SPECTROPHOTOMETRIC STUDY OF STABILITY CONSTANT OF SUBSTITUTED BENZOTHIAZOLYL AND BENZIMIDAZOLYL DERIVATIVES WITH RARE METAL IONS.

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Abstract: Substituted benzothiazolyl and benzimidazolyl derivatives synthesized by using microwave as a green approach. Structures were confirmed by spectral and CHN analysis. Some of the synthesized compounds were further implemented for the spectrophotometric study with La^{3+}, Sm^{3+} and Pr^{3+} rare earth metal ions by Job's methods to judge the nature of complex and metal-ligand stability constant.

Keywords: Stability constant, Lanthanides, Spectrophotometry.

Introduction:

The spectrophotometric methods are used to evaluate association and dissociation constants provided that there is difference in the absorption between the ionic and molecular forms of substances. Spectrophotometric experiment includes knowledge of possible interferences that may absorb at the wavelength of the sample. The wavelength at which the absorption by the absorption by the sample is measured is then chosen to be some wavelength remote from the absorption by interfering compounds. The method is much less susceptible than colorimetry to operator error and to interferences from compounds encountered in the sample itself. Spectrophotometry is currently used in all routine analytical labs and In undoubtedly will be for many years to come. Initially spectrophotometer were used to ascertain the concentrations of simple colored solutions, such as potassium permanganate. Over the years, it became recognized that many metals react with organic reagents to form intensely coloured complexes. Very selective and sensitive analytical procedures have been developed for the determination of trace metal components in solutions with concentrations as 1 ppm and less. Obtaining reproducible results by means of spectrophotometric analysis often required attention, skill and a considerable knowledge of chemistry. The equipment is generally inexpensive and most laboratories are able to handle this type of analytical work. Many workers have determined metal-ligand stability constants.

Heterocyclic compounds have gained immense importance in human life because of their variety of applications, particularly these compounds have been successful tested against several diseases and therefore have acquired medicinal importance in recent years. The heterocyclic compounds have wide applications in medicinal chemistry, pharmaceutical chemistry. Nitrogen and Sulfur containing heterocyclic compounds have been found to possess a wide variety of biological activities. Activities in biological field through antimicrobial of Benzothiazolyl and benzimidazolyl substituted derivatives have wide range of biological applicability[1-8].

Asha Mathew et al[9] determined the Ne (III), Sm (III), Ga(III), Te (III), Dy (III), and Ho (III) in miceller media spectrophotometrically. Raghuwanshi et al[10] investigated the confirmation complex formation by isosbestic point method and Job's method between Cu(II) and isoxazolines spectrophotometrically. The lanthanide compounds have significant importance in everyday life11-12. Spectrophotmetric determination of copper (II), Silver(I), and paladium (II) with 4-(2,6-diamino-4-pyrimidylazo) phenol done by Ishwar Singh et al[13].

In the previous decades lanthanide compounds have remarkable importance their use in various organic technical processes led to a rapid growth in the field of complexes. In the present work an attempt has been made to study confirmation of complex formation and stability constant of La(III), Sm(III) & Pr(III) with substituted benzothiazoles and benzimidazoles in the constant ionic strength of 0.1 M at various percentages of binary solvent-water mixture at 30±0.1ºC, applying Job's method of continuous variation and dilution method spectrophotometrically.

Experimental:

Acetone-water, Dioxan-water and DMSO-water mixtures were used in the preparation of desired lignad solutions. The metal nitrates of La, Sm and Pr were used for the stock solution. The metal-ligand stability constants of some substituted benzothiazolyl and benzimidazolyl derivatives were determined spectrophotometrically. Absorption are measured by using BioEra's Single Beam UV-Visible Spectrophotometer (cat No. BI/CISP/SB-S-03). Equimolar solution of La(III), Pr(III), Sm(III) and ligand (substituted benzothiazolyl and benzimidazole derivatives) (0.1M) were mixed in different ratios to prepare Job's

solution. Volume of each solution was made upto 10 ml after adjusting the appropriate pH and maintaining constant ionic strength (μ= 0.1 M) in addition to wavelength of maximum (λmax) some other wavelengths were selected as proposed by Vosburgh and Robert Gold[14].
Job's curves were constructed from which metal-ligand stability constant was calculated and same procedure was repeated for remaining metal ions.

Systems-

The following some systems were chosen for determining the metal-ligand stability constant and confirmation of complexes spectrophotometrically-

1. Job's Method of continuous variation-
    a. La (III), Pr (III), Sm (III)-1c
    b. La (III), Pr (III), Sm (III)-2b

Where, 1c- (1-Benzothiazol-2-l-[1,2]diazetidine-3-ylidene)-phenyl-amine,
2b- (1,2-Dihydro-benz[4,5]imidazo[2,1-c][1,2,4]triazin-3-ylidene)-(4-phenyl-thiazole-2-yl)-amine

The metal ligand stability constant calculated by using following formula-

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

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

where,
x- Concentration of complex in any metal ligand solution.
a- Initial concentration of metal ion in particular solution.
b- Initial concentration of ligand in particular solution.

RESULT AND DISCUSSION

Continuous variation method which is used to determine complex equilibrium in solution. The maximum of curves corresponding to stoichiometry of two species at high concentration. Peak of the curve represents mole fraction of ligands bound to molecules from the curves equilibrium constant may be determined under the conditions of constant ionic state and constant pH. These are presented in fig 1 to 8.

The spectral curves of La(III), Pr(III), Sm(III) with substituted benzothiazolyl and benzimidazolyl derivaties in Acetone-water, Dioxan-water and DMSO-water mixtures in the constant ionic strength of 0.1M at various percentages of binary solvent mixture are represented in fig.1 to fig. 8 The measurements were carried out at 340 nm and pH -4.6 on plotting measured absorbance against % composition of the two constituents of the complex gives a characteristic plot indicating formation of a more stable complex. The composition of the complex was calculated from the point of intersection of the tangents to the curve and was found to be 1:1.

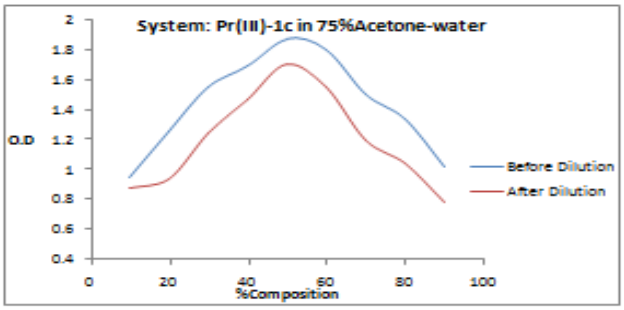

Fig. 1

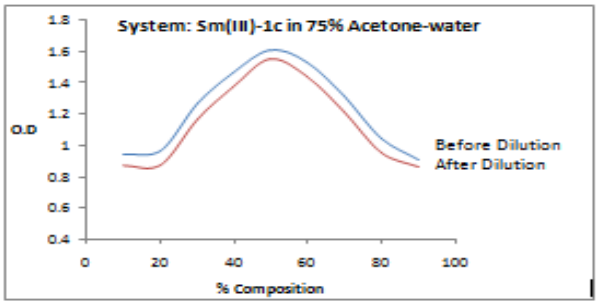

Fig. 2

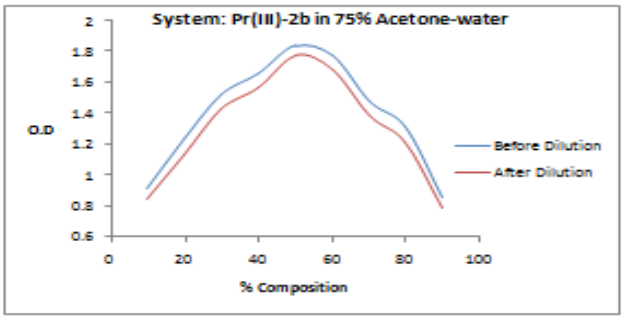

Fig. 3

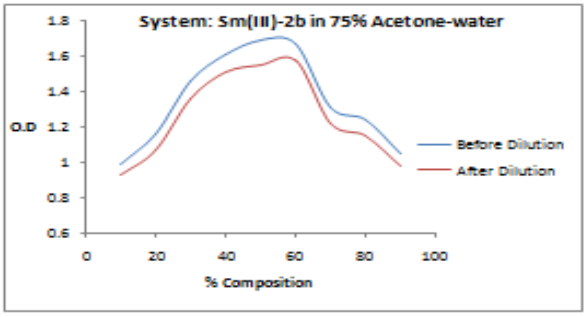

Fig.4

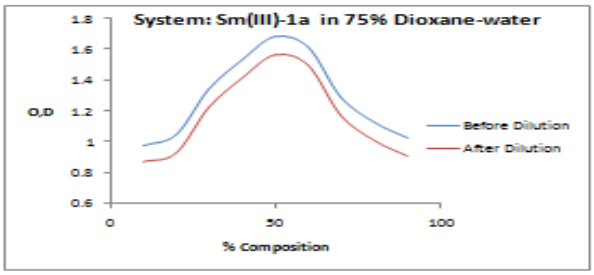

Fig.5

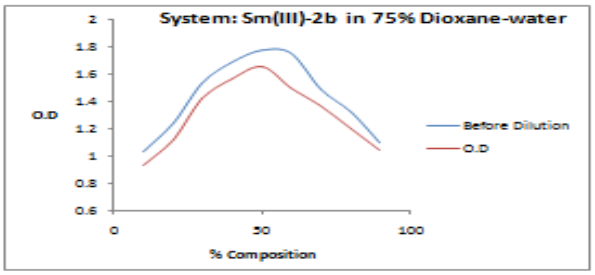

Fig.6

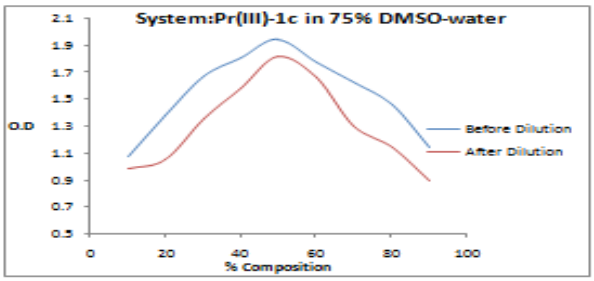

Fig.7

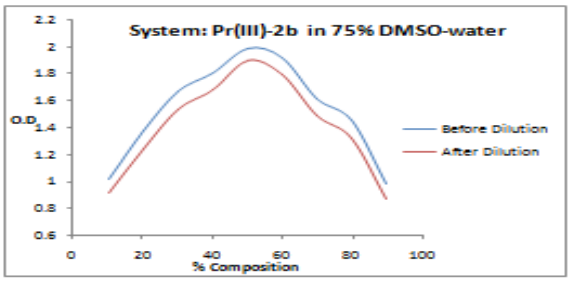

Fig.8

The metal-ligand stability constants indicate the logK values obtained in different binary solvent mixtures follows the order,

DMSO-Water> Acetone-Water> Dioxan-Water

Table.1- Calculated metal-ligand stability constant

System	log K		
	75% Acetone	75% Dioxan	75% DMSO
La (III)-1c	3.223	3.220	3.484
La (III)-2b	3.192	2.706	3.233
Pr (III)-1c	3.413	3.475	3.487
Pr (III)-2b	3.223	1.885	3.247
Sm (III)-1c	3.239	3.355	3.245
Sm (III)-2b	3.487	3.151	3.183

The metal ligand stability constants of substituted benzothiazolyl and benzimidazolyl derivatives in binary solvent system with La(III), Pr(III) and Sm(III) indicates the strong tendency of complex formation. The log k values obtained in binary solvents follows the order DMSO-Water> Acetone-Water > Dioxane-Water.
The stability order of complexes for compound 1a with metal ions in acetone-water and dioxane-water follows the same trend as Pr-1c > Sm-1c > La-1c whereas for DMSO-water Pr-1c > Sm-1c ≈ La-1c for Dioxane-water and Acetone-water but the stability trend for compound 2b is variable.

Lanthanides generally form dipositive, tripositive and tetrapositive ions. The tripositive state is most stable state. The lanthanides are stable in solid as well as in solution state. The present study includes tripositive ions bonding between lanthanides ions and coordinating ligands depend on electronegativity of bonding atoms in ligands. The complex formation in case of ligand 1c and 2b the complex formation site maybe through N atom which gives variable trends.

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