Comparative Spectrophotometric Determination of Neodymium (III), Praseodymium (III), Samarium (III) and Terbium (III) in Aqueous and Micelle Media

Uwanta Emaime Jimmy[1, *], Nicholas Eno-obong Sunday[2], Ikpe Edidiong Emmanuel[1], Ocheni Adejoh[3], Ukoha Pius Onyeoziri[2]

[1]Department of Chemistry, Faculty of Physical Sciences, Akwa Ibom State University, Ikot Akpaden, Nigeria

[2]Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, University of Nigeria, Nsukka, Nigeria

[3]Department of Chemistry, Faculty of Natural Sciences, Kogi State University, Anyigba, Nigeria

Email address:

emaimeuwanta@gmail.com (Uwanta Emaime Jimmy), emaimeuwanta@aksu.edu.ng (Uwanta Emaime Jimmy),
eno-obong.nicholas.pg78610@unn.edu.ng (Nicholas Eno-obong Sunday), pius.ukoha@unn.edu.ng (Ukoha Pius Onyeoziri),
ochenades@yahoo.com (Ocheni Adejoh)

[*]Corresponding author

Abstract: This research work titled comparative spectrophotometric determination of neodymium (III), praseodymium (III), samarium (III) and terbium (III)in aqueous and micelle media using schiff base was carried out with the aim to use a simple, rapid and sensitive spectrophotometric method for the determination of Nd (III), Pr (III), Sm(III) and Tb(III) using the Schiff base 2,2′-((1E,1′E)-(1,2-phenylenebis(azanlylidene)bis (methanylylidene))diphenol (BSOPD) as a ligand. Spectral and absorbance measurements were carried out using UV/Visible Spectrophotometer (Jenway model no.: 6305) with 1-cm matched quartz cells. This method of experiment was based on the formation of green coloured complexes, upon the reaction of Nd(III) and Pr(III) and a brown coloured complexes for Sm(III) and Tb(III) having a maximum absorbance of 376, 386, 384 and 380 nm respectively. The comparative analysis of the complexes formed in aqueous and in micellar media were investigated in this study. In the obtained results, it was discovered that, Beer's law was obeyed in the concentration ranges of 0.001 - 0.02 ppm. The molar absorptivity was found to be in the range of 7,776- 23,197 and 27,087 $dm^3mol^{-1}cm^{-1}$ and the Sandell's sensitivity for the compounds analyzed were in the ranges of 6.13-19.34 µg cm^{-2}. The increase in absorbance in the presence of the surfactants is due to micelle formation. The reactants were bound in a small volume of stern layer of the micelle leading to a greater increase in concentration effect. This effect in concentration reaches a maximum before decreasing due to dilution effect occasioned by increase in metal ion concentration.

Keywords: Schiff Base, Metal Complexes, Lanthanides, Stoichiometry, Spectrophotometer

1. Introduction

The study on the importance of lanthanide in science and in various branches of technology is growing rapidly globally. The lanthanides elements constitute a group in the periodic table with extremely similar chemical properties that make their separation and analytical determination challenging [1-4]. Schiff bases are derived from the aromatic amines and aldehydes, have a wide variety and are important class of ligands in coordination chemistry; and find extensive applications in different fields, for example; inorganic, biological and analytical chemistry [5]. Schiff bases are weak bases and are readily hydrolysed by dilute mineral acids, but not by aqueous alkalis and they also play an important role in coordination chemistry as they easily form stable complexes with most transition metal ions and salts are formed by them through coordination of the electrons on nitrogen atom of

azomethine group [5]. Spectrophotometric methods, as trace analysis technique, have been advocated as one of the best for the quantitative determination of lanthanide metal ions. The methods can determine metals in the range 10^{-3}-10^{-6} mol/litre with a 2% approximate precision and with intermediate speed. Spectrophotometric determination of metals in micellar media is introduced to improve the molar absorptivities, sensitivities and substitute the previous steps of toxic solvent extraction. Surfactant molecules and micelles are designed as 'organized assembles' which show some specific characteristics. They are non-toxic compared to some organic solvents used to solubilize metal complexes, easy to use, optically transparent. Surfactant molecules and micelles solubilize, concentrate and compartmentalize chemical species. They also change dissociation constant, oxidation-reduction properties, offer unique reaction media and influence transport properties [6]. Surfactants enhance the analytical characteristics of chromophoric chelating organic reagents and thus increase the sensitivity of the determination, decrease the equilibration time of the reaction and increase the stability of the complex. Therefore, the micellar solution can be used as a medium for spectrophotometric determination of metal ions [6]. Several researchers studied spectrophotometric procedure for the determination of metal ion representative from the three sub groups of lanthanide series namely Neodymium (III) and samarium (III) of cerium group; Gadolinium (III) and Terbium (III) of Terbium family and Dysprosium (III) and Holmium (III) of Yttrium family using 1-(2-pyridylazo)-2-naphthol (PAN) as chromogenic reagent in micellar media, in the work, an intense red coloured ML_3, type of complex (L=PAN and M = Ln^{3+}) was formed in the pH range 8.5 - 9.5 and was also observed that Nd, Pr, Sm and Tb(III) react with 1-(2-pridlazo)-2-naphthol (PAN) in the presence of surfactant with low molar absorptivity [7]. Dhepe and Zade who under took a research work on the spectrophotometric study of ternary complex forming system of some lanthanide metal ions with Eriochrome cyanine R in presence of Cetyl pjadaxum bromide of micro determination reported that Eriochrome Cyanine R (ECR) a member of triphenylmethane type of dye, reported to form green coloured complexes with lanthanide was used for micro determination of these metal ions [8]. Addition of cationic surfactant, Cetylpyridinium bromide (CPB), a cationic surfactant sensitized the colour reactions of Gd(III), Tb(III), Dy(III), Ho(III) and Lu(III) with ECR. Formation of water soluble, highly coloured ternary complexes with a considerable bathochromic shift of about 50 nm in presence of surfactant was observed. Optimum reaction conditions and other analytical parameters were also evacuated [8-9]. Stoichiometric ratio 1:3:3 of Ln: ECR: CPB were responsible for the observed rise in molar absorptivity and sensitivity [9-13]. Uwanta et al also reported from their research work that, the Schiff base (BSOPD) was successfully prepared and was used to synthesis new metal complexes of Nd(III), Sm(III) and Tb(III); the complexes had been characterized by physical methods and spectroscopic techniques [14-15]. However, in this study, Schiff base BSOPD was used to assess the spectroscopic determination of some lanthanides: Nd(III), Pr(III), Sm(III) and Tb(III) complexes, as well as a comparative analysis of the complexes formed in aqueous and micellar media.

2. Materials and Methods

Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results. To eliminate possible contamination from detergents or other sources, all glass wares and polyethylene material used were soaked with a 1M nitric acid for 48 h and then rinsed several times with deionized water before use.

2.1. Apparatus

Beakers, conical flask and test tubes (pyrex), spectral and absorbance measurements were carried out using UV/Visible spectrophotometer (Jenway model no.: 6305) with 1-cm matched quartz cells, pH meter (Jenway model no.: 3510).

2.2. Reagents

All the reagents and solvents used were of analytical grade and were used as supplied unless otherwise stated.

2.3. Preparation of Stock Solutions

Nd(III) solution (0.001 moldm^{-3}): Accurately weighed 0.0219 g of Nd(NO$_3$)$_3$.6H$_2$O (Sigma Aldrich 99%) was dissolved in minimal amount of deionised water in a beaker and transfer to a 50 cm^3 volumetric flask. The solution was made up to mark using deionised water to give 0.001 mol dm^{-3} solution.

Pr(III) solution (0.001moldm^{-3}): Accurately weighed 0.0218 g of Pr(NO$_3$)$_3$.6H$_2$O (Sigma Aldrich 99%) was dissolved in minimal amount of deionised water in a beaker and transfer to a 50 cm^3 volumetric flask. The solution was made up to mark using deionised water to give 0.001moldm^{-3} solution.

Sm(III) solution (0.001moldm^{-3}): Accurately weighed 0.0128 g of SmCl$_3$ (Sigma Aldrich 99%) was dissolved in minimal amount of deionised water in a beaker and transfer to a 50 cm^3 volumetric flask. The solution was made up to mark using deionised water to give 0.001 moldm^{-3} solution.

Tb(III) solution (0.001moldm^{-3}): Accurately weighed 0.0133 g of TbCl$_3$ (Sigma Aldrich 99%) was dissolved in minimal amount of deionised water in a beaker and transfer to a 50 cm^3 volumetric flask. The solution was made up to mark using deionized water to give 0.001 moldm^{-3} solution.

BSOPD solution (0.001moldm^{-3}): Accurately weighed 0.0158 g of dried BSOPD was dissolved in minimal amount of DMF in a beaker and transfer to a 50 cm^3 volumetric flask. The solution was made up to mark using DMF to give 0.001 moldm^{-3} solution.

SDS (sodium dodecyl sulphate) solution (0.01 moldm^{-3}): Accurately weighed 0.029 g of SDS was dissolved in minimal amount of deionised water in a beaker and transfer to a 10 cm^3 volumetric flask. The solution was made up to

mark using deionized water to give 0.02 moldm^{-3}.

CTAB solution (0.02 moldm^{-3}): Accurately weighed 0.027 g of SDS was dissolved in minimal amount of deionised water in a beaker and transfer to a 10 cm^3 volumetric flask. The solution was made up to mark using deionized water to give 0.02 moldm^{-3}.

Triton X-100 solution (0.02 moldm^{-3}): Accurately measured 0.06 cm^3 from a 1.63 moldm^{-3} of Triton X-100 was dissolved in minimal amount of deionised water in a beaker and transfer to a 10 cm^3 volumetric flask. The solution was made up to mark using deionised water to give 0.02 moldm^{-3}.

2.4. Spectrophotometric Determination of Metal Ions in Micellar Media

Procedure: Requisite volumes of solution of (5x10^{-6}moldm^{-3}) of BSOPD in surfactant and 1x10^{-6}moldm^{-3} of Ln^{3+} solution was mixed in a 10 cm^3 capacity flask in a 5:1[BSOPD] /Ln^{3+} ratio, and 1cm^3 of appropriate buffer

solution. The mixture was then made up to 10 cm^3 with deionized water. The solution was allowed to stand for 25 min before scanning at 250-800 nm. The surfactants were sodium dodecylsulphate (SDS) as anionic surfactant, cetyltrimethylammonium bromide (CTAB) as a cationic surfactant and Triton X-100 as non-ionic surfactant.

2.5. Effect of Reagent Concentration

The effect of concentration of the ligand BSOPD was investigated for Nd(III), Pr(III), Sm(III) and Tb(III) metal ions. A fixed concentration of the metal was used with varying concentrations of the ligands from 1x10^{-5}- 2x10^{-4} moldm^{-3}. The plots of absorbance versus concentration of ligand are shown in Figure 1 shown below. It was observed that, the absorbance kept increasing with increase in the concentration of the ligand. Therefore, for subsequent work the concentration of the ligand was kept more than five times of the metal ion concentration so that all the metal ions could be used up.
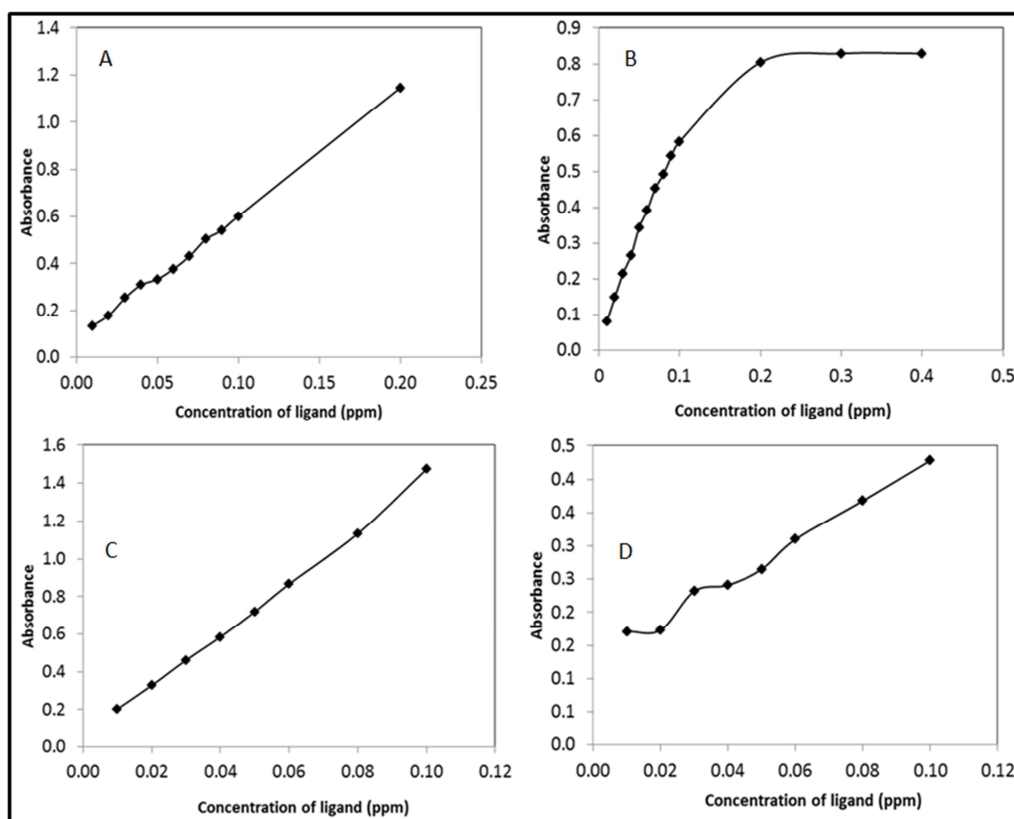

Figure 1. *Plots of absorbance versus concentration of ligand for the formation of Metal-BSOPD complex (A) Nd-BSOPD (B) Pr-BSOPD (C) Sm-BSOPD (D) Tb-BSOPD.*

3. Results and Discussion

3.1. Calibration Graphs and Detection Limit

A calibration curve was plotted for Nd(III), Pr(III), Sm(III) and Tb(III) in BSOPD in aqueous and micellar media according to the general procedure described previously. Beer's law is obeyed from 0.001 - 0.02 ppm for aqueous

medium and 0.001 - 0.006 ppm in micellar media, the limit of detection (LOD) and quantification (LOQ) for Nd(III), Pr(III), Sm(III) and Tb(III) were obtained at the range of 0.02 - 0.22 and 0.03 - 0.65 ppm respectively in aqueous medium. The LOD and LOQ were obtained in the range 0.004 - 0.03 and 0.10 - 0.09 ppm respectively in micellar media. The calibration sensitivity (ppm) was in the range 3.42-23.99 for aqueous medium and 9.61-89.04 for micellar media. The spectrophotometric study of ternary complex forming system

of some rare earth with bromopyrogallol red in presence of cetyldimethylethylammonium bromide for micro determination and that Beer's law was obeyed between 0.81-1.81 ppm [16]. The method was simple, rapid and highly sensitive for the spectrophotometric determination of yttrium, neodymium, europium, terbium and ytterbium. The results obtained in this study for Beer's law were in supports with the findings of other researchers obtained for Beer's law which the values were between 0.05-2.00 ppm in a spectrophotometric determination of samarium (III) with chrome azurol S in the presence of cetylpyridinium chloride [16-17]. These results were also in accordance with the earlier findings by Ojeda et al. who reported in their studies on the complexation of Ga(III) with 2-hydroxy-5-T-butylphenol-4'-methoxy-azobenzene (HR) that the

coordination compound of gallium with synthesized azoreagents-HR was obtained and it was for the first time [18]. It was established that including organic phase (of extract) directly into the flame increases the sensitivity of determination of gallium a few times and Beer's law was observed within 1 - 10 mg/ml of gallium concentrations.

3.2. The Effect of pH

The effect of pH on the complexation of the metal ions with BSOPD was studied between pH 1-13. Complexation reaction of Nd with BSOPD was maximal at pH 9, Pr with BSOPD at pH 9, Sm with BSOPD at pH 10 and Tb with BSOPD at pH 11. At pH 9, 10 and 11, it is expected that the ligand will exist as;

$$H_2L \text{ or } L^{2-} + H^{2+}$$

Under this condition ligation of H_2L to Ln (Nd, Pr, Sm and Tb) will be favoured due to strong electrostatic interaction between the positively charge Ln^{3+} and L^{2-} to form a highly stable chelate. The complexation is favoured in weakly basic conditions.

3.3. Comparative Analysis of the Degree of Determination of the Metal Ions in Different Surfactants

The effect of three kinds of surfactants, namely sodium

dodecyl sulphate (SDS) (anionic), cetyl trimethyl ammoniumbromide (CTAB)(cationic) and Triton X-100 or Polyethylene-di-isobutyl-glycol-ether (TX-100)(non-ionic) were studied at different concentrations, for the determination of Nd(III), Pr(III), Sm(III) and Tb(III) using BSOPD at 35-60°C, 5-10 min, 9-11 pH with 0.001 ppm of metal ion concentration. A comparative analysis of the complexes is presented in Table 1 below.

Table 1. Comparative analysis of complexes in BSOPD in various concentrations of different micelle.

Micellar media	Complex	Conc. (ppm)	λ_{max}	ε_{max} (dm^{3}mol^{-1}cm^{-1})
SDS		0.4	376.0	44,000
		1	372.5	53,000
		5	420.0	46,000
CTAB		0.4	376.0	59,000
		1	376.0	58,000
	Nd-BSOPD	5	376.5	54,000
		0.4	354.5	79,000
		1	454.0	1,000
Triton X-100		5	377.5	54,000
			426.5	4,000
			377.5	47,000
			426.5	4,000
SDS		0.4	375.5	67,000
		1	375.5	64,000
		5	376.5	49,000
CTAB		0.4	376.0	55,000
		1	376.5	50,000
	Pr-BSOPD	5	376.5	52,000
		0.4	376.5	64,000
		1	559.5	3,000
Triton X-100		5	354.5	46,000
			584.4	2,000
			332.5	55,000
			574.0	3,000

Micellar media	Complex	Conc. (ppm)	λ_{max}	ε_{max} ($dm^3mol^{-1}cm^{-1}$)
SDS		0.4	373.5	56,000
		1	373.5	61,000
		5	375.0	67,000
CTAB		0.4	373.5	80,000
		1	371.0	57,000
	Sm-BSOPD	5	376.0	49,000
		0.4	375.5	57,000
		1	545.5	2,000
Triton X-100		5	363.5	68,000
			566.0	2,000
			376.0	59,000
			566.0	2,000
SDS		0.4	367.5	55,000
		1	370.0	50,000
		5	373.0	60,000
CTAB		0.4	366.5	63,000
	Tb-BSOPD	1	373.0	62,000
		5	372.5	70,000
		0.4	362.5	70,000
Triton X-100		1	566.0	1,000
		5	354.5	82,000
			368.0	59,000

Table 2. *Data for comparative analysis of complexes in micellar media and in aqueous medium.*

[Micelle] (ppm)	Complex	$[Ln^{3+}]$ (ppm)	λ_{max} (nm)	ε_{max} $dm^3mol^{-1}cm^{-1}$	$[Ln^{3+}]$ (ppm)	λ_{max} (nm)	ε_{max} $dm^3mol^{-1}cm^{-1}$	% Increase in ε_{max}
Triton X-100 0.4	Nd-BSOPD	0.001	354.5	79,000	0.001	354.5	69,000	14.49
SDS 0.4	Pr-BSOPD	0.001	375.5	67,000	0.001	375.5	64,000	4.69
CTAB 0.4	Sm-BSOPD	0.001	373.5	80,000	0.001	373.5	63,000	26.98
Triton X-100	Tb-BSOPD	0.001	354.5	82,000	0.001	354.5	59,000	38.98

A comparative analysis of complexes in micellar media and in aqueous medium was studied at the same λ_{max} to ascertain the effect of micelles on molar absorptivity's of Nd(III), Pr(III), Sm(III) and Tb(III) using BSOPD. The results is presented in Table 2 above showed that at 354.5 nm, 0.001 ppm, Nd(III) in Triton X-100 surfactant (0.4 ppm) with BSOPD gave ε_{max} of 79,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} of Nd(III) is 69,000 $dm^3mol^{-1}cm^{-1}$ and this indicates a 14.49% increase in ε_{max}. At 375.5 nm, 0.001 ppm, Pr(III) in SDS surfactant (0.40 ppm) with BSOPD gave ε_{max} of 67,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} of Pr(III) is 64,000 $dm^3mol^{-1}cm^{-1}$ and this indicates a 4.69% increase in ε_{max}. At 373.5 nm, 0.001 ppm, Sm(III) in CTAB surfactant (0.4 ppm) with BSOPD gave ε_{max} of 80,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} is 63,000 $dm^3mol^{-1}cm^{-1}$ and this indicates a 26.98% increase in ε_{max}. At 354.5 nm, 0.001 ppm, Tb(III) in Triton X-100 surfactant (1 ppm) with BSOPD gave ε_{max} of 82,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} is 59,000 $dm^3mol^{-1}cm^{-1}$ and this indicates a 38.98% increase in ε_{max} as shown in Table 2 above.

Table 3. *Selected analytical parameters in aqueous medium using BSOPD.*

Parameter	Nd(III) complex	Pr(III) complex	Sm(III) complex	Tb(III) complex
λ_{max} (nm)	376.00	386.00	384.00	380.00
Molar absorptivity ($dm^3mol^{-1}cm^{-1}$)	12.675	23.197	7.776	13.006
Calibration sensitivity (ppm)	12.67	23.19	7.78	13.03
Time (min.)	10	5	5	10
pH	9	9	10	11
Temperature (°C)	50	35	40	60
Analytical sensitivity (ppm)	59	66	79	82
Limit of Detection (ppm)	0.06	0.05	0.04	0.04
Limit of Quantification (ppm)	0.17	0.15	0.13	0.12
Linear dynamic range (ppm)	0.002-0.02	0.0008-0.02	0.0008-0.02	0.001-0.02
Intercept	0.464	0.447	0.116	0.101

The selected analytical parameters obtained with optimization experiments in aqueous medium using BSOPD for Nd(III), Pr(III), Sm(III) and Tb(III) using BSOPD is presented on Table 3 above. The results is presented in Table 3 above showed that, λ_{max} (nm) values gave 376.00 for Nd (III), 386.00 for Pr(III), 384.00 for Sm(III) and 380.00 for Tb(III) complexes. The molar absorptivity ($dm^3mol^{-1}cm^{-1}$) values gave 12.675 for Nd (III), 23.197 for Pr(III), 7.776 for Sm(III) and 13.006 for Tb(III) complexes. Time (min.) were 10 mins. for Nd (III), 5mins. for Pr(III), 5 mins. for Sm(III) and 10 mins. for Tb(III) complexes. The pH values gave 9 for Nd (III), 9 for Pr(III), 10 for Sm(III) and 11 for Tb(III) complexes. Temperature (°C) values gave 50 for Nd(III), 35 for Pr(III), 40 for Sm(III) and 60 for Tb(III) complexes. The

analytical sensitivity (ppm) values gave 59 for Nd (III), 66 for Pr(III), 79 for Sm(III) and 82 for Tb(III) complexes. The limit of detection (ppm) values gave 0.06 for Nd (III), 0.05 for Pr(III), 0.04 for Sm(III) and 0.04 for Tb(III) complexes. The limit of quantification (ppm) values gave 0.17 for Nd (III), 0.15 for Pr(III), 0.13 for Sm(III) and 0.12 for Tb(III)

complexes. The linear dynamics range (ppm) gave values within the range of 0.002-0.02 for Nd (III), 0.0008-0.02 for Pr(III), 0.0008-0.02 for Sm(III) and 0.001-0.02 for Tb(III) complexes. The intercept values were 0.464 for Nd(III), 0.447 for Pr(III), 0.116 for Sm(III) and 0.101 for Tb(III) complexes.

Table 4. Selected Parameters in micellar media using BSOPD.

Parameter	Nd(III) complex	Pr(III) complex	Sm(III) complex	Tb(III) complex
λ_{max}	354.50	375.50	373.50	354.50
Molar absorptivity ($dm^3mol^{-1}cm^{-1}$)	84.630	27.087	34.925	89.040
Calibration sensitivity (ppm)	84.63	27.08	34.92	89.04
Surfactant (ppm)	Triton X-100 (0.4)	SDS (0.4)	CTAB (0.4)	Triton X-100 (1)
Time (min.)	10	5	5	10
pH	9	9	10	11
Temperature (°C)	50	35	40	60
Analytical sensitivity (ppm)	229.35	171.40	245.92	234.75
Limit of detection (ppm)	0.01	0.02	0.01	0.01
Limit of quantification (ppm)	0.04	0.06	0.04	0.04
Linear dynamic range (ppm)	0.0004-0.006	0.0004-0.006	0.0004-0.006	0.0004-0.006
Intercept	0.356	0.110	0.119	0.332

However, the selected analytical parameters obtained with optimization experiments in micelle media using BSOPD for Nd(III), Pr(III), Sm(III) and Tb(III) using BSOPD is presented on Table 4 above. The results is presented in Table 4 above showed that, λ_{max} (nm) values gave 354.50 for Nd(III), 375.50 for Pr(III), 373.50 for Sm(III) and 354.50 for Tb(III) complexes. The molar absorptivity ($dm^3mol^{-1}cm^{-1}$) values gave 84.630 for Nd (III), 27.087 for Pr(III), 34.925 for Sm(III) and 89.040 for Tb(III) complexes. The surfactant (ppm) values gave Triton X-100 (0.4) for Nd(III), SDS (0.4) for Pr(III), CTAB (0.4) for Sm(III) and Triton X-100 (1) for Tb(III) complexes. The time (min.) were 10 mins. for Nd (III), 5mins. for Pr(III), 5 mins. for Sm(III) and 10 mins. for Tb(III) complexes. The pH values gave 9 for Nd (III), 9 for Pr(III), 10 for Sm(III) and 11 for Tb(III) complexes. Temperature (°C) values gave 50 for Nd(III), 35 for Pr(III), 40 for Sm(III) and 60 for Tb(III) complexes. The analytical sensitivity (ppm) values gave 229.35 for Nd (III), 171.40 for Pr(III), 245.92 for Sm(III) and 234.75 for Tb(III) complexes. The limit of detection (ppm) values gave 0.01 for Nd (III), 0.02 for Pr(III), 0.01 for Sm(III) and 0.01 for Tb(III) complexes. The limit of quantification (ppm) values gave 0.04 for Nd(III), 0.06 for Pr(III), 0.04 for Sm(III) and 0.04 for Tb(III) complexes. The linear dynamics range (ppm) gave values within the range of 0.0004-0.006 for Nd (III), 0.0004-0.006 for Pr(III), 0.0004-0.006 for Sm(III) and 0.0004-0.006 for Tb(III) complexes. The intercept values were 0.356 for Nd(III), 0.110 for Pr(III), 0.119 for Sm(III) and 0.332 for Tb(III) complexes.

4. Conclusions

In this research work, the comparative spectrophotometric determination of Nd(III), Pr(III), Sm(III) and Tb(III) in aqueous and micelle media using BSOPD as ligand, enhancement of molar absorptivity in the presence of surfactants is due to increase of absorbance at the λ_{max} of the complexes. The increase in absorbance in the presence of the

surfactants is due to micelle formation. The reactants are bound in a small volume of stern layer of the micelle leading to a greater increase in concentration effect. This effect reaches a maximum before decreasing due to dilution effect occasioned by increase in metal ion concentration. The degree of enhancement varies with surfactants.

Conflict of Interests

Acknowledgements

References

[1] Jenka, T. C.; Bailey, M. D.; Hovey, J. L.; Fernando, S.; Basnayake, G.; Cross, M. E.; Li, W and Allen, M. J. (2018). First Use of a Divalent Lanthanide for Visible-light promoted photoredox catalysis. *Chem. Sci,* 9, 1273-1278. Doi 10.1039/C75C024799.

[2] McGill, I. (2005,). "Rare Earth Elements" Ullmann's Encyclopedia of Industrial Chemistry, (31) Weinheim. Wiley-VCH. 191.

[3] Livergood, R. (2005). Rare Earth Elements: A Wrench in the Supply Chain (PDF) Center for Strategic and International Studies.

[4] Haxel, G.; Hedrick, J. and Orris, J. (2006). Rare earth element critical resources for high technology. Reston (VA) United States Geological Survey USGS fact sheet, 087-02 (PDF).

[5]   Spinu, C.; Pleniceanu, M. and Tigae, C. (2008). Biologically Active Transition metal Chelates with a 2-Thiophenecarboxaldehyde-Derived Schiff Base: Synthesis, Characterization, and Antibacterial Properties. *Turk. J. Chem.*, 32, 487.

[6]   Drozd, A. V and Baskir, I. M. (2002). Simultaneous Determination of Zinc and Cadmium with 1-(2-naphthol in aqueous micellar solution using Two Dimensional Absorption Spectra. *J. Anal Chem.,* 57, 1, 12-14.

[7]   Mathew, A. V.; Kumar, K.; Rao, I. M.; Satyanarayana, A. and Shyamala, P. (2012). Spectrophotometric determination of neodymium (III), samarium (III), dysprosium(III), holmium(III) in micellar media. *Ind. J. chem. Techno.*, 19, 331-336.

[8]   Dhepe, A. S. and Zade, A. B. (2011). Spectrophotometric study of ternary complex forming systems of some lanthanide metal ions with Eriochrome Cyanide R in presence of Cetylpyridinium Bromide for micro-determination. *E-journal of Chemistry*, 8 (3), 1264-1274. DOI: 10.1155/2011/871685.

[9]   Belsare, G. W.; Zade, A. B.; Kalbende, P. P. and Belsare, P. U. (2012). Spectrophotometric study of ternary complex forming systems of some rare earths with bromopyrogallol red in presence of cetyldimethylammonium bromide for micro-determination. *Der Pharma Chemica.*, 4 (3), 1226 -1238.

[10] Athira, C. J.; Sindhu, Y.; Sujamol, M. S and Mohanan, K. (2011). Synthesis and spectroscopic characterization of some Lanthanide (111) nitrate complexes of ethyl 2-[2-(1-acetyl-2-oxopropyl)azo]-4,5-dimethyl-3-thiophenecarboxylate. *Jour. serb. chem. soc.*, 76 (2), 249-261.

[11] Dik, T. A.; Kostyuk, N. N and Trebikov, A. O. (2003). Spectrophotometric determination of Sm (III) content in hydrochloric acid solution. *Jour. Appl. Spectro.*, 70, 729-732.

[12] Gadzhieva, S. R; Chyragov, F. M and Guscinov, F. E. (2005). Spectrophotometric study of the complexation of Samarium (III) with disodium 2-(2-hydroxy -3-sulfo-5-nitrophenylazo) naphthalene-1,8-dihydroxy-3,6-disulfonate in the presence of cetyltrimethylammonium bromide. *Jour. Anal. Chem.*, 60, 819-821.

[13] Mohanan, K.; Athira, C. J; Sindhu, Y and Sujamol, M. S. (2009). Synthesis, spectroscopic characterization and thermal studies of some Lanthanide (III) nitrate complexes with a hydrazo derivative of 4-aminoantipyrine. *Journal of rare-earths.*, 27 (5), 705.

[14] Ratre, P. and Kumar, D. (2013). Spectrophotometric Determination of Trace Amounts of Samarium in Environmental Samples. *American International Journal of Research in Formal, Applied & Natural Sciences*. USA. AURFAN 13-254, 110-118.

[15] Uwanta, E. J.; Ukoha, P. O. and Ekwere, I. O. (2020). Synthesis and Characterization of Neodymium (III), Samarium (III) and Terbium (III) Complexes Containing Bis(Salicylaldehyde)Orthophenylenediamine as Ligand. *Scientific Research Journal* (SCIRJ), 8 (6), 5-10. http://dx.doi.org/10.31364/SCIRJ/v8.i6.2020.P0620XX

[16] Uwanta, E. J.; Johnson, A. S.; Ukoha, P. O. and Emmanuel, J. U. (2021). Neodymium (III) and Samarium (III) Complexes of 2, 2'-((1E,1'E) - (1,2 Phenylene bis(Azanlylidene)bis(Methanylylidene)) diphenol ligand: Synthesis, Characterization and Biological activity. *Oriental Journal of Chemistry*, 37 (3), 575-582. http://dx.doi.org/10.13005/ojc/370308

[17] Soylak, M. and Turkoglu, D. (2000). Spectrophotometric determination of Samarium (III) with chrome azurol S in the presence of cetylpyridium chloride. *Talanta,* 53, 125-129. https://doi.org/10.1016/S0039-9140(00)00386-6

[18] Ojeda, C. B.; Torres, A. G.; Rojas, F. S. and Pavon, J. M. C. (1987). Fluoremetric determination of trace amount of gallium in biological tissues. *Analyst*, 112, 1499-1506. https://doi.org/10.1039/AN9871201499