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**CHELATION STUDY OF PRASEODYMIUM, NEODYMIUM,
SAMARIUM AND GADOLINIUM WITH
TETRAETHYLENEPENTAAMINEHEPTAACITIC ACID**

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TURQUIE

CHELATION STUDY OF PRASEODYMIUM, NEODYMIUM, SAMARIUM AND GADOLINIUM WITH TETRAETHYLENEPENTAAMINEHEPTAACITIC ACID

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ABSTRACT

A quantitative spectrophotometric study of the interaction between tetraethylenepentaamine-heptaacetic acid (TPHA) with trivalent praseodymium, neodymium, samarium, and gadolinium was carried out. The effect of pH on the chelate formation was studied. The mole ratio of each complex was determined and the stability constants of the chelates were calculated. A proposed analytical procedure for determination of trivalent praseodymium, neodymium, samarium, and gadolinium was given. TPHA was found to form the 1:1 chelates with the studied ions in the range of pH lies between 2.7 and 10.5. The obtained stability constants were found to be 17.3, 17.6, 18.2, and 18.6 for PrIII, NdIII, Sm III and Gd III chelates respectively.

INTRODUCTION

Lanthanides are well known to form strong complexes with several colourless and coloured chelating agents. The intensity of absorption maximum of complexes increases and slightly displaces to longer wavelength compared to the free metal ion. However, for certain elements, absorption maximum is displaced to shorter wavelength. Zielinski et al [1] determined, spectrophotometrically, lanthanides using methylthymol blue. The reaction between lanthanides and arsenazo III, at pH 4-5, was investigated [2]. Kotoucek et al [3] showed that gallocyanine [C.I. Mordant blue 10] methyl ester reacted with lanthanides in aqueous 10, 20 and 30 % ethanol to form 1:3 (metal:ligand) complexes with well defined absorption maximum. Determination of traces of rare earth elements in water using 2-hydroxy-2-methylpropionic acid was reported [4].

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Several other organic indicators such as pyrogallol red and diphenylguanidine [5], dicarboxyarsenazo III [3,3'-(1,8-dihydroxy-3,6-disulpho-2,7-naphthylene-bisazo) bis-(4-arsenobenzoic acid) [6], chlorosulphophenol M [3-(5-chloro-2-hydroxy-3-sulphophenylazo)-6-(3-sulphophenylazo) chromotropic acid] [7] and orthanilic B [3-(phenylazo)-6-(2-sulphophenylazo)-chromotropic acid] [8] were also applied for the spectrophotometric determination of lanthanides.

However, most of these methods are not sensitive enough for analytical application as the formed complexes are unstable and non reproducible. Moreover, there is a large error in determining one lanthanide in presence of another and many other ions interfere.

On the other hand, spectrophotometric determination of rare earths in solution of polyaminopolycarboxylic acids seems to be more effective, stable and sensitive. Mishchenko and Poluetkov [9] studied the absorption spectra of aqueous complexes of lanthanides with EDTA. Addition of EDTA increases the band intensity about 1.1-2.6 leading to an increase in the sensitivity of detection. The optimal conditions for the determination are 0.1 M EDTA at pH 8-9 and lanthanide concentration of 10 mg (as oxide)/ml.

It has been noticed that the stability of metal chelates increases by increasing co-ordinating groups in the order EDTA, DCTA, DTPA and TTHA. This is due to the increase of affinity of the ligand for the lanthanide ion.

The present work illustrates spectrophotometric study of the interaction between Pr(III), Nd(III), Sm(III) and Gd(III) and tetraethylenepentaminehepta-acetic acid (TPHA). A proposed method for analytical determination of the studied elements is also given.

EXPERIMENTAL

Materials

The experimental conditions and the optical methods were previously published [10]. Solutions of Pr (III), Nd(III), Sm(III) and Gd(III) were prepared from the respective chloride salts. All pH measurements were carried out using a combined glass-calomel electrode. Absorption spectra were measured in the range of wavelength from 210 nm to 700 nm.

Preparation of solutions

Trivalent lanthanide solutions were prepared by dissolving accurate weight of the lanthanide chloride in bidistilled water to obtain solution of $1 \times 10^{-3}M$ except for Gd(III) where the concentration was $5 \times 10^{-4}M$.

The TPHA solution was prepared by dissolving an accurate weight of tetra sodium salt of TPHA in bidistilled water to obtain $10^{-2} M$ solution. From this stock solution different concentrations were prepared by appropriate dilutions. The stock solution of TPHA was standardized against a standard copper sulphate solution using murexide as indicator[11].

The chelate solution was prepared by mixing equal volumes of the metal ion and TPHA solutions. The required pH was then adjusted using carbonate free sodium hydroxide solution.

RESULTS AND DISCUSSION

Variation of the absorption of ($Ln^{+3} + TPHA$) as a function of pH

The characteristic absorption bands of an aqueous solution of Pr (III), Nd (III), Sm(III) and Gd(III) are located at wavelength range from 250 nm to 700 nm. TPHA absorbs in the ultraviolet region and its absorbance is negligible at $\lambda \geq 260$ nm. The absorption spectra of a mixture of $10^{-3} M$ of Pr (III), Nd(III) and Sm(III) or $5 \times 10^{-4} M$ of Gd(III) with $5 \times 10^{-2} M$ of TPHA were shifted to longer wavelength as the pH of the mixture solutions increased. Within certain pH range, the position of the absorption maximum remains constant (Table I). The obtained spectra of the chelates are shown in Fig. 1. The pH at which the complex was completely formed in case of gadolinium was in

Table I
Characteristics of lanthanide-TPHA chelates

ion	$\lambda(\text{nm})$ ion	ϵ ion	$\lambda(\text{nm})$ complex	ϵ complex	pH interval	pK
Pr (III)	442	0.94×10^3	458	3.0×10^3	3.7-10.5	17.3
	466	0.56×10^3	469	1.6×10^3		
	478	0.36×10^3	485	1.4×10^3		
Nd (III)	518	0.24×10^3	522	1.3×10^3	3.5-10.5	17.6
	571	0.40×10^3	580	2.3×10^3		
Sm (III)	370	0.15×10^3	375	1.5×10^3	3.2-10.5	18.2
	400	0.48×10^3	409	3.1×10^3		
Gd (III)	272	0.96×10^3	274	5.6×10^3	2.7-10.5	18.6
	275	0.60×10^3	276	3.0×10^3		

more acidic region than that of praseodymium. This is apparently because gadolinium has more basic properties and therefore the formation of its complexes take place in more acidic region. At $\text{pH} > 10.5$ the absorbance decreased due to the formation of hydroxy complexes. The molar absorptivities of each chelate is given in Table I.

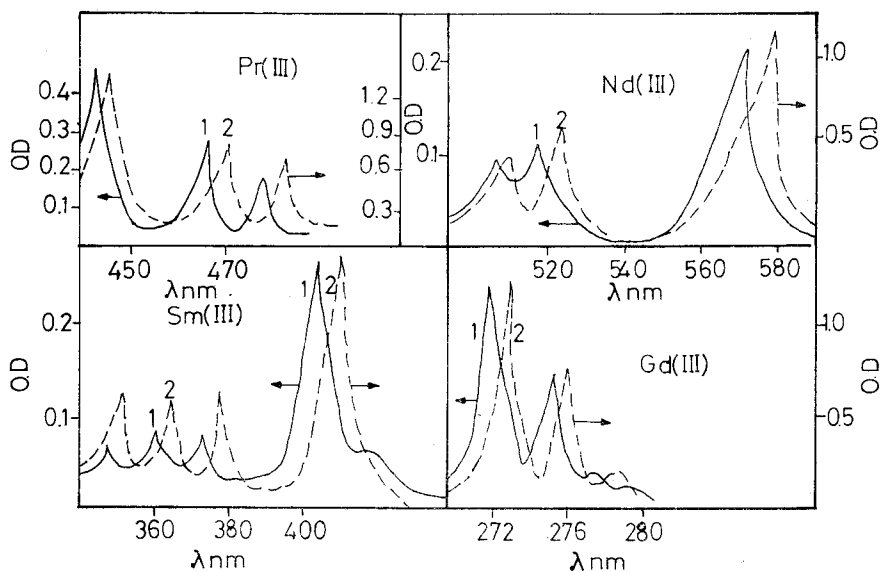


Fig. 1: Absorption spectra of some lanthanides and their TPHA chelates.

- 1- $[\text{Ln}^{+3}] = 5 \times 10^{-4} \text{ M}$, $[\text{Gd III}] = 2.5 \times 10^{-4} \text{ M}$
 2- $(\text{Ln}^{+3} + \text{TPHA})$ at $\text{pH } 3.5$

Determination of the composition of the chelates

The mole ratio method was first applied in which the concentration of Pr(III), Nd(III), Sm(III) and Gd(III) was kept constant at 10^{-3} M (Gd III at $5 \times 10^{-4} \text{ M}$) and TPHA concentration was varied between 10^{-5} M to $4 \times 10^{-3} \text{ M}$. The pH being maintained at $\text{pH } 3.5, 7.5$ and 9.5 . The obtained curves (Fig. 2) show that the discontinuity occurs at a mole concentration ratio $[\text{Ln III}] : [\text{TPHA}]$ equal to 1:1 suggesting that the composition of the complex is 1:1. No evidence was found for other ratios.

The continuous variation method was also applied in which a series of solutions were prepared by mixing different concentrations of Pr(III), Nd(III), Sm(III) and Gd(III) in such a way that the sum of their con-

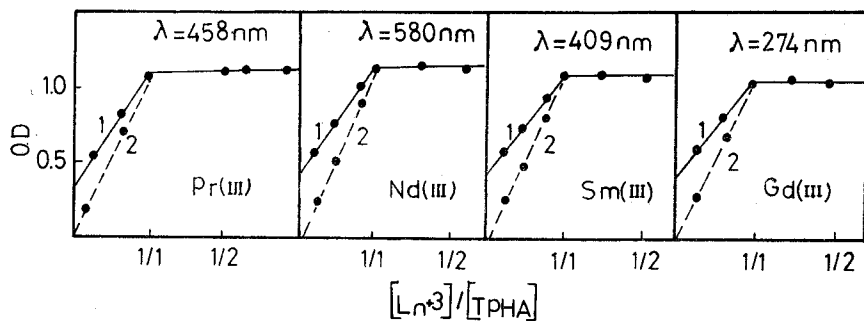


Fig. 2: Variation of the optical density, at the characteristic maxima of each complex, with $[\text{Ln}^{+3}] / [\text{TPHA}]$
 1- pH = 3.5 2- pH = 7.5 or 9.5

centration remained constant at 10^{-3} M (5×10^{-4} M in case of Gd(III)). The method was applied at pH 3.5, 7.5 and 9.5. Fig. 3 shows that the the maximum occurs at $[\text{Ln III}] / [\text{Ln III}] + [\text{TPHA}]$ equal to 0.5 which confirms that the composition of the chelates is 1:1. The stability constants were then calculated and the values are grouped in Table I. The stability constant of the 1:1 chelate increased from Pr(III) to Gd(III). It was suggested by many authors that the bonding in the chelates is purely electrostatic and therefore the stability of these complexes would be determined only by the radius of the cation present. Therefore the stability constant value should then be expected to vary linearly with Z^2/r or more generally with $1/r$ (where Z is the atomic number and r is

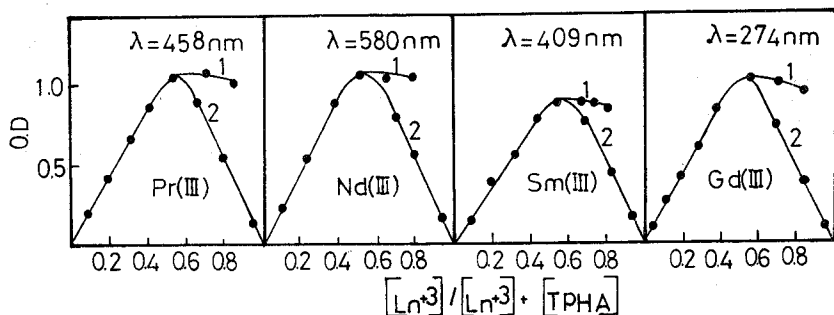


Fig. 3: Variation of the optical density, at the characteristic maxima of each complex, with $[\text{Ln}^{+3}] / [\text{Ln}^{+3}] + [\text{TPHA}]$
 1- pH = 3.5 2- pH = 7.5 or 9.5

the radius of the cation present). The stability constants of the metal chelates of TPHA was slightly lower than that of DTPA. This may be attributed to the overcrowding of the donor groups around the metal ion leading to a mutual repulsion. The overcrowding prevents the donor groups to enter to the central ion, thus lower stability of the formed complex may be expected.

Effect of other ions

The effect of other ions was investigated at pH 9.0. Foreign ions were added after preparing the chelate solution. The method is selective for the studied ions where Sr(II), Ca(II), Co(II), Co(III), Ni(II), Cu(II), Zn (II), Ce (III), UO_2^{+2} , PO_4^{-3} , SO_4^{-2} and nitrate do not interfere.

Analytical procedure

A suitable aliquot containing 10–100 μg of lanthanide element and 2 ml of 0.1 M TPHA was completed to 10 ml with bidistilled water. The pH of solutions was adjusted with carbonate free sodium hydroxide to 9. The absorbance of the mixed solutions was measured at the characteristic maximum of each complex (Table I). The lanthanide concentration was calculated from a previously prepared calibration curve for each element.

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