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Solvent Extraction and Separation of Trivalent Lanthanides Using Cyphos IL 104, a Novel Phosphonium Ionic Liquid as Extractant

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ABSTRACT

Solvent extraction of trivalent lanthanides from chloride solution using a novel ionic liquid Cyphos IL 104 (triethyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate or [R₄PA]) has been investigated, while comparing the results with that of its precursors triethyl(tetradecyl)phosphonium chloride [R₄PCl or Cyphos IL 101], Cyanex 272 [HA] and their equimolar mixture. The results also indicate very high extractability of Cyphos IL 104 toward trivalent lanthanides. Unlike the conventional acidic extractants, extraction of trivalent lanthanides with Cyphos IL 104 increases the equilibrium pH of the aqueous phase due to the preferential extraction of acid over the lanthanide ions. Extraction mechanism has been established by studying the extraction of neodymium(III) with the ionic liquid as a function of the concentrations of Cyphos IL 104 and chloride ions. Separation studies of trivalent lanthanides from a mixed solution containing 1×10^{-4} M each of La, Nd, Gd, and Lu with Cyphos IL 104 or Cyanex 272 indicate that Cyphos IL 104 is a better extractant in terms of extraction coefficient, but Cyanex 272 exhibits better selectivity toward heavier lanthanides. The prospects of stripping and regeneration of ionic liquid (Cyphos IL 104) have also been discussed in the present study.

KEYWORDS

Ionic liquid; Cyphos IL 104; Cyphos IL 101; Cyanex 272; lanthanides

Introduction

Solvent extraction (SX) is one of the hydrometallurgical techniques used for separating desired metal ions from the aqueous solutions of mixed metal ions. However, numerous stages are required for their separation from each other to achieve the desired purity, especially in the case of rare earth metals (REMs). REMs or the lanthanides are important ingredients for the modern technological growth, as they are widely used in electric vehicle batteries, electronics, powerful magnets of devices and wind turbines, phosphors of fluorescent lamps, catalysts of petroleum refining industries, etc.^[1] All these applications often require pure/specific REMs. But, in nature, due to similar physical and chemical properties, all the lanthanide elements occur as a single chemical entity, and are difficult to separate from each other.^[2] To achieve efficient separation of lanthanide ions, various types of extractants (e.g., cationic, anionic, and solvating) have been investigated.^[3–12]

Among the extractants, acidic (cationic) extractants generally exhibit better extraction efficiency and selectivity.^[13] As such, many acidic extractants such as D2EHPA, PC88A, Cyanex 272, Cyanex 301 etc. have been investigated for the separation of different pairs of trivalent lanthanide ions.^[14–18] However, extraction of metal ions with the acidic extractants is associated with the release of H⁺ ions into the aqueous phase, which adversely affects the extraction efficiency. In order to prevent this problem, acidic extractants saponified with sodium hydroxide or ammonia solution are generally used for the extraction of trivalent lanthanides and other metals. Although better extraction efficiencies and selectivity have been reported with saponified extractants,^[19–21]

certain drawbacks are associated with the process: (1) saponified extractant loses its saponification value after first contact with aqueous phase, which hinders the similar extraction behavior in further steps;^[22] (2) higher degree of saponification results in emulsification and third-phase formation during extraction;^[23] (3) a large amount of ammonium or sodium ions releases to the aqueous phase during extraction, which increases the salt concentration of the effluent.^[23–26]

Literature survey also indicates the use of various primary (RNH_2), secondary (R_2NH), and tertiary (R_3N) amines, and the quaternary ammonium salts (R_4N^+) for the separation of lanthanides.^[5,27–29] The usefulness of amines as extractants depends on the ability of the metal ions to form anionic species in the aqueous phase, which are extracted by amines in an anion exchange process. Among the neutral organophosphorous extractants, tri-*n*-butyl phosphate (TBP),^[9,10] tri-*n*-octyl phosphine oxide (TOPO), tributyl phosphine oxide (TBPO),^[7] Cyanex 923,^[30] etc., have been used for the separation of trivalent lanthanides. But during the extraction with TBP, it entraps water in the organic phase due to its solubility in the aqueous phase.^[31] Therefore, newer reagents are worth investigating to explore the possibility of obviating the aforementioned drawbacks.

Recently, ionic liquids (ILs) have emerged as a new class of extractants comprising bulky organic cations and the organic/inorganic anions. The advantages of ILs are that these are liquids over a wide range of temperature and are strongly hydrophobic, thereby partitioning the extracted metal complexes efficiently into the organic phase. As they are nonvolatile in nature, they may be considered as “a green solvent.” Besides the scope of preparing a variety of ILs of specific properties by combining different sets of cations and anions, they may not release H^+ ions into the raffinate unlike conventional acidic extractants. So the steps such as the neutralization of released acid or the saponification of extractant can be avoided.^[32–35]

The initial investigation on the use of ionic liquids as diluents has focused on the imidazole-based compounds with anions like NTf_2^- (bis(trifluoromethylsulfonyl)imide) or PF_6^- (hexafluorophosphate) for the extraction of different metals, including lanthanides.^[36,37] Use of ILs as diluents require the use of the additional extractant in the ionic liquid phase to facilitate the extraction process.^[38–41] By contrast, use of ILs as diluents makes the organic phase highly viscous, which leads to problems in phase separation and metal recovery. During the extraction, loss of imidazolium cation, such as $[\text{C}_8\text{mim}]^+$, to the aqueous phase was found to be a major drawback, making the imidazole-based ILs unsuitable for an environment-friendly process.^[42] Efforts were made to control the loss of imidazolium cations by adding complexing agents or replacing them with a new kind of ILs.^[40,43–44] The fluorinated ILs such as 1-butyl-3-methylimidazolium hexafluoro-phosphate, $[\text{C}_4\text{mim}][\text{PF}_6]$, and 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl) imide, $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ have shown good extraction efficiency for lanthanides and actinides, but the fluorinated anions are not suited for economic and environmental reasons.^[45] Therefore, recently, ionic liquids of combination of quaternary ammonium or phosphonium cations and nonfluorinated anions have been put forward for the investigation of IL as extractant in molecular diluents in SX process.^[46–47]

Although a few studies are reported using ionic liquids as extractants for separating the lanthanides and other metals,^[22–24,47–51] the underlying processes and mechanism of extraction with ILs are not well understood. Earlier a phosphonium-based ionic liquid, Cyphos IL 104, Trihexyl (tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate) was applied for the extraction of lactic acid.^[52] Separation studies of some metals such as Pd(II) , Ni(II) , Co(II) , and Cu(II) were also reported in the literature by using Cyphos IL 104.^[48,53–54] However, no systematic studies have been reported on the extraction and separation of trivalent lanthanides using Cyphos IL 104. Therefore, the aim of present study is to investigate the extraction behavior and mechanism using Cyphos IL 104 as an extractant for the separation of light (La(III) and Nd(III)), middle (Gd(III)), and the heavy (Lu(III)) lanthanides from a chloride solution.

Experimental

Stock solutions of La(III), Nd(III), Gd(III), and Lu(III) were prepared by dissolving their respective oxides in a minimum amount of concentrated hydrochloric acid and diluting it with distilled water to the required volume. Initial lanthanide concentration was maintained at 1×10^{-4} M for all the extraction studies. Chloride concentration in the aqueous phase was maintained by adding the required amount of sodium chloride. The extractants, Cyphos IL 104 (trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate) or $[R_4P^+][A^-]$ and Cyphos IL 101 (trihexyl(tetradecyl) phosphonium chloride), were procured from Sigma-Aldrich. Cyanex 272 (2,4,4-(trimethylpentyl) phosphinic acid) was kindly provided by Cytec, Canada. The chemical structure and properties of solvent extraction reagents used in the present investigation are given in Fig. 1 and Table 1. All the organic-phase solutions were prepared by dissolving a weighed amount of required extractant in commercial-grade kerosene. All other chemicals were of analytical-grade reagents.

Solvent extraction experiments were carried out by shaking equal volumes of aqueous and organic phases of known concentrations for 30 min in a glass-stoppered vial with the help of a rotospin shaker (Revotek, India) at 303 K and 30 rpm. All the experiments were performed in duplicate and uncertainties with error bar are included in each figure. Preliminary experiments show that the extraction equilibrium was attained within 5 min. The solutions after equilibration were transferred to a separating funnel and allowed to settle for phase separation. The metal concentration in the aqueous phase was analyzed by ICP-OES (Varian, Vista-MPX). The concentration of the metal in the organic phase was then obtained by material balance. These concentrations were used to determine the distribution ratios (D) and the

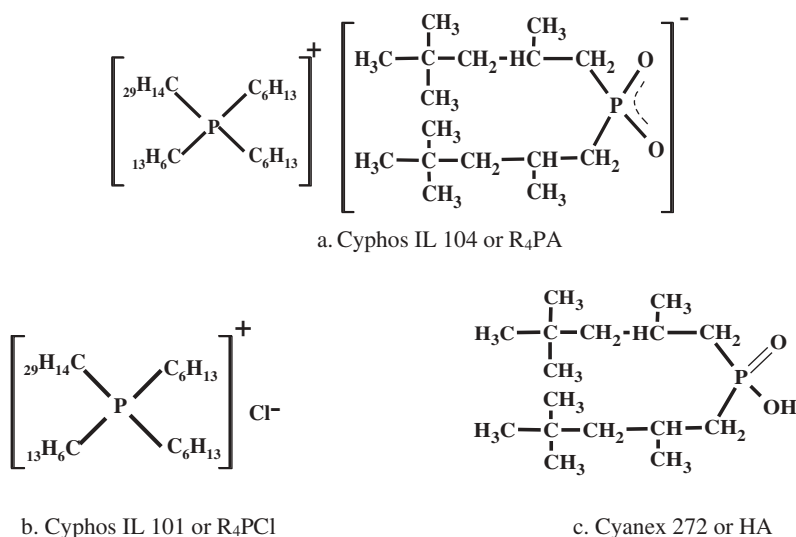


Figure 1. Chemical structure of Cyphos IL 104 (R_4PA), Cyphos IL 101 (R_4PCl), and Cyanex 272 (HA).

Table 1. Properties of solvent extraction reagents.^[55]

Properties	Cyphos IL104	Cyphos IL 101	Cyanex 272
IUPAC name	Trihexyl(tetradecyl) phosphonium bis (2,4,4-trimethylpentyl) phosphinate	Trihexyl(tetradecyl)phosphonium chloride	Bis(2,4,4-trimethylpentyl) phosphinic acid
Appearance	Pale yellow liquid	Colorless to yellow liquid	Colorless to light amber liquid
Molecular weight	773.27 g/mol	519.31 g/mol	290.42 g/mol
Density	0.895 g/mL	0.8819 g/ml	0.92 g/mL
Viscosity	806 mPa.S at 25°C	1824 mPa.S at 25°C	142 mPa.S at 25°C

percentage extraction. The percentage extraction (%E), distribution ratio (D), and separation factor (β) were determined by using the following equation:

$$\%E = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

$$D = \frac{C_i - C_f}{C_i} \quad (2)$$

$$\beta = \frac{D_1}{D_2} \quad (3)$$

where C_i and C_f are the concentrations of metal ions in the aqueous phase before (I = initial) and after (f = final) extraction, respectively. D_1 and D_2 are the distribution ratios of the metal ions M_1 and M_2 , respectively.

Results and discussion

In order to examine the extraction behavior of Cyphos IL 104 toward trivalent lanthanides, solvent extraction of neodymium(III) from an aqueous solution containing 1×10^{-4} M Nd(III) at different initial pH (1 to 5) with 0.003M Cyphos IL 104 in kerosene at a phase ratio O/A = 1:1 was investigated; results are depicted in Fig. 2. For comparison, solvent extraction of neodymium(III) was also carried out with Cyphos IL 101 and Cyanex 272, being the precursors of Cyphos IL 104, using their 0.003M concentrations including their equimolar mixture (0.003M each) under similar conditions (Fig. 2). It was observed that extraction of neodymium(III) with Cyphos IL 104 increased with the increase in initial pH of the aqueous phase. However, with Cyphos IL 101, Cyanex 272 or their equimolar mixture extraction of neodymium(III) was negligible in the entire range of pH studied. The difference in extraction efficiency may be due to

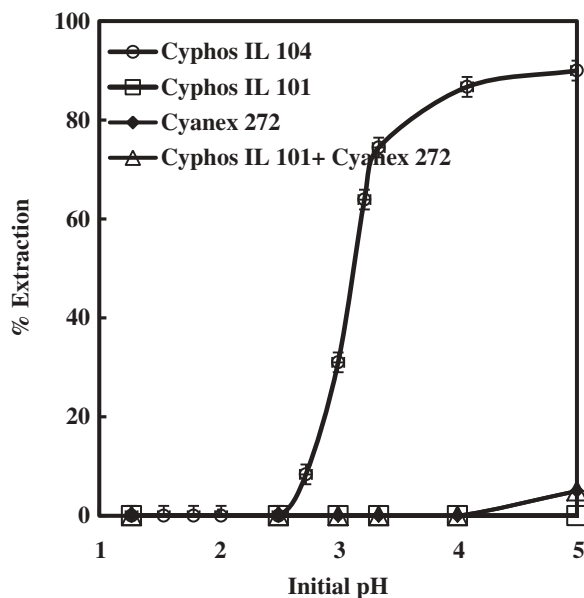


Figure 2. Effect of initial pH on the extraction of neodymium(III) by Cyphos IL 104, Cyphos IL 101, Cyanex 272 and equimolar mixture of Cyphos IL 101 and Cyanex 272. Aqueous phase: 1×10^{-4} M Nd(III), 0.1M Cl^- , Organic phase: 0.003M respective extractant, equilibrium time = 30 min.

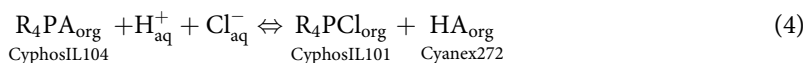
Table 2. Equilibrium pH of the aqueous phase after extraction of neodymium(III) with Cyphos IL 104 and its different constituents.

Initial pH	Equilibrium pH			
	Cyphos IL 104	Cyphos IL 101	Cyanex 272	Cyphos IL 101+ Cyanex 272
1.3	1.3	1.3	1.3	1.3
2.5	3.8	2.5	2.3	2.3
3.0	4.2	3.0	2.9	2.9
3.3	4.6	3.4	3.1	3.1
4.0	5.0	4.0	3.9	3.9
5.0	5.5	4.9	4.9	4.8

variation in the equilibrium pH of the aqueous phases in these cases. The values of equilibrium pH of the aqueous phase are given in Table 2.

Equilibration of neodymium(III) solutions with Cyphos IL 101 did not exhibit any change in pH. As can be seen (Fig. 2), extraction of neodymium(III) with Cyphos IL 101 was also negligible. This is because Cyphos IL 101 extracts metal ions by anion exchange mechanism^[51,54,56–57], and neodymium(III) does not form any anionic species under the studied experimental conditions. When neodymium(III) was extracted with Cyanex 272 or equimolar mixture of Cyphos IL 101 and Cyanex 272, the equilibrium pH decreased due to the release of H⁺ ions from Cyanex 272. The decrease in pH actually reduced the extraction efficiency of Cyanex 272. Under the pH range (initial pH 1 to 5) studied, a maximum of 5% Nd(III) was extracted with Cyanex 272 alone and with the equimolar mixture of Cyphos IL 101 and Cyanex 272. In the case of extraction of neodymium(III) with Cyphos IL 104, the equilibrium pH increased significantly. The increase in equilibrium pH, as mentioned in our previous publication,^[55] is because of the preferential extraction of H⁺ ions over neodymium(III) by Cyphos IL 104. The affinity of ammonium- and phosphonium-based ionic liquids to capture protons from aqueous solutions causing abrupt increase in pH of the aqueous solution and decrease in the available ionic liquid for extraction of metal ions have been reported by many researchers.^[47,48] Cieszyńska and Wisniewski,^[53] while extracting palladium(II) from hydrochloric acid with Cyphos IL 104, have confirmed the formation of dimer of bis(2,4,4-trimethylpentyl)phosphinic acid in the organic phase by ³¹P NMR studies of the extracted complex by extracting the H⁺ ions with the phosphinate part of the ionic liquid. However, the extent of affinity of ionic liquid for acid is not reported anywhere.

In order to understand the relation between increase in equilibrium pH and neodymium(III) extraction, a plot of concentration of H⁺ ions in the organic phase (after acid extraction) along with extraction of neodymium(III) with 0.003M Cyphos IL 104 at different initial pH is presented in Fig. 3. The concentration of H⁺ ions in the organic phase was calculated from the difference in initial and equilibrium pH of the extraction system. Hydrochloric acid extraction by Cyphos IL 104, which dissociates Cyphos IL 104 into Cyphos IL 101 and Cyanex 272, can be represented as^[55]



Conjugate acid of phosphinate ion (A[−]), that is, bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272 or HA), being a weak acid (pK_a = 6.37)^[58] and hydrophobic in nature (Partition constant, K_d = 53),^[59] H⁺ ions present in the aqueous phase are first extracted by Cyphos IL 104. After acid extraction, neodymium(III) starts getting extracted by the remaining Cyphos IL 104. The numbers in parentheses (Fig. 3) indicate the concentration of unutilized Cyphos IL 104 after acid extraction. Up to the initial pH of 2.5 (≥0.003M H⁺), Cyphos IL 104 (0.003M) was completely utilized for the extraction of HCl, and no neodymium(III) extraction was detected. Above the initial pH of 2.5 (<0.003M H⁺), Cyphos IL 104 was not completely utilized for the extraction of H⁺ ions. And the unutilized Cyphos IL 104 extracted neodymium(III) into the organic phase. Therefore, as the initial pH increased, the availability of Cyphos IL 104 for neodymium extraction also increased. Thus, in the initial pH range of 2.7 to 5.0, neodymium(III) extraction increased from 8% to 90%.

The mechanism for extraction of neodymium(III) with Cyphos IL 104 may be represented as

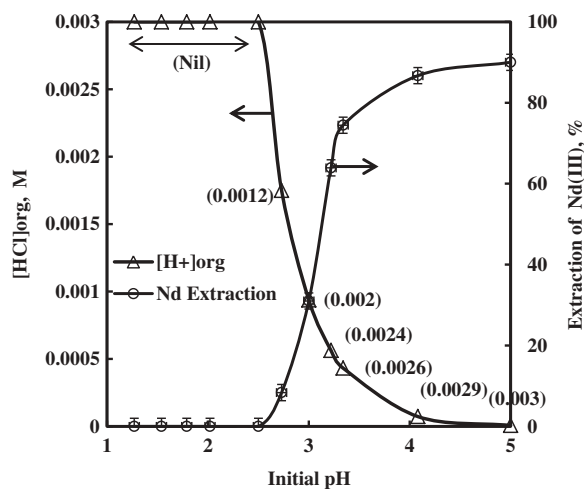


Figure 3. Effect of initial pH on HCl and neodymium(III) extraction. Aqueous phase: 1×10^{-4} M Nd(III), 0.1M Cl^- , Organic phase: 0.003M Cyphos IL 104, equilibration time = 30 min.



$$K_{\text{Nd}} = \frac{[\text{NdA}_3]_{\text{org}} [\text{R}_4\text{PCL}]_{\text{org}}^3}{[\text{Nd}_{\text{aq}}^{3+}] [\text{Cl}_{\text{aq}}^-]^3 [\text{R}_4\text{PA}]_{\text{org}}^3} \quad (6)$$

$$K_{\text{Nd}} = \frac{D \cdot [\text{R}_4\text{PCL}]_{\text{org}}^3}{[\text{Cl}_{\text{aq}}^-]^3 [\text{R}_4\text{PA}]_{\text{org}}^3} \quad (7)$$

$$\text{where } D = \frac{[\text{NdA}_3]_{\text{org}}}{[\text{Nd}_{\text{aq}}^{3+}]}$$

$$\log D = \log K_{\text{Nd}} + 3 \left\{ \log [\text{R}_4\text{PA}_{\text{org}}] + \log [\text{Cl}_{\text{aq}}^-] - \log [\text{R}_4\text{PCL}_{\text{org}}] \right\} \quad (8)$$

In order to establish the aforementioned extraction mechanism, solvent extraction of neodymium(III) with Cyphos IL 104 in kerosene as a function of Cyphos IL 104 concentration and chloride ion concentration was studied. Extraction of neodymium(III) from 0.1M Cl^- solution containing 1×10^{-4} M Nd(III) at initial pH 5.0 increased with increase in Cyphos IL 104 concentration in the range 0.0025–0.007M (Fig. 4). Similarly, the extraction of neodymium(III) at initial pH 5.0 with constant initial Cyphos IL 104 concentration (0.003M) increased with increase in chloride ions concentration in the aqueous phase in the range 0.0003–0.001M (Fig. 5). It may be noted here that when 0.003M Cyphos IL 104 was contacted with the sodium chloride solutions (0.0003–0.1M) in absence of a trivalent lanthanide, extraction of chloride or sodium ion into the organic phase was not observed. Taking into consideration the acid extraction (Eq. 4) as well as that of neodymium(III) extraction (Eq. 5), equilibrium concentrations of Cyphos IL 104, Cl^- , and Cyphos IL 101(R_4PCL) were calculated and plots of $\log D$ vs. $\{\log [\text{R}_4\text{PA}]_{\text{org}} + \log [\text{Cl}^-]_{\text{aq}} - \log [\text{R}_4\text{PCL}]_{\text{org}}\}$ were drawn for both the extractant and the chloride variation experiments. When Cyphos IL 104 concentration was varied (0.0025–0.007M), plot of $\log D$ vs. $\{\log [\text{R}_4\text{PA}]_{\text{org}} + \log [\text{Cl}^-]_{\text{aq}} - \log [\text{R}_4\text{PCL}]_{\text{org}}\}$ had slope of ~ 3 (Fig. 6). For chloride variation experiments, plot of $\log D$ vs. $\{\log [\text{R}_4\text{PA}]_{\text{org}} + \log [\text{Cl}^-]_{\text{aq}} - \log [\text{R}_4\text{PCL}]_{\text{org}}\}$ also had a slope of ~ 3 (Fig. 7), but with negative sign. Negative sign of the slope is because as the extraction of neodymium(III) increases with increase in chloride ion concentration, equilibrium concentration of R_4PCL increases and at the same time equilibrium concentration of R_4PA decreases,

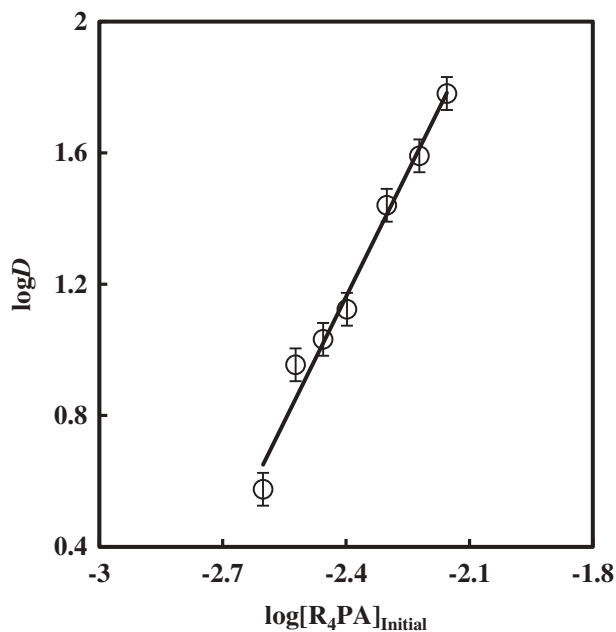


Figure 4. Effect of Cyphos IL 104 concentration on the extraction of neodymium(III). Aqueous phase: 1×10^{-4} M Nd(III), 0.1M Cl^- , Initial pH = 5.0 ± 0.05 , $t = 30$ min.

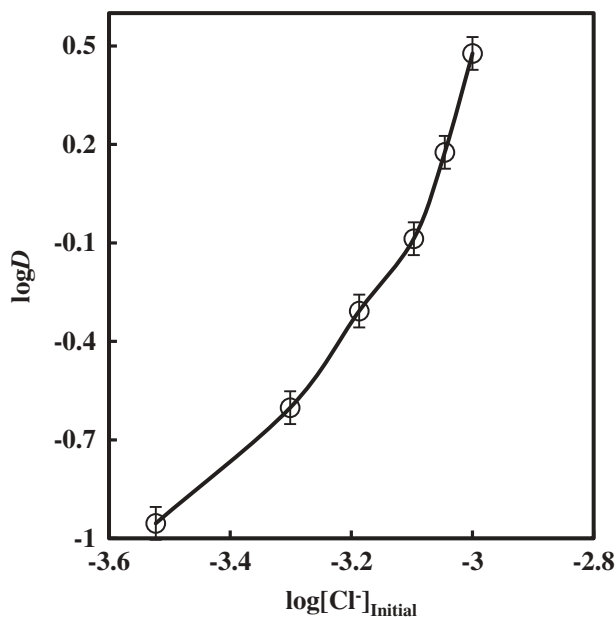


Figure 5. Effect of initial chloride ion concentration on the extraction of neodymium(III). Aqueous phase: 1×10^{-4} M Nd(III), Organic phase: 0.003M Cyphos IL 104 in kerosene, Initial pH = 5.0 ± 0.05 , $t = 30$ min.

which results in overall decrease of $\{\log[R_4PA]_{org} + \log[Cl^-]_{aq} - \log[R_4PCL]_{org}\}$ with increase in the chloride ion concentration. Slope values of ~ 3 for the plots of $\log D$ vs. $\{\log[R_4PA]_{org} + \log[Cl^-]_{aq} - \log[R_4PCL]_{org}\}$ in case of both Cyphos IL 104 concentration and chloride ion concentration variation experiments confirm

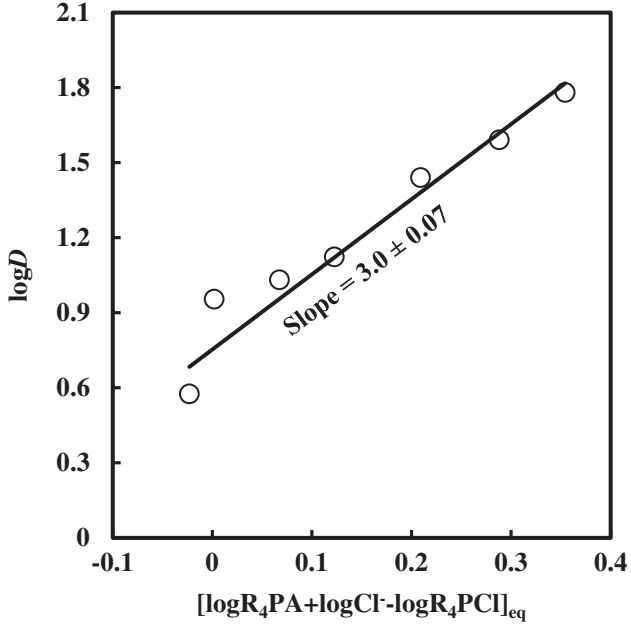


Figure 6. Effect of equilibrium concentrations of R_4PA , Cl^- and R_4PCl on the extraction of neodymium(III) while varying initial concentration of Cyphos IL 104 (R_4PA). Aqueous phase: 1×10^{-4} M Nd(III), 0.1M Cl^- , Initial pH = 5.0 ± 0.05 , $t = 30$ min.

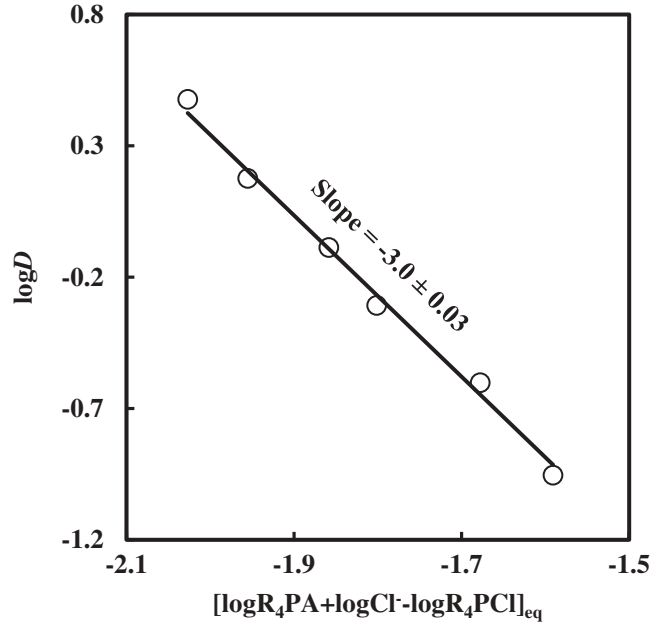


Figure 7. Effect of equilibrium concentrations of R_4PA , Cl^- and R_4PCl on the extraction of neodymium(III) while varying initial concentration of chloride ion in the aqueous phase. Aqueous phase: 1×10^{-4} M Nd(III), Organic phase: 0.003M Cyphos IL 104 in kerosene, Initial pH = 5.0 ± 0.05 , $t = 30$ min.

the extraction mechanism as expressed in Eq. (5). Equilibrium constant (K_{Nd}) value for neodymium(III) extraction with Cyphos IL 104 was calculated to be 5.7.

Separation of trivalent lanthanides with Cyphos IL 104

In order to study the mutual separation, solvent extraction of trivalent lanthanides from 0.1M chloride solution at different initial pH (in the range 1.0–5.0) containing 1×10^{-4} M each of La(III), Nd(III), Gd(III), and Lu(III) with 0.003M Cyphos IL 104 was investigated. As stated earlier, due to the preferred H^+ extraction, equilibrium pH of the aqueous phase increased (Table 3). Extraction of trivalent lanthanides with respect to varying equilibrium pH is depicted in Fig. 8. It is evident from these data that the order of solvent extraction of trivalent lanthanides with Cyphos IL 104 followed the order of their ionic radii ($Lu(III) > Gd(III) > Nd(III) > La(III)$). At the initial pH 5.0 (with the Eq. pH 5.5), logD values for Lu(III), Gd(III), Nd(III), and La(III) have been found to be 2.4, 2.2, 0.9, and -0.5, respectively corresponding to the extraction of 99.9% Lu(III), 99.9% Gd(III), 90% Nd(III), and 22% La(III). Separation factors obtained between different pairs of trivalent lanthanides from their mixed solutions by using Cyphos IL 104 at different equilibrium pH are given in Table 3 up to two significant figures.

Table 3. Separation factors of different pair of lanthanides from a mixed solution at varying pH with Cyphos IL 104.

Initial pH	Eq. pH	Separation factor (β)					
		Lu/Gd	Lu/Nd	Lu/La	Gd/Nd	Gd/La	Nd/La
2.5	3.8	25	40	40	2	2	1
2.7	4.0	10	20	70	2	7	3
3.0	4.2	85	470	1500	6	18	3
3.5	4.8	1	120	900	120	900	8
4.0	5.0	1	40	500	40	500	10
4.5	5.3	1	13	350	10	350	25
5.0	5.5	1	30	900	20	600	30

Aqueous: 1×10^{-4} M Ln(III), 0.1M Cl^- , Organic: 0.003M Cyphos IL 104, $t = 30$ min

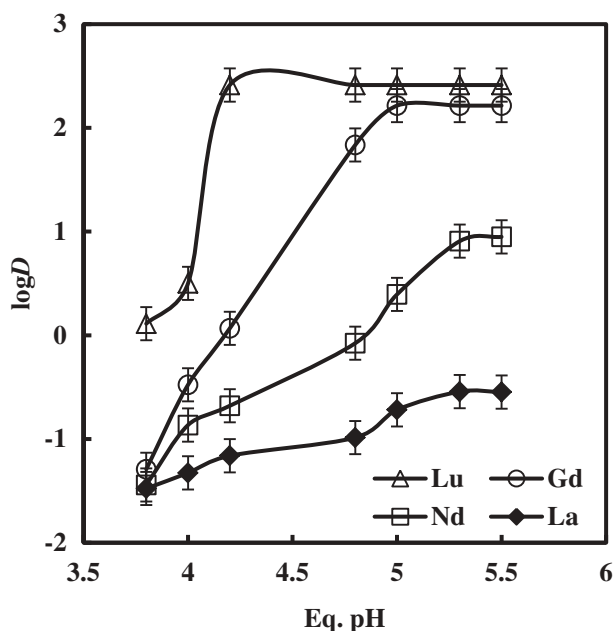


Figure 8. Effect of equilibrium pH on extraction of La(III), Nd(III), Gd(III), and Lu(III) from their mixed solution with Cyphos IL 104. Aqueous phase: 1×10^{-4} M Ln(III), 0.1M Cl^- , Organic phase: 0.003M Cyphos IL 104, $t = 30$ min.

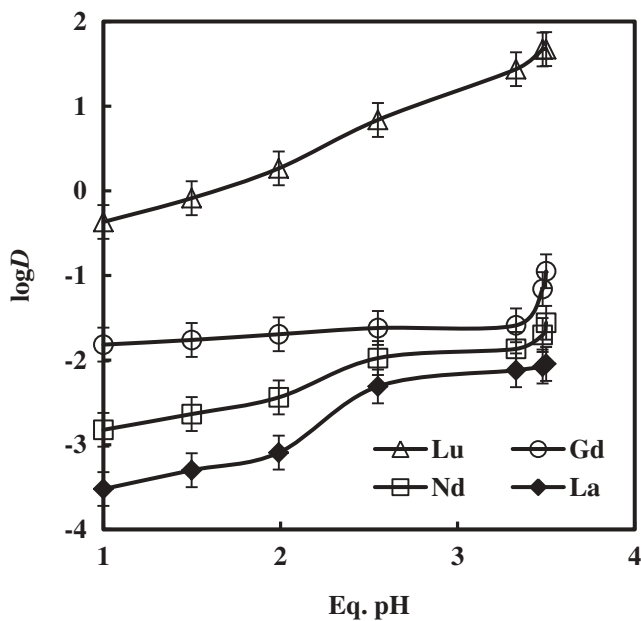


Figure 9. Effect of equilibrium pH on extraction of La(III), Nd(III), Gd(III), and Lu(III) from their mixed solution with Cyanex 272. Aqueous phase: 1×10^{-4} M Ln(III), 0.1M Cl^- , Organic phase: 0.003M Cyanex 272, $t = 30$ min.

Being the anionic precursor of Cyphos IL 104, 0.003M Cyanex 272 was also examined to extract trivalent lanthanides from 0.1M chloride solutions of different initial pH (1.0 to 5.0) containing 1×10^{-4} M each of La(III), Nd(III), Gd(III), and Lu(III). Extraction of the lanthanides with respect to the equilibrium pH of aqueous phase is depicted in Fig. 9. At the initial pH of 5.0 (Eq. pH 3.5) with 0.003M Cyanex 272, logD values of 1.7, -0.9, -1.5, and -2.0 were obtained for Lu(III), Gd(III), Nd (III), and La(III), respectively, corresponding to the extraction of 98% Lu, 10% Gd(III), 2.7% Nd(III), and 0.9% La(III). When compared (Figs. 8 and 9), the extraction efficiency of Cyphos IL 104 for trivalent lanthanides was found to be better than that of Cyanex 272. However, selectivity for heavier lanthanides was found to be better with Cyanex 272 than with Cyphos IL 104. This may be attributed to the difference in extraction mechanism of the two extractants. As explained earlier, in the case of Cyphos IL 104, the increase in initial pH increases the availability of the free Cyphos IL 104, resulting in the increased extraction of trivalent lanthanides. By contrast, equilibrium pH of the aqueous phase decreases in case of Cyanex 272, which suppresses the extraction of lighter lanthanides, and heavier lanthanides (lutetium (III) in this case) are selectively extracted. The separation factors calculated for different pairs of trivalent lanthanides from their mixed solutions by using Cyanex 272 as extractant at different equilibrium pH are given in Table 4. With Cyanex 272, separation factors obtained between lutetium and lighter lanthanides were found to be much higher

Table 4. Separation factors of different pair of lanthanides from a mixed solution at varying pH with Cyanex 272.

Initial pH	Eq. pH	Separation factor (β)					
		Lu/Gd	Lu/Nd	Lu/La	Gd/Nd	Gd/La	Nd/La
1.0	1.0	30	300	1400	10	50	5
1.5	1.5	50	350	1600	8	35	5
2.0	2.0	90	500	2300	6	25	4
2.6	2.5	300	650	1400	2	5	2
3.7	3.3	1100	2000	3600	2	3	2
4.5	3.4	680	2400	5600	3	8	2
5.0	3.5	400	1700	5200	4	12	3

in comparison to Cyphos IL 104. Therefore, it can be concluded that Cyphos IL 104 has higher extraction efficiency, but its precursor Cyanex 272 has better selectivity toward heavier lanthanides.

Separation factor values obtained for different pairs of the lanthanides with Cyphos IL 104 and Cyanex 272 can be compared with those of commonly used commercial extractants such as D2EHPA, EHEHPA, and Cyanex 923 (Table 5).^[60–62] Data clearly show that Cyphos IL 104 exhibits better extraction efficiency toward lanthanides as compared to the conventionally used extractants. It is also important to note that separation of the heavier lanthanide, Lu(III) from the light/middle lanthanides (La(III), Nd(III), Gd(III)) can be better achieved with Cyphos IL 104 as compared to the other reagents such as D2EHPA and EHEHPA. However, selectivity of heavier lanthanides was found to be better with Cyanex 272 than that of Cyphos IL 104. Separation factor between the lighter lanthanides such as Nd(III) and La(III) is substantially higher with the Cyphos IL 104 (Table 5) as compared to all other reagents. Thus, by using Cyphos IL 104, heavier lanthanides can be separated as a group from the lighter lanthanides; this can also be used for achieving better separation efficiency among the lighter lanthanides.

Loading capacity of Cyphos IL 104 for Lu(III), Gd(III), Nd(III), and La(III)

The loading capacity of Cyphos IL 104 (0.003M) was determined by contacting the organic phase repeatedly with the fresh aqueous solutions containing 13.2 mg/L La(III), 10.7 mg/L Nd(III), 13.8 mg/L Gd(III), and 17 mg/L Lu(III) at a phase ratio (O/A) of 1 and initial aqueous phase pH 5.0 ± 0.05 . After nine contacts, Cyphos IL 104 was found to be loaded with 3.50 mg/L La(III), 14.42 mg/L Nd(III), 25.16 mg/L Gd(III), and 76.63 mg/L Lu(III). As can be seen in Fig. 10, 0.003 M Cyphos IL 104 was saturated with Gd(III), Nd(III), or La(III) in only two contacts, whereas saturation of Cyphos IL 104 with Lu(III) was not achieved even in nine contacts. The higher loading capacity of Cyphos IL 104 for Lu(III) clearly indicates preference of this solvent for Lu(III) with a prospect of its selective extraction from other trivalent lanthanides present in the aqueous solution. Thus, Cyphos IL 104 can be effectively used for the separation of heavy lanthanides from other lanthanides.

Stripping of trivalent lanthanides from the loaded Cyphos IL 104

Stripping of lanthanides from the loaded Cyphos IL 104 obtained from loading capacity experiment was performed by varying the concentration of HCl in the range 0.5–2.5 M (Fig. 11). It was observed that stripping of trivalent lanthanides increased with increase in the hydrochloric acid concentration. When the loaded organic containing 3.5 mg/L La(III), 14.4 mg/L Nd(III), 25.2 mg/L Gd(III), and 76.6 mg/L Lu(III) was contacted with 0.5 M hydrochloric acid, 89% La(III), 43% Nd(III), 32% Gd(III), and 21% Lu(III) were stripped from the organic phase. The stripping of the trivalent lanthanides follows the order La(III) > Nd(III) > Gd(III) > Lu(III). The stripping order further confirms the strong interaction between the heavy lanthanides and Cyphos IL 104. When hydrochloric acid concentration was increased to 2.5 M, all the extracted lanthanides were stripped from the organic phase without any selectivity.

Table 5. Comparison of separation factor of Cyphos IL 104 from some conventional extractants.

Extractant	Experimental conditions	Separation factor (β)						Reference
		Lu/Gd	Lu/Nd	Lu/La	Gd/Nd	Gd/La	Nd/La	
Cyphos IL 104	10^{-4} M Ln^{3+} , 0.003M Cyphos IL 104, 0.1M Cl^- , Initial pH = 5.0 (Eq. pH = 5.5)	1	30	900	20	600	30	Present study
Cyanex 272	10^{-4} M Ln^{3+} , 0.003M Cyanex 272, 0.1M Cl^- , Initial pH = 5.0 (Eq. pH = 3.5)	400	1700	5200	4	12	3	Present study
D2EHPA	1g dm^{-3} Ln^{3+} , 0.05M D2EHPA, 0.1M HCl	9.55	175	425	18.3	44.6	2.43	[60]
EHEHPA	1gm dm^{-3} Ln^{3+} , 0.2M EHEHPA, 0.1M HCl	20.7	119	199	5.74	9.52	1.67	[60]
Cyanex 923	10^{-4} M Ln^{3+} , 0.5M Cyanex 923, 0.001M HCl	—	—	—	1.3	16	12	[61]
Cyanex 272	0.1g/L Ln^{3+} , 0.5M Cyanex 272, Eq. pH = 1.75	81	730	1900	9	23	2	[62]

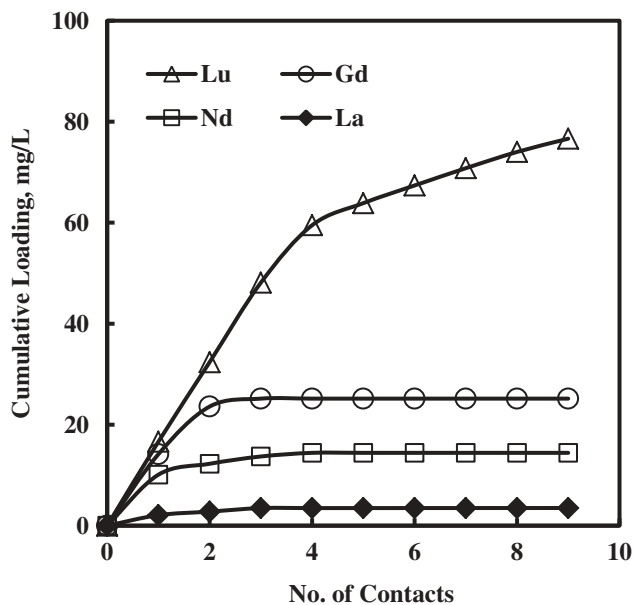


Figure 10. Cumulative loading of 0.003 M Cyphos IL 104 in 9 contacts. Aqueous phase: 13.2 mg/L La^{3+} , 10.7 mg/L Nd^{3+} , 13.8 mg/L Gd^{3+} and 17 mg/L Lu^{3+} , 0.1M Cl^- , Initial pH = 5.0, t = 30 min.

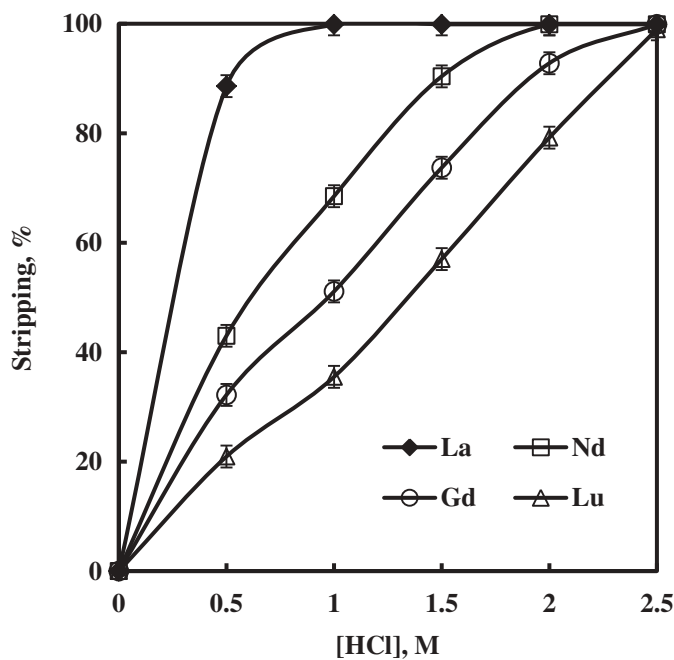
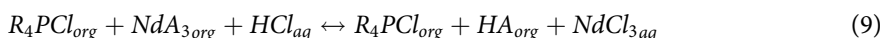


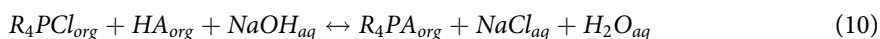
Figure 11. Effect of hydrochloric acid concentration on the stripping of Lu(III), Gd(III), Nd(III), and La(III) from IL. Cyphos IL 104 (mg/L): 3.5 La(III), 14.4 Nd(III), 25.2 Gd(III), and 76.6 Lu(III); O/A = 1.

Regeneration of Cyphos IL 104 and prospects of recycling

For economic and environmental reasons, the extractants used in the solvent extraction processes must be regenerated and reused for further extraction. In order to investigate the regeneration ability, 0.003M Cyphos IL 104 was contacted with 1×10^{-4} M Nd(III) at pH 5.0 to extract neodymium(III) into the organic phase. The loaded Cyphos IL 104 was completely stripped with 0.1 M HCl. However, when the stripped organic phase was used again for the extraction of neodymium(III) from 1×10^{-4} M Nd(III) solution at pH 5.0, extraction efficiency decreased substantially. The decrease in extraction efficiency may be accounted for the protonation of the ionic liquid (Cyphos IL 104) during the stripping process. The stripping of Nd(III) from the loaded Cyphos IL 104 with HCl may be represented as



Therefore, after stripping with 0.1 M HCl, the organic phase was neutralized with 0.1 M NaOH solution. The regenerated Cyphos IL 104 exhibited the same extraction efficiency as that of the virgin Cyphos IL 104. This neutralization stage can be shown as



The process of extraction–stripping–regeneration was repeated five times. Each time the regenerated Cyphos IL 104 exhibited comparable extraction efficiency with Cyphos IL 104. Thus, Cyphos IL 104 can be considered as a stable system for solvent extraction of trivalent lanthanides from the chloride solutions.

Conclusions

The extraction of trivalent lanthanides from their chloride solutions using Cyphos IL 104 as an extractant is accompanied by the increase in equilibrium pH of the raffinate, reflecting the affinity of the extractant toward H^+ ions. After acid extraction, the unutilized Cyphos IL 104 participates in the extraction of the trivalent lanthanides. The mechanism for the extraction of trivalent lanthanides with Cyphos IL 104 has been evaluated by slope analysis method. Cyphos IL 104 shows better extraction efficiency in comparison to its precursors Cyphos IL 101, Cyanex 272, or their equimolar mixture. Interestingly, during the extraction of trivalent lanthanides from a mixed solution containing La(III), Nd(III), Gd(III), and Lu(III) with Cyphos IL 104 or Cyanex 272, the higher extraction efficiency is exhibited by Cyphos IL 104, although its precursor Cyanex 272 exhibits better selectivity toward heavier lanthanides. Cyphos IL 104 can, however, be applied for the separation of lighter lanthanides with that of the heavier lanthanides. From the stripping studies, it is found that trivalent lanthanides loaded in the Cyphos IL 104 phase can be easily stripped with dilute HCl. But stripping with HCl leads to protonation of Cyphos IL 104, forming Cyphos IL 101 and Cyanex 272. Therefore, Cyphos IL 104 can be regenerated with the same extraction efficiency by washing the stripped organic phase with a dilute sodium hydroxide solution.

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References

1. Clapper, J.R. Worldwide Threat Assessment of the US Intelligence Community, March 12, 2013, pp. 1–34.
2. Gupta C.K.; Krishnamurthy N. *Extractive Metallurgy of Rare Earths*; CRC Press: United States of America; 2005, pp. 1–484.
3. Abdeltawab, A.A.; Nii, S.; Kawaizumi, F.; Takahash, K. Separation of La and Ce with PC-88A by counter-current mixer-settler extraction column. *Sep. Puri. Technol.* 2002, 26(2–3), 265–272.
4. El-Hefny, N.E.; El-Nadi, Y.A.; Daoud, J.A. Equilibrium and mechanism of samarium extraction from chloride medium using sodium salt of Cyanex 272. *Sep. Purif. Technol.* 2012, 75(3), 310–315.
5. El-Yamani, I.S.; Shabana, E.L. Solvent extraction of lanthanum(III) from sulfuric acid solutions by Primene JMT. *J. Less Common Met.* 1985, 105(2), 255–261.
6. Gaudernack, B.; Hannestad, G.; Hundere, I. Process for separating yttrium values from the lanthanides. U.S. Patent US3751553A, August 7, 1973.
7. Khopkar, P.K.; Narayanankutty, P. Extraction of some trivalent lanthanides and americium(III) by neutral organophosphorous extractants from thiocyanate solutions. *J. Inorg. Nucl. Chem.* 1972, 34(8), 2617–2625.
8. Li, H.; Guo, F.; Zhang, Z.; Li, D.; Wang, Z. A new hydrometallurgical process for extracting rare earths from apatite using solvent extraction with P₃₅₀. *Proceedings of Rare Earths'04 in Nara Japan (J. Alloy Compd.* 2006, 408–412, 995–998).
9. Peppard, D.F.; Driscoll, W.J.; Siromen, S.J.; Mason, G.W. Fractional extraction of the lanthanides as their di-alkyl orthophosphates. *J. Inorg. Nucl. Chem.* 1957, 4(5–6), 334–343.
10. Peppard, D.F.; Driscoll, W.J.; Sironen, R.J.; McCarty, S. Nonmonotonic ordering of lanthanides in tributyl phosphate-nitric acid extraction system. *J. Inorg. Nucl. Chem.* 1957, 4(5–6), 326–333.
11. Weiwei, W.; Xianghan, W.; Shulan, M.; Hongfei, L.; Deqian, L. Extraction and stripping of ytterbium(III) from H₂SO₄ medium by Cyanex 923. *J. Rare Earths*, 2006, 24(6), 685–689.
12. Yin, J.; Hu, B.; He, M.; Jiang, Z. Determination of trace rare earth elements in environmental samples by low temperature electrothermal vaporization inductively coupled plasma mass spectrometry after synergistic extraction with dimethylheptyl methyl phosphate and 1-phenyl-3-methyl-4-benzoyl-pyrazalone-5. *Anal. Chim. Acta* 2007, 594(1), 61–68.
13. Xie F.; Zhang T. A.; Dreisinger D.; Doyle F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* 2014, 56, 10–28.
14. Basualto, C.; Valenzuela, F.; Molina, L.; Munoz, J. P.; Fuentes, E.; Sapag, J. Study of the solvent extraction of the lighter lanthanide metal ions by means of organophosphorus extractants. *J. Chil. Chem. Soc.* 2013, 58(2), 1785–1789.
15. Kim, J.S.; Kumar, B.N.; Lee, J.Y.; Kantam, M.L.; Reddy, B.R. Separation and recovery of light rare-earths from chloride solutions using organophosphorus based extractants, *Separ. Sci. Technol.* 2012, 47(11), 1644–1650.
16. Morais, C.A.; Ciminelli, V.S.T. Process development for the recovery of high grade lanthanum by solvent extraction. *Hydrometallurgy* 2004, 73(3–4), 237–244.
17. Radhika, S.; Kumar, B.N.; Kantam, M.L.; Reddy, B.R. Liquid–liquid extraction and separation possibilities of heavy and light rare-earths from phosphoric acid solutions with acidic organophosphorus reagents. *Sep. Purif. Technol.* 2010, 75(3), 295–302.
18. Radhika, S.; Kumar, B.N.; Kantam, M.L.; Reddy, B.R. Solvent extraction and separation of rare-earths from phosphoric acid solutions with TOPS99. *Hydrometallurgy* 2011, 110(1–4), 50–55.
19. Banda, R.; Jeon, H.; Lee, M. Solvent extraction separation of Pr and Nd from chloride solution containing La using Cyanex 272 and its mixture with other extractants. *Sep. Purif. Technol.* 2012, 98, 481–487.
20. Banda, R.; Jeon, H.S.; Lee, M.S. Solvent extraction separation of La from chloride solution containing Pr and Nd with Cyanex 272. *Hydrometallurgy* 2012, 121–124, 74–80.
21. Thakur, N.V. Separation of neodymium from lighter rare earths using alkyl phosphonic acid, PC 88A. *Hydrometallurgy* 1993, 34(1), 99–108.
22. Coll, M.T.; Fortuny, A.; Kedari, C.S.; Sastre, A.M. Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant. *Hydrometallurgy* 2012, 125–126, 24–28.
23. Sun, X.; Ji, Y.; Hu, F.; He, B.; Chen, J.; Li, D. The inner synergistic effect of bifunctional ionic liquid extractant for solvent extraction. *Talanta* 2010, 81(4–5), 1877–1883.
24. Sun, X.; Ji, Y.; Zhang, L.; Chen, J.; Li, D. Separation of cobalt and nickel using inner synergistic extraction from bifunctional ionic liquid extractant (Bif-ILE). *J. Hazard. Mater.* 2010, 182(1–3), 447–452.
25. Wang, L.; Huang, X.; Yu, Y.; Xiao, Y.; Long, Z.; Cui, D. Eliminating ammonia emissions during rare earth separation through control of equilibrium acidity in a HEH(EHP)-Cl system. *Green Chem.* 2013, 15, 1889.
26. Yin, S.; Wu, W.; Bian, X.; Zhang, F. Effect of complexing agent lactic acid on the extraction and separation of Pr (III)/Ce(III) with di-(2-ethylhexyl) phosphoric acid. *Hydrometallurgy* 2013, 131–132, 133–137.
27. Khopkar, P.; Mathur, J. N. Extraction of trivalent actinides and lanthanides by tertiary and quaternary amines from concentrated chloride solutions. *J. Inorg. Nucl. Chem.* 1981, 43, 1035–1040.

28. Hsu, K.H.; Huang, C.H.; King, T.C.; Li, P.K. Separation of praseodymium and neodymium in high purity (99.9%) by counter-current exchange extraction and its mechanism. In Proceedings of International Solvent Extraction Conference'80 (ISEC'80), Liege, Belgium, 1980, 2, 80–82.
29. Huang, C.H.; Jin, T.Z.; Li, B.G.; Li, J.R.; Xu, G.X. Studies on extraction mechanism of the rare earths with quaternary ammonium salts. In Proceedings of Int. Solvent Extr. Conf., ISEC'86, Dechema, Frankfurt, 1986, 215–221.
30. Reddy, M.L.P.; Varma, R.L.; Ramamohan, T.R.; Sahu, S.K.; Chakravorty, V. Cyanex 923 as an extractant for trivalent lanthanides and yttrium. *Solvent Extr. Ion Exch.* 1998, 16(3), 795.
31. Mishra, S.; Ganesh, S.; Velavendan, P.; Pandey, N.K.; Mallika, C.; Mudali, U.K.; Natarajan, R. Thermodynamics of solubility of tri-*n*-butyl phosphate in nitric acid solutions. *Adv. Chem. Eng. Res.* 2013, 2(3), 55–60.
32. Deng, Y. *Ionic Liquids — Properties, Preparation and Application*; SINO-PEC Press: Beijing, China; 2006, pp. 334–344 (in Chinese).
33. Reddy, R.G. Novel applications of ionic liquids in materials processing. *J. Phys.: Conference Series* 2009, 165, 012076, 1–6.
34. Guo-cai, T.; Jian, L.; Yi-xin, H. Application of ionic liquids in hydrometallurgy of nonferrous metals. *T. Nonferr. Metal Soc.* 2010, 20, 513–520.
35. Zhang, S.; Lu, X. *Ionic Liquids from Fundamental Study to Industrial Application*; Science Press: Beijing; 2006, pp. 12–16 (in Chinese).
36. Yang, F.; Kubota, F.; Baba, Y.; Kamiya, N.; Goto, M. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. *J. Hazard. Mater.* 2013, 254–255, 79–88.
37. Yoon, S.J.; Lee, J.G.; Tajima, H.; Yamasaki, A.; Kiyono, F.; Nakazato, T.; Tao, H. Extraction of lanthanide ions from aqueous solution by bis(2-ethylhexyl)phosphoric acid with room temperature ionic liquids. *J. Ind. Eng. Chem.* 2010, 16(3), 350–354.
38. Rout, A.; Venkatesan, K.A.; Srinivasan, T.G.; Rao, P.R.V. Liquid–liquid extraction of Pu(IV), U(VI) and Am (III) using malonamide in room temperature ionic liquid as diluent. *J. Hazard. Mater.* 2012, 221–222, 62–67.
39. Rout, A.; Kotlarska, J.; Dehaen, W.; Binnemans, K. Liquid–liquid extraction of neodymium(III) by dialkylphosphate ionic liquids from acidic medium: the importance of the ionic liquid cation. *Phys. Chem. Chem. Phys.* 2013, 15(39), 16533–16541.
40. Sun, X.; Ji, Y.; Guo, L.; Chen, J.; Li, D. A novel ammonium ionic liquid based extraction strategy for separating scandium from yttrium and lanthanides. *Sep. Purif. Technol.* 2011, 81(1), 25–30.
41. Villemain, D.; Didi, M.A. Extraction of rare earth and heavy metals, using ionic solvents as extraction medium (A review). *Orient. J. Chem.* 2013, 29(4), 1267–1284.
42. Dietz, M.L.; Dzielawa, J.A. Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: implications for the 'greenness' of ionic liquids as diluents in liquid–liquid extraction. *Chem. Commun.* 2001, 20(20), 2124–2125.
43. Luo, H.; Dai, S.; Bonnesen, P.V.; Buchanan, A.C.; Holbrey, J.D.; Bridges, N.J.; Rogers, R.D. Extraction of cesium ions from aqueous solutions using calix[4]arene-bis(tert-octylbenzo-crown-6) in ionic liquids. *Anal. Chem.* 2004, 76(11), 3078–3083.
44. Sun, X.Q.; Peng, B.; Chen, J.; Li, D.Q.; Luo, F. An effective method for enhancing metal-ions' selectivity of ionic liquid-based extraction system: Adding water-soluble complexing agent. *Talanta* 2008, 74(4), 1071–1074.
45. Rout, A.; Binnemans, K. Liquid–liquid extraction of europium(III) and other trivalent rare-earth ions using a non-fluorinated functionalized ionic liquid. *Dalton Trans.* 2014, 43(4), 1862–1872.
46. Regel-Rosocka, M. Extractive removal of zinc(II) from chloride liquors with phosphonium ionic liquids/toluene mixtures as novel extractants. *Sep. Purif. Technol.* 2009, 66(1), 19–24.
47. Rout, A.; Venkatesan, K.A.; Srinivasan, T.G.; Rao, P.R.V. Ionic liquid extractants in molecular diluents: Extraction behavior of europium (III) in quaternary ammonium-based ionic liquids. *Sep. Purif. Technol.* 2012, 95, 26–31.
48. Castillo, J.; Coll, M.T.; Fortuny, A.; Donoso, P.N.; Sepúlveda, R.; Sastre, A.M. Cu(II) extraction using quaternary ammonium and quaternary phosphonium based ionic liquid. *Hydrometallurgy* 2014, 141, 89–96.
49. Kogelnig, D.; Stojanovic, A.; Jirsa, F.; Korner, W.; Krachler, R.; Keppler, B.K. Transport and separation of iron (III) from nickel(II) with the ionic liquid trihexyl(tetradecyl)phosphonium chloride. *Sep. Purif. Technol.* 2010, 72(1), 56–60.
50. Regel-Rosocka, M.; Cieszyńska, K.; Wiśniewski, M. Extraction of zinc(II) with selected phosphonium ionic liquids. *Przem. Chem.* 2006, 85, 651–654 (in Polish).
51. Wellens, S.; Thijs, B.; Binnemans, K. An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids. *Green Chem.* 2012, 14(6), 1657–1665.
52. Schlosser, S.; Martak, J. Extraction of lactic acid by phosphonium ionic liquids. *Sep. Purif. Technol.* 2007, 57(3), 483–494.

53. Cieszynska, A.; Wisniewski, M. Extractive recovery of palladium (II) from hydrochloric acid solutions with Cyphos IL 104. *Hydrometallurgy* 2012, *113-114*, 79–85.
54. Rybka, P.; Regel-Rosocka, M. Nickel (II) and cobalt (II) extraction from chloride solutions with quaternary phosphonium salts. *Separ. Sci. Technol.* 2012, *47*(9), 1296–1302.
55. Kumari, A.; Sinha, M.K.; Sahu, S.K.; Pandey, B.D. Investigation of a novel ionic liquid, Cyphos IL 104 for the solvent extraction of mineral acids. *Hydrometallurgy* 2015, doi:[10.1016/j.hydromet.2015.09.016](https://doi.org/10.1016/j.hydromet.2015.09.016).
56. Regel-Rosocka, M.; Wisniewski, M. Selective removal of zinc(II) from spent pickling solutions in the presence of iron ions with phosphonium ionic liquid Cyphos IL 101. *Hydrometallurgy* 2011, *110*(1–4), 85–90.
57. Regel-Rosocka, M.; Nowak, Ł.; Wiśniewski, M. Removal of zinc(II) and iron ions from chloride solutions with phosphonium ionic liquids. *Sep. Purif. Technol.* 2012, *97*, 158–163.
58. Wang, X.; Li, W.; Meng, S.; Li, D. The extraction of rare earths using mixtures of acidic phosphorous-based reagents or their thio-analogues. *J. Chem. Technol. Biotechnol.* 2006, *81*, 761–766.
59. Biswas, R.K.; Habib, M.A.; Singha, H.P. Colorimetric estimation and some physico-chemical properties of purified Cyanex 272. *Hydrometallurgy* 2005, *76*, 97–104.
60. Sato, T. Liquid-liquid extraction of rare-earth elements from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy* 1989, *22*, 121–140.
61. Gupta, B.; Malik, P.; Deep, A. Solvent extraction and separation of tervalent lanthanides and yttrium using cyanex 923. *Solvent Extr. Ion Exc.* 2003, *21*(2), 239–258.
62. Swain, B.; Otu, E.O. Competitive extraction of lanthanides by solvent extraction using Cyanex 272: Analysis, classification and mechanism. *Sep. Purif. Technol.* 2011, *83*, 82–90.