

Solvent extraction of praseodymium(III) from acidic nitrate medium using Cyanex 921 and Cyanex 923 as extractants in kerosene

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Abstract: Solvent extraction of praseodymium(III) from acidic nitrate medium by the neutral organophosphorous extractants Cyanex 921 and Cyanex 923 in kerosene was studied. The effects of various parameters like equilibration time, nitric acid concentration, nitrate ion concentration, extractant concentration, temperature, and nature of diluents on the extraction behavior of Pr(III) were investigated. The extraction of 0.001 M Pr(III) was quantitative (93%) from the aqueous phase containing 0.001 M HNO₃ and 0.1 M KNO₃ using 0.5 M Cyanex 921/1 M Cyanex 923. On the basis of slope analysis, the compositions of the extracted species were formulated as Pr(NO₃)₃.2Cyanex 921 and Pr(NO₃)₃.Cyanex 923. The percentage of extraction of Pr(III) was found to decrease with increases in temperature. The standard enthalpy and entropy changes were negative owing to the complexation with decrease in randomness without a compensatory disruption of the hydration sphere of the metal ion. Mineral acids like hydrochloric acid (0.008 M) and sulfuric acid (0.03/0.02 M) were effective for the stripping of Pr(III) from the loaded organic phase with 0.5 M Cyanex 921/1 M Cyanex 923.

Key words: Solvent extraction, Pr(III), acidic nitrate, Cyanex 921, Cyanex 923, stripping

1. Introduction

The rare earth metal group comprises the lanthanide elements from lanthanum to lutetium. They are essential for many applications in the chemical, metallurgical, optical, electronic, and ceramic industries. In most of these uses, the rare earths are responsible for high technological performance, by either participating in the intermediate manufacturing processes or integrating the finished products. As a consequence of these facts, research in the field of rare earths has become important. Praseodymium is a light rare earth metal usually found in 2 different kinds of ores, i.e. monazite and bastanasite.¹ A number of techniques are available for the estimation of Pr³⁺ in the aqueous phase.^{2,3} Solvent extraction is presently one of the major techniques used on the industrial scale for the separation and recovery of metals at micro and macro level. It plays a significant role as a separation technique because of its successful application in organic, pharmaceutical, and nuclear industries and hydrometallurgy.

The organophosphorous compounds have been extensively employed in solvent extraction and separation of rare earth elements.^{4,5} Solvating extractants have an atom capable of donating electron density to a metal in the formation of an adduct. Extractants of this type are basic in nature and facilitate extraction by coordinating with the metal and simultaneously replacing molecules of water of hydration. The extractive ability

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of neutral organophosphorous compounds increases in the order phosphates < phosphonates < phosphinates < phosphine oxides. Among these, the neutral phosphine oxide extractants have found wide applications in the purification and recovery of rare earths because of their higher stability, lower aqueous solubility, and rapid phase disengagement.^{6,7} Cyanex 921 is a solid extractant composed of tri-n-octyl phosphine oxide (93%) with average molecular weight 386. Cyanex 923 is a straight chain neutral extractant comprising a mixture of 4 trialkyl phosphine oxides with average molecular weight 348. It has low solubility in water and miscibility with all commonly used hydrocarbons.⁸ Gupta et al.⁹ have studied the extraction behavior of trivalent lanthanides along with Y(III) using Cyanex 923 in toluene and predicted the extraction species as $\text{Ln}(\text{NO}_3)_3 \cdot 2\text{Cyanex 923}$. Awwad et al.¹⁰ have investigated the extraction of Eu(III) from nitrate medium using Cyanex 921 in toluene. They reported the composition of the extracted species as $\text{Eu}(\text{NO}_3)_3 \cdot 3\text{Cyanex 921}$ and the extraction increased with increases in pH. The solvent extraction of cerium(IV) from simulated H_2SO_4 leaching of bastnaesite by Cyanex 923 was studied by Liao et al.¹¹ The results showed that Cyanex 923 can extract Ce(IV) as $\text{Ce}(\text{HSO}_4)_2\text{SO}_4 \cdot 2\text{Cyanex 923}$. The results also showed that temperature did not affect the extraction process. Reddy et al.¹² have studied the extraction of lanthanum from ammonium thiocyanate medium using tri-n-octyl phosphine oxide (TOPO) and dibenzyl sulfoxide (DBSO) in carbon tetrachloride. They reported decreases in extraction with increases in the metal ion concentration and temperature. The composition of the extracted species was found to be $\text{La}(\text{SCN})_3 \cdot 3\text{TOPO}$. Cyanex 923 has been suggested to be an efficient extractant for the trivalent lanthanides and yttrium as reported by Reddy et al.¹³ Hui et al.¹⁴ demonstrated the extraction of lanthanum with purified Cyanex 923 in heptane from nitrate medium by the Arsenazo III method. The results showed that the extraction process is controlled by both chemical reaction and diffusion.

The authors have already reported the extraction of Nd(III) from dilute nitric acid medium using Cyanex 272 and its binary mixture with Cyanex 921/Cyanex 923¹⁵ and using Cyanex 921 as extractant from acidic nitrate medium.¹⁶ As rare earths belong to the category of hard acids, according to the hard soft acid base concept (HSAB), they have affinity for the hard donor ligands containing oxygen donor atoms. Since Cyanex 921 and Cyanex 923 both have more electronegative oxygen as the donor atom, they can extract the metal from the aqueous to the organic phase. In the present investigation, an attempt was made to study the extraction of Pr(III) using Cyanex 921 and Cyanex 923 in kerosene from acidic nitrate medium, since there are no reports on the detailed study of this extraction system. The effects of various parameters like equilibration time, acid concentration, nitrate ion concentration, extractant concentration, temperature, and diluents on the extraction of Pr(III) were investigated. The nature of the extracted species was ascertained by evaluating the distribution ratio (D) while varying the extractant and nitrate ion concentration on the basis of slope analysis. Stripping studies were carried out to recover the metal from the loaded organic phase. The efficiencies of both extractants were compared.

2. Results and discussion

2.1. Effect of equilibration time

The extraction equilibrium of 0.001 M Pr(III) from 0.001 M HNO_3 and 0.1 M KNO_3 using 0.1 M Cyanex 921 and 0.1 M Cyanex 923 was studied at different intervals of time varying from 2 to 60 min. The equilibrium was reached in 20 min as shown in Figure 1. The extraction of Pr(III) was 58.4% with 0.1 M Cyanex 921 and 57.6% with 0.1 M Cyanex 923 in 20 min. A further increase in shaking time up to 60 min had no adverse effect on the extraction. Therefore, in all experiments a 20-min shaking time was maintained.

2.2. Effect of nitric acid concentration

The effect of nitric acid concentration on the extraction of 0.001 M Pr(III) from 0.1 M KNO_3 using 0.1 M Cyanex 921 and 0.1 M Cyanex 923 was studied in the concentration range from 0.001 M to 0.04 M. It was observed that the percentage of extraction of 0.001 M Pr(III) increased from 58.5% to 69.2% with 0.1 M Cyanex 921 and from 57.6% to 64.3% with 0.1 M Cyanex 923 with an increase in nitric acid concentration from 0.001 M to 0.008 M and then decreased with further increases in nitric acid concentration (Figure 2). The decrease in the extraction of metal with increases in acid concentration may be due to the extraction of acid by the neutral organophosphorous extractants.¹⁷ In order to examine the extraction of HNO_3 by neutral extractants (Cyanex 921/Cyanex 923) under the present extraction conditions, experiments were carried out in the absence of Pr(III) in the aqueous phase and it was observed from the data given in Table 1 that with an increase in HNO_3 molarity acid extraction increases.

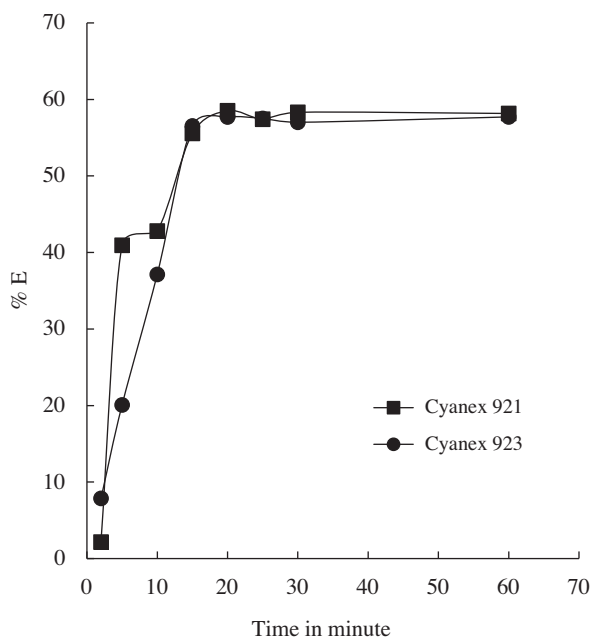


Figure 1. Effect of equilibration time on the extraction of 0.001 M Pr(III) from 0.001 M HNO_3 and 0.1 M KNO_3 using 0.1 M Cyanex 921 and 0.1 M Cyanex 923 in kerosene.

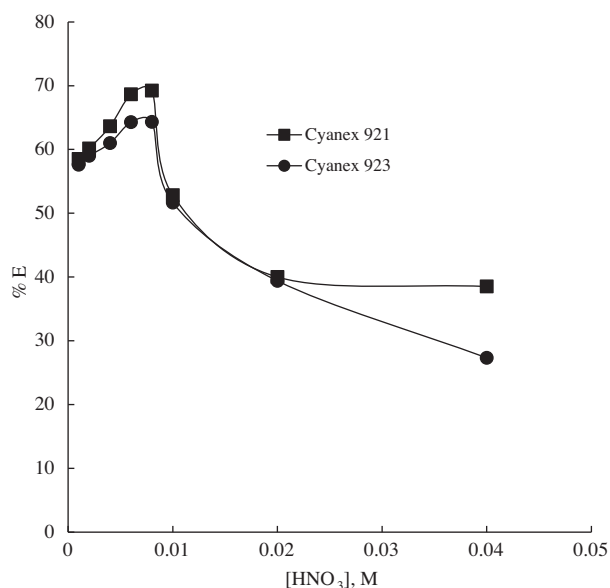


Figure 2. Effect of nitric acid concentration on the extraction of 0.001 M Pr(III) from 0.1 M KNO_3 using 0.1 M Cyanex 921 and 0.1 M Cyanex 923 in kerosene.

Table 1. Effect of Cyanex 921/Cyanex 923 on extraction of HNO_3 from 0.1 M KNO_3 in the absence of Pr(III).

[HNO_3], M	% Extraction	
	Cyanex 921	Cyanex 923
0.01	32.0	34.5
0.02	57.0	42.8
0.04	72.4	67.5

2.3. Effect of nitrate ion concentration

The involvement of nitrate ion in the extracted complex was studied by varying the nitrate ion concentration from 0.3 M to 1 M by adding required amounts of KNO_3 with a constant H^+ ion concentration (0.001 M)

in the aqueous phase for the extraction of 0.001 M Pr(III) with 0.1 M Cyanex 921 and 0.1 M Cyanex 923. The percentage of extraction of metal increased from 60% to 90.3% for Cyanex 921 and from 60% to 83.9% for Cyanex 923 with an increase in nitrate ion concentration from 0.3 M to 0.6 M and then decreased with further increases in concentration in both cases.¹⁶ The linear plot of log D versus log $[\text{NO}_3^-]$ (Figure 3) yielded a slope of 2.8 with 0.1 M Cyanex 921, whereas with 0.1 M Cyanex 923 a slope of 2.6 was obtained (in the range 0.3 M-0.6 M), which indicates third-power dependence of nitrate ion concentration, revealing the presence of 3 nitrate ions in the extracted complex. The increase in extraction due to the increase in the concentration of nitrate ions may be attributed to a common ion effect as metal nitrate species have been extracted.¹⁸ The formation of extractable metal complexes depends on the activity of water molecules in the aqueous phase. Due to the addition of excess potassium nitrate to the aqueous phase the activity of water molecules decreases and thus decreases the extraction of metals into the organic phase.¹⁹

2.4. Effect of extractant concentration

Extraction of 0.001 M Pr(III) from 0.001 M HNO_3 and 0.1 M KNO_3 was carried out by varying the extractant concentrations in the range 0.01–0.5 M of Cyanex 921 and 0.01–1 M of Cyanex 923 in kerosene. It was observed that with respect to the effect of extractant concentration in the organic phase the recovery of Pr(III) increased from 0.6% to 92.6% and from 5.7% to 92.8% with increases in Cyanex 921 and Cyanex 923 concentrations, respectively. The plot of log D versus log [Extractant] (Figure 4) yielded a slope of 1.8 with Cyanex 921 and 1.0 with Cyanex 923. The slope values of 1.8 and 1.0 indicated the average number of Cyanex 921 and Cyanex 923 in the extracted complexes to be 2 and 1, respectively.

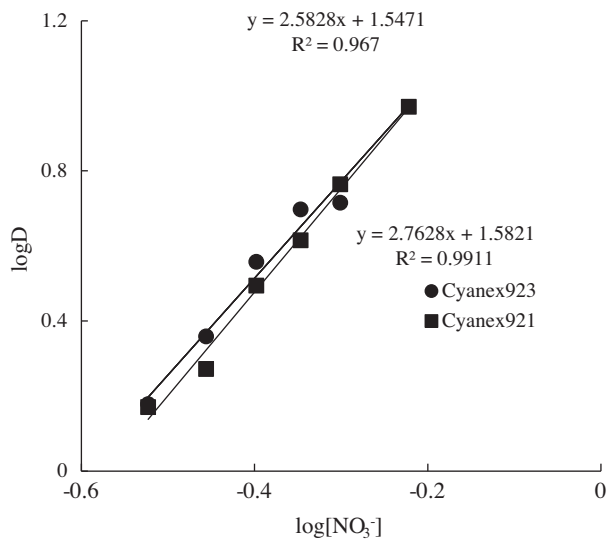


Figure 3. Plot of log D versus log $[\text{NO}_3^-]$ for the extraction of 0.001 M Pr(III) from 0.001 M HNO_3 using 0.1 M Cyanex 921 and 0.1 M Cyanex 923.

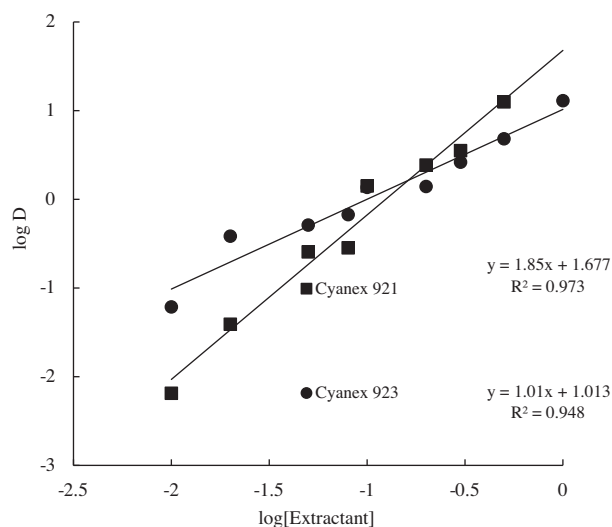
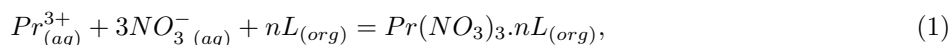


Figure 4. Plot of log D versus log [extractant] for the extraction of 0.001 M Pr(III) from 0.001 M HNO_3 and 0.1 M KNO_3 .

2.5. Extraction equilibrium

Based on the slope analysis results, the extraction equilibrium can be proposed as



where L stands for Cyanex 921 or Cyanex 923 and the distribution ratio D can be written as

$$D = [Pr(NO_3)_3.nL]_{(org)}/[Pr^{3+}]_{(aq)}, \quad (2)$$

where $n = 2$ for Cyanex 921 and $n = 1$ for Cyanex 923.

The extraction equilibrium constant can be represented as

$$K_{ex} = [Pr(NO_3)_3.nL]_{(org)}/[Pr^{3+}]_{(aq)}[NO_3^-]_{(aq)}^3[L]_{(org)}^n. \quad (3)$$

From the value of K_{ex} the change in standard free energy of the extraction process (ΔG_{ex}°) was calculated using the following relation:

$$\Delta G_{ex}^\circ = -RT \ln K_{ex} \quad (4)$$

From various experimental observations the average values of extraction equilibrium constants were calculated and using these in Eq. (4) the values of ΔG_{ex}° were obtained and are presented in Table 2. The negative values of change in standard free energy show that the extraction processes under consideration are spontaneous.

Table 2. Extraction equilibrium constants and change in standard free energy for the system of 0.001M Pr(III) from acidic nitrate medium using Cyanex 921/Cyanex 923 in kerosene.

Extraction systems	Cyanex 921		Cyanex 923	
	$K_{ex(Average)}$	ΔG_{ex}° (kJ/mol)	$K_{ex(Average)}$	ΔG_{ex}° (kJ/mol)
HNO ₃ variation	1.39×10^5	-28.89	1.28×10^4	-23.15
KNO ₃ variation	2.41×10^5	-28.57	2.46×10^4	-23.90
Extractant variation	2.47×10^5	-27.62	2.81×10^4	-23.71

2.6. Effect of temperature

The effect of temperature on the extraction of 0.001 M Pr(III) from 0.001 M HNO₃ and 0.1 M KNO₃ with 0.1 M Cyanex 921 and 0.1 M Cyanex 923 was studied by varying the temperature from 298 K to 338 K. It was observed that with an increase in temperature the extraction decreased from 58.4% to 17% and from 57.6% to 23% when Cyanex 921 and Cyanex 923 were used as extractants, respectively. This may be due to the decreased stability of the extracted metal complex at higher temperature. The standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were calculated by plotting the $\log K_{eq}$ vs. $1000/T$ using the Van't Hoff equation:

$$\log K_{eq} = -\Delta H^\circ/2.303RT + \Delta S^\circ/2.303R \quad (5)$$

From the graph (Figure 5), the ΔH° and ΔS° were found to be $-35.2 \text{ kJ mol}^{-1}$ and $-19.3 \text{ J K}^{-1} \text{ mol}^{-1}$ for 0.1 M Cyanex 921, whereas for 0.1 M Cyanex 923 the values were $-30.4 \text{ kJ mol}^{-1}$ and $-23.2 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The negative values of ΔH° and ΔS° indicate the extraction to be exothermic and formation of a stable complex in the extraction process. This may be due to the displacement of some water molecules or because of the loss in entropy during complexation, which is larger than the gain in entropy due to dehydration.

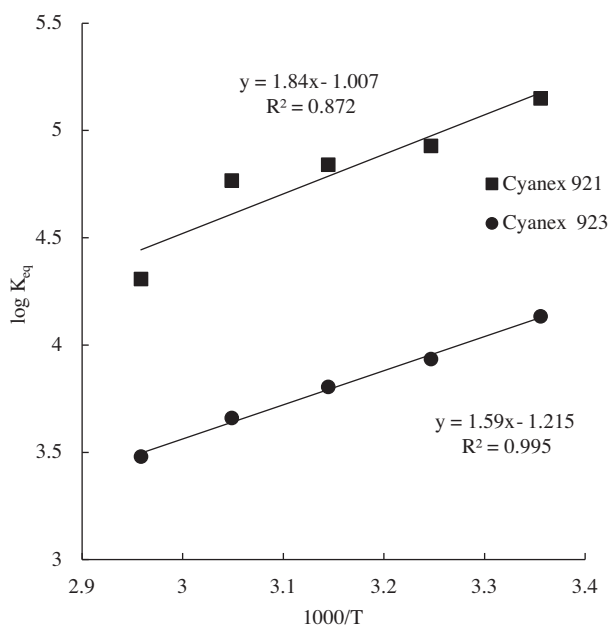


Figure 5. Plot of $\log K_{eq}$ versus $1000/T$ for the extraction of 0.001 M Pr(III) from 0.001 M HNO_3 and 0.1 M KNO_3 using 0.1 M Cyanex 921 and 0.1 M Cyanex 923.

2.7. Effect of diluents

The selection of extractant and diluent are 2 important aspects of a successful solvent extraction system. A radioactive or ionizing environment can destroy the diluent or the extractant. The diluent as well as the extractant should be completely incinerable in order to minimize waste production. The diluent has to be cheap, give practically negligible losses, and should have good solubility to the extractant. The nature of the diluent influences the attractive energies between the extracted species and the organic phase. In this context, the effect of diluents (kerosene, benzene, toluene, xylene, and chloroform) on the extraction behavior of 0.001 M Pr(III) with 0.1 M Cyanex 921/0.1 M Cyanex 923 from 0.001 M HNO_3 and 0.1 M KNO_3 was investigated (Table 3). The results confirmed that the extraction of Pr(III) was maximum when kerosene was used as diluent, which follows the same trend as reported by El-Nadi.²⁰ The percentage of extraction decreased with increases in the dielectric constants of diluents. Although benzene, toluene, xylene, and chloroform have higher dielectric constants than kerosene, the percentage of extraction of Pr(III) was lowest in benzene. This may be because of the lower solubility of the extracted species in the organic phase or may be due to different interactions between diluents and extractants that occur in aromatic and nonaromatic diluents.²¹

Table 3. Effect of diluents on the extraction of Pr(III) using 0.1 M Cyanex 921 and 0.1 M Cyanex 923.

Diluents	Dielectric constant	D_1 (Cyanex 921)	D_2 (Cyanex923)
Kerosene	1.8	1.41	1.36
Benzene	2.28	Turbidity	0.05
Toluene	2.39	0.16	0.096
Xylene	2.54	0.29	Turbidity
Chloroform	4.81	0.22	0.38

2.8. Stripping

The loaded organic phase was prepared by mixing 100 mL of aqueous solution containing 0.001 M Pr(III), 0.001 M HNO₃, 0.1 M KNO₃, and organic solution of 0.5 M Cyanex 921 or 0.1 M Cyanex 923. After phase separation, the loaded organic was filtered through 1PS phase separation paper. Various concentrations of acids (HCl and H₂SO₄) were used as strippants to recover the metal from the loaded organic phase containing 0.131 g/L Pr(III). It was found that 0.008 M HCl and 0.03 M H₂SO₄ can effectively recover 100% of the metal from the loaded organic phase of 0.5 M Cyanex 921, whereas from the loaded organic phase of 1 M Cyanex 923, 0.008 M HCl and 0.02 M H₂SO₄ can effectively strip the metal (Table 4).

Table 4. Stripping of praseodymium(III) from the loaded organic phase.

Organic phase	0.5 M Cyanex 921		1 M Cyanex 923	
	HCl % Stripping	H ₂ SO ₄ % Stripping	HCl % Stripping	H ₂ SO ₄ % Stripping
0.001	75.8	61.5	50	32.4
0.005	91.6	82.4	90.2	83
0.008	100	83.6	100	92
0.01	45	85.8	62.3	95
0.02	33	91.2	29.4	100
0.03	31	100	25	99.2

In conclusion, solvent extraction of Pr(III) from acidic nitrate medium was studied using neutral organophosphorous reagents, i.e. Cyanex 921 and Cyanex 923, in kerosene. Metal transfer to organic phase follows the solvation mechanism. With 0.5 M Cyanex 921 the extraction was 92.6%, whereas with 0.5 M Cyanex 923 it was 92.8%. Under similar experimental conditions, Cyanex 921 showed better extractability for Pr(III) as compared to Cyanex 923, which may be due to the higher molecular weight of the former. On the basis of slope analysis results, the stoichiometry of the metal species in the organic phase was proposed to be Pr(NO₃)₃.2Cyanex 921 and Pr(NO₃)₃.Cyanex 923. The extraction process was accompanied by a decrease in enthalpy and entropy. Kerosene was found to be the best diluent for the extraction of Pr(III) under the present experimental conditions. Pr(III) was stripped effectively using 0.008 M HCl and 0.03 M H₂SO₄ from the loaded organic phase of 0.5 M Cyanex 921 and from 1 M Cyanex 923 with 0.008 M HCl and 0.02 M H₂SO₄.

3. Experimental

3.1. Materials

The stock solution of Pr(III) (0.01 M) was prepared by dissolving its oxide in a small volume of concentrated nitric acid and then heating to remove excess acid and diluting to 100 mL with double distilled water. Cyanex 921 and Cyanex 923 supplied by the Cytex Canada Inc. (gift sample) were used without further purification. Distilled kerosene was used as diluent. Organic phase solution was prepared by dissolving the required amount of the extractants in kerosene and then diluting to the required concentration. All other reagents used were of analytical grade.

3.2. Methods

Metal distribution equilibria were determined by means of a technique in which equal volumes (10 mL) of aqueous and organic phases were contacted in a separating funnel and shaken with the help of a mechanical

shaker for 20 min. After the disengagement of phases, the aqueous phase was analyzed to determine the metal concentration by the Arsenazo III method using an ELICO UV-VIS spectrophotometer. Concentration of Pr(III) in the organic phase was calculated from the mass balance using the measured concentration of metal in the aqueous phase before and after extraction. The distribution ratio (D) was calculated from the ratio of the metal concentration in the organic phase to that in the aqueous phase after extraction. The percentage of extraction (% E) was determined from the D value as $100(D/D + 1)$. The temperature variation studies were performed by shaking equal volumes of aliquots in a thermostat shaker by maintaining a particular temperature for the required time. The stripping percentage was calculated as $\% \text{ Stripping} = [C_s / (C_o - C)] \times 100$, where C_o is the original metal ion concentration in the aqueous phase before extraction, C is the metal ion concentration in the aqueous phase after extraction, and C_s is the metal ion concentration after stripping.

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