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Spectroscopic determination of neodymium (III), praseodymium (III), samarium (III) and Terbium (III) in aqueous and micelle media using 2,2′- ((1E,1′E) - (1,4 phenylenebis (Azanylylidene)) Bis (Methanylylidene)) diphenol (BSPPD) as ligand

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ABSTRACT

Lanthanide metals, as well as other heavy metals, are toxic and have an accumulative effect in biotic and abiotic organisms emanating from drug, electronic, glass, laser, electrical, nuclear, ceramic, and metallurgical industries. This study 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)-(1,4-phenylenebis (azanylylidene)) bis (methanylylidene)) diphenol (BSPPD). The objectives of this study were; to synthesize Nd(III), Pr(III), Sm(III) and Tb(III) complexes of BSPPD, to characterize the ligands and their metal complexes on the basis of melting point, conductivity, thermogravimetry, infra-red, nuclear magnetic resonance (1H and 13C) and UV-Visible spectroscopy and analyse the potentials of BSPPD as spectrophotometric reagents for Nd(III), Pr(III), Sm(III) and Tb(III) based on their interaction with Schiff bases. The analysis of the complexes formed in aqueous and micellar media was investigated in this study. Spectral and absorbance measurements were carried out using a UV-Visible Spectrophotometer (Jenway: 6305) with 1-cm matched quartz cells. The method of experiment used was based on the formation of dark brown coloured complexes upon the reaction of Nd(III), Sm(III), Tb(III) and reddish brown coloured complexes for Pr(III), with the highest absorbance of 368, 373, 372 and 374 nm, respectively. Beer's law was obeyed from 0.001-0.02 ppm for aqueous medium and 0.001-0.01 ppm in micellar media as observed in this study. The molar absorptivity was observed within the ranges of 341-25993 $dm^3mol^{-1}cm^{-1}$ for aqueous medium and 9601-84944 $dm^3mol^{-1}cm^{-1}$ for micellar media.

Keywords: *BSPPD, Lanthanides, Metal complexes, Schiff base, Stoichiometry, UV- visible spectrophotometer, Nuclear magnetic resonance (1H and 13C).*

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Highlights of this paper

- 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)-(1,4-phenylenebis (azanylylidene)) bis (methanylylidene)) diphenol (BSPPD).
- To synthesize Nd(III), Pr(III), Sm(III) and Tb(III) complexes of BSPPD.
- To characterize the ligands and their metal complexes on the basis of melting point, conductivity, thermogravimetry, infra-red, nuclear magnetic resonance (^{1}H and ^{13}C) and UV-Visible spectroscopy and analyse the potentials of BSPPD as spectrophotometric reagents for Nd(III), Pr(III), Sm(III) and Tb(III) based on their interaction with Schiff bases.
- The analysis of the complexes formed in aqueous and in micellar media was investigated in this study.

1. INTRODUCTION

The global interest in Schiff base metal complexes has been increasing over the years, and this is due to the ease of synthesizing them and the diverse range of applications (Midya, Chakraborty, & Chattopadhyay, 2025). Schiff base complexes have found ready application in spectrophotometry, catalysis, medicine, metallurgy and magnetic materials (Uwanta, Sunday, Emmanuel, Adejoh, & Onyeoziri, 2023). Schiff bases have extensive applications in different fields of chemistry, for example, inorganic, biological and analytical chemistry (Abdulaziz & Almomani, 2016; Chandramouli, Shivanand, Nayanbhai, Bheemachari, & Udupi, 2012; Geethalaksmi & Theivarasu, 2016; Uwanta et al., 2023). Schiff bases are derived from aromatic amines and aldehydes and have a wide range of varieties, which are an important class of ligands in coordination chemistry (Kavitha et al., 2018; Spinu, Pleniceanu, & Tigae, 2008). The lanthanide elements constitute a group in the periodic table which has extremely similar chemical properties, which makes their separation and analytical evaluation a challenging one (Haxel, Hedrick, & Orris, 2002; Jenks et al., 2018; Mohanan, Athira, Sindhu, & Sujamol, 2009; Ratre & Kumar, 2013). Some lanthanide (III) metal complexes of Schiff bases have been synthesized and characterized by melting point, Fourier Transform Infra-red (FTIR), Nuclear magnetic Resonance (NMR), Ultra-violet and Visible (Uv-Vis) and Mass spectra spectroscopes (Jia, Li, Chen, Liu, & Tong, 2019). Lanthanide complexes have been universally researched for their distinctive photophysical properties (Pedra, Kitagawa, & Hasegawa, 2020). Some of these complexes have been used in medicine as tools in biomedical analysis, as magnetic resonance imaging (MRI) contrast agents, catalysis, material sciences and nuclear power generation (Aime et al., 2006; Kahn et al., 2003). Earlier findings by some researchers have reported that 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 (Dhepe & Zade, 2011). Uwanta et al. (2023) also reported in their earlier findings that the Schiff base (BSOPD) was successfully prepared and was used to synthesize new metal complexes of Nd(III), Sm(III) and Tb(III); the complexes had been characterized by physical methods and spectroscopic techniques (Uwanta, Johnson, Ukoha, & Emmanuel, 2021; Uwanta, Ukoha, & Ekwere, 2020; J. E. Uwanta et al., 2023). Therefore, this research work is designed to take up the analytical study of Nd(III), Pr(III), Sm(III) and Tb(III) with BSPPD in different micellar media which would determine these metal ions at trace levels, as well as a comparative analysis of the complexes formed in aqueous and micellar media.

2. MATERIALS AND METHODS

Accurate quality assurance procedures were carried out in this study in order to obtain reliable results. Possible contamination were eliminated using detergents or other sources; all glassware and polyethylene material used were soaked with a 1M nitric acid for 48 h and then washed and rinsed several times with deionized water before use as stated in the standard method (Association of Official Analytical Chemists (AOAC), 1998).

2.1. Apparatus

Conical flask, test tubes (pyrex), beakers and volumetric flask, 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), Weighing balance (Model no.: S-METLER, E-2000, Zurich analytical balance, Switzerland).

2.2. Reagents

All the reagents used in this research work were of analytical grade and were used as supplied unless otherwise stated.

2.3. Preparation of Stock Solutions

All the methods used for the preparation of stock solutions in this research work were according to that of the previous findings (Uwanta et al., 2023).

2.4. Spectrophotometric Evaluation of Metal ions in Micellar Media

Requisite volumes of solution of ($5x10^{-6}moldm^{-3}$) of BSSPD in surfactant and $1x10^{-6}moldm^{-3}$ of Ln^{3+} solution were mixed in a 10 cm^3 capacity flask in a 5:1[BSSPD] /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 an anionic surfactant, cetyltrimethylammonium bromide (CTAB) as a cationic surfactant and Triton X-100 as a non-ionic surfactant.

2.5. Effect of pH on the Formation of Complex

The variation of absorbance with pH was studied by reacting $1x10^{-4}$ $moldm^{-3}$ solution of Nd(III) with $2x10^{-4}$ $moldm^{-3}$ solution of the ligand BSPPD. For the other metal ions Pr(III), Sm (III) and Tb (III) 1x10-4 $moldm^{-3}$ solution of metal solution was reacted with $1x10^{-4}$ $moldm^{-3}$ solution of ligand BSPPD over the pH range of 1-13. The mixtures were allowed to react for a given time and at a given temperature of the different metal ions in the ligand solution. The absorbances were taken at the specified λ_{max} of the metal complex under study and plotted against the pH.

2.6. Concentration of Reagent on the Formation of Complex

The concentration of the 2,2′-((1E,1′E)-(1,4-phenylenebis (Azanylylidene)) bis (Methanylylidene)) diphenol (BSPPD) ligand was investigated for Nd (III), Pr (III), Sm (III) and Tb (III) metal ions to identify its effect. Varying concentrations of the ligand (BSPPD) ($1x10^{-5}$-$1x10^{-4}$ $moldm^{-3}$) were reacted with a fixed amount of Nd(III), Pr(III), Sm(III) or Tb(III). The mixture was allowed to react for 5 min at 50 °C, and the absorbance was taken at 374 nm for Nd(III) in BSPPD. For Pr(III) in BSPPD, the time of reaction was 5 min at 35 °C, and absorbance was taken at 373 nm. For Sm(III) in BSPPD, the time of reaction was 5 min at 50 °C, and absorbance was taken at 372 nm. For Tb(III) in BSPPD, the time of reaction was 5 min at 60 °C, and absorbance was taken at 373 nm. The absorbances were plotted against the various concentrations of the reagents. The plots of absorbance versus concentration of ligand are shown in Figures 1-4. It was observed that the absorbance kept increasing with an increase in the concentration of the ligand. Therefore, for subsequent work, the concentration of the ligand was kept more than five times the metal ion concentration so that all the metal ions could be used up.

3. RESULTS AND DISCUSSION

Beer's law was obeyed in this study from 0.0008-0.02 ppm for aqueous medium and 0.0006-0.006 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 0.1-0.09 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 the ternary complex forming system of some rare earths with bromopyrogallol red in the presence of cetyldimethylethylammonium bromide for micro determination, and that Beer's law was obeyed between 0.81-1.81 ppm (Uwanta et al., 2021). The method used 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 support with the findings of other researchers obtained for Beer's law, which were between 0.05-2.00 ppm in a spectrophotometric determination of samarium (III) with chrome azurol S in the presence of cetylpyridinium chloride (Soylak & Türkoğlu, 2000; Uwanta et al., 2021). Belsare, Zade, Kalbende, and Belsare (2012) also carried out a spectrophotometric study of a ternary complex-forming system of some rare earths with bromopyrogallol red in the presence of cetyldimethylethylammonium bromide for micro-determination and that Beer's law was obeyed between 0.81-1.81 ppm (Belsare et al., 2012). Soylak and Türkoğlu (2000) obtained in their findings an adherence to Beer's law between the ranges of 0.05-2 ppm in a spectrophotometric determination of samarium (III) with chrome azurol S in the presence of cetylpyridinium chloride (Soylak & Türkoğlu, 2000).

3.1. Ligand Concentration

The concentration of the chelating reagents of 2,2′-((1E,1′E)-(1,4-phenylenebis (Azanylylidene)) bis (Methanylylidene)) diphenol (BSPPD) was investigated for the Nd (III), Pr (III), Sm (III) and Tb (III) metal ions to know its effect. A fixed concentration of the metal was used with different concentrations of the ligands from $1x10^{-5}$-$2x10^{-4}$ $moldm^{-3}$. The absorbance values versus concentration of ligand (ppm) are shown in Figures 1-4.

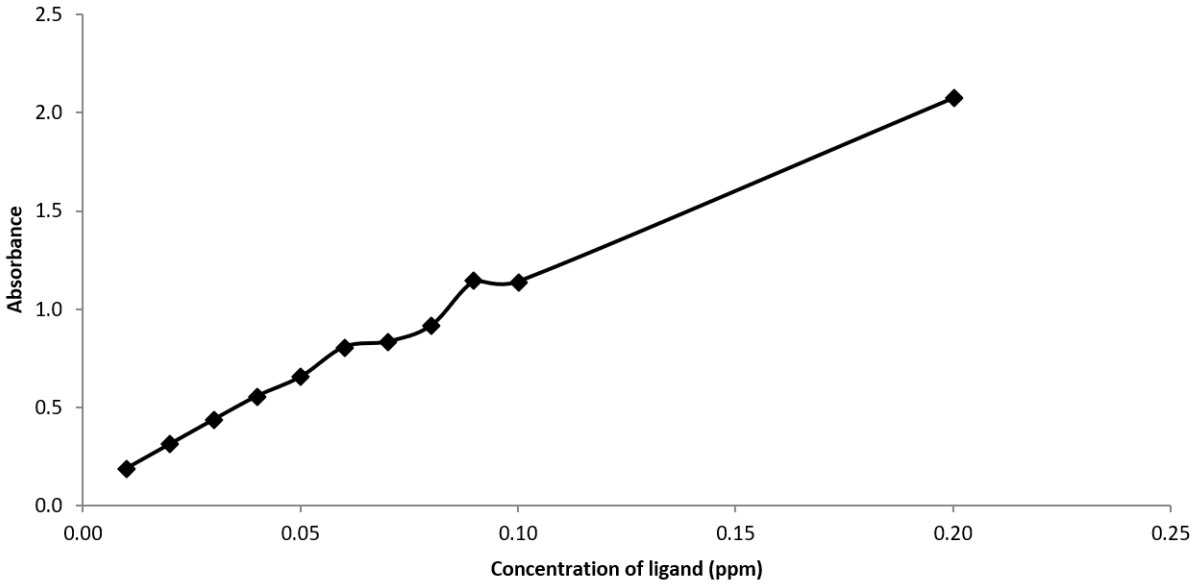

Figure 1. Absorbance values versus concentration of ligand (ppm) for the formation of Nd-BSPPD complex.

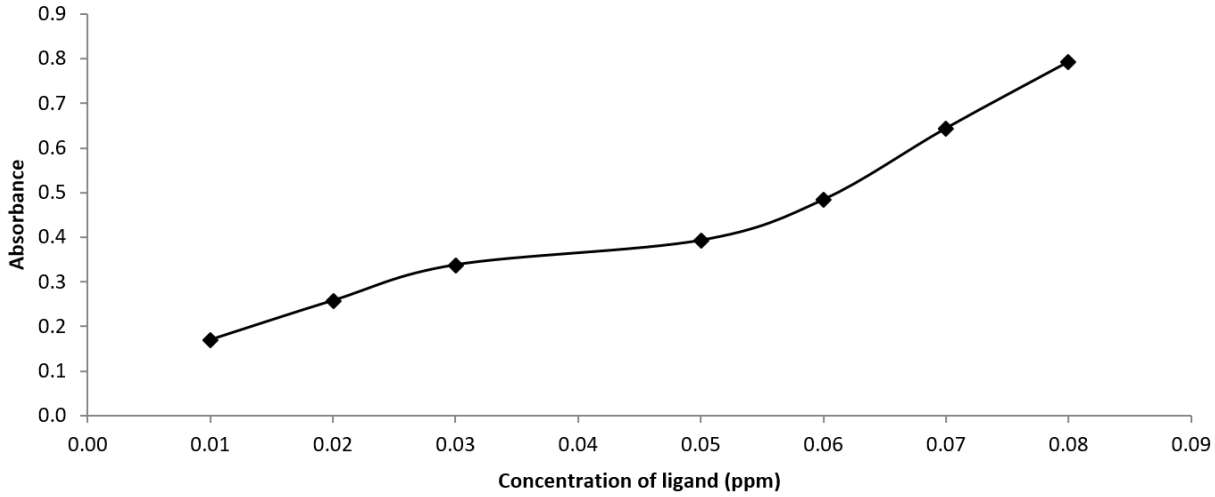

Figure 2. Absorbance values versus concentration of ligand (ppm) for the formation of Pr-BSPPD complex.

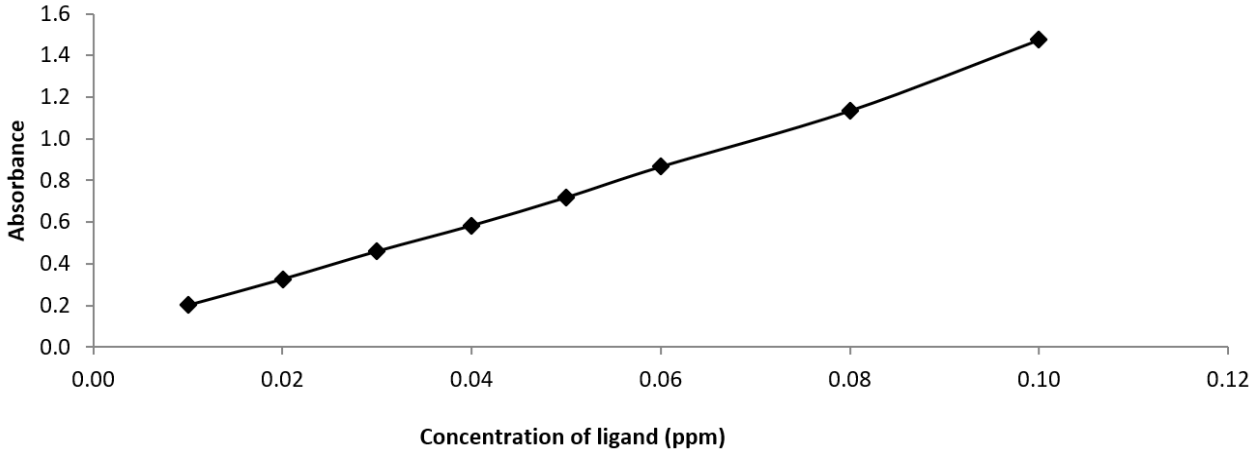

Figure 3. Absorbance values versus concentration of ligand (ppm) for the formation of Sm-BSPPD complex.

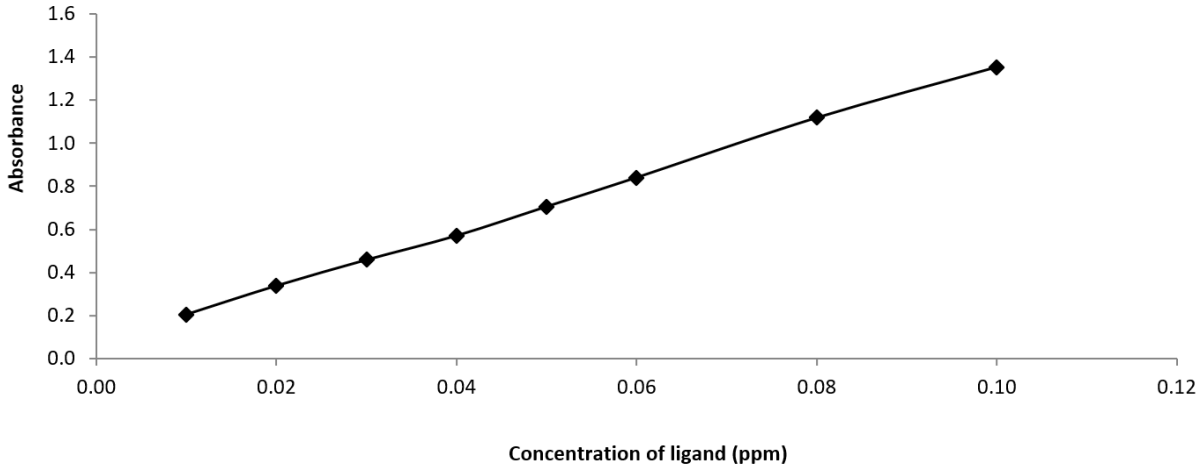

Figure 4. Absorbance values versus concentration of ligand (ppm) for the formation of Tb-BSPPD complex.

It was observed that the absorbance kept increasing with an increase in the concentration of the ligand. Therefore, for subsequent work, the concentration of the ligand was kept more than five times the metal ion concentration so that all the metal ions could be used up.

3.2. pH

The pH effect on the complexation of the metal ions with BSPPD was observed between pH 1 and 13. Complexation reaction of Nd with BSPPD at pH 9, Pr with BSPPD at pH 9, Sm with BSPPD at pH 10 and Tb with BSPPD at pH 10, as shown below. At pH 9, 10, and 11, it is expected that the ligand will exist as reported in the previous study Uwanta et al. (2023). Under this condition, ligation of H_2L to Ln (Nd, Pr, Sm and Tb) will be favoured due to the strong electrostatic interaction between the positively charged Ln^{3+} and L^{2-} to form a highly stable chelate. The complexation is favoured in weakly basic conditions.

The variation of absorbance with pH for Nd(III), Pr(III), Sm(III) and Tb(III) complexes in BSPPD is shown in Figures 5-8. Similar reaction was obtained for the complexation of Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III) with 1-(2-pyridylazo)-2-naphthol (PAN) (Mathew, Kumar, Shyamala, Satyanarayana, & Rao, 2012).

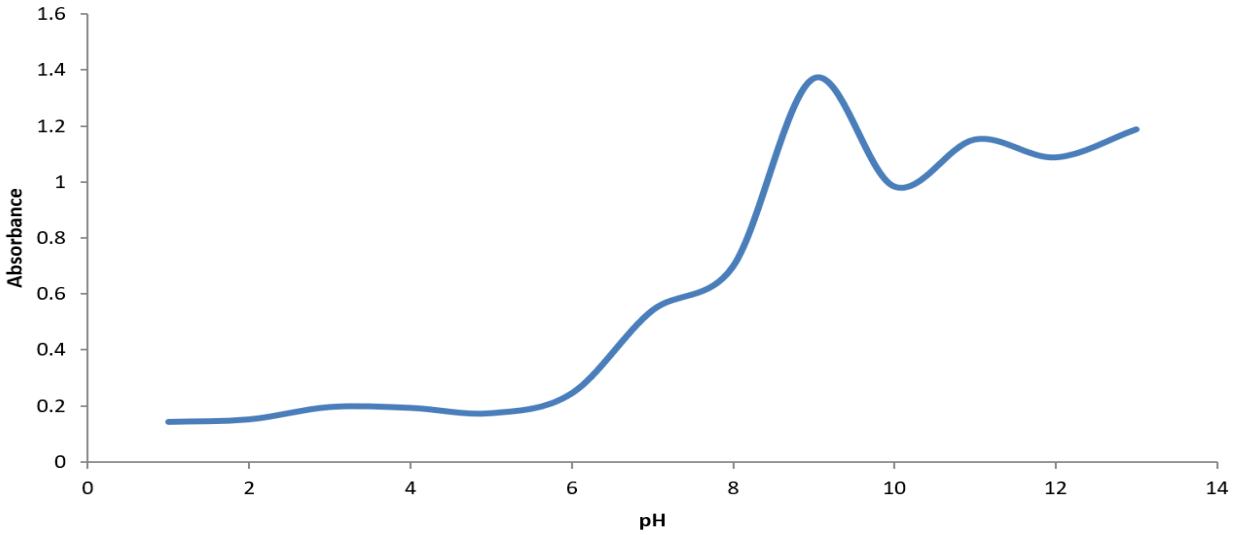

Figure 5. Variation of absorbance with pH for the formation of Nd-BSPPD complex.

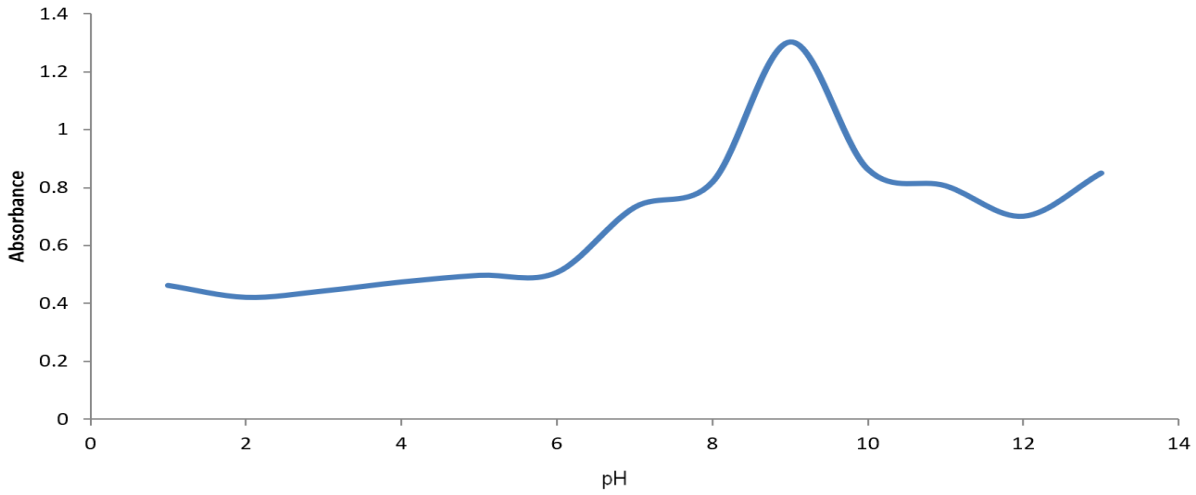

Figure 6. Variation of absorbance with pH for the formation of Pr-BSPPD complex.

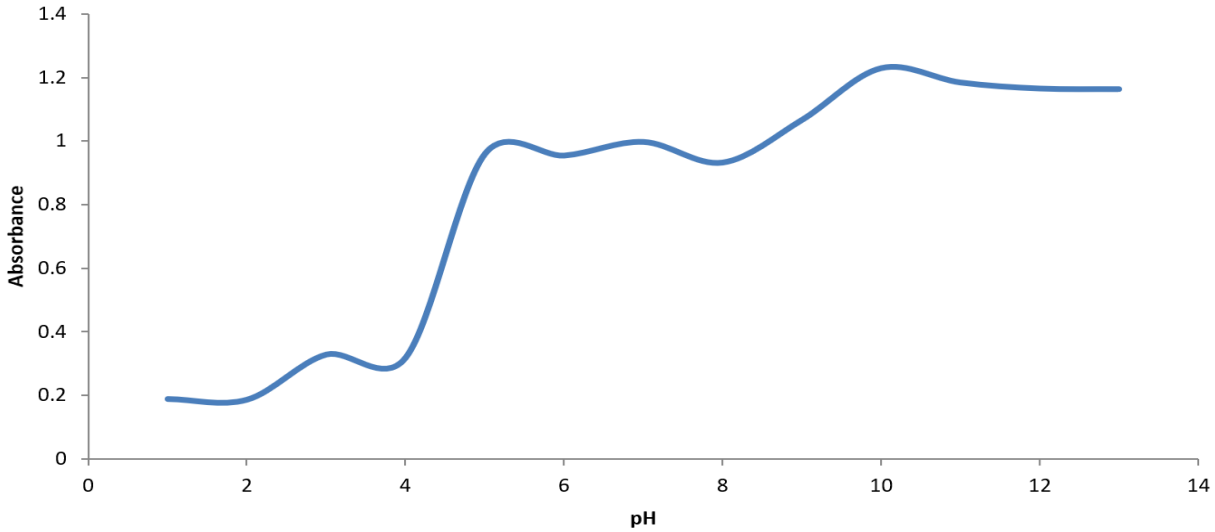

Figure 7. Variation of absorbance with pH for the formation of Sm-BSPPD complex.

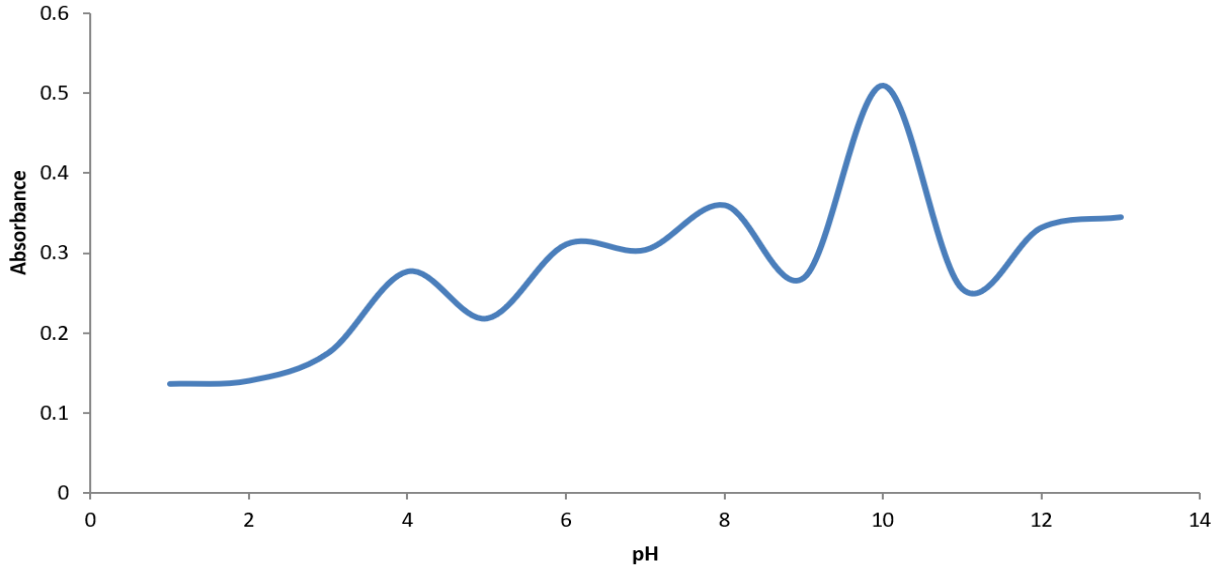

Figure 8. Variation of absorbance with pH for the formation of Tb-BSPPD complex.

3.3. Analysis of the Degree of Assessment of the Metal ions in Different Surfactants

Three types of surfactants, namely sodium dodecyl sulphate (SDS) (anionic), cetyl trimethyl ammonium bromide (CTAB)(cationic) and Triton X-100 or Polyethylene-di-isobutyl-glycol-ether (TX-100)(non-ionic) were investigated in this study. A fixed amount of Nd(III), Pr(III), Sm(III) or Tb(III) was determined in different concentrations of SDS, CTAB or Triton X-100 using BSPPD were analysed at different concentrations, for the determination of Nd(III), Pr(III), Sm(III) and Tb(III) using BSPPD at 35-60 ^{o}C, 5-10 min, 9-11 pH with 0.001 ppm of metal ion concentration. The λ_{max} (nm) of the complexes in Triton X-100 using BSPPD were in the range 370-379 with molar absorptivities ($dm^3mol^{-1}cm^{-1}$) in the range 42000-69000. The λ_{max} (nm) of the complexes in CTAB using BSPPD was in the range 305.0-376.5 with molar absorptivities ($dm^3mol^{-1}cm^{-1}$) in the range 2000-65000. The λ_{max} (nm) of the complexes in SDS using BSPPD was in the range 349.0-377.0 with molar absorptivities ($dm^3mol^{-1}cm^{-1}$) in the range 22,000-65m000. A comparative analysis of the complexes is presented in Table 1.

Table 1. Results of comparative analysis of complexes using 2,2′-((1E,1′E)-(1,4-phenylenebis (Azanylylidene)) bis (Methanylylidene)) diphenol (BSPPD) in various concentrations of different micelle.

S/N	Micellar media	Complexes	Concentration (ppm)	λ_{max} (nm)	ε_{max} ($dm^3mol^{-1}cm^{-1}$)
1	SDS		0.4	354.0	45,000
		Nd-BSPPD	1	376.5	58,000
			5	377.0	61,000
				421.5	22,000
2	CTAB	Nd-BSPPD	0.4	375.5	36,000
			1	376.0	43,000
			5	376.5	40,000
3	Triton X-100	Nd-BSPPD	0.4	378.0	55,000
			1	378.0	61,000
			5	580.0	1,000
				375.0	69,000
4	SDS	Pr-BSPPD	0.4	354.5	40,000
			1	377.0	50,000
			5	349.0	65,000
				553.0	13,000
5	CTAB	Pr-BSPPD	0.4	340.0	15,000
			1	305.0	6,000
			5	355.6	2,000
6	Triton X-100	Pr-BSPPD	0.4	378.0	62,000
			1	379.0	63,000
			5	378.0	48,000
				377.0	40,000
7	SDS	Sm-BSPPD	0.4	370.0	60,000
			1	377.0	55,000
			5	580.0	1,000
8	CTAB	Sm-BSPPD	0.4	376.5	46,000
			1	376.5	48,000
			5	376.0	54,000
9	Triton X-100	Sm-BSPPD	0.4	370.0	48,000
			1	378.0	59,000
			5	375.0	59,000
10	SDS	Tb-BSPPD	0.4	370.0	50,000
			1	377.0	60,000
			5	377.0	52,000
11	CTAB	Tb-BSPPD	0.4	376.0	39,000
			1	354.0	46,000
			5	376.5	65,000
12	Triton X-100	Tb-BSPPD	0.4	370.0	45,000
			1	378.0	49,000
			5	378.0	42,000

Table 2. Results of comparative analysis of complexes in micellar media and in aqueous medium using 2,2′-((1E,1′E)-(1,4-phenylenebis (azanylylidene)) bis (methanylylidene)) diphenol (BSPPD).

S/N	Micellar media					Aqueous medium		
1.	**[Micelle] (ppm)**	**Complex**	**$[Ln^{3+}]$ (ppm)**	**λ_{max} (nm)**	**ε_{max} ($dm^3mol^{-1}cm^{-1}$)**	**$[Ln^{3+}]$ (ppm)**	**λ_{max} (nm)**	**ε_{max} ($dm^3mol^{-1}cm^{-1}$)**
2.	Triton X-100(5)	Nd-BSPPD	0.001	375.00	69,000	0.001	375.00	59,000
3.	SDS (5)	Pr-BSPPD	0.001	349.00	65,000	0.001	349.00	36,000
4.	SDS (1)	Sm-BSPPD	0.001	370.00	60,000	0.001	370.00	38,000
5.	CTAB (5)	Tb-BSPPD	0.001	376.50	65,000	0.001	376.50	54,000

Table 2 presents the results obtained for the comparative analysis of complexes in micellar media and in aqueous medium was studied at the same λ_{max} to determine the effect of micelles on molar absorptivity's of Nd(III),

Pr(III), Sm(III) and Tb(III) using BSPPD showed that at 375.00 nm, 0.001 ppm, Nd(III) in Triton X-100 surfactant (5 ppm) with BSPPD gave ε_{max} of 69,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} is 59,000 $dm^3mol^{-1}cm^{-1}$. This indicates a 16.95 % increase in ε_{max}. At 349.00 nm, 0.001 ppm, Pr(III) in SDS surfactant (5 ppm) with BSPPD gave ε_{max} of 65,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} is 36,000 $dm^3mol^{-1}cm^{-1}$. This indicates an 80.56 % increase in ε_{max}. At 370.00 nm, 0.001 ppm, Sm(III) in SDS surfactant (1 ppm) with BSPPD gave ε_{max} of 60,000 dm3mol-1cm-1. In the absence of surfactant, the ε_{max} is 38,000 $dm^3mol^{-1}cm^{-1}$. This indicates a 57.89 % increase in ε_{max}. At 376.5 nm, 0.001 ppm, Tb(III) in CTAB surfactant (5 ppm) with BSPPD gave ε_{max} of 65,000 $dm^3mol^{-1}cm^{-1}$. In the absence of surfactant, the ε_{max} is 54,000 $dm^3mol^{-1}cm^{-1}$. This indicates a 20.37 % increase in ε_{max}. The enhancement of molar absorptivity in the presence of surfactants is due to an increase in absorbance at the λ_{max} of the complexes (Mathew et al., 2012). The increase in absorbance in the presence of the surfactants is due to micelle formation. The reactants are bound in a small volume of the Stern layer of the micelle, leading to a greater increase in concentration effect. This effect reaches a maximum before decreasing due to the dilution effect occasioned by an increase in metal ion concentration. The degree of enhancement varies with surfactants and ligands.

Table 3. Results of analytical parameters in aqueous medium using 2,2′-((1E,1′E)-(1,4-phenylenebis (azanylylidene)) bis (methanylylidene)) diphenol (BSPPD).

S/N	Parameters	Complexes			
		Nd(III)	Pr(III)	Sm(III)	Tb(III)
1.	λ_{max} (nm)	374.00	373.00	372.00	374.00
2.	Molar absorptiviy ($dm^3mol^{-1}cm^{-1}$)	3421	25993	17205	12252
3.	Calibration sensitivity (ppm)	3.42	25.99	17.30	12.16
4.	Time (min)	5	5	5	5
5.	pH	9	9	10	10
6.	Temperature ^oC	50	35	35	35
7.	Analytical sensitivity (ppm)	15	188	75	120
8.	Limit of Detection (ppm)	0.22	0.02	0.02	0.03
9.	Limit of Quantification (ppm)	0.65	0.05	0.05	0.03
10.	Linear dynamic range (ppm)	0.0008-0.02	0.0008-0.01	0.0008-0.01	.0.001-0.02
11.	Intercept	0.256	0.200	0.264	0.117

The results of the various analytical parameters obtained with optimization experiments in aqueous medium using BSPPD for Nd(III), Pr(III), Sm(III) and Tb(III) are presented in Table 3. The obtained results, as shown in Table 3, showed that λ_{max} (nm) values gave 374.00 for Nd (III), 373.00 for Pr(III), 372.00 for Sm(III) and 374.00 for Tb(III) complexes. The molar absorptivity ($dm^3mol^{-1}cm^{-1}$) values gave 3421 for Nd (III), 25993 for Pr(III), 17205 for Sm(III) and 12252 for Tb(III) complexes. Time (min.) was 5 mins. for Nd (III), 5mins. for Pr(III), 5 mins. for Sm(III) and 5 mins. for Tb(III) complexes. The pH values gave 9 for Nd (III), 9 for Pr(III), 10 for Sm(III) and 10 for Tb(III) complexes. Temperature (^oC) values gave 50 for Nd (III), 35 for Pr(III), 35 for Sm(III) and 35 for Tb(III) complexes. The analytical sensitivity (ppm) values gave 15 for Nd (III), 188 for Pr(III), 75 for Sm(III) and 120 for Tb(III) complexes. The limit of detection (ppm) values gave 0.22 for Nd (III), 0.02 for Pr(III), 0.02 for Sm(III) and 0.03 for Tb(III) complexes. The limit of quantification (ppm) values gave 0.65 for Nd (III), 0.05 for Pr(III), 0.05 for Sm(III) and 0.03 for Tb(III) complexes. The linear dynamics range (ppm) gave values within the range of 0.0008-0.02 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 0.256 for Nd (III), 0.200 for Pr (III), 0.264 for Sm (III) and 0.117 for Tb (III) complexes.

Table 4. Results of analysed parameters in micellar media using 2, 2′-((1E,1′E)-(1,4-phenylenebis (Azanylylidene)) bis (Methanylylidene)) diphenol (BSPPD).

S/N	Parameters	Complexes			
		Nd(III)	Pr(III)	Sm(III)	Tb(III)
1.	λ_{max}	375.00	349.00	370.00	376.50
2.	Molar absorptivity ($dm^3mol^{-1}cm^{-1}$)	84944	21284	9601	24203
3.	Calibration sensitivity (ppm)	84.94	21.28	9.61	24.20
4.	Surfactant (ppm)	Triton X-100 (5)	SDS (5)	SDS (1)	CTAB (5)
5.	Time (Min)	5	5	5	5
6.	pH	9	9	10	10
7.	Temperature ^{o} C	50	35	35	35
8.	Analytical sensitivity (ppm)	268.79	851.2	113.06	260.22
9.	Limit of detection (ppm)	0.01	0.004	0.03	0.01
10.	Limit of quantification (ppm)	0.04	0.01	0.09	0.04
11.	Linear range (ppm)	0.0004-0.006	0.0006-0.006	0.0006-0.006	0.0006-0.006
12.	Intercept	0.216	0.041	0.091	0.112

Based on the results in Table 4, it was observed that some analytical parameters were obtained with optimization experiments in micelle media using BSPPD for Nd(III), Pr(III), Sm(III) and Tb(III). The obtained results showed that λ_{max} (nm) values gave 375.00 for Nd (III), 349.00 for Pr(III), 370.00 for Sm(III) and 376.50 for Tb(III) complexes. The molar absorptivity ($dm^3mol^{-1}cm^{-1}$) values gave 84630 for Nd (III), 27087 for Pr(III), 34925 for Sm(III) and 89040 for Tb(III) complexes. The surfactant (ppm) values gave Triton X-100 (5) for Nd (III), SDS (5) for Pr(III), SDS (1) for Sm(III) and CTAB (5) for Tb(III) complexes. The time (min.) used was 5 mins. Each of the four parameters, namely: Nd (III), Pr(III), Sm(III) and Tb(III) complexes. The pH values gave 9 for Nd (III), 9 for Pr(III), 10 for Sm(III) and 10 for Tb(III) complexes. Temperature (^{o}C) values gave 50 for Nd (III), 35 for Pr(III), 35 for Sm(III) and 35 for Tb(III) complexes. The analytical sensitivity (ppm) values gave 268.79 for Nd (III), 851.20 for Pr(III), 113.06 for Sm(III) and 260.22 for Tb(III) complexes. The limit of detection (ppm) values gave 0.01 for Nd (III), 0.004 for Pr(III), 0.03 for Sm(III) and 0.01 for Tb(III) complexes. The values of the limit of quantification (ppm) were 0.04 for Nd (III), 0.01 for Pr(III), 0.09 for Sm(III) and 0.04 for Tb(III) complexes, respectively. The range of linear dynamics (ppm) gave concentrations within the range of 0.0004-0.006 for Nd (III), 0.0006-0.006 for Pr(III), 0.0006-0.006 for Sm(III) and 0.0006-0.006 for Tb(III) complexes. In this study, the concentrations of intercept were 0.216 for Nd (III), 0.041 for Pr(III), 0.091 for Sm(III) and 0.112 for Tb(III) complexes, respectively.

4. CONCLUSION

In conclusion, Schiff base ligands BSPPD were synthesized and isolated in 75.40 % yield. The Nd(III), Pr(III), Sm(III) and Tb(III) complexes were also synthesized and their complexes in BSPPD were in 58.50-70.00 % yield. Maximum conditions for the formation of the complexes in BSPPD were Nd (III) time 5 min, temperature 50 ^{o}C and a pH of 9. Pr(III) time 5 min, temperature 35 ^{o}C and a pH of 9. Sm (III) time 5 min, temperature 35 ^{o}C and a pH of 10. Tb(III) time 5 min, temperature 35 ^{o}C and a pH of 10. The ligands and the complexes were characterized by 1H- and 13C-NMR, IR, Uv-Vis and elemental analysis. BSPPD were used successfully to determine Nd, Pr, Sm and Tb in aqueous medium and micellar media. The limit of detection in aqueous medium was 0.02-0.22 ppm, but was enhanced to 0.004-0.03 ppm in micellar media. Molar absorptivities ($dm^3mol^{-1}cm^{-1}$) in aqueous medium were 3421-25,993 but were enhanced to 9601-89,040 in micellar media. Therefore, it was observed that the increase in absorbance in the presence of the surfactants was due to micelle formation. The reactants are bound in a small volume of the stern layer of the micelle, which produces a high concentration effect, and the effect reaches its peak before reducing due to the dilution effect occasioned by the high concentration of metal ion and this level of enhancement increment was observed to have varied with surfactants.

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