Development of efficient extraction and separation systems for scandium

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Development of efficient extraction and separation systems for scandium

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Chapter 1. Introduction

1-1 Rare earth elements

1-1-1 Rare earth elements sources and current situation

Rare earth elements (REEs) series are a group of seventeen chemical elements, in the periodic table group 3 as shown in Table 1-1, including scandium (Sc), yttrium (Y) and the fifteen lanthanides (lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu)). These elements have similar chemical properties and can be found in the same ore deposits [1,2]. They are named rare earth elements, some of them are very plentiful in nature, such as Ce, which is as abundant as Copper in Earth's Crust [1-10]. However due to their geochemical properties, they are still named as "rare earth".

In 1787, Lieutenant Carl Axel Arrhenius discovered "ytterbite" (gadolinite), starting the REEs chapter in the history of science [9]. The REEs are often subclassified into "light-group" (LREEs including Sc, La, Ce, Pr, Nd, Pm, Sm, Eu and Gd) and "heavy-group" (HREEs including Y, Tb, Dy, Ho, Er, Tm, Yb and Lu) based on the electronic configurations of REEs [1-3]. Electronic configuration and radius of each trivalent REE are listed in Table 1-2.

Talbe1-1 periodic table

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57~ 71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89~ 103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides 57~71			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides 89~103			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Table 1-2 The ionic radius of rare earth elements

Element	Atomic number	Atomic weight	Electron config	Crystallized ionic radius (Å)		
				Ln^{2+}	Ln^{3+}	Ln^{4+}
Sc	21	44.95591	$(3d4s)^3$		0.885	
Y	39	88.90585	$(4d5s)^3$		1.040	
La	57	138,9055	$4f^0(5d6s)^3$		1.172	
Ce	58	140.155	$4f^1(5d6s)^3$		1.15	1.01
Pr	59	140.90765	$4f^2(5d6s)^3$		1.13	0.99
Nd	60	144.24	$4f^3(5d6s)^3$	1.43	1.123	
(Pm)	61	(145)	$4f^4(5d6s)^3$		1.11	
Sm	62	150.36	$4f^5(5d6s)^3$	1.36	1.098	
Eu	63	151.965	$4f^6(5d6s)^2$	1.331	1.087	
Gd	64	157.25	$4f^7(5d6s)^3$		1.078	
Tb	65	158.92534	$4f^{88}(5d6s)^3$		1.063	0.90
Dy	66	162.5	$4f^9(5d6s)^3$	1.21	1.052	
Ho	67	164.93032	$4f^{10}(5d6s)^3$		1.041	
Er	68	167.26	$4f^{11}(5d6s)^3$		1.030	
Tm	69	168.9432	$4f^{12}(5d6s)^3$	1.17	1.020	
Yb	70	173.04	$4f^{14}(5d6s)^2$	1.16	1.008	
Lu	71	174.967	$4f^{14}(5d6s)^3$		1.001	

REEs are applied in many industrial materials, such as electronic materials (Nd, Dy, Sm…), alloy and aeronautical materials (Sc), automotive materials (Nd, Dy, Sm…), nuclear materials (Zr, Hf, Sc…), and so on as shown in Table 1-3 [11-13]. REEs have analogous electronic configurations, with the outer three electrons as Sc $(3d4s)^3$, Y $(4d5s)^3$, La $(5d6s)^3$ as shown in Table 1-2 [2,13]. Thus, REEs are difficult to separate from each other, especially for those with a high purity to use in scientific researches and industrial applications.

Table 1-3 Applications of REEs in various fields.

Application	21 Sc	39 Y	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Magnets			○		○	◎		◎		○	○	○					
Phosphors/ Luminescence	○	○		○	○	○			○	○	○		○	○	○	○	
Metal alloys/ baeetries	○		○	○	○	○		○									
Glass/Polishing/ Ceramics		○	○	○	○	○											
Optical disc										○	○	○					
Capacitor		○	○			○											
Catalyst	○	○	○	○	○	○											

China as the world's leading producer since early 1990s [5], had dominated about 95% of the REEs supply production until 2010. The prices for many REEs had risen significantly since then. Therefore, development of efficient extraction and separation methods for REEs not only from each other, but also from other metals has been desired in the world [3-4, 5-8, 10,13]. Among them, scandium has attracted a lot of attention on its application and consequently the separation [14,15].

1-1-2 Sources of Sc and its application

Scandium (Sc), with atomic number 21 is a silvery-white metallic rare earth element. It was discovered in 1879 from the minerals euxenite and gadolinite of Scandinavia [5]. Sc belongs to LREEs and its electronic configurations is $(3d4s)^3$. The supply of Sc is very limited every year. Since no scandium mine was found, Sc is produced as a byproduct from mines in China (titanium and rare earth), Kazakhstan (uranium), Russia (apatite), and Ukraine (uranium), as a result with low concentration from each mine [4,16-18]. Nonetheless, Sc is widely utilized in industries, such as televisions and fluorescent energy-saving lamps [19,20], alloys [21-23], catalyst [24,5], fuel cell [26,27] etc., making Sc very expensive. Therefore, the extraction and separation of Sc from other metals has become very important to maintain the continuous enough supply.

1-2 Extraction methods for metal separation

Metals exhibit different chemical and physical properties [11,15]. Therefore, extraction and separation of metals from others metals can be done by chemical or physical methods. In chemistry, hydrometallurgy is a very useful method for obtaining target metals from ores or urban mines. It comprises liquid-liquid extraction (LLE) [28-30], solid-phase extraction (SPE) [31-35], and liquid-membrane extraction (LME) [36-38] etc. The former two methods are widely used in hydrometallurgical processes.

1-2-1 Liquid-liquid extraction

In industry, liquid-liquid extraction (solvent extraction) is an effective method for separation and purification of metals. LLE can be used in easy operation with simple equipments, and in continuous extraction and separation processes. Normally, LLE process consists of target metals' transferring from a feed phase to another phase containing an extractant, which forms a hydrophobic complex with target metal ions (Figure 1-1). The medium salt, pH condition, solvents, and extractants (mainly) are important factors in the liquid-liquid extraction process. In general, organic solvents are used as the water-immiscible phase. Therefore, the use of environmentally friendly solvents, which are harmless and less volatile, has been desired. Most recently ionic liquids have attracted much attention as an alternative to organic solvents as described later.

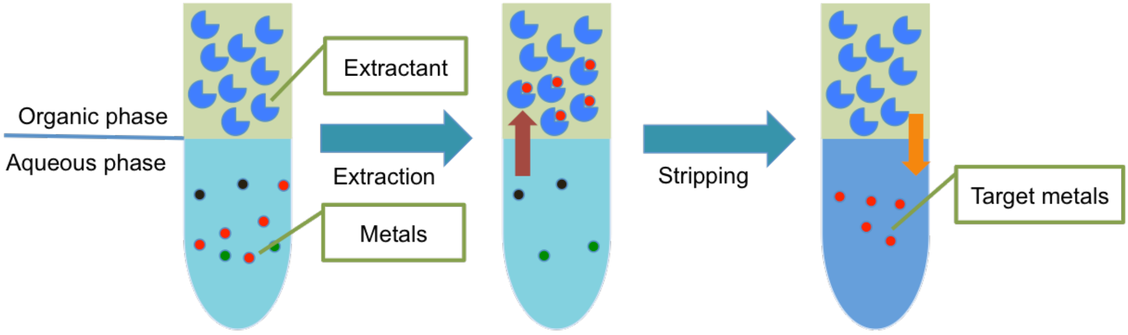
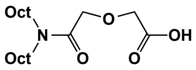
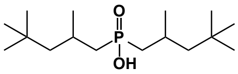
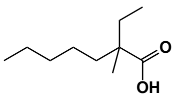
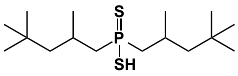
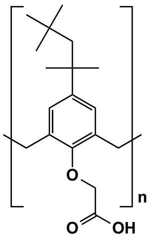
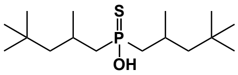
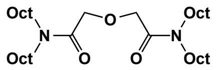
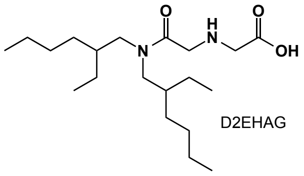
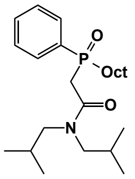
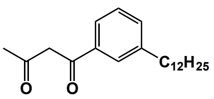
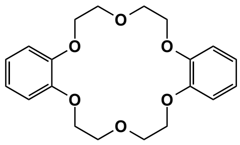
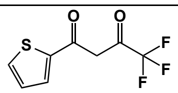
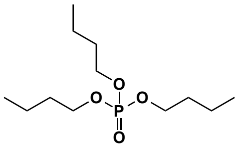
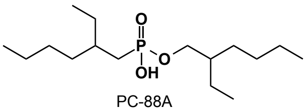
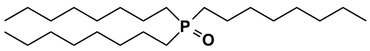


Figure 1-1 Liquid-liquid extraction (LLE) process.

1-2-1-1 Extractants

The liquid-liquid extraction is one of the most promising methods for the separation of metal ions. The extraction efficiency, critical for LLE, is strongly affected by the properties of the extractants used. The extractants can be characterized as acidic and neutral extractants. Many extractants have been employed in the extraction and separation of metal ions as shown in Table 1-4. For the extraction of metal ions, *N,N,N',N'*-tetraoctyldiglycolaminde (TODGA) was synthesized and applied for the extraction and separation of Zr(IV) and Hf (IV) from nitrate aqueous solutions by Saleh et al [39]. The neutral organophosphorus compounds such as octyl(phenyl)-*N,N*-diisobutylcarbamoyl-methyl phosphine oxide (CMPO) was used on transuranic extraction (TRUEX) process and it showed increase the extraction efficiency for the trivalent actinides and lanthanides, due to its high performance of phosphoryl group by Mincher et al. [40]. The organic organophosphorus compounds di(2-ethylhexyl)phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ether (PC-88A) were successfully used to separate Ti(IV) from Fe(III), Al(III), V(V), Ce(IV), Mg(II), and Mn(II) by Singh et al [41].

Table 1-4 the structure of some extractants.

Type	Structure	Type	Structure
Acidic extractants (extraction with protonation)	 **DODGAA**	Acidic extractants (extraction with protonation)	 **Cyanex 272**
	 **Versatic 10**		 **Cyanex 301**
	 **Calix[4]arene carboxyl derivatives**		 **Cyanex 302**
		Neutral extractants (extraction without protonation)	 **TODGA**
	 D2EHAG		 **CMPO**
	 LIX 54		 Dicyclohexano-18-crown-6 derivatives
	 HTTA		 **TBP**
	 PC-88A		 TOPO

1-2-1-2 Synergistic extraction

As described above, many extractants have been synthesized and reported. Furthermore, selective extraction of metals with synergistic extractants, by using two kinds of extractants, has been reported. Synergistic extraction systems have obtained more and more attention in recent years. It not only enhances the extraction efficiency, but also improves the selectivity, even the stripping performance of target metal ions. So far, many synergistic extraction systems have been investigated and applied. A significant synergistic extractant system consisting of LIX 63 and Ionquest 801 was developed to recover germanium over other metals in aqueous solutions (Nusen et al.) [42]. Synergistic primary amine and neutral organophosphorus derivatives Cyanex 923 and Cyanex 925 were investigated for extracting zinc(II) and cadmium(II) from a hydrochloric acid solution. The extraction rate followed the order: Zn(II) > Cd (II), and the synergistic effects followed N1923 + Cyanex 925 > N1923 + Cyanex 923 (Luo et al.) [43].

1-2-2 Solid phase extraction

With the sustainable development of science, the separation, the preconcentration and the recovery of metal resources from minerals or urban mines are becoming significantly challenging in technology. Various procedures for the separation and preconcentration of metal ions from their matrix, such as liquid-liquid extraction, solid-phase extraction (SPE), ion exchange, flotation, and cloud-point extraction etc. have been extensively developed [44]. The liquid-liquid extraction is widely used in industry for the separation and purification of metal ions. However, this reagent and solvent consuming procedure always imposes several environmental problems because of the toxicity and volatility of the organic solvent. The SPE approach has been sometime promoted, due to its simplicity, rapidity, high recovery, low consumption and controllability. The fundamental principle of SPE is the target metal ions from the aqueous phase being bound to solid phase, and being desorbed in the other solution, as shown in Figure 1-2. The adsorption process can also be done through a column that contains an adsorbent. The retained metals are eluted from the solid phase by an aqueous washing solvent. Abundant solid support materials, such as silica gel [45-47], chitosan [34], resin [48-51], and polymer [52-55] have been applied in solid-phase extraction of metal ions. Furthermore, a variety of ligands or functional groups are modified onto a solid support as an effect adsorbent for the purpose of adsorption and enrichment of metal ions. The preparation of new solid phase extraction with specially functional groups has obtained much attention since it has more efficient selectivity and adsorbability. In many adsorbents, resin and silica gel can be easily modified with other organic functional groups because they can be chemically modified and their principal parts have higher stability.

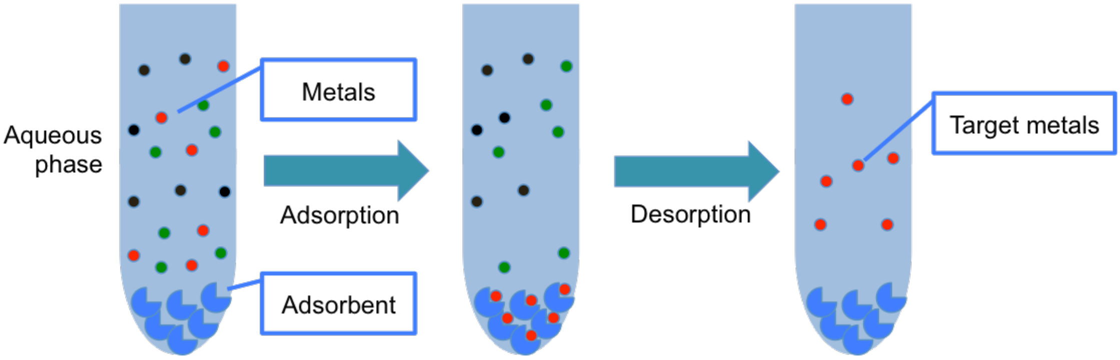


Figure 1-2 Solid-phase extraction process.

A new chelating resin, which was modified from Amberlite XAD-16 linked 1,6-bis(2-carboxy aldehyde phenoxy)butane group for adsorption of Cu(II) and Cd(II) (Oral et al.) [56]. Silica gels are always to be modified for preconcentation metal ions, such as carboxymethyl chitosan (CMCS) grafted with β-cyclodextrin (CMCS-g-CD) modified silica gel adsorption of cadmium (Lü et al.) [57]. 3-chloropropyltrimethoxysilane modified silica gels with 8-aminoquioline and 2-aminopyridine were investigated for preconcentration Ca(II), Mg(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) in aqueous samples (Soliman et al.) [58].

1-2-3 New extraction systems

1-2-3-1 Ionic liquid (as a diluent)

The environmental issue is a major challenge, thus, the “green” chemistry has become more important in science and industry fields. Liquid-liquid extraction (LLE) is a widely used significant method of separation and purification of metals by using an aqueous phase and organic phase process. However, the toxic or volatile organic compounds (VOCs) used as reagent and solvent in the LLE procedure, have several environmental problems. Recently, room temperature ionic liquids (TRILs or ILs) with low melting point salts are used. ILs are composed of organic cations (imidazolium, pyridinium, ammonium and phosphonium) and inorganic anion (tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), chloride (Cl^-)), indeed an organic anion (trifluoromethylsulfonate (OTf^-), bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-) as shown in Figure 1-3.

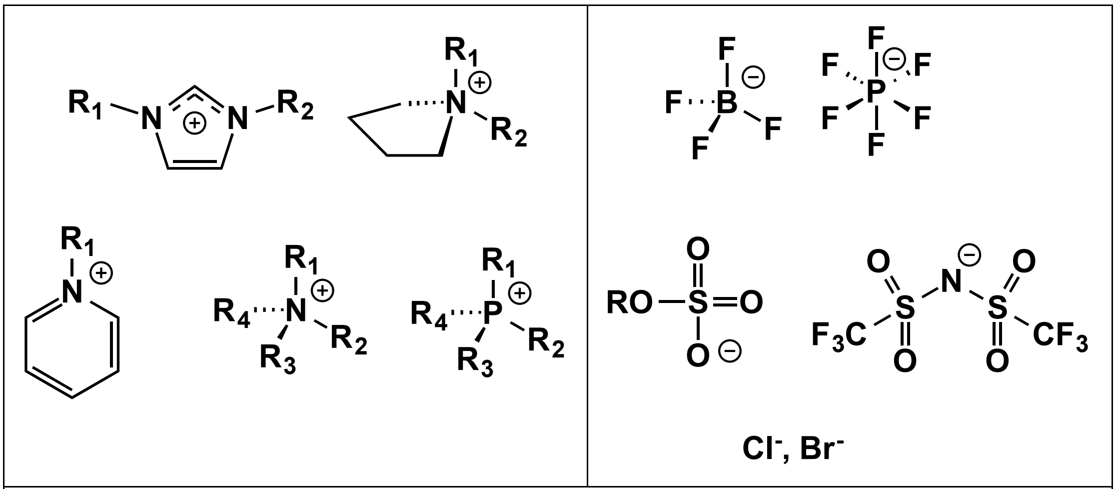


Figure 1-3 Structure of typical ionic liquids

ILs have attracted increasing attention as “green” solvent alternatives to common organic solvents. Due to the unique properties of ILs, such as less-volatility, less-flammability and thermal stability, ILs can be applied in numerous synthetic, catalytic [59,60], biochemical application [61,62], electrochemical [63-65], and extraction processes [66,67]. In extraction and separation processes, it is required for ILs to be immiscible in water and dissolve various organic and inorganic species. The ILs have a potential to fulfill the requirement because the physico-chemical properties are tunable by varying the combination of constituents cations and anions. ILs can easily extract organometallic compounds due to the “like dissolve like” principle.

ILs are designer solvents. Thus, task-specific ionic liquids (TSILs), which have a specific functional group, have received much attention because they are easily synthesized and modified. TSILs having a functional group of a high affinity to a target metal ion can be applied in liquid-liquid extraction without a conventional extractant and a diluent (detailed description can be found in Section 1-2-3-2).

1-2-3-2 Functional ionic liquid

As described previously, ionic liquids-based extraction processes have been highlighted during last decades. In addition, task-specific ionic liquids or functional ionic liquids (FILs) containing a functional cation and/or anion become series of functional liquid. Because ILs can be designed, extraction and separation of metal ions by using FILs are becoming a great challenge. Modification of FILs can be divided into three classes:

(**i**) Cation modified: Visser et al. reported the extraction of mercury (Hg^{2+}) and cadmium (Cd^{2+}) by using the task-sepcific ILs, which were functioned with thiourea, thioether and urea, undiluted or diluted with 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) from aqueous solutions [68,69]. Extraction of Hg^{2+} from chloride aqueous solutions with 1,3-diethylimidazole-2-thione (C_2ClmT) ILs, which has the thione group, was reported by Lu et at [70]. Luo et at. synthesized a new FILs containing aza-18-crown-6-ether group and reported the separation of Cs^+ and Sr^+ [116]. Sengupta et al. examined the extraction of Am(III), Pu(IV), Pu(VI), Np(IV), Np(VI), and U(VI) into diglycolamide-functionalized TSIL (DGA-TSIL) from nitrate aqueous solutions, the functional group similar to TODGA [71].

(**ii**) Anion modified: In 2010, Egorov et al. reported the extraction of transition metal ions (Fe3+, Cu2+, Ni2+, and Mn2+) by using a FILs, which has the salicylate anion group [72].

(**iii**) Cation and anion both modified: Sun et al. synthesized quaternary ammonium salts based bi-functionalized ionic liquid with dialkylphosphate and carboxylate anion and studied the extraction and separation of REEs [73] (detailed description at 1-3).

Designed FILs as an extractant is expected to give a high efficiency.

1-3 Extraction and separation of REEs

As described in **1-1**, the development of an efficient method for the mutual separation of REEs or the separation from other metals has been desired. For the separation of REEs, hydrometallurgy processes such as liquid-liquid extraction (LLE) and solid-phase extraction (SPE) as described in **1-2** are very significant technology in scientific research and industry.

For industrial applications, the purification of REEs is strongly required and the extractant is one of the most important factors in the LLE system, to obtain the high extraction and separation efficiencies. Synergistic extraction systems have also been employed. Recent advances of extractants and synergistic extraction systems for the separation and purification of REEs are listed in Table 1-5 and Table 1-6, respectively.

Table 1-5 extraction of extractants for REEs

Year	Author	Solvent and medium	Extractants or their derivatives	Metal ions	Stripping	Ref.
2007	Mowafy *et al.*	Benzene/nitrate	TODGA, THDGA	U, Th, La, Nd, Eu, Am, Sr, Ba, Co	-	[74]
2007	Naganawa *et al.*	*n*-hexane/nitrate	DODGAA	14 lanthanides	-	[75]
2008	Petrova *et al.*	C_6H_6/chloride	Crown-ethers	14 lanthanides	-	[76]
2012	Lu *et al.*	Chloroform/ nitrate	Calix[4]arene derivatives	Th, Yb, Gd, La	-	[77]
2013	Amorin *et al.*	1,2-dichloroethane/ nitreate	CMPO derivatives	Am, Eu	-	[78]
2014	Shimojo *et al.*	isooctane/nitrate	DODGAA	14 lanthanides	HNO_3	[79]
2014		isooctane/nitrate		54 metal ions	HNO_3	[80]
2014	Baba *et al.*	*n*-dodecane/nitrate	D2EHAG Versatic acid 10	Sc, La, Nd, Eu, Dy, Y	H_2SO_4	[81]

Table 1-6 Synergistic extraction of REEs.

Year	Author	Solvent/ medium	Extractants	Metal ions	Stripping	Ref.
2008	Huang *et al.*	Kerosene/ sulfate	HDEHP/ HEH, EHP	Nd, Sm	-	[82]
2008	He *et al.*	$CHCl_3$/ Chloride	tBu[4]CH2COOH/ N1923	Eu, Pr, Yb	HCl	[83]
2008	Zhang *et al.*	Kerosene/ sulfate	DEHPA/ HEH/EHP	La, Nd, Sm, Gd	-	[84]
2009	Jia *et al.*	*n*-heptane/ chloride	CA12/ C301	14 lanthanides	-	[85]
2009	Tong *et al.*	Benzene/ chloride	HPMBP/ CA12	14 lanthanides	-	[86]
2009	Tong *et al.*	*n*-heptane/ Chloride	CA-100/ Cyanex 301,302	14 lanthanides	HCl	[87]
2011	Nasab *et al.*	Kerosene/ nitrate, chloride, sulfate	Cyanex 272, Cyanex 302/ TBP	Th, Fe, Ce, La, Y	EDTA	[88]
2012	El-Nadi *et al.*	Kerosene/ Nitrate	TOPO/ TRPO	La, Nd, Y	HNO_3	[89]
2012	Tian *et al.*	*n*-heptane/ nitrate	CA-100/ 8-hydroxyquinoline	14 lanthanides and Y	HNO_3	[90]
2013	Tian *et al.*	Heptane/ nitrate	HQ/ Cyanex 301, Cyanex302	La, Nd, Sm, Tb, Ho, Tm, Y	-	[91]
2013	Tong *et al.*	Kerosene/ sulfate	Cyanex 923/ Cyanex 272, P204,P507	Ce(IV), Th(IV)	-	[92]
2014	Liu *et al.*	Kerosene/ Chloride	Cyanex 272/ Alamine 336, TEHA, TOA	Pr, Nd	HCl, H_2SO_4	[93]
2015	Mohammadi *et al.*	*n*-heptane/ Chloride	D2EHPA/ EHEHPA	Y, Dy, Nd	-	[94]

New extraction systems are applied to the separation of REEs. In addition, due to defects of organic solvent in LLE, such as volatility and harmfulness of organic compounds, environmentally friendly ionic liquids have attracted much attention in a liquid-liquid extraction process. ILs are used as an alternative to organic solvents to reduce the environmental loads. Furthermore the efficient separation performance was found in some ILs systems. Recent studies of liquid-liquid extraction using ILs as the extraction solvents are shown in Table 1-7. Furthermore, ILs can be modified with efficient functional groups to cation and/or anion constituents. Thus, functional ionic liquids are expected to be more efficient in the extraction and separation of REEs. Several studies of functional ionic liquids are shown in Table 1-8.

Table 1-7 extraction of REEs in ILs systems.

Year	Author	ILs	Extractants/notes	Metal ions	Medium	Ref.
2008	Turanov *et al.*	[C_4mim][PF_6], [C_4mim][Tf_2N]	TPMDPO, Ph_2Et_2, Bu_2Et_2	Ln, Y	Nitrate ClO_4^-	[95]
2008	Kubota *et al.*	[$C_n$mim][Tf_2N] (n=8, 12)	PC-88A	Y, Eu, Ce, La	Nitrate	[96]
2008	Hirayama *et al.*	[C_4mim][Tf_2N]	HTTA / 18C6	La, Eu, Lu	Chloride	[97]
2008	Shimojo *et al.*	[$C_n$mim][Tf_2N] (n=2, 4, 6)	TODGA	Ln	Nitrate	[98]
2008	Zuo, *et al.*	[C_8mim][PF_6]	-	Ce, Th, Gd, Yb	Nitrate	[99]
2008	Zuo, *et al.*	[C_8mim][PF_6]	primary amine N1923	Th / Rare earths	Sulfate	[100]
2009	Zuo *et al.*	[C_8mim][PF_6]	D2EHPA	Ln, Sc, Y, Th	Nitrate	[101]
2009	Mallah *et al.*	[$C_n$mim][Tf_2N] (n=4, 6)	HYD	Sm, Eu, Gd, Dy	Nitrate	[102]
2010	Mallah *et al.*	[C_6mim][Tf_2N]	PAN / HYD	Sm, Eu, Gd, Dy	Nitrate	[103]

Table 1-7 extraction of REEs in ILs systems.

2010	Kubota *et al.*	[C$_n$mim][Tf$_2$N] (n=4, 8, 12)	DODGAA/SLM	Y, Eu,Zn (fluorescent powder)	Nitrate	[104]
2010	Yoon *et al.*	[C$_n$mim][PF$_6$] (n=2, 4), [C$_4$mpy][PF$_6$]	D2EHPA	Ce, Nd, Sm, Dy, Yb	Chloride	[105]
2010	Okamura *et al.*	[C$_4$mim][Tf$_2$N]	HTTA, HTTA-18C6, -DC18C6, -DB18C6, -15C5	Ln	Chloride	[106]
2011	Rout *et al.*	[C$_8$mim][Tf$_2$N]	D2EHPA, HDEHDGA / masking DTPA	Eu, Am	Nitrate	[107]
2011	Baba *et al.*	[C$_8$mim][Tf$_2$N]	DODGAA / SLM	Nd, Dy, Fe (magnet)	Nitrate	[37]
2011	Kubota *et al.*	[C$_n$mim][Tf$_2$N] n=4,8,12	DODGAA	Y, Eu,Zn (fluorescent powder)	Nitrate	[108]
2012	Yang *et al.*	[C$_8$mim][Tf$_2$N]	DODGAA	Ln	Sulfate	[109]

Table 1-8 Functional ionic liquid extraction of REEs

Year	Author	ILs / diluent	Extractants/notes	Metal ions	Medium	Ref.
2009	Liu *et al.*	[C$_n$mim][PF$_6$] (n=4, 8),	Cyphos IL 104	Y, Dy, Ho, Er, Yb	Nitrate	[110]
2010	Sun *et al.*	[A336][CA-100]	[A336][CA-100]	Sc, Y, Eu, Ce	Nitrate	[111]
2010	Odinets *et al.*	CMPO-modified ILs	CMPO-modified IL	U, Pu, Eu, Am	Nitrate	[112]
2010	Mehdi *et al.*	[C$_4$mim][hfac]	[C$_4$mim][hfac]	Nd, Co, Cu	Tf$_2$N$^-$	[113]

Table 1-8 Functional ionic liquid extraction of REEs

2011	Wang *et al.*	[A336][CA-100]	[A336][CA-100]	Ln,Y	Chloride	[114]
2011	Olivier *et al.*	Ac-functionalized ILs	Ac-functionalized ILs	Eu, Tb	Chloride	[115]
2011	Rout *et al.*	*n*-dodcean, tetradecaen, hexadecaene	[A336][DEHP], [A336]DGA]	Eu, Am	Nitrate	[116]
2012	Vicente *et al.*	-	[DMImC$_n$P(O)Ph$_2$] [NTf$_2$]/[PF$_6$] (n=2,3,4,6,8)	La, Eu	hfa	[117]
2012	Yang *et al.*	*n*-heptane	[A336][P204], [A336] [P507]	Y, Eu, Gd, Ce, Tb	Nitrate	[118]
2013	Mohapatra *et al.*	[C$_4$mim][PF$_6$], [C$_4$mim][Tf$_2$N]	DGA-based TSIL	Eu, Am, Pu, Np, UO$_2$, Sr, Cs	Nitrate	[119]
2013	Rout *et al.*	[C$_6$mim][DEHP], [C$_6$mpyr][DEHP], [N4444][DEHP]	[C$_6$mim][DEHP], [C$_6$mpyr][DEHP], [N4444][DEHP]	Nd	Nitrate	[120]
2014	Sun *et al.*	heptane	[N2222][EHEHP], Cyanex 923	La, Nd, Eu, Dy, Er	Chloride	[121]
2014	Sun *et al.*	heptane	[Nnnnn][DEHP], (n=2,4,6,8)	La, Nd, Eu, Dy, Er	Chloride	[122]
2015	Dong *et al.*	*n*-heptane	[N1888][EHEHP]	Lu, Yb, Tm, Er, Y, Ho	Sulfate	[123]
2015	Shkrob *et al.*	[Hbet][NTf$_2$], [Hcar][NTf$_2$], [Chol][NTf$_2$]	[Hbet][NTf$_2$], [Hcar][NTf$_2$], [Chol][NTf$_2$]	Eu, Am, Ln	Nitrate	[124]

Solid-phase extraction (SPE) is a useful low-cost process for preconcentration and recovery of trace metal ions from aqueous solutions. As the solid materials contain silica gel, chitosan, and polymer etc. Furthermore, the solid support materials can be modified with functional groups to improve its selectivity and adsorbability for target metal ions. Thus, the adsorption of REEs has been investigated using functional solid materials since last decade as shown in Table 1-9.

Table 1-9 solid-phase extraction of

Year	Author	Medium	Main part	Functional group	Metal ions	Ref.
2007	Zhang *et al.*	Nitrate	Silica gel	Acetylacetone	Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb ,Lu	[125]
2008	Suzuki *et al.*	Nitrate	Resin	Tertiary pyridine	Lu, Gd, Eu, Sm, Nd, Pr, Ce, La	[126]
2010	Dave *et al.*	Chloride	Amberlite XAD-4 resin	MADB18C6	La, Nd, Sm	[127]
2013	He *et al.*	Nitrate	Polymer	Chelating-	La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu, Th	[128]
2013	Turanov *et al.*	Nitrate	Carbon inverse opals	Tetraphenylmethylenediphosphine dioxide	14 lanthanides, U, Th	[129]
2014	Roosen *et al.*	Nitrate	Chitosan biopolymers	EDTA-, DTPA-	Pr, Nd, Dy	[34]
2014	Xu *et al.*	Nitrate	Silica gel	*iso*butyl-BTP	Am, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb	[130]
2014	Roosen *et al.*	Nitrate	Chitosan-silica	EDTA-, DTPA-	La, Nd, Eu, Dy, Lu	[131]
2015	Galhoum *et al.*	Chloride	Chitosan	Diethylenetriamine	Nd, Dy, Yb	[132]
2015	Ogata *et al.*	Chloride	Silica gel	Diglycol amic acid	14 lanthanides, Al, Ca, Cu, Fe, Zn	[32]

1-3-1 Extraction and separation of Scandium

In the previous section, recent advances of extraction systems for REEs are described. A variety of extraction methods have been studied for REEs separation, however, the reports on Sc are few (Table 1-10) because no scandium mine has been found, and Sc is produced as a byproduct from mines of low concentration of Sc. The isolation of Sc is very complex and difficult.

Hydrometallurgy technique, such as liquid-liquid extraction and solid-phase extraction, are effective methods for the separation and purification of Sc. For constructing the efficient solvent extraction of Sc, the selection of the extractants is very important. However, Sc has the lowest coordination number, smallest ionic radius, and highest Lewis acidity among the REEs group (RE^{3+}). Therefore, the affinities of Sc to the extractant differ substantially from that of the other REEs. The affinity of Sc to PC-88A and D2EHPA, which are typical extractants for REEs, is very high, but the stripping of the metal is difficult. To establish an efficient separation of Sc, the development of novel extraction and separation systems are desired.

Table 1-10 Extraction and separation of Sc

Year	Authors	Extractants (adsorbents)	Metals	Medium	Stripping (desorption)	Ref.
2011	Sun *et al.*	Cyanex925/ [A336][NO_3]	Sc, La, Ce, Eu, Y, Yb	Nitrate	HNO_3	[133]
2011	Turanov *et al.*	Bis(diphenylphosphorylmethylcarbamoyl)alkanes	Sc, Y, 14 lanthanides	HCl, HNO_3, $HClO_4$	-	[134]
2012	Abbasi *et al.*	Nialidixic acid (HNA)	Cu, Fe, Ni, Mn, Sb, Co, Sc, Y, Nd, Eu	Perchlorate	HNO_3	[135]
2013	Fujinaga *et al.*	Oxidized Phoslex DT-8	Sc, Zr, Ti, Y, Al, Fe	Chloride	HCl	[136]
2013	Hosomoni *et al.*	Modified Escherichia coli	Sc, Y, 14 lanthanides	HEPES	-	[137]
2014	Wang *et al.*	D2EHPA,/TBP	Fe, Ti, Sc, Zr, Ga, Al, Ca, V,Cr	Sulfate, chloride, nitrate	NaOH	[138]
2014	Zhao *et al.*	HTTA/TOPO	Sc, La, Y, Dy, Eu, Nd	Nitrate	HNO_3	[139]
2015	Depuydt *et al.*	[$P_{444}C_1COOH$] [Cl]	Sc	Chloride	HCl	[140]
2015	Onghena *et al.*	[Hbet][Tf_2N]	Sc, Y, La, Ce,Nd, Dy, Al, Fe, Ca, Ti, Na	Chloride, nitrate	HCl oxalic acid	[141]
2015	Zhong *et al.*	N235, HDEHP/TBP	Sc, U, Fe, Mn, Zr, Ti, Th	Chloride	NaOH	[142]

1-4 Thesis organization

This thesis describes the development of the extraction based techniques for the separation and recovery of scandium (Sc) from aqueous resources containing rare earth metals (REEs) or other metal ions.

The present graduation thesis mainly consists of five chapters, which are the general introduction in Chapter 1, the research achievements in Chapter 2, Chapter 3, and Chapter 4 the general conclusion in Chapter 5, and the references and acknowledgement in the end.

Introduction (Chapter 1) is a summary description on the separation and recovery of Sc from the resources. The hydrometallurgical separation techniques such as liquid-liquid extraction, solid-phase extraction, and the use of novel “green” solvents, ionic liquids, are included.

In Chapter 2, synergistic extraction of Sc in REEs was examined by using β-diketone reagent (HTTA) and organophosphine oxide (TOPO) in *n*-dodecane and ionic liquids.

In Chapter 3, novel functional ionic liquids (FILs) bearing three kinds of amic acid type functional groups were synthesized and applied the separation of Sc.

In Chapter 4, novel adsorbents for the separation of Sc were developed by modifying a functional group of a high affinity to Sc, to three kinds of base materials.

Chapter 5 describes the overall conclusions based on the results in Chapter 2 to Chapter 4.

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Chapter 2. Separation of scandium by synergistic extraction systems

2-1 Separation of scandium from transition metals by a synergistic extraction system with 2-thenoyltrifluoroacetone and tri-*n*-octylphosphine Oxide

2-1-1 Introduction

As described in chapter 1, Sc has been produced in a trace amount as a kind of byproduct materials in some ores in China, Kazakhstan, Russia and Ukraine [1]. Thus Sc is hard to be purified and recovered and insufficient to meet the growing demand. This fact leads to a very high price of Sc. The extraction and separation of Sc has recently become an important research topic [2], although laboratory studies on the separation process remain few. Liquid-liquid extraction process consists of target metals' transferring from a feed phase to another phase by the extractant and forming hydrophobic complex. The extractant plays a key role in the separation of target metal ions; therefore, the selection of an appropriate extractant is often critical in determining success of the extraction process. However, it has been difficult to find an appropriate extractant for Sc. Organophosphorous extractants such as D2EHPA and PC-88A, which are typical extractants for REEs, show very high affinity to Sc, and the stripping efficiency in the systems is consequently low [3-5]. Therefore, the development of more effective extraction and separation systems of Sc in industrial production has been attracted much attention.

The extraction of rare earth metals including Sc with 2-thenoyltrifluoroacetone (HTTA) was investigated as described later [6]. As the pKa 5.60 ± 0.23 of HTTA, which is a β-diketone, is relatively high [7,8], the metal ions are readily stripped to an aqueous solution in the mild acid conditions. However, the extraction ability is low because of the high pKa. To improve the extraction and/or separation efficiency, synergistic extraction that is extraction with two or more different extractants is often effective. Neutral phosphate derivatives such as tri-*n*-octylphosphine oxide (TOPO) and tri-butyl phosphate (TBP) are often used as a synergistic reagent [9-12]. In this study, we applied the synergistic system of HTTA with the co-extractant TOPO to the extraction and separation of Sc from a sulfuric acid solution derived from ore refining, which contains a variety of transition metals such as Mn, Al, Zn, Ni, Co, and Fe. An analytical reagent HTTA was used as a model of the commercial extractant having β-diketone such as LIX54 (1-(3-dodecylphenyl)butane-1,3-dione Figure 2-1-1) [13]. In the present work, the effect of adding TOPO on the extraction ability and the selectivity of Sc was examined to show the potential use of β-diketone with TOPO system to the recovery of Sc.

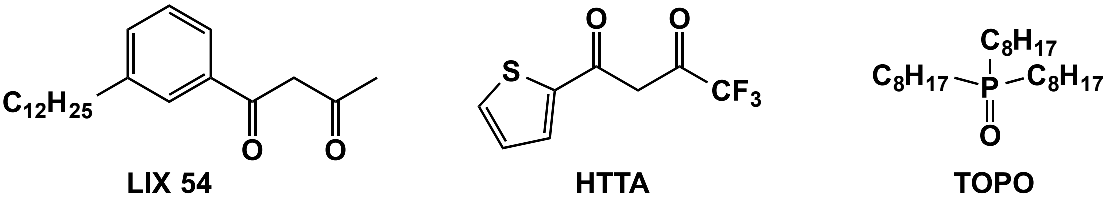


Figure 2-1-1 Molecular structures of extractants

2-1-2 Experiment

2-1-2-1 Reagents

Extractants HTTA and TOPO were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). *n*-Dodecane, ammonium sulfate and sulfuric acid were provided by Kishida Chemical Co., Ltd (Osaka, Japan). All the other chemicals were of analytical grade. The molecular structures of the extractants used are shown in Figure 1.

2-1-2-2 Liquid–liquid extraction procedure

Aqueous feed phases containing 0.1 mmol/L of each of Sc and other transition metals (Al, Mn, Fe, Co, Ni, and Zn) were prepared by dissolving the sulfate salts of the metals in 0.2 mol/L H_2SO_4 and 0.2 mol/L ammonium sulfate. The pH values of the aqueous phases were adjusted by mixing the two solutions. Extraction phases were prepared by dissolving a given amount of HTTA and/or TOPO in the organic solvent (*n*-dodecane).

Equal volumes (3 ml) of the organic extraction phase and the feed phase were poured into a sealed tube. After mixing for 60 s in a vibrating mixer, the mixture solution was gently shaken at 298 K for 12 h in a temperature-controlled bath to attain equilibrium. The equilibrium pH of the resulting aqueous phase was measured by a pH meter (HM-60 G, DKK-TOA Co.). The stripping of metal ions from the extraction phase was also examined by using acid solutions in a similar manner as the extraction procedure. Metal concentrations in the aqueous phases were determined by using an inductively coupled plasma (ICP)-atomic emission spectrometer (Optima 8300; Perkin Elmer Inc., MA, USA). The extraction ratio for the metal ions (*E* [-]) was calculated by Eq. (2-1-1):

$$E = \frac{[M]_{ex.eq}}{[M]_{aq.0}} = \frac{[M]_{aq.0} - [M]_{aq.eq}}{[M]_{aq.0}} \tag{2-1-1}$$

The distribution ratio *D* [-] was defined as shown in Eq. (2-1-2):

$$D = \frac{[M]_{ex.eq}}{[M]_{aq.eq}} = \frac{[M]_{aq.0} - [M]_{aq.eq}}{[M]_{aq.eq}} \tag{2-1-2}$$

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

The separation factor β was calculated by Eq. (2-1-3):

$$\beta_{Sc/Fe} = \frac{D_{Sc}}{D_{Fe}} \tag{2-1-3}$$

2-1-3 Results and discussion

2-1-3-1 Synergistic extraction with HTTA and TOPO in sulfate medium

The extraction ratios of metal ions extracted into the organic phase with HTTA alone, and with HTTA and TOPO are shown in Figure 2-1-2. As is shown in Figure 2-1-2(a), Sc^{3+} was selectively extracted from the other metals except Fe^{3+}, and quantitative extraction was achieved at pH >3 in the aqueous phase. Adding TOPO as a co-extractant enhanced the extraction efficiency of Sc^{3+} as shown in Figure 2-1-2(b), and furthermore, the extraction of Fe^{3+} was decreased drastically. Thus it was found that Sc^{3+} could be separated from Fe^{3+} without the precipitation or reduction method. Moreover, Sc^{3+}could be separated from Al^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}, although adding TOPO enhanced the extraction of some metal ions coexisting in the aqueous solution. A synergistic extractant system with β-diketone and TOPO was suggested to be useful for the separation and recovery of Sc^{3+} from ores having Sc as a byproduct and transition metals.

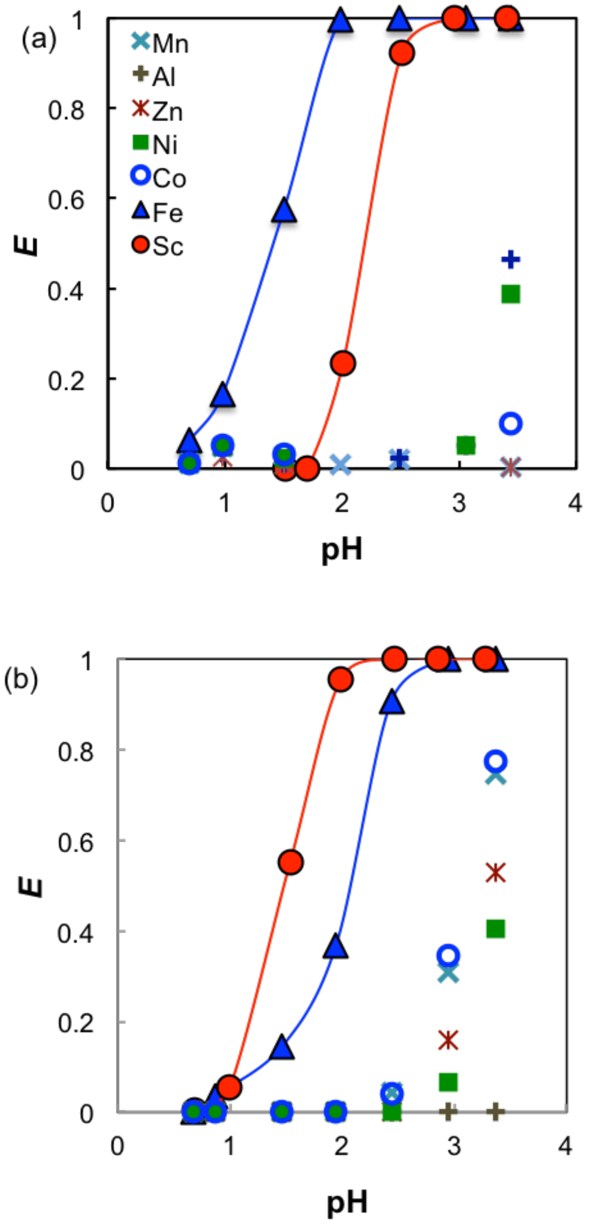


Figure 2-1-2 Extraction behavior of metal ions using (a) HTTA alone and (b) HTTA and TOPO in *n*-dodecane. Aqueous phase: 0.1 mmol/L M^{n+}, *n*-dodecane phase: (a) [HTTA] = 10 mmol/L; (b) [HTTA]=[TOPO]=10 mmol/L

2-1-3-2 Extraction mechanism in the synergistic system

The extraction mechanism of Sc^{3+} with HTTA and TOPO was investigated by the slope analysis. Figure 2-1-3 shows the logarithmic plots of the distribution ratio, *D*, of Sc^{3+} with HTTA and TOPO as a function of pH in the aqueous phase (a) and the HTTA concentration (b) and the TOPO concentration (c). The plots of log*D* versus pH showed a linear relationship with a slope of 3, and the relationship between log*D* and log[HTTA] at constant TOPO concentration was linear with a slope of 3 for extraction of Sc^{3+}. The results suggest that three protons are released from the HTTA molecules into the aqueous phase to form neutral complexes with Sc^{3+}. Furthermore, log*D* against log[TOPO] at constant HTTA concentration showed a linear correlation with slope 1 for Sc^{3+}. The results demonstrated that Sc^{3+} was extracted as the complex with three HTTA and one TOPO molecule in the synergistic system as expressed by Eq. (2-1-4):

$$Sc^{3+} + 3HTTA + TOPO \leftrightharpoons Sc(TTA)_3TOPO + 3H^+ \qquad (2\text{-}1\text{-}4)$$

where the equilibrium constant, Kex of the Eq.(2-1-4) is expressed by Eq. (2-1-5):

$$K_{ex} = \frac{[M]_{ex.eq}[H^+]^3}{[M]_{aq.eq}[HTTA]^3[TOPO]} = D\frac{[H^+]^3}{[HTTA]^3[TOPO]} \qquad (2\text{-}1\text{-}5)$$

and the following relational expression is obtained:

$$\log D = \log K_{ex} + 3\log[HTTA] + \log[TOPO] + 3pH \qquad (2\text{-}1\text{-}6)$$

Considering that Sc^{3+} is extracted with 3 HTTA, as described in the previous report [6], the enhancement of Sc extraction by the addition of TOPO seems to be plausible from Eq. (2-1-4). To clarify the synergistic effect on the Sc extraction more precisely, the extraction behavior of Eu^{3+}, which is in the same rare earth group, was also examined and plotted in Figures 3 along with Sc^{3+}. The plots of log*D* versus pH and log[HTTA] for each metal ion showed the same linear correlation with slope 3, however the slope of the linear relationship between log*D* and log[TOPO] for Eu^{3+} is 2, thus the extraction reaction is expressed by Eq. (2-1-7):

$$Eu^{3+} + 3HTTA + 2TOPO \leftrightharpoons Eu(TTA)_3(TOPO)_2 + 3H^+ \qquad (2\text{-}1\text{-}7)$$

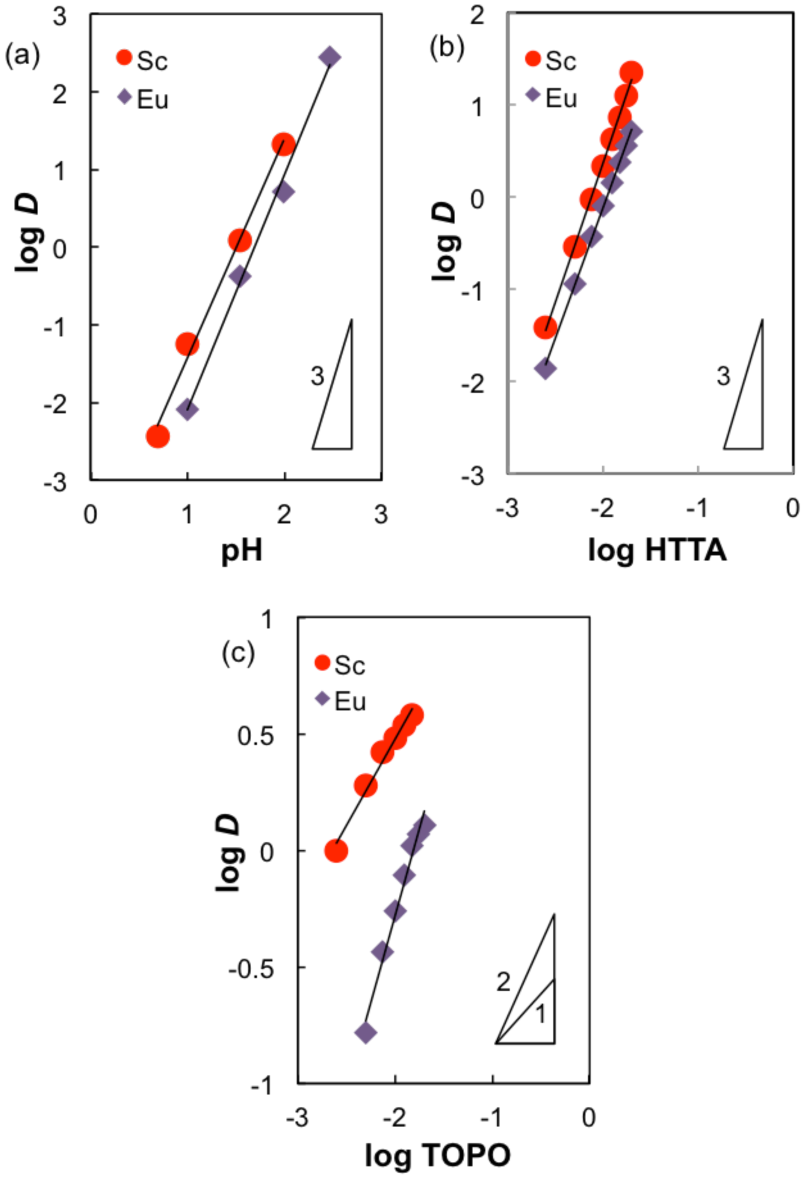


Figure 2-1-3 Slope analyses of $Sc^{3+}$and Eu^{3+} extraction in the synergistic HTTA and TOPO system in *n*-dodecane. a) log*D*–pH, b) log*D*–log[HTTA], c) log*D*–log[TOPO]. Organic phase: (a) [HTTA] = [TOPO] = 10 mmol/L; (b) [TOPO] = 10 mmol/L; (c) [HTTA] = 10 mmol/L. Aqueous phase: 0.1 mmol/L M^{n+}

In the HTTA alone system, Sc, of which ionic radius is much smaller and coordination number is lower than the other rare earth metal ions, is coordinately saturated with 3 HTTA and extracted selectively from rare earth metal ions, while in the synergistic system, the extraction of Eu^{3+} strongly enhanced compared to Sc^{3+}, because more TOPO molecules are involved in the extracted species of Eu^{3+} to be coordinatively saturated.

The synergistic effect was also observed for extraction of Co^{2+}, Mn^{2+} and Zn^{2+}, whereas the efficiencies of Fe^{3+} and Al^{3+} were decreased in the mixed extractant system.

To confirm the synergistic effect, the Continuous Variation Method (Job's plot) was employed for Sc^{3+} and Fe^{3+}, where the total concentration of HTTA and TOPO was maintained at 20 mmol/L and the extraction equilibrium was measured at various molar ratios of HTTA to the total extractant. As shown in Figure 2-1-4, the extraction degree of Sc^{3+} reached a maximum value when the ratio of HTTA was 0.75, that is, the ratio of HTTA and TOPO in the organic phase was 3:1, proving the validity of Eq. (2-1-4). Under the experimental conditions (pH 1.7), the extraction of Sc^{3+} was not observed in both only TOPO and only HTTA systems, therefore the mixture of the extractants was demonstrated to offer a significant synergistic effect for Sc^{3+}. For the extraction of Fe^{3+}, the addition of TOPO decreased the extraction efficiency from that with HTTA alone. The separation factor, $\beta_{Sc/Fe}$, defined as the ratio of distribution ratio D for Sc and Fe, is given in Figure 2-1-4.

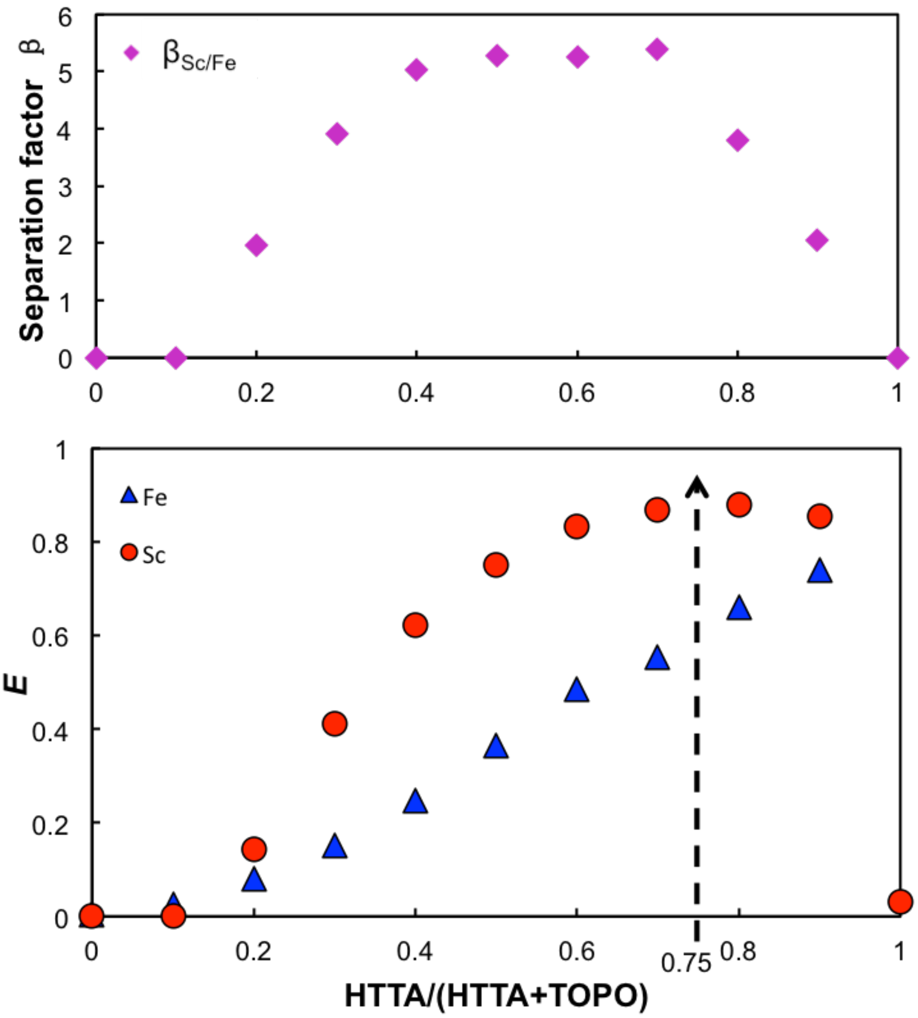


Figure 2-1-4 Continuous variation method for Sc and separation factor $\beta_{Sc/Fe}$ with HTTA and TOPO in *n*-dodecane

Organic phase:[HTTA] + [TOPO] = 20 mmol/L; Aqueous phase: 0.1 mmol/L Sc^{3+}, pH1.7

2-1-3-3 Stripping

Stripping of Sc^{3+} from the extraction phase was performed in the synergistic extraction system. As shown in Figure 2-1-5, quantitative stripping of Sc^{3+} was reached by using 1mol/L HCl or 1mol/L H_2SO_4, however 1mol/L HNO_3 could not recover the metal ion completely. The extraction behavior of rare earth metals from the nitrate media was examined as described later, and it was shown that the synergistic extraction mechanism for Sc^{3+} was different from Eq. (2-1-4) [6]. The adduct formation with a nitrate ion was observed in the extracted species where the number of HTTA coordinated to Sc was decreased to two and the extraction was significantly enhanced compared to that from the sulfuric media shown in the present study. That is, Sc^{3+} was slightly extracted even at 1mol/L HNO_3. It was suggested that stripping of Sc^{3+} proceeded via the reverse reaction of the extraction reaction.

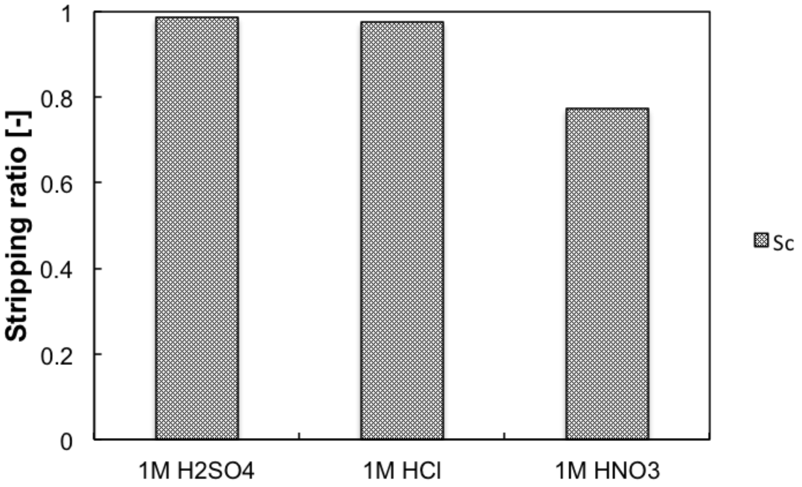


Figure 2-1-5 Stripping of Sc from organic phase

(Organic phase: [HTTA] = [TOPO] = 10 mmol/L, $[Sc^{3+}]_0$ = 0.1 mmol/L)

2-1-4 Conclusion

A synergistic extractant HTTA and TOPO was employed for extraction and separation of Sc^{3+} from a sulfuric solution containing common metal ions, such as Al^{3+}, Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. It was found that extraction efficiency of Sc^{3+} was low and Fe^{3+} was extracted more selectively than Sc^{3+} when only HTTA was used. The addition of TOPO enhanced Sc^{3+} extraction, and furthermore it reversed the order of the selectivity by inhibiting the extraction of Fe^{3+}. The extraction stoichiometry of Sc^{3+} complex with the mixed extractant was revealed to be 3:1:1 for HTTA, TOPO and Sc, respectively. The synergistic effect of Sc was confirmed experimentally and theoretically. Stripping of Sc^{3+} was achieved by using 1mol/L HCl or 1mol/L H_2SO_4. Based on the results obtained, it was demonstrated that a combination of a β-diketone and the synergistic extractant TOPO is a promising extractant system for recovering Sc from ores containing Sc as a byproduct.

2-2 Synergistic extraction of rare-earth metals and separation of scandium using in an ionic liquid system

2-2-1 Introduction

2-Thenoyltrifluoroacetone (HTTA), which contains a β-diketone and a hydrophobic trifluoromethyl group, is an effective extractant [14]. The extraction with HTTA has been studied in combination with the synergistic reagents, because the extraction efficiency of HTTA for REEs is low. Neutral phosphate derivatives such as tri-butyl phosphate (TBP) or tri-*n*-octyl phosphine oxide (TOPO) are generally not used alone because of the problems associated with own extraction efficiency. However, examples of coextractants have been reported for liquid–liquid processes [9-12]. In the previous section, extraction and separation of Sc from the other transition metals were investigated. The synergistic extraction was observed for Sc, and the separation was found to be possible in this system. In this study, separation of scandium and other rare earth metals was examined using the synergistic extraction system. The extraction mechanism for the metal ions was investigate in n-dodecane systems.

Ionic liquid (ILs) have sometimes been used as novel diluents during liquid–liquid extractions [15-18]. The physico-chemical properties of ILs are tunable because the combination of constituent ions can be adjusted. This can lead to distinct improvements in the reagent performance. Several IL extraction systems, including HTTA, have been used for the extraction of REEs, and synergistic extraction has been reported using HTTA and a neutral 18-crown-6 [19,20].

In the present study, we examine the potential for synergistic extraction of REEs with HTTA and TOPO mixtures. Specifically, the selective separation of Sc is documented using IL 1-butyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide ([C_4mim][Tf2N]) as a diluent. The synergistic effects on the separation of these metals in the IL system were assessed by comparing with that in a conventional organic system.

2-2-2 Experimental

2-2-2-1 Reagents

Extractants 2-thenoyltrifluoroacetone (HTTA) and tri-*n*-octyl phosphine oxide (TOPO) were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). A hydrophobic IL [C_4mim][Tf_2N] (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) ([bmim][Tf_2N]) was obtained from Sigma-Aldrich Co. and a water-soluble IL [C_4mim][Cl] (1-butyl-3-methylimidazolium chloride) was procured from Kanto Chemical Co. Inc. *n*-Dodecane was provided by Kishida Chemical Co., Ltd. All other chemicals were of analytical grade. The molecular structures of the extractants and IL [C_4mim][Tf_2N] are shown in Figure 2-2-1.

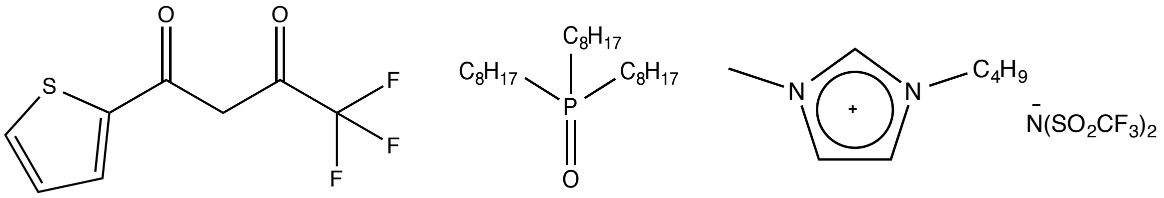

HTTA TOPO [C_4mim][Tf_2N]

Figure 2-2-1 Molecular structures of extractants and ionic liquid used

2-2-2-2 Liquid–liquid extraction procedure

Aqueous feed phases containing 0.1 mmol/L of each of six rare-earth metal ions (Sc, Y, La, Nd, Eu, and Dy) were prepared by dissolving the nitrate salts of the metals in 0.1 mol/L HNO_3 and in 0.1 M *N*-(2-hydroxyethyl)piperazine-*N'*-(2-ethanesulfonic acid) solution (HEPES). The pH values of the aqueous phases were adjusted by mixing the two. Solutions of high acidity were prepared using an appropriate concentration of HNO_3, and the nitrate ion concentration was adjusted through the addition of NH_4NO_3 solution. The concentration of [C_4mim] in an aqueous phase was adjusted by dissolving appropriate amount of [C_4mim][Cl] to the aqueous phase. The extraction phases were prepared by dissolving a given amount of HTTA and/or TOPO in an IL ([C_4mim][Tf_2N]) or the selected organic solvent (*n*-dodecane).

Equal volumes of the IL or organic extraction phase and the feed phase were poured into a sealed tube. After mixing for 60 s in a vibrating mixer, the combinations were gently shaken at 298 K for 12 h in a temperature-controlled bath to attain equilibrium. The mixture was then centrifuged at 8000 rpm for 5 min so that the two phases separated. The equilibrium pH of the resulting aqueous phase was measured by a pH meter (HM-60 G, DKK-TOA Co.). The stripping of metal ions from the extraction phase was also examined using HNO_3 solution. Metal concentrations in the various aqueous phases were determined using an inductively coupled plasma (ICP)-atomic emission spectrometer (Optima 5300; Perkin Elmer Inc.). The extraction ratio for the REEs (*E* [-]) was calculated by Eq. (2-2-1),

$$E = \frac{[\mathrm{M}]_{\mathrm{ex.eq}}}{[\mathrm{M}]_{\mathrm{aq.0}}} = \frac{[\mathrm{M}]_{\mathrm{aq.0}} - [\mathrm{M}]_{\mathrm{aq.eq}}}{[\mathrm{M}]_{\mathrm{aq.0}}} \qquad (2\text{-}2\text{-}1)$$

and the distribution ratio *D* was defined as shown in Eq. (2-2-2),

$$D = \frac{[\mathrm{M}]_{\mathrm{ex.eq}}}{[\mathrm{M}]_{\mathrm{aq.eq}}} = \frac{[\mathrm{M}]_{\mathrm{aq.0}} - [\mathrm{M}]_{\mathrm{aq.eq}}}{[\mathrm{M}]_{\mathrm{aq.eq}}} \qquad (2\text{-}2\text{-}2)$$

where [M] is the rare-earth metal concentration, and subscripts aq and ex indicate the feed aqueous and extraction phases respectively. The subscripts 0 and eq denote the initial and equilibrium states.

2-2-3 Results and discussion

2-2-3-1 Synergistic extraction with HTTA and TOPO in the *n*-dodecane system

Figure 2-2-2 shows the REE extraction ratios to *n*-dodecane for systems containing (a) only HTTA and (b) a mixture of HTTA and TOPO. As can be seen in Figure 2-2-2(a), Sc was selectively extracted relative to the other REEs with HTTA alone, and quantitative extraction was achieved at pH >3. Adding TOPO enhanced the extraction of Sc dramatically but the extraction of other REEs was more strongly enhanced so that the selectivity for Sc consequently decreased (Figure 2-2-2(b)). We confirmed that the REEs were not extracted by TOPO alone under the same experimental conditions (data not shown). The improvement in the extraction ratios of the rare-earth ions was, therefore, attributed to a synergistic effect between the two extractants.

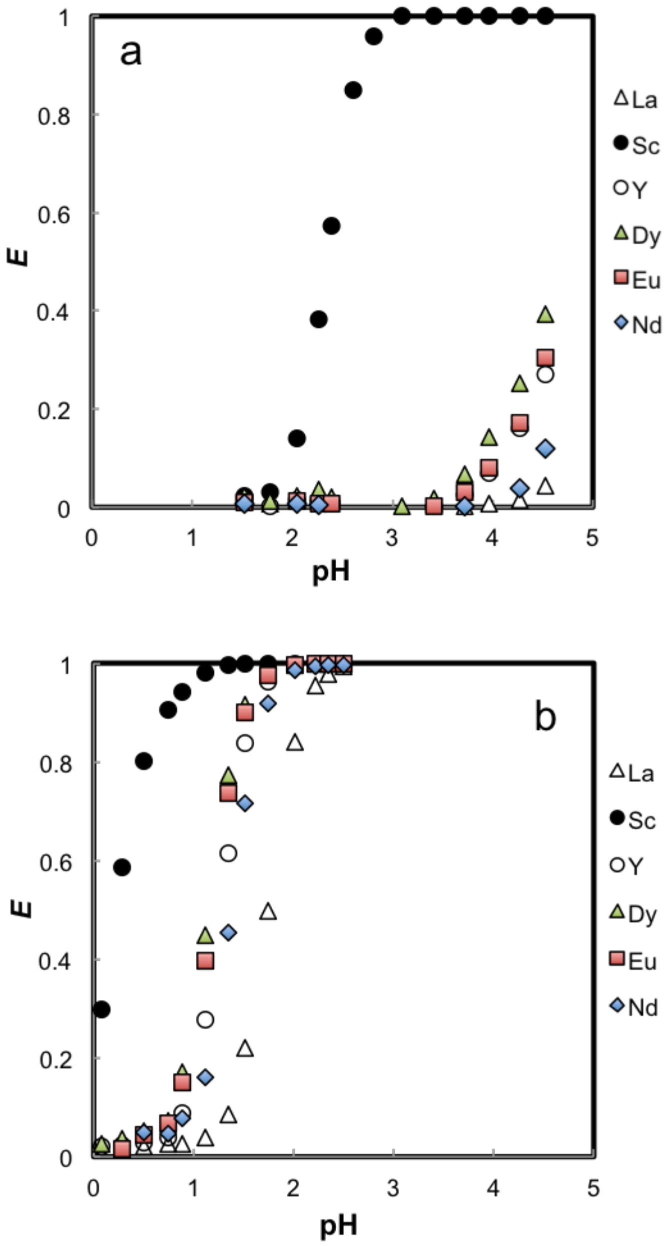


Figure 2-2-2 Rare earth metal extraction efficiencies using (a) only HTTA and (b) HTTA and TOPO in *n*-dodecane. Aqueous phase: 0.1 mmol/L M^{3+}, *n*-dodecane phase: (a) [HTTA] = 10 mmol/L, (b) [HTTA]=[TOPO]=10 mmol/L

2-2-3-2 Synergistic extraction with HTTA and TOPO in an ionic liquid system

The extraction of REEs was also examined for the IL system. As is shown in Figure 2-2-3(a), all REEs examined were extracted when the IL containing only HTTA was used at pH >3. No selectivity for specific REEs including Sc was observed, in contrast with the extraction efficiencies found in the *n*-dodecane system shown in Figure 2-2-2(a). As shown in Figure 2-2-3(b), however, the addition of TOPO to HTTA in the IL yielded improved REE extraction efficiencies. This was especially true in the case of Sc, for which the extraction was significantly larger than that of the other REEs. Lanthanides are not extracted at all by TOPO acting alone in [C_4mim][Tf_2N] under the experimental conditions. Similar results have been reported previously by Yang et al. [9]. It was confirmed that Sc was also rarely extracted at the hydrogen ion concentration range from 1.5 to 0.2 mol/L where the extraction curve of Sc was toward quantitative extraction. Therefore, the combination of the two extractants used in our study must have played an important role, causing a synergistic effect. However, a slight difference in the extraction efficiency of each metal ion using TOPO affected the selectivity in the binary HTTA-TOPO extraction system. Ours is the first report of a combination of HTTA and TOPO showing significantly a synergistic effect on the extraction and separation of Sc into an IL.

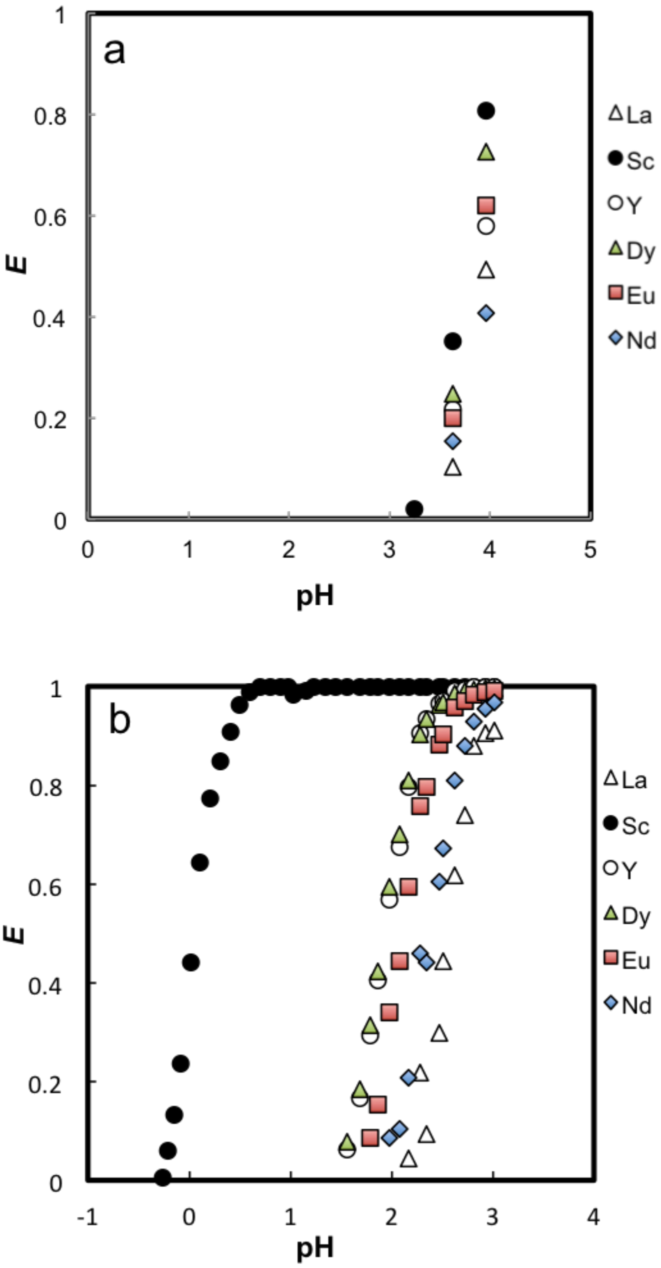


Figure 2-2-3 Rare earth metal extraction efficiencies using (a) only HTTA and (b) HTTA and TOPO in the ionic liquid (IL) system. Aqueous phase: 0.1 mmol/L M^{3+}, IL phase:(a) [HTTA] = 10 mmol/L, (b) [HTTA]=[TOPO]=10 mmol/L

2-2-3-3 Investigating the extraction mechanism in the synergistic system

Organic solvent system

Slope analysis was conducted to clarify the REE extraction mechanism operating in the synergistic extraction system. β-Diketones such as HTTA are widely used to extract a variety of metal ions by acting as chelating agents. The mechanism involved in the extraction of trivalent REE ions with HTTA in organic solvents follows Eq. (2-2-3) [14].

$M^{3+}(aq) + 3HTTA(o) \leftrightharpoons M(TTA)_3(o) + 3H^+(aq)$ (2-2-3)

The synergistic extraction equilibrium with HTTA and a co-extractant S is reported to be represented by Eq. (2-2-4) [12,21].

$M^{3+}(aq) + 3HTTA(o) + nS(o) \leftrightharpoons M(TTA)_3Sn(o) + 3H^+(aq)$ (2-2-4)

The experimental data are provided in Figure 2-2-4 for the extraction of the REEs with a mixture of HTTA and TOPO. Figure 2-2-4(a) shows the relationship between log*D* and the pH in the aqueous phase at equilibrium for the extraction of Eu^{3+} and Sc^{3+} with HTTA and TOPO. A linear relationship was obtained with a slope of 3 for Eu^{3+}, indicating that three protons were released during the extraction reaction. The result applies for all of the REE ions examined in this study, except Sc^{3+}, for which the relationship deviated from slope 3. The effects of the HTTA and TOPO concentrations on the distribution ratio, *D*, were also examined. Plots of log*D* against log[HTTA] at constant TOPO concentration and of log*D* against log[TOPO] at constant HTTA concentration showed linear correlations. The slopes were 3 and 2, respectively, for Eu^{3+} while a value of 2 was obtained for Sc^{3+} in each correlation. These results are presented in Figures 2-2-4(b) and (c). This suggests that the extracted species in the synergistic HTTA and TOPO system had a stoichiometry of 3:2:1 (HTTA:TOPO:M, M = Y, La, Nd, Eu, and Dy) and 2:2:1 for Sc^{3+}. The synergistic extraction reaction in the n-dodecane system can, therefore, be expressed as

$$M^{3+}(aq) + mHTTA(o) + nTOPO(o) + xNO_3^-(aq) \leftrightharpoons M(TTA)_m(TOPO)_n(NO_3)_X(o) + mH^+(aq) \quad (2\text{-}2\text{-}5)$$

Based on Eq. (2-2-5), D is represented by Eq. (2-2-6)

$$\log D = \log K_{ex} - m\log[H^+] + m\log[HTTA] + n\log[TOPO] + x\log[NO_3^-] \quad (2\text{-}2\text{-}6)$$

where m, n, and x are 3, 2, and 0 for REEs, except Sc^{3+} for which the values of 2, 2, and 1 were obtained. K_{ex} is the equilibrium constant of Eq. (2-2-5). The logarithmic *D* of Sc^{3+} was confirmed to be proportional to the logarithm of nitrate ion concentration, and no significant effect of the nitrate ion concentration on the extraction of Eu^{3+} was observed under the given experimental conditions (Figure 2-2-4(d)).

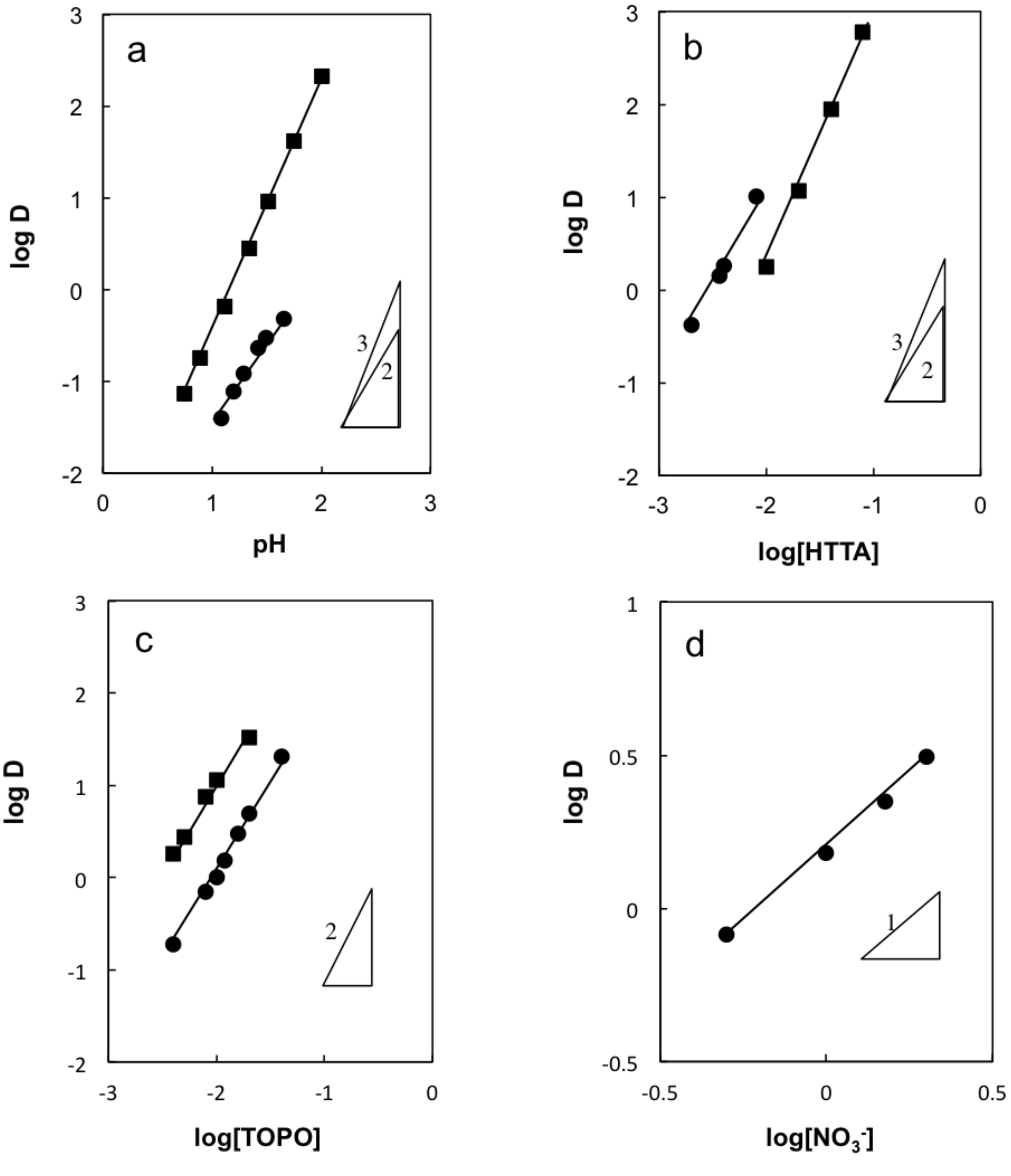


Figure 2-2-4 Slope analyses of $Sc^{3+}$and Eu^{3+} extraction in the synergistic HTTA and TOPO system in *n*-dodecane. a) log*D*–pH, b) log*D*–log[HTTA], c) log*D*–log[TOPO], (d) log*D*-log[NO_3^-](Sc^{3+}). Organic phase: (a) [HTTA] = [TOPO] = 10 mmol/L; (b) [TOPO] = 10 mmol/L; (c) [HTTA] = 10 mmol/L (Sc^{3+}) and 20 mmol/L (Eu^{3+}); (d) [HTTA] = [TOPO] = 3 mmol/L (pH=1). Aqueous phase: 0.1 mmol/L M^{3+}. (■:Eu^{3+},●:Sc^{3+})

The ionic radius of Sc is much smaller than that of the other REEs; Sc also has a lower coordination number (6 or 8) than do the other REEs (6-12). Therefore, the complex of Sc^{3+} with HTTA alone is coordinatively saturated and is hydrophobic. Therefore, it was selectively distributed into the organic phase. In the synergistic system, the REEs, except Sc^{3+}, formed coordinatively saturated complexes with more HTTA ligands and two TOPO adducts. Therefore, the distribution of the REEs was considered to be enhanced compared to Sc^{3+}. It is likely that the involvement of the TOPO molecule in the extracted species produces a selective advantage for REEs other than Sc in conventional organic systems.

Ionic liquid system

The extraction of REE ions with HTTA in an IL has previously been studied [19,22], and the metal extraction reaction was described by Eqs. (2-2-7) and (2-2-8):

$$M^{3+}(aq) + 3HTTA(IL) \leftrightharpoons M(TTA)_3(IL) + 3H^+(aq) \quad (2\text{-}2\text{-}7)$$

$$M^{3+}(aq) + 4HTTA(IL) + C_4mim^+Tf_2N^-(IL) \leftrightharpoons M(TTA)_4C_4mim\ (IL) + 4H^+(aq) + Tf_2N^-(aq) \quad (2\text{-}2\text{-}8)$$

In the HTTA system, the extraction capability for Sc^{3+} was significantly low compared to that in *n*-dodecane. HTTA solubilized more effectively in the IL than in the organic solvent; therefore, the distribution of HTTA to the aqueous phase must be lower in the IL phase than in the *n*-dodecane phase. Metal ions react with extractants in the aqueous side of the aqueous and organic interface; therefore the IL system exhibits lower extraction efficiency than the *n*-dodecane system. Furthermore, the complex formation of Sc^{3+} with more extractant molecules as expressed by Eq. (2-2-8) is difficult compared to that of Eu^{3+}. The addition of TOPO, however, strongly enhanced the extraction efficiency of REEs; this is especially true in the case of Sc^{3+}. Slope analysis was also conducted for synergistic extraction with a mixture of HTTA and TOPO. Figures 2-2-5(a), (b), and (c) show the relationships between log*D* and pH, log*D* and log[HTTA], and log*D* and log[TOPO], respectively. Clear linear correlations were observed, with slopes of 2, 2, and 3 for Eu^{3+}, indicating that two protons were released during the extraction process. As for Sc^{3+}, the slopes of the relationships between log*D* and log[HTTA] or log[TOPO] were 1 or 3, although the dependency on the proton concentration at high acidity was not analyzed because it was difficult to accurately estimate the effect of proton concentrations in a high acid concentration range. The stoichiometry of the synergistic extractants in the IL system was found to be 2:3:1 for Eu^{3+} and 1:3:1 for Sc^{3+} (HTTA:TOPO:M), respectively, under the present experimental conditions. Furthermore, it was expected that the nitrate and component ions of IL contributed to metal extraction for satisfying the electrical neutrality. Therefore, the synergistic extraction reaction in the IL can be expressed as Eq. (2-2-9):

$$M^{3+}(aq) + mHTTA(IL) + nTOPO(IL) + xNO_3^-(aq) + (3\text{-}m\text{-}x)C_4mim^+Tf_2N^-(IL) \leftrightharpoons$$
$$M(TTA)_m(TOPO)_n(NO_3^-)_xTf_2N^-_{(3\text{-}m\text{-}x)}\ (IL) + (3\text{-}m\text{-}x)C_4mim^+(aq) + mH^+(aq) \quad (2\text{-}2\text{-}9)$$

Eq. (2-2-10) is readily derived from Eq. (2-2-9).

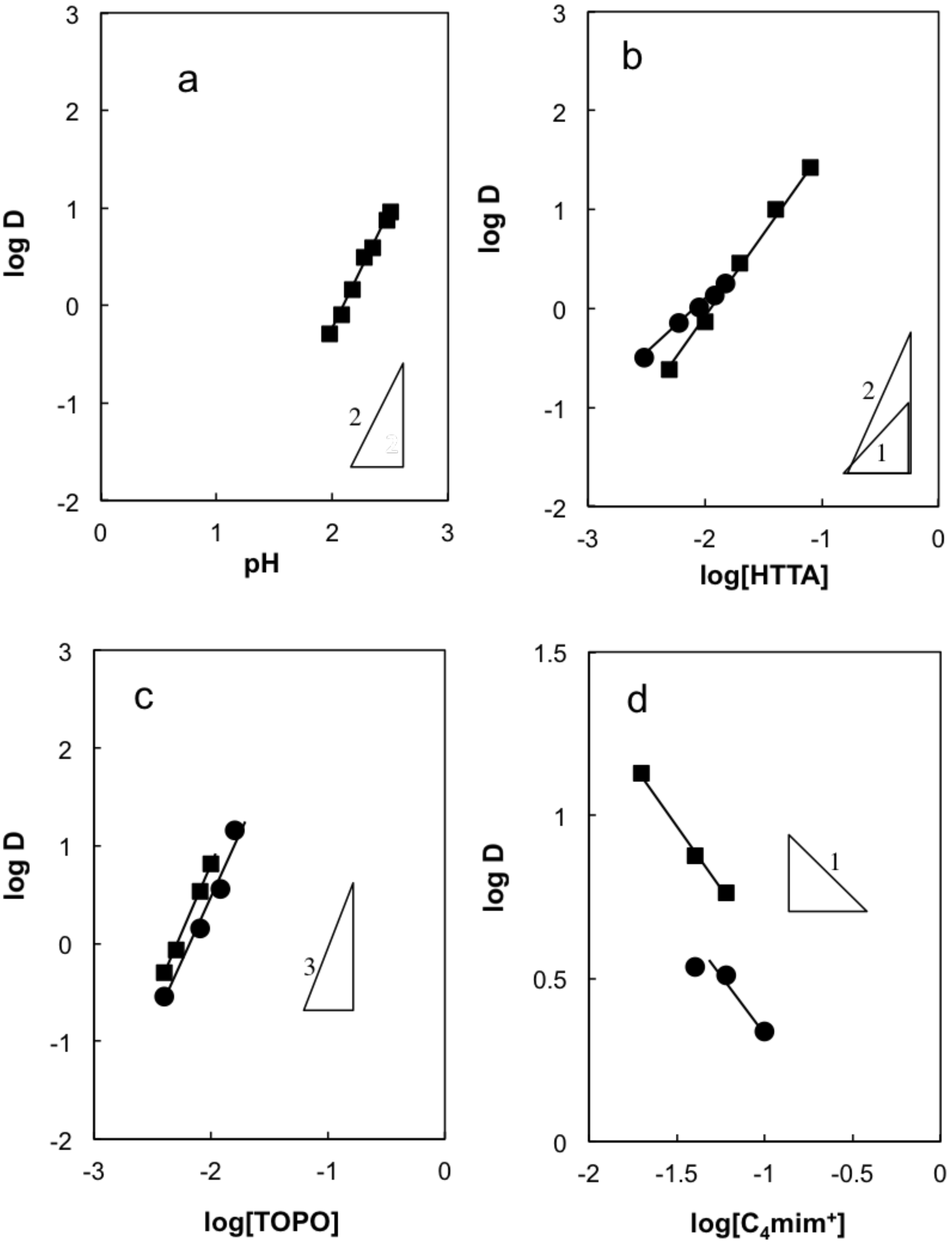
$$\log D = \log Kex - m\log[H^+] + m\log[HTTA] + n\log[TOPO] + x\log[NO_3^-]$$
$$+ (3\text{-}m\text{-}x)\log[C_4mim^+] \quad (2\text{-}2\text{-}10)$$

where *Kex* is the equilibrium constant from Eq. (2-2-9).

To confirm the contributions from the nitrate ions or the major component ions of the IL, the effect of the NO_3^- or $[C_4mim^+]$ concentrations in the aqueous phase on the distribution ratio was examined, where hydrophilic $[C_4mim][Cl]$ was added to the aqueous phase as a source of $[C_4mim^+]$. As shown in Figure 2-2-5(d), a decrease in *D* against $[C_4mim^+]$ concentration was observed for Eu^{3+} and Sc^{3+}. An influence is also apparent for Sc^{3+}, that is, log*D* was proportional to $\log[NO_3^-]$ for Sc^{3+} at higher nitrate concentration range (Figure 2-2-5(e)), though $[NO_3^-]$ contributed little to the extraction for Eu^{3+} (data not shown). Therefore, in the IL system, the extraction proceeded via cation exchange of metallic complex $M(TTA)_m(TOPO)_n(NO_3)_x^{3-m-x}$ with the imidazolium cation of the IL. The extracted species are interpreted to be $Eu(TTA)_2(TOPO)_3^+$ and $Sc(TTA)(TOPO)_3(NO_3)^+$ under the present experimental conditions. The extracted species were considered to pair with the IL anion in the IL phase. The extraction reactions for REEs, except Sc^{3+}, and then for Sc^{3+} itself, may consequently be expressed as Eqs. (2-2-11) and (2-2-12), respectively:

$$M^{3+}(aq) + 2HTTA(IL) + 3TOPO(IL) + C_4mim^+Tf_2N^-(IL) \leftrightharpoons$$
$$M(TTA)_2(TOPO)_3Tf_2N(IL) + C_4mim^+(aq) + 2H^+(aq) \quad (2\text{-}2\text{-}11)$$

$$\mathrm{Sc^{3+}(aq) + HTTA(IL) + 3TOPO(IL) + NO_3^{-}(aq) + C_4mim^{+}Tf_2N^{-}\,(IL) \rightleftharpoons Sc(TTA)(TOPO)_3(NO_3)Tf_2N(IL) + C_4mim^{+}(aq) + H^{+}(aq)} \quad (2\text{-}2\text{-}12)$$



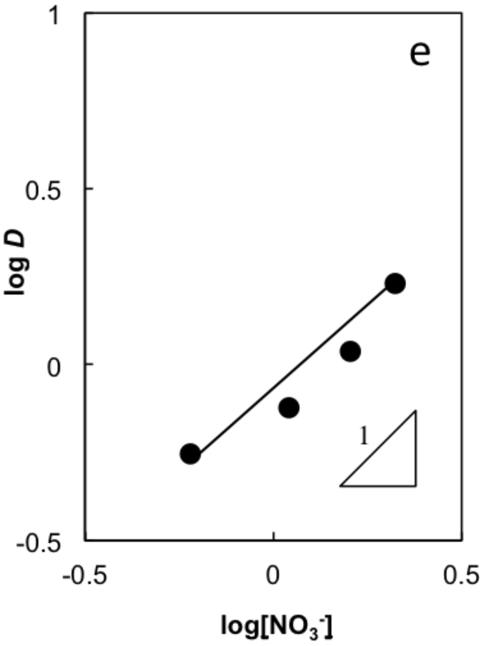


Figure 2-2-5 Slope analyses of Sc^{3+} and Eu^{3+} extraction in the synergistic HTTA and TOPO systems in the IL. a) log*D*–pH; b) log*D*–log [HTTA]; c) log*D*–log[TOPO]; d) log*D*-log[C_4mim]; e) log*D*-log[NO^{3-}]. Organic phase: (a) [HTTA] = [TOPO] = 10 mmol/L; (b) [TOPO] = 10 mmol/L; (c) [HTTA] = 10 mmol/L (Sc^{3+}) and 20 mmol/L (Eu^{3+}); (d) [HTTA] = [TOPO] = 10 mmol/L; (e) [HTTA] = [TOPO] = 2 mmol/L (pH=1)
Aqueous phase: 0.1 mmol/L M^{3+} (■:Eu^{3+},●:Sc^{3+})

In the synergistic system, the extraction was enhanced especially for Sc because the coordination sphere of Sc^{3+} was saturated with the extractants and nitrate. Moreover, solubilization of the Sc complex into the IL phase was considerably higher than that of the Eu^{3+} complex because the latter is larger in size. The release of an imidazolium cation into the aqueous phase accelerated the partitioning of the metal complexes. Finally, it should be noted that complete segregation of Sc^{3+} from the other REEs could be obtained in the synergistic IL extraction system.

2-2-3-4 Stripping

Stripping from the extraction phase was performed by 3mol/L HNO_3 for both extraction systems. Quantitative stripping was achieved using 3mol/L HNO_3 in the organic system in Figure 2-2-6. The stripping can be attributed partly to a lack of dissociation of HTTA, as well as to the inhibition of the coordination of TOPO because of the interaction of its coordination sites with H^+ under high acidity. In the IL system, the stripping of Sc^{3+} was achieved by 3mol/L HNO_3 in Figure 2-2-7. However, the other REEs proved more difficult to remove despite their lower extractability. A potential interpretation is that the non-Sc complexes do not solubilize uniformly into the bulk IL phase in the extraction step.

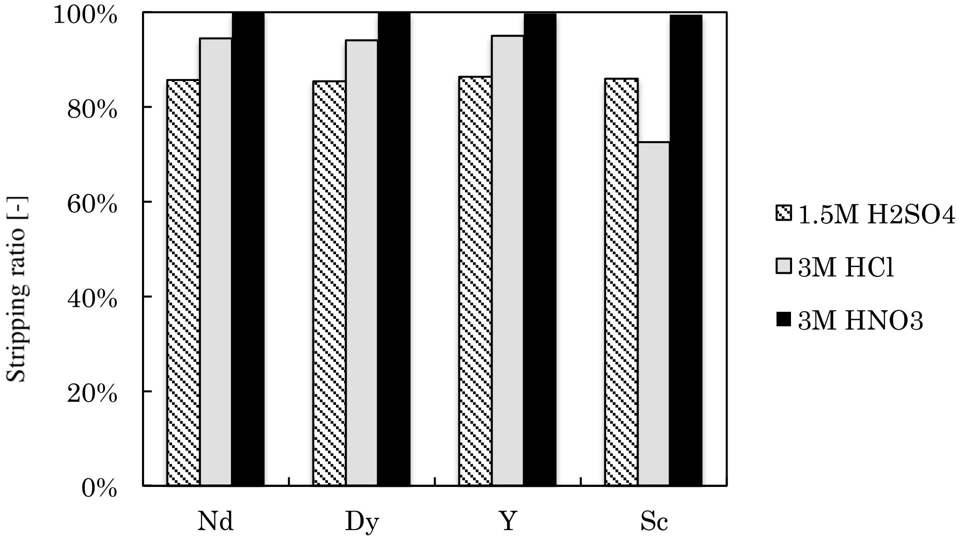


Figure 2-2-6 The extraction of REEs in organic solvent system (HTTA 10 mmol/L and TOPO 10 mmol/L in *n*-dodecane) Stripping of REEs in the organic solvent system

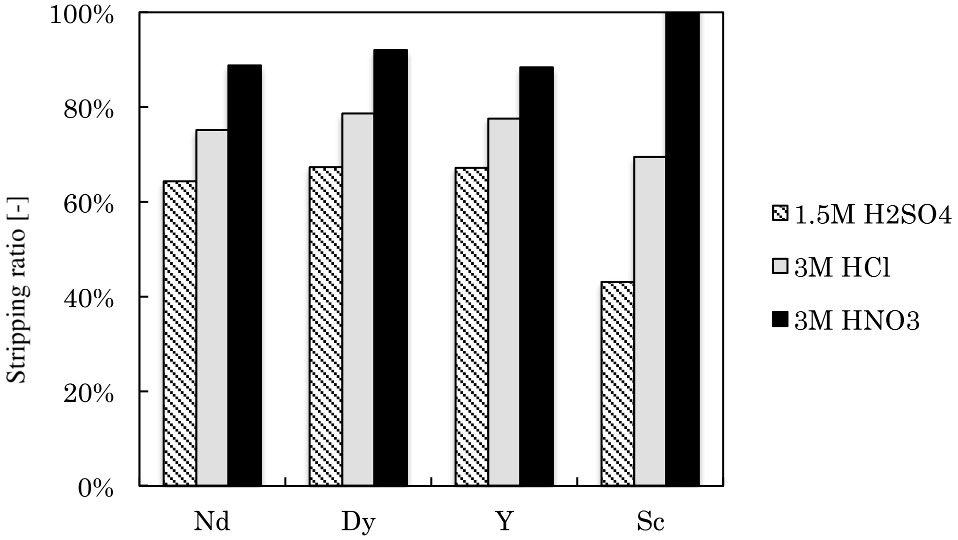


Figure 2-2-7 The extraction of REEs in ILs system (HTTA 10 mmol/L and TOPO 5 mmol/L in $[C_4mim][Tf_2N]$) Stripping of REEs in the ILs system

2-2-4 Conclusion

We investigated the synergistic extraction of REEs using a combined β-diketone (HTTA) and phosphine oxide (TOPO), and found that the synergistic effects were different in an IL and in an organic solvent. The extraction efficiencies of the rare-earth metals were enhanced by the synergistic effect in the organic medium, while the selectivity for Sc^{3+} was reduced. However, our synergistic extraction improved both the extraction efficiencies and the selectivity in the IL; this was particularly true for Sc over the other REEs, in the IL.

2-3 Conclusion

Liquid-liquid extraction of metal ions including REEs and common metals using synergistic extractant HTTA and TOPO was investigated in sulfate or nitrate media. The synergistic effects were obtained for REEs and some other transition metals. Adding TOPO increased the extraction efficiency of REEs with HTTA and depressed the extraction of Fe(III). An ionic liquid, [C_4mim][Tf_2N], was applied to a diluent as alternative to n-dodecane used in this study. The synergistic effect with TOPO for Sc was significantly larger than that for other REEs in contrast to the effect observed in the n-dodecane system. The difference in the extraction behavior of Sc and other REEs was suggested to be caused by the difference in the ionic radius, the coordination number and so on. The synergistic extractant system with β-diketone such as HTTA and neutral TOPO should be useful to extract and separate Sc from other metals.

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Chapter 3. Development of functional ionic liquid with amic acid groups

3-1 Introduction

In liquid-liquid extraction (LLE), the separation performance is affected by the properties of the extractant used in the process [1,2]. Many extractants have been synthesized and employed in the extraction and separation of metal ions. Novel extractants, *N,N*-dioctyldiglycol amic acid (DODGAA) was found to effectively separate LEEs from other metals [3-5]. *N*-[*N*,*N*-di(2-ethylhexyl)aminocarbonylmethyl] glycine (D2EHAG), which was developed by Baba et al., showed a high separation efficiency for nickel (Ni) and cobalt (Co) from manganese (Mn) and selective extraction of scandium (Sc) from the other rare earth elements (REEs) was possible[6-7].

Liquid-liquid extraction is the most efficient technology for the recovery of REEs, however, the use of a large amount of organic solvents has several environmental problems due to their toxicity and volatility etc. Room temperature ionic liquids (TRILs or ILs) are organic salts, which have advantages such as less-volatility, less-flammability etc. In Chapter 2, an imidazolium based IL ([C_4mim][Tf_2N]) was applied to the extraction solvent as an alternative to *n*-dodecane, and the extraction and separation performance of Sc was found to be improved compared to that in the n-dodecane system. ILs sometimes improve the extraction performance as just described. However, it has been difficult to find an extractant suitable for the ILs. As described in introduction section, ILs usually consist of an organic cation (imidazolium, pyridinium, ammonium and phosphonium) and an inorganic anion or an organic anion (tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), chloride (Cl^-), (trifluoromethylsulfonate (OTf^-), and bis[(trifluoromethyl)sulfonyl]imide (NTf_2^-)). Imidazolium bis[(trifluoromethyl)sulfonyl]imide was reported to have extracting ability by itself for Au and Pt [8]. Extraction and separation of metal ions by using ILs as an extractant are promising but facing great challenges [9,10], although water immiscible ILs including the imidazolium bis[(trifluoromethyl)sulfonyl]imide have been applied to the extraction of metal ions or organic compounds as the solvents. A great appeal of ILs is that they can be designed and synthesized.

Task-specific ionic liquids (TSILs) or functional ionic liquids (FILs), which bear a functional group in the IL constituents (Figure 3-1), have received much attention [11-16]. The diglycolamide-functionalized FIL was synthesized by Sengupta et al. and the extraction behavior of several actinide ions was examined [12]. The betainium bis(trifluoromethylsulfonyl)imide [Hbet][Tf_2N] was synthesized by Onghena *et al*. and the extraction property of Sc(III) was investigated [16].

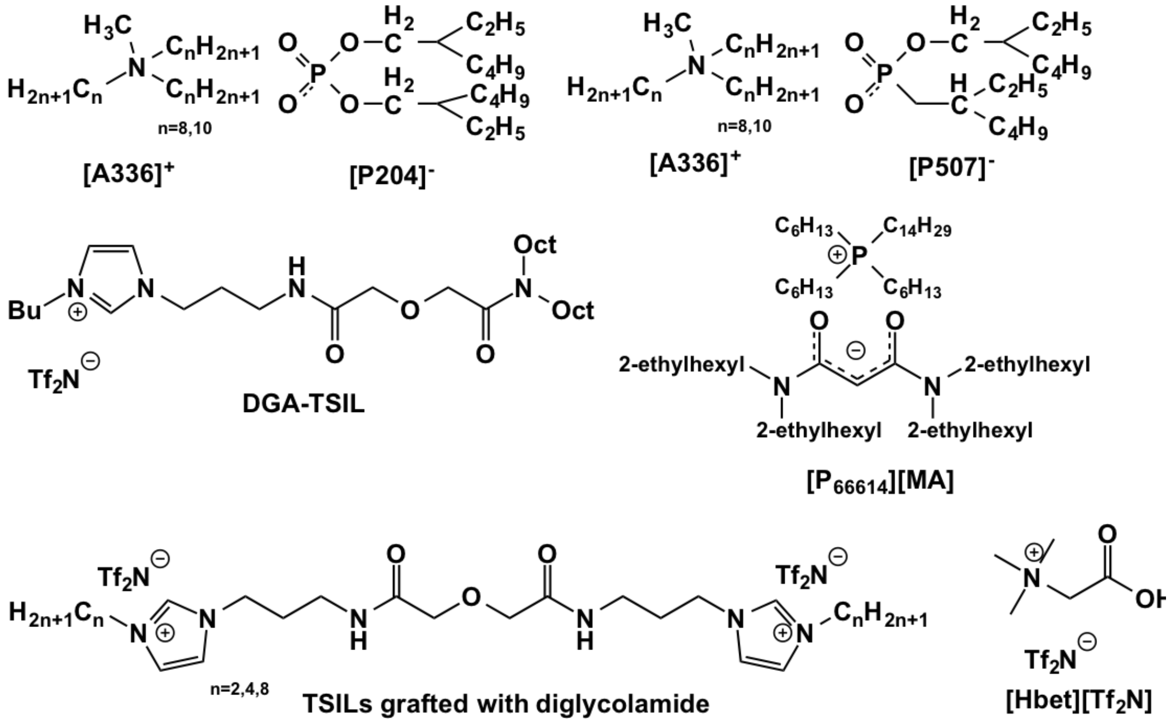
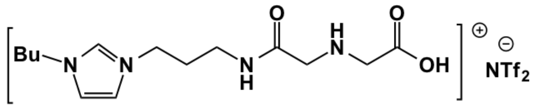
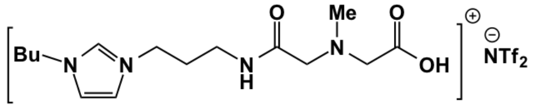


Figure 3-1 Functional ionic liquids

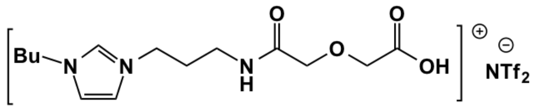
In this work, three new FILs bearing three types of amic acid groups [AGAPbim][Tf_2N], [ASAPbim][Tf_2N] and [DAAPbim][Tf_2N] shown in figure 3-2 were synthesized. A functional group, aminocarbonylmethylglycine of [AGAPbim][Tf_2N] is the moiety of the extractant D2EHAG, which has a high affinity to scandium ion, and [ASAPbim][Tf_2N] is the derivative of [AGAPbim][Tf_2N]. Another FILs [DAAPbim][Tf_2N] has a functional group of the extractant DODGAA, which is selective for rare earth metals. The extraction behavior of metal ions including Sc was examined by using FILs to show the usefulness of the modification of ILs with a functional group of a high affinity to target metal ions.



[AGAPbim][Tf$_2$N]



[ASAPbim][Tf$_2$N]



[DAAPbim][Tf$_2$N]

Figure 3-2 Molecular structures of FILs synthesized

3-2 Experimental

3-2-1 Reagents

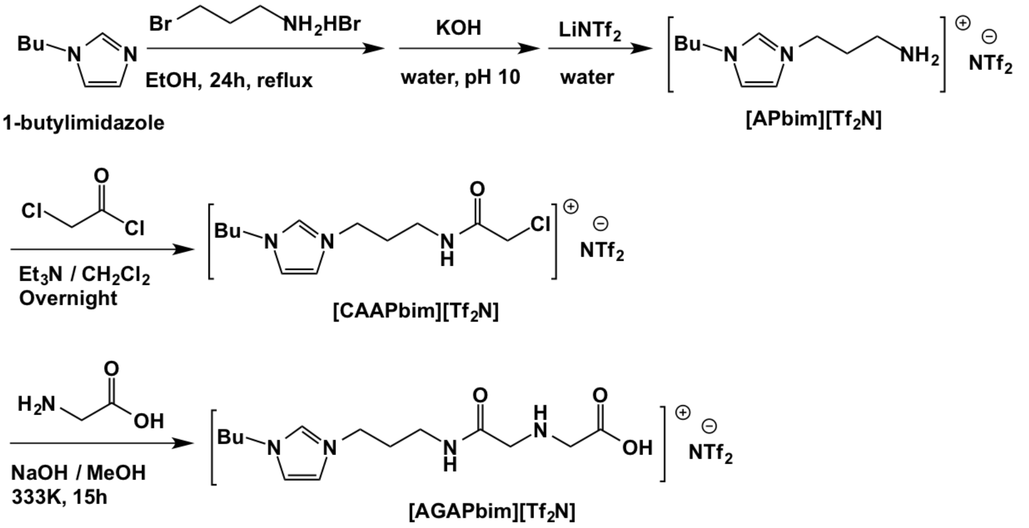
Chloroacetyl chloride (>98.0%), and diglycolic acid anhydride (98%) were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Triethylamine (>99.0%), 3-bromo-1-propylamine hydrobromide (95.0%), and the hydrophobic IL [C_4mim][Tf_2N] (1-butyl-3-methylimidazolium-bis(trifluoromethyl- sulfonyl)imide) were purchased from Wako Pure Chemical Industries (Osaka, Japan). Glycine (>99.0%) was from Kishida Chemical Co., Ltd. (Osaka, Japan). 1-Methyl imidazole (>98%) and 4-methylmorpholine-2,6-dione (>97%) were obtained from Sigma-Aldrich Co., Ltd. Lithium bis[(trifluoromethyl)sulfonyl]imide (>99.7%) was obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Sulfuric acid (5 mol/L), ammonium sulfate (99.5%), cobalt sulfate 7-hydrate (99.0%), and Chromium ammonium sulfate (97%) were from Kishida Chemical Co., Ltd. Nickel sulfate hexahydrate (99.0%), iron sulfate (99.5%), manganese sulfate pentahydrate (99.0%), calcium sulfate dihydrate (98.0%), aluminium sulfate (85.0%), and magnesium sulfate heptahydrate(99.5%) were obtained from Wako Pure Chemical Industries. Scandium sulfate (99.9%) was from Mitsuwa Chemical Co., Ltd. (Osaka, Japan).

3-2-2 Analysis of new functional ionic liquids

Nuclear magnetic resonance spectra (NMR; AVANCE II 300, Bruker, Germany) were recorded for ^{1}H NMR (300MHz) in deuterated chloroform ($CDCl_3$), dimethyl sulfoxide-D6, and methanol-D4.

3-2-3 Synthesis of FILs

Synthesis of [AGAPbim][Tf_2N]



Scheme 3-1 synthesis of [AGAPbim][Tf_2N]

[AGAPbim][Tf_2N] was synthesized according to the Scheme 3-1. [APbim][Tf_2N] (1-butyl-3-propylamineimidazoliumbis[(trifluoromethyl)sulfonyl] imide) was synthesized by the reaction of 1-butylimidazole and 3-bromo-1-propylaminehydrobromide as shown in Scheme 3-1 [17-19]. Reagent 1-butylimidazole (10mmol, 1eq) was dissolved in ethanol, and then the ethanol solution of 3-bromo-1-propylamine hydrobromide (10mmol, 1eq) was added. After the mixture solution was refluxed under the nitrogen for 24 h, the ethanol is removed in *vacuo* and the solid residue was dissolved in water. The pH value of the solution was adjusted to 10 by the addition of potassium hydroxide. The product imidazolium bromide was then separated from the KBr by evaporation of water, followed by extracting with ethanol-tetrahydrofuran. The obtained solution was concentrated under vacuum and then [APbim][Tf_2N] was obtained by

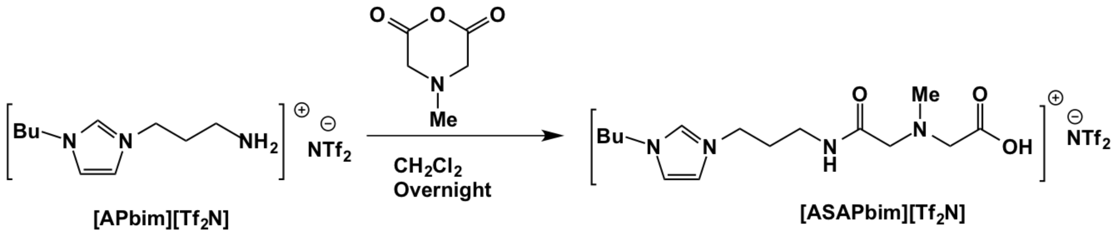
subsequent ion exchange with $LiNTf_2$ (15mmol, 1.5eq), in 90% yield.
[APbim][Tf_2N]: ^1H NMR (300 MHz, CDCl3) δ 10.22 (s, H, NC*H*N), 7.87 (s, H, NC*H*C), 7.57 (s, H, NC*H*C), 4.55 (m, 2H, NCH_2CCH_2), 4.38 (m, 2H, NCH_2CH_2), 2.77 (m, 2H, $NCH_2CH_2CH_2NH_2$), 1.93 (m, 2H, $NCH_2CH_2CH_2NH_2$), 1.74 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.39 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.96 ($NCH_2CH_2CH_2CH_3$).

[CAAPbim][Tf_2N] (1-butyl-3-(3-(2-chloroacetamido)propyl) imidazolium bis[(trifluoromethyl)sulfonyl]imide) was synthesized from amine-supported ionic liquid [APbim][Tf_2N] and chloroacetyl chloride in dichloromethane (DCM) solution under nitrogen gas [20]. Chloroacetyl chloride (10mmol, 2eq) was added slowly to the DCM solution of [APbim][Tf_2N] (5mmol,1eq) and triethylamine (Et_3N) (10mmol, 2eq) at 273K, followed by stirring overnight at room temperature. The resulting mixture was washed with low concentration hydrochloride (0.1 mol/L) to remove amine. The DCM phase was washed by deionized water several times. The organic solution was concentration under vacuum. The compound [CAAPbim][Tf_2N] was extracted by chloroform and obtained after removing chloroform, in 69% yield.
[CAAPbim][Tf_2N]: ^1H NMR (300 MHz, CDCl3) δ 9.16 (s, H, NC*H*N), 7.78 (s, 2H, NC*H*C), 4.17 (m, 4H, $NCH_2CH_2CH_2$), 4.01 (s, 2H, $COCH_2Cl$), 3.11 (m, 2H, $NCH_2CH_2CH_2NH_2$), 1.98 (m, 2H, $NCH_2CH_2CH_2NH_2$), 1.79 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.27 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.91 ($NCH_2CH_2CH_2CH_3$).

[AGAPbim][Tf_2N] (1-butyl-3-(3-(2-((carboxymethyl)amino)acetamido)propyl) imidazolium bis[(trifluoromethyl)sulfonyl]imide) was synthesized by the intermediate [CAAPbim][Tf_2N] and glycine in methanol solution under nitrogen gas. Glycine (4mmol, 2eq) was dissolved in the methanol solution with sodium hydroxide (NaOH) (4mmol, 2eq) and [CAAPbim][Tf_2N] (2mmol, 1eq) was added by dropwise to the mixture solution, followed by stirring for 15 h at 333K. The resulting solution was concentrated in vacuum to remove methanol. The obtained organic phase was dissolved in ethyl acetate (AcOEt) and washed by 1 mol/L sulfuric acid solution and deionized water several times. The AcOEt was removed in vacuum.
[AGAPbim][Tf_2N] was obtained as a dark brown liquid (36% yield).

[AGAPbim][Tf$_2$N]: ^{1}H NMR (300 MHz, CDCl3) δ 9.13 (s, H, NC*H*N), 7.80 (s, 2H, NC*H*C), 4.18 (m, 4H, NCH_2CH$_2$CH$_2$), 3.92 (s, 2H, COCH_2NH), 3.76 (s, 2H, NHCH_2COOH), 3.12 (m, 2H, NCH$_2$CH_2CH$_2$NH), 1.98 (m, 2H, NCH$_2$CH$_2$CH_2NH), 1.79 (m, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.27 (m, 2H, NCH$_2$CH$_2$CH_2CH$_3$), 0.91 (NCH$_2$CH$_2$CH$_2$CH_3).

Synthesis of [ASAPbim][Tf$_2$N]

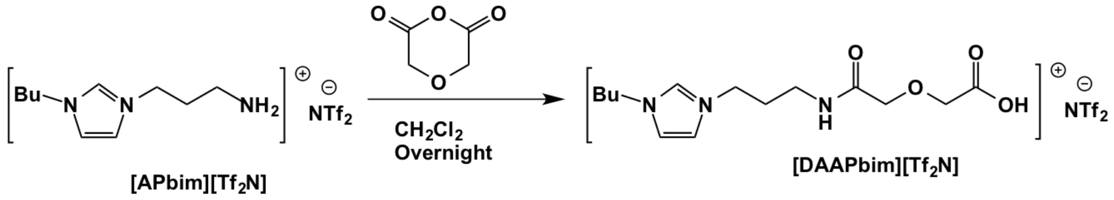


Scheme 3-2 synthesis of [ASAPbim][Tf$_2$N]

[ASAPbim][Tf$_2$N] (1-butyl-3-(3-(2-((carboxymethyl)(methyl)amino)acetamido) propyl) imidazolium bis[(trifluoromethyl)sulfonyl]imide) was synthesized by [APbim][Tf$_2$N] and 4-methylmorpholine-2,6-dione according to Scheme 3-2: 4-methylmorpholine-2,6-dione (2.4mmol, 1.2eq) dissolved in DCM was added to the solution of [APbim][Tf$_2$N] (2mmol, 1eq) in DCM, and the mixture was stirred at room temperature overnight. The solvent in the resultant mixture was removed in vacuum. The solid residue was dissolved in AcOEt and was washed with deionized water several times. The organic solution was dried in vacuum. The resulting compound was a yellow liquid in 38% yield.

[ASAPbim][Tf$_2$N]: ^{1}H NMR (300 MHz, CDCl3) δ 9.14 (s, H, NC*H*N), 7.77 (s, 2H, NC*H*C), 4.16 (m, 4H, NCH_2CH$_2$CH$_2$), 4.01 (s, 2H, COCH_2NH), 3.96 (s, 2H, NHCH_2COOH), 3.15 (m, 2H, NCH$_2$CH_2CH$_2$NH), 2.89 (s, 3H, CH$_2$NCH_3CH$_2$), 1.98 (m, 2H, NCH$_2$CH$_2$CH_2NH), 1.79 (m, 2H, NCH$_2$CH_2CH$_2$CH$_3$), 1.27 (m, 2H, NCH$_2$CH$_2$CH_2CH$_3$), 0.91 (NCH$_2$CH$_2$CH$_2$CH_3).

Synthesis of [DAAPbim][Tf_2N]



Scheme 3-3 synthesis of [DAAPbim][Tf_2N]

[DAAPbim][Tf_2N] (1-butyl-3-(3-(2-(carboxymethoxy)acetamido)propyl)imidazolium bis[(trifluoromethyl)sulfonyl]imide) was synthesized from [APbim][Tf_2N] (2mmol,1eq) and diglycolic acid anhydride (4mmol,2eq) [2] as shown in scheme 3-3. The synthesis of [DAAPbim][Tf_2N] was similar to that of [ASAPbim][Tf_2N]. The resultant colorless liquid [DAAPbim][Tf_2N] was obtained in 51% yield.

[DAAPbim][Tf_2N]: ^{1}H NMR (300 MHz, CDCl3) δ 8.91 (s, H, NC*H*N), 7.62 (s, 2H, NC*H*C), 4.22 (m, 4H, $NCH_2CH_2CH_2$), 4.22 (s, 2H, $COCH_2O$), 4.01 (s, 2H, $COCH_2COOH$), 3.31 (M, 2H, $NHCH_2CH_2CH_2NH$), 2.14 (m, 2H, $NCH_2CH_2CH_2NH$), 1.89 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.38 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.98 (m, 3H, $NCH_2CH_2CH_2CH_3$).

3-2-4 Extraction procedure

The aqueous feed phases were prepared by 0.1mol/L sulfuric acid solution and 0.1 mol/L ammonium sulfate solution containing 0.1mmol/L of metals (Mg^{2+}, Al^{3+}, Ca^{2+}, Sc^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+}). The pH values of the aqueous phase were adjusted by mixing the two solutions. As the extraction phase, [AGAPbim][Tf_2N] was used undiluted or diluted in the ionic liquid [C_4mim][Tf_2N]. Extraction experiments were carried out in a sealed tube with 50mg FILs alone in contact with 3ml aqueous metals solutions or 1.5ml [C_4mim][Tf_2N] containing 10mmol/L concentration of [AGAPbim][Tf_2N] with 1.5ml metals containing aqueous solutions. The mixture was shaken for 60s in a vibrating mixer, and then gently shaken at 298K for 12h in a temperature-controlled shaking bath to reach equilibrium. The resultant mixture was centrifuged at 8000rpm for 5min at 298k, and the aqueous phase was separated. The equilibrium pH of the aqueous phase was measured by a pH meter (HM-60 G, DKK-TOA Co.). The metal concentrations in the aqueous phases were determined by using an inductively coupled plasma (ICP)-atomic emission spectrometer (Optima 8300; Perkin Elmer Co., MA, USA). The extraction ratio *E* (-) was calculated by Eq. (3-1),

$$E = \frac{[M]_{ILs.eq}}{[M]_{aq.0}} = \frac{[M]_{aq.0} - [M]_{aq.eq}}{[M]_{aq.0}} \tag{3-1}$$

where [*M*] is the metals concentration, and subscripts aq and ILs indicate the aqueous phase and the ionic liquid phase, 0 and eq denote the initial and the equilibrium state, respectively.

3-3 Results and discussion

Figure 3-3(a) shows the extraction behavior of the metal ions with undiluted [AGAPbim][Tf_2N]. The extraction was promoted with increasing the pH of the aqueous feed solution, suggesting that the extraction proceeds via proton exchange of the functional groups of the imidazolium IL with a metal cation. It was found that the quantitative extraction of Sc^{3+} was achieved at about pH > 1.5 under the experimental conditions. Sc^{3+} was selectively extracted to [AGAPbim][Tf_2N]. The extractant D2EHAG, which includes the same functional group as [AGAPbim][Tf_2N], was reported to show a high affinity to Sc^{3+} [7]. As describ in Chapter 4, a novel adsorbent, PA-AG, was prepared by introducing the aminocarbonylmethylglycine group to a resin [21]. The similar extraction behavior of the metal ions except Fe^{3+} was observed for [AGAPbim][Tf_2N] as that with the novel adsorbent PA-AG. Metal extraction increased in the order of $Sc^{3+} > Fe^{3+} > Ni^{2+} > Co^{2+} >$ other metal ions, whereas PA-AG was observed to adsorb Fe^{3+} as well as Sc^{3+}. In the [AGAPbim][Tf_2N] extraction system, the extraction mechanism of Fe^{3+} was suggested to be different from that in the adsorption mechanism. Thus the novel FIL was considered to be both an extractant and the solvent. It was found that Sc^{3+} could be separated from other transition metals.

The extraction of metal ions was also examined with [AGAPbim][Tf_2N] dissolved in [C_4mim][Tf_2N] as a diluent. As shown in Figure 3-3(b), the similar selectivity for the metal ions was observed as that using undiluted [AGAPbim][Tf_2N], although the extraction curve shifted to the right because the concentration of aminocarbonylmethylglycine group was lower than that of undiluted [AGAPbim][Tf_2N]. The volume of the [AGAPbim][Tf_2N] used without dilution was about 0.03mL, that is, enrichment of Sc was suggested to be possible to [AGAPbim][Tf_2N].

The extraction behavior of metal ions, by [ASAPbim][Tf_2N] is shown in Figure 3-3(c). The signs of the extraction of Fe^{3+} was observed, however, Sc^{3+} was little extracted under the present experimental conditions. The extractability and selectivity of [ASAPbim][Tf_2N] for Sc^{3+} was worse than that of [AGAPbim][Tf_2N] under the same extraction conditions. The difference in the performance between the two FILs is considered to be caused by the difference in the category of amine group in the center of the functional group. Compared to the secondary amine of [AGAPbim], tertiary amine of [ASAPbim] has less affinity to the hard metal ions like Sc, and the metal complex with the tridentate ligands was less stable due to the steric hindrance caused by the bulky alkyl group.

Figure 3-3(d) shows the metal extraction behavior of [DAAPbim][Tf_2N], which has the diglycol amic acid functional group. Extractant DODGAA, which has a diglycol amic acid group in the molecule, has a high selectivity to rare earth metal ions including Sc against to other metal ions, however, the extraction ability of Sc is not so high compared to that using D2EHAG having aminocarbonylmethylglycine. The structure of the former functional group is rigid to recognize Sc ion of small size. The extraction ability for Sc^{3+} is low compared to that of the latter functional group, of which structure is very flexible [7].

The extraction of metal ions with FTLs shown in Fig. 3-3 seems to reflex the affinity of the functional group introduced to metal ions.

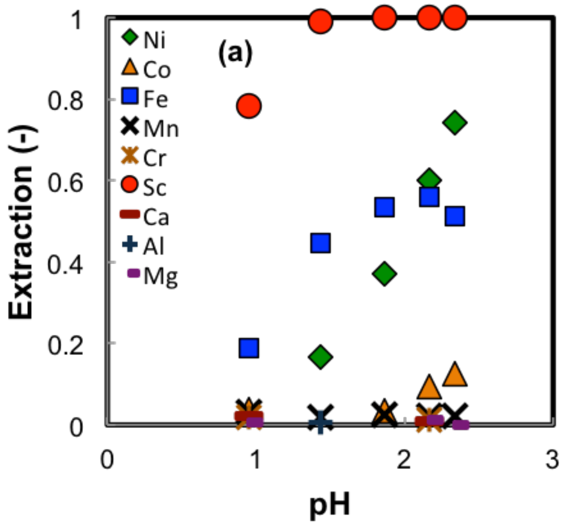


Figure 3-3-(a) extraction behavior of metal ions using [AGAPbim][Tf_2N] alone, FILs = 50mg, Aqueous phase: [M] = 0.1mmol/L, [SO_4^{2-}] = 0.1mol/L

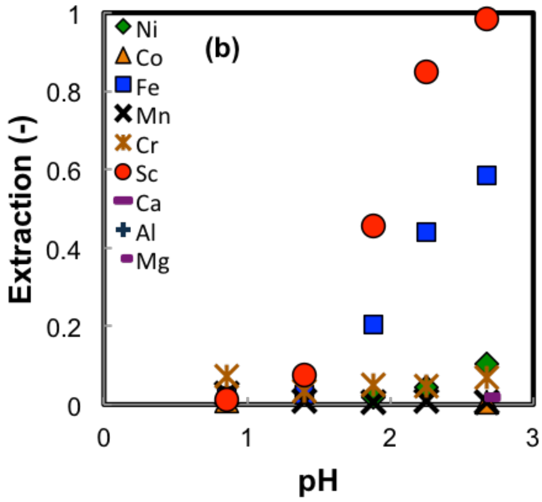


Figure 3-3-(b) extraction behavior of metal ions using [AGAPbim][Tf_2N] in [C_4mim][Tf_2N] = 10mmol/L, Aqueous phase: [M] = 0.1mmol/L, [SO_4^{2-}] = 0.1mol/L.

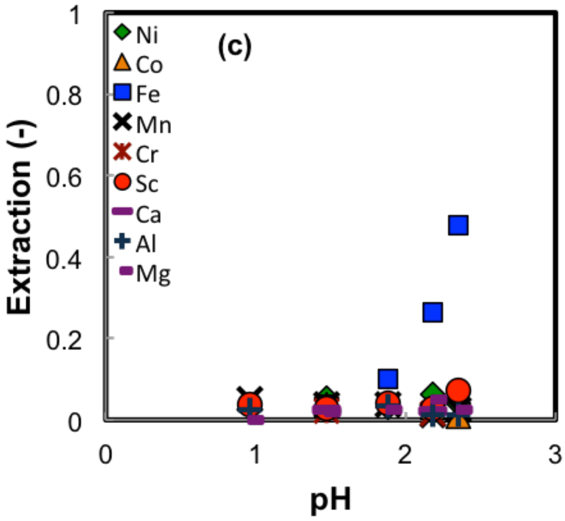


Figure 3-3-(c) extraction behavior of metal ions using [ASAPbim][Tf_2N] alone, FILs = 50mg, Aqueous phase: [M] = 0.1mmol/L, [SO_4^{2-}] = 0.1mol/L

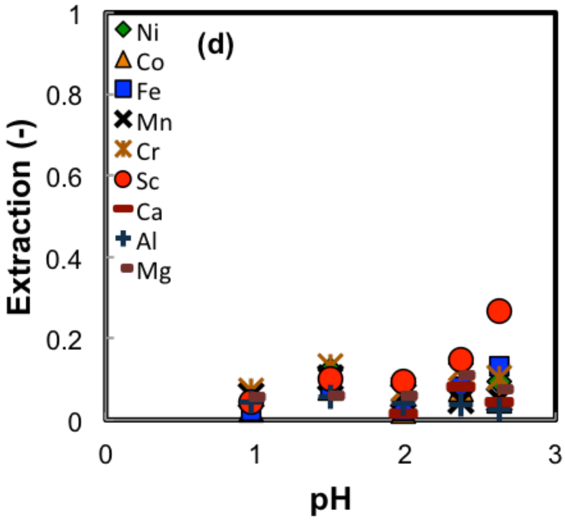


Figure 3-3-(d) extraction behavior of metal ions using [DAAPbim][Tf_2N] alone, FILs= 50mg, Aqueous phase: [M] = 0.1mmol/L, [SO_4^{2-}] = 0.1mol/L

3-4 Conclusion

New functional ionic liquids were synthesized, and the extraction behavior of metal ions was examined using the FILs undiluted and/or diluted in an IL [C_4mim][Tf_2N]. The extraction performance of FILs was shown to depend on the performance of the functional groups introduced in the ILs. Among the FILs, [AGAPbim][Tf_2N] exhibited a high extraction and separation performance for Sc^{3+} to other metal ions including Fe^{3+}. It was demonstrated that an ionic liquid having a high affinity for the target Sc ion could be prepared by introducing an aminocarbonylmethylglycine as the functional group.

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Chapter 4. Development of novel adsorbent bearing aminocarbonylmethyl glycine and its application to scandium separation

4-1 Introduction

Hydrometallurgical techniques such as liquid–liquid extraction and solid-phase extraction are used widely for the separation and purification of REEs. Liquid–liquid extraction, also termed solvent extraction, provides easy operation with simple equipment, enables the construction of continuous separation process and can provide a high throughput. The key to establishing a successful metal separation process is the selection of an excellent extractant, which recognizes a target metal ion selectively and efficiently [1]. For rare earth metals, 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ether (PC-88A) [2,3] and 2-methyl-2-ethylheptanoic acid (Versatic 10) [4,5], have been used as industrial extractants. A new extractant, *N*,*N*-dioctyldiglycol amic acid (DODGAA) [6-8], which shows a high affinity to REE ions, has been developed. However, it has been difficult to find an effective extractant for the separation and recovery of Sc. Recently, a novel extractant, *N*-[*N*,*N*-di(2-ethylhexyl)amino carbonylmethyl]glycine (D2EHAG) [9,10], to meet this demand was developed.

Solid-phase extraction technology, known as ion exchange or the adsorption method, is another choice for the separation and high-purity concentration of trace metal ions. This method avoids the use of organic solvents that impact the environment, and has come to the forefront in recent years [11-14]. Few commercial ion exchange resins or adsorbents exist to separate Sc efficiently from other metal ions. In this study, we have developed a novel adsorbent that bears functional groups that recognize Sc. This adsorbent contains the same functional group as the extractant D2EHAG. Inorganic silica is often used in the laboratory as the support material to immobilize functional groups, since it is easily available, readily modified and the adsorption behavior of metal ions is readily evaluated. Therefore, many adsorbents based on silica gel have been studied for metal ion adsorption [15-19]. In this work, we have immobilized the aminocarbonylmethylglycine functional group on silica gel with amino groups as reaction sites. For practical use, however, silica gel as a packed bed is problematic in terms of a pressure drop and chemical resistance. Therefore, a commercially available amine-supported organic resin has been used as the support material [11,12]. In this study, silica gels were used to confirm the fundamental information on synthesis and the metal adsorption. The novel adsorbent, which is modified with the functional group, for practical use was prepared based on the resin, and its adsorption behavior for metal ions that include Sc was examined. The applicability of the functionalized adsorbent is discussed for Sc separation.

4-2 Experimental

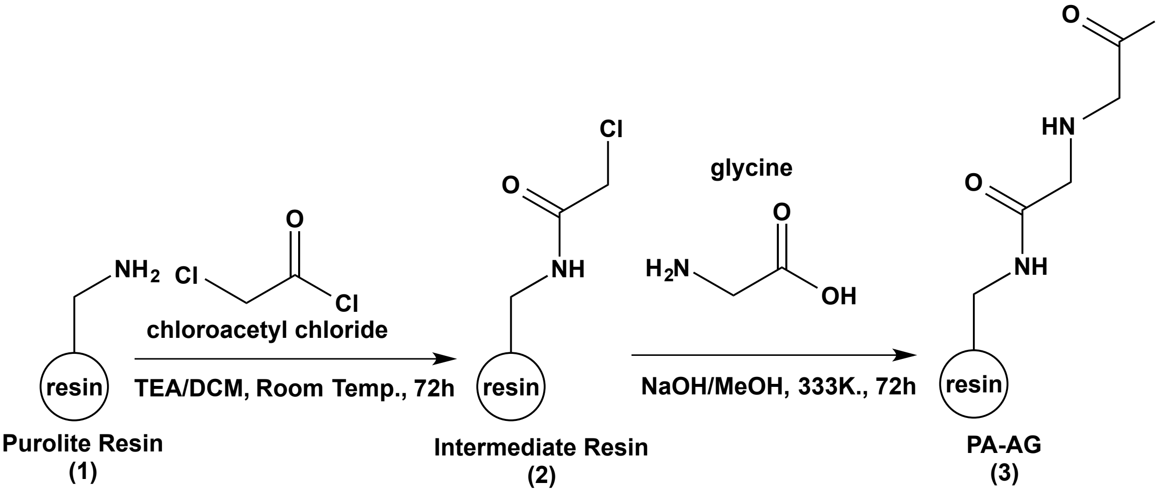
4-2-1 Reagents

3-Aminopropyl silica gel (~0.6–1.3 mmol/g, 75~150μm) (abbreviated as Si_1) and 3-(ethylenediamino)propyl silica gel (~0.7–1 mmol/g, the size is comparable with Si_1) (Si_2) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) as adsorbent support materials. A commercial primary amine-supported resin, Purolite A110 (PA, Purolite Corp., PA, USA), which is made of polystyrene that is crosslinked with divinylbenzene, was supplied by Sumitomo Metal Mining Co., Ltd. (Tokyo, Japan). Commercial PA is a weak base anion exchange resin with a total capacity of 2.0 eq/L, and the size is 300~1200μm. Chloroacetyl chloride (> 97%) and triethylamine (> 99%) were obtained from Wako Pure Chemical Industries (Osaka, Japan). Glycine (> 99%) was purchased from Kishida Chemical Co., Ltd (Osaka, Japan). Metal ion stock solutions were prepared from their metal sulfates. All other reagents and solvents were of analytical grade and were used as received.

4-2-2 Adsorbent synthesis

Novel adsorbents were prepared by modifying PA or silica gels with amine groups. According to the synthesis of D2EHAG in a previous report [13], adsorbent-bearing aminocarbonylmethylglycine was synthesized in two reaction steps as shown in Scheme 4-1. Before synthesis, PA resin was dehydrated at 333 K for 48 h, and its mass decreased by 50%. The amount of supported amino groups in the resin was estimated by neutralization titration to be 5.49 mmol/g. In the first step, intermediate chloroacetamide-supported resin (2) was synthesized by adding three equivalent amounts of chloroacetyl chloride to the original resin PA (1) in dichloromethane containing triethylamine (3 eq), followed by stirring for 72 h at room temperature. The resulting mixture was filtered, and the residual product was washed with 0.1 mol/L HCl, methanol and deionized water until the rinse solution was neutral. An intermediate resin (2) was obtained. In the second step, the intermediate product (2) was added to a methanol solution of glycine (5 eq) and sodium hydroxide (5 eq) as alkaline catalyst, and the reactants were stirred for 72 h at 333 K. The resulting mixture was filtered and washed with 1.0 mol/L H_2SO_4, methanol and deionized water as above described. The resultant product was dried and aminocarbonylmethylglycine-immobilized resin (PA-AG) was obtained.

Preliminary to the synthesis of PA-AG, silica gel-based adsorbents that support aminocarbonylmethylglycine, Si_1-AG and Si_2-AG were prepared by modifying the corresponding base materials, Si_1 and Si_2, to determine the synthesis approach described above. Here, the amount of supported amino groups on the original silica gels was estimated from the mass percentage of nitrogen by elemental analysis of 0.97 and 1.59 mmol/g, respectively.



Scheme 4-1 Synthesis of adsorbents

4-2-3 Adsorbent analysis

Adsorbent chemical characteristics were analyzed by Fourier-transform infrared (FT-IR) spectrometry (Spectrum 65, PerkinElmer Co., MA, USA). FT-IR spectra were recorded from 4000–600 cm^{-1} and were measured by attenuated total reflection. The averaged spectra were obtained at a resolution of 4 cm^{-1}.

The amounts of amino groups in the original PA and aminocarbonylmethylglycine group introduced to the PA were determined by neutralization titration using an automatic potentiometric titrator (AT-710S, Kyoto Electronics Manufacturing Co., Ltd., Kyoto, Japan).

4-2-4 Procedure for adsorption and desorption experiments

Batch adsorption experiments were carried out in a sealed tube with 50 mg (dry basis) adsorbent in contact with 5 mL metal ion-containing aqueous solution, where the solution was prepared by diluting metal stock solution, and the pH was adjusted by using 0.1 mol/L sulfuric acid and ammonium sulfate solution. The sample solution was shaken by horizontal axis rotation using a rotary mixer (15 rpm, NRC-D20, Nisshin Rika Co., Tokyo, Japan) at room temperature (~298K) for a given time. After filtration, the metal ion concentration in the filtrate, C_f (mg/L), was determined using an inductively coupled plasma-atomic emission spectrometer (Optima 8300; Perkin Elmer Co., MA, USA), and the adsorption ratio for each metal ion, A (-) was calculated from:

$$A = (C_0 - C_f)/C_0 \qquad (4\text{-}1)$$

where C_0 (mg/L) is the initial metal concentration. The adsorption capacity q (mg/g) was calculated from:

$$q = (C_0 - C_f)V/M \qquad (4\text{-}2)$$

where V is the volume of solution (L) and M is the dry mass of adsorbent (g). Metal ion desorption from the adsorbent was also examined as the similar way as adsorption experiment using 5mL sulfuric acid solution, and the desorption ratio De (-) was defined as follows:

$$De = C_{de}/C_{ad} \qquad (4\text{-}3)$$

where C_{ad} expresses (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 Adsorbent characterizations

Microscopy revealed that the synthesized resin maintained its spherical shape and size compared with the original resin (data not shown).

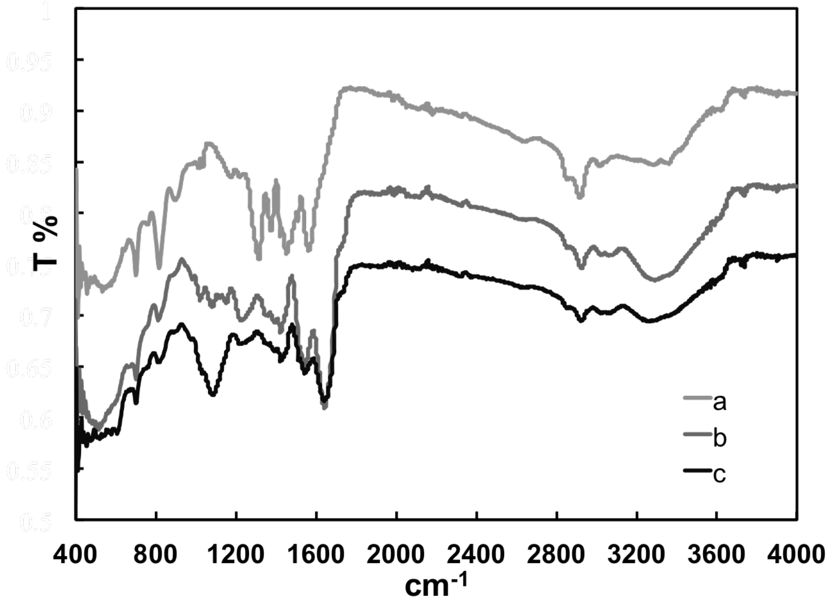


Figure 4-1 FT-IR spectra of original PA (a), synthesized PA-AG (b) and Sc-loaded PA-AG (c)

Figure 4-1 shows FT-IR spectra for the unmodified and modified resins. The IR bands at 3270 cm^{-1} and 3340 cm^{-1} that are associated with the primary amine of the original resin (a) disappeared, and a characteristic band attributable to secondary amine -NH- and solid-state amide appeared at ~3000–3500 cm^{-1} in the modified resin, PA-AG (b). The IR peak at 1580 cm^{-1} for the N-H bending vibration of amine (a) disappeared, and that at 1540 cm^{-1} for the carboxyl anion and C-O stretching vibrations in the carboxyl group, and the peak at 1655 cm^{-1}, which is attributed to -CO-NH-, appeared (b). The spectrum at ~1300–1450 cm^{-1} is attributed to the bending vibration of C-H and O-H, that at ~950–1300 cm^{-1} is assigned to the stretching vibration of C-O and that at ~900–1200 cm^{-1} is attributed to -O-H bending and C-O stretching vibration (b). The spectra revealed that the amine of the original PA was modified with the aminocarbonylmethylglycine group. The spectrum of Sc-loaded resin was also measured (c). Compared with that of the synthesized resin (b), peak intensities at ~3000–3500, 1655, 1540 and 1230 cm^{-1} were weakened, and a significant change in peak shape around 900–1200 cm^{-1} was observed, which suggests that the secondary amine, carboxylic and carbonyl groups of modified aminocarbonylmethylglycine are involved in complex formation. The strong peak at ~1100 cm^{-1} suggests the existence of sulfate ions.

The characteristic peaks of aminocarbonylmethylglycine were also observed for two silica gel based adsorbents, Si_1-AG and Si_2-AG.

Based on the neutralization titration results, the amount of carboxyl group on modified resin was estimated to be 2.87 mmol/g. The amount of amino group supported on the original resin was estimated to be 5.49 mmol/g, where an amine that is different from the reactive primary amine seemed to be contained. More than 52% of the effective amine of the original resin was modified with aminocarbonylmethylglycine group. Neutralization titration cannot be used as for silica gel-based adsorbents because silica gel has a poor chemical resistance, especially in alkali solution.

4-3-2 Effect of contact time

Figure 4-2 shows the kinetic behavior of the adsorption ratio of Sc and Ni on the novel adsorbents. Adsorption equilibrium of Ni was achieved at ~480 min for the commercial resin-based adsorbent PA-AG. For the silica-based adsorbents, Si_1-AG and Si_2-AG, equilibrium was reached within 60 min for Ni. PA-GA took longer to reach equilibrium because metal ion diffusion in the pores of styrenic macroporous resin is considered to affect the adsorption rate. The time to reach equilibrium for Sc was confirmed to be shorter than that for Ni in liquid-liquid extraction with D2EHAG having the same functional group as the adsorbent, the equilibrium for Sc was concluded to be attained. Henceforth, adsorption equilibrium was measured after shaking for 720 min.

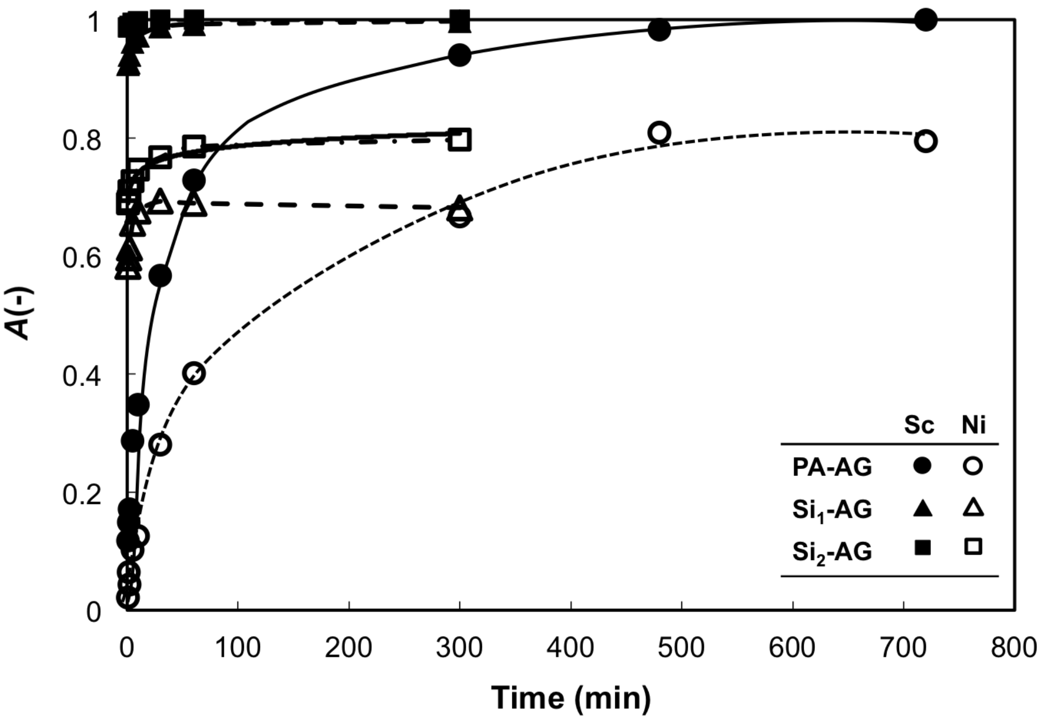


Figure 4-2 Effect of contact time on Sc and Ni adsorption onto adsorbents (adsorbents: 50 mg, aqueous phase: 5 mL, [M] = 10 mg/L, pH 3.0 after adsorption, $[SO_4^{2-}]$ = 0.1 mol/L)

4-3-3 Metal ion adsorption behavior

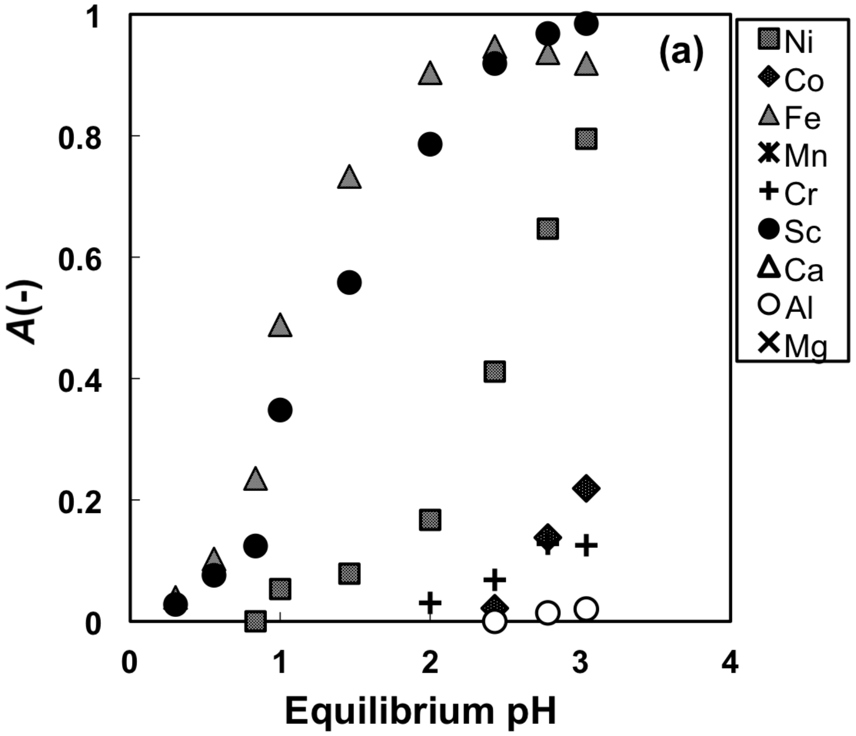
The adsorption behavior of metal ions from a sulfuric acid solution that contained Mg^{2+}, Al^{3+}, Ca^{2+}, Sc^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+} was examined. As shown in Figure 4-3(a), metal ion adsorption on the modified resin PA-AG was promoted with increasing pH of the feed aqueous solution. Sc^{3+} was adsorbed selectively from the other metal ions except for trivalent Fe^{3+}, and quantitative adsorption was achieved above pH > 2.5. Metal ion adsorption increased in the following order: $Fe^{3+} \geq Sc^{3+} > Ni^{2+} > Co^{2+} > Al^{3+}$ and the other metal ions. The FT-IR spectrum for the Sc-loaded resin in Figure 4-1(c) shows that the secondary amine, carboxylic and carbonyl groups are involved in Sc ion capture, which leads to a high in ion selectivity. Few metal ions were adsorbed on the original resin PA. These results suggest that the resin was modified with the metal affinity groups of D2EHAG. In liquid-liquid extraction with D2EHAG

[10], the extraction from nitric acid media was reported to proceed via the reaction as follows:

$$Sc^{3+} + 2(HR)_2 = ScR_3HR + 3H^+ \qquad (4\text{-}4)$$

The modified resin functioned as a cation exchanger by acid dissociation and metal ion adsorption was similar to that of liquid–liquid extraction with the extractant, D2EHAG [13,14], which contains the same functional group. As described later, Sc^{3+} forms complexes with sulfate ions such as $Sc(SO_4)^+$ and $Sc(SO_4)_2^-$. Considering the results described above, adsorption and desorption was though to proceed by the reaction of Sc^{3+} and also $Sc(SO_4)^+$ with aminocarbonylmethylglycine of the resin. The driving force is the proton dissociation and association of the carboxyl moiety in the functional group.

The separation of Sc^{3+} and Fe^{3+} seems to be difficult. The precipitation fractionation generates a sludge, which may cause to co-precipitate. The adsorption behavior of divalent Fe^{2+} was examined, where 10 mmol/L hydrazine was added to the feed solution that contains Fe^{2+} to avoid Fe^{2+} oxidation to Fe^{3+}. As shown in Figure 4-3(b), divalent Fe^{2+} was rarely extracted in the pH range where Sc^{3+} was extracted. Sc^{3+} separation from iron ions may be possible by reducing trivalent Fe^{3+} to divalent Fe^{2+}.


(a)
A(-)
Equilibrium pH
Ni
Co
Fe
Mn
Cr
Sc
Ca
Al
Mg
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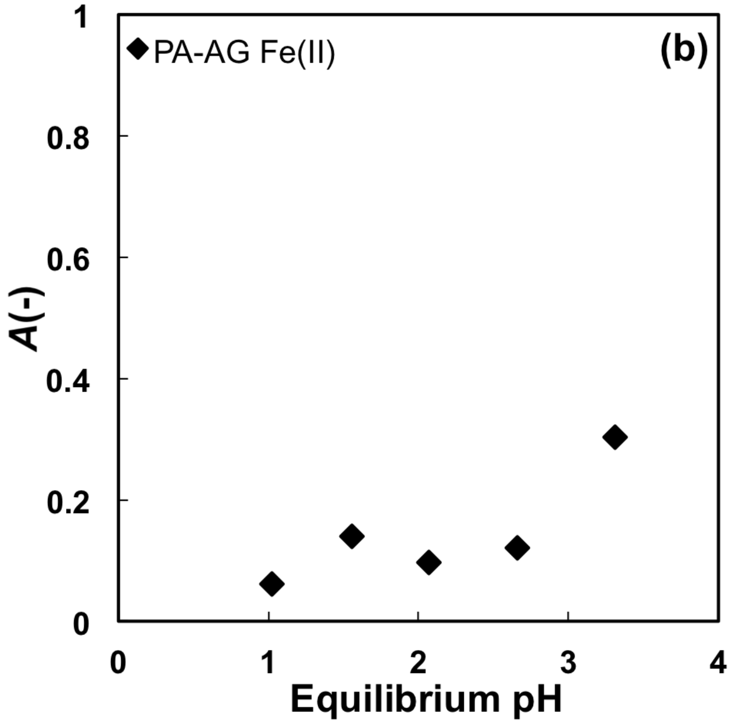
0.2
0.4
0.6
0.8
1
0
1
2
3
4


(b)
PA-AG Fe(II)
A(-)
Equilibrium pH
0
0.2
0.4
0.6
0.8
1
0
1
2
3
4

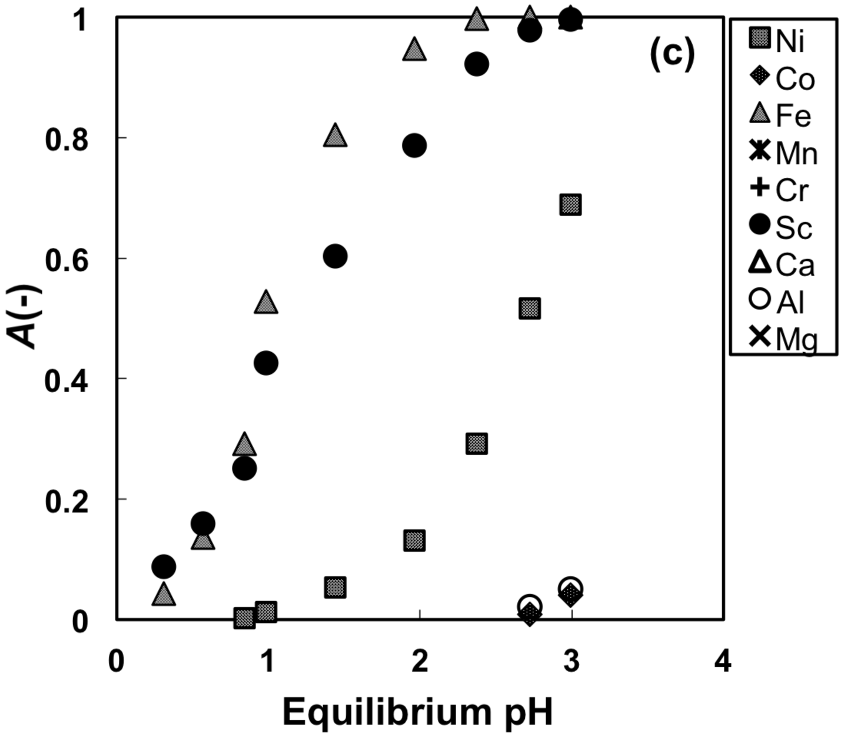


Figure 3 Adsorption behavior of various metal ions onto novel adsorbents PA-AG (a), adsorption of Fe(II) by PA-AG (b), Si_1-AG (c) (adsorbents: 50 mg, aqueous phase: 5 mL, [M] = 10 mg/L, $[SO_4^{2-}]$ = 0.1 mol/L, (b) $[N_2H_4]$ = 10 mmol/L was added)

The adsorption behavior observed was similar to that for Si_1-AG (Figure 4-3(c)) and Si_2-AG (data not shown). The adsorption performance of the latter adsorbent was higher compared with that of the former according to the amount of amine groups on the corresponding original silica gel. The performance was found to depend on the amount of reaction site amines, consequently the amount of the aminocarbonylmethylglycine groups, on the support material.

The effect of sulfate salt in aqueous solution on $Sc^{3+}$and Ni^{2+} adsorption was examined. As shown in Figure 4-4, the adsorption performance decreased with increase in sulfate salt concentration, because sulfate ions, which interact with metal ions in aqueous solution, increase accordingly. Sc^{3+} interacts strongly with sulfate ions compared with the other metal ions such as Ni^{2+} and Co^{2+}. (logarithmic stability constants of 1:1 and 1:2 complexes are 2.59, 4.97 for Sc and 1 (1:1) for Ni (*I*=0.5, 298 K), respectively [20]. According to the stability constants, the concentration ratio of cationic species, Sc^{3+} and $Sc(SO_4)^+$, is about 30%, at 0.1M sulfate ion concentration, however the anionic species $Sc(SO_4)_2^-$ occupy more than 90% of the total at 0.5mol/L sulfate ion concentration. For Ni, free Ni ion is predominant at lower sulfate ion concentration. The adsorption of Ni decreased extremely in a high sulfate concentration, due to the increase in the neutral species. A high selectivity for Sc could be obtained by choosing appropriate adsorption conditions.

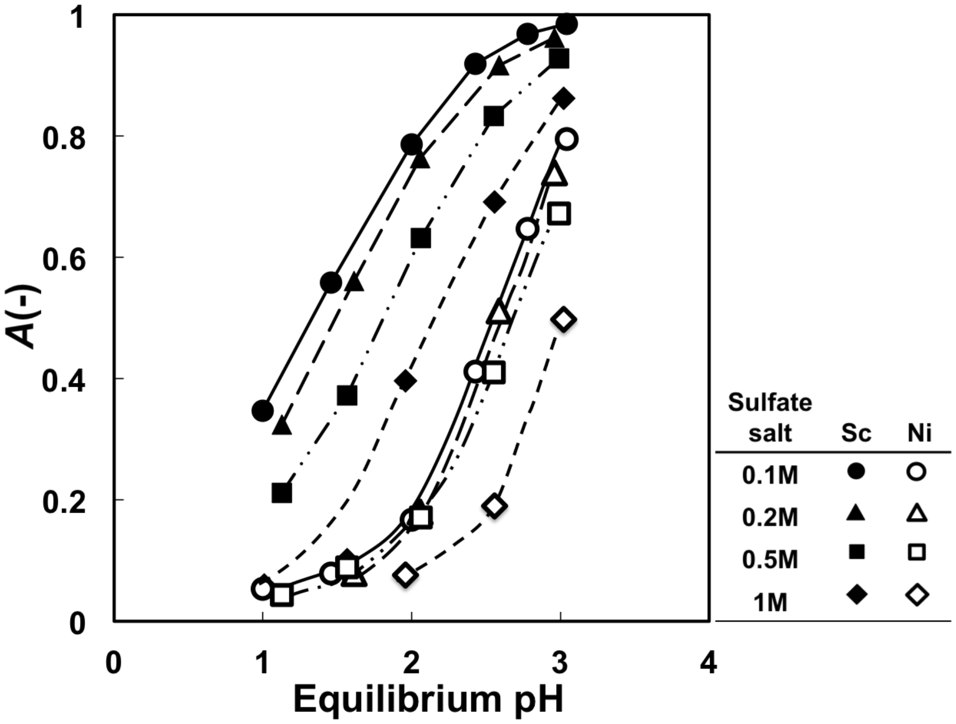


Figure 4-4 Effect of SO_4^{2-} concentration on metal ion adsorption on to PA-AG

(adsorbents: 50 mg, aqueous phase: 5 mL, [M] = 10 mg/L)

4-3-4 Scandium adsorption isotherm

A Sc adsorption isotherm was measured at 298 K by varying the initial concentration of Sc^{3+} at equilibrium pH 3. As shown in Figure 4-5, the adsorption capacity for Sc^{3+} at equilibrium, q_e (mg/g), increased with increase in equilibrium concentration of Sc^{3+} in aqueous solution to reach a constant value, which suggests a Langmuir-type adsorption. The value of the plateau region of the curve gives the maximum adsorption capacity, q_m (mg/g).

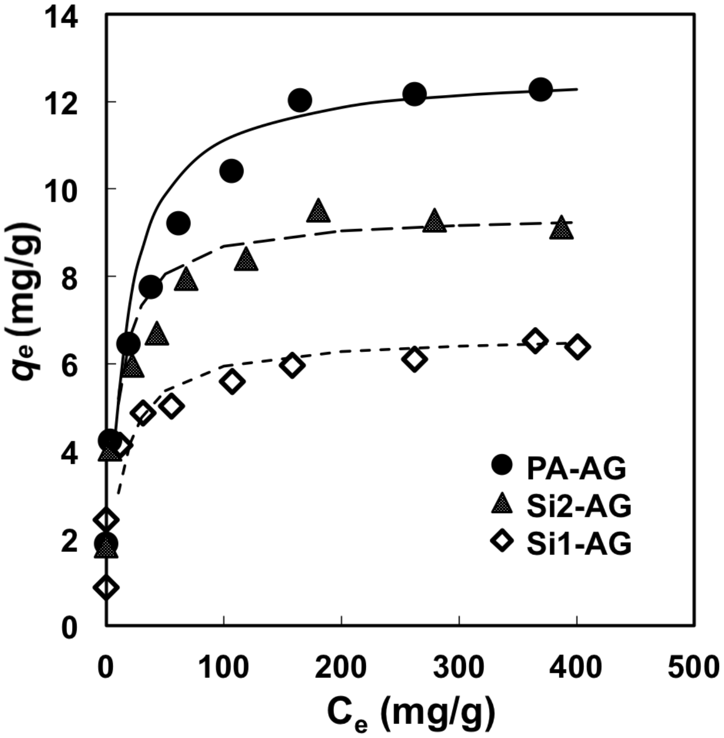


Figure 4-5 Adsorption isotherms of Sc on adsorbents

(adsorbents: 50 mg, aqueous phase: 5 mL, equilibrium pH 3, $[SO_4^{2-}]$ = 0.1 mol/L)

The Langmuir isotherm expressed by Eq. (4-5) is rewritten as Eq. (4-6):

$$q_e = K_L q_m C_e / (1 + K_L C_e) \tag{4-5}$$

$$C_e / q_e = (1/K_L\, q_m) + (1/q_m) C_e \tag{4-6}$$

where K_L is the adsorption equilibrium constant (L/mg). Subscript e denotes the equilibrium state. Langmuir plots based on Eq. (4-6) show straight lines for Sc on modified resins, and q_m and K_L were obtained from the plots listed in Table 4-1. The amount of aminocarbonylmethylglycine groups on the support material is thought to affect adsorption performance. The q_m values of other adsorbents recently developed was listed together in Table 4-1. These adsorbents required the higher pH of the feed solution in nitrate media, due to the pK_a of their functional groups, though they seem to show the adsorption performance as well or better compared to that of our resin base adsorbent in sulfate media.

Table 4-1 Langmuir constants (K_L) and adsorption capacities (q_m)a of novel adsorbents compared with q_m of other adsorbents.

Adsorbents	q_m (mg/g)	K_L (L/mg)	r^2
PA-AG	12.72 (0.28mmol/g)	0.069	0.996
Si_1-AG	6.65 (0.15mmol/g)	0.084	0.994
Si_2-AG	9.43 (0.21mmol/g)	0.117	0.997
Ion-imprinted PMAA[b]	12.8 (0.28mmol/g)	-	-
SOJR[c]	27.0 (0.60mmol/g)	-	-

a: pH 3, $[SO_4^{2-}]$=0.1 M.
b: pH 5, HNO_3 media, polymer particles synthesized by MMA(methacrylic acid), EGDMA(ethylene glycol dimethacrylate) and/Sc(III) ion-8-hydroxyquinoline[21]
c: pH 4, HNO3, saponified product of orange juice residue[22]
r^2: correlation coefficient.

4-3-5 Desorption and reuse of adsorbents

We carried out desorption experiments of Sc from adsorbents by washing with sulfuric acid. Figure 4-6 shows the effect of acidic concentration on Sc desorption behavior. The desorption ratio increases with increasing acidic concentration and quantitative Sc desorption was achieved with 1 mol/L H_2SO_4. The high desorption ratio from the adsorbent is attributed to protonation of the functional group with acids. The novel adsorbent works as a cation exchange resin. To examine the reusability of new adsorbent, five times adsorption–desorption tests were performed repeatedly under the same experimental conditions. As shown in Figure 4-7, no obvious decline in performance was observed in each time from the first to fifth adsorption test. Thus the adsorbent could be used in practical applications.

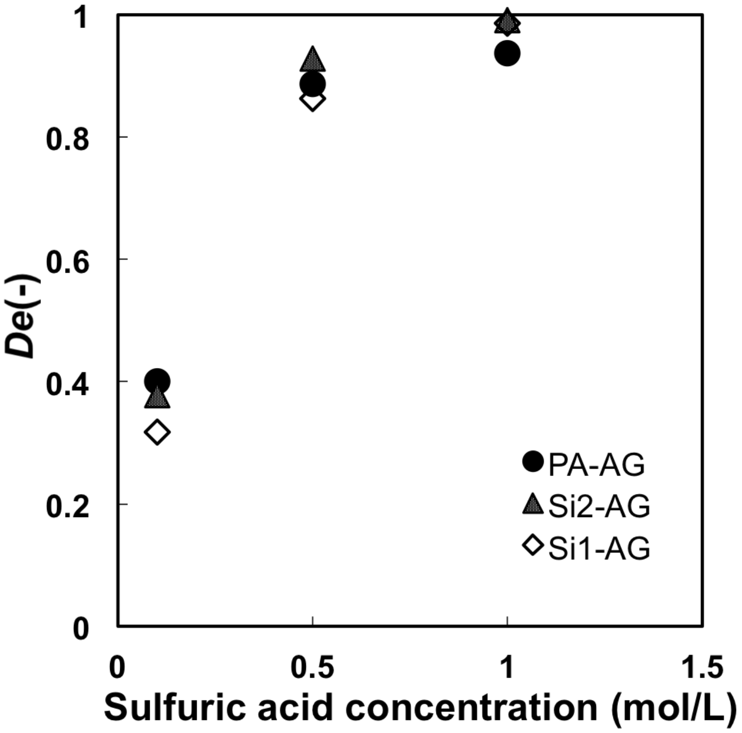


Figure 4-6 Desorption behavior of Sc from adsorbents

(Sc-loaded adsorbents: 30 mg, aqueous phase: 3 mL, H_2SO_4).

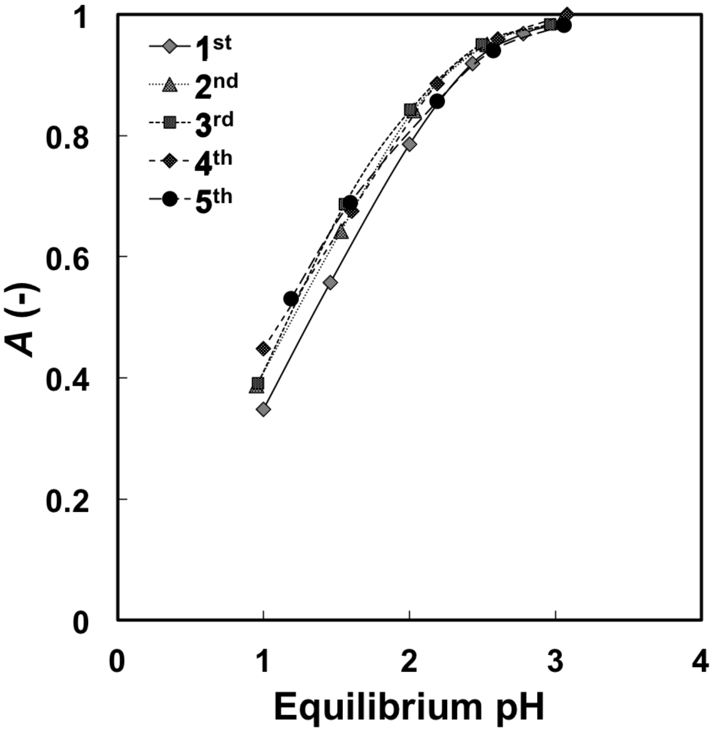


Figure 4-7 Recyclability of modified resin PA-AG for adsorption of Sc, PA-AG 50 mg

(aqueous phase: 5 mL, [M] = 10 mg/L, $[SO_4^{2-}]$ = 0.1 mol/L).

4-4 Conclusion

We have prepared a novel adsorbent, which was modified with an aminocarbonylmethylglycine functional group on a commercial styrenic resin PA. The modified adsorbents removed Sc selectively over the other transition metals such as Mg, Al, Ca, Sc, Cr, Mn, Co, Ni and Fe(II), by reducing Fe(III) to Fe(II) in sulfuric acid solution. Sc was desorbed readily from the adsorbents by using 1 mol/L H_2SO_4. The functional group immobilized on the support material served as an ion exchanger like the corresponding extractant, which has a high affinity for Sc. Adsorbent reuse was possible, and the potential use of the commercial resin-based adsorbent was demonstrated in terms of chemical resistance.

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Chapter 5 Conclusions

This thesis is aiming for the development of novel hydrometallurgical separation systems for the recovery of scandium. Three subjects to achieve the purpose were summarized as follows:

In Chapter 2, liquid-liquid extraction of REEs by using an β-diketone extractant 2-thenoyltrifluoroaceton (HTTA) and a neutral synergistic extractant tri-*n*-octylphosphine oxide (TOPO) was examined in *n*-dodecane (organic solvent) and [C_4mim][Tf_2N] (ionic liquid). In the organic solvent system, the addition of TOPO enhanced the extraction of all the REEs with HTTA. In the ionic liquid system, the selectivity for Sc against the other REEs was significantly improved. The difference in the extraction ability in the two solvent systems was explained by the extraction mechanism. The synergistic extractant system was applied to the recovery of Sc from other transition metals existing in the leaching solution of an ore. It was found that Sc could be selectively recovered from the other metal ions including Fe^{3+}.

In Chapter 3, novel functional ionic liquids (FILs) were synthesized with the three kinds of amic acid groups. The extraction behavior of metal ions (including Mg^{2+}, Al^{3+}, Ca^{2+}, Sc^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+}) with FILs was examined. The FIL bearing aminocarbonylmethylglycine of a high affinity for Sc could selectively extract Sc^{3+} from other transition metals including Fe^{3+}, from which separation was difficult with the aminocarbonylmethylglycine contained extractant D2EHAG.

In Chapter 4, novel adsorbents for Sc were prepared by introducing a functional group aminocarbonylmethylglycine of a high affinity for Sc onto organic resin and silica gels. The adsorption behavior of metal ions including Sc was examined, and it was proved that the resin based adsorbent could be used in the practical separation of Sc.

Overall, the effective hydrometallurgical separation systems for Sc have been developed based on the liquid-liquid extraction employing synergistic systems, new functional ionic liquid systems and solid-phase extraction with novel adsorbents.

List of abbreviation

E: extraction ratio
D: distribution ratio
S: stripping ratio
β: separation ratio
C: concentration
ex: extraction
M: metal
LLE: liquid-liquid extraction
init: initial state
eq: equilibrium state
aq: aqueous phase
org: organic phase
ILs: ionic liquid phase
strip: stripping phase
SPE: solid-phase extraction
LME: liquid-membrane extraction

REEs: rare earth elements
Sc: scandium
Y: yttrium
La: lanthanum
Ce: cerium
Pr: praseodymium
Nd: neodymium
Pm: promethium
Sm: samarium
Eu: europium
Gd: gadolinium
Tb: terbium
Dy: dysprosium
Ho: holmium
Er: erbium
Tm: thulium
Yb: ytterbium
Lu: lutetium

TRILs: room temperature ionic liquids
TSILs: task-specific ionic liquids
FILs: functional ionic liquids
ILs: ionic liquids
C_4mim: 1-butyl-3-methylimidazolium
C_6mim: 1-hexyl-3-methylimidazolium
HNO_3: nitric acid
HCl: hydrochloric acid
HNA: Nialidixic acid
BF_4: tetrafluoroborate
PF_6: hexafluorophosphate
OTf: trifluoromethylsulfonate
NTf_2: bis[(trifluoromethyl)sulfonyl]imide
mpy: 4-methylpyridinium
C_8mim: 1-octyl-3-methylimidazolium
H_2SO_4: sulfuric acid
$HClO_4$: perchloric acid

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