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Research Article

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Spectrophotometric studies of thiazolyl substituted Schiff's bases in binary solvent mixtures at 30±0.1^{0}C

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ABSTRACT

The stability constants of complexes of rare metals La(III), Pr(III) & Sm(III) with 2-[3-(4-methoxy phenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methyl phenol (MPPTMP-I), 2-[3-phenyl-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methoxy phenol (PPTMP-I) & 2-[3-(4-chlorophenyl)-1-(4-phenyl-thiazol-2-ylimino)-allyl]-4-methyl-phenol (CPTMP- I) in binary solvent dioxane-water mixture at 30±0.1^{0}C, by applying Job's method of continuous variation spectrophotometrically.

Keywords: Spectrophotometry, stability constant, substituted thiazolyl schiff's bases, rare metal ions.

INTRODUCTION

Spectroscopy deals with the study of measurement of interaction between radiation energy and matter particles. Spectrophotometric methods can be used to evaluate dissociation and association constants provided that there is a pronounced difference in the absorption between the molecular and ionic forms of substances. One of the most spectacular effects of complex formation is the change of spectral properties. The reasons for light absorption by complexes are as follows.
1) The excitation of electrons of both metal ion and ligand is influenced by their interaction.
2) The electrons of transition metal ions are easily excited and consequently absorbed in the visible region i.e. these ions give coloured compounds.
3) The electron systems of non transition metal ions and of the ligands are more stable, excitation of electrons require more energy and thus these species absorbs in the ultraviolet range of spectrum.
4) Owing to the interaction of central metal ion and the ligand the charge transfer from the ligand to metal ion may occur on irradiation. This phenomenon is the reason for so called charge transfer spectra in the visible and near ultraviolet region.

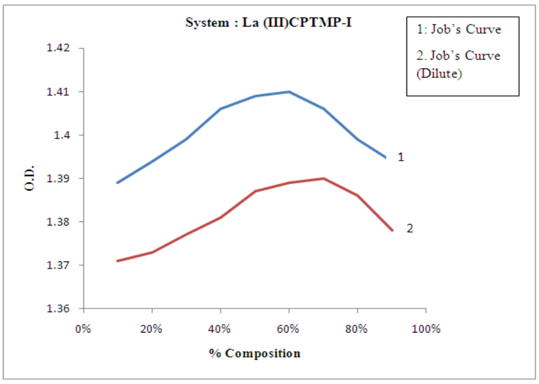
Many workers[1-5] have reported their results on metal-ligand stability constants. Raghuvanshi et al [6] studied the confirmation of complex formation by isobestic point method and Job's method between Cu(II) and substituted isoxazolines spectrophotometrically. The lanthanide compounds have remarkable importance in everyday life [7-8] More explicitly in the previous decades their use in various organic technical processes led to a rapid growth especially in the field of complexes. Spectrophotometric determination of Ne (III), Sm(III), Ga(III),Te(III), Dy(III) & Ho(III) in miceller media done by Asha Mathew et al[9] . In the present study an attempt has been made to study stability constants of La(III), Pr(III) & Sm(III) with substituted thiazoles in the constant ionic strength of 0.1M at various percentages of binary solvent -water mixture at 30±0.1^{0}C, applying Job's method of continuous variation and dilution method spectrophotometrically to compare the results with pH-metric determination.

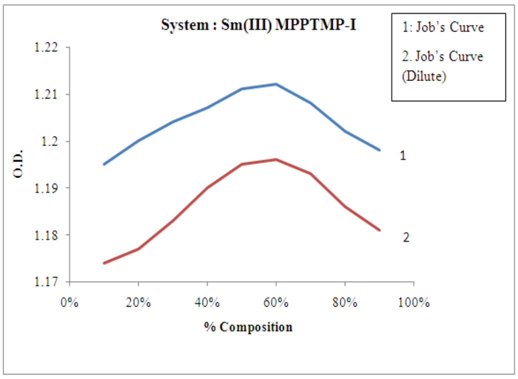
EXPERIMENTAL SECTION

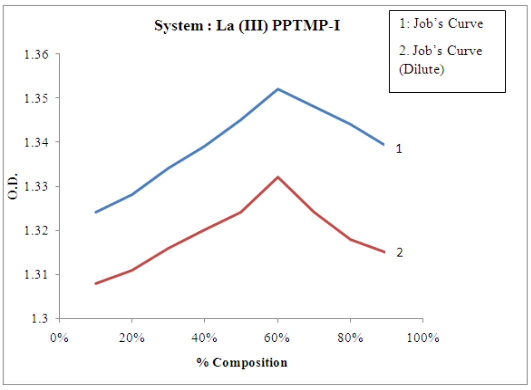
Dioxane water were used in the preparation of desired ligand solutions. The metal nitrates were used to prepare stock solutions. All the pH measurements were performed on a equiptronics micrometer (Model EQ-621) with accuracy ±0.01units. All the spectrophotometric measurements were carried out with UV-Visible spectrophotometer model-106, systronic make with ±5 nm accuracy ,spectral range between 340-960 nm, using 1.00 cm quartz cell and ionic strength was maintained by adding appropriate quantity of potassium nitrate solution. Standard solution of La(III), Pr(III) & Sm(III) 0.01 M was added in varying proportions to get different compositions of metal-ligand solutions. λmax was determined using one of the compositions. At a constant wavelength λmax, metal-ligand stability constant was determined. Complex formation have been studied by McBryde[11] and Banerjee[12]. The composition of complexes at different pH were confirmed by Job's method as modified by Vosburgh and Gold[13]. The data of absorption and percentage composition of metal ion and ligand solution at constant pH were used and curves were constructed. The stability constant values determined by pH-metry were further compared with spectrophotometric calculated values.

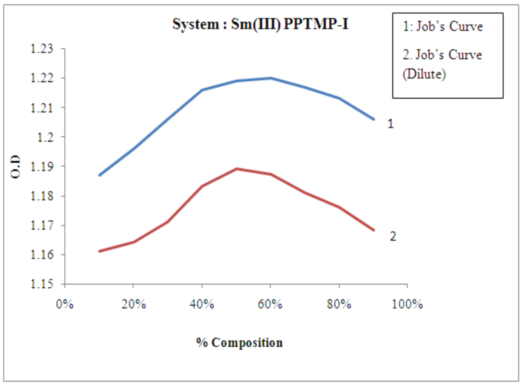
RESULTS AND DISCUSSION

The spectral curves of the reaction mixtures of La(III), Pr(III) & Sm(III) with substituted thiazoles in the constant ionic strength of 0.1M at various percentages of binary solvent mixture are represented in (Fig.1). The measurements were carried out at 430 nm and pH = 4.1. On plotting measured absorbance against mole fractions of the two constituents of the complex gives a characteristic triangular plot indicating formation of a more stable complex [14] .The composition of the complex was calculated from the point of intersection of the tangents to the curve [15] and was found to be 1:1.









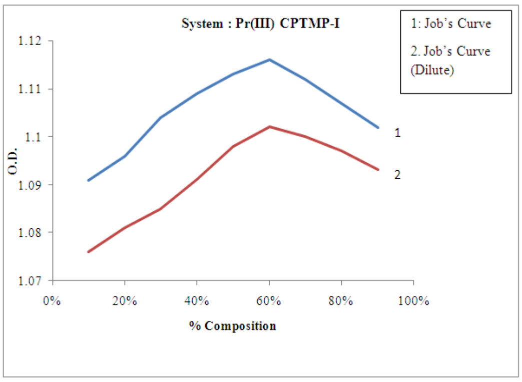


Fig. 1 : Job's curve and Job's curve after dilution of equimolar solution of La(III), Pr(III) & Sm(III) with MPPTMP-I, PPTMP-I & CPTMP-I at 430nm and pH= 4.1.

The stability constants of the complexes were calculated from the following relation:

$$K = \frac{x}{(a - x)(b - x)}$$

$$k = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

Here,
X – Concentration of complex in any metal ligand solution.
a – Initial concentration of metal in particular solution.
b - Initial concentration of ligand in particular solution.

Table 1: Comparision of stability constants of rare metals with thiazolyl substituted schiff's bases by pH metry and spectrophotometry

System	Technique	
	pH metry	Spectrophotometery
	Log K	Log K
La(III) MPPTMP-I	2.959	2.956
Pr(III) MPPTMP-I	2.956	2.996
Sm(III) MPPTMP-I	2.67	2.668
La(III) PPTMP-I	2.081	2.032
Pr(III) PPTMP-I	3.933	3.939
Sm(III) PPTMP-I	3.961	3.956
La(III) CPTMP-I	2.572	2.521
Pr(III) CPTMP-I	2.357	2.328
Sm(III) CPTMP-I	2.668	2.668

Lanthanide form complexes with oxygen or oxygen plus nitrogen containing chelating ligands. Bonding between lanthanide ions and coordinating ligands depends on electronegativity of bonding atoms in monodentate ligands. But complex formation in bi or polydentate ligands in the presence of water is usually successful only with the ligands that form chelate rings through oxygen atoms[16]. There is no specific trend in metal-ligand stability constant. This is due to variation in polar nature of solvents and solvent-solvent interactions. Values of stability constants are nearly same for all the three metal ions for the ligands with methoxy and chloro substituted groups whereas for the ligand PPTMP variable results were reported.

Complexes involving multidentate ligands are more stable i.e. formation of chelated complex is more favourable. The spectrophotometrically calculated values of stability constants are supported by pH-metrically determined stability constants values as represented in table-1, which confirms the complex formation tendency of rare metal ions with thiazolyl substituted schiff's bases.

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