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E: ISSN NO.: 2455-0817 *Remarking An Analisation*

Spectrophotometric determination Europium$^{(III)}$ and Terbium$^{(III)}$ as its1- (2-pyridylazo)-2-Naphthol Complex with a Mixture of Naphthalene and Benzophenone

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Abstract

The growing importance of rare earth metals in nuclear chemistry and metallurgy necessitated the development of methods for their rapid determination on the microgram scale. The fundamental condition of spectrophotometric determination of rare earth metals with 1-(2-pyridylazo)-2-naphthol (PAN) were described by Shibata. Solvent extraction behavior of lanthanide ions was investigated using PAN as a cheating agent at pH 9.0 in aqueous Benzene and 20 % ethanol medium at 28±1^{0}C. This paper deals with the spectrophtometric determination of Europium$^{(III)}$ and Terbium$^{(III)}$ with PAN. The complexes of Europium$^{(III)}$ and Terbium$^{(III)}$ with PAN were extracted in molten binary mixture of naphthalene-benzophenone (3:1) from aqueous solutionat the pH 8.5.

Keywords: Extraction, 1-(2-Pyridylazo)2- Naphthol, Naphthalene, Benzophenone, Spectrophotometer.

Introduction

This new method of extraction is essentially a liquid-liquid extraction at elevated temperature followed by solid-liquid separation at room temperature. In this technique the metal chelates are precipitated in aqueous solution in microgram quantities which can be easily extracted into molten organic substances. Just as in case of their liquid-liquid extraction using organic solvents. The metal chelates formed in aqueous solution can be extracted by adsorption on polycrystalline substance obtained on cooling. Thus the method has been named as analysis by solid-liquid separation/extraction.

The azo dyes have been considered as very sensitive spectrophotometric agents for various transition metal and lanthanide. Anderson and Nickless[5] have reviewed the analytical applications of heterocyclic dye stuff and closely related compounds in which the heteroatom and any hydroxyl groups are involved in chelation with metal ion.

Solid extraction and homogeneous extraction of metal as 1-(2-pyridylazo)2- naphthol chelates into molten naphthalene and chloroform have been compared by Lobanov and Espi[6]. The solid-liquid extraction of the complexes of praseodymium $^{(III)}$ and Neodymium $^{(III)}$ with PAN in a mixture of polycrystalline naphthalene and benzophenone have been reported by Vyas[7].

Aim and Scope of the Study

The azo dyes have always been considered as very sensitive spectrophotometric agents for various Lanthnide such as Eu$^{(III)}$ and Tb$^{(III)}$. Anderson and Nickless have revived the analytical applications of heterocyclic dye stuffs and closely related compounds in which the hetero atom and any hydroxyl groups are involved in chelation with metal ions. It has been shown the extraction ratio of more than 90 % is achieved during solid-liquid extraction procedures is a single step.

Review of Literature

As stated earlier, Funjnaga, Kuwamoto and Nakayama31 presented the new mothod of solid-liquid separation in 1969 in which the liquid-liquid extraction at elevated temperature was followed by solid-liquid separation at room temperature. The basis studies solid-liquid extraction useses solid organic compound as the immiscible phases.

It has some advantage as compound the liquid-liquid extraction. The preconcentration of metal ion in very small volume of organic phase is achieved. This method is very rapid and the extraction`s upto maximum extent are achieved in one single operation. The binary solid mixture of organic substance which have considerably lower melting point can be used for example, naphthalene with diphenyl or benzophenone.

The composition and extraction equilibrium constant of rare earth metal complexs of 1-(2-Pyridylazo) 2-Naphthol have been investigated by several workers[1-4]. Most of these metal chelates are insoluble in water and find application in the extraction of lanthanons into inorganic solvents and their Spectrophotometric determination[10-12]. The ultraviolet and visible absorption spectrum of the dyes has been studied as a function of pH by Pease and Williams[13],

Many of these chelates are insoluble in water but can be extracted into various organic solvents. This phenomenon has been investigated in detail by Berger and Elvers[14], Shibata[15-16] and Betteridge, Fernando and Freiser[17], Golden and Guillot[18], Frederic and Daniel[19], Marmodee and Goojer[20], Moreau and Vitorge[21],Barkleit and Kretzschmar[22].

Materials

Preparation of Stock Solution

The stock solution (250 ml) of Europium$^{(III)}$ and Terbium($^{III)}$ Nitrate were prepared by dissolving requisite amount of their oxide (99.9 %, E.Merck Darmstand) in small amount of concentrated nitric acid and were evaporated to dryness. The viscous mass was redissolved and diluted with double distilled water. The stock solution was standardized complexometrically with disodium salt of ethylenediamine tetra acetic acid (EDTA; BDH, Analar) using xylenol orange as an indicator. EDTA solution was standardized by general procedure described by Vogel[8].ion were stored in polthene bottles and were diluted before use in each experiment. Xylenol orange (BDH) indicator solution (0.1%) was prepared by suspending 0.1 gm in 1:1 (v/v) ethanol water mixture.

Standardization of Europium / Terbium solutions

The procedure by Lyle and Rahman[9] was used for the above purpose. A 10 ml of Europium / Terbium nitrate solution were taken in separate conical flasks and diluted to 40 ml with double distilled water. Few drop of freshly prepared Xylenol orange indicator along with a drop Pyridine was added, followed by addition of 1.0 ml of acetic acid acetate buffer for fixing the pH between 5.5-6.5. The wine red coloured solution was then titrated with EDTA solution. The titration was continued until the colour sharply changed from red to yellow. Xylenol orange gave accurate and very precise titres values.

Chelating Reagents

A 0.01 M solution of (PAN) 1-(2-Pyridylazo) 2-Naphthol. (Recrystallized from 50% v/v aqueous methanol, M.P. 136-137^{o}C) was prepared by dissolving accurately weighed amount of it in pure methanol.

Solid-organic Extractants

Naphthalene

Naphthalene analytical reagent grade was further purified by sublimation. The sublimed product melted at 80 ± 0.1^{o}C. Molten naphthalene was used as an extractant. The solid naphthalene was used in a 20% solution of naphthalene in acetone was prepared for those experiments where polycrystalline naphthalene was required.

Benzophenone

Recrystallized benzophenone melting at 48^{o} C was used in the solid state.

Apparatus

pH-Meter

The pH measurements were carried with an Elico model digital pH-meter with combined glass and calomel electrodes (accuracy±0.01 pH) at 28±0.5^{o}C.

Ultra-Violet and Visible Spectrophotometer

The measurements of optical density of solution were carried out with help of Beckmann DU U.V and visible spectrophotometer, equipped with the quartz cell of 1 cm. path length.

Methods

Procedure

Lanthanide metal ions such as Eu$^{(III)}$ and Tb$^{(III)}$ have been extracted as their PAN complex by molten mixture of naphthalene and benzophenone. Aliquots containing 10 µg. of metal ion Eu$^{(III)}$ or Tb$^{(III)}$ are transferred in a tightly stoppered Erlemeyer flask (100 ml) and were diluted to 40 ml with distilled water, the complexing reagent solution 1-(2-Pyridylazo)-2-Naphthol was added followed by the addition of few drops of dilute aqueous ammonia solution in order to render the solution alkaline. The sample solution was warmed to 60^{o}C on a water bath and allowed to stand for 30 minutes at room temperature. A mixture of naphthalene and benzophenone (3:1) weighing 2.0 gm was added to the reaction mixture and heated to 52-54^{o}C. The solid binary mixture melted completely, the solution was stirred vigorously for few minutes till the molten mixture solidified again. It was washed several times with cold water and finally dried at 25-30^{o}C. The solid molten mixture leaded with metal complex was dissolved in ethereal solution and exactly 10ml solution was made in a volumetric flask. A portion of it was taken in quartz photometric cell and optical density was measured against reagent blank solution.

Beer`s Law, Sensitivity and Reproducibility

The complexes of Europium $^{(III)}$ and Terbium $^{(III)}$ with PAN were extracted in molten binary mixture of naphthalene–benzophenone (3:1) from aqueous solutions at the pH-8.5. The adsorption spectra of these extracts in the ethereal solution were recorded in the visible range 450-600nm. The absorption maxima fig. 1 were observed at 530 and 550 nm for Europium $^{(III)}$ and Terbium $^{(III)}$which are given in table 1. The molar absorptivity of PAN- Europium $^{(III)}$ and Terbium $^{(III)}$ extracts in ether at the λ max was found to be 5.690x10^{4} and 6.754x10^{4}. The concentration of Europium $^{(III)}$ and Terbium $^{(III)}$ metal ions were varied from 0.5 to 20µg under optimum experimental condition. The optical density of ethereal solution of naphthalene – benzophenone extracts, was

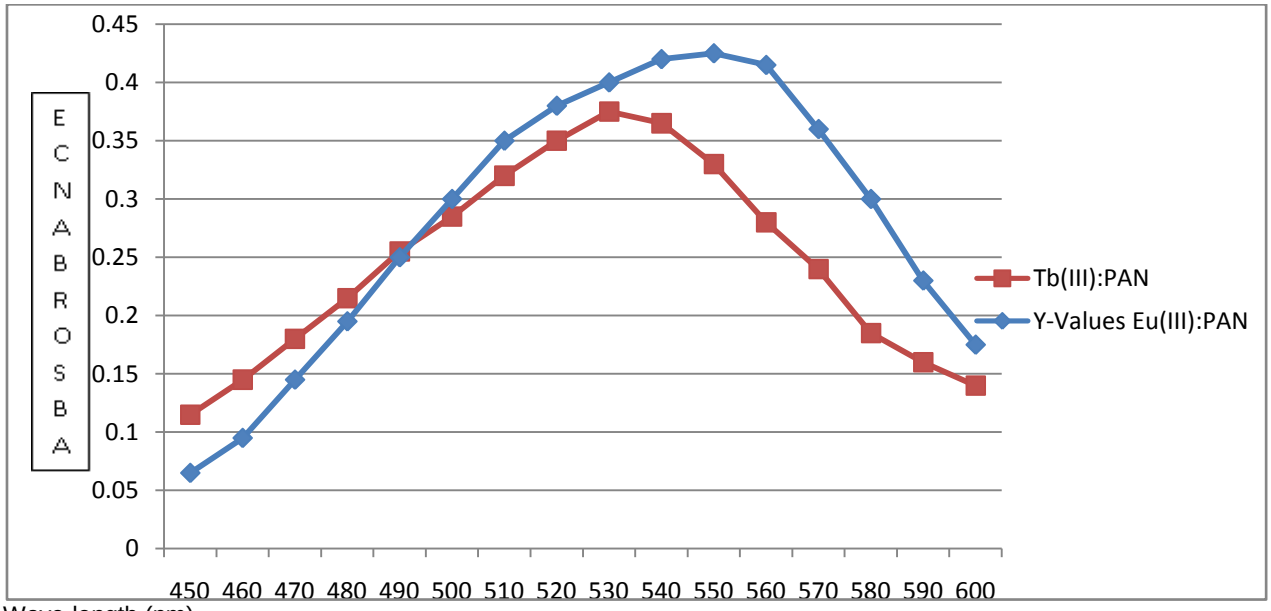
measured at 530 and 550 nm respectively. The calibration curves were plotted between absorbance and metal ion concentration. A linear relationship, over concentration range 0.5 to 16µg of Europium $^{(III)}$ and Terbium $^{(III)}$ ions per 10 ml ether was observed, (table 2). fig.2. the mean absorbance of five replicate determination was determined, and the mean deviation and relative mean error and Sandell sensitivity were calculated which are given in the table 3.

Table: 1

Absorbance vs. Wave length data for Europium $^{(III)}$ and Terbium $^{(III)}$ –PAN complexes extracted into molten naphthalene -Benzophenone

Wave Length(nm)	Absorbance of Extracts in ether $Eu^{(III)}$:PAN	Absorbance of Extracts in ether $Tb^{(III)}$:PAN
450	0.115	0.065
460	0.145	0.095
470	0.180	0.145
480	0.215	0.195
490	0.255	0.250
500	0.285	0.300
510	0.320	0.350
520	0.350	0.380
530	0.375	0.400
540	0.365	0.420
550	0.330	0.425
560	0.280	0.415
570	0.240	0.360
580	0.185	0.300
590	0.160	0.230
600	0.140	0.175

Fig.1 Absorbance Spectra for $Eu^{(III)}$/$Tb^{(III)}$:PAN Complex in Naphthalene-Benzophenone

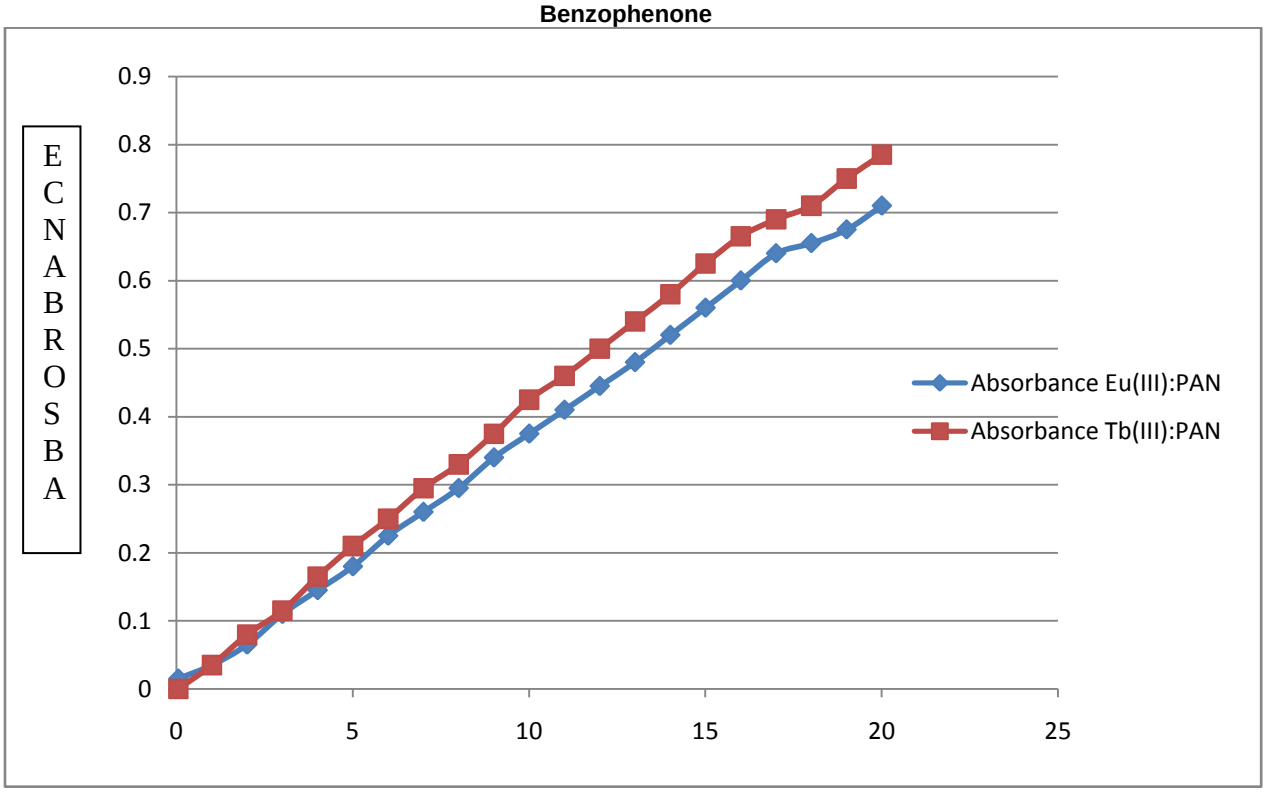


Wave-length (nm)
$Eu^{(III)}$/$Tb^{(III}$-10 µg.
PAN-4.0 ml, 0.01M
pH-8.50
Reference-Reagent Blank

Table no: 2
Metal ion concentration vs. Absorbance data for extraction of Europium$^{(III)}$ and Terbium$^{(III)}$ –PAN complexes extracted into molten naphthalene -Benzophenone

Conc.of Metal ion µg/10 ml. in aqueous phase	Absorbance of Extracts in ether Eu$^{(III)}$:PAN (530 nm)	Absorbance of Extracts in ether Tb$^{(III)}$:PAN (550 nm)
0.05	0.015	0.015
1.00	0.035	0.035
2.00	0.065	0.080
3.00	0.110	0.115
4.00	0.145	0.165
5.00	0.180	0.210
6.00	0.225	0.250
7.00	0.260	0.295
8.00	0.295	0.330
9.00	0.340	0.375
10.00	0.375	0.425
11.00	0.410	0.460
12.00	0.445	0.500
13.00	0.480	0.540
14.000	0.520	0.580
15.00	0.560	0.625
16.00	0.600	0.665
17.00	0.640	0.690
18.00	0.655	0.710
19.00	0.675	0.750
20.00	0.710	0.785

Fig.2 Absorbance Vs Metal Ion Concentration Plot for Eu$^{(III)}$/Tb$^{(III)}$:PAN Complex Extracted In Naphthalene-Benzophenone



PAN-4.0 ml, 0.01M
pH-8.50
λ max nm for Eu$^{(III)}$:PAN, λ max nm for Tb$^{(III)}$:PAN,
Reference-Reagent Blank

Table: 3
Spectral Characteristics Of $Eu^{(III)}/Tb^{(III)}$: PAN Chelates Extracted Into Molten Naphthalene – Benzophenone Ether

Metal Complexes	λ Max (nm)	Mean Absorbance	Molar Absorptivity Ex 10^4 litmol^{-1} Cm^{-1}	Sandell,s Sensitivity Sx10^{-3} µg cm^{-2}	Concentration Range µg/10Ml	Relative Mean Error%
EU $^{(III)}$: PAN	530	0.375	5.6990	2.7	0.5-20	0.53
Tb $^{(III):}$ PAN	550	0.425	6.7546	2.3	0.5-20	0.47

Result and Discussion

The absorption maximum of these extracts in the ethereal solution was recorded in the visible range 450-600 nm. The optimum pH range for the quantitative extraction of $Eu^{(III)}/Tb^{(III}$was found to be 8.5-10.5. the effect of $Eu^{(III)}/Tb^{(III}$-PAN ration was studied spectrophotometrically by using mole-ratio method. The results indicated the formation of a 1:3 ($Eu^{(III)}/Tb^{(III}$:PAN) complex in accordance with the composition reported in literature[1-3]. The absorption maxima fig.1 were observed at 530 nm for $Eu^{(III)}$ and 550 nm for $Tb^{(III}$ respectively.

Conclusion

The molar absorptivity and Sandell`s sessitivity values indicate the higher degree of sensitivity of PAN as complexing and spectrophotometric agent. The metal ion concentration as low as 0.5 ppm can be recovered by employing the PAN complexing and extracting reagent. The relative mean error (<1%) indicates that the method adopted for extraction, possess high degree of precision.

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