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Synergistic extraction of Nd(III) with mixture of 8-hydroxyquinoline and its derivative with di-2-ethyl hexyl phosphoric acid in different diluents

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Abstract−Solvent extraction of neodymium (III) from chloride medium with synergistic mixture of 8-hydroxyquinoline or 2-methyl-8-hydroxyquinoline and di-2-ethyl hexyl phosphoric acid was investigated in different diluents. Effect of various experimental parameters such as pH, extractant concentration, diluents and temperature was studied. Role of diluents on extraction of neodymium is explained in terms of activity coefficient adopting Hildebrand regular solution theory. The negative value of enthalpy change suggests that the extraction of ternary system is exothermic. The IR data for the extracted species also substantiated the nature of extracted species as observed by slope analysis method.

Keywords: Neodymium, Synergistic Extraction, D2EHPA, 8-Hydroxyquinoline, Diluent, Ternary Extraction

INTRODUCTION

Rare earth elements are pivotal for their uses in green energy technology such as wind turbines, electric vehicle, and energy efficient lighting devices. Neodymium is one of the important members of the rare earth family due to its wide uses in colorant for glass, in welding goggles and more recently also in laser crystals. Presently, neodymium is mostly employed in the manufacturing of permanent magnets in green energy technology areas [1]. The continuous miniaturization of electric motors, hard disks and wind turbines is causing increasing demand for high-performance neodymium-iron-boron magnets (NdFeB). The supply risk for the rare-earth elements (REEs) used in these magnets is a growing concern, and cumulative demand of Nd-Fe-B permanent magnet in clean energy sector has resulted in bracketing the neodymium in critical materials category by US DOE [2]. Generally, solvent extraction is used to separate and purify rare earths on industrial scale. Organophosphorus extractants such as di-2-ethylhexyl phosphoric acid (D2EHPA), 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A), trioctylphosphine oxide (Cyanex921) are used to separate neodymium from different types of aqueous streams [3-7]. New class of neutral extractants such as TEHDGA (N,N,N′,N′-tetra-2-ethylhexyl diglycolamide) and TODGA (N, N, N′, N′-tetraoctyl glycomide) has also been explored for rare earths separation studies [8-10]. The extraction and separation of rare earths from used NdFeB permanent magnets by ionic liquid trihexyl(tetradecyl)phosphonium nitrate from nitrate medium was described by Riano et al. [11]. The extraction behavior of neodymium and other rare earths from nitric acid media by the functionalized ionic liquid trioctylmethylammoniumdioctyldiglycolamate was investigated [12]. A new recycling process for (microwave) roasted NdFeB magnets is proposed, based on the carboxyl-functionalized ionic liquid: betainiumbis(trifluoromethylsulfonyl)imide [13]. A detailed review on the recycling of Dy and Nd from permanent magnetic material by solvent extraction method using D2EHPA and PC88A was highlighted [14]. The synergistic solvent extraction of Neodymium(III) with mixture of triisooctylamine (Alamine 308) and bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302) in kerosene from chloride solutions has been investigated [15].

Though different extraction systems have been studied, separation of rare earths from aqueous solution still is challenging and difficult. Researchers working worldwide to develop a selective extractant system which can separate and purify one of the rare earths from a host of other rare earths. However, till date no suitable extractant has been synthesized. Consequently, exploring the various combinations of known extractants opens up an avenue to find a suitable and effective combination of extractants for rare earths extraction and separation. 8-Hydroxyquinoline (HQ: abbreviated as oxine in the present work) and its derivative is one of those classes of extractant which are known to have good extraction ability for various metal ions [16,17], and have been widely using in analytical chemistry and hydrometallurgy. 8-Hydroxyquinoline has also been applied to the extraction of rare earth elements [18]. Contrary to the single extractant systems, synergistic solvent extraction system comprised of two solvents combinations offers more selectivity and improvement in extraction efficiency for rare earths. Oxine was used as synergistic extractant in combination with cyanex301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) for extraction of rare earth elements [19]. A binary mixture of sec-octylphenoxyacetic acid (CA12) and HQ was applied to the synergistic extraction of all the lanthanides and yttrium from nitrate medium [20]. Liquid-liquid extraction of Pr(III) and Nd(III) using HQ in chloride-acetate medium was already studied in presence of PC88A [21]. The effect of diluent on the extraction efficiency indicates that with increasing dielectric constant, the extraction efficiency decreases. As well, the results indicate that HQ alone cannot separate Pr and Nd; how-

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ever, as a mixed extractant with PC88A separation can be achieved. Addition of methanol in the water phase eight-coordinated mixed ligand adducts was formed instead of six-coordinated chelate in extraction of La(III), Gd(III) and Lu(III) species with 5,7-dihalogeno derivatives of 8-hydroxyquinoline [22]. Extraction behavior of certain trivalent lanthanides in chloroform medium with 8-quinolinol in presence of 1,10-phenanthroline and 4,4′-di(5-nony1)-2.2′-bipyridine (DNBP) was studied, and the difference of synergistic efficiency was attributed to the steric effect of the nonyl-groups in DNBP [23].

Though references are available in literature, there is scanty reporting available on Nd(III) separation. Therefore, it is desirable to investigate the extraction behavior of Nd(III) metal ion with synergistic mixture of D2EHPA with HQ and its derivative from chloride medium. The effects of several parameters like pH, extractant concentration, temperature and nature of diluents were studied extensively. Diluents play a very important role in mixed extraction, and the magnitude of formation constant of ternary adduct changes with nature of diluents. Dielectric constants of the media were found to have no specific role on the trend of such extraction [24]. However, as the activity coefficients of the chemical species are very sensitive to the medium, the role of diluents was studied in terms of their effect on activity co-efficient. The latter were calculated by adopting Hildebrand regular solution theory [25], and a systematic correlation between formation constant of adduct and nature of solvent was achieved. Results have been interpreted in the light of experimental equilibrium data obtained in the present investigation.

EXPERIMENTAL

1. Reagents and Apparatus

A stock solution of neodymium oxide was prepared by dissolving the neodymium oxide (>99.9% purity, IREL, India) in minimum concentrated hydrochloric acid and evaporated to near dryness. Subsequently, it was dissolved in distilled water followed by addition of few drops of hydrochloric acid to avoid hydrolysis of RE. Free acid content in rare earth stock solution was determined by precipitating rare earth with disodium oxalate followed by titration with standard NaOH using phenolphthalein as an indicator. The stock solutions were diluted to the desired concentrations when necessary. D2EHPA (95% diester) was procured from Heavy Water Board, India, PC88A (95% diester) was procured from Daihachi Chemical Co., Japan, Cyanex272 (bis (2,4,4-trimethylpentyl) phosphinic acid) was supplied by Cyanamid Canada, TBP (tri-n-butyl phosphate), TOPO (tri-octyl phosphine oxide), Cyanex923 (a mixture of four trialkyl phosphine oxides :R_3PO, $R_2R'PO$, RR'_2PO and R'_3PO where R is n-octyl and R′ is n-hexyl chain), Commercially available Aliquat 336 (tri capryl ammonium chloride) was used as supplied, and Alamine336, oxine and 2-methyl-oxine were obtained from M/S Sigma Aldrich, USA. These extractants were used as received. The organic diluents and other chemicals used in the present study were of AR grade. A digital pH-meter, Systronics model 335, was used for the pH measurements and ICP-AES (JY Ultima 2) instrument was used to determine the concentration of neodymium in aqueous solutions. A Bruker Alpha Platinum - ATR was used for IR measurement.

2. Extraction Procedures

Extraction experiments were carried out by equilibrating 5 mL aqueous containing Nd(III) solution and 5 mL extractant of desired concentration and shaken for 30 min in a mechanical shaker. Time of equilibrium had been previously optimized. The organic and aqueous phases were allowed to settle and then disengaged. After the separation of the two phases, the concentration of Nd(III) in the aqueous phase was determined by ICP-AES. The concentration of Nd(III) in the organic phase was obtained by mass balance. The equilibrium *pH* was maintained at 2.5, which was optimum for the maximum extraction, and desired *pH* was adjusted by addition of HCl and NH_4OH. All the extraction experiments were in triplicate at room temperature (27±1 °C) except for temperature variation experiments. Care was taken to keep the temperature constant (±<0.5 °C) throughout extraction studies by monitoring at regular intervals using a thermometer and by preheating the solutions. The distribution ratio (D*)* was calculated as follows:

$$D=\frac{[Nd^{3+}]_o}{[Nd^{3+}]_a}$$

where 'o' and 'a' represent organic and aqueous phases, respectively. Percentage extraction (%E) was calculated as (100D/1+D) at phase ratio (O/A)=1. The parameter governing the synergistic effect known as synergistic co-efficient (*S.C*) of adduct was evaluated by using the following equation [26]:

$$S.C=\log (D_{mix}/D_s+D_0)$$

where D_{mix}, D_s and D_0 represent the distribution ratio for ternary system, with individual ligands, namely, oxine or 2-methyl oxine and D2EHPA, respectively. However, pure HQ individually extracts the metal ion to a very negligible extent, so here $D_s=0$.

Material balance was checked in preliminary experiment from the difference of total metal ion concentration and that left in aqueous solution after the extraction, which was found to be same obtained after stripping the extracted organic phase.

To strip the metal ion, loaded organic phase was equilibrated with HCl of different concentrations, at room temperature for 30 min. After separating the aqueous solution from the organic phase, Nd(III) concentrations were estimated to evaluate the stripping ratio. The percentage of stripping(S) was calculated as follows:

$$S=\frac{[Nd^{3+}]_a}{[Nd^{3+}]_o}\times 100$$

RESULTS AND DISCUSSION

1. Screening of Extractants

The extraction behavior of Nd(III) was investigated by evaluating different extractants [Table 1]. The extraction of Nd(III) follows the order D2EHPA>PC88A>Cyanex 272 for acidic extractant system, while for basic extractant the Aliquat336 gave slightly better D than Alamine336. In the case of neutral extractants there was not much difference in D value. Amongst all the systems investigated, D2EHPA gave higher D compared to others. This may be possibly due to higher acidic strength of D2EHPA. In case of syn-

Table 1. Distribution ratio of Nd(III) using different extractant, at a fixed *pH* 2.5 in dodecane diluent

Binary system	D_0	Ternary system	D_{mix}
Nd(III) - TBP	0.25	Nd(III) - TBP - Oxine	0.28
Nd(III) - TOPO	0.24	Nd(III) - TOPO - Oxine	0.31
Nd(III) - Cyanex923	0.18	Nd(III) - Cyanex923 - Oxine	0.32
Nd(III) - D2EHPA	0.44	Nd(III) - D2EHPA - Oxine	1.86
Nd(III) - PC88A	0.21	Nd(III) - PC88A - Oxine	1.22
Nd(III) - Cyanex272	0.05	Nd(III) - Cyanex272 - Oxine	0.28
Nd(III) - Aliquat336	0.18	Nd(III) - Aliquat336 - Oxine	0.25
Nd(III) - Alamine336	0.26	Nd(III) - Alamine336 - Oxine	0.29

ergistic mixture with TBP, TOPO and Cyanex 923, D value was almost constant. It seems that at relatively lower pH range the difference in basicity of neutral extractants does not play any significant role. Oxine in combination with D2EHPA resulted in higher extraction. The addition of HQ enhanced the extraction, which may be attributed to the replacement of residual water molecule by HQ compound, rendering the ternary adduct more lipophilic. Similar observation was reported for the extraction of rare earths with HQ when it was used with acidic extractant [21]. Based on these observations D2EHPA+HQ mixture was selected for further investigation in the present work.

2. Synergistic Extraction of Neodymium with D2EHPA in Presence of 8-Hydroxyquinoline or 2-Methyl-8-hydroxyquinoline

2-1. Effect of Feed Acidity

Fig. 1 illustrates the variation of extraction of Nd metal as a function of aqueous feed pH synergistic mixture of D2EHPA and oxine. It is evident that extraction increased from 5% to ~65% with the increase in pH from 1 to 2.5 and thereafter it remained constant. The increase in extraction of Nd(III) metal ion may be attributed to the cationic exchange mechanism where the extraction of Nd(III) takes places with the exchange of hydrogen ions of dimer D2EHPA in nonpolar diluent dodecane. Similar observation was reported for the extraction of Dy(III) from chloride medium with EHEHPA as an extractant [27]. Beyond pH 2.5 the extraction was almost constant, which may be due to the solvating nature of oxine. Based on this study a pH of 2.5 was selected for further investigation.

2-2. Effect of Extractant Concentrations

The extractions of Nd(III) from aqueous chloride media at pH 2.5 were studied in terms of effect of D2EHPA concentration in different diluents at a fixed concentration of oxine on the distribution ratio of Nd(III). The plot of log D vs log [D2EHPA] is shown in Fig. 2. The extraction of Nd(III) was found to increase with increase in D2EHPA concentration irrespective of diluent. This may be explained by the release of more water molecules from the inner sphere of metal ion, by the ligand as the latter is known to be better chelating agent than water. It is well known that the organic extractant D2EHPA exists as dimer in nonpolar diluent. For binary extraction system, the possible extraction of Nd(III) may be described by the following equation as reported elsewhere [28,29]:

$$Nd^{3+}_{aq}+(n+p)/2\ [H_2A_2]_{org} \xrightleftharpoons{K} [NdA_n\ (HA)_p]_{org}+nH^+ \tag{1}$$

The equilibrium constant for Nd(III) and D2EHPA binary system of Eq. (1) is given by

$$K=\frac{[Nd\ A_n\ (HA_p)]_{org}[H^+]^n}{[Nd^{n+}]_{aq}\ [H_2A_2]^{(n+p)/2}_{org}} \tag{2}$$

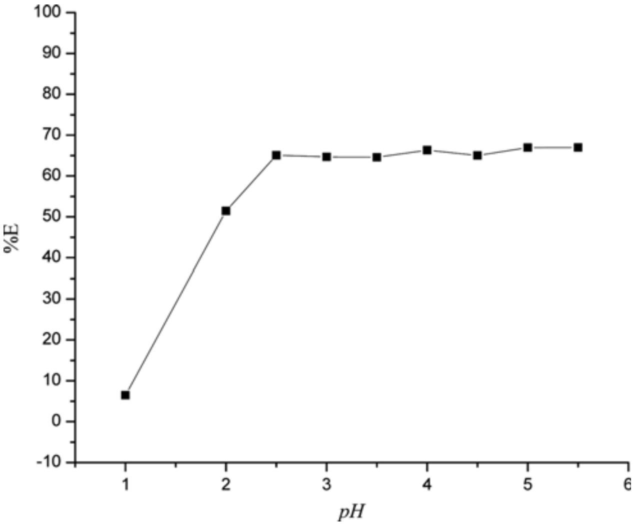

Fig. 1. Influence of pH on %E in ternary complex with fixed concentration of D2EHPA and Oxine in dodecane diluent.

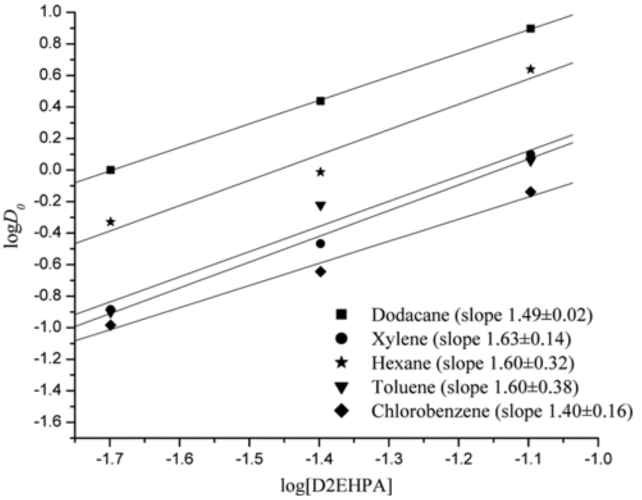

Fig. 2. Effect of concentration of D2EHPA on distribution ratio (D_0) of Nd(III) in several diluents.

$$K=\frac{D_0[H^+]^n}{[H_2A_2]^{(n+p)/2}_{org}} \tag{3}$$

$$\log K=\log D_0-(n+p)/2\,\log[H_2A_2]_{org}-n\,pH \tag{4}$$

Eq. (4) can be used to obtain the dependency of pH and extractant concentration. The nature of the extracted species was established by slope analysis technique. The log-log plot of D_0 against D2EHPA concentration yielded straight line with slope ~1.5 for all diluents (Fig. 2).

$(n+p)/2=1.5$, and $(n+p)=3$.

Further taking into consideration of the data presented in Fig. 1, the plot of $\log D_0$ vs pH had rendered a slope ~3, so n=3 and subsequently p=0. So Eq. (1) can be written as:

$$Nd^{3+}_{aq}+1.5\,[H_2A_2]_{org}\overset{K}{\rightleftharpoons}[NdA_3]_{org}+3H^+ \tag{5}$$

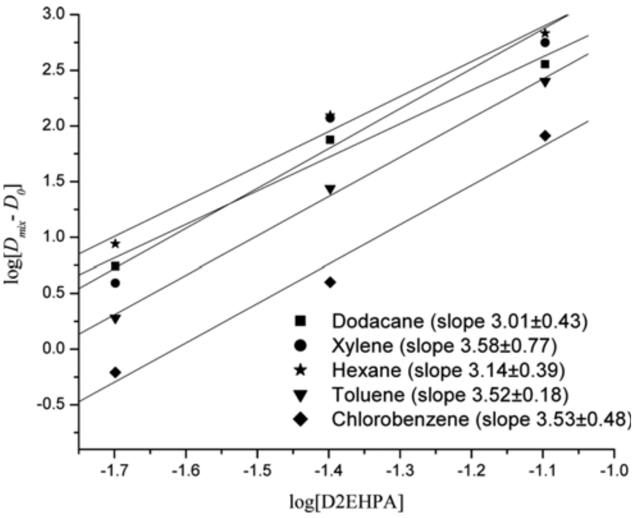

Fig. 3. Effect of concentration of D2EHPA on $\log[D_{mix}-D_0]$ of Nd(III) in presence of fixed concentration of oxine in several diluents.

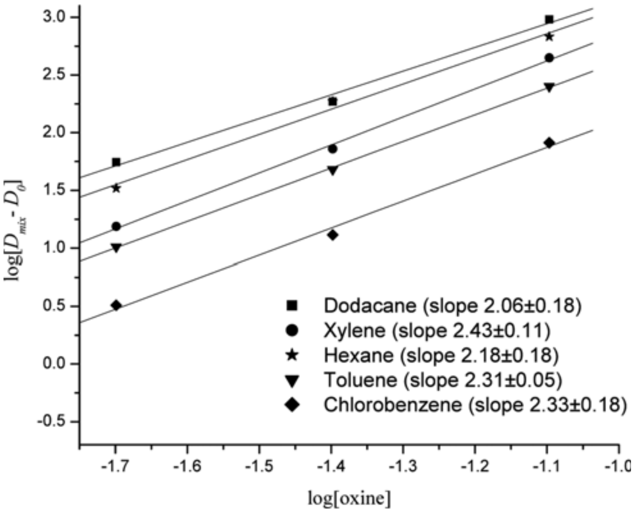

Fig. 4. Effect of concentration of oxine on $\log[D_{mix}-D_0]$ of Nd(III) in presence of fixed concentration of D2EHPA in several diluents.

In case of ternary extraction (D2EHPA+oxine system), the log-log plot of ($D_{mix}-D_0$) against D2EHPA concentration (Fig. 3) at a fixed 8-hydroxyquinoline concentration (8×10^{-2} mol lit^{-1}) yielded straight line of slope ~3. Donor concentration (HQ) was varied by keeping D2EHPA concentration at 8×10^{-2} mol lit^{-1} to understand the mechanism of ternary extraction. The results obtained are shown in Fig. 4 as plot of log [$D_{mix}-D_0$] against log [HQ], where they show a straight line with a slope of ~2 for all the diluents studied. This suggests the dependency of 2 moles w.r.t one mole of Nd(III) and the nature of extracted species formed is of the type $[NdA_3(HA)_3\cdot(HQ)_2]$org in the organic phase. Similar observation and conclusions were obtained with D2EHPA+2-methyl oxine system in different diluents as illustrated in Fig. 5 and Fig. 6. Thus, the possible synergistic extraction of Nd(III) may be described by the following equation:

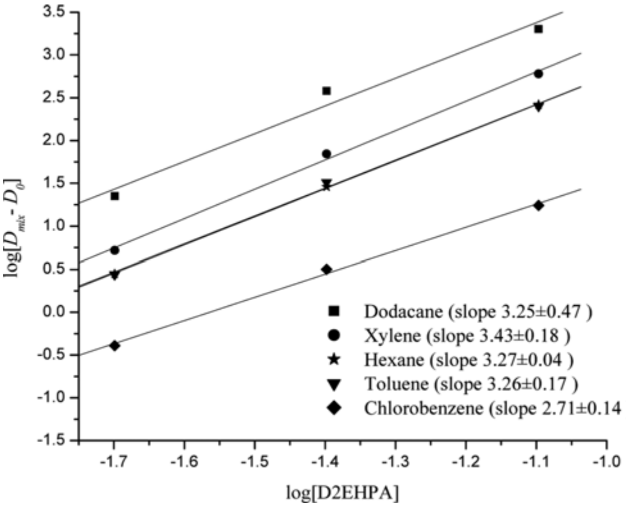

Fig. 5. Effect of concentration of D2EHPA on $\log[D_{mix}-D_0]$ of Nd(III) in presence of fixed concentration of 2-methyl oxine in several diluents.

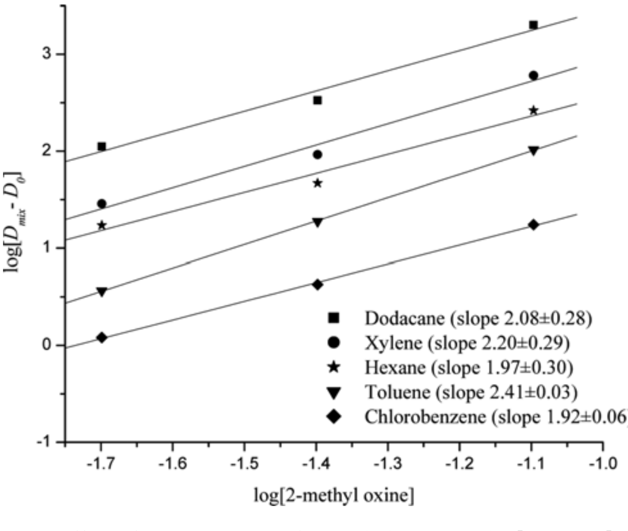

Fig. 6. Effect of concentration of 2-methyl oxine on $\log[D_{mix}-D_0]$ of Nd(III) in presence of fixed concentration of D2EHPA in several diluents.

Table 2. Equilibrium constants in different organic diluents for binary and ternary systems

Diluents	Nd(III)-D2EHPA	Nd(III)-D2EHPA-Oxine		Nd(III)-D2EHPA-2-methyl oxine	
	log K	log K′	log K_S	log K′	Log K_S
Dodecane	−9.91	−0.54	10.45	−1.29	11.20
Xylene	−11.51	−0.73	12.25	−0.77	12.28
Hexane	−10.43	−0.82	11.25	−0.40	10.84
Toluene	−11.59	−0.39	11.98	−0.39	11.98
Cholobenzene	−11.99	−0.10	11.88	−0.78	11.21

$$Nd_{aq}^{3+}+3[H_2A_2]_{org}+2[HQ]_{org} \xrightleftharpoons{K'} [NdA_3(HA)_3\ (HQ)_2]_{org}+3H^+ \quad (6)$$

The ternary extraction constant ‘K′’ associated with distribution ratio of ternary adduct (D_{mix}) by the following equation:

$$\log K'=\log (D_{mix}-D_0)-3\log[H_2A_2]-2\log\ [HQ]-3pH \quad (7)$$

And hence according to the previous literature [29],

$$\log K_s=\log K'-\log K \quad (8)$$

where K_s=adduct formation constant of ternary system in organic phase.

All these equations and reaction schemes were found to be almost equally applicable to both the two donors dissolved in different diluents. The equilibrium constants for both two donors are shown in the Table 2, which indicates formation of strong ternary adduct for both oxine and 2-methyl oxine complex in xylene media.

Synergistic coefficients (S.C) for both Nd(III)-D2EHPA-oxine and Nd(III)-D2EHPA-2-methyl oxine in different diluents were evaluated. The extractant concentration was varied in the range 0.01 M to 0.08 M for 0.01 M Nd_2O_3 in hydrochloric acid at pH 2.5. The synergistic coefficient values obtained with different diluents with 0.08 M ligand+0.08 M donor concentrations are in Table 3, which clearly shows that the xylene is the best solvent for both the systems.

Table 3. Synergistic extraction of Nd(III) with D2EHPA-oxine/2-methyl oxine in different diluents

Diluents	Nd(III)-D2EHPA	Nd(III)-D2EHPA-Oxine
	Synergistic coefficient	
Dodecane	1.67	2.41
Xylene	2.65	2.68
Hexane	2.20	1.79
Toluene	2.34	2.34
Cholobenzene	2.18	1.51

2-3. IR Spectrum

To further confirm the composition of the extracted complexes, infrared spectrum measurement was taken and some peak absorptions data are shown in Table 4. The characteristic absorption of D2EHPA is 1,278 cm^{-1} was attributed to P=O vibrations and 1043 cm^{-1} attributed to P-O-C vibration, which shifted to the lower wave numbers to 1,036 cm^{-1} in the metal complex. The spectra (Fig. 10) show peaks at 1,466 and 1,378 cm^{-1} due to the C-H deformation vibrations and peaks at the interval 2,853-2,957 cm^{-1} corresponding to the 2-ethylhexyl group.

2-4. Influence of Temperature on the Synergistic Extraction

Temperature effect is the most complex factor affecting the synergistic extraction process. The influence of temperature on distribution ratios was studied with the ligand in presence of donors separately in different organic diluents, keeping concentration of Nd(III) and extractant concentration constant. The changes in enthalpy (ΔH_f^0), entropy (ΔS_f^0) and free energy (ΔG_f^0) of each of the extraction system were evaluated using the following equation:

$$\log K'=\frac{-\Delta H_f^0}{2.303\ RT}+\frac{\Delta S_f^0}{2.303\ R} \quad (9)$$

The plot of logK′ against 1/T yields a straight line, with a slope ΔH_f^0 and ΔS_f^0 were evaluated by using the slope value and intercept of the straight line. Such results are shown in Fig. 7 and Fig. 8 for D2EHPA-oxine and D2EHPA-2-methyl oxine systems, respectively. The calculated values of the thermodynamic parameters for both the systems are in Table 5. The data shows that extraction proceeds spontaneously in the forward direction ($\Delta G_f^0<0$) for ligands with both of the two donors in all diluents except chlorobenzene. As the metal ion Nd(III) itself is hard acid and the ligand contains hard donor center (O) complex formation involve hard - hard interaction, as per Pearson's HSAB principle, and the interaction between the cation and the ligands provides a negative enthalpy

Table 4. IR characteristic peak of extraction complex

Sample	P=O cm^{-1}	OH cm^{-1}	P-O-C cm^{-1}
D2EHPA	1278	1465	1043
Nd^{3+} - D2EHPA	-	1462	1036
D2EHPA - Oxine	1278	1465	-
Nd^{3+} - D2EHPA - Oxine	-	1462	1035
D2EHPA - 2-methyl oxine	1259	1466	-
Nd^{3+} - D2EHPA - 2-methyl oxine	-	1466	1034

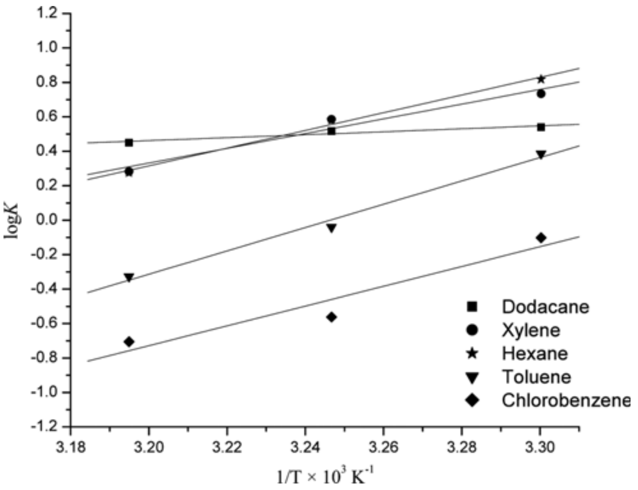

Fig. 7. Effect of temperature on equilibrium constant of Nd(III) - D2EHPA - oxine complex.

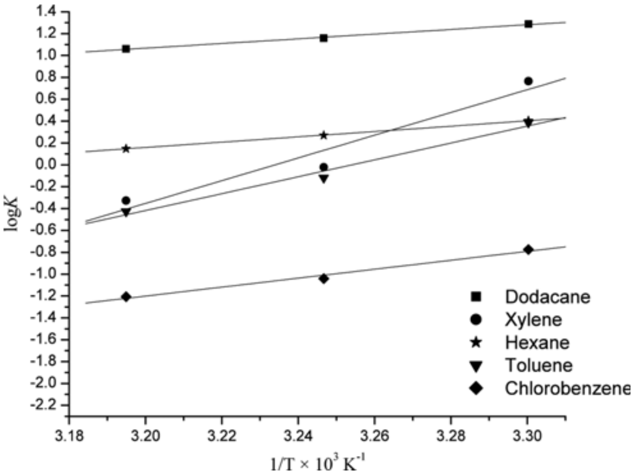

Fig. 8. Effect of temperature on equilibrium constant of Nd(III) - D2EHPA - 2-methyl oxine complex.

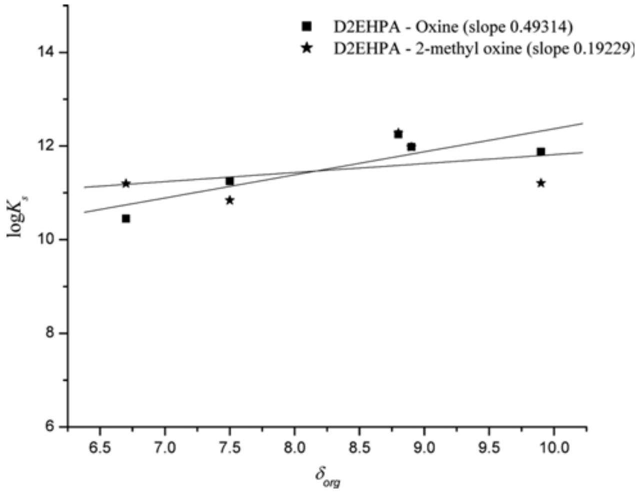

Fig. 9. Plot of logK_s vs δ_{org} in synergistic extraction of Nd^{3+} in different diluents.

contribution ($\Delta H_f^0<0$) due to formation of the cation-anion bonds, and this bonding decreases the randomness of the system, resulting in negative entropy contribution ($\Delta S_f^0<0$) [30,31]. Overall ternary complex formation therefore proceeds via outer sphere mechanism as the expansion of co-ordination shell of f-block metal is permitted. Similar exothermic nature of extraction for rare earths from chloride medium with organophosphorous extractant dinonyl phenyl phosphoric acid was reported by Anitha et al. [32].

2-5. Diluent Effect

Experimental outcomes predict that the nature of organic diluents has an important role in controlling the degree of synergism, which varies widely with the diluents. Such variation of synergistic effect cannot be explained by the dielectric constants of solvents. However, Hildebrand's regular solution theory can be applied to explore the nature of the solvents deciding the extent of synergism [26]. In several previous investigations, the application of this concept was made successfully. From regular solution theory, it has been possible to calculate the activity and activity coefficient of interacting species with the aid of the knowledge of solubility parameters and molar volumes. Accordingly, adduct formation constant logK_s is related to the solubility parameter of diluent, as below [31].

$$\log K_s = 2B\ \delta_{org} + \text{constant} \quad (10)$$

$$B = 1/2.303\ RT\ [V_{adduct}\cdot\ \delta_{adduct} - V_{chelate}\cdot\ \delta_{chelate} - V_{donor}\cdot\ \delta_{donor}\ ] \quad (11)$$

where, V=molar volumes of adduct, chelate and donor

Table 5. Calculated thermodynamic parameters

Ternary system	Solvent	ΔH (k Jmol^{-1})	ΔS (JK^{-1} mol^{-1})	ΔG (k Jmol^{-1})
Nd(III) - D2EHPA - Oxine	Dodecane	−16.31	−43.35	−3.17
	Xylene	−81.74	−255.22	−4.41
	Hexane	−98.29	−308.50	−4.81
	Toluene	−129.56	−420.58	−2.12
	Chlorobenzene	−110.42	−365.48	0.32
Nd(III) - D2EHPA - 2-methyl oxine	Dodecane	−41.10	−111.10	−7.44
	Xylene	−198.96	−643.42	−4.00
	Hexane	−46.62	−146.14	−2.34
	Toluene	−147.77	−480.88	−2.06
	Chlorobenzene	−78.30	−273.53	4.58

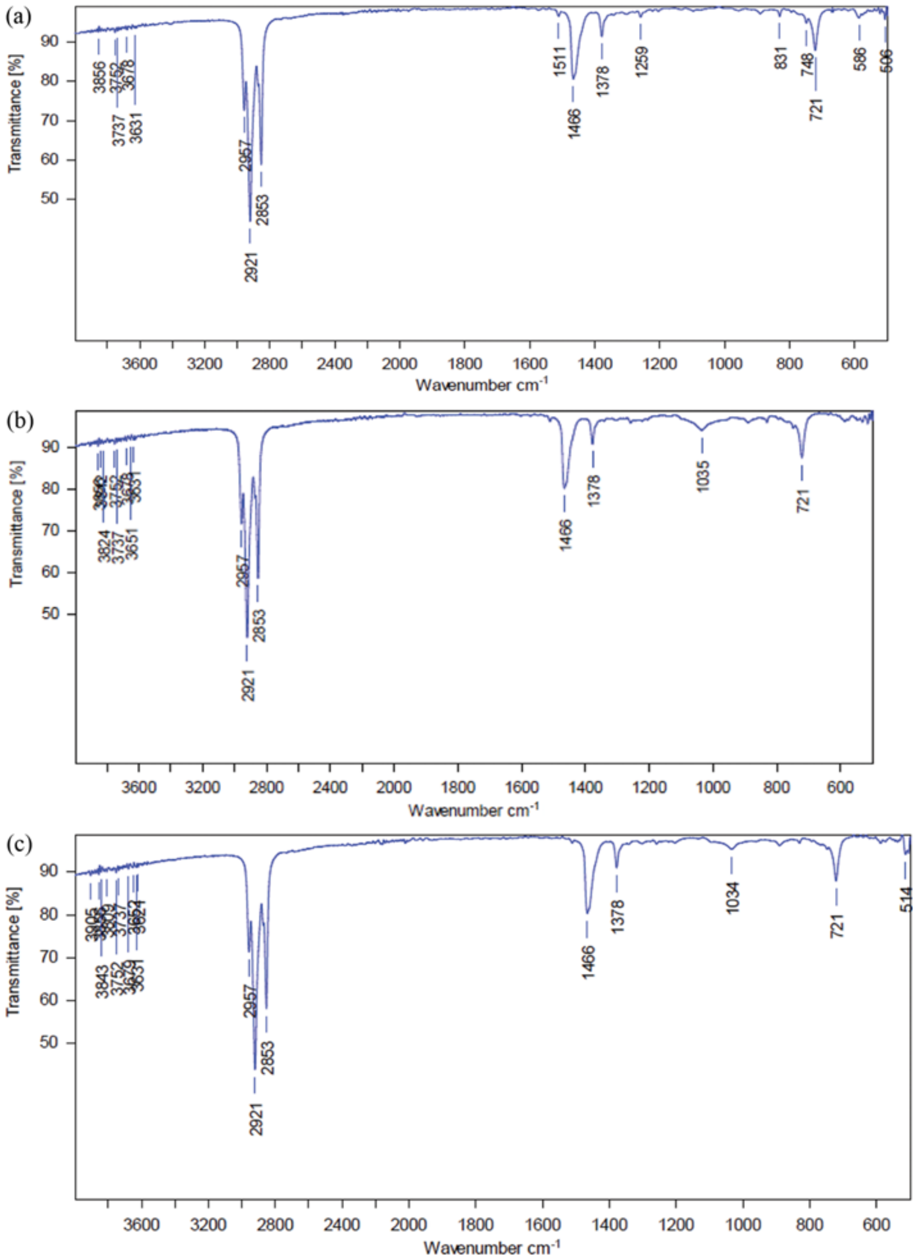

Fig. 10. IR spectra (a) Spectra due to D2EHPA - 2-methyl oxine, (b) Spectra due to Nd^{3+} - D2EHPA - oxine, (c) Spectra due to Nd^{3+} - D2EHPA - 2-methyl oxine.

δ=solubility parameter of adduct, chelate and donor

Both V and δ depend on diluent nature and the constant term is independent on diluents.

In the present investigation, experimentally determined logK_s in each solvent was plotted against solubility parameters (δ_{org}) of respective diluents (Fig. 9), and the slope of the resulting straight line was equated to '2B' from which δ_{adduct} was calculated using above relation. Solubility parameter of the ternary adduct was also calculated theoretically, adopting a previous method. A comparison of δ_{adduct} values in Table 6 obtained theoretically and experimentally for two types of ternary complexes involving oxine and 2-methyl oxine establishes the validity of the regular solution theory in these systems. Wu et al. also investigated the effect of diluents on the separation of Pr and Nd from chloride-acetate medium by 8-hydroxyquinoline with and without EHEHPA as an added synergist [21].

2-6. Stripping

Nd(III) was stripped from the extract (D2EHPA- Oxine) at a

Table 6. Solubility parameter (δ_{adduct}) of ternary system

Ligand - Donor system	δ_{adduct} ($J^{1/2}$ $cm^{-3/2}$)	
	Theoretical	Present work
D2EHPA - Oxine	7.94	9.04
D2EHPA - 2-methyl oxine	8.03	8.41

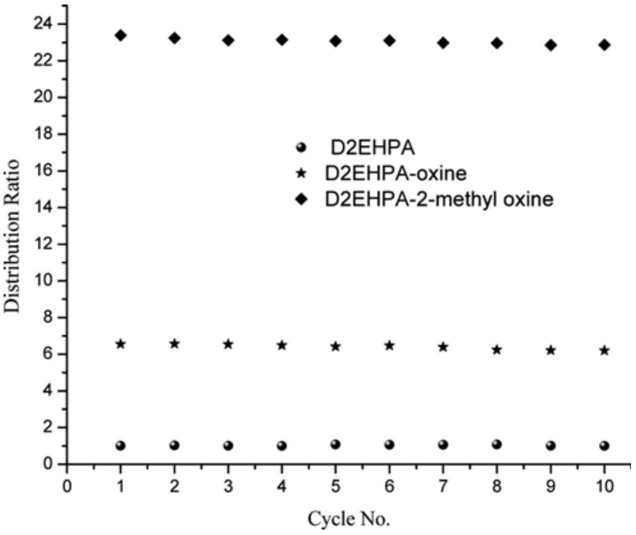

Fig. 11. Effect of reusability of D2EHPA and D2EHPA - oxine/ 2-methyl oxine solvents on distribution ratio of Nd(III).

phase ratio(O/A) of 1 with different concentration of HCl in the range of 0.5 M to 3 M. Quantitative stripping (>99%) of Nd(III) was achieved with 1 M and above concentration of HCl. Interestingly, the complete stripping of Nd(III) from organic phase D2EHPA requires 6 M of HCl [6], whereas in the case of synergistic mixture with oxine, relatively much lower concentration of HCl was found to be effective.

2-7. Reusability Test of the Extraction Systems

The extraction reusability of the extraction systems, namely 0.02 M D2EHPA, 0.02 M D2EHPA+0.08 M Oxine and 0.02 M D2EHPA+ 0.08 M 2-methyl oxine dissolved in dodecane, was investigated for extraction of Nd(III) from chloride medium at pH 2.5 by repeated extraction and stripping with 4 M HCl at O/A ratio of 1. The values of distribution ratio as a function of cycle (extraction and stripping) are shown in Fig. 11. It is evident the extraction systems were quite stable even after 10 cycles of operation of extraction and stripping, where in each case the D values obtained were almost constant.

CONCLUSION

Extractions of Nd(III) through the synergistic combination of D2EHPA and oxine derivatives have been studied extensively. Effects of different diluents in such extractions were compared, and measurements of extraction equilibrium constants show that xylene is the best solvent for both of the two systems (ligand-donor). Diluent effects were correlated with respective solubility parameter adopting regular solution theory of Hildebrand. Influence of temperature indicates an expansion of coordination shell in ternary extract, which is very often shown by f-block elements. Slope analysis method confirms the formation of neutral extracted species of the type $[NdA_3(HA)_3\ (HQ)_2]_{org}$ in the organic phase of D2EHPA and oxine.

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