Synergistic Extraction of Erbium (III) by n-Octyl Phenyl Phosphinic Acid (OPPA) with Oxine and 2-Methyl Oxine in Different Diluents

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Abstract

The synergistic extraction of erbium (III) was investigated using n-octyl phenyl phosphinic acid (OPPA) in combination with oxine and 2-methyl oxine in different diluents. The extraction efficiencies of these synergistic extractants for erbium were measured as a function of extractant concentration, pH, temperature and diluents. The composition of extracted species determined by slope analysis method indicates the formation of $[Er(HA_2)_3(HOX)]_{org}$ complex and was also confirmed by Infrared spectroscopy. Based on the experimental data, the values of the equilibrium constants as well as synergistic coefficients have been calculated. Both the donors (oxine/2-methyl oxines) exhibited almost similar synergistic effect with OPPA. The extraction of erbium with these solvents was exothermic in nature. Diluent dependency on synergism for OPPA-oxine/2-methyl oxine system was explained in terms of regular solution theory of Hildebrand. Experimentally determined solubility parameter of ternary adduct was correlated with theoretically obtained values.

Key words: OPPA, oxine, 8-hydroxyquinoline, erbium, synergistic extraction

Introduction:

The rare earth elements (REE) or lanthanides, scandium as well as yttrium, are a group of elements that have become increasingly important in number of high-tech applications including hybrid cars, wind turbines, magnets, phosphors, lasers, optical fibers etc. Erbium is one of the promising REE and used extensively for up-conversion materials, displays, corrosion resistant coatings, as a tritium permeation barrier for nuclear reactors, solar films, antireflection coating material, bio imaging etc.[1,2]. The high value of REE depends on its effective individual

separation, which is very challenging to accomplish owing to low separation factors between the adjacent REE because of their similar chemical properties. Among the techniques used, solvent extraction is extensively used in the commercial processing of rare-earth compounds. Several extractants have been used in the past to separate REE from various aqueous streams.

Lanthanides (III) because of their typical hard Lewis acid character, were extracted in early stages by organophosphorus ligands, which act as hard Lewis bases and thereby impose high extraction power for the REE having high coordination number[3]. Similarly, 8-hydroxyquinoline (HOX) and its derivatives also achieve a high degree of extraction under favorable condition. The extraction efficiencies of these compounds have been extensively investigated on the extraction of REE[4]. Alternatively, synergistic extraction systems have been applied to rare earths, where a significant increase in the extraction efficiency of REE was observed in combination of two extractants. The extractant having higher distribution ratio with the metal ion of interest is considered as the main extractant while the other is referred as donor.

The systematic synergistic solvent extraction of erbium has been carried out with neutral type of extractants[5-6]. The synergistic effect in the extraction of gadolinium, dysprosium and erbium with a ternary system consisting of tri-n-butyl phosphate (TBP) and tricaprylylmethyl ammonium chloride (Aliquat336) in xylene from thiocyanate solution was described along with the composition of extracted species[7]. The effect of various process parameters like pH, concentration of NH_4SCN, Aliquat336 and TBP on distribution ratios have been described. Neutral organophosphorus compounds with a phosphoryl complexing center were found to cause synergistic shifts in the extraction of Nd(III) and Er(III) from chloride based solutions by acidic extractant 3,5-diisopropylsalicylic acid. The extracted neodymium and erbium complexes had the composition NdA_3L_2 and ErA_3L_2, where HA=3,5-diisopropylsalicylic acid and L is a neutral organophosphorus compound[8].

Though synergistic extraction of Er has been reported, investigations with acidic extractant namely, n-octyl(phenyl)phosphinic acid (OPPA) has not been reported so far, particularly in combination with 8-hydroxyquinoline (HOX), commonly known as oxine. Solvent extraction of cobalt and nickel from aqueous sulphate medium was explored using OPPA in n-dodecane[9]. Extraction behavior of Y(III) from hydrochloric acid medium by OPPA in different diluents was investigated in detail and higher extraction was observed with low dielectric constant diluents. Extraction behavior of lanthanides with OPPA was investigated in detail where OPPA was found to be promising extractant for separation of heavier rare earths from the lighter rare earths[10]. The degree of synergism is correlated to stability of the adduct formed, which in turn depends on the nature of extractants as well as on the type of organic diluent used. Thus, the proper choice of

diluent is very important for synergistic enhancement. The dielectric constants of solvents alone cannot explain such type of variation of synergistic effect. Akiba et. al.[11] had shown the effect of diluent on synergic extraction of europium by the mixture of thenoyltrifluoroacetone and tri-*n*-octyl phosphine oxide by evaluating adduct formation constants. They found the adduct formation constant is correlated with one of the physical properties of the diluent, solubility parameter (δ_{org}) for the overall reaction, which is useful in selection of diluents in solvent extraction. The formation constants of the tributyl phosphate (TBP) adduct with the tris-thenoyltrifluoroacetone (TTA) chelate in several diluents was evaluated for scandium extraction and was described in the light of solubility parameter concept[12]. The activity coefficients of the chemical species vary with the medium, the correlation between the formation constant and the nature of diluent becomes necessary as per Hildebrand regular solution theory[13].

In the present work, the extraction of erbium with n-octyl(phenyl)phosphinic acid (OPPA) in combination with oxine or 2-methyl oxine from chloride solution was explored. This new synergistic extraction system has not been reported so far for erbium and is being reported for the first time. The main objective is to study the extraction behavior of Er(III) from chloride medium by the synergistic extractant(OPPA-HOX) in different diluents under various extraction process parameters like pH, extractant and donor concentration, temperature etc. The solubility of different diluents under the study in OPPA-HOX-Er has been evaluated to understand the effect of the diluents on the extent of synergism.

Experimental:

Materials and Methods

Erbium (III) chloride stock solution of known concentration was prepared by dissolving vacuum dried Er_2O_3 in Conc. HCl followed by evaporating excess HCl. The solution is made up to known volume and pH was adjusted to ~2 with HCl. The stock solution was diluted to the desired concentrations whenever necessary. The extractant OPPA was synthesized as described elsewhere [14]. The Synthesized OPPA extractant was estimated using potentiometry in 75% ethanol and was found to be 99% pure with dibasic acid content below detection limits. Elemental analysis of OPPA was performed on a Thermofinnigan Flash EA TM 1112 elemental analyser. The results were as follows: C–66.67% (theoretical 66.12%), H–9.50% (9.12%) and P–11.58% (12.18%). Oxine and 2-methyl-oxine were purchased from M/s Sigma Aldrich, USA and were used without any purification, pH measurements were carried out using a digital pH-meter, Systronics model 335 and concentration of erbium in aqueous solutions were determined by ICP-OES (JY Ultima 2). IR measurements were carried out using A Bruker Alpha Platinum–ATR.

Procedure

Organic phase was prepared by dissolving appropriate amount of OPPA extractant in desired diluent. The initial pH of the feed (aqueous) solution was adjusted to 2 before the equilibration experiment was carried out. Aqueous solutions (10 ml) containing 0.01 M Er(III) ions was contacted with 0.1 M OPPA (10ml) in n-dodecane for 30 minutes in a mechanical shaker at a certain temperature. After phase separation of organic and aqueous phases, equilibrium pH of the raffinate solutions was measured. The solutions were diluted as required with electronic grade dilute HNO_3 and analysis of erbium was carried out with ICP-OES make Jobin Yvon inductively coupled plasma-atomic emission spectrometer. The erbium concentration in the organic solutions were calculated by material balance. The error in the analysis was within ±1.0%. All experiments were performed in triplicate and average data is reported. The stripping studies were carried out with 3.5 M HCl. To determine the effect of temperature on distribution ratio, experiments were performed in a thermostat (±0.5 ^{o}C) with mechanical shaking for 30 min. Temperature was varied in the range of 300 to 333 K. The aqueous phases were separated and analyzed for metal ions. The distribution ratio (*D)* was calculated as follows,

$$D = \frac{Er(III)_{org}}{Er(III)_{aq}} \tag{1}$$

where 'org' and 'aq' represent organic and aqueous phases respectively. The synergistic co-efficient (*S.C*) of adduct, which governs the synergistic effect is evaluated by using the following equation [15].

$$S.C = log\frac{D_{mix}}{D_0+D_1} \tag{2}$$

where D_{mix}, D_0 and D_1 represent the distribution ratio for ternary system, with individual ligand (OPPA) and with individual donor (oxine or 2-methyl oxine) respectively.

Results and Discussion:

Influence of pH

Preliminary experiments were performed to monitor the effect of equilibrium pH on the extraction of Er(III) with OPPA and its mixture with oxine/2-methyl oxine. It was observed that the extraction of Er(III) increased in agreement with equation (5) with increase in pH. However at pH beyond 3, precipitation was observed. Hence all experiments were performed at feed pH 2 for feed solution.

Extraction of Er(III) using OPPA

OPPA concentration was varied from 0.01–1.0 M in different diluents to understand its effect on extraction behaviour of Er(III). The pH of initial feed solution was kept constant at 2 and the data was generated at O/A ratio of 1. The log D vs log [OPPA] plot for Er in different diluents is

shown in Fig. 1. The nature of the extracted species was established by slope analysis technique. The plots were straight lines with slope ~3, no changes in the slopes were observed. This confirms that the stoichiometry of Er(III)–OPPA complexes does not change with the diluent. The extraction of Er(III) was found to increase with increase in OPPA concentration irrespective of diluent. This is obviously due to making metal ion sphere more lipophilic by the ligand OPPA. Under the present experimental condition, oxine or 2-oxine show only a poor extraction trend towards Er(III).

Extraction of Er(III) with OPPA in presence of fixed concentration of oxine or 2-methyl oxine

In the case of ternary extraction (OPPA+oxine), the effect of OPPA on the extraction of Er(III) was studied keeping the oxine concentration constant (0.08 M) at O/A=1. The extraction of Er(III) increased with OPPA concentration irrespective of diluents. Fig. 2 shows the extraction of Er(III) using OPPA and oxine using several diluents. The log $(D_{mix}-D_0)$ against log [OPPA] plot show straight lines for all diluents with slopes corresponding to ~3. This clearly indicates the presence of three bidentate chelating groups of OPPA, (H_2A_2), denoted as dimer of OPPA in non-polar diluent, surrounding the Er(III) cation in the ternary extraction system. Similar results were obtained for Er(III) extraction with OPPA+2-methyl oxine system, with fixed concentration of 2-methyl oxine (0.08 M) and variation in OPPA concentration as shown in Fig. 3. The synergistic co-efficient (*S.C*) of adduct formed by Er(III) with OPPA and donor are evaluated and tabulated in Table 1. In all the diluents studied synergistic coefficient values increased with increase in concentration of diluents up to 0.08 M and for a given concentration the synergism followed the order: toluene > methyl isobutyl ketone > nitrobenzene > dichloromethane > petrofin.

Extraction of Er(III) with oxine/2-methyl oxine OPPA in presence of fixed concentration of OPPA

The effect of donor concentration (oxine or 2-methyl oxine) at fixed concentration of OPPA concentration (0.02 mol/L) in the organic phase in various diluents on extraction of Er(III) at O/A=1 were investigated to evaluate the stoichiometry of donor molecules (HOX) in Er-OPPA-HoX complex. The results are illustrated in Fig. 4 and Fig. 5. The slope of straight lines of the plot of log $(D_{mix}-D_0)$ vs. log (oxine or 2-methyl oxine) correspond to ~1, indicating that one mole of oxine or 2-methyl oxine is present in the extracted moiety in the organic phase. Based on these observations of slope analysis technique, it is evident that the nature of the extracted species in

the organic phase is found to be [Er(HA$_2$)$_3$(HOX)]. Thus, the probable synergistic extraction of Er(III) may be described by the following equations:

$$Er^{3+}_{aq} + 3[H_2A_2]_{org} \overset{K}{\Leftrightarrow} [Er(HA_2)_3]_{org} + 3H^+ \tag{3}$$

$$Er^{3+}_{aq} + 3[H_2A_2]_{org} + [HOX]_{org} \overset{K'}{\Leftrightarrow} [Er(HA_2)_3 (HOX)]_{org} + 3H^+ \tag{4}$$

The extraction equilibrium constant for the binary system K is related to distribution coefficient D_0 is expressed by the following equation:

$$\log K = \log D_0 - 3 \log [H_2A_2] - 3\, pH \tag{5}$$

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

$$\log K' = \log (D_{mix}\text{-}D_0) - 3 \log [H_2A_2] - \log [HOX] - 3\, pH \tag{6}$$

and hence,

$$\log K_s = \log K' - \log K \tag{7}$$

where K_s is the overall formation constant of ternary adduct. The equilibrium constant, ternary extraction constant and overall formation constants were evaluated for both Er-OPPA-oxine and Er-OPPA-2-methy oxine systems and are illustrated in the Table 2. This clearly indicates formation of strong ternary adduct for both oxine and 2-methyl oxine complex in toluene media.

IR spectrum of Erbium complex with oxine

Infrared spectra of OPPA and its extraction with erbium(III), the ternary extracted species is shown in Fig. 6. The characteristic absorption of OPPA is 1215 cm^{-1} designated to P=O vibrations, which shifted to o 1170 cm^{-1} in the Er(III)-OPPA complex.

Thermodynamic parameters of erbium extraction with OPPA-oxine and OPPA-2-methyl oxine

The effect of temperature is one of the factors affecting the synergistic extraction process. The thermodynamic parameters were deduced for Er(III) extraction by OPPA + Oxine/2-methyl oxine in different diluents by performing experiments at different temperature with fixed feed and extractant concentrations. The change in enthalpy (ΔH^0_f), entropy (ΔS^0_f) and free energy (ΔG^0_f) of each of the extraction system were evaluated using following equation

$$\log K' = \frac{-\Delta H^0_f}{2.303\, RT} + \frac{\Delta S^0_f}{2.303\, R} \tag{8}$$

The linear variation of $\log K'$ against 1/T in different diluents are shown in Figs. 7 and 8, and determined values of ΔH^0_f and ΔS^0_f are tabulated in Table 3.

The interaction between hard acid (Er(III)) with hard donor center (O) results in hard-hard interaction as per Pearson's HSAB principle, and this interaction between the cation and the ligands provides a negative enthalpy contribution ($\Delta H^0_f < 0$). The decrease in the randomness of the system, resulting due to formation of the cation-anion bonds, contributed negatively to the entropy component. ($\Delta S^0_f < 0$) [16]. Overall ternary complex formation therefore proceeds via outer sphere mechanism as the expansion of co-ordination shell of f-block metal is permitted. Such a mechanism is favored by enthalpy change as there is no breakage in M-H$_2$O bond.

Diluents dependency

The synergistic effect is known to be strongly diluent dependent [17] as is confirmed by the data presented in Table 1. Such change in distribution ratios could not be explained by dielectric constants of solvents [18]. Arichi[19] reported that only ligands containing a polar group or atom yield high distribution ratios. Also the aromatic compounds are more efficient than corresponding aliphatic compounds. In the present case, the nature of the solvents deciding the extent of synergism can be explained based on the Hildebrand's regular solution theory [13]. The activity and activity coefficient of interacting species can be calculated based on the regular solution theory, using solubility parameters and molar volumes data. Accordingly adduct formation constant K_s is related to the solubility parameter of diluent by the following equation [11].

$$\log K_s = 2B\, \delta_{org} + \text{constant} \tag{9}$$

$$\text{where, } B = 1/\, 2.303\, RT\, [\, V_{adduct.}\, \delta_{adduct} - V_{chelate.}\, \delta_{chelate} - V_{donor.}\, \delta_{donor}\,] \tag{10}$$

and, V = molar volumes of adduct, OPPA(chelating agent) and HOX(donor)

  δ = adduct solubility parameter, OPPA(chelating agent) and HOX(donor)

Both V and δ depend on nature of diluent used in extraction and constant term in equation (9) is independent of diluent.

A slope of '2B' was observed for both the adducts formed by OPPA-Oxine/2-methyl oxine systems. In Fig. 9, the slope obtained from the plot of adduct formation constant for Er(III) with OPPA-oxine/2-methyl oxine in different diluents vs solubility parameters (δ_{org}) is used in estimating the δ_{adduct}. A comparison of δ_{adduct} values (Table 4) obtained both 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.

Conclusions:

The effect of diluents in extraction behaviour of Er from nitric acid medium by synergistic solvent mixture of OPPA as ligand and oxine/2-methyl oxine as donor was investigated in detail. Both the donors (oxine/2-methyl oxines) exerted almost similar synergistic effect with OPPA.

Among the diluents studied, toluene gave a better synergism in comparison to other diluents. The extraction of erbium with these solvents was exothermic in nature. The composition of extracted species determined by slope analysis method indicated the formation of $[Er(HA_2)_3(HOX)]_{org}$ complex and was also confirmed by Infrared spectroscopy. Solubility parameter for the ternary adducts formed in Er-OPPA-Oxine/2-methy oxine system in different diluents were experimentally determined and were compared well with the theoretical calculated values establishing the validity of the solution theory of Hildebrand.
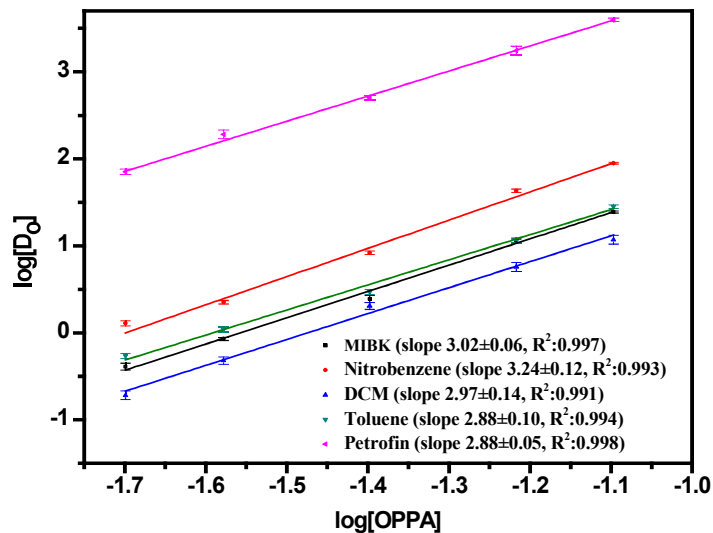
Fig. 1 Variation of distribution ratio of Er(III) in different diluents with concentration of OPPA (Concentration of Er(III) in the feed: 0.01M, O/A:1,Temperature:27°C)
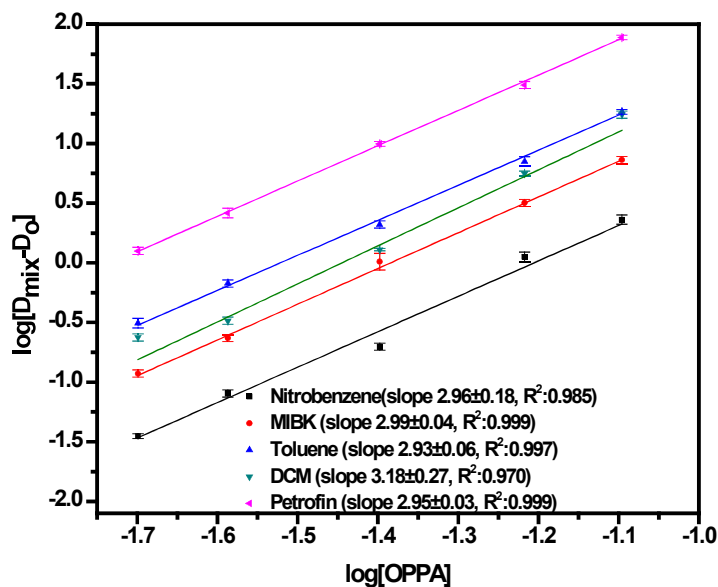

Fig. 2. Effect of OPPA concentration on extraction of Er(III) in constant concentration of oxine.

(Er(III) in the feed: 0.01M, oxine :0.08 M, O/A:1,Temperature:27°C)
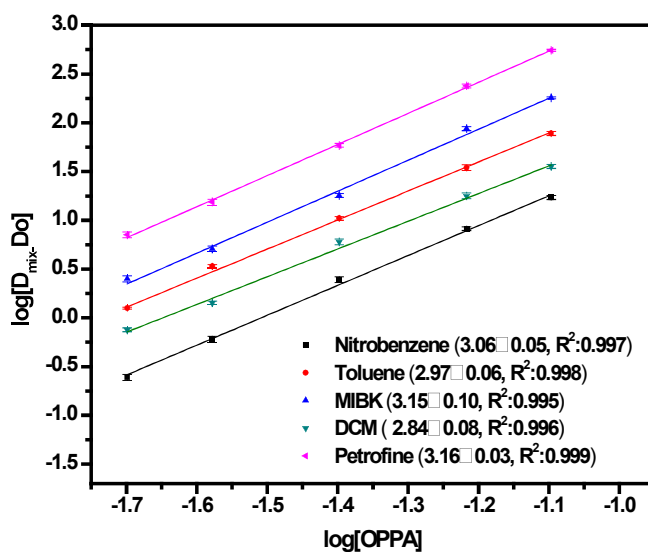
Fig. 3 Effect of concentration of OPPA on Er(III) extraction in presence of fixed concentration of 2-methyl oxine

(Concentration of Er(III) in the feed: 0.01M, 2-methyl oxine :0.08 M, Temperature:27°C)
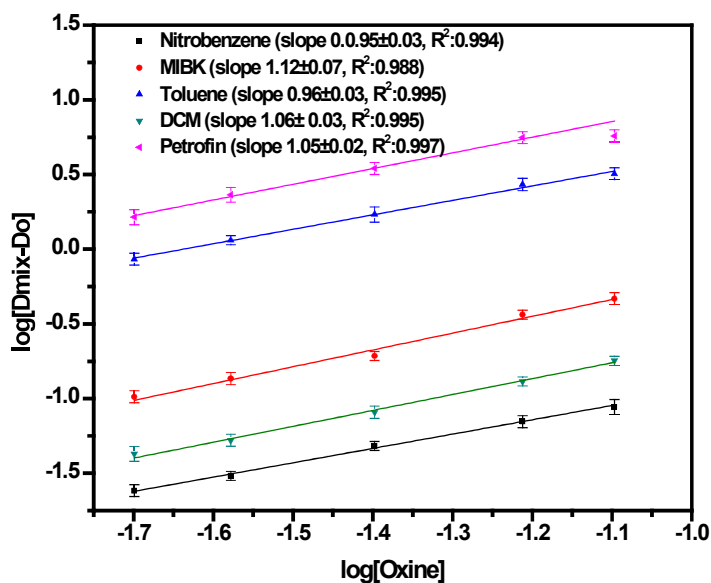

Fig. 4 Effect of concentration of oxine on Er(III) extraction in presence of fixed concentration of OPPA

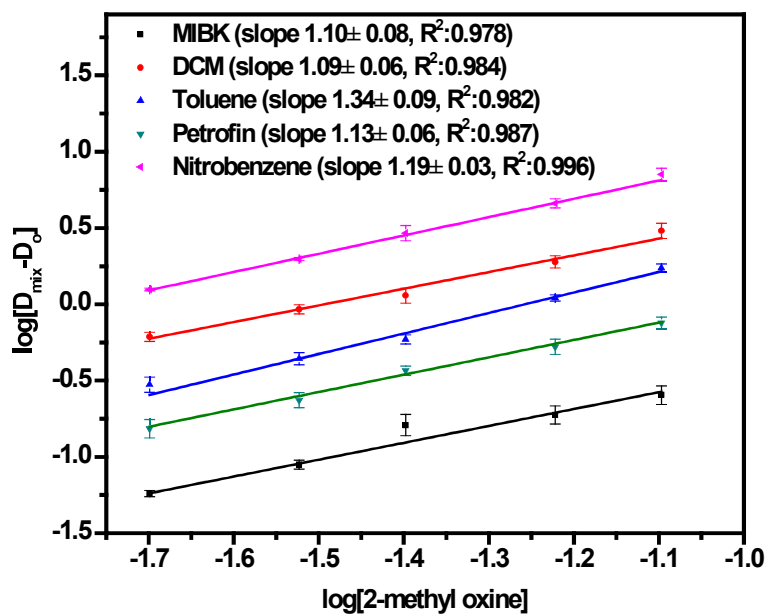**(Er(III) in the feed: 0.01M, OPPA :0.02 M, O/A:1,Temperature:27°C)**

Fig. 5 Effect of concentration of 2-methyl oxine on Er extraction in Er-OPPA-2-methyl oxine system

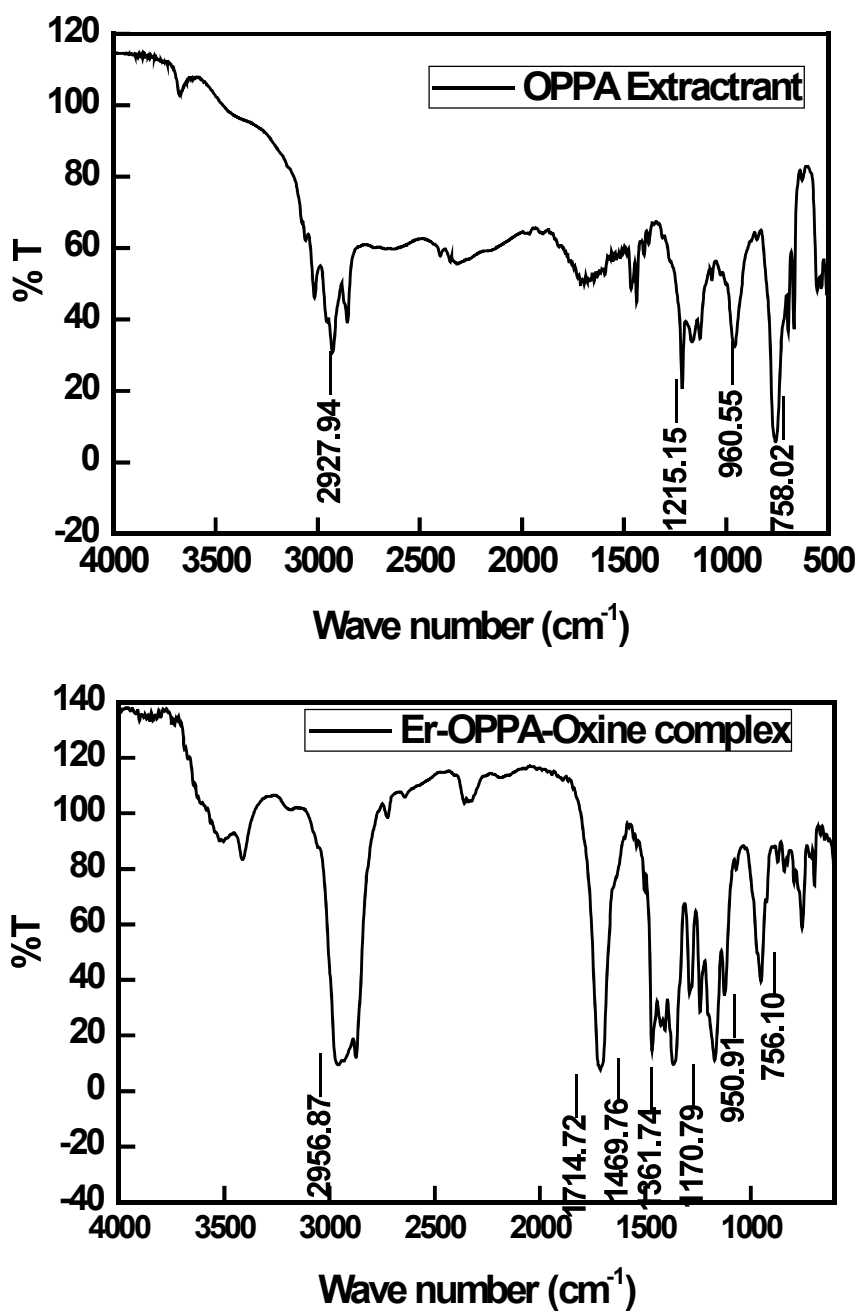**(Er(III) in the feed: 0.01M, OPPA :0.02 M, O/A:1,Temperature:27°C)**

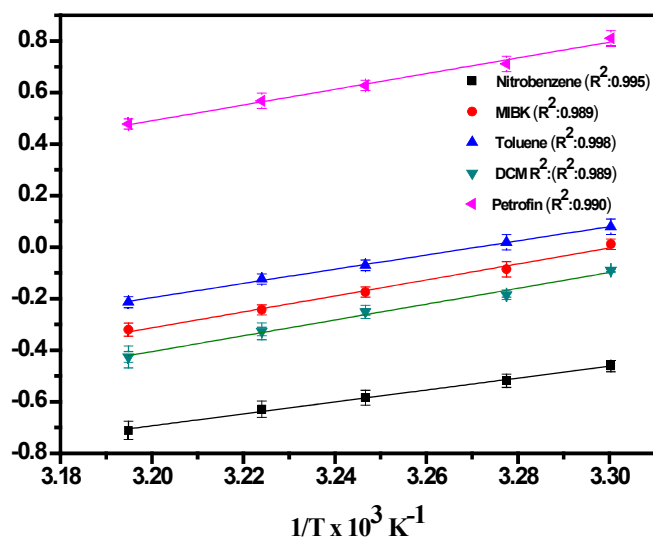**Fig. 6 IR Spectra of extractant OPPA and Er³⁺-OPPA-oxine complex**

Fig. 7 Variation of equilibrium constant of Er(III) – OPPA – Oxine complex with temperature.

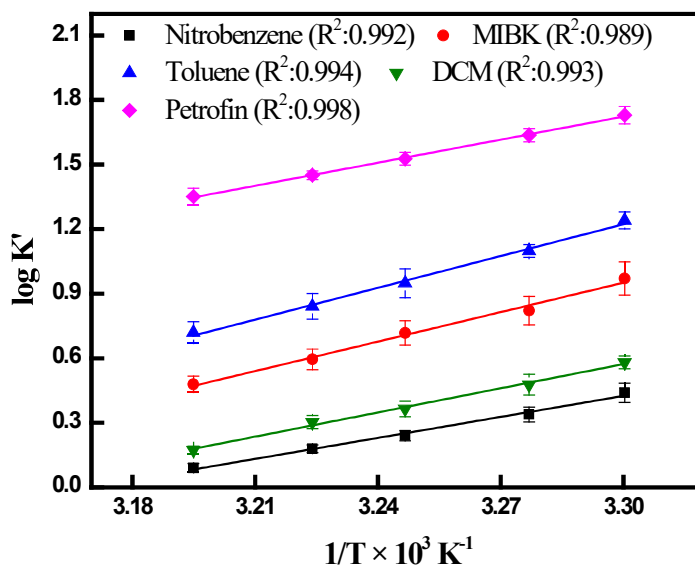**(Er(III) in the feed: 0.01M, OPPA :0.02 M, Oxine: 0.08M, O/A:1)**

Fig. 8 Effect of temperature on equilibrium constant of Er(III) – OPPA – 2-methyl oxine complex

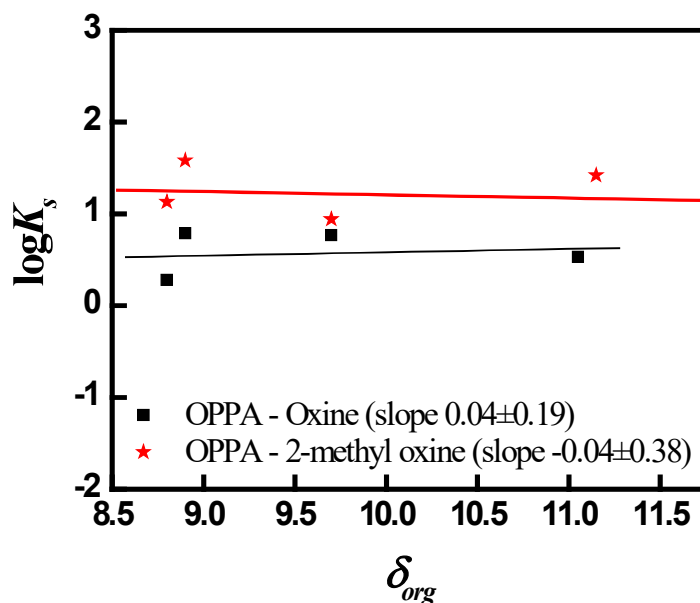**(Er(III) in the feed: 0.01M, OPPA :0.02 M, Oxine: 0.08M, O/A:1)**

Fig. 9 The variation of log K_s vs δ_{org} in synergistic extraction of Er^{3+} in different diluents

TABLE 1: Synergistic extraction of Er(III) at fixed concentration of OPPA (0.02 M) with varying concentration of donor

Diluents	Concentration of oxine or 2 methyl oxine[M]	S.C (oxine system)	S.C (2-methyl oxine system)
Nitrobenzene	0.02	0.02 ± 0.001	0.22 ± 0.013
	0.04	0.03 ± 0.001	0.35 ± 0.017
	0.08	0.10 ± 0.003	0.49 ± 0.046
Methyl isobutyl ketone	0.02	0.03 ± 0.002	0.27 ± 0.013
	0.04	0.07 ± 0.002	0.36 ± 0.008
	0.08	0.17 ± 0.003	0.72 ± 0.049
Toluene	0.02	0.74 ± 0.045	0.41 ± 0.010
	0.04	0.99 ± 0.050	0.99 ± 0.04
	0.08	1.25 ± 0.065	1.00 ± 0.05
Dichloromethane	0.02	0.03 ± 0.001	0.11 ± 0.012
	0.04	0.06 ± 0.002	0.22 ± 0.014
	0.08	0.15 ± 0.004	0.38 ± 0.007
Petrofin	0.02	0.01 ± 0.001	0.01 ± 0.001
	0.04	0.02 ± 0.001	0.01 ± 0.001
	0.08	0.03 ± 0.002	0.04 ± 0.002

TABLE 2: Equilibrium constants for binary and ternary systems

Diluents	Er(III) –OPPA system	Er(III) –OPPA – Oxine system		Er(III) –OPPA – 2-methyl oxine system	
	$\log K$	$\log K'$	$\log K_s$	$\log K'$	$\log K_s$
Nitrobenzene	-0.98± 0.026	-0.45 ± 0.015	0.53 ± 0.0	0.44± 0.034	1.42± 0.060
Methyl isobutyl ketone	-0.16± 0.003	0.02± 0.001	0.18± 0.00	0.97± 0.048	1.13± 0.051
Toluene	-0.74± 0.041	0.05± 0.006	0.79± 0.04	1.24± 0.029	1.98± 0.070
Dichloromethane	-0.86± 0.035	-0.09± 0.006	0.77± 0.04	0.54± 0.023	1.40± 0.060
Petrofin	1.39± 0.035	0.81± 0.006	-0.57± 0.0	1.73± 0.02	0.34± 0.056

TABLE 3: Results of Thermodynamic parameters

Ternary System	Diluents	ΔH (k J mol^{-1})	ΔS (JK^{-1} mol^{-1})	ΔG (k J mol^{-1})
Er(III) – OPPA – Oxine	Nitrobenzene	-38.40±1.55	-135.52±3.12	-1.24±0.03
	Methyl isobutyl ketone	-56.38±2.71	-185.92±4.25	-0.32±0.01
	Toluene	-47.81±0.29	-156.84±0.95	-0.29±0.02
	Dichloromethane	-53.76±2.27	-179.24±4.42	-1.61±0.02
	Petrofin	-60.25±1.36	-183.24±7.91	-4.73±0.03
Er(III) – OPPA – 2-methyl oxine	Nitrobenzene	-62.19±2.31	-197.22±5.13	-2.44±0.02
	Methyl isobutyl ketone	-87.26±2.66	-269.90±5.12	-5.49±0.03
	Toluene	-94.08±2.67	-287.09±4.05	-7.03±0.04
	Dichloromethane	-71.67±1.78	-225.60±4.98	-3.32±0.02
	Petrofin	-68.32±2.14	-192.66±3.96	-9.95±0.03

TABLE 4: Solubility parameter (δ_{adduct}) of ternary system

Ternary System	δ_{adduct} (J$^{1/2}$ cm$^{-3/2}$)	
	Theoretical	**Present work**
OPPA – Oxine	8.51	8.93
OPPA – 2-methyl oxine	8.58	8.70

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