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Solvent Extraction and Separation of Nd, Pr and Dy from Leach Liquor of Waste NdFeB Magnet Using the Nitrate Form of Mextral®336At in the Presence of Aquo-Complexing Agent EDTA

Aarti Kumari ^{1,2}, Kamala Kanta Sahu ^{1,2} and Sushanta Kumar Sahu ^{1,2,*}

¹ Metal Extraction & Recycling Division, CSIR-National Metallurgical Laboratory, Jamshedpur 831007, India; aartikumari0809@gmail.com (A.K.); kksahu@nmlindia.org (K.K.S.)

² Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

* Correspondence: sushanta29@gmail.com; Tel.: +91-647-234-5273

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Abstract: Solvent extraction and separation of Pr, Nd and Dy from a synthetic leach solution of spent NdFeB magnet from wind turbines in the presence of aquo-complexing agent Ethylenediaminetetraacetic acid (EDTA) was studied using the nitrate form of Mextral®336At ([336At][NO₃]) as an extractant. The effect of different process parameters such as pH, extractant, nitrate, and EDTA concentrations on the extraction of Pr, Nd and Dy was studied. The extraction of these rare earths elements follows the order Pr > Nd > Dy, whereas EDTA forms stable complexes in the order Dy > Nd > Pr. The synergy of these two effects improved the selectivity among these elements as compared to when no aquo-complexing agent was used. The mechanism of extraction of rare earth elements was established by slope analysis method. The Fourier-Transform Infrared Spectroscopy (FTIR) spectra of [336At][NO₃] and extracted Nd complex were recorded to understand the interaction of extractant with rare earth metal ions in the organic phase.

Keywords: Spent NdFeB magnet; Solvent extraction; Extractant; EDTA; Separation factor

1. Introduction

Superior magnetic properties make NdFeB magnets suitable for various applications such as the hard drive of computers, amplifiers, MRI machines, and wind turbines. The NdFeB magnet industry is growing globally at a rate of 20% each year [1]. However, primary resources of rare earth elements are limited and they occur together in mineral deposits, which make their separation tedious and lead to over production of less demanding rare earth metals. For 1 MW of electricity generation, typically 250–650 kg of NdFeB magnets are required for the generators of wind turbines [2,3], and the life span of such magnets is only ~10 years. Furthermore, during shaping of the magnets, 20–30% of the magnet is wasted as sludge. Thus, there is huge generation of waste magnet which can serve as a potential source of Nd, Pr and Dy. Processing of spent magnets for the recovery of rare earth elements will reduce the burden on primary resources and their separation will be simpler, as these resources do not contain all rare earth elements.

A variety of approaches, such as liquid metal extraction, flux method, and chemical vapor transport method, have been attempted in the past for the recovery of rare earth elements from spent NdFeB magnets [4–6]. These processes are highly energy intensive and rare earth products obtained are in an impure form. The hydrometallurgical process is known as the most suitable method for obtaining metal of desired purity. Studies were carried out for selective recovery of rare earths from spent NdFeB magnets using a variety of mineral acids (H₂SO₄, HNO₃, HCl etc.) to obtain rare earth

(Nd³⁺, Pr³⁺ and Dy³⁺) in aqueous solution. However, individual separations of these metal ions are still a difficult task.

The solvent extraction process is the most suitable method for the separation of individual rare earths. Various studies have been carried out for the separation of rare earths using cation exchange extractants. Different cation exchange (acidic) extractants including Cyanex 272, D2EHPA, PC88A, and Cyanex 301 have been studied for the separation of La, Pr and Nd [7]. Cyanex 272 showed the best extraction efficiency among all extractants. The separation of heavy rare earths (Y, Dy, Tb and Gd) from crude concentrate using 2-ethylhexylphosphonic acid, mono-2-ethylhexyl ester (EHEHPA) as the extractant have also been studied [8]. Using two cycles of extraction, scrubbing and stripping, nuclear grade Dy₂O₃ was produced with more than 98% recovery. Acidic extractants release H⁺ ions in the aqueous phase, which lowers the extraction efficiency of extractants. Therefore, various studies have been carried out for the separation of rare earths using acidic extractants saponified by NaOH or NH₃ solution [9,10]. The extraction of Nd(III) from chloride media have been studied using 40% saponified PC88A [11]. Similarly, extraction studies have been carried out for the separation of La, Ce, Pr and Nd using saponified PC-88A to obtain Nd₂O₃ oxide of purity >97% [12]. Although better separation can be achieved by using saponified extractants, the possibility of emulsification and third phase formation were found as major drawbacks during the extraction process. In addition, release of Na⁺ or NH₄⁺ ions into the aqueous phase during extraction also affects the environment adversely [13]. To solve these problems, many separation studies were carried out by a mixture of acidic extractants with amine based extractants. Separation studies of Pr and Nd were carried out using a mixture of Cyanex 272 and different amine extractants such as Alamine 336, TOA, TEHA and Aliquat 336 [14,15]. The mixture of Cyanex 272 and Alamine 336 showed the maximum synergistic factors of 14.2 for Pr and 12.2 for Nd by using a 0.5 mole fraction of Cyanex 272 [14]. Attempts were also made by using neutral and anion exchange extractants for the separation of praseodymium, neodymium and dysprosium.

In the last decade, ionic liquid has emerged as a future solution for the separation of metal ions. Ionic liquid is the organic salt consisting of an organic cation and organic or inorganic anion, with a melting point below 100 °C. Various studies were carried out for the extraction of Nd, Pr and Dy using a variety of ionic liquids used as extractant or diluents. The extraction study of Pr, Nd and Dy derived from spent NdFeB magnet was carried out with TBP by using ionic liquid Aliquat nitrate ([A336][NO₃] or R₄N·NO₃) as diluent [16]. A significant extraction of Nd(III) was obtained in the ionic liquid phase through repeated extraction. Another ionic liquid, trihexyl(tetradecyl)phosphonium nitrate was used for the separation of cobalt from rare earths (Nd, Dy) [17]. The detailed extraction study of Nd with Cyanex 923 was carried out in presence of ionic liquid containing the bis(trifluoromethylsulfonyl)imide anion with five different cations. It was found that ionic liquids with hydrophilic cation, [C₄mim][Tf₂N] and [N₁₄₄₄][Tf₂N], extract Nd(III) efficiently in comparison with hydrophobic cations [18]. Other ionic liquids, such as [Hbet][Tf₂N] and DODGAA, were also explored for the extraction of rare earths [19,20]. Some key extractant systems used in the literature for the separation of praseodymium, neodymium and dysprosium are summarized in Table 2.

For effective separation of chemically similar rare earth ions, new extraction systems were developed by adding water soluble complexing agent in the aqueous phase. The complexing agents form the thermodynamic stable chelate complex, which consequently enhances the selectivity of one metal ion by masking other ions in the aqueous phase. This kind of system could be very useful for the separation of adjacent rare earth ions such as praseodymium and neodymium. In Table 1, different extraction systems were summarized for separation of rare earths (mainly Pr, Nd and Dy) in the presence of water-soluble complexing agents. Several cation exchange extractants, such as D2EHPA, HEHEHPA, and P204 were studied in the presence of different complexing agents (lactic acid, citric acid, formic acid, acetic acid, EDTA, DTPA etc.) for the separation of rare earth ions [21–23]. The separation of La, Pr and Nd using Cyanex 272 and PC88A was studied by adding the complexing agent EDTA to the aqueous solution [24]. The separation studies were carried out at two pH conditions (2.8 and 4.9), with and without EDTA addition. It was found that the extraction of

Pr and Nd was suppressed by the addition of EDTA, which enhances the possible separation between Pr/Nd and La. Similarly, the separation of Ce, La, Pr and Nd was studied with acidic extractant P2O4 in the presence of two complexing agents: Lactic acid and citric acid [25]. The experiments for the separation of two adjacent rare earths Pr and Nd in D2EHPA-HCl-LA (lactic acid) extraction system have also been carried out [26]. The maximum separation factor for Nd/Pr was obtained as 1.57 by using 0.6M lactic acid in aqueous solution at pH 3.5. An extraction and separation study of Ce (III) and Pr(III) was carried out with P2O4 by adding different ratios of citric acid and lactic acid in aqueous solution as the complexing agent [27]. It was found that with an increase in the ratio of citric acid:lactic acid, the separation factor increased and the maximum separation factor value was achieved as 5.78. Overall, it was observed that separation studies of rare earths were mostly carried by using acidic extractants in the presence of complexing agents.

There is scant information available on the separation behavior of rare earths using ionic liquid extractants in the presence of complexing agents. Rare earth ions forms stable anionic species in the aqueous phase; therefore, quaternary ammonium salts (R_4N^+) may be effective for the separation of rare earth ions [28–31]. Therefore, in the present investigation, it is aimed to study the extraction of rare earth metal ions with an ionic liquid, trioctyl-methyl-ammonium nitrate, or $R_4N \cdot NO_3$, in the presence of complexing/masking agent EDTA and to understand the influence of complexing agent on the separation of Pr, Nd and Dy. For this, the effect of pH, extractant concentration, and EDTA concentration were studied in detail. The extraction percentage and separation factor values were calculated for each experiment in order to determine the selectivity between Pr, Nd and Dy. The mechanism of extraction of metal ions with $R_4N \cdot NO_3$ was also explored. FTIR (Fourier-Transform Infrared Spectroscopy) analysis was also carried out to comprehend the interaction of rare earth ions in the loaded organic phase.

Table 1. Different extractant systems for separation of rare earths in presence of water-soluble complexing agents.

Rare Earths	Extractant	Diluent	Aqueous Medium	Water-soluble Complexing Agent	Remarks	Reference
La, Pr and Nd	Cyanex 272, PC88A	Escaid 110	Chloride	EDTA	PC88A has higher extraction efficiency than Cyanex 272. Addition of EDTA in aqueous phase suppressed the extraction of Pr and Nd due to formation of anionic complexes.	[24]
La, Ce, Pr, Nd	P2O4	Kerosene	Chloride	Lactic acid, Citric acid	The separation factors for Ce/La, Pr/La and Nd/La were enhanced for the system containing both complexing agents, i.e., lactic acid and citric acid.	[25]
Pr and Nd	D2EHPA	Kerosene	Chloride	Lactic acid	Distribution ratio and separation factor increased by decreasing acidity and increasing lactic acid concentration. Best separation factor for Nd/Pr achieved was 1.57 at 0.6 M lactic acid concentration and pH 3.5.	[26]
Ce and Pr	P2O4	Kerosene	Chloride	Lactic acid Citric acid	The distribution ratio increased with increase in ratio of citric acid: lactic acid. The maximum separation factor of 5.78 was achieved.	[27]
Pr and Nd	D2EHPA	ISOPAR M	Nitrate	EDTA, DTPA	The extraction degree of Nd and Pr in DTPA is higher than EDTA. Effects of mixtures of EDTA and DTPA on the extraction were also evaluated. Studies carried out in electrostatic liquid-liquid contactor. The best separation factor was achieved as 2.	[39]
Nd, Pr (didymium solution)	[A336] [NO ₃]	naphtha-100	Nitrate	DTPA	DTPA forms 1:1 complex with rare earth ions, which helps in the separation of Nd-Pr. In 45 stage, 95% recovery of Nd was obtained with purity > 99%.	[40]
Light and Heavy Rare Earths	[A336][NO ₃]	-	Nitrate	EDTA	The addition of 0.2 M EDTA in 11 M nitrate aqueous solution enhanced the separation possibility between light and heavy rare earths as chelating agent forms stable complexes with Heavy rare earths.	[41]
Heavy Rare Earths	CA-100	-	Chloride	EDTA	Selective separation of Yttrium from impurities (Ho, Er, Tm, Yb, Lu due to formation of EDTA-Yttrium complex.	[22]
Nd, Dy, Fe, Co	[A336][SCN]	toluene	Chloride	EDTA	EDTA was used as stripping agent for the separation of Fe and Co from the deep eutectic solvent containing Nd, Dy, Fe, B and Co.	[42]

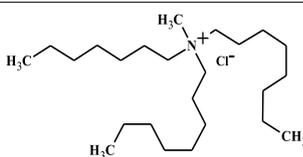
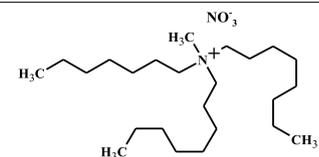
Table 2. Different solvent extractant systems related to the separation of praseodymium, neodymium and dysprosium.

Rare Earths	Extractant	Diluent	Aqueous Medium	Remarks	Reference
La, Nd, Pr	Cyanex 272, D2EHPA, PC88A, Cyanex 301	Escaid 110	Chloride	Cyanex 272 showed the best extraction efficiency among all extractants. The separation of La, Nd and Pr improved by using saponified extractant.	[7]
Y, Dy, Tb, Gd	EHEHPA	Kerosene	Chloride	Dy ₂ O ₃ were produced with more than 98% recovery. Two concentrates yttrium (>93%, 1st cycle) and terbium (>54%, 2nd cycle) were also produced.	[8]
Nd	PC88A and 40% saponified PC88A	Kerosene	Chloride	Distribution co-efficient was increased significantly by using saponified extractant.	[11]
La, Ce, Pr, Nd	Saponified PC-88A	Kerosene	Chloride	Nd ₂ O ₃ of >97% purity were produced using extraction, scrubbing and stripping steps.	[12]
Pr and Nd	Mixture of Cyanex 272 and amine extractants (Alamine 336, TOA and TEHA)	Kerosene	Chloride	Equimolar Combination of Cyanex 272 and Alamine 336 showed the best extraction ability and the maximum synergistic effect for Pr and Nd separation.	[14]
Nd	[A336] [DGA]	[A336] [NO ₃]	Nitrate	Extraction of Nd was found better by using [A336][DGA] in [A336][NO ₃] in comparison to HDGA in [A336][NO ₃], at pH values > 2	[29]
Nd, Eu, Tm	HDEHP	Benzene	Chloride, sulfate, nitrate	Antagonistic effects were observed the mixtures of HDEHP+TBP and HDEHP+TOPO	[32]
Dy	PC88A	Shellsol D70	Nitrate	The experimental equilibrium data were correlated with chemically based model.	[33]
Pr, Nd, La, Ce, Sm	20% saponified PC88A+iso-decanol	Kerosene	Chloride	Nd ₂ O ₃ were produced with recovery of >85% having purity >96% using 6 extractions, 18 scrubbing and 6 stripping stages. The separation factor for Nd/Pr was obtained as 1.64.	[34]
Nd, Pr, Ce and La	[A336] [NO ₃]	Shellsol AB	Nitrate	Mini plant trial were carried out with 190 L of feed solution to obtain 95% Nd ₂ O ₃ using 8 extractions, 6 scrubbing and 6 stripping stages.	[35]
Nd	Cyanex 921	Kerosene	Nitrate	With the aqueous phase containing 0.001 mol/L HNO ₃ and 0.1 mol/L KNO ₃ , 98% of Nd(III) was extracted using 0.5M extractant.	[36]
Pr, Nd, Dy	TBP	[A336][NO ₃]	Nitrate	By using 1.8M TBP, 95 g/L of Nd loaded in the ionic liquid phase at pH 2. Complete extraction of rare earths (Nd, Pr and Dy) in two contacts.	[16]
Nd, Dy, Co	trihexyl(tetradecyl)phosphonium nitrate	-	Nitrate	After separation of Cobalt, Na ₂ EDTA along with NH ₄ NO ₃ were used for selective stripping of Dy. By precipitation process, Nd ₂ O ₃ , Dy ₂ O ₃ and CoO were obtained with purities of 99.6%, 99.8% and 99.8%, respectively.	[17]
Nd	Cyanex 923	[C ₄ mim][Tf ₂ N], [N ₁₄₄₄][Tf ₂ N], [P ₆₆₆₁₄][Tf ₂ N], [C ₁₀ mim][Tf ₂ N], [N ₁₈₈₈][Tf ₂ N].	Nitrate	Ionic liquids with hydrophilic cation, [C ₄ mim][Tf ₂ N] and [N ₁₄₄₄][Tf ₂ N] extract Nd(III) efficiently by ion-exchange mechanism. Hydrophobic cation extract Nd(III) less efficiently due to its low solubility in the aqueous phase.	[18]
Nd	[Hbet][Tf ₂ N]	-	Chloride Nitrate, bis(trifluoromethylsulfonyl)imide	Extraction was possible from chloride, nitrate and bis(trifluoromethylsulfonyl)imide medium with similar distribution ratios.	[19]
Nd, Dy, Fe	DODGAA	[C ₈ mim][Tf ₂ N]	Nitrate	DODGAA showed higher selectivity for Dy and Nd compared with Fe through an SLM impregnated with the ionic liquid, [C ₈ mim][Tf ₂ N].	[20]
Nd, Fe	Cyphos IL 101	-	Chloride	More than 99% of iron selectively extracted in organic phase. Best separation factor of Nd/Fe was obtained as 8 × 10 ⁵ .	[37]
Nd	[C ₆ mim][DEHP], [C ₆ mpyr][DEHP], [N ₄₄₄₄][DEHP]	[C ₆ mim][NTf ₂], [C ₆ mpyr][NTf ₂], [N ₁₄₄₄][NTf ₂]	Nitrate	The extraction behaviour with [C ₆ mim][DEHP] and [C ₆ mpyr][DEHP] was found to be different in comparison with [N ₄₄₄₄][DEHP], particularly for pH in the extraction process.	[38]

2. Materials and Methods

A stock solution containing 0.12 M Nd, 0.03 M Pr, and 0.002 M Dy was prepared by dissolving appropriate amounts of the respective rare earth chlorides in distilled water. For solvent extraction studies, the stock solution was diluted 10 times and nitrate concentration was maintained by the addition of an appropriate amount of sodium nitrate. Ethylenediaminetetraacetic acid (EDTA) was used as the complexing/ masking agent, and was also added in appropriate quantities while diluting the stock solution. The pH of the aqueous solution was maintained by the addition of HNO₃ or NaOH solutions whenever required. Solvent extraction studies were carried out using the nitrate form of Mextral®336At ([³³⁶At][NO₃]) as extractant. Mextral®336At in chloride form ([³³⁶At][Cl]) was obtained from Kopper Chem, Chongqing, China which is basically trioctyl-methyl-ammonium chloride (R₄N·Cl). Prior to solvent extraction studies, trioctyl-methyl-ammonium nitrate (R₄N·NO₃) was prepared by converting trioctyl-methyl-ammonium chloride (Mextral®336At) into nitrate form by mixing with 2.5 M NaNO₃ solution three times in order to ensure complete exchange of chloride ions by nitrate ions [41]. The exchange was also confirmed by analysis of chloride ion in aqueous raffinate by Volhard's test. After three contacts with NaNO₃ solution, a negligible amount of chloride ions was detected in the raffinate. The properties of chloride (R₄N·Cl or [³³⁶At][Cl]) and nitrate form (R₄N·NO₃ or [³³⁶At][NO₃]) of Mextral®336At are given in Table 3. Commercial grade kerosene and iso-decanol were used as diluent and phase modifier, respectively. All other chemicals used in the experiments were of analytical grade.

Table 3. Properties of solvent extraction reagent.

Properties	Mextral®336At or [³³⁶ At][Cl]	[³³⁶ At][NO ₃]
IUPAC name	Trioctyl-methyl-ammonium chloride (C ₂₅ H ₅₄ NCl)	Trioctyl-methyl-ammonium nitrate (C ₂₅ H ₅₄ N ₂ O ₃)
Appearance	Yellow cream	Yellow liquid
Molecular weight	404.1 g/mol	430.7
Density	0.88–0.89 g/mL	0.90–0.95 g/mL
Structure		

Solvent extraction experiments were carried out by shaking 10 mL of each aqueous feed and organic phase solution for 15 min in a glass-stoppered vial with the help of a roto-spin shaker (Revotek, Kolkata, India) at room temperature (298 ± 2K) and 30 rpm. After equilibration, the solution was allowed to settle for a few minutes to ensure complete phase separation. All the solvent extraction experiments were performed in duplicate. Eutech pH 510 was used to measure pH of aqueous solutions before and after the experiments. The concentration of metal ions in the raffinate was analyzed by ICP-OES (Thermo Scientific, Waltham, MA, USA). The metal ions extracted into the organic phase were determined by material balance. From these values, the extraction percentage (%E), distribution coefficients (D) and separation factors (β) were calculated using Equations (1)–(3):

$$\%E = \frac{M_i - M_f}{M_i} \times 100 \quad (1)$$

$$D = \frac{M_i - M_f}{M_f} \quad (2)$$

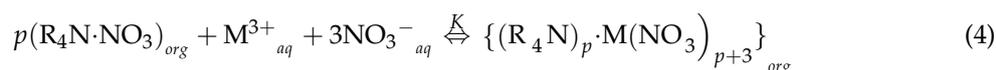
$$S.F. = \frac{D_1}{D_2} \quad (3)$$

where M_i and M_f represents the initial concentration of metal ions in the aqueous feed and final concentration of metal ions in the raffinate. The extraction percentage (%E) determines the efficiency of the extraction. The distribution coefficient (D) represents the ratio of metal ions transferred to organic phase to remaining metal ions in the raffinate solution. The separation factor (β) determines the selectivity of one lanthanide (Ln) ion over other, where D_1 and D_2 are the distribution coefficient of metal ions Ln_1 and Ln_2 , respectively.

3. Results and Discussion

The spent NdFeB magnet of wind turbines received from Regen Power Tech. Ltd, Chennai, India. contained 23.2% Nd, 5.6% Pr, 0.42% Dy, 67.3% Fe, 1% B, and other traces of elements like Al and Co as minor impurities. As mentioned in our earlier publication [43], a process was developed to selectively recover rare earth elements by leaching with 0.5 M HCl at 368 K and 100 g/L pulp density for 300 min. The leach solution contained 0.12 M Nd, 0.03 M Pr and 0.002 M Dy along with only 0.0002 M Fe and other minor impurities. Iron and other impurities were removed by precipitation at pH 3.5. In the present investigation, solvent extraction and separation of rare earth elements from 10 times diluted synthetic leach solution containing 0.012 M Nd, 0.003 M Pr and 0.0002 M Dy from nitrate medium with [336At][NO₃] was studied.

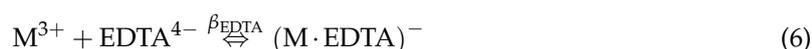
Extraction of rare earth elements from nitrate solution with [336At][NO₃] may be expressed as



where M^{3+} represents Nd³⁺, Pr³⁺ or Dy³⁺. The equilibrium constant K can be written as

$$K = \frac{[(R_4N)_p \cdot M(NO_3)_{p+3}]}{[R_4N \cdot NO_3]^p [M^{3+}]_{aq} [NO_3^-]^3} \quad (5)$$

The aqueous phase complexation of rare earth elements with EDTA is governed by the following equilibrium expression:



The stability constant, β_{EDTA} can be expressed as

$$\beta_{EDTA} = \frac{[(M \cdot EDTA)^-]}{[M^{3+}][EDTA^{4-}]} \quad (7)$$

From Equations (5), (6) and (7), the distribution ratio D of metal ion can be written as

$$D = \frac{K [R_4N \cdot NO_3]^p [NO_3^-]^3}{\{1 + \beta_{EDTA} \cdot [EDTA^{4-}]\}} \quad (8)$$

At very low concentrations of EDTA compared to metal ion concentration, particularly Nd and Pr concentration, formation of EDTA complex in the aqueous phase may be neglected and distribution ratio D can be rewritten as

$$D = K [R_4N \cdot NO_3]^p [NO_3^-]^3 \quad (9)$$

By taking the logarithm of both sides as

$$\log D = \log K + p \log [R_4N \cdot NO_3] + 3 \log [NO_3^-] \quad (10)$$

3.1. Effect of pH on Solvent Extraction of Nd, Pr and Dy

The effect of pH in the range of 0.1 to 5.0 on the solvent extraction of rare earth elements from 6 M NaNO₃ solution containing 0.012 M Nd, 0.003 M Pr, 0.0002 M Dy, and 0.0001 M EDTA with 0.43 M nitrate form of Mextral®336At (R₄N·NO₃) in kerosene was studied. It was found that aqueous feed pH had no significant effect on solvent extraction of rare earth elements, and the extraction of Pr, Nd and Dy remained almost constant at 91%, 85% and 42%, respectively, in the entire range of pH studied (Figure 1). It is clear from Figure 1 that the extraction of rare earth elements followed the order Pr > Nd > Dy and preferred to extract light rare earth elements first. This may be due to the fact that the stability of hydrated ions in the aqueous phase follows the order Pr < Nd < Dy. Therefore, the least soluble hydrated Pr³⁺ ion is easily dehydrated and converted to easily extractable species [28].

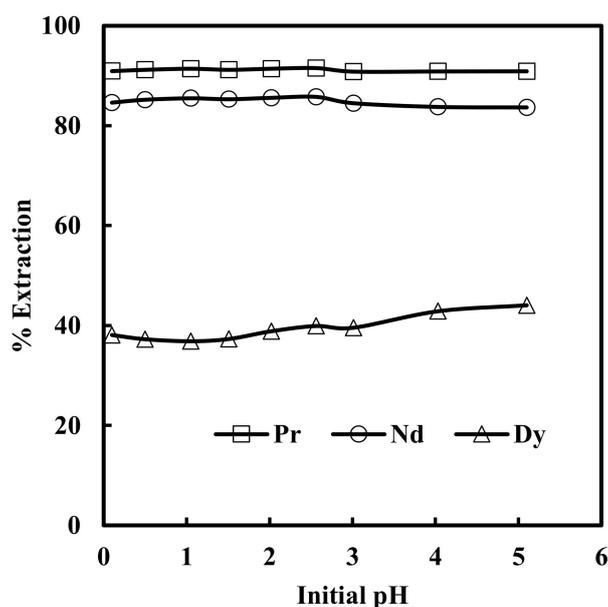


Figure 1. Effect of initial pH of aqueous feed solution on extraction of Pr, Nd and Dy by [336At][NO₃]. Aqueous phase: [NO₃⁻] = 6 M, [EDTA] = 0.0001 M. Organic phase: [336At][NO₃] = 0.43 M + 10% iso-decanol in kerosene.

3.2. Effect of [336At][NO₃] Concentration on Solvent Extraction of Nd, Pr and Dy

Here, solvent extraction of rare earth elements, from a 6 M NaNO₃ solution containing 0.012 M Nd, 0.003 M Pr, 0.0002 M Dy, and 0.0001 M EDTA with varying concentrations of [336At][NO₃] (in the range of 0.07–0.73 M) at constant aqueous feed pH of 3, was studied. Beyond 0.73 M [336At][NO₃] concentration, the organic phase was found to be comparatively viscous and phase separation was difficult. The results are depicted in Figures 2 and 3. It was found that extraction of Nd, Pr and Dy increased with an increase in [336At][NO₃] concentration, and 90% Pr, 82% Nd and 39% Dy were extracted with 0.43 M [336At][NO₃] (Figure 2). The extraction of Pr and Nd was found to be >95% along with 80% extraction of Dy by using 0.73 M [336At][NO₃]. The plot of log*D* vs. log[336At][NO₃] for Pr and Nd (Figure 3) had slopes of 3 and 2.8, respectively, with a correlation coefficient of 0.99, indicating association of 3 moles of the extractant for the extraction of 1 mole of metal ions into the organic phase (Equation 10). Separation factors between different pairs of rare earth elements (Pr/Dy, Nd/Dy and Pr/Nd) at varying concentrations of [336At][NO₃] were calculated and are shown in Figure 4. It was found that the separation factors for each pair of rare earth elements increased with an increase in [336At][NO₃] concentration up to 0.43 M. At 0.43 M [336At][NO₃], the separation factor values were 15.1 for Pr/Dy, 7 for Nd/Dy and 2.1 for Pr/Nd.

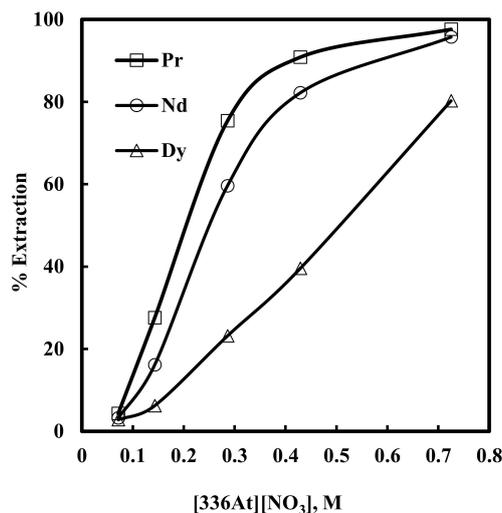


Figure 2. Effect of concentration of $[336\text{At}][\text{NO}_3]$ on extraction of Pr, Nd and Dy in presence of EDTA. Aqueous phase: $\text{pH} = 3$, $[\text{NO}_3^-] = 6 \text{ M}$, $[\text{EDTA}] = 0.0001 \text{ M}$. Organic phase: $[336\text{At}][\text{NO}_3] = 0.07\text{--}0.73 \text{ M} + 10\%$ iso-decanol in kerosene.

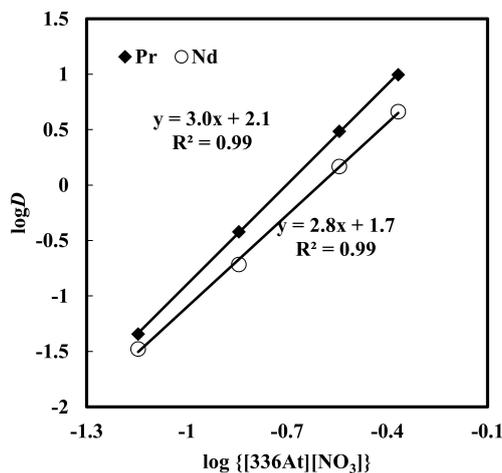


Figure 3. Effect of concentration of $[336\text{At}][\text{NO}_3]$ on distribution ratio. Aqueous phase: $\text{pH} = 3$, $[\text{NO}_3^-] = 6 \text{ M}$, $[\text{EDTA}] = 0.0001 \text{ M}$. Organic phase: $[336\text{At}][\text{NO}_3] = 0.07\text{--}0.43 \text{ M} + 10\%$ iso-decanol in kerosene.

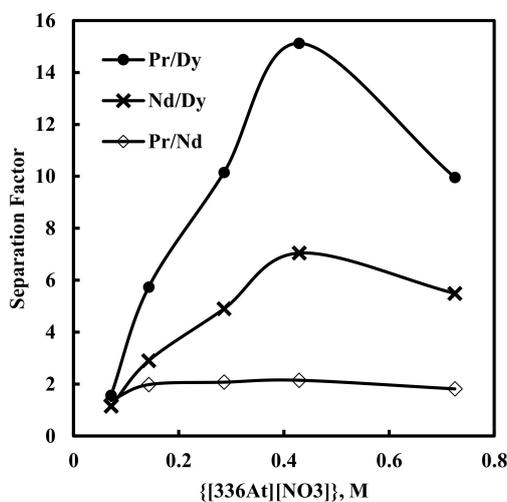


Figure 4. Effect of concentration of $[336\text{At}][\text{NO}_3]$ on separation factors. Aqueous phase: $\text{pH} = 3$, $[\text{NO}_3^-] = 6 \text{ M}$, $[\text{EDTA}] = 0.0001 \text{ M}$. Organic phase: $[336\text{At}][\text{NO}_3] = (0.07\text{--}0.73 \text{ M}) + 10\%$ iso-decanol in kerosene.

3.3. Effect of Nitrate Concentration on Solvent Extraction of Nd, Pr and Dy

Solvent extraction of rare earth elements under varying concentrations (1–6 M) of NaNO₃ in solutions containing 0.012 M Nd, 0.003 M Pr, 0.0002 M Dy, and 0.0001 M EDTA, with 0.43 M [336At][NO₃], was studied. The results depicted in Figure 5 show that the extraction of Pr, Nd and Dy increased with an increase in nitrate concentration in the aqueous phase. When nitrate concentration increased from 1 to 6 M, rare earth extraction increased from 3% to 90% for Pr, 1.9% to 82% for Nd and 0.8% to 39% for Dy. The plot of log*D* vs. log[NO₃[−]] for Pr and Nd (Figure 6) had slopes of 3.1 and 2.9, respectively. This indicates the involvement of 3 moles of nitrate ions for the extraction of one mole of metal ion into the organic phase. The overall reaction mechanism can be represented as

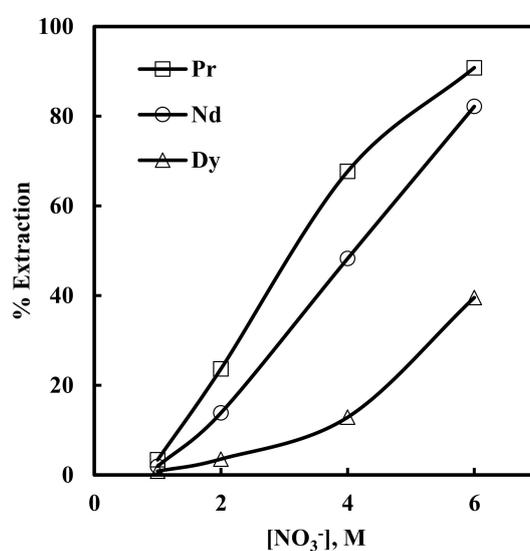
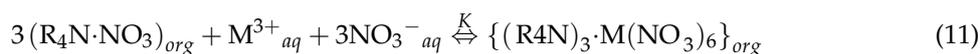


Figure 5. Effect of nitrate ion concentration on the extraction of Pr, Nd and Dy in the presence of EDTA. Aqueous phase: pH = 3, [EDTA] = 0.0001 M. Organic phase: [336At][NO₃] = 0.43 M + 10% iso-decanol in kerosene.

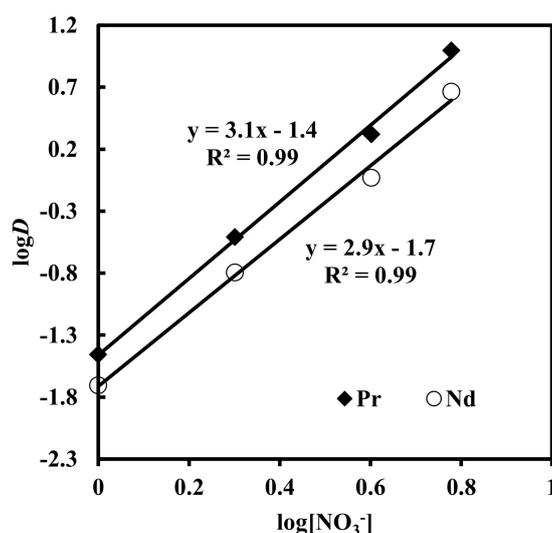


Figure 6. Effect of concentration of nitrate ion on distribution ratio. Aqueous phase: pH = 3, [EDTA] = 0.0001 M. Organic phase: [336At][NO₃] = 0.43 M + 10% iso-decanol in kerosene.

The separation factor values for different pairs of rare earth ions against various nitrate concentration are shown in Figure 7.

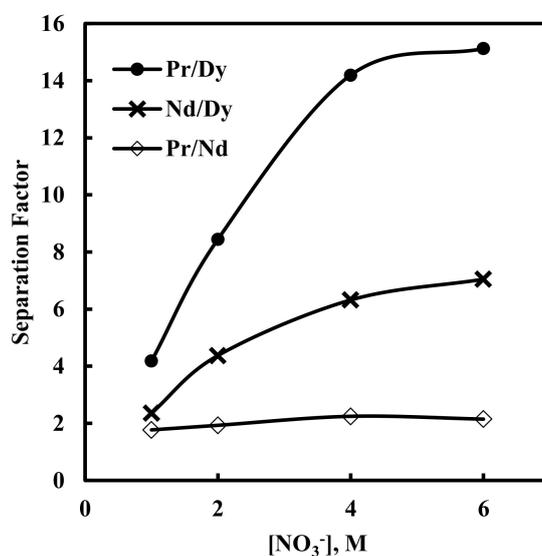


Figure 7. Effect of nitrate ion concentration on separation factors. Aqueous phase: pH = 3, [EDTA] = 0.0001 M. Organic phase: [336At][NO₃]= 0.43 M + 10% iso-decanol in kerosene.

3.4. Effect of EDTA on Solvent Extraction of Nd, Pr and Dy

In order to investigate the effect of complexing agent EDTA, solvent extraction of rare earth elements were studied from 6 M NaNO₃ solutions containing 0.012 M Nd, 0.003 M Pr, and 0.0002 M Dy, with 0.43 M [336At][NO₃], and varying concentrations of EDTA in the range of 0.0001–0.005 M in the aqueous phase (assuming EDTA will make 1:1 complex with the rare earth ions). The results are depicted in Figure 8. It is clear from Figure 8 that the extraction of rare earth metal ions decreased with an increase in EDTA concentration. This is due to the fact that EDTA forms thermodynamically stable complexes with rare earth metal ions in the aqueous phase and suppresses their further extraction into the organic phase, as shown in Equation 6.

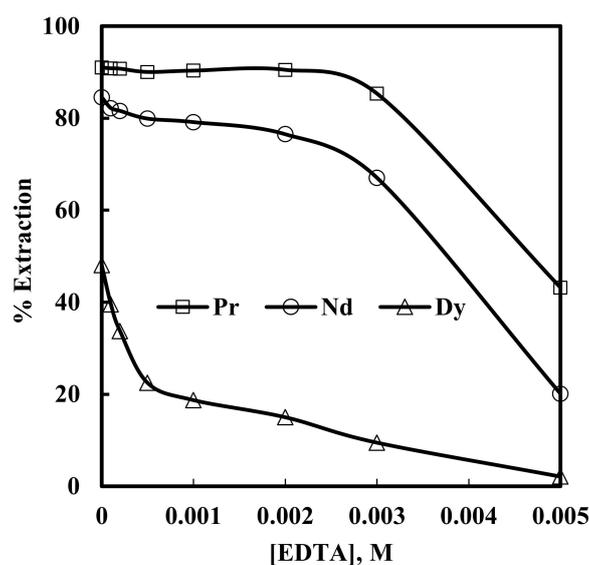


Figure 8. Effect of EDTA concentration on the extraction of Pr, Nd and Dy. Aqueous phase: pH = 3, [NO₃⁻] = 6 M. Organic phase: [336At][NO₃] = 0.43 M + 10% iso-decanol in kerosene.

The plot of separation factor values against EDTA concentrations is shown in Figure 9. It is interesting to observe that separation factor values for Pr/Dy and Nd/Dy increased with an increase in EDTA concentration up to 0.003 M EDTA. Conversely, when EDTA was not used in the aqueous solution, the separation factor values for Pr/Dy, Nd/Dy and Pr/Nd were found to be 10.9, 5.9 and 1.8, respectively. However, when 0.003 M EDTA was used as the complexing agent, separation factor values increased to 55.6, 19.4 and 2.9, respectively (Table 4). Beyond 0.003 M EDTA the separation factor values decreased continuously. The stability constants ($\log \beta_{\text{EDTA}}$) of Pr, Nd and Dy ions with EDTA are 16.17, 16.48 and 18.01, respectively [44]. Dysprosium forms a stable complex with EDTA, in comparison with Pr and Nd. Therefore, in the present investigation, EDTA preferentially masked Dy ions present in the aqueous solution and increased the separation values for Pr/Dy and Nd/Dy up to 0.003 M EDTA. Beyond 0.003 M EDTA, Pr and Nd were also effectively masked by EDTA, thereby decreasing the separation factor values. At 0.003 M EDTA, separation factor values obtained for Pr/Dy and Nd/Dy were 55.6 and 19.4, respectively. The separation factor for Pr/Nd (2.9) was almost constant, as shown in Figure 9, due to a very small difference in their stability constant with EDTA. Comparisons of separation factor values for Pr/Nd obtained in the present investigation with the values reported in the literature are given in Table 5. It is clear from Table 5 that the use of EDTA as a complexing agent improved the separation factor for Pr/Nd.

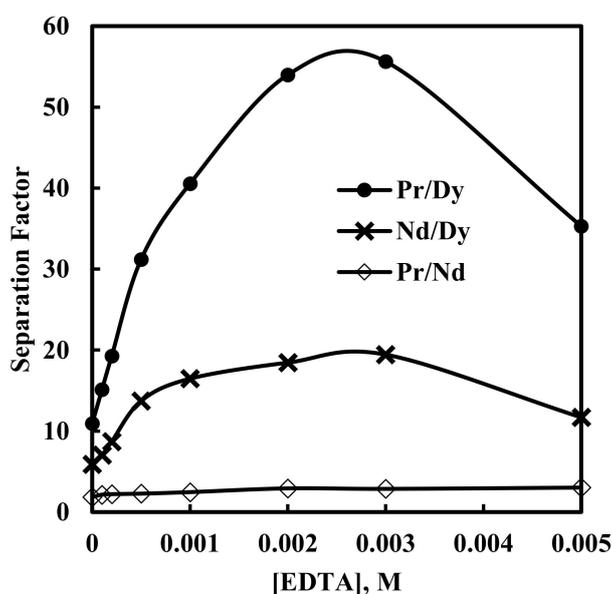


Figure 9. Effect of EDTA concentration on separation factors. Aqueous phase: pH = 3, $[\text{NO}_3^-] = 6 \text{ M}$. Organic phase: $[\text{336At}][\text{NO}_3] = 0.43 \text{ M} + 10\% \text{ iso-decanol}$ in kerosene.

Table 4. Extraction and separation behavior of Pr, Nd and Dy with and without EDTA, using $[\text{336At}][\text{NO}_3]$ as extractant. Aqueous phase: pH = 3, $[\text{NO}_3^-] = 6 \text{ M}$. Organic phase: $[\text{336At}][\text{NO}_3] = 0.43 \text{ M} + 10\% \text{ iso-decanol}$ in kerosene.

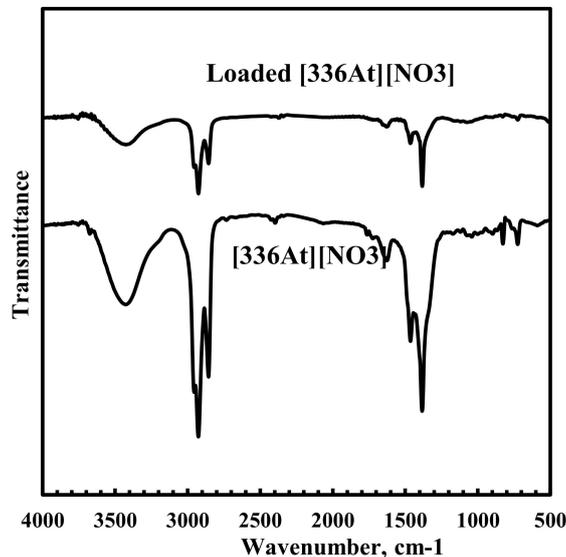
In Aqueous Solution	% Extraction			Separation Factor (β)		
	Pr	Nd	Dy	Pr/Dy	Nd/Dy	Pr/Nd
Without adding EDTA	91	84.5	48	10.9	5.9	1.8
0.003M EDTA	85	67	9.5	55.6	19.4	2.9

Table 5. Comparison of separation factors obtained for Pr and Nd in different studies.

Separation Studies	Separation Factor for Pr and Nd	Reference
0.43 M [A336][NO ₃] in kerosene from 6 M NaNO ₃ using 0.003 M EDTA as chelating agent	2.9	(present investigation)
0.5 M [A336][NO ₃] in xylene from 4 M NaNO ₃ aqueous solution	2.04	
0.2 M EHEHPA in toluene from 0.4 M NaNO ₃ aqueous solution	1.27	[35]
0.2 M D2EHPA in toluene from 0.4 M NaNO ₃ aqueous solution	1.25	
1 M D2EHPA in kerosene from aqueous solution of pH 3.5 using 0.6 M Lactic acid as chelating agent	1.57	[26]

3.5. FTIR Spectra of [336At][NO₃] and Nd Loaded [336At][NO₃]

In order to understand the interaction between representative rare earth ion Nd³⁺ and [336At][NO₃], FTIR absorption spectra of [336At][NO₃] were recorded and are shown in Figure 10. Although both the spectra are very similar, it was found that the characteristic peak at 1462 cm⁻¹ corresponding to N–CH₂ symmetric vibration of [336At][NO₃] shifted to 1450 cm⁻¹ and became broader in the Nd loaded [336At][NO₃]. This confirms the interaction of Nd(III) with nitrate ions of [336At][NO₃], which led to a broadening of the peak due to N–CH₂ symmetric stretching vibration. Furthermore, the characteristic peak at 1382 cm⁻¹ due to N–O asymmetric stretching vibration in [336At][NO₃] shifted to 1372 cm⁻¹ in the Nd loaded [336At][NO₃]. This indicates the interaction of nitrate groups with Nd³⁺ ion during extraction. This result supports the extraction mechanism as shown in Equation (4).

**Figure 10.** FTIR spectra for [336At][NO₃] and Nd loaded [336At][NO₃].

4. Conclusions

The solvent extraction separation studies of praseodymium, neodymium and dysprosium obtained from NdFeB magnet leach liquor were performed by using ionic liquid, [336At][NO₃] in the presence of complexing agent EDTA. It was found that the extraction of rare earths with [336At][NO₃] in the organic phase follows the order Pr > Nd > Dy, whereas the complex formation stability of EDTA with rare earth ions in the aqueous solution follows the order Dy > Nd > Pr. This established the possibility of efficient separation of rare earths by using [336At][NO₃] in the presence of complexing agent EDTA. With the addition of EDTA in the aqueous phase (upto 0.003 M), the extraction of rare

earths decreased due to the masking effect, but the separation factor enhanced significantly. However, it is required to understand the interaction of rare earth metal ions and $[336\text{At}][\text{NO}_3]$ at the molecular level considering dielectric constant of diluents and viscosity of the extractant. Furthermore, the effect of other aquo-complexing agents, such as lactic acid and citric acid, may also be investigated.

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