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Highly Proficient Extractive Studies on The Behaviour of Neodymium (III) Assisted By 2-Octylaminopyridine from Weak Succinate Media

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ABSTRACT

The extraction behaviour studies of neodymium(III) from sodium succinate medium at pH 7.5 with 2-octylaminopyridine in xylene. The extracted neodymium(III) was stripped with 0.1 M HCl from the organic phase and determined by arsenazo. Physicochemical parameters like diluents study, phase ratio, and loading capacity to name a few were optimized for the quantitative extraction of neodymium(III). Neodymium(III) was selectively extracted and separated from binary and ternary mixtures.

Keywords: - Extraction, Neodymium (III), 2-octylaminopyridine, Succinate media.

I. INTRODUCTION

Neodymium is one most abundant element in earth crust but never occur in nature as a native element, its main source is ores of Monazite, Xenotime and Bastnaesite [1]. Neodymium is used as a permanent magnet, neodymium, boron, and iron tetragonal alloy ($Nd_2Fe_{14}B$) have been used in a wide range of applications requiring high coercive force and high energy product (e.g. Hybrid electric vehicles and miniature high capacity hard disk drives) [2,3]. Neodymium is rare and valuable therefore their recycling and extraction are mandatory for technical, environmental, economic, and resource conservation reasons.

Separation of neodymium from natural resources by environmentally friendly approaches is most significant. Therefore, man strategies for the isolation of neodymium have been developed. Among which solvent extraction is the most often used technique. Different extractants have been used for the extraction of neodymium such as 8-hydroxyquinoline [4], Cyanex 921 [5], trioctylphosphine oxide (TOPO) and trialkylphosphine oxide [6], 2-ethylhexylphosphoric acid [7]. Tributylposphate in supercritical carbon dioxide solvent has been successfully used for the quantitative recovery of neodymium [8]. Mono-2-ethylhexyl ester [9]. The extractantdialkylphospate in the ionic liquid has been studied for the extraction of neodymium [10].

Long-chain crown ethers such as poly[dibenzo-18-crown-6] [11], dicycloheano-18-crown-6 [12], and TODGA [13] were used.

As per as the robustness of the work is concerned. In earlier work, Nd(III) was extracted with different extractants. However those required either mineral acid media, the high time of extraction, high concentration of extractant, etc. Whereas in the present method, the extraction was carried out in 0.005 M sodium succinate at pH – 7.5, and extractant concentration was 0.05 M indicating the method is relatively eco-friendly and a step ahead towards green Chemistry.

The proposed study aimed to develop a more greener and precise method for the extraction of Nd(III). Efforts have been made to optimize the extraction system. The novelty of the system lies in the minimum use of concentration of extractant and use of greener weak acid media. The method has a good recovery of solvent and does not require too much of instrumentation.

II. EXPERIMENTAL

Apparatus

Digital spectrophotometer optimized α was used for the absorption measurement using 1 cm quartz cells. An Elico digital pH meter model LI-127 was used to measure the pH. METLER TOLEDO was used for weighing operations model ML-204/-01 having accuracy 1×10^{-4} g.

Reagents

Standard Neodymium(III) 500 µg/ml stock solution

The stock solution of neodymium (III) was prepared to dissolve 1.165 g. of neodymium oxide in 40 ml of perchloric acid and the final volume was brought to 1000 ml with double distilled water.

2-Octylaminopyridine (2-OAP)

2-OAP was synthesized by Borsch and Petrukhin [14] and the working extractant solution having molarity (0.05M) was prepared in xylene.

Arsenazo-I

Arsenazo-I **(0.05**% w/v) was prepared by dissolving 0.05 g. of arsenazo-I (s. d. Fine-chem limited) in water.

Triethanolamine buffer

Added 200 ml 15% triethanolamine in 160 ml of 1M HNO_3 and 40 ml of water. Adjust the pH of the solution to 7.2 with dilute NH_3 or HNO_3.

All reagents and metal salts used are of analytical grade and their solutions were prepared in water and mineral acid.

Recommended Procedure

A solution containing 75 µg neodymium(III), was made to 0.005 M w/v with sodium succinate, and pH was brought to 7.5 with dilute mineral acid and base by maintaining total dilution volume to 25 ml and then transferred to 125 ml separatory funnel to this added 10 ml 0.05 M 2-OAP in xylene as an extractant and shaken for 5 min, two phases were allowed to disengage. The neodymium(III) extracted in the organic phase was stripped with 0.1 M HCl (3 × 10) ml as a strippant solution.

The stripped solution containing neodymium(III) was evaporated to moist dryness. To this added 5% sulphosalicyclic acid. After two minutes added 5 ml of the Arsenazo-I [15] (0.05% w/v) solution, 10 ml of triehanolamine buffer, water to 40 ml, and ammonia till the pH was 7.2. Transfer the solution to a 50 ml volumetric flask, diluted up to the mark with water, and measured the absorbance at 580 nm using reagent solution as a reference.

III. RESULTS AND DISCUSSION

Effect of pH

The formation of a complex of metal with a particular extractant and the subsequent extraction was greatly influenced by the pH of the solution. The influence of the pH on the extraction of neodymium(III), was studied in the range from 1-10 (Fig. 1). The required H^+ ion concentration at various pH was reached by adding dil. HCl or NaOH. The extraction of ion-pair complex of neodymium(III) was increased with pH and became quantitative in the pH range 7.0 - 8.2, above this optimum pH range neodymium(III) extraction decreases. Therefore 7.5pH was selected throughout the experiment.

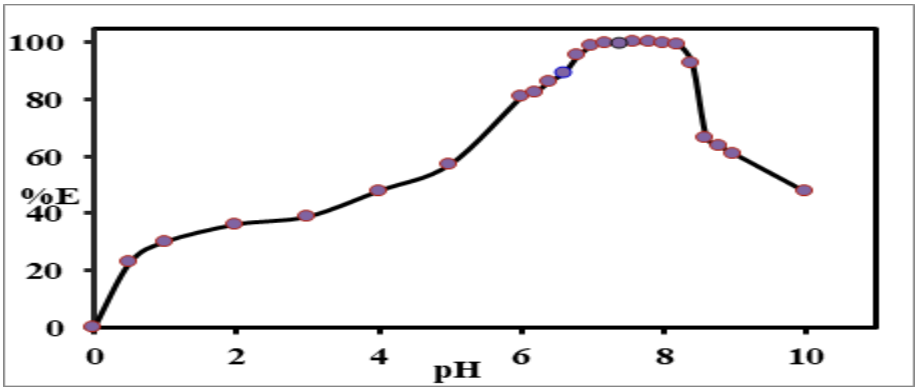

Fig. 1 Effect of pH on extraction of Nd(III) - 2-OAP complex.

Influence of 2-OAP concentration on extraction of neodymium(III)

The concentration of extractant is one of the most important factors for the extraction of any metal. Hence extraction performance of neodymium(III) greatly depended on the concentration of 2-OAP. To elucidate the effect of 2-OAP concentration on the neodymium(III) extraction, the experiment was carried out at a various concentration of 2-OAP from 0.001- 0.10 M (Fig. 2), and other parameters such as pH 7.5, 0.005 M sodium succinate, phase ratio 2.5:1 were kept constant and extraction was carried out. The results illustrate that the extraction commences at 0.001 M 2-OAP concentration and becomes quantitative in the range of 0.04-0.06 M,

further increase in concentration beyond 0.06 M there was a decrease in the extraction of neodymium(III). For the further study, 10 ml of 0.05 M 2-OAP was adopted as an optimum concentration of extractant for the quantitative extraction of neodymium(III). The recycling capacity of the reagent for quantitative extraction of neodymium(III) was observed to be three times.

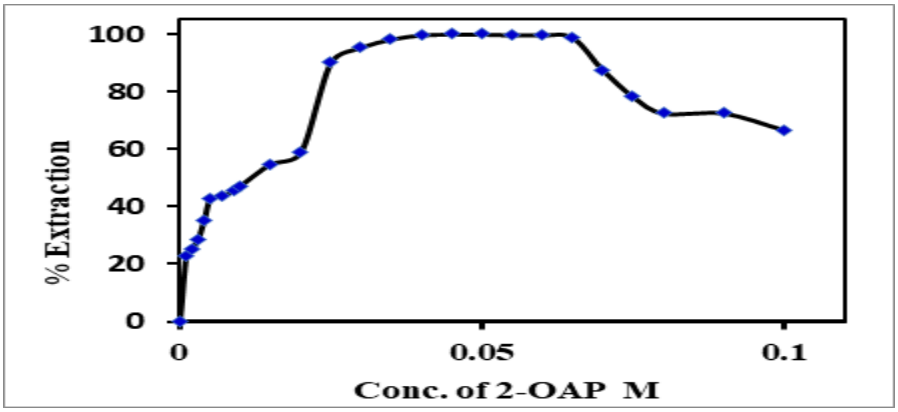

Fig. 2 Impact of conc. of 2- OAP on extraction of Nd(III)

Impact of weak organic acid concentration

The extraction of neodymium(III) was investigated at pH 7.5 with 10 ml of 0.05 M 2-OAP in xylene in the presence of a varying concentration of different weak organic anions like acetate, succinate, malonate and citrate. Quantitative extraction of neodymium(III) was found from succinate media. The weak acid curve of sodium succinate indicates that quantitative extraction was taking place in the concentration range of 0.003 to 0.010 M. In general procedure 0.005 M sodium succinate was recommended throughout the experiment (Fig. 3). The salicylate, malonate, citrate, and ascorbate do not give quantitative extraction of neodymium(III) as there was no formation of stable ion-pair complexes.

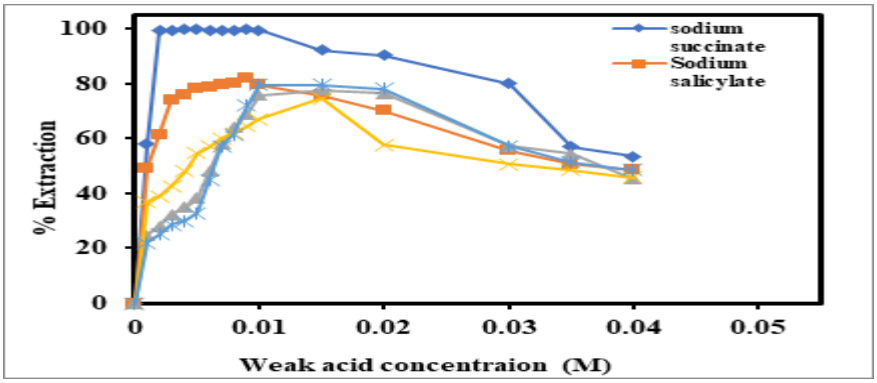

Fig. 3 Impact of weak organic acid concentration

Metal Loading Capacity

The extraction behaviour of neodymium(III) was studied concerning the metal loading capacity was demonstrated at a varying concentration of neodymium(III) in the range 25 µg to 900 µg. The analysis elucidates that the nearly hundred percent extractions take place in the range of 25 to 700 µg. It means up to 700 µg of neodymium(III) 10 ml of 0.05 M 2-OAP is sufficient and after 700 µg neodymium(III) decrease in

extraction demonstrates that there might be a deficiency of 2-OAP. Thus this study indicates that 700 µg of neodymium(III) is a maximum capacity for 10 ml 0.05 M 2-OAP.

Impact of stripping reagents on the extraction of neodymium(III)

Stripping is a back extraction and is reverse to that of extraction. If the extraction took place in a basic medium, usually the acidic strippants become more efficient and vice versa. The loaded organic phase of 2-OAP, was back-extracted with various stripping reagents as shown in Fig. 4. The results demonstrate that, the extraction efficiency of the different stripping reagents like ammonia buffer, water, ammonia, HCl, H_2SO_4 and HNO_3. The study illustrates that neodymium(III) was extracted with 2-OAP in xylene and stripped out completely with HCl, while other reagents showed incomplete stripping of neodymium(III) from the loaded organic phase. Therefore, the stripping of neodymium(III) from the loaded organic phase was carried out with 0.1 M HCl (3 × 10 ml) solution. The stripping mechanism-

[2-OAPH+Nd (succinate)$^{-}{}_2$ $_+$3 HCl⇌ 2-OAP +$NdCl_3$ +2 succinic acid

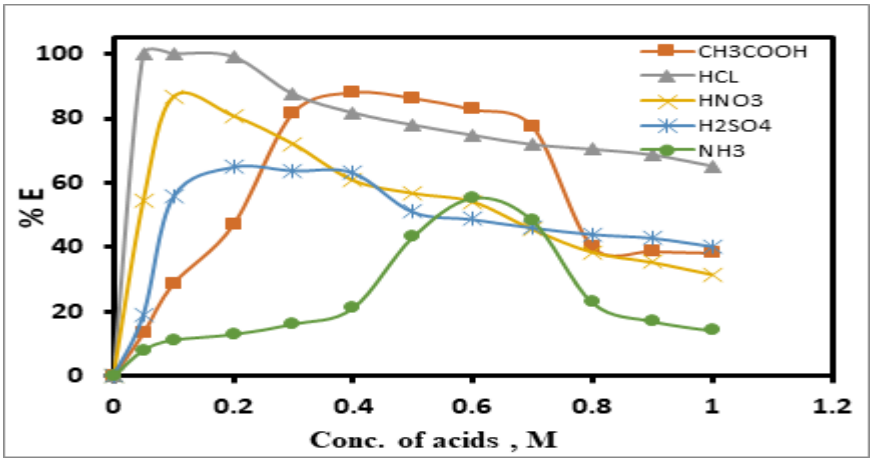

Fig. 4 Impact of strippants on extraction of Nd(III)

Solvent Study

The use of suitable solvents is very important in solvent extraction. The different solvents were studied such as amyl alcohol, 1,2-dichloroethane, xylene, n-butanol, kerosene, methyl *iso*butylketone, chloroform, toluene, benzene, carbon tetrachloride (Fig. 5). The extraction of neodymium(III) was found to be quantitative in xylene and toluene with 0.05 M 2-OAP. It was found that there was no significant relationship between dielectric constant and percentage extraction. Hence xylene was selected as a solvent for extraction of neodymium(III) which has low cost and showed clear phase separation.

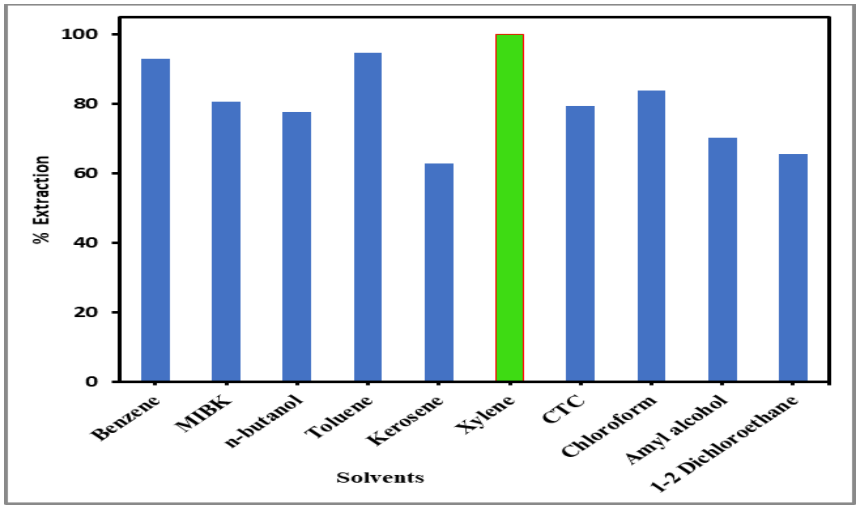

Fig. 5 Effect of solvents

Effect of organic to aqueous volume ratio

The different volume of aqueous phase to non-aqueous phase was examined by keeping organic phase volume fixed. The analysis was carried out in the range of 1:1 to 1:30. The study reveals that 1:1 to 1:6 ratios give quantitative extraction of neodymium(III). Beyond 1:6 ratio the distribution ratio decreases because of lack of 2-OAP extractant due to an increase in volume (Fig. 6). Therefore 1:2.5 ratio of organic to aqueous was recommended for the proposed method for practical suitability and to avoid the losses of chemicals.

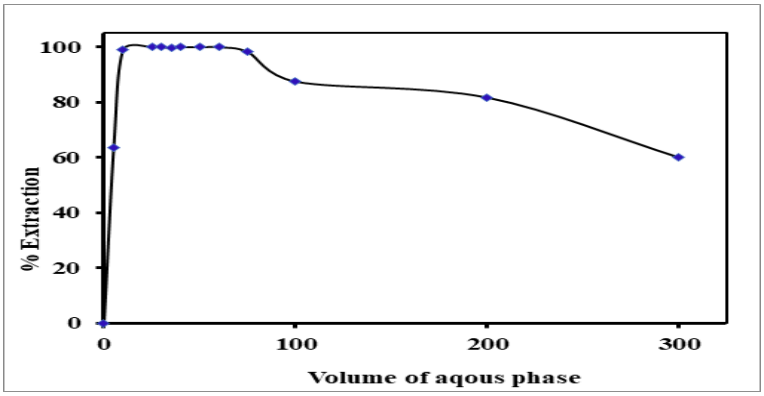

Fig. 6 Effect of organic to aqueous volume ratio

Stoichiometry of extracted species

The mechanism of extraction of neodymium(III) was proposed by evaluating the experimental information and based on slope ratio study. The plot of log $D_{[Nd(III)]}$ Vs log $C_{[\text{succinate}]}$ at fixed pH 5.5 and 9.5 was linear with slopes 2.02 and 2.03 respectively. This illustrates that two succinate ions react with one Nd(III) species (Fig. 7). The plot of log $D_{[Nd(III)]}$ Vs log $C_{[2\text{-OAP}]}$ at fixed pH 5.5 and 9.5 showed a slope of 1.18 and 1.09 respectively. This illustrates that one mole of 2-OAP takes part in reaction with one mole of neodymium(III) (Fig. 8). Therefore the slope ratio method proposes the possible combination of species as 1:2:1 (Metal: succinate: 2-OAP). The probable mechanism of extraction based on the slope ratio analysis method was as follows

$$Nd(III) + 2\ succinate^{2-} \rightleftharpoons [Nd(succinate)_2]^-_{aq} \quad (1)$$

$H^+ + 2\text{-}OAP_{org.} \rightleftharpoons 2\text{-}OAPH^+_{org.}$ (2)

$2\text{-}OAPH^+_{org} + [Nd(succinate)_2]^-_{aq} \rightleftharpoons [2\text{-}OAPH{+}Nd(succinate)^{-2}]$ (3)

$[2\text{-}OAPH{+}Nd(succinate)^{-2}] + 3HCl \rightleftharpoons 2\text{-}OAP + NdCl_3 + 2$ succinic acid (4)

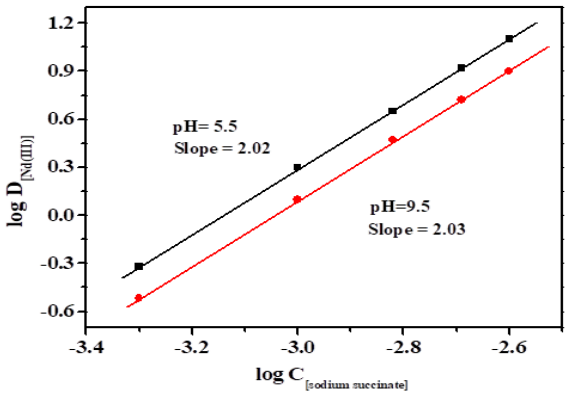

Fig.7 Plot $\log D_{[Nd(III)]}$ Vs $\log C_{[succinate]}$

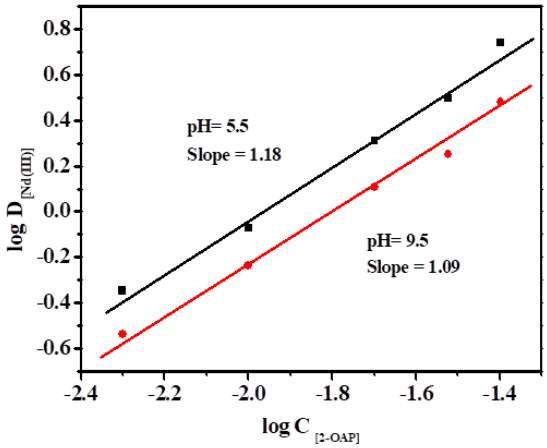

Fig. 8 Plot of log D [Nd(III)] Vs $\log C_{[2\text{-}OAP]}$

IV. APPLICATIONS

Separation of neodymium(III) from associated metal ions

The influence of commonly associating ions in the ore samples on the extraction recovery of neodymium(III) was studied. Various salts and metal ions were added individually to a solution containing 75 µg of neodymium(III) in 25 ml aqueous volume and an extraction procedure was employed. The tolerance limit of the associating ions, defined as the largest amount making the recovery of neodymium(III) less than 95 %. Most of the metal ions and anions do not interfere in the extraction of the neodymium(III) even at the milligram level. The versatility of the proposed method was checked by carrying out extraction of neodymium(III) with various associated metal ions such as Zr(IV), Ce(IV), Y(III),Th(IV), La(III),Gd(III), Sm(III), Cd(II), Pb(II), Ba(II), Ru(III), Se(IV), Mg(II), Sr(II), Mo(VI), U(VI), V(V), Zn(II), Ca(II), Cr(VI),

W(VI), Ti(IV), Nb(V), Co(II), Mn(II), Fe(II), Ta(V), Ni(II), Eu(III), Pd(II), As(III), Cu(II), Bi(III), Te(IV) and Sb(III) with 10 ml of 0.05 M 2-OAP in xylene from 0.005 M succinate medium (Table 1). Added metal ion was estimated by a classical method using a selective reagent spectrophotometrically whereas neodymium (III) was determined spectrophotometrically by the Aresnazo-I method.

Table 1 The influence of foreign ions on extraction of neodymium(III)

Tolerance limit in mg	Foreign ions added
0.5	Gd(III) [f]
1	U(VI)[a], V(V) [a], Fe(II), Ta(v)[a], Ce (IV) [a], Pb(II) [b], Al(III) [d], Ni(II) [c]
2	La(III), Y(III), Mo(II), Zr(IV)[a] , Zn (II), Ba(II), Mn(II), Sb(II), Ru(III), Th(IV)[a]
3	Se(IV), Bi(III), Te(IV), Co(II), Eu(III)
4	Mg(II)
5	Cd(II), Ti(IV), Nb(V), Cu(II)
7	Pd(II)
10	Sr(II), Cr(VI), Sm(III) [e], W(VI), Fluoride, Nitrite, phosphate, EDTA
15	Ascorbate, Tartarate, Iodide, Thiourea, Chloride, Salicylate, Thiocyanate
25	Acetate, Nitrate, Thiosulphate, Citrate, Ca(II), Sulphate, Succinate
50	Bromide , Oxalate ,

a = Fluoride, b = thiosulphate, c = thiocyanate, d = oxalate, e = ascorbate ,
f = thiourea

Separation of neodymium(III)from ternary mixture

A ternary mixture of neodymium (III) with Th(IV) Zr(IV):La(III) Ce(IV): Cd(II), Fe(II): Th(IV), Fe(II): Th(IV), Y(III) :Y(III), La(III) : Sm(III), U (VI): Zr(IV), Mo(VI): Eu(III), U(VI):BI(III), La(III):U(VI), Ce(IV) and U(VI) Th(IV) were prepared and analyzed by general procedure (Table 2).

Table 2 Separation of neodymium(III) from synthetic mixtures.

Metal ions	Amount taken in μg	% Recovery of Nd(III)*	RSD, %
Nd(III)	75	99.75	0.07
Th(IV)	40		
Zr(IV)	400		
Nd(III)	75	99.72	0.15
La(II)	250		
Ce(IV)	300		
Nd(III)	75	99.68	0.07
Bi(III)	300		

La(III)	250		
Nd(III)	75	99.75	0.17
Th(IV)	40		
Ce(IV)	300		
Nd(III)	75	99.78	0.10
Y(III)	75		
La(III)	250		
Nd(III)	75	99.62	0.19
Eu(III)	150		
U(VI)	200		
Nd(III)	75	99.78	0.16
Sm(III)	200		
U(VI)	200		
Nd(III)	75	99.48	0.13
Zr(IV)	400		
Mo(VI)	150		
Nd(III)	75	99.58	0.09
Fe(III)	400		
Cd(II)	40		
Nd(III)	75	99.62	0.11
Y(III)	75		
Th(IV)	40		
Nd(III)	75	99.72	0.15
U(VI)	200		
Ce(IV)	300		
Nd(III)	75	99.70	0.17
U(VI)	200		
Th(IV)	40		

* Average five determinations

Added metal ions remained in a non-organic phase whereas from loaded non-aqueous phase containing neodymium(III) was back-extracted with 0.1 M HCl (3 × 10) ml and determined spectrophotometrically by arsenazo-I. To check and confirm the accuracy of the method average three determinations were carried out.

V. CONCLUSION

I]. The ion-pair complex of neodymium(III) succinate with the 2-OAP in xylene was good enough for separating the various binary, ternary mixtures which are commonly associated with it.

II]. During extraction of neodymium(III) there was no need for the addition of any surfactant or modifier for quantitative extraction in a single step from weak acid media at 7.5 pH and at room temperature.

III]. The neodymium(III) from the loaded organic phase of 2-OAP was back-extracted by stripping the non-aqueous phase with 0.1 M HCl (3 × 10 ml) solution.

IV]. The extractant 2-OAP was extended for separating the neodymium(III) from binary and ternary mixtures.

V]. The strippants used for the separation are simple.

VI]. The probable composition of the proposed method was 1:2:1 (metal: succinate: 2-OAP extractant).

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