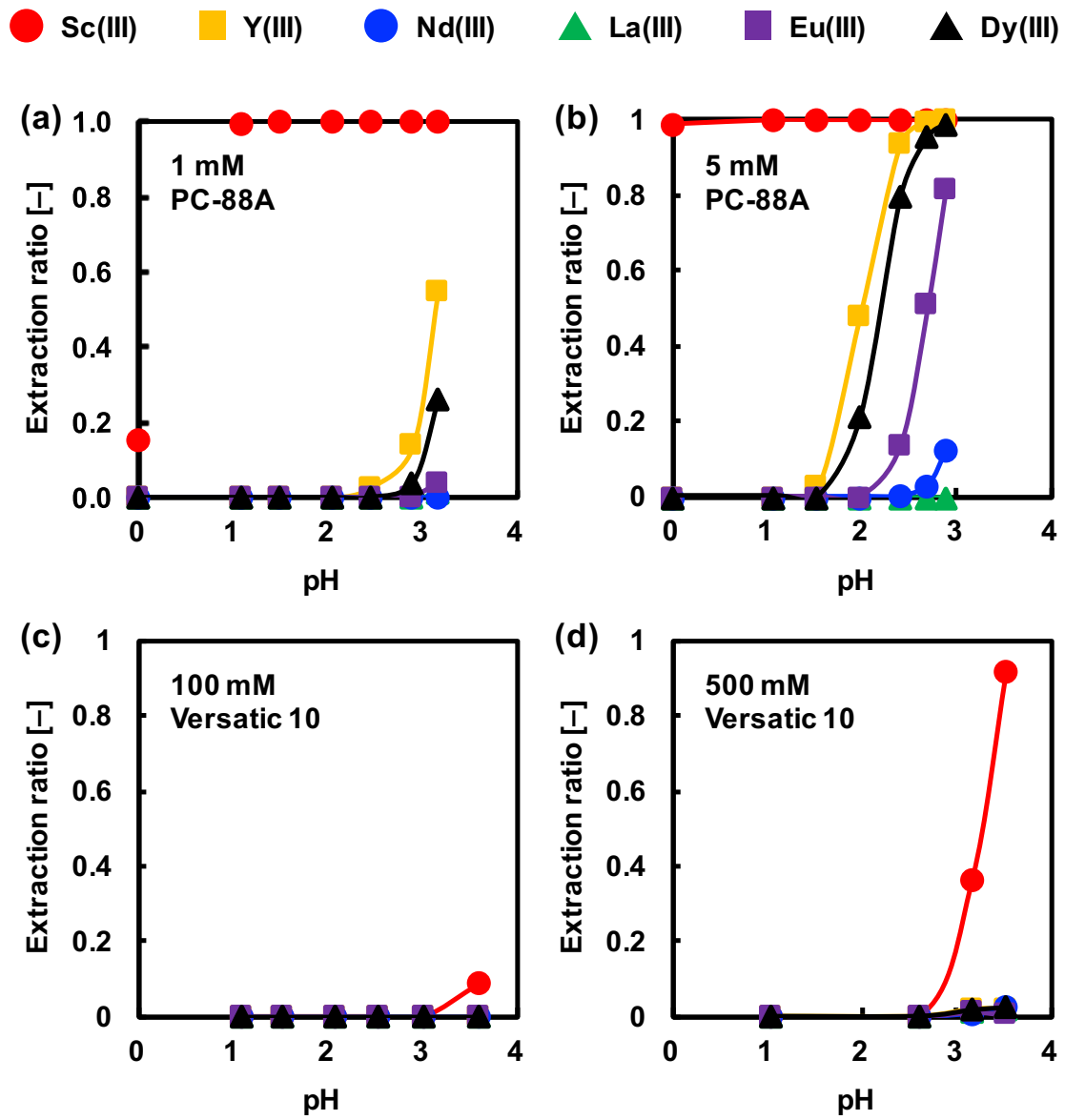


Figure 2.4. Extraction of 0.1 mM REE ions using (a) 1 mM PC88A, (b) 5 mM PC88A, (c) 100 mM Versatic 10, and (d) 0.5 M Versatic 10 (0.1 M nitrate media, organic/aqueous ratio = 1, 1 h shaking at 160 rpm and room temperature, and n-dodecane as the organic phase).

2.3.3. pH isotherm for the binary extractant

The extraction isotherm equilibrium of the binary mixture of PC88A and Versatic 10 was investigated. Figure 2.5 shows the effect of adding Versatic 10 to 1 and 5 mM PC88A on the distribution ratios of Sc^{3+}. Adding Versatic 10 increases the pH of extraction and decreases the extraction efficiency. When 100 mM Versatic 10 is added to 1 mM PC88A, the extraction curve shifts right compared with that of PC88A alone. Quantitative extraction of Sc is achieved

at around pH 2 and no extraction is observed at around pH = 0. The extraction performance decreases with increasing molar ratio of Versatic 10 in the mixed extractant. For 5 mM PC88A, addition of more than 0.5 M Versatic 10 is required to ensure the quantitative stripping in this system. It is clear that addition of Versatic 10 to PC88A causes the antagonistic effect, that is, the distribution ratio of the metal ions using the binary mixture is lower than that using only PC88A. However, we achieved selective extraction of scandium at an appropriate pH using the binary mixture (PC88A and Versatic10 at molar ratio 100). This suggests that using the binary mixture for extraction, the difficulties arising from using PC88A alone will be overcome, such as high acid consumption in the stripping process and the precipitate formation associated with the metal loading could be reduced by adding Versatic 10, as described later.

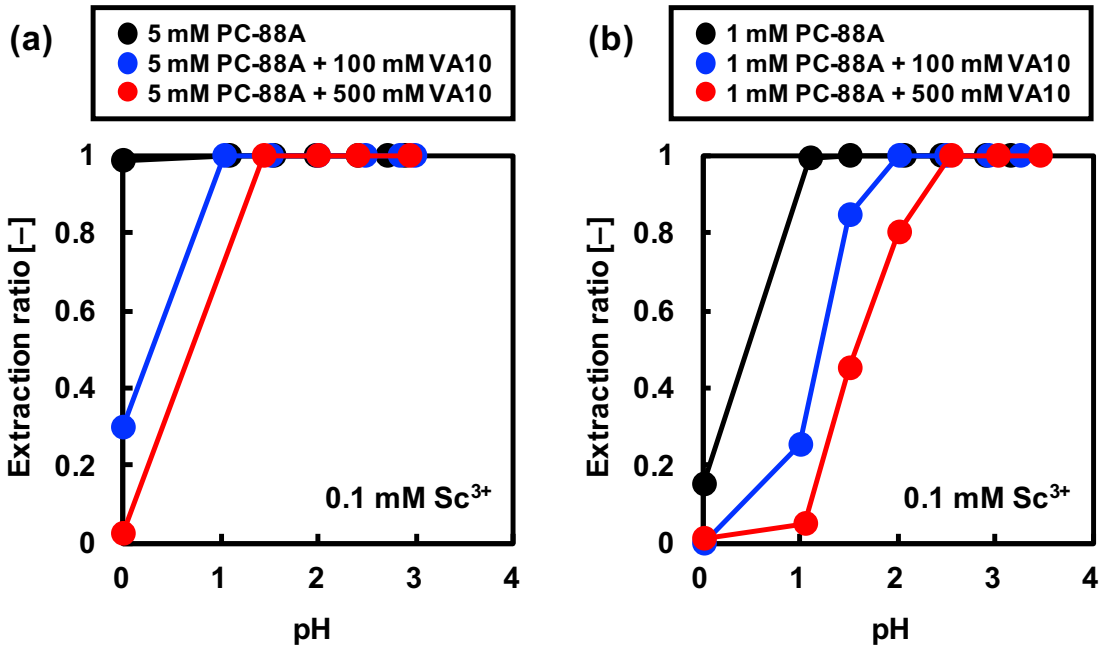


Figure 2.5. Extraction of 0.1 mM Sc^{3+} using (a) 5 mM PC88A, 5 mM PC88A/100 mM Versatic 10, and 5 mM PC88A/0.5 M Versatic 10, and (b) 1 mM PC88A, 1 mM PC88A/100 mM Versatic 10, and 1 mM PC88A/0.5 M Versatic 10 (0.1 M nitrate media, organic/aqueous ratio =1, 1 h shaking at 160 rpm and room temperature, and n-dodecane as the organic phase).

2.3.4. Slope analysis

Trivalent cationic extraction can be generally expressed by the following equation:

$$M^{3+} + 3HR_{(o)} \rightleftharpoons MR_{3(o)} + 3H^{+} \qquad (2.3)$$

However, phosphonic and carboxylic acids are known to exist as dimers.[18] Therefore, we can write the extraction equation for scandium in the individual PC88A as follow:

$$M^{3+} + 3H_2R_{2\,(o)} + \rightleftharpoons M(HR_2)_3 + 3H^+,\ K_{ex} \qquad \textbf{(2.4)}$$

In the presence of Versatic 10, PC88A interacts with Versatic 10 as described later. If Versatic 10 is involved in the extraction reaction, the extraction with the association form of PC88A and Versatic 10 like heterodimer could also occur under the experimental conditions as follows.

$$M^{3+} + 3H_2RA_{\,(o)} + \rightleftharpoons M(HRA)_{3,\,(o)} + 3H^+,\ K_{ex,m} \qquad \textbf{(2.5)}$$

where H_2R_2 and H_2RA are dimeric PC88A and the associate with Versatic 10, and K_{ex} and $K_{ex,m}$ are the equilibrium constant for Eqs. (2.4) and (2.5), respectively. The distribution ratio D is expressed by the Eq. (2.6);

$$D = ([M(HR_2)_3] + [M(HRA)_3])/[M] = (K_{ex}[H_2R_2]^3 + K_{ex,m}\,[H_2RA]^3)/[H]^3 \qquad \textbf{(2.6)}$$

Extraction of REEs using PC88A was reported to proceed with the relationship $D = K_{ex}[(HR)_2]^3[H^+]^{-3}$ at low organic loading with metal ions and at low acidity, that is, extracted species is $M(HR_2)_3$.[15,19-21] We investigated the extraction mechanism of PC88A alone under low scandium loading and low aqueous acidity. As shown in Figure 2.6 (a) and (b), the slope of the plot of log D against pH is almost equal to 3, and the slope of log D against log $[H_2R_2]_{(o)}$ is also 3, where the dimer concentration was calculated using the dimerization constant 3000 L/mol.[22] Based on these results, the extracted Sc complex with individual PC88A can be expressed as $Sc(HR_2)_3$.

Dimer equation calculations and new effect on mechanism

$$\boldsymbol{2HR \rightleftharpoons (HR)_2}$$

$$\boldsymbol{HR_0 = 2(HR)_2 + HR}$$

$$\boldsymbol{HR = HR_0 - 2(HR)_2}$$

$$\boldsymbol{K_d = {[(HR)_2]}/{[HR_0 - 2(HR)_2]^2}}$$

$Kd=3*10^{3}\ dm^{3}/mol$

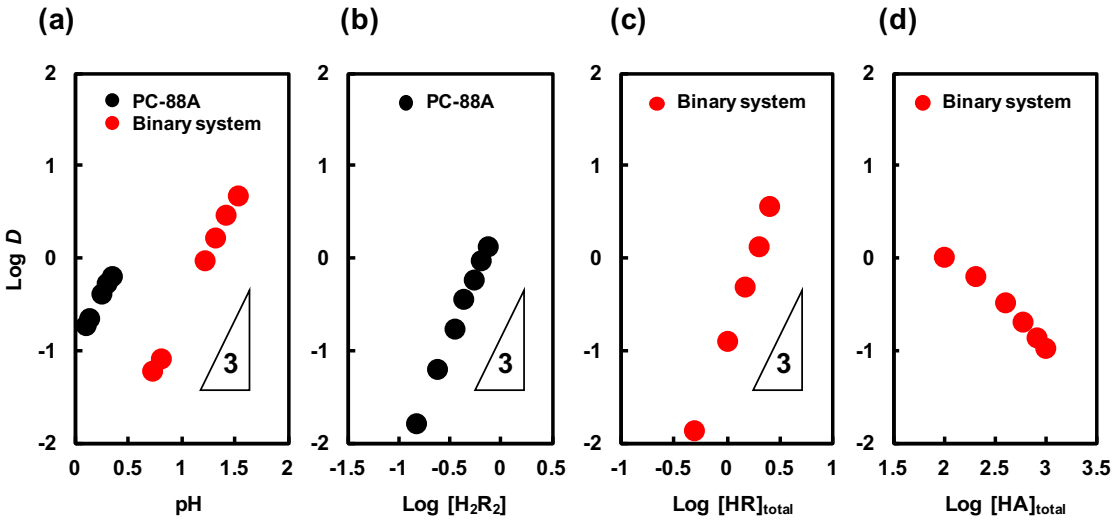


Figure 2.6. (a) Plots of log *D* against pH for 1 mM PC88A and the binary mixture. (b) Plot of log *D* against log $[H_2R_2]$ for a system containing only PC88A; [PC88A] = 0.5–2 mM at pH_{eq} = 0.06. (c) Plot of log *D* against log $[HR]_{total}$ for the binary mixture; [PC88A] = 0.5–2.5 mM and [Versatic 10] = 100 mM at pH_{eq} = 0.8 and (d) Plot of log *D* against log $[HA]_{total}$; [Versatic 10] = 100–950 mM and [PC88A] = 1 mM at pH_{eq} = 1.2 in *n*-dodecane with 1 h shaking at 160 rpm and room temperature. HR and HA are referred to PC88A and versatic 10, respectively.

For the binary mixture (1 mM PC88A/100 mM Versatic 10), the plot of log *D* against pH is a straight line with a slope of 3 as for PC88A alone (Figure 2.6(a)). Figure2.6 (c) shows the plot of log *D* against log$[HR]_{total}$, where $[HR]_{total}$ is the total concentration of PC-88A. A straight line with a slope near 3 is obtained, suggesting that the major extracted species is $Sc(HRA)_3$, because most PC88A is expected to interact with Versatic 10 and the concentration of the associate increases in proportion to the initial PC88A concentration under the experimental conditions. Furthermore, *D* is found to decrease with increasing the concentration of Versatic 10, as shown in Figure 2.6(d). Versatic 10 alone cannot extract Sc^{3+} under the experimental conditions. It can get involved in the extraction of the metal ion in the presence of PC88A as the dimer with PC88A. The addition of Versatic 10 leads to decrease the concentration of PC88A dimer, which has a high affinity to REE ions, increasing the association

form of which coordination ability is lower than that of dimeric PC88A. Thus Versatic 10 shows a negative effect on the extraction of REEs, including Sc^{3+}.

In particular, the extraction efficiency of Sc significantly decreases by adding Versatic 10 (Figures 2.5). An antagonistic effect has also been reported for extraction of indium by a mixture of D2HEPA and octanoic acid,[23] which is compatible with this study.

A loading test for Sc^{3+} was performed to help understanding the extraction mechanism for the individual PC88A (1 mM) and binary extractant (1 mM PC88A+100 mM Versatic10) systems. Figure 2.7 shows the relationship between the concentration of loaded Sc^{3+} and the initial concentration in the aqueous phase at pH 2, where quantitative extraction of Sc^{3+} can be attained for both extractant systems where, Versatic 10 alone shows zero extraction. Although the loading capacity is the same for the two systems up to near 0.2 mM loading, the binary system has a lower loading capacity after 0.2 mM owing to possible interaction between the extractants. The precipitation was appeared before 0.2 mM loading when using PC88A alone and increased upon higher loading, however addition of Versatic 10 to PC88A delays the formation of the precipitation as shown in Figure 2.7. The phosphinate polymer precipitate was reported upon loading the organic phase containing acidic organophosphorous extractants with rare earths that caused many drawbacks in the industrial applications. [15]

The effect of nitrate ion in the feed solution was also examined. A negative effect on Sc extraction was observed, which is considered to be caused by decreasing the tetravalent Sc ion content due to the complex formation with nitrate ion as illustrated in Figure 2.8.

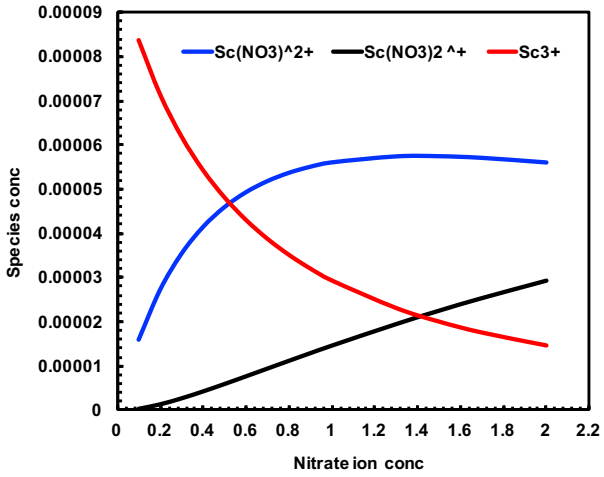


Figure 2.8. Scandium ion speciation in aqueous nitrate solution dependent on the nitrate ion concentration.

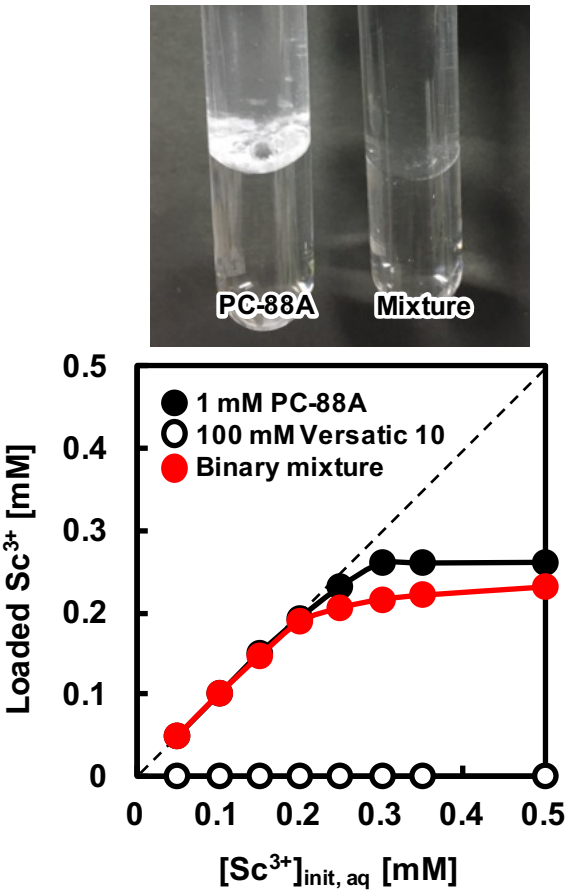


Figure 2.7. Sc^{3+} loading tests on 1 mM PC88A, 1 mM PC88A/100 mM Versatic 10, and 100 mM Versatic 10 at pHeq = 2 from 0.1 M nitric. The picture shows the precipitate occurred using only PC88A and vanish using the binary system at the same experimental conditions.

An experimental loading capacity that exceeds the maximum theoretical loading (0.166 mM) with PC88A could be due to the change in the extraction mechanism with high metal loading. Tomita et al.[24] reported formation of a 1:6 complex of D2EHPA at a high extractant concentration, and a 1:3 complex formed at high loading where solid crystals appeared. They found that the complex formed between one metal ion and three D2EHPA monomers at high metal loading has high density and rapidly agglomerates to form a polymeric film. Therefore, the high loading capacity of PC88A may be because of participation of monomers in the extraction process at high metal concentration. In the presence of Versatic 10, it could overcome the deficiency of PC88A because Versatic 10 molecules participate as the modifier and enable the Sc complex to be solubilized in the organic phase, although the loading capacity of the extraction phase is limited because of the ability of PC88A to form the 1:3 complex. However, further work is required to confirm the nature of the extracted species in the organic phase.

2.3.5. NMR analysis

Acidic extractants such as PC88A and Versatic10 are known to form dimers, respectively, in low polarity diluents. However, in the mixture extractant system, the two extractants have potentially interact with each other in the solvent. To clarify the interaction, we recorded NMR spectra for the individual extractants and their mixture in the organic solvent. ^{1}H NMR data for PC88A, Versatic 10, and 50% PC88A+ 50% Versatic 10 are shown in Figure 2.9. The chemical shifts of ^{1}H NMR spectra of PC88A and Versatic 10 exhibited at 12.00 ppm and 12.66 ppm, that are attributed to the presence of the hydrogen atom in P-O-H and C-O-H, respectively. However, in the mixture extractants, the signal due to the hydrogen bonding of proton in carboxylic acid disappeared and only one chemical shift exhibited at 12.05 ppm that is almost the same as that appeared in individual PC-88A. The relative proton number for the signal at 12 ppm against that at 3.9 ppm attributed to the ester group O-CH_2 of the binary extractants system is near 1:2 in individual PC-88A, while in the mixture extractants, that is approximated to be 1:1, suggesting the heterodimer of PC-88A with Versatic 10 is formed in

the mixture extractant system. The results support the extraction mechanism for the binary extractant system that Versatic10 participates the extraction of scandium ions as the association form with PC88A.

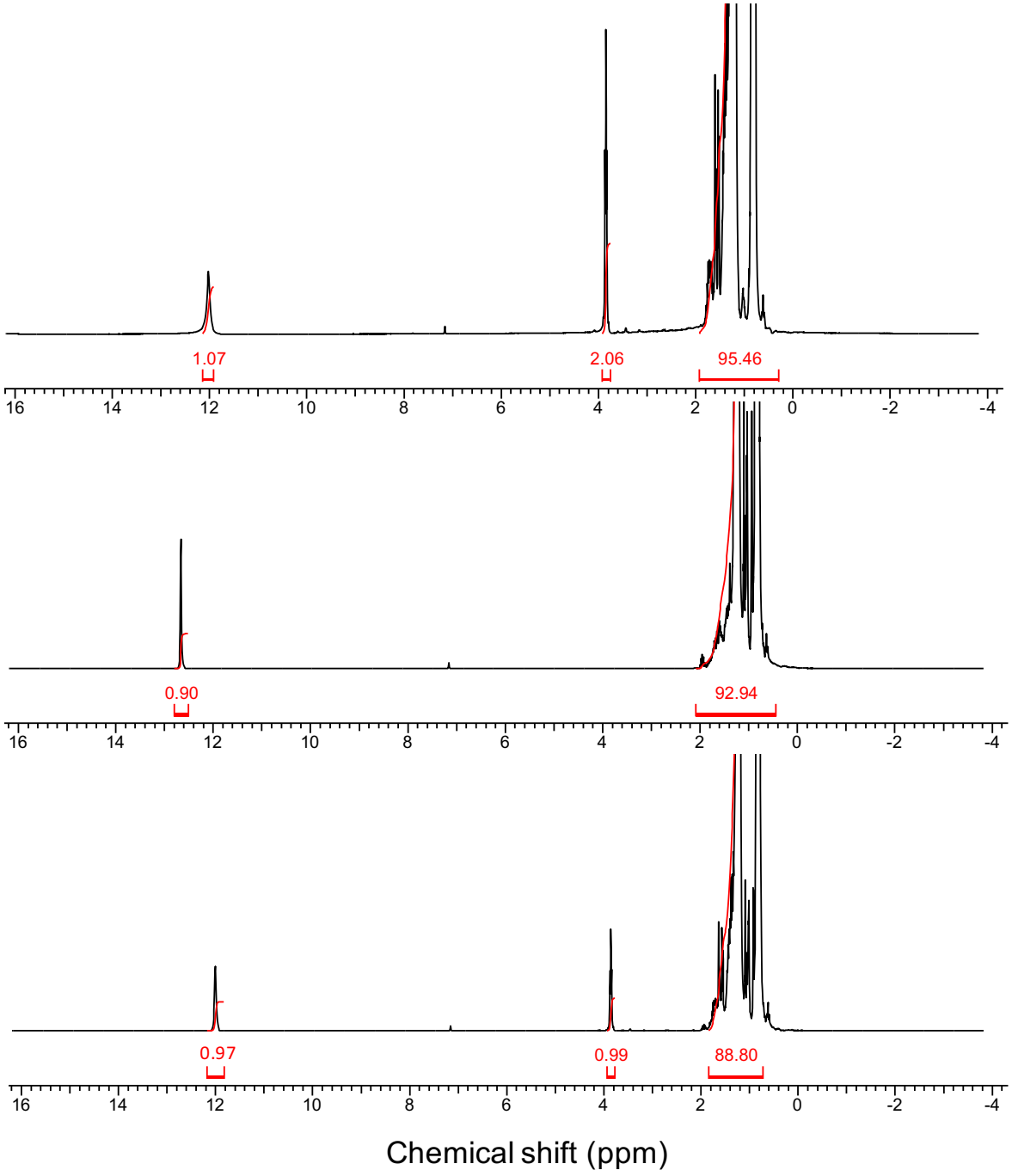


Figure 2.9. ^{1}H NMR of PC88A, Versatic 10, and PC88A/Versatic 10 binary mixture in n-hexane (300 MHz, C6D6).

2.3.6 FT-IR analysis

Acidic extractants such as PC88A and Versatic10 are known to form dimers in low polarity diluents. We recorded IR spectra of the individual extractants and mixtures before loading with scandium ions. All of the organic phase samples were prepared in carbon tetrachloride. A solution of 0.5 M PC88A in carbon tetrachloride was prepared and the IR spectrum was recorded before the extraction process. PC88A/Versatic 10 mixtures were then prepared by adding 0.5 M Versatic 10 to PC88A, and the IR spectra were recorded (with a KBr cell) (Figure 2.10). With addition of Versatic 10, the band of the P=O group shifts from 1218 cm^{-1} for 0.5 M PC88A to 1202.69 cm^{-1} for 0.5 M PC88A and (0.5 M PC88A/0.5 M Versatic 10), respectively. Moreover, the stretching band of the O–H bond changes from 2366 cm^{-1} to 2348 cm^{-1}. After addition of Versatic 10, the C–O–P vibration changes from 1037.46 cm^{-1} to 1033.84 cm^{-1}, while the P–O peak shifts from 980.18 cm^{-1} to 983.91 cm^{-1}. With addition of Versatic 10, the wavenumber of the band at 875.11 cm^{-1} that corresponds to stretching of P–O(H) bonds in PC88A increases by 25 cm^{-1}, and become broader with addition of 0.5 M Versatic 10. A new band appears at 728.88 cm^{-1}, which may indicate the change in the (P=O)–OH group vibration because of hydrogen bond formation between PC88A and Versatic 10. The change in the OH bond frequency of PC88A after addition of Versatic 10 could also be an indication of interaction between the two extractants. The out of plane stretching band of O–H of Versatic 10 at 946.87 cm^{-1} is not observed for the 0.5 M PC88A/0.5 M Versatic 10 mixture, which may be because of interference with the strong band of the C–O–P group.

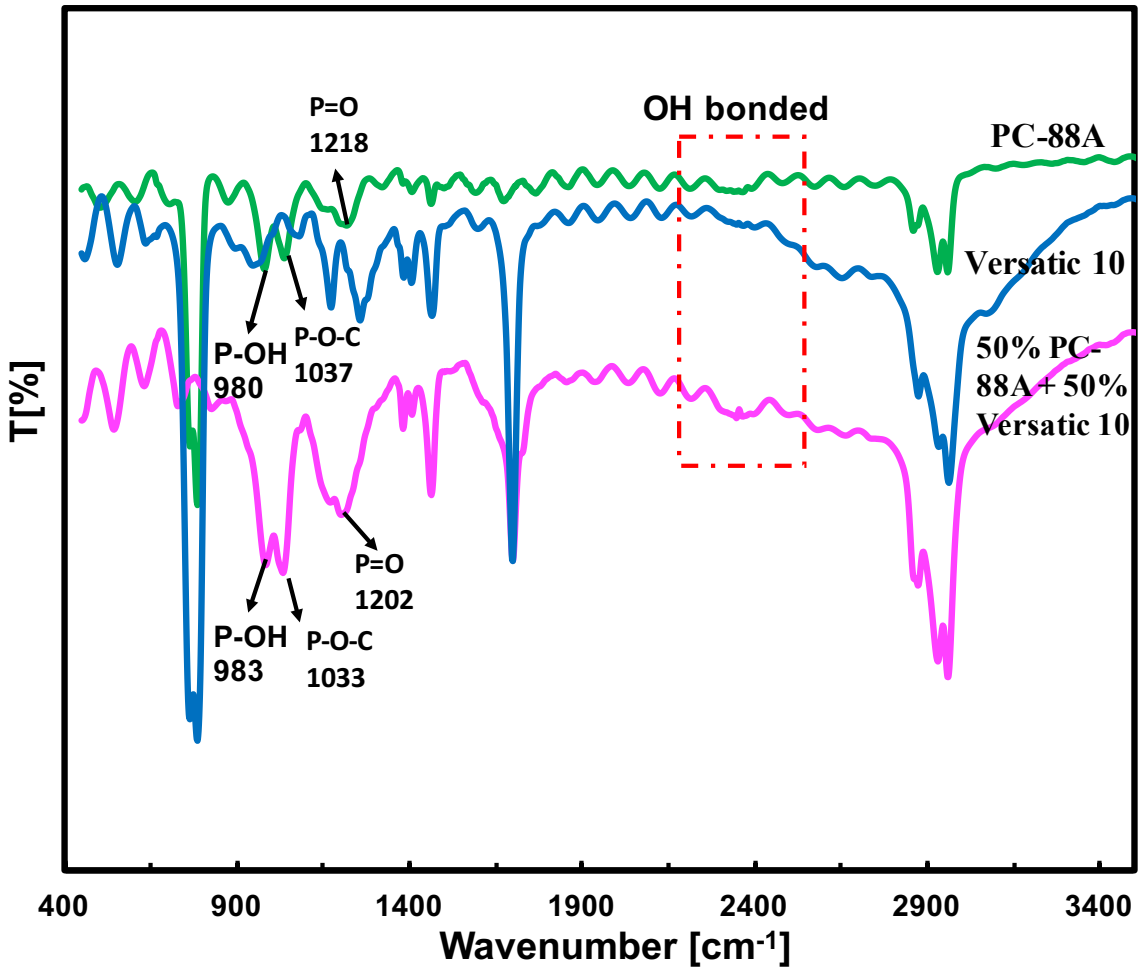


Figure 2.10 FT-IR spectra of PC88A, Versatic 10, and PC88A/Versatic 10 binary mixtures: (a) 0.5 M PC88A, (b) 0.5 M Versatic 10, (c) 0.5 M Versatic 10/0.1 M PC88A, (d) 0.5 M PC88A/0.1 M Versatic 10, and (e) 0.5 M PC88A/0.5 M Versatic 10. The diluent for all of the organic phases is carbon tetrachloride in KBr cell.

2.3.7 Separation of Sc from common ions

The extraction of Sc from common ions was investigated from 0.1 mM nitrate media. The selective extraction of Sc along with Fe ions was observed as shown in Figure 2.11. However, the extraction process requires improving the separation factors between Sc and Fe(III). The reduction of Fe (III) was carried out by 10 mM hydrazine to minimize its extraction. The results confirmed that both of them can be extracted by the binary system.

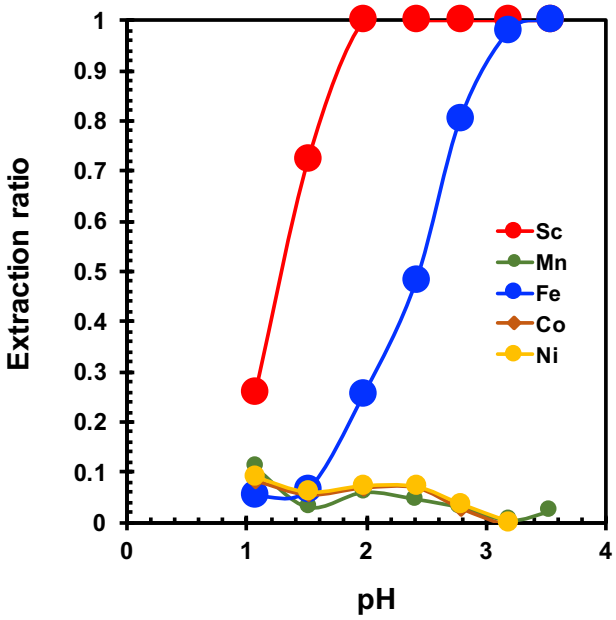


Figure 4. Extraction ratio of foreign ions using the binary extracatnt 1mM PC88A and 100 mM Versatic 10. 0.1 mM metal ions, Fe (III) is used, and 1 h shaking time at room temp.

2.4. Stripping of Sc from the loaded organic phase

Based on the extraction results, the PC88A system does not allow simple stripping of Sc from the loaded organic phase. Using the 1 mM PC88A/100 mM Versatic 10 binary extractant system, which is the best combination to achieve selective extraction of scandium at an appropriate pH, a stripping test was performed for the loaded organic phase containing 0.1 mM Sc^{3+} at an organic/aqueous ratio of 1 and room temperature. The stripping efficiency was compared for different acids: 1 M each of H_2SO_4, HNO_3, and HCl. The stripping efficiency tends to increase in the order $HNO_3 \approx HCl > H_2SO_4$ (Figure 2.12 (b)). Figure 2.12 (a) shows the Sc^{3+} stripping efficiencies in the PC88A and binary extractant systems as a function of acid concentration using HNO_3. The results show that 95% Sc is stripped from the binary mixture with 0.75 M HNO_3, whereas only 48.7% Sc is stripped from the PC88A system with the same nitric acid concentration. Using 1 mM PC88A alone, a higher concentration of nitric acid is required to achieve complete stripping of Sc^{3+}. With addition of Versatic 10 to PC88A, complete stripping of Sc is achieved with low acid consumption by a single stripping operation.

Therefore, the stripping efficiency is greatly improved by using a PC88A/Versatic 10 binary mixture compared with using PC88A alone.

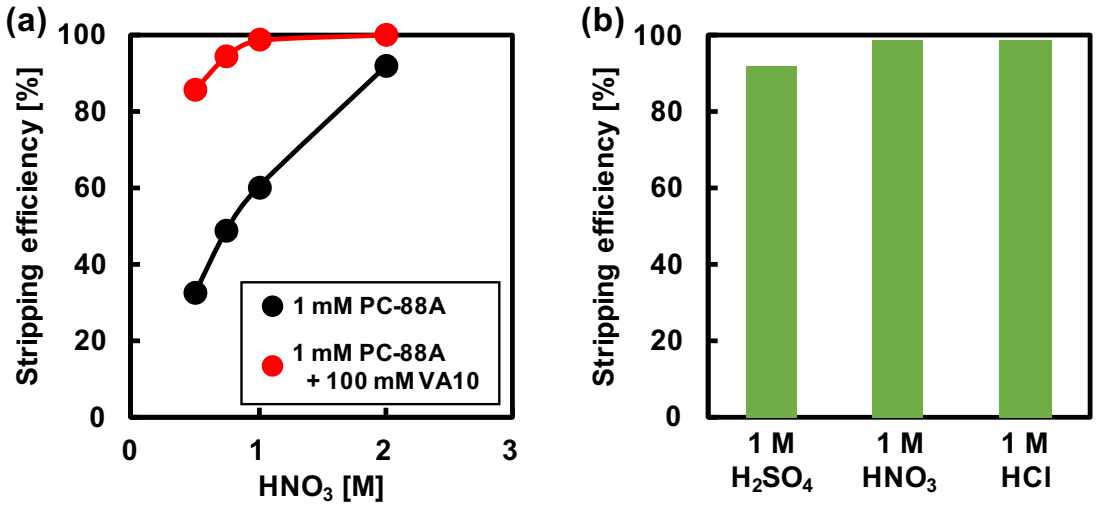


Figure 2.12. Stripping efficiency from 0.1 mM Sc^{3+}. (a) Sc^{3+} stripping efficiencies from the 1 mM PC88A and 1 mM PC88A/100 mM Versatic 10 loaded organic phases using nitric acid. (b) Comparison of the stripping efficiencies of different mineral acids for the loaded.

2.5. Conclusion

We have investigated extraction of REEs using PC88A alone and PC88A mixed system with Versatic 10. Addition of Versatic 10 to PC88A increases the pH at which extraction begins and decreases the distribution coefficient of Sc while maintaining high separation efficiency. Owing to the antagonistic effect, Sc^{3+} is selectively extracted over other REEs at pH = 2, and stripping of Sc^{3+} can be successfully achieved in a single step with a mild acidic solution, such as 1 M HNO_3. Slope analysis, loading tests show the possibility of participation of Versatic 10 in the extraction reaction, and the extracted species could be $Sc(HR_2)_3$ and $Sc(HAR)_3$ at low metal loading under low acidic conditions. However, the results suggest that the stoichiometry of the extracted species changes at high metal loading. In the PC88A alone system under high loading, a polymeric phase is observed, but it is not observed using the binary mixture, indicating that Versatic 10 acts as a modifier. NMR spectroscopy results suggest a possible interaction between the two extractants in the organic phase through changes in intermolecular hydrogen bonds, which causes the antagonistic effect. The new binary system achieves high

selectivity, high loading efficiency, and prevents crud formation at the interface, indicating its potential for economic industrial applications.

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Chapter 3

A polymer inclusion membrane composed of the binary carrier PC-88A and Versatic 10 for the selective separation and recovery of Sc

3.1. Introduction

The demand for rare earth metals (REMs) has been steadily increasing due to their unique physical and chemical characteristics and extensive usage in various life sectors, e.g., adding small amount of REMs to steels can improve their heat, corrosion and oxidation resistance.[1] Scandium is one of the REMs, which has an essential role in many application areas such as aluminium alloys, semiconductors and future fuel-cells.[2] The price of scandium is considerable and it is produced mainly as a by-product, therefore, there is an urgent need for the development of dedicated and efficient separation techniques to sustain the growing demand for this metal. Solvent extraction is one of the industrially established separation methods to recover REMs from aqueous solutions.[3,4] However, it has still some significant drawbacks such as requiring relatively complex equipment, consuming high amounts of solvents, involving multi-stage extraction processes, extensive energy consumption, and limited ligand selection.[5]

In recent years, liquid membrane technologies have attracted much attention in the separation and recovery of metal ions from aqueous solutions[6] because of their high energy efficiency, flexibility, low cost, easily satisfying environmental pollution regulations, and offering controlled membrane permeability. There are several kinds of liquid membranes for metal separation from aqueous liquors, such as supported liquid membranes (SLMs), emulsion liquid membranes (ELMs), bulk liquid membranes (BLMs), and polymer inclusion membranes (PIMs).[7] In the present study, we have focused on PIMs due to several important advantages they offer compared to the other types of membrane mentioned above.

PIMs are liquid membranes which consist of a base polymer (usually poly(vinyl chloride), PVC or cellulose triacetate, CTA), a carrier (often a commercial solvent extractant) which is immobilized between the entangled chains of the base polymer, and a plasticizer, if necessary.[8-10] PIM-based separation is considered as a highly promising technique because of the high

stability, selectivity, efficiency, and durability of PIMs.[11] The outstanding performance of PIMs in comparison with the other types of liquid membranes is expected to lead to the development of novel industrial separation processes in the near future. PIMs have already been shown to be applicable to the separation of some REMs [12-14], actinides[15,16] as well as other metals[17-24]. However, there have been no reports so far on scandium separation using PIMs because of the lack of suitable extractants/carriers. There are several good extractants with high extraction affinity for scandium[25], however, back-extraction is known to be difficult when such extractants are used. To establish a successful membrane separation system, the efficiency of back-extraction is equally important as that of extraction.

In our previous solvent extraction study as in chapter 2[26], we found that a binary extractant composed of PC-88A and Versatic 10 showed a good performance for both the selective extraction and efficient back-extraction of scandium. Chapter 3 reports on the development, optimization and characterization of the first PIM for the selective separation of scandium ion from other REM ions.

3.2. Experimental

3.2.1. Reagents and chemicals

PC-88A and Versatic 10 were supplied by Daihachi Chemical (Osaka, Japan) and Japan Epoxy Resin (Tokyo, Japan) (currently Mitsubishi Chemical Corporation), and used without further purification. CTA used as the PIM base-polymer, dioctylphthalate (DOP) and 2-nitrophenyloctyl ether (2NPOE) used as plasticizers were purchased from Sigma-Aldrich (St Louis, USA). The salts of the REMs studied were provided by Aldrich and used in the preparation of the feed solutions. Sulfuric acid, nitric acid and ammonium nitrate were purchased from Kishida Chemical (Osaka, Japan).

3.2.2. Membrane preparation

In this study, PIMs using CTA as the base-polymer and 2NPOE or DOP as the plasticizer were prepared as previously described.[27] A homogeneous solution containing the required amount of CTA (20-70 wt%), the plasticizer (0-40 wt%) and the mixed carrier (0 - 40 wt%) with a total mass of 400 mg was dissolved in 10 mL dichloromethane as shown in Figure 3.1.

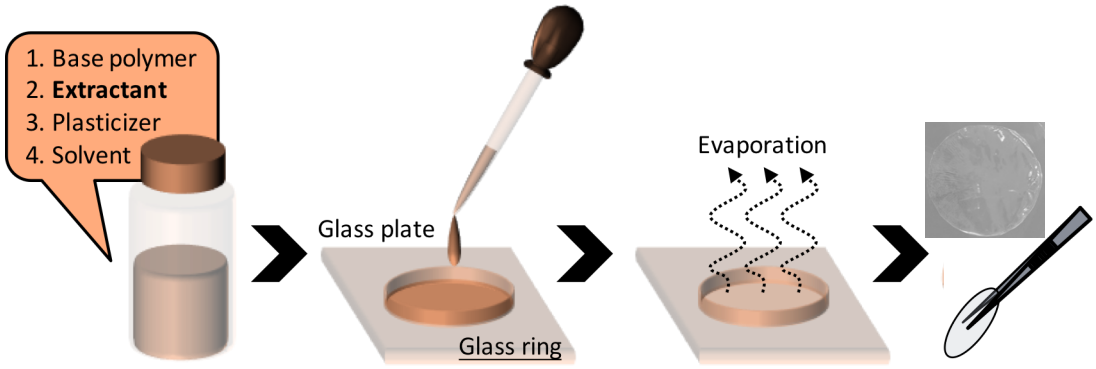


Figure 3.1. Schematic representation for the preparation of membrane at bench scale.

The ratio of PC-88A and Versatic 10 was also varied. The solution was then poured into a 7.5 cm in diameter glass ring positioned on a flat glass plate, and covered with a filter paper and a watch glass to allow the slow evaporation of the solvent overnight. The prepared membranes were transparent with a soft surface and a good mechanical strength as shown in Figure 3.2. Membrane thickness was measured using Digimatic Micrometer MDC-25 MX (Mitutoyo, Japan) and the corresponding value was calculated as the average of 10 spots across the membrane diameter. The average thickness of the membranes used in all experiments was 60±5 µm.

Figure 3.2. A photo image of a prepared membrane.

3.2.3. Membrane extraction and back-extraction experiments.

The PIM extraction experiments were conducted by immersing a circular segment of the membrane with an average mass of 80 mg in a 50 mL of an aqueous feed solution in a glass flask covered with Parafilm. To evaluate the effect of parameters on the PIM performance, all experiments were performed at a constant pH 4, unless otherwise stated. All extraction experiments were performed at a stirring rate of 90 rpm at 25 ^{o}C using a thermostated orbital shaker (EYELA NTS-4000, Tokyo Rikakikai Co., Ltd., Tokyo, Japan). The aqueous feed solutions were prepared by dissolving metal salts in mixtures of 0.1 M HNO_3 and 0.1 M NH_4NO_3 solutions. The pH of the feed solutions was adjusted by varying the ratio of the HNO_3 and NH_4NO_3 solutions. The pH during the extraction experiments was measured at predetermined times by using a pH meter (H-M-60 G, DKK-TOA, Japan). Samples (1 mL) were taken periodically from the feed solution and replaced with the same volume of the initial feed solution. Metal concentrations were analyzed by inductively coupled plasma - atomic emission spectrometry (ICP-AES, Optima 8300; Perkin Elmer, USA).

The kinetics of the PIM extraction was described by the following first order equation:

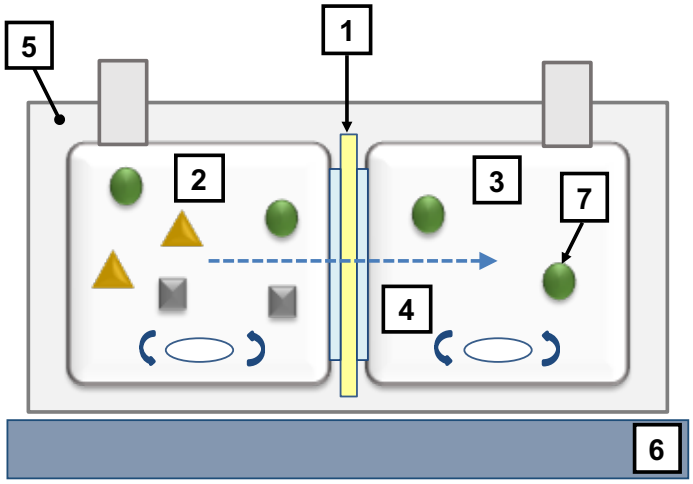
$$ln\left(\frac{[M^{3+}]_f}{[M^{3+}]_{f,0}}\right) = -kt \qquad (3.1)$$

where t is the time (h), $[M^{3+}]_{f,0}$ and $[M^{3+}]_f$ are the concentrations of the REM ion in the feed solution at times 0 (original solution) and t, respectively, and k is the kinetic rate constant (h^{-1}) for the metal uptake into the membrane.

The back-extraction experiments were conducted by immersing the loaded membrane with a REM ion into a sulfuric acid receiving solution.

3.2.4. Membrane transport experiment

Metal transport experiments were performed using a transport system consisting of two jacketed glass compartments with the PIM sandwiched between them as shown in Figure 3.3. The membrane apparatus is designed for analyzing a transport behavior, and the same apparatus was used for the study on supported liquid membrane (SLM) experiments[28,29]. The two compartments were filled with the feed and receiving solutions (50 ml each). The diameter of the membrane exposed to the solutions was 25.0 mm (effective surface area of 4.9×10^{-4} m^2). The solutions in both compartments were mechanically stirred at 300 rpm during the experiments using magnetic stirrers (KH-55D, Vidrex, Japan) and small crosshead magnets (8 x φ10). Samples (1 ml) were taken from the ports of both glass compartments at predetermined times and analyzed by ICP-AES. The samples were replaced with the same volume of the corresponding fresh solutions. Temperature of both compartments was kept constant at 25 ^oC by continuously circulating water through the compartments' jackets from a water bath with a thermoregulator (RCB-1200, EYELA, Japan). The feed solution containing initially 0.1 mM metal ion(s) and the receiving solution were prepared as described earlier. As in the extraction



1. **Polymer inclusion membrane (PIM)**
2. **Feed solution**
3. **Receiving solution**
4. **Stirring magnets**
5. **Water bath**
6. **Magnetic stirrer**
7. **Metal ions**

Figure 3.3 Schematic diagram of the PIM transport cell.

experiments, it was assumed that the transport kinetics was first order (Equation (1)). The permeability coefficient (P), initial flux J_0 (mol m^{-2} s^{-1}) and recovery factor RF (%) were determined by Equations (2) -(4), respectively.

$$P = \frac{V}{A} k \tag{3.2}$$

$$J_0 = P\,[M^{3+}]_0{}^f \tag{3.3}$$

$$RF(\%) = \frac{[M^{3+}]_0{}^f - [M^{3+}]^f}{[M^{3+}]_0{}^f}\,100 \tag{3.4}$$

where V (m^3) is the volume of feed solution, A (m^2) is the membrane surface area exposed to each of the two solutions, and superscript f refers to the feed solution.

3.2.5. Membrane characterization

The morphology of the PIMs studied was examined by imaging their cross-sections using scanning electron microscopy (SEM, Inspect S50 XT microscope, type: FB 2017/12- FEI,

USA). The membrane samples were first immersed into liquid nitrogen for 15 min, then were cut into small rectangular pieces to be fixed onto the sample holder, and finally were coated with palladium (MSP-15 Magnetron Sputter Hitachi, Japan). SEM images at two different scales were taken.

3.3. Results and discussion

3.3.1. Optimization of the PIM composition

The optimization of the composition of the CTA-based PIM containing PC-88A and Versatic 10 was based on extraction and back-extraction experiments involving PIMs with different compositions.

3.3.1.1. Carrier

Initially, PIMs containing either PC-88A or Versatic 10 were studied. Figure 3.4(a) shows the transient concentration of REM ions ($[M^{3+}]$) of interest in the feed solution normalized with respect to their initial concentrations ($[M^{3+}]_0$) during extraction experiments at pH 1 involving PIMs containing different concentrations of the extractant PC-88A and 30% of the plasticizer DOP. The results showed that Sc^{3+} was selectively extracted into the membranes and the extraction rate and amount extracted increased with increasing the PC-88A concentration. Upon increasing PC-88A concentration in the PIM up to 10%, the extracted amount of Sc^{3+} gradually increased and quantitative extraction of Sc^{3+} into a PIM containing 10% PC-88A was achieved after 24 h of extraction. In experiments with feed solutions at pH 4 other REMs were also extracted and this lowered the extraction rate and the amount of Sc^{3+} extracted. However, it was difficult to back-extract Sc^{3+} from the PC-88A containing PIMs regardless of the concentration of PC-88A as shown in Figure 3.4(b) where the transient concentration of Sc^{3+} is normalized with respect to the initial concentration in the feed solution ($[Sc^{3+}]_0$). The inability to back-extract quantitatively Sc^{3+} from the PIM would be a serious obstacle in developing a PIM-based separation technology for this metal.

The membrane extraction of REM ions was also carried out using PIMs with Versatic 10 alone as the carrier. The extraction ability of the extractant Versatic 10 for Sc^{3+} is considerably

lower than that of PC-88A[25] and therefore the extraction experiments involving Versatic 10-based PIMs were conducted at feed solution pH of 4 rather than 1 (Figure 3.5(a)). As expected, the back-extraction of Sc^{3+} from the Versatic 10-based PIMs was found to be better than that from the PC-88A-based membranes (Figure 3.5(b)).

It has been proven that the use of binary extractants in extraction systems[30] can improve their ability to selectively and reversibly extract specific target metal ions. In chapter 2, we have found that the binary extractants PC-88A and Versatic 10 are suitable for both the selective extraction and efficient back-extraction of Sc^{3+}. [26.] It was confirmed that Sc is extracted via the exchange by three protons in the binary extractant system. The reaction seemed to involve PC-88A dominantly, and Versatic 10 was considered to reduce the affinity of PC-88A to Sc. This result improved the back-extraction efficiency. Therefore, the possibility of using this binary extractant as the carrier of a CTA-based PIM was examined as a part of chapter 3. It was expected that the presence of Versatic 10 would improve the stripping efficiency of Sc^{3+} from the PIM with the binary extractant compared to the PIM containing only PC-88A while keeping the high selectivity of the latter membrane.

The extraction and back-extraction characteristics of CTA-based PIMs containing 30 wt% DOP as plasticizer and both PC-88A and Versatic 10 as the binary carrier in concentrations equal to 10 wt%, 20 wt%, 30 wt%, and 40 wt% were studied. The ratio between the two extractants was varied, while all the extraction experiments were conducted with the same initial feed solution which includes 0.1 mM and maintained pH of 4. Best extraction was achieved at this pH value in a series of experiments where the initial pH was varied between 1 and 4. It should be noted that in the course of the extraction process the pH decreased from 4 to around 3.3. As shown in Figure 3.6, the extraction of Sc^{3+} was enhanced by increasing the PC-88A concentration of the membrane, however, the back- extraction of Sc^{3+} was depressed as a result of this. Moreover, increasing the Versatic 10 percentage over that of PC-88A was found to be effective for improving the back-extraction efficiency. Both quantitative extraction and back-extraction were achieved with a PIM containing 40 wt% carrier.

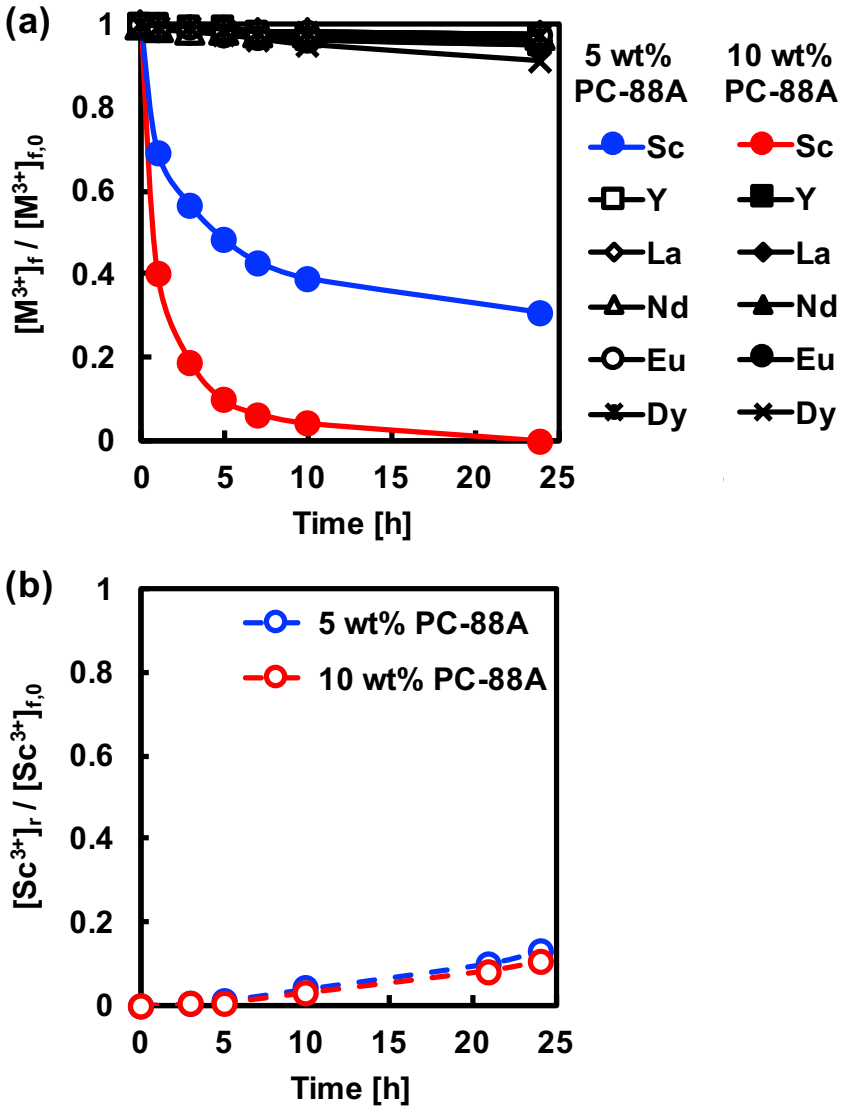


Figure 3.4 (a) Normalized transient concentrations in the feed solution of the REM ions studied during the PIM extraction experiments. (b) Normalized transient Sc^{3+} concentration in the 1 M sulfuric acid receiving solution during the PIM back-extraction experiment. Experimental conditions: CTA-based PIMs composition - 5 or 10 wt% PC-88A and 30 wt% DOP; PIM mass and thickness – 80 mg and 60 ±5 μm, respectively; Feed solution volume, initial composition and pH – 50 mL, 0.1 mM of each of the REM ions studied and 1, respectively.

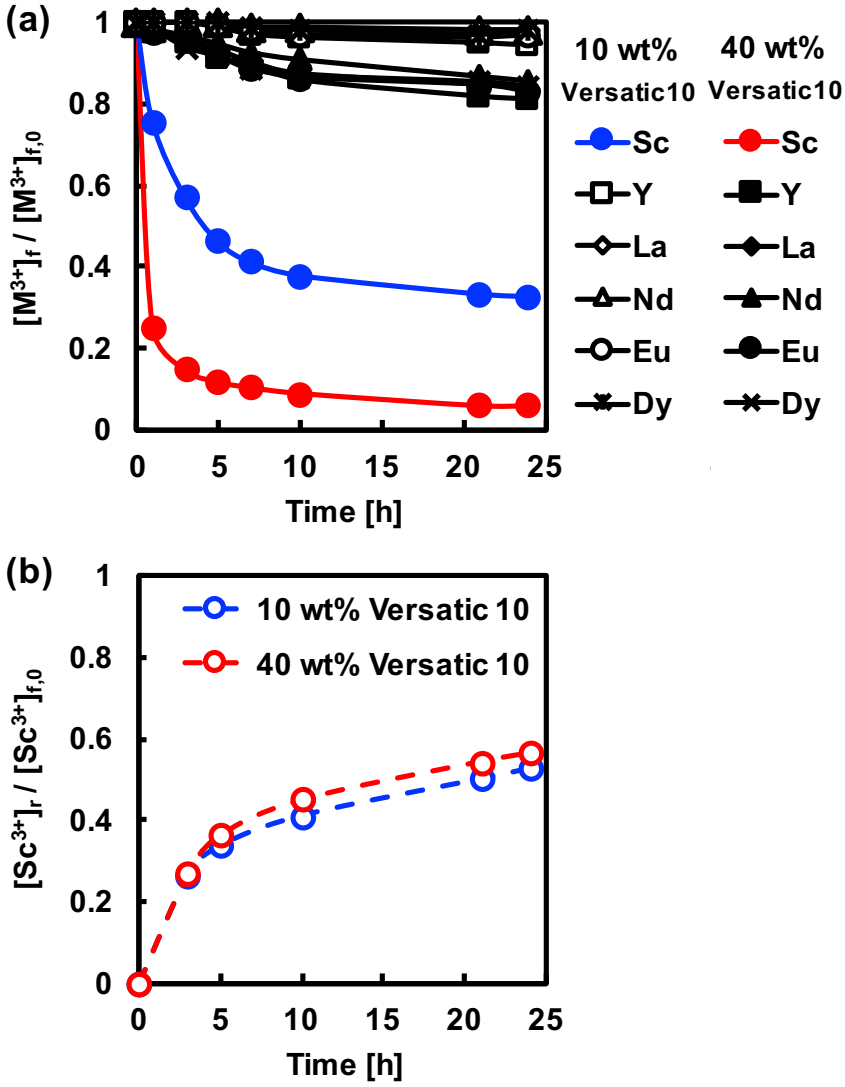
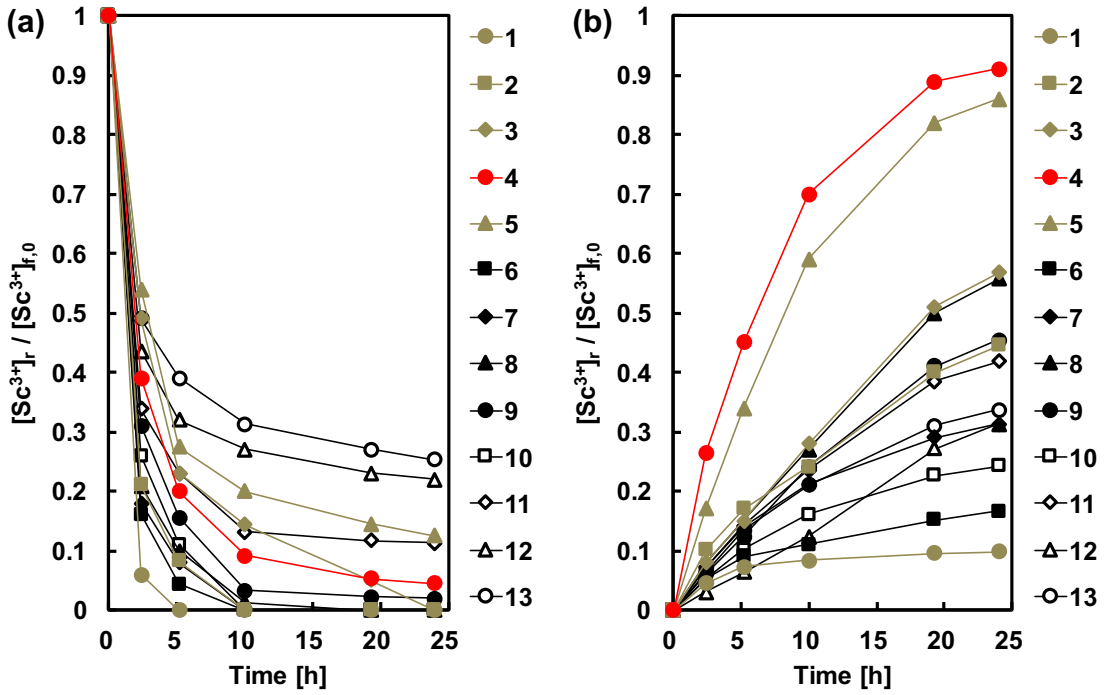


Figure 3.5. (a) Normalized transient concentrations in the feed solution of the REM ions studied during the PIM extraction experiments. (b) Normalized transient Sc^{3+} concentration in the 1 M sulfuric acid receiving solution during the PIM back-extraction experiment. Experimental conditions: CTA-based PIMs composition - 10 or 40 wt% Versatic 10 and 30 wt% DOP; PIM mass and thickness – 80 mg and 60 ±5 μm, respectively; Feed solution volume, initial composition and pH – 50 mL, 0.1 mM of each of the REM ions studied, 4, respectively.



Binary carrier composition (wt%)

No.	1	2	3	4	5	6	7	8	9	10	11	12	13
PC-88A	20	10	6	4	2	15	10	6	4	10	4	5	2
Versatic 10	20	30	34	36	38	15	20	24	26	10	16	5	8
Total	40					30				20		10	

Figure 3.6. (a) Normalized transient Sc^{3+} concentration in the feed solution during the PIM extraction experiments. (b) Normalized transient Sc^{3+} concentration in the 1 M sulfuric acid receiving solution during the PIM back-extraction experiments. Experimental conditions: CTA-based PIMs composition - binary extractant (composition in the above table) and 30 wt% DOP. Remaining experimental conditions as in Figure 3.5.

(4 wt% PC-88A + 36 wt% Versatic 10), 30 wt% CTA and 30 wt% DOP. PIM with concentration of the carrier greater than 40 wt%, was found to be mechanically unstable and therefore the combination of4 wt% PC-88A and 36 wt% Versatic 10 was selected as the optimum carrier composition. The results mentioned above demonstrated the importance of controlling the ratio between the two extractants for achieving efficient extraction and back-extraction of Sc^{3+}. The initial rate constant (k) values calculated by Eq. (1) for different carrier compositions in the membrane are summarized in Table 3.1.

Table 3.1, Rate constant (k) values for Sc^{3+} extraction in PIMs of different carrier composition. Remaining experimental conditions as in Figure 3.5.

Carrier compositions	DOP (wt%)	k [h^{-1}]
10 wt% PC-88A	30	0.29
40% Versatic10	30	0.36
4 wt% PC-88A + 36 wt% Versatic 10	30	0.55
4 wt% PC-88A + 36 wt% Versatic 10	40	0.86

3.3.1.2. Plasticizer and polymer

CTA-based PIMs containing 4 wt% PC-88A and 36 wt% Versatic 10 as the binary extractant and DOP or 2NPOE as the plasticizer in the concentration range of 0 - 40 wt% were studied. The experimental results suggested that the membrane extraction rate increased upon increasing the percentage of the plasticizer in the membrane (data not shown). The best extraction and back-extraction efficiency was achieved when using 40 wt% DOP. The extraction and back-extraction results obtained at this PIM composition are shown in Figure 3.8, and the initial extraction rate constant values are listed in Table 3.1. It can be expected that by increasing the plasticizer concentration, the viscosity of the membrane phase will decrease thus provide more opened polymer structures and lower membrane diffusion coefficients.[31] The PIMs prepared with 2NPOE as the plasticizer were less flexible than those containing DOP. In addition, DOP is the less expensive plasticizer. Therefore, DOP was considered to be more suitable plasticizer for preparing the PIMs with the optimal composition.

On the other hand, CTA-based PIMs containing PC-88A/ Versatic 10 binary extractants were transparent, mechanically strong and flexible, whilst PVC-based PIMs containing the same binary carrier are oily and PVDF based PIMs are cloudy as shown in Figure 3.7 Furthermore, the adsorption desorption experiments were carried out from 40 wt% carrier (4 wt% PC-88A + 36 wt% Versatic 10), 30 wt% PVC/ or PVDF and 30 wt% DOP that attained

89% and 95% extraction, 60% and 68% stripping for PVC and PVDF membranes, respectively. The results indicate that CTA is the best candidate as base polymer selection with the chosen extractants in this chapter.

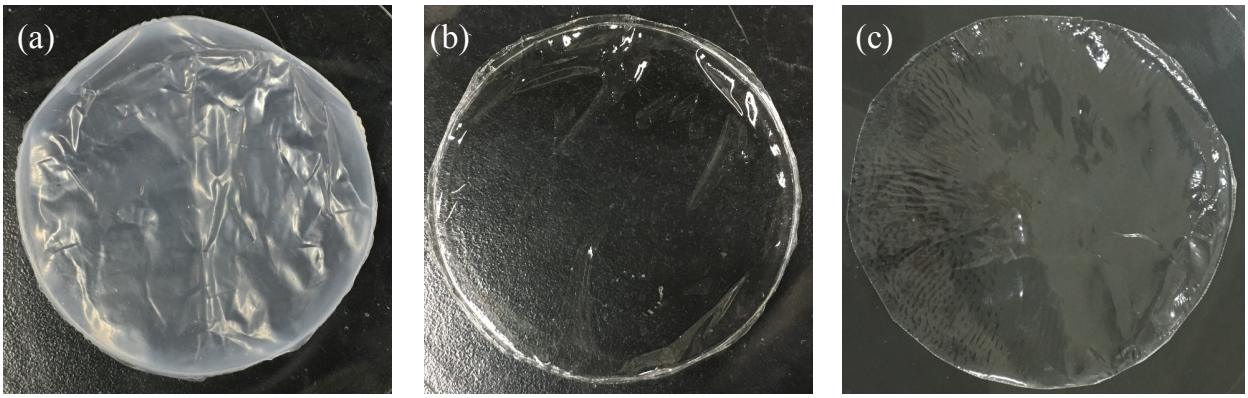


Figure 3.7. Pictures of the prepared membranes using (a) PVDF, (b) PVC and (c) CTA as base polymer with 40 wt% carrier (4 wt% PC-88A + 36 wt% Versatic 10), and 30 wt% DOP.

3.3.1.3 Stripping reagent

Three different mineral acids (HCl, HNO_3 and H_2SO_4) were studied for their suitability as stripping reagents for Sc^{3+} and it was established that their stripping efficiency increased in the order HNO_3 > HCl > H_2SO_4. However, when we used the nitric and hydrochloric acids as the receiving solution in membrane permeation experiments, the pH values in the feed phase drastically dropped down. Therefore, in the membrane permeation experiments, sulfuric acid was selected due to its high hydrophilicity, which protected the acid permeation from the receiving phase to the feed one.

3.4. Membrane characterization by SEM

The morphology of PIMs with different compositions was investigated using high resolution SEM. Figure 3.9 showed SEM cross-sectional images at two scales; magnification 2000x and 10000x of CTA-based PIMs containing DOP (a and a'); PC-88A, Versatic 10 and DOP (b and b'); and PC-88A and Versatic 10 without DOP (c and c'). All the membranes shown in Fig 3.9

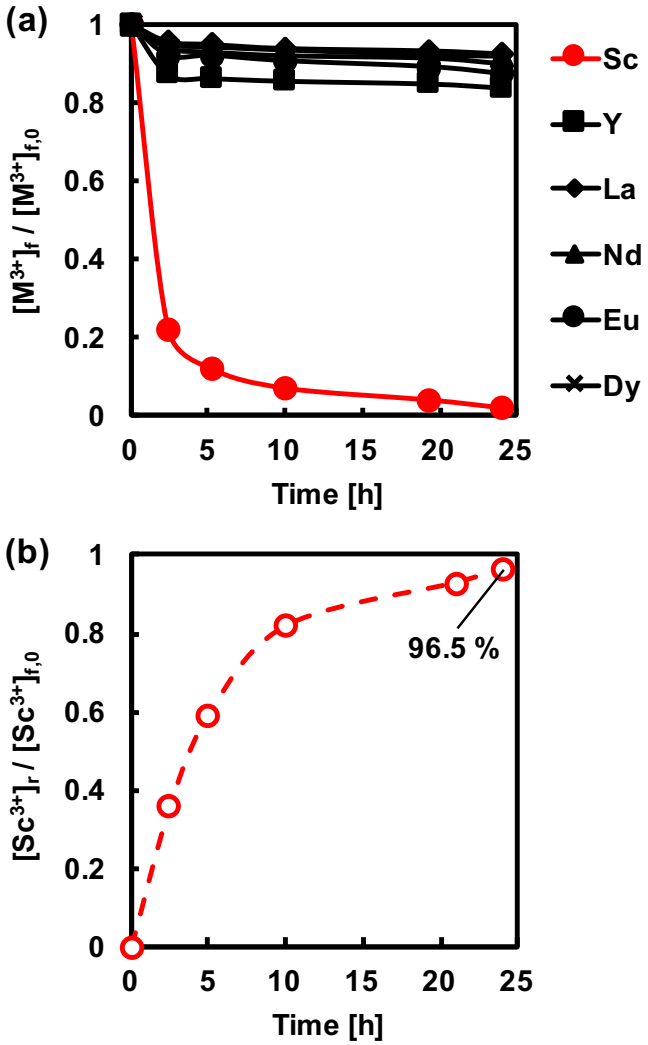


Figure 3.8. (a) Normalized transient concentrations in the feed solution of the REM ions studied during the PIM (4 wt% PC-88A and 36 wt% Versatic 10) extraction experiments. (b) Normalized transient Sc^{3+} concentration in the 1 M sulfuric acid receiving solution during the PIM back-extraction experiments. Remaining experimental conditions as in Fig. 3.5 except for the DOP concentration which was 40 wt%.

were transparent as shown in Fig. 3.2. The SEM images of CTA-based PIM with only DOP revealed a homogenous and uniform membrane structure (Fig. 3.9 (a')). The SEM image of the PIM binary system composed of 4 wt% PC-88A and 36 wt% Versatic 10 with 30 wt% DOP as the plasticizer, which offered the best Sc^{3+} ion transport, exhibited a well-oriented multilayer fibrous structure (Fig. 3.9(b')). That of the same PIM binary system but without DOP (Fig. 3.9(c')) are characterized by a non-uniform cracked structure thus illustrating the critical role of the plasticizer in forming a uniform and homogeneous PIM and explaining the poor

permeability of this PIM. Consequently, it can be concluded that by adding a plasticizer, both the uniformity and permeability of the membranes increases significantly. Moreover, the PIMs prepared with DOP were thinner with a low density (compared (b) to (c)) that would further promote high membrane permeability. These results are in agreement with the study of Manzak et al. [32] about the role of the plasticizer in constructing more flexible and softer PIMs and in minimizing the intermolecular interaction forces in their polymer scaffolds thus resulting in higher membrane permeability.

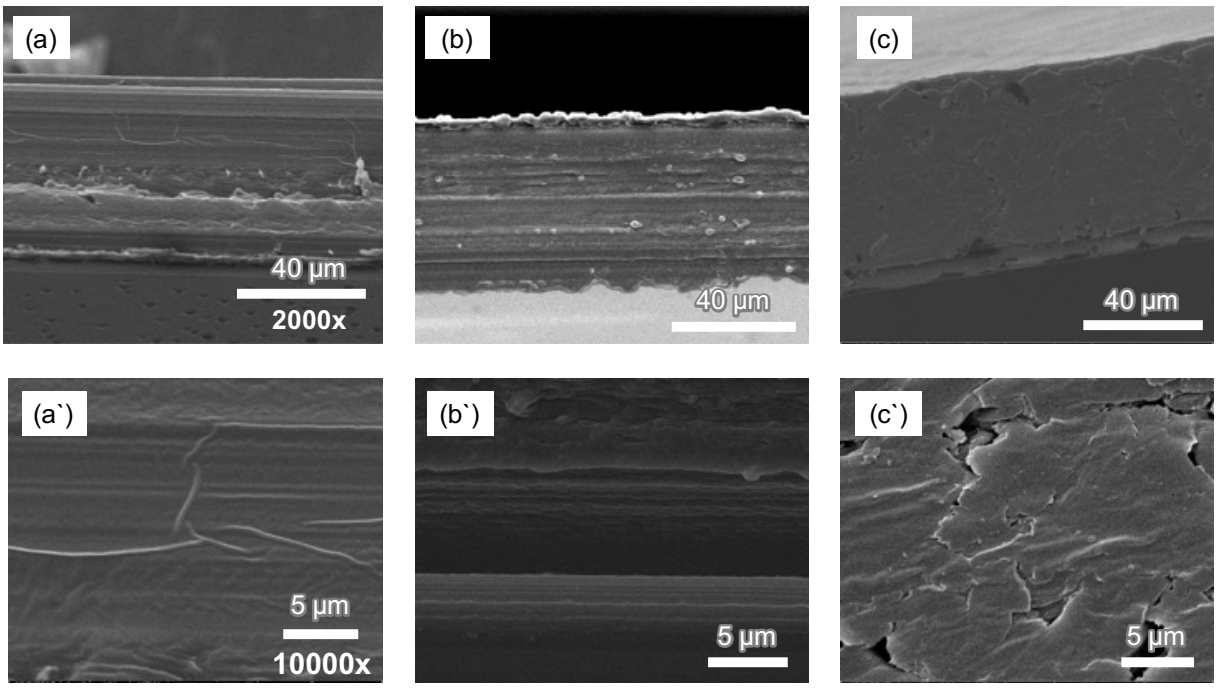


Figure 3.9. SEM cross section micrographs at two scales: magnification 2,000x and 10,000x of CTA-based PIMs with 30 wt% DOP (a and a'); 4 wt% PC-88A, 36 wt% Versatic 10 and 30 wt% DOP (b and b'); and 4 wt% PC-88A and 36 wt% Versatic 10 (c and c').

3.5. Membrane transport experiments

Membrane transport experiments of metal ions were conducted using PIMs with total binary carrier concentration of 40 wt%, where the ratio between PC-88A and Versatic 10 was varied. When maintaining the percentage of Versatic 10 constant and varying the PC-88A percentage between 1 and 3 wt%, incomplete extraction of Sc was observed from a nitrate acid feed solution at pH 4, while more than 6 wt% PC-88A enhanced the transport of the other REM ions studied over that of Sc^{3+} into the 1 M sulfuric acid receiving solution. Therefore, the membrane

composition of 40 wt% (4 wt% PC-88A + 36 wt% Versatic 10), 40 wt% DOP and 20 wt% CTA, already selected as optimal for the extraction and stripping of Sc^{3+}, was found to be optimal for its transport as well.

A PIM with the optimal composition mentioned above but without the plasticizer DOP showed very poor permeability for Sc^{3+} in transport experiments.

As described before, the extraction of Sc proceeds via the exchange by three protons in the binary extractant system.[26] Membrane transport of the metals is thought to proceed by the following mechanism: the extraction reaction with a cation exchange occurs at the membrane surface of the feed side, followed by the diffusion of the metal species in the membrane from the feed to the receiving side where the metal ion is recovered into the receiving phase.

The driving force in the membrane transport is the concentration gradient of hydrogen ions (Figure 3.10) between the feed and the receiving solution. As described before, and therefore the highly acidic conditions in the receiving solution were crucial for obtaining effective transport across the membrane. The percentage of Sc^{3+} recovery after a 24 h of transport was about 36% when a 1 M H_2SO_4 receiving solution was used and this value slightly increased with increasing the H_2SO_4 concentration to 2 mol L^{-1}. However, a decline of the transport efficiency was observed when 3 M H_2SO_4 was used as shown in Table 3.2. This result was contrary to the Le Chatelier's principle according to which with increasing of the concentration gradient of hydrogen ions the extraction rate should increase accordingly.[33] However, when the sulfuric acid concentration was higher than 2 mol L^{-1}, co-extraction of the acid was observed, which caused a decrease in the pH of the feed solution.

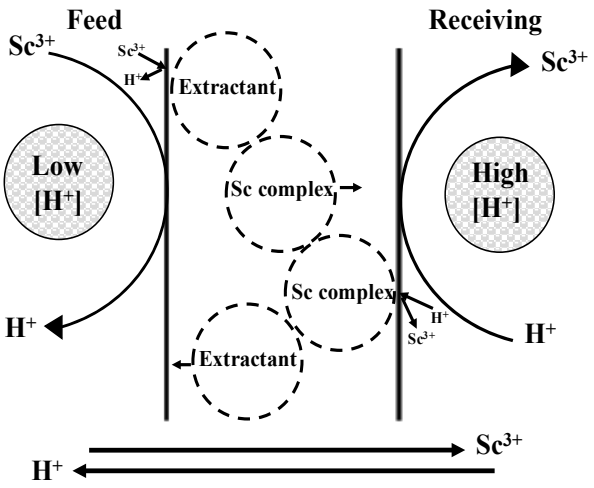


Figure 3.10. Schematic illustration of counter- transport.

Table 3.2, Effect of acid type and concentration in the receiving solution on the transport efficiency for the Sc^{3+} ion and the pH change of the feed solution after 24 h of transport. Remaining experimental conditions as in Figure 3.8.

Acids	pH_f		Remaining % of Sc in feed	Recovery % of Sc in receiving
	t =0 h	t = 24 h		
1 M H_2SO_4	4	3.33	15.7	35.7
2 M H_2SO_4	4	3.21	2.5	39.8
3 M H_2SO_4	4	3.12	23.5	18.2
1 M HCl	4	<zero	59.7	12.5
1 M HNO_3	4	<zero	68.8	4

When the receiving solution contained 1 M HCl or 1 M HNO_3, very small amount of Sc^{3+} was recovered after a 24 h operation, as summarized in Table 3.2. The drop in the pH value in the feed solution to around zero after 6 h of transport was observed, which was due to the fast transport of acids into the feed solution.

Figure 3.11 shows the transport behavior of REM ions including Sc^{3+} through the CTA-based PIM with the optimal composition and a receiving solution containing 1 M H_2SO_4. It was found that Sc^{3+} concentration in the feed phase decreased relatively fast, while in the receiving phase, the concentration gradually increased. The difference in the metal permeation behavior in both phases was considered to be the fact that the metal transport was dominated by the diffusion in the membrane. Therefore, an increase in the metal permeation into the receiving phase has a lag time in the initial stage (Fig. 3.11). After 96 h from the start of the transport experiment, Sc^{3+} was quantitatively recovered in the receiving solution with a recovery factor of 96.7%, and only a small amount of other REM ions was transported through the membrane. These results demonstrate that the binary carrier membrane containing PC-88A and Versatic 10 is suitable for the selective and quantitative recovery of Sc^{3+} from its nitrate solutions containing other REM ions into a 1 M H_2SO_4 receiving solution. The kinetic parameters for the successful transport were calculated and listed in Table 3.3.

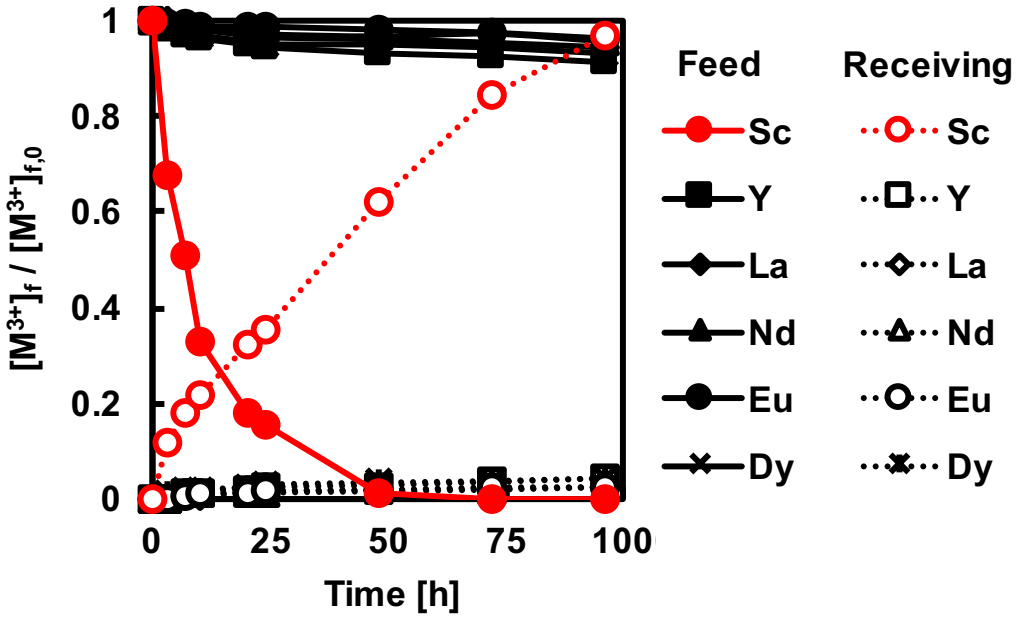


Figure 3.11. Transport of REM ions across a PIM of optimal composition. Experimental conditions as in Figure 3.8.

Table 3.3 Kinetic parameters for Sc^{3+} transport. Experimental conditions as in Fig. 3.11.

K (h^{-1})	V (m^3)	A (m^2)	$[Sc^{3+}]_0^f$ (mol/L)	P (m/h)	J_0 (mol/m^2s)
0.0664	$5 \cdot 10^{-5}$	$4.9 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$6.77 \cdot 10^{-3}$	$1.88 \cdot 10^{-7}$

For comparison, the transport behavior was examined using different nitrate ion activity in the feed phase from 0.01-0.5 M by adding KNO_3 salt which has low flux. The results illustrated that the increase of nitrate ion in the feed phase supported the transfer of protons from receiving phase (pH was estimated through time intervals). For example, upon using 0.2 M nitrate media, pH dropped in the feed phase from 4 to 2.43 after 24h and the extraction reaction was suppressed accordingly. Whilst, the increase of nitrate ion concentration more than 0.5 M leaded to zero stripping percentage in the receiving phase. However, the transport of Sc was carried out from chloride and sulfate media feed solutions, indicating that the best transport results of Sc could be obtained only from nitrate media. Furthermore, the transport experiment was performed with and without plasticizer in the PIM. The effective factors to succeed the transport experiments were the ratio between PC-88A and Versatic 10 as well as the presence of DOP (plasticizer) to enhance the ion dipole interaction.

The variation of sulfate ion concentration in the receiving phase was also studies from 0.1 M to 2.5 M controlled by the addition of NH_4SO_4 to the receiving phase which is thought to affect the metal transport by forming sulfate complexes. The transport of Sc was decreased with increasing sulfate ion concentration, but the transport of other REEs was promoted at high sulfate ion concentration. Finally, the best conditions for running the transport experiment are, 0.1 M nitrate media metal ions as feed phase and 1 M sulfuric acid as receiving phase solution for effective extraction and recovery of Sc ion from the feed phase containing rare earth metal ions with a recovery factor of 96.7%. These results demonstrate the efficiency of this system for the selective recovery of Sc from aqueous solution of other rare earth metal ions.

3.6. Conclusions

This chapter reports the development of the first PIM with a binary carrier consisting of PC-88A and Versatic 10 and its use for the selective separation and pre-concentration of Sc^{3+} from nitrate solutions containing other REM ions. The use of the binary carrier allowed easier stripping of Sc^{3+} from the PIM and thus enabled the construction of a successful membrane permeation system for Sc^{3+}. The transport efficiency of the PIM was found to depend on both the membrane and receiving solution compositions which were optimized as 4 wt% PC-88A + 36 wt% Versatic 10, 40 wt% DOP and 20 wt% CTA for the PIM and 1 M H_2SO_4 for the receiving solution. The results obtained in this study illustrate the potential of binary carrier PIMs for the separation and pre-concentration of target chemical species.

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Chapter 4

A Novel Binary-Extractant-Impregnated Resin for Selective Recovery of Scandium

4.1. Introduction

Recently, scandium has received much attention because of its increasing demand, and its price has increased from 2.54 US$/g in 2009[1] to 4.6 US$/g in 2016[2]. Scandium is a cutting-edge material, and it is used in solid oxide fuel cells,[3] organic chemistry catalysts[4], high-intensity discharge lamps, and as an alloying agent[5]. Scandium is a rare earth element, which refers to the scarcity of concentrated deposits and it occurring in trace amounts. As a result, scandium is recovered as a byproduct from residues and tailing wastes, which often contain much higher concentrations of Fe, Al, and other metals.[6,7] Scandium is conventionally concentrated by precipitation, although the product purity is a matter of concern. Currently, solvent extraction (SX) is widely used to purify scandium from leachates containing large amounts of impurities. Many extractants had been investigated for separation of scandium, such as di-2-ethylhexyl phosphoric acid,[8] tributyl phosphate,[9] ionic liquids,[10] *N*-[*N*,*N*-di(2-ethylhexyl) aminocarbonylmethyl] glycine,[11] and Cyanex series extractants.[12] Inspite of the several advantages of SX, some difficulties, such as phase separation, third phase formation, and loss of extractants, are not easily overcome, especially for organophosphorus extractants. Among the methods used for scandium separation, ion exchange (IX) exhibits high adsorption capacity and low maintenance costs.[13] However, the conventional IX method is not suitable for concentration of low scandium concentration solutions containing impurities owing to the loss of resin performance caused by contaminants.[14] Therefore, impregnated resins are promising because they combine the advantages of SX and IX by incorporating an extractant that can be selectively recognize a specific metal ion into the polymer matrix. The key for efficient recovery of the targeted metal ion is the functional group of the extractant and its affinity for a specific metal ion.

The impregnated-resin technique can overcome the problems of scandium recovery by SX. However, reports dealing with Sc separation are limited. Organophosphorus extractants are

popular for recovery of Sc. Separation of Sc by a HDEHP known as (D2HEPA)-impregnated resin (Lewatit VP OC 1026) [15] and a HEHEHP known as (PC-88A)-impregnated resin (XAD-7)[16] has been investigated. However, elution of the adsorbed metals was difficult, and the Sc–HEHEHP complex could only be eluted with 4-methyl-2-pentanone. A review article suggested that the scandium elution efficiency increases in the order Na_2CO_3 > $NaHCO_3$ > $(NH_4)_2CO_3$ > NH_4F>H_2SO_4 > $Na_2S_2O_3$ > HCl > Na_2SO_4.[17] Other research has shown that scandium can be effectively eluted from an iminodiacetate resin using ethylenediaminetetraacetic acid, diglycolic acid, or carboxylic acids.[18] Smirnov et al, succeeded in eluting adsorbed Sc from a phosphorous-containing IX resin using 180 g/l Na_2CO_3.[19] A recent study using Lewatit TP 260 and Lewatit TP 209 chelating resins and a Lewatit TP 272 solvent-impregnated resin reported selective adsorption of Sc over Fe(III) and Al(III). [20] However, they could not recover Sc even with highly concentrated acids owing to resin breakage and solvent leakage, indicating that elution strategies need further improvement.

In Chapter 2 and 3 [21,22] we performed extraction of Sc from other rare earth ions by SX with a polymer inclusion membrane using a binary-extractant system with a long alkyl chain carboxylic acid and an organophosphonic ester. In SX, the binary-extractant system allowed high-efficiency stripping using a mild acidic solution, which was difficult using the organophosphonic ester extractant alone. The binary system is promising for selective recovery of Sc from other rare earth ions. However, it needs further improvement to completely overcome precipitate formation, which occurs in the high metal-loaded organic phase. In Chapter 4, we introduced the binary-extractant system into solvent-impregnated XAD-7HP resins. Our aim is to create an efficient impregnated resin for pre-concentration and recovery of Sc using the binary-extractant concept. We expect that binary-extractant-impregnated resins will overcome the problems of third phase and precipitate formation, and allow selective extraction and high elution of Sc suitable for industrial application.

4.2. Experimental

4.2.1. Reagents

The PC-88A and Versatic 10 extractants were purchased from Daihachi Chemical Co., Ltd. (Osaka, Japan) and Japan Epoxy Resin (Tokyo, Japan) (currently Mitsubishi Chemical Corporation), respectively. Amberlite XAD-7HP, which is an acrylic ester co-polymer without any ligands, was supplied by Organo Corporation (Tokyo, Japan)., and its physical properties are listed in Table 4.1 The metal nitrate salts for the aqueous feed solutions were provided by Sigma-Aldrich (St. Louis, USA). Nitric acid and ammonium nitrate were purchased from Kishida Chemical Co., Ltd. (Osaka, Japan). All of the other chemicals were of analytical grade.

Table 4.1 Physical properties of Amberlite XAD-7HP.

Physical property	Value
Superficial area	450 m^2g^{-1}
Resin porosity	0.55
Particle size	20/60 mesh-250/850 µm
Pore volume	0.97-1.14 cm^3g^{-1}
Pore size	85-90 Å
Skeletal density	1.24 gcm^{-3}

4.2.2. Preparation of the Extractant impregnated resin

The Amberlite XAD-7HP resin was first washed with ethanol:hydrochloric acid:water (2:1:1) solution overnight to remove impurities and residual monomers. The resin was then rinsed several times with distilled water and dried in a vacuum oven at 60 °C for 5 h. The desired amount of the single or binary extractant was dissolved in 10 ml of chloroform, and 1 g of the resin was then added and the mixture was stirred overnight. The chloroform was removed by evaporation and the resins were dried in vacuo for 4 h. The amount of loaded sorbent per gram of resin was determined from the weight change before and after the loading process. It was found that 0.55 g of both extractants could be loaded per gram of resin, although more than 0.95 g impregnation leads to an oily surface, as shown in Figure 4.1.

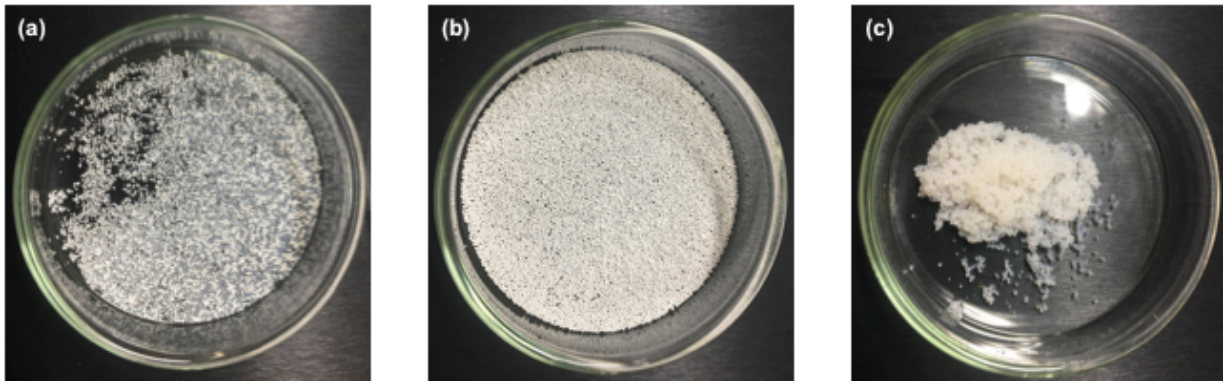

Figure 4.1 (a) XAD-7HP resin before treatment. (b) XAD-7HP resin loaded with 0.55 g of both extractants per gram of resin. (c) XAD-7HP resin loaded with 0.95 g of both extractants per gram of resin.

Leakage of the extractants from the resins was tested by shaking the impregnated resins with 0.01 M hydrochloric acid for one week. Leakage from the resins was negligible under the present experimental conditions.

4.2.3. Adsorption procedure

The adsorption experiments were performed in batches using 50 mg of the EIR to investigate the loading capacity, kinetics, and selective separation and pre-concentration process. Aqueous feed phases containing 0.1 mM of each of Sc and other rare earth ions (Y^{3+}, La^{3+}, Nd^{3+}, Dy^{3+}, and Eu^{3+}) or transition metals (Al^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, etc) were prepared by dissolving the nitrate salts of the metals in 0.1 M HNO_3 or 0.1 M ammonium nitrate solution. The pH values of the aqueous phases were adjusted by mixing the two solutions. In the adsorption experiments, the ratio of the solution volume to the resin was kept constant at 100 ml/g, except for the loading capacity test where the ratio was 40 ml/g. Untreated XAD-7HP was also used for comparison. For all of the experiments, the solutions were shaken for 1 h at 298 K by horizontal axis rotation using a rotary mixer (15 rpm, NRC-D20, Nisshin Rika Co., Tokyo, Japan). The resultant solutions after adsorption were filtered off and analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 8300, Perkin Elmer Inc., MA, USA).. The degree of adsorption of the metal ions was calculated by

$$A = (C_0 - C_f)/C_0, \quad \textbf{(4.1)}$$

where A (-) is the degree of adsorption, C_0 (mg/l) is the initial concentration of the metal, and C_f is the concentration of the metal in the aqueous solution after equilibration with the impregnated resin. The adsorption capacity q (mg/g) was calculated by

$$q = (C_0 - C_f) \times V/M, \quad \textbf{(4.2)}$$

where V is the volume of the solution (L) and M is the dry mass of adsorbent (g). Desorption from the metal-loaded EIR was performed using various mineral acids. The metal ion desorption degree from the adsorbent De (-) was calculated in a similar way to the adsorption experiments:

$$De = C_{de}/C_{ad}, \quad \textbf{(4.3)}$$

where C_{ad} represents $(C_0 - C_f)$ in the adsorption step and C_{de} (mg/l) is the metal concentration in the desorbing solution.

4.3. Results and Discussion

4.3.1. Sc removal using the EIR containing a single extractant

Adsorption and desorption of the rare earth metal ions were investigated using EIRs containing either PC-88A or Versatic 10. Initially, the amount of PC-88A or Versatic 10 impregnated in the resin was varied from 0.05 to 1.6 mmol/g, and the adsorption experiments were performed from pH 1 to 3.5. Figure 4.2(a) shows extraction of the metal ions with the EIR containing 0.05 mmol/g PC-88A as a function of the pH of the aqueous solution. Sc adsorbs to the extractant-impregnated resin with high efficiency in all pH range, and Sc selectively adsorbs in preference to the other rare earth ions in the low pH range. The selectivity for Sc decreases with increasing amount of impregnated PC-88A. The adsorption behavior of the metal ions with the EIR containing 0.75 mmol/g Versatic 10 is shown in Figure 4.2(b). The EIR with Versatic 10 is highly selective for Sc, although the affinity of Versatic 10 for rare earth ions is much lower than that of PC-88A (Wang and Cheng, 2011). A higher amount of extractant impregnated in the resin and a higher pH are required to achieve quantitative extraction of Sc compared with PC-88A. No adsorption of metal ions is observed with untreated XAD-7HP. Desorption from each EIR was tested with nitric acid. The results reveal the difficulty of Sc recovery from the impregnated resins even under highly acidic conditions (Figure 4.3).

4.3.2. Binary-extractant-impregnated resin

Based on the individual adsorption behavior, the amount of PC-88A impregnated into the resin was fixed at 0.05 mmol/g, while the amount of the second component Versatic 10 was varied

from 0 to 1.6 mmol/g. Batchwise adsorption and desorption experiments using the binary EIR were performed. Figure 4.4(a) shows the effect of the amount of impregnated Versatic 10 on the desorption behavior. The stripping efficiency increases with increasing amount of Versatic 10, although impregnation of too much Versatic 10 makes stripping difficult, similar to the case using the single extractant EIR resins. In SX with only PC-88A or Versatic 10,

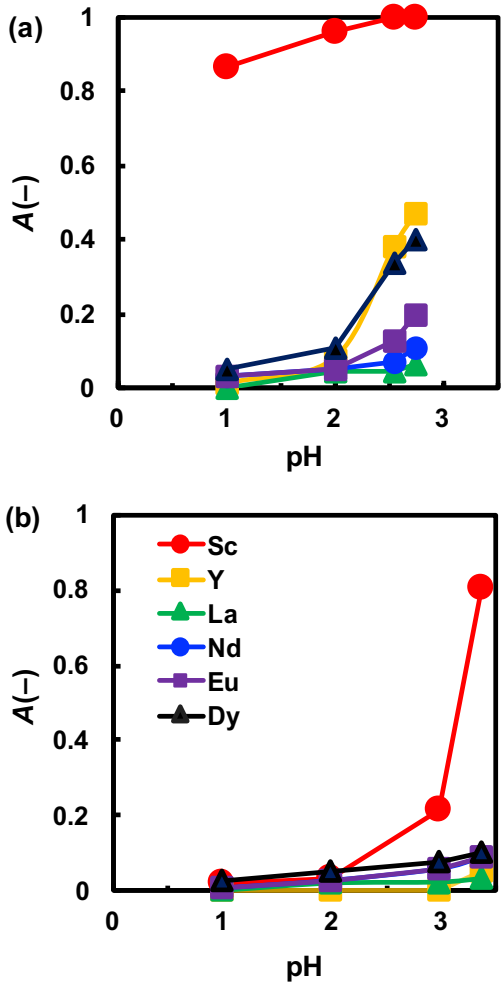

Figure 4.2. Adsorption of rare earth metal ions as a function of pH for (a) 0.05 mmol/g PC-88A and (b) 0.75 mmol/g Versatic 10 impregnated XAD-7HP (50 mg resin, 5 ml aqueous solution with initial concentration of 0.1 mM metal ions, and 1 h shaking at room temperature).

Sc is extracted with three dimer extractants. For the binary-extractant system, NMR analysis (data not shown) suggests that Sc is extracted with hetero dimers with the two extractants. The complex with the two extractants is not rigid, and it is unstable compared with that formed with the individual extractants. Therefore, Sc is considered to be readily stripped with a mildly acidic solution. Thus, it is concluded that the resin with 0.05 mmol/g PC-88A and 0.75 mmol/g

Versatic 10 is the best combination for quantitative desorption of Sc (optimum condition) (Figure 4.4(a)).

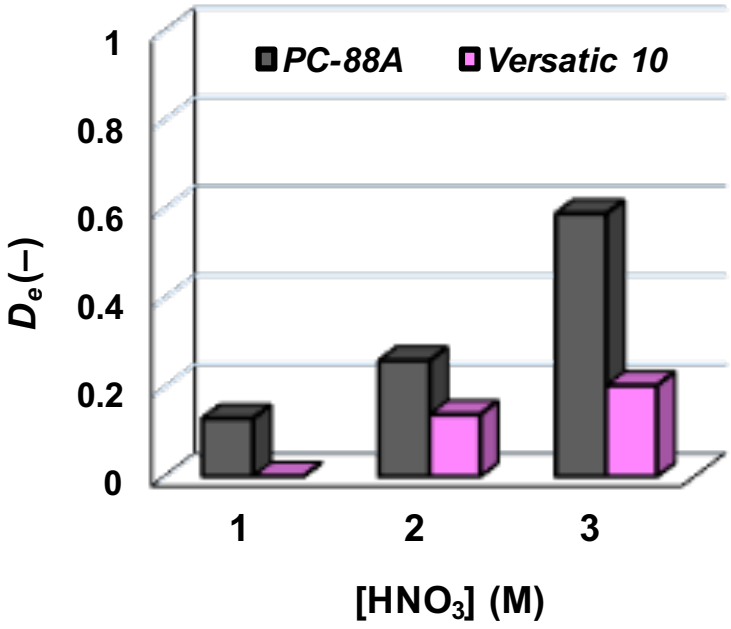

Figure 4.3. Desorption of Sc ions from (a) 0.05 mmol/g PC-88A and (b) 0.75 mmol/g Versatic 10 impregnated XAD-7HP (50 mg resin, 5 ml aqueous solution with initial concentration of 0.1 mM metal ions at pH 2.75 and 3.4 for PC-88A and Versatic 10, respectively, and a1 h shaking at room temperature)

The desorption efficiency with the optimum combination was also investigated using H_2SO_4 and HCl. H_2SO_4 provides a higher recovery yield than using the other mineral acids. The stripping efficiency increases in the order H_2SO_4 > HNO_3 > HCl (Figure 4.4(c)). Figure 4.4(b) shows the effect of the pH on the adsorption behavior of rare earth ions to the optimum binary EIR. The binary system can selectively adsorb Sc over other rare earth metals and quantitative desorption from the loaded resin can be achieved. A few studies[24-25] have reported the advantages of the binary-extractant system compared with single-extractant systems for SX, and using two extractants leads to new characteristics in the extraction and stripping processes. Based on the previous studies, choosing the best combination of the two extractants is crucially important to improve the desorption performance, which is an obstacle for application of impregnated resins to industrial separation.

4.3.3. Adsorption isotherm

The adsorption isotherm was investigated in a wide range of initial Sc(III) concentrations at pH 2.75 under the optimum conditions (Figure 4.5). The obtained data were subsequently applied to the Langmuir isotherm model:

$$\frac{1}{q} = \frac{1}{K_1 q_{\mathrm{m}}} \times \frac{1}{C_{\mathrm{e}}} + \frac{1}{q_m}, \qquad \textbf{(4.4)}$$

where C_{e} is the equilibrium concentration of Sc in the solution (mg/L), q is the amount of adsorbed Sc ions at equilibrium (mg/g), as defined by Eq. (2), K_1 is the Langmuir constant, q_{m} is the maximum adsorption capacity (mg/g), respectively.

Plots of $1/C_{\mathrm{e}}$ versus $1/q$ was constructed to determine whether the experimental data fit the Langmuir isotherms. The determination coefficient R^2 value for scandium adsorption on these resins is close to 1, indicating that this model can be applied to express Sc adsorption on the impregnated XAD-7HP. Langmuir isotherm suggests the homogeneous sorption, indicating the homogeneous distribution of extractant molecules on the polymeric support. It was noted that doubling (1.6 mmol/g) of tripling (2.4 mmol/g) the amount of the impregnated binary extractant has an insignificant effect on the REEs adsorption. However, the high extractant loading reduce the hinderance of the hydrophobic surface of the polymer pores against the fast contact between the hydrophilic metal ions and the extractant in the resin. Thus, filling the pores could be essential when hydrophobic resins are used.[26]

The maximum adsorption capacity and K_1 estimated are listed in Table 4.2. The adsorption capacities and elution performance for various extractant-impregnated resins are summarized in Table 4.3.

Table 4.2 Parameters of the Langmuir isotherm for adsorption of scandium on the EIR.

Extractant in EIR mmol/g	q_m **mg/g**	K_1	$\mathbf{R^2}$
0.8	48	$3.9*10^{-4}$	0.99

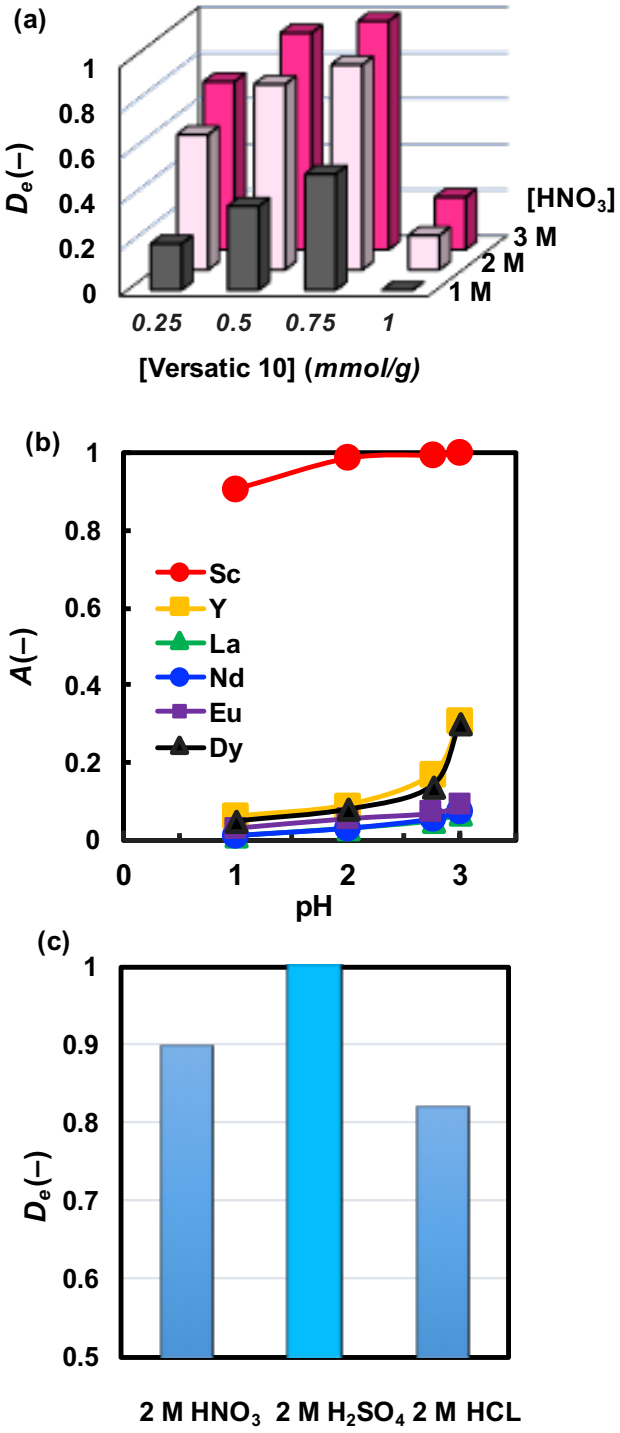

Figure 4.4. (a) Changes in the Sc desorption ratios as a function of the amount of Versatic 10 added to 0.05 mmol/g PC-88A for various HNO3 concentrations. (b) Effect of pH on adsorption of rare earth ions by the optimum EIR (c) Desorption from the 0.05 mmol/g PC-88A/0.75 mmol/g Versatic 10 impregnated resin (optimum) using various mineral acids. (50 mg resin, 5 ml aqueous solution with initial concentration of 0.1 mM metal ions, and 1 h shaking at room temperature). Adsorption was performed from aqueous solution at pH 2.75 prior to desorption (Figure 4.3 (a))

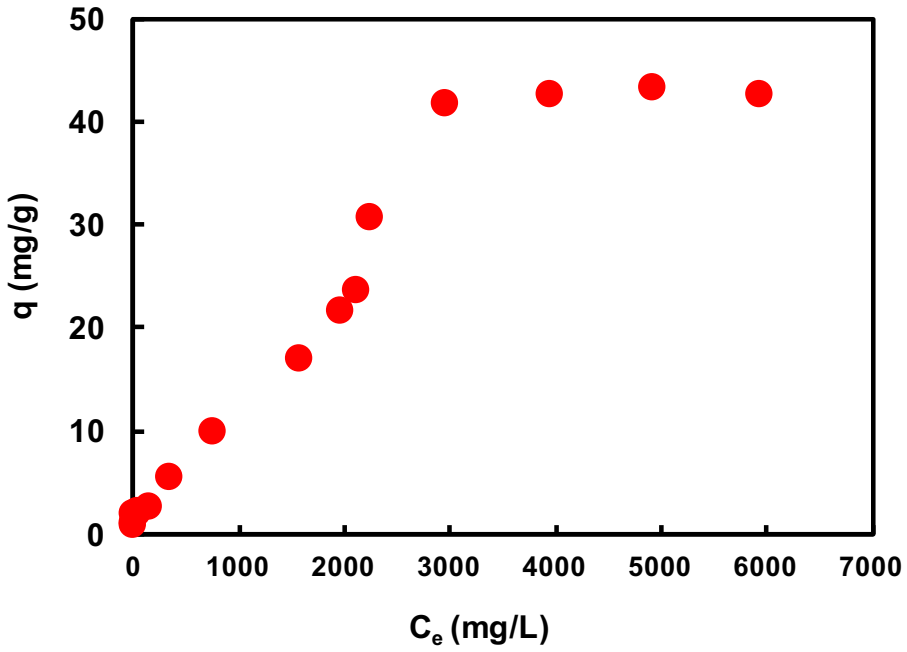

Figure 4.5. Sc adsorption equilibrium isotherm (50 mg resin, 2 ml aqueous solution, and 1 h shaking at room temperature).

Table 4.3 Adsorption capacities and elution performance of Sc for various extractant-impregnated resins.

Resin	Extractant	Adsorption capacity (mg/g)	Elution	Refs
XAD-7	[A336][CA-100]	1.888	0.3 M HNO_3	27
XAD-7	$[C_8mim][PF_6]$ +Cyanex923	44.64	Not mentioned	28
TP 272	Cyanex 272	Around 10	Not mentioned	20
XAD-7HP	PC-88A+ Versatic 10	48	2M H_2SO_4	This work

4.3.4. Sorption kinetics

The effect of the contact time on adsorption of Sc(III) was investigated by varying the contact time from 2 to 60 min using 50 mg of the optimum binary EIR and 5 ml of a solution containing 50 mg/l Sc. Adsorption of Sc increases with increasing contact time, and equilibrium is achieved at about 20 min with maximum loading of 2.9 mg Sc. The kinetics of Sc adsorption on the binary-extractant-impregnated resin is considered to be relatively high. The pseudo-first- and pseudo-second-order rate laws were applied to the adsorption kinetics of Sc on the EIR:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\log t \quad (4.5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4.6)$$

where q_e and q_t are the amount of Sc (mg/g resin) adsorbed on the EIR at equilibrium and time t, and k_1 and k_2 are the rate constants for pseudo-first- or pseudo-second-order adsorption, respectively.

The rate constants and coefficients of determination (R^2) for both kinetics laws are given in Table 4.4. The R^2 value for the pseudo-second-order equation is close to 1. Moreover, comparison of the values of the experimental and calculated adsorption capacities shows that there is a good match with pseudo-second-order kinetics. Therefore, pseudo-second-order kinetics is more suitable for expressing the adsorption reaction.

Table 4.4 Rate constants for pseudo-first- and pseudo-second-order kinetics of Sc adsorption on the binary EIR.

Constants of kinetic expression			
Pseudo first-order rate			
k_1, t/s^{-1}	calculated $\mathbf{q_e}$, mg/g	empirical $\mathbf{q_e}$, mg/g	R^2
0.98	1.98	2.95	0.98
Pseudo second-order rate			
k_2, $m/g.mg^{-1}.s^{-1}$	calculated $\mathbf{q_e}$,mg/g	empirical $\mathbf{q_e}$, mg/g	R^2
6.163	3.05	2.95	0.997

Initial Sc concentration:50 mg/l

4.3.5. Thermodynamic study

The effect of the temperature on adsorption of Sc on the binary EIR was investigated in the range 23–50 °C. The amount of adsorbed Sc increases with increasing reaction temperature (data not shown). The thermodynamic equilibrium constant K_d was calculated by

$$K_d = \frac{(C_0 - C_e)V}{mC_e}, \quad (4.7)$$

This value was then used to calculate the apparent thermodynamic parameters:

$$\ln K_{\mathrm{d}} = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (4.8)$$

$$\Delta G = \Delta H - T\Delta S, \quad (4.9)$$

where ΔH is the enthalpy change (kJ/mol), ΔS is the entropy change (J/(mol K)), R is the gas constant (8.314 J/(mol K)), T is the absolute temperature (K), and ΔG is the free energy change (kJ/mol).

The calculated apparent thermodynamic parameters for Sc(III) sorption on the binary EIR are ΔH = 18.5 kJ/mol, ΔS = 68.9 J/(mol K), and ΔG = −0.277 kJ/mol. The positive value of ΔH confirms the endothermic character of this adsorption process. The negative value of ΔG indicates the spontaneous nature of adsorption on the resin. The positive value of ΔS indicates increased randomness at the solid–solution interface during adsorption.[29]

4.3.6. Sorption of interfering metal ions

Some common impurity metals, such as Fe(III), Al(III), and Zr (IV), tend to compete with Sc(III) for adsorption on the active binding sites. Thus, it is crucial for the successful adsorption system to separate Sc from these impurities. The binary-extractant system developed in this study was investigated for separation of Sc from other metal ions (Figure 4.6). Sc can be selectively separated from all of the contaminant metal ions at pH 0.5 without the need for iron reduction or scrubbing treatment. The results confirm that the newly developed binary-extractant resin has a stronger affinity for Sc than Fe, Zr, and Al. The most recent study achieved higher selectivity of Sc than Fe using an EIR.[20] However, reduction of Fe was required prior to the adsorption step and Sc could not be recovered with highly concentrated acids owing to solvent leakage. Therefore, this binary-extractant resin is promising for recovery or pre-concentration of Sc from industrial effluents and wastes containing ferric ions.

4.3.7. Recycling and re-use of Extractant impregnated resin

Metal desorption and resin recycling are critical issues in industrial separation processes using resins. Recovery of the loaded Sc ions was quantitatively achieved using 2 M sulfuric acid. The reusability of the binary resin was confirmed by applying two rinsing steps with 0.1 M HCl, and then five adsorption experiments were performed under the same experimental

conditions. No obvious change in the impregnated-resin performance is observed from the first to the fifth adsorption recycle tests. Thus, the newly developed binary-extractant-impregnated resin is suitable for practical use.

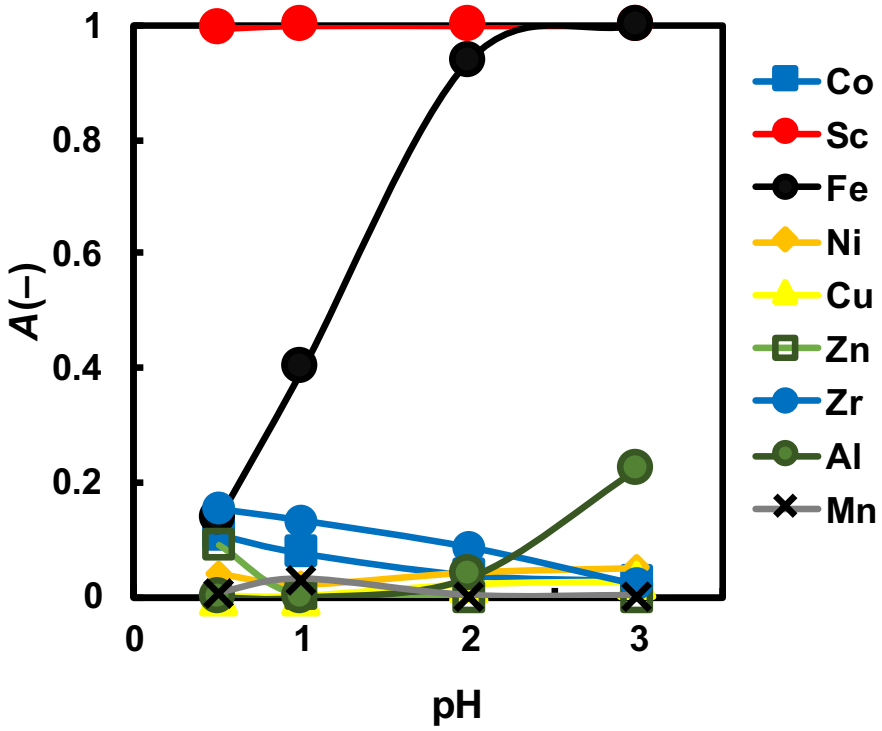

Figure 4.6. Degree of adsorption of the interfering metals on the optimum binary EIR (50 mg resin, 5 ml aqueous solution with initial concentration of 0.1 mM metal ions, and 1 h shaking at room temperature).

4.4. Conclusion

A mixture of the commercial extractants PC-88A and Versatic 10 has been successfully impregnated into the XAD-7HP resin. Several unique characteristics are obtained by applying the binary-extractant system to the extractant impregnated resin (EIR). Desorption of the loaded Sc can be quantitatively achieved using 2 M sulfuric acid, which is a problem for conventional impregnated resins. The newly designed EIR was used for separation and recovery of Sc^{3+} from a nitrate medium containing common metal ions, such as Al^{3+}, Fe^{3+}, Zr^{4+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}. Sc can be selectively recovered from the REEs and other impurities ions, and reduction of the iron ions or applying a scrubbing treatment is not required. The maximum loading capacity of the binary EIR for adsorption of Sc is 48 mg Sc/g resin for 0.8 mmol/g binary-extractant-impregnated XAD-7HP resin. The impregnated resin

adsorbs Sc according to the Langmuir isotherm and second-order kinetics. Based on the results, PC-88A and Versatic 10 impregnated in the XAD-7HP resin shows promising adsorption performance for recovering Sc from tailing and industrial wastes.

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Chapter 5

Conclusion

Due to the high prices and increased applications of rare earths, the world is focusing on new strategies for their recovery from effluents and industrial wastes that usually contain many contaminants. Therefore, the development of an efficient and environmental friendly separation system of REEs including scandium is crucial to sustain the continuous demand. Organophosphorus extractants such as EHEHPA commercially known as PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) is widely used for the recovery of various metal ions from the alternative sources (mainly industrial wastes) including REEs. The use of PC88A in conventional solvent extraction suffers from many problems. The need for developing an efficient extractant system with good stripping ability for rare earths especially for scandium is crucial for the industrial applications. For this reason, a binary system is utilized to create a new promising strategy for REEs extraction. **Chapter 1** described the general introduction on the current states and issues related to rare earth separation.

In the thesis, the binary system composed of PC88A and Versatic 10 was developed for the extraction and recovery of scandium (**chapter 2**), and applied the extractant system to a polymer inclusion membrane(PIM) (**chapter 3**) and extractant impregnated resin (**chapter 4**).

In chapter two, the extraction behavior of rare earth metal ions was screened using several binary systems composed mainly PC-88A and another extractants. Among them, a combination of PC-88A and Versatic 10 is the best candidate to attain both extraction and stripping under favorable conditions. 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 appropriate pH and allowed stripping using a mild acid concentration. The extraction behavior was analyzed and the results suggested that the participation of Versatic 10 in the extraction reaction, and the extracted species could be $Sc(HR_2)_3$ and $Sc(HAR)_3$ at low metal loading under low acidic conditions (HR:PC-88A, HA:Versatic10). The FT-IR and NMR results supported the extraction mechanism for the binary extractant system that Versatic 10 participates in the extraction of scandium ions as the association form with PC88A through changes in intermolecular hydrogen bonds. This causes an antagonistic effect and facilitates efficient scandium stripping from the extractant solution.

Chapter 3, reported the development of the first PIM from the binary carrier PC-88A/Versatic 10 for the separation and recovery of Sc. The optimum PIM was decided by

studying many membrane compositions of PC-88A/Versatic 10 ratio, polymer and plasticizer. The amount of extracted or recovered Sc metal ions depends on many process parameters such as pH of feed phase, acid concentration of feed phase and PIM composition that accordingly change the flux and the process kinetics. Finally, Scandium was selectively and quantitatively transported into the receiving phase against the concentration gradient from other rare earth metal ions through binary system PIM. The newly binary mixture inclusion membrane of Versatic 10 and PC-88A gives transparent and stable membrane, promoting the best desorption ability and overcoming the solvent extraction deficiencies such as flooding, and third phase formation.

The fourth chapter, a mixture of the commercial extractants PC-88A and Versatic 10 has been successfully impregnated into the neutral XAD-7HP resin. Using the individual extractant, the selective adsorption of Sc was possible, however the desorption was very difficult. In the binary extractant system, the desorption ratio was increased with increasing the amount of impregnated Versatic 10, and the best combination for the quantitative desorption of Sc was found to be 0.05 mmol/g PC-88A and 0.75 mmol/g Versatic 10. This binary-extractant-impregnated concept could provide a new way to develop novel ion-exchange resins for metal separation. Sc can be selectively separated from all of the contaminant metal ions such as Al^{3+}, Fe^{3+}, Zr^{4+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} at pH 0.5. The good reusability of the resin was confirmed by five times repeated use in the recycling operation. The results demonstrated PC-88A and Versatic 10 impregnated in the XAD-7HP resin is a promising technique for recovering Sc from tailing and industrial wastes.

The major findings in this work relate to the increased understanding of three different techniques using mixture extractant systems for the separation of rare earth elements. The results from this work show that the antagonistic interactions dominated in the mixed mixture, could be relevant to industrial separations. The development of new mixed or synergistic solvents is the way forward from the perspective of process improvements. The results suggest a bright future for the next generation of selective mixed extractants.

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