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Toward Greener Separations of Rare Earths: Bifunctional Ionic Liquid Extractants in Biodiesel

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Ionic liquids (ILs) containing quaternary phosphonium cations and phosphonic acid anions were explored as novel extractants for rare earths (RE) separation. They were considered to be bifunctional ionic liquid extractants (bif-ILEs), since both cations and anions of ILs were involved in the extraction. Trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate (Cyphos IL 104), as a bif-ILE, together with propylene carbonate (PC), dimethyl carbonate (DMC), and soybean oil methyl ester (SBME, biodiesel) as diluents was employed in the extraction of RE(III) from aqueous solutions. Acidified Cyphos IL 104 (HNO_3-Cyphos IL 104) exhibited high solubility in three diluents, and higher extraction efficiency than bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) because of the coextraction of RE(III) by quaternary phosphonium cation and phosphonic acid anion in organic phase. Additionally, this coextraction mechanism could eliminate the loss of IL. The physical properties and miscibility test results indicated that SBME was an excellent solvent for RE(III) extraction. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2338–2346, 2010

Keywords: extraction, ionic liquid, Cyphos IL 104, rare earths, soybean oil methyl ester

Introduction

Replacement of conventional solvents with green solvents has been widely studied in organic synthesis, catalysis, electrochemistry, and solvent extraction.[1,2] ILs are generally considered as green solvents due to their high-thermal stability, very low flammability, and negligible vapor pressure.[3–6] The ionic nature of ILs results in a variety of extraction mechanisms, including solvent ion-pair extraction, ion exchange, and simultaneous combinations of these.[7,8] In most articles, hydrophobic ILs with imidazolium cation are frequently used as diluent in solvent extraction systems.[9–11] Dietz et al. reported that, with the cation exchange mechanism, the increase of Sr(II) extraction was accompanied by increasing solubilization of IL in the aqueous phase, as the strontium-crown ether complex ($Sr{\cdot}CE^{2+}$) was exchanged for $C_n mim^+$.[12] Another example was using 2-thenoyl trifluoroacetone/$C_4mim^+Tf_2N^-$ system for Lanthanide(III) extraction. Lanthanide complexes in $C_4mim^+Tf_2N^-$ were formed by the exchange of the IL anions into the aqueous phase.[13] Ion exchange extraction systems accompanied by loss of the IL components to the aqueous phase poses a significant problem

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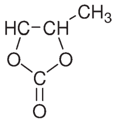
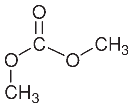
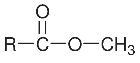
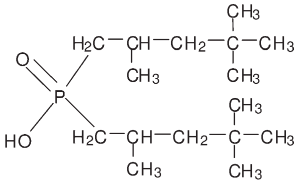
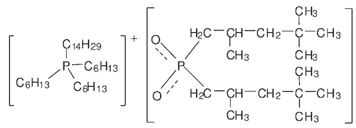
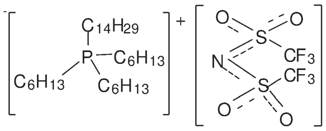
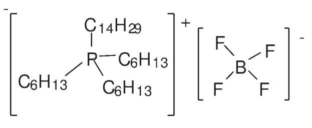
Table 1. Chemical Structures of Solvents Used in this Study

			
propylene carbonate (PC)	dimethyl carbonate (DMC)	soybean oil methyl ester (SBME)	bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272)
			
trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate (Cyphos IL104)	tetradecyl(trihexyl) phosphonium bistriflamide (Cyphos IL109)	tetradecyl(trihexyl)phosphonium tetrafluoroborate (Cyphos IL111)	
$P_{6,6,6,14}{}^{+}PO_2R_2^{-}$ (R = $CH_2CH(CH_3)CH_2C(CH_3)_3$)	$P_{6,6,6,14}{}^{+}N(CF_3SO_2)_2^{-}$	$P_{6,6,6,14}{}^{+}BF_4^{-}$	

in potential applications of ILs in liquid/liquid extraction, both from a cost and environmental perspective.[14] Phosphonium ILs have been used as effective extractants for the removal of organic acids and metal ions.[15–19] In these studies, phosphonium ILs containing simple anions, such as Cl^- or NO_3^- were used to extract metal ions by anion exchange mechanism, which was analogous to the extraction with quaternary ammonium salts. Solvent extraction of $PdCl_4^{2-}$ and $ZnCl_4^{2-}$ with tetradecyl(trihexyl)phosphonium chloride (Cyphos IL 101) by an ion-exchange mechanism was studied by Cieszyńska et al. and Regel-Rosocka et al.[20,21] Trihexyl (tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate (Cyphos IL 104) has recently been explored as an effective extractant for lactic acid.[15] To date, there are no reports on the use of Cyphos IL 104 in metal extraction systems.

It is important to select a suitable phosphonium ILs diluent for obtaining an optimum extraction process. In recent years, more and more constraining environmental regulations have been adopted to limit the use of industrial solvents responsible for volatile organic compounds (VOCs) emission and greenhouse gas production.[22] Biodiesel has the potential to dramatically reduce the amount of environmentally-polluting VOCs released to the atmosphere.[23] It is an excellent solvent for its high biodegradability, low toxicity, and low-vapor pressure, hence, many environmental and safety problems associated with organic solvents are avoided. Recently, biodiesel has been used in a wide range of food, pharmaceutical, and cosmetic industries,[24–26] more importantly, it can be used as a replacement or additive to mineral diesel.[27] Biodiesel can be manufactured from any product containing fatty acids, such as vegetable oil or animal fats.[28–30] Biodiesel produced by the transesterification of soybean oil and methanol in the presence of alkaline catalyst is better known as soybean oil methyl ester (SBME).

We herein report the separation of RE(III) with phosphonium ILs and three green organic solvents system using the principles of green chemistry as a guide. Compared to Cyphos IL 104, tetradecyl(trihexyl) phosphonium bistriflamide (Cyphos IL 109), tetradecyl(trihexyl)phosphonium tetrafluoroborate (Cyphos IL 111), and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272), HNO_3-Cyphos IL 104 is the most effective extractant for the separation of Y(III) from heavy rare earths (HRE(III)). The cation and anion of HNO_3-Cyphos IL 104 form complexes with RE(III) via a coordinating mechanism. HNO_3-Cyphos IL 104 acts as the bifunctional ionic liquid extractant (bif-ILE) in the extraction reaction. The high-separation factors suggest HNO_3-Cyphos IL 104/SBME system would be of practical value in the separation of Y(III) from HRE(III).

Experimental

Chemicals

The Cyphos IL 104 (>95.0%), Cyphos IL 109 (>97.0%), Cyphos IL 111 (>97.0%), and Cyanex 272 (>85.0%) were kindly supplied by the Cytec Canada, Inc. (Table 1). Dimethyl carbonate (>99.0%) and propylene carbonate were purchased from Acros and Aldrich. All other chemicals used were of analytical grade (Beijing Beihua Fine Chemicals Co., Ltd.). Stock solutions of trivalent rare earth ions were prepared by dissolving RE_2O_3 (>99.9%) in nitric acid. Deionized water was used in the preparation of SBME, HNO_3 acidified Cyphos IL 104 and all solutions.

Preparation of soybean oil methyl ester (SBME)

Soybean oil (300 mL) was taken into a flask together with the mixture of 81 mL of absolute methanol and 2.7 g of NaOH and stirred for 50 min at 50°C. After cooling down to room-temperature, the upper layer was separated from the lower layer and washed thoroughly with deionized water. The sample was then purified by vacuum distillation which yielded a pale yellow oil.[28] A Karl Fisher titration showed that product contained 0.0983% w/w water.

Nitric acid modification of Cyphos IL 104

Cyphos IL 104 (19.4 mmol) was mixed with HNO_3 at the molar ratios of 1:1, 1:2, 1:3, 1:4, 1:5, and 1:6, respectively,

Table 2. The Formation of HNO_3 Acidified Cyphos IL 104

$n_{IL\text{-}104}$ mmol	C_{HNO_3}[a] (mol L^{-1})	V_{HNO_3}[b] (mL)	n_{HNO_3}[c] (mmol)	$n_{HNO_3} : n_{IL\text{-}104}$
19.4	3.233	6.0	17.5	0.9:1
19.4	3.233	12.0	34.9	1.8:1
19.4	3.233	18.0	48.5	2.5:1
19.4	3.233	24.0	58.2	3.0:1
19.4	3.233	30.0	77.6	4.0:1
19.4	3.233	36.0	77.6	4.0:1

[a] Concentration of nitric acid used for the acidification of Cyphos IL 104.
[b] Volume of nitric acid used for the acidification of Cyphos IL 104.
[c] Acid content in HNO_3 acidified Cyphos IL 104 was determined by titration in ethanol media of the organic phase with phenolphthalein as indicator.

and the mixture was shaken for 30 min at room-temperature. The aqueous solution was removed after shaking and centrifugation. After acidification, it was repeatedly washed with deionized water. The sample was dried in a vacuum at 70°C for 24 h. A clear pale yellow liquid was obtained. Acid content in HNO_3 acidified Cyphos IL 104 was determined by titration in ethanol media of the organic phase with phenolphthalein as indicator (Table 2).

Methods

All electrospray ionisation-mass spectrometric (ESI-MS) measurements were performed by a Finnigan MAT LCQ ion trap mass spectrometer (San Jose, CA, USA) equipped with a Finnigan electrospray source and capable of analyzing ions up to *m*/*z* 2000. Viscosity measurements were performed with a rotational viscometer (Model NDJ-7, Shanghai Balance Instrument Factory, China). The water content was determined using a Karl Fisher titration (Model WA-1C, Jiangsu-Jiangfen Electroanalytical Instrument Co., Ltd., China.).

The miscibility test between phosphonium ILs and organic solvents was performed by shaking sealed glass tubes containing a mixture of 1 g phosphonium IL and 1 mL organic solvent for 30 min. The glass tube was then placed in a temperature-controlled water tank at 25°C, and then inspected visually for an interface. The systems that appeared as a clear, homogeneous phase without any visible interface, turbid suspension were considered as miscible system. For the scope of this work, other systems were considered as partially miscible system, in that they usually exhibited two phases with an obvious interface. The phase separations were usually complete within a few minutes. The results of all miscibility tests are shown in Table 3.

In the equilibrium experiments, 1 mL of organic phase containing various concentrations of Cyphos ILs with 5 mL aqueous solutions were placed in equilibrium tubes and shaken mechanically for 40 min to ensure complete equilibration at 25 ± 1°C. Sodium nitrate was added to avoid any third-phase formation. The concentration of sodium nitrate in the test solution varied from 0.05 to 0.60 mol L^{-1}.

Table 3. Miscibility Test Between Cyphos ILs and Organic Solvents at 25°C[a]

ILs	SBME	PC	DMC
Cyphos IL 104	M	PM	PM
HNO_3-Cyphos IL 104	M	M	M
Cyphos IL 109	M	M	M
Cyphos IL 111	M	M	M

[a] 1 g Cyphos IL 104, HNO_3-Cyphos IL 104, Cyphos IL 109 or Cyphos IL 111 was mixed with 1 mL solvents. 'M' indicates miscible and 'PM' indicates partially miscible.

After phase separation, the concentration of RE(III) in the aqueous phase was determined by volume titration using EDTA.[31] The extraction efficiency (*E*) was calculated by

$$E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e represent the initial and final concentrations of metal ions in aqueous phase.The distribution ratio (*D*) was defined as follows

$$D = \frac{C_0 - C_e}{C_e} \times \frac{volume\ of\ aqueous\ phase}{volume\ of\ organic\ phase} \tag{2}$$

Experimental results, done in duplicate, agree within 5% of their mean.

Results and Discussion

Acidification of Cyphos IL 104

Significantly improved RE(III) extraction efficiency can be well obtained simply by acidifying the Cyphos IL 104 with HNO_3. The acidification of Cyphos IL 104 was studied under different ratios of Cyphos IL 104 to HNO_3. Table 2 indicated that the saturated HNO_3 acidified Cyphos IL 104 was formed with a HNO_3: Cyphos IL 104 complex ratio of 4:1. 30 mL of HNO_3 (3.233 mol L^{-1}) acidified Cyphos IL 104 (abbreviated as HNO_3-Cyphos IL 104) with the form of $(P_{6,6,6,14}{}^{+}PO_2R_2^{-})\cdot(HNO_3)_4$ was used for the following study. There was no water found in HNO_3-Cyphos IL 104, as measured by Karl Fisher titration.

We have compared the extraction capacities of HNO_3-Cyphos IL 104 and unacidified Cyphos IL 104 for Y(III). The extraction experiments showed that HNO_3-Cyphos IL 104 was more suitable for the extraction of Y(III) than Cyphos IL 104. The Cyphos IL 104 was weak alkaline and induced the deposition of yttrium in the aqueous phase. So white sediment appeared in the remanent solutions at higher pH values (pH>1.8) with 0.1 mol L^{-1} unacidified Cyphos IL 104 in SBME. In the following extraction experiments, Y(III) solutions at pH values lower than 1.8 were used in Cyphos IL 104/SBME system. As for HNO_3-Cyphos IL 104, the maximum extraction was obtained at pH 5.6, and there

Table 4. Comparison Results of Cyphos IL 104, HNO_3-Cyphos IL 104 and Cyanex 272 for Y(III) extraction ($[Y^{3+}]$ = 0.201 mmol L^{-1}, C_{NaNO_3} = 0.1 mol L^{-1})

Organic phase	C[a] (mol L^{-1})	pH_0	$E_{Y^{3+}}$ %	*D*
Cyphos IL 104 in SBME	0.02	1.6	6.5	0.3
	0.05	1.6	14.8	0.9
	0.10	1.6	34.0	2.6
HNO_3-Cyphos IL 104 in SBME	0.02	5.6	83.0	24.5
	0.05	5.6	99.1	525.4
	0.10	5.6	99.5	1055.8
Cyanex 272 in SBME	0.02	2.7	1.2	0.1
	0.05	2.7	19.7	1.2
	0.10	2.7	63.9	8.8

[a] The concentration of Cyphos IL 104, HNO_3-Cyphos IL 104 or Cyanex 272 in SBME.

Table 5. Effect of the Diluent on the Percentage Extraction of 0.201 mmol L^{-1} Y(III)

	$E_{Y^{3+}}$ %			
Diluents	Cyphos IL 104[a]	HNO_3-Cyphos IL 104[b]	Cyphos IL 109[c]	Cyphos IL 111[c]
SBME	34.0	99.5	51.6	40.1
PC	–	99.6	59.3	55.4
DMC	–	99.2	52.7	48.3

[a] Conditions: 0.10 mol L^{-1} Cyphos IL104 in diluents, $C_{NaNO_3} = 0.1$ mol L^{-1}, $pH_0 = 1.6$.
[b] Conditions: 0.10 mol L^{-1} HNO_3-Cyphos IL104 in diluents, $C_{NaNO_3} = 0.1$ mol L^{-1}, $pH_0 = 5.6$.
[c] Conditions: 0.25 mol L^{-1} Cyphos IL109 or Cyphos IL111 in diluents, $C_{NaNO_3} = 0.1$ mol L^{-1} $pH_0 = 5.6$.

was no white precipitate formed in the solution. The extraction capability of Y(III) with Cyphos IL 104 and HNO_3-Cyphos IL 104 were studied at their optimum individual pH and the results are listed in Table 4. The extraction efficiencies of HNO_3-Cyphos IL 104 and Cyphos IL 104 were 83.0–99.5% and 6.5–34.0% at different phosphonium ILs concentrations, respectively. It was found that the extraction capacity of Cyphos IL 104 for Y(III) from nitrate solution could be enhanced significantly due to the nitric acid acidification.

Extraction of Y(III) in different diluents

As we know, phosphonium ILs are based on relatively large alkyl quaternary phosphonium cations, and therefore, tend to have high viscosities due to their large molecular weights.[32] Phosphonium ILs need to be diluted with an appropriate solvent in order to reduce viscosity. Three solvents namely propylene carbonate (PC), dimethyl carbonate (DMC), and SBME were selected to observe any changes in the extraction of Y(III) with varying diluents (Table 5). Some of these physical properties of the diluents are shown in Table 6.[33–35] The physical properties of diluents such as density, viscosity, and surface tension are responsible for a good and fast phase separation. In addition, a diluent with no or low volatile at room-temperature and high-boiling point is preferred.[36] HNO_3-Cyphos IL 104 and diluents PC, DMC or SBME are miscible in all proportions. The viscosity of three dilutents is low, resulting in a fast and obvious phase separation at room-temperature. The solubility of the organic solvent in water is one of the most important parameters, which should be as low as possible. PC and DMC have solubilities in water of 17.5 and 13.9 wt %, respectively. The concentration of phosphonium IL has become very high because of the loss of diluent to the aqueous phase during the extraction. That is why the extraction efficiencies of Y(III) using PC and DMC were slightly higher than using SBME. SBME with a boiling point of 366°C at 760 mmHg

Table 6. Physical Properties of PC, DMC and SBME Used in this Study

Solvent	Density (g cm^{-3}) 25°C	Viscosity (mPa·s) 25°C	Boiling point (°C)	Vapor pressure (mm of Hg at 20°C)	Solubility in water	Ref.
SBME	0.880	1.400	366	<2	–	33
PC	1.200	2.512	240	0.03	17.5%	34,35
DMC	0.861	0.409	90	42	13.9%	34,35

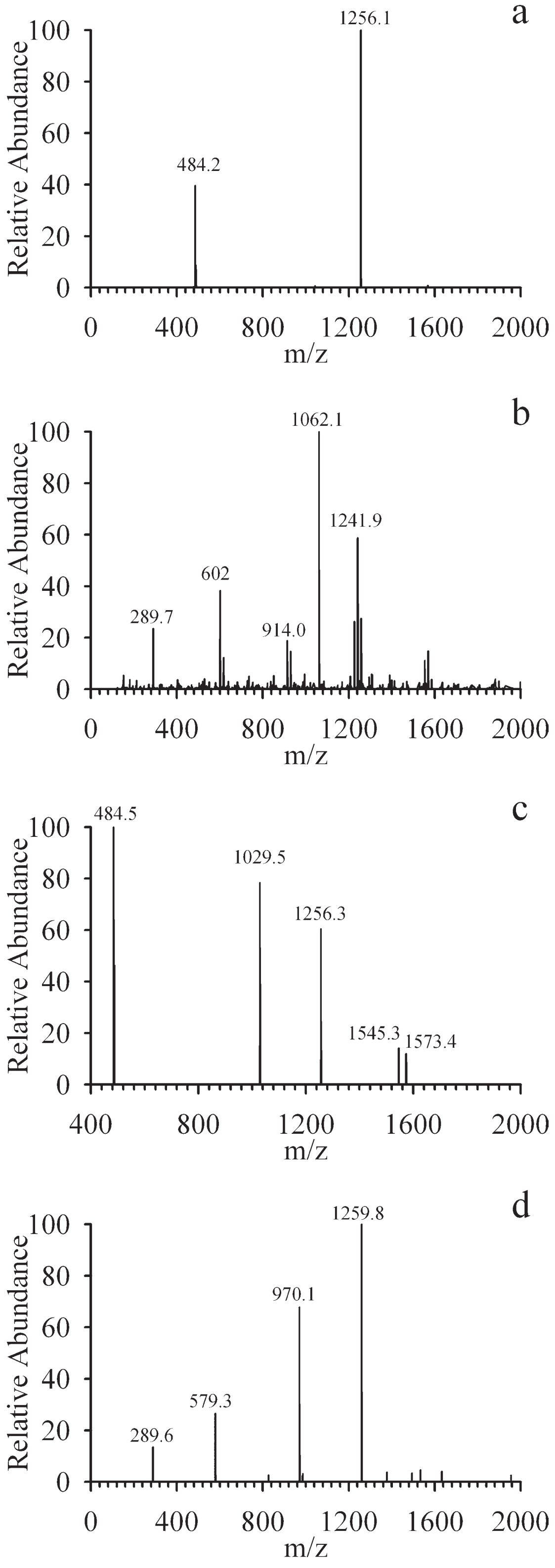


Figure 1. ESI positive (a, c), and negative (b, d) ion mass spectrum of Cyphos IL 104 (a, b), and HNO_3-Cyphos IL 104 (c, d).

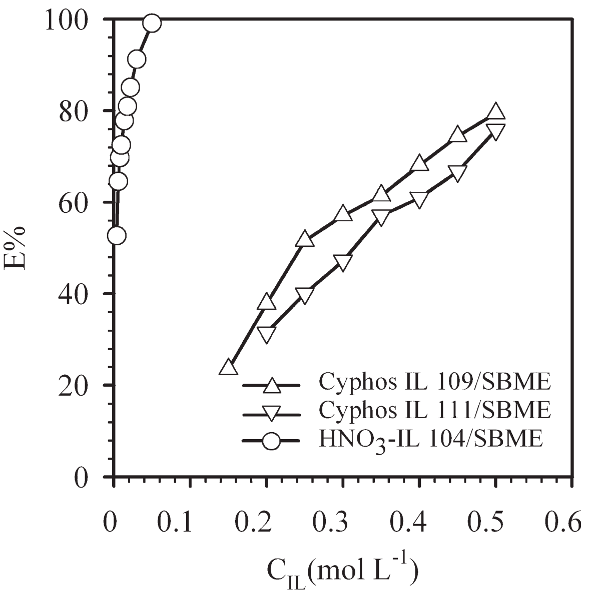


Figure 2. Effect of IL anions on the extraction of Y(III).

($C_{NaNO3} = 0.1$ mol L^{-1}, $pH_0 = 5.6$).

is insoluble in water.[24] As a kind of recycling and green-clean solvent, SBME was preferred as the best diluent for the extraction of RE(III), hence many environmental and safety problems associated with organic solvents could be avoided.

Extraction of Y(III) with a bif-ILE

ESI-MS was employed for the analysis of Cyphos IL 104 and HNO_3-Cyphos IL 104 (Figure 1). The positive mode of HNO_3-Cyphos IL 104 showed major m/z peaks at 484.5 and 1029.5 (Figure 1c). The first peak corresponded to the single cation $P_{6,6,6,14}{}^+$, and the second one to the aggregate of two cations and one nitrate ion, $[(P_{6,6,6,14})_2NO_3]^+$. The peaks of the ion $PO_2R_2^-$ (m/z 289.6), and its deprotonated ion $[H(PO_2R_2)_2]^-$ (m/z 579.3) were obserbed in the negative mode (Figure 1d). Therefore, we concluded that both the dimer of the cation and the anion existed in HNO_3-Cyphos IL 104.

Cyanex 272 is a widely used metal extractant, which is a protonated form of the Cyphos IL104 anion.[37] The extraction of Y(III) with HNO_3-Cyphos IL 104 and Cyanex 272 was performed at their individual optimum pH (Table 4). HNO_3-Cyphos IL 104 was more efficient than Cyanex 272, indicating that not only the anion, but also the cation was involved in the extraction.

Acidified Cyphos IL 109 and Cyphos IL 111 cannot be used for the extraction of Y(III), as we found that their extraction efficiencies were significantly lower compared to the Cyphos IL 109 and 111. As discussed earlier, Cyphos IL 104 was not suitable for the effective extraction of Y(III) from aqueous solution. HNO_3-Cyphos IL 104, Cyphos IL 109 and Cyphos IL 111 were selected to study the effect of IL anions on the extraction of metal ions from aqueous solutions (Figure 2). For Cyphos IL 109 and Cyphos IL 111, the dominant mechanism was proposed to be the anion exchange. The ion-pair formed between quaternary phosphonium cation and the anionic complex of Y^{3+} and NO_3^- suggested that the quaternary phosphonium cation was involved in the extraction. HNO_3-Cyphos IL 104 had the best extraction capacity of 91.2% at 0.01 mol L^{-1}, whereas the extraction efficiencies of ILs with anions BF_4^- and Tf_2N^- were lower. This result demonstrated that the extraction of HNO_3-Cyphos IL 104 was extremely dependent on the coextraction of Y(III) with cation and anion. The mechanism of Y(III) extraction showed quite different due to the different structures of three phosphonium ILs. The HNO_3-Cyphos IL 104 could be considered to be a bif-ILE, because both cation and anion were involved in the extraction.

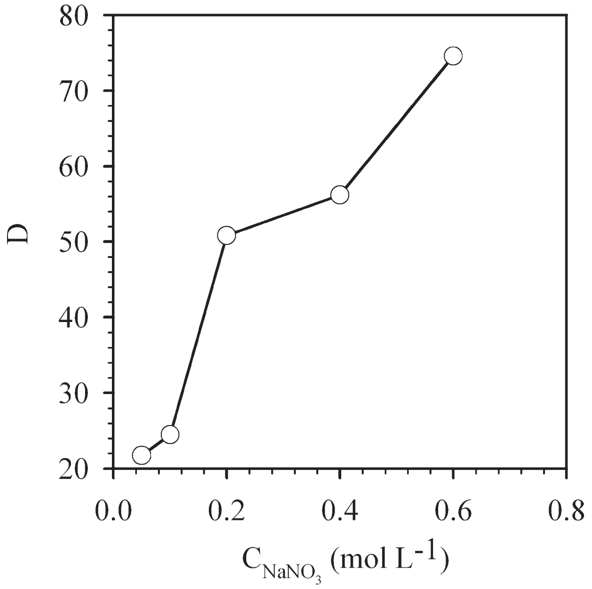


Figure 3. Effect of sodium nitrate concentration on the distribution ratio of Y(III).

($[Y^{3+}] = 0.201$ mmol L^{-1}, $pH_0 = 5.6$, 0.02 mol L^{-1} HNO_3-Cyphos IL 104 in SBME).

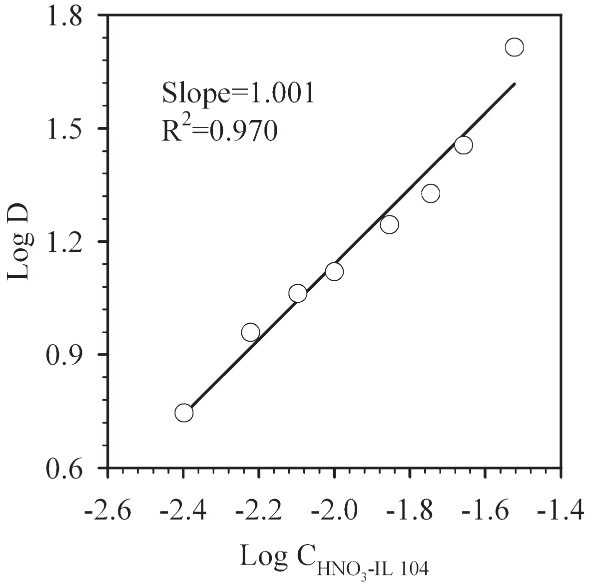


Figure 4. Slop analysis of Y(III) extraction as a function of the concentration of HNO_3-Cyphos IL 104 in SBME.

($[Y^{3+}] = 0.201$ mmol L^{-1}, $C_{NaNO3} = 0.1$ mol L^{-1}, $pH_0 = 5.6$).

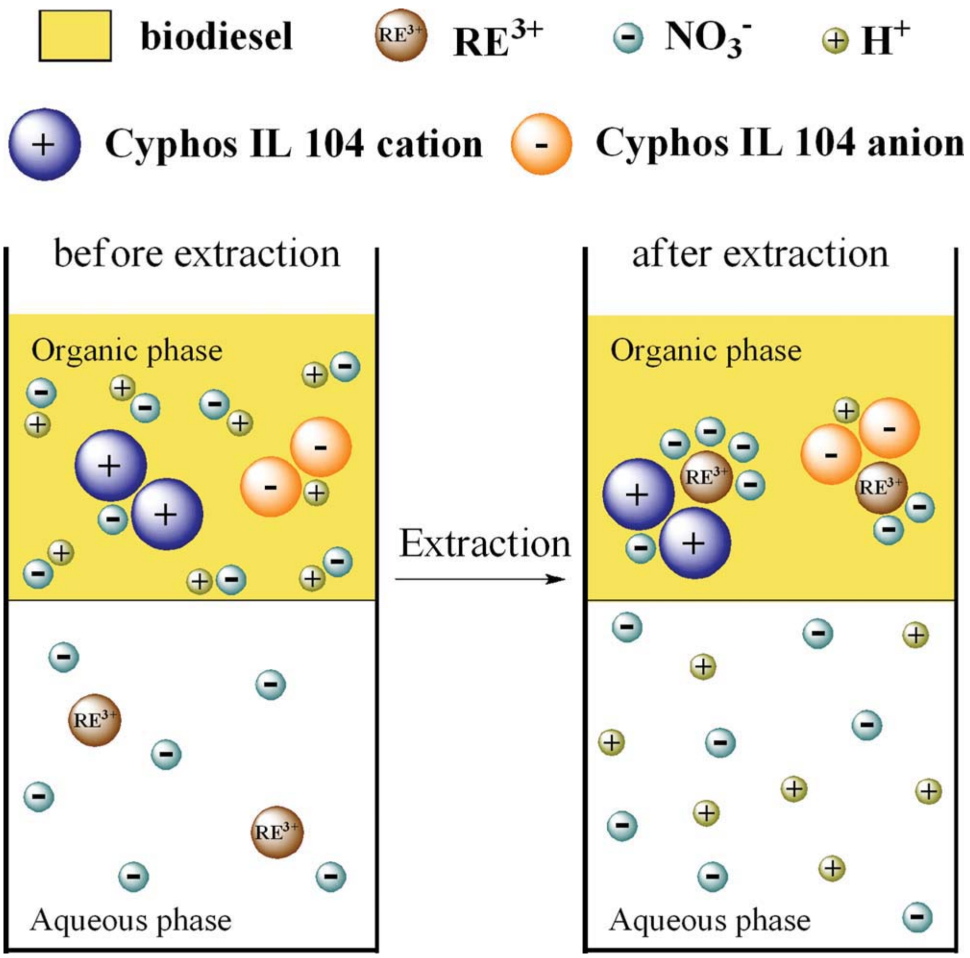


Figure 5. Schematic illustrating the extraction mechanism of RE(III) by bif-ILE.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

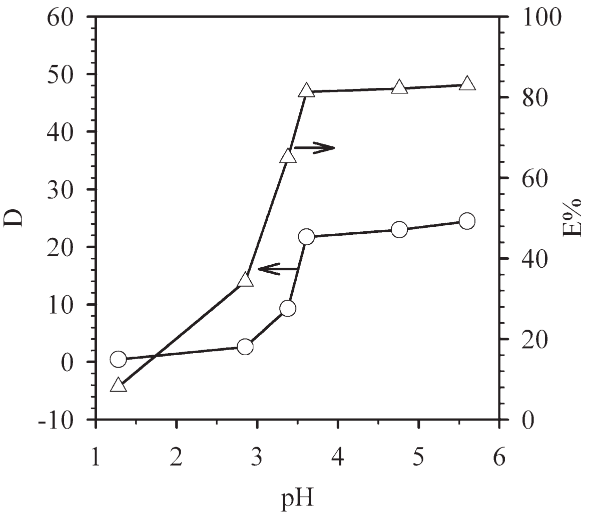


Figure 6. Effect of initial pH on the extraction of 0.201 mmol L^{-1} Y(III) by 0.02 mol L^{-1} HNO$_3$-Cyphos IL 104 in SBME.

(C_{NaNO3} = 0.1 mol L^{-1}).

Meanwhile, nitrate ions in HNO_3 acidified Cyphos IL 104 played a key role in the extraction reaction. The effect of sodium nitrate concentration in aqueous phase was studied in the concentration range of 0.05–0.60 mol L^{-1} with 0.02 mol L^{-1} HNO_3-Cyphos IL 104/SBME. As shown in Figure 3, the distribution ratio greatly increased with the increase of sodium nitrate concentration. Nitrate ions in HNO_3-Cyphos IL 104 was expected to alter the coordination environment of Y(III). They were coordinated to the metals and form complexes with Y(III). Nitrate ions in the aqueous phase may facilitate the formation of complexes and significantly increase the distribution ratios of Y(III). High-water solubility of the studied phosphonium ILs would lead to the formation of reverse micelles.[16] Sodium nitrate can avoid the

Table 7. Stripping of Y(III) with 0.02 mol L^{-1} EDTA after extraction with 0.1 mol L^{-1} HNO_3-Cyphos IL 104 in SBME ($[Y^{3+}]$ = 0.201 mmol L^{-1}, C_{NaNO_3} = 0.1 mol L^{-1})

Extraction cycles	$[Y^{3+}]$ (mmol L^{-1})			
	Initial	Final	$E_{Y^{3+}}$ %	*D*
1	0.201	0.00095	99.5	1055.8
2	0.201	0.00157	99.2	633.0
3	0.201	0.00182	99.1	546.0

Table 8. Separation factors (β)[a] between RE(III)

RE_1/RE_2	Y/Gd	Y/Tb	Y/Dy	Y/Ho	Er/Y	Tm/Y	Yb/Y	Lu/Y
β^b	6.17	8.57	40.81	14.55	1.83	2.06	10.92	4.60
β^c	–	–	–	1.36	1.75	6.54	6.82	7.96

[a] β is the ratio of distribution (D) of two metals measured under the same condition.

[b] Conditions: 0.02 mol L^{-1} HNO_3-Cyphos IL 104 in SBME at $pH_0 = 3.6$, [RE(III)] = 0.201 mmol L^{-1}.

[c] Studied by Sun et al.,[42] conditions: 0.04 mol L^{-1} Cyanex 272 in *n*-heptane at $pH_0 = 2.7$, [RE(III)] = 5.038 mmol L^{-1}.

third-phase formation in phosphonium ILs extraction systems as a result of interaction between reverse micelles.

For exploring the extraction mechanism by HNO_3-Cyphos IL 104, the conventional slope analysis method was adopted. As shown in Figure 4, plot of log D vs. log [HNO_3-Cyphos IL 104] produced a straight line with a slope of 1.001 for Y(III). This could be explained by the coexistence of cation and anion complexes with Y(III).[38] Figure 5 illustrates the extraction mechanism of RE(III) by HNO_3-Cyphos IL 104. As disscussed earlier, the cation and anion of HNO_3-Cyphos IL 104 existed as $[(P_{6,6,6,14})_2NO_3]^+$ and $[H(PO_2R_2)_2]^-$. Both of them were involved in the RE(III) extraction.

The influence of initial pH value on the extraction of Y(III) with HNO_3-Cyphos IL 104 in SBME was studied in the pH range from 1.3–5.6 (Figure 6). The extraction percentage increased sharply with the increase of pH and reached a platform at pH larger than 3.6. At high acidity, there was relatively little extraction of Y(III) which might be due to the fact that the high concentration of H^+ can inhibit the formation of complexes.

The toxicity of phosphonium ILs was important to the green separation of RE(III). Stock et al. reported nonhalide phosphonium salts containing bulky cations were relatively benign as compared to pyridinium or imidazolium salts.[39] The contamination of the aqueous phase by components of ILs was a serious problem that limited the application of ILs in solvent extraction.[12,14] This problem had not occurred in our study due to the the hydrophobicity of this bif-ILE, and its high utility and recycle of both cation and anion.

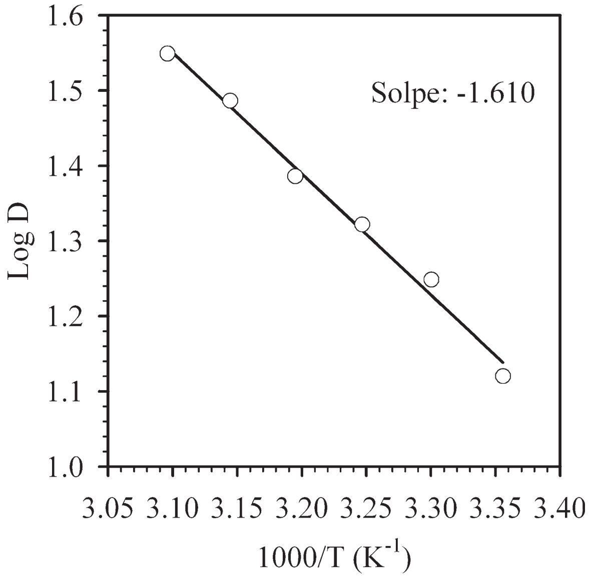


Figure 7. Effect of experimental temperature on the extraction of Y(III) with HNO_3-IL 104.

($C_{HNO_3\text{-IL 104/SBME}} = 0.01$ mol L^{-1}, $C_{Y(III)} = 0.201$ mmol L^{-1}, $C_{NaNO_3} = 0.1$ mol L^{-1}).

Stripping of metal ions and the reuse of Cyphos IL 104 were also studied. The stripping agent used in this investigation was EDTA (0.02 mol L^{-1}, 5 mL). Organic phase loaded with Y(III) was rinsed with deionized water to remove the excessive EDTA. As shown in Table 7, 99.1% of Y(III) was removed by 0.1 mol L^{-1} Cyphos IL 104/SBME from solution in the third cycle. After three extraction/stripping cycles, the same sample of Cyphos IL 104/SBME could still keep its extraction capacity.

Separation of Y(III) from HRE(III)

It is widely known that the separation and purification of Y from HRE by liquid-liquid extraction is difficult for their similar chemical properties.[40] Cyanex 272, a protonated form of the Cyphos IL 104 anion, is a well-known and popular solvent for the extraction of cobalt from nickel in both sulfate and chloride media.[41,42] Sun et al. reported that Cyanex 272 mixed with 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5 (HPMBP) or sec-nonylphenoxy acetic acid (CA-100) in *n*-heptane was efficient to synergistic of RE(III) from HCl medium.[40,43] It is interesting to note that the ß value of Yb/Y in HNO_3-Cyphos IL 104/SBME system (Table 8) was large enough that Yb could be effectively separated from Y; and the ß values Y/Gd (6.17), Y/Tb (8.57), Y/Dy (40.81), Y/Ho (14.55), Er/Y (1.83), Tm/Y (2.06), Lu/Y (4.60) indicated that Y can be separated from other HRE. HNO_3-Cyphos IL 104 has successfully improved ß values of Y/Ho and Yb/Y in comparison with Cyanex 272 as reported by Sun et al.[40]

Thermodynamic studies

The extraction of Y(III) with HNO_3-Cyphos IL 104 in SBME (0.01 mol L^{-1}) was carried out at temperatures between 25°C and 50°C. The log D vs. (1/T) plot is shown in Figure 7, giving a slope of −1610.0. The change of enthalpy of the reactions ΔH can be determined according to the following equation

$$\frac{\Delta \log D}{\Delta(1/T)} = -\frac{\Delta H}{2.303R} \qquad (3)$$

where R is the gas constant, T is the temperature (K). ΔH is 30.82 kJ mol^{-1}. The positive ΔH value confirmed the endothermic nature of the extraction process. This suggested that the extraction was more favorable at high-temperature. The thermal stability of the mixture of bif-ILE and SBME contributed to the extraction of metals at higher-temperatures.

Conclusions

HNO_3-Cyphos IL 104, as a bif-ILE with unique propeties, exhibited a high capacity to extract RE(III) from aqueous solutions. It was found to be the most appropriate extractant among four ILs studied for the separation of Y(III) from HRE(III). SBME, as a safe and environmentally friendly solvent, has potential to replace conventional solvents in metal extraction. It was observed that Y(III) was extracted with HNO_3-Cyphos IL 104 in SBME by forming complicated neutral complexes. Nitrate ions were coordinated into organic complexes for the extraction of RE(III). HNO_3-Cyphos IL 104 was a successful bif-ILE, which have high-extraction groups and quaternary phosphonium/ammonium ILs property.

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