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Spectrophotometric evaluation of stability constants of titanium, molybdenum, iron and aluminium with gallacetophenone phenylhydrazone

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ABSTRACT

Stability constant of metal complexes of gallacetophenone phenylhydrazone (GPPH) are determined using spectrophotometric method. Stability constant of complexes are determined at 30°C, by maintaining the ionic strength constant using 0.1M NaNO₃. The stoichiometry of the complexes is determined by Job's method. It has been verified thoroughly by Asmus method. For the metals, the order of stability constant is found to be Fe(II) > Ti (IV) > Mo (VI) > Al (III). The log k values of the complexes of Fe (II), Ti (IV), Mo (VI) and Al (III) are calculated to be 8.84, 8.44, 7.17 and 3.50 respectively by Asmus method. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Stability constant;
Gallacetophenone
phenylhydrazone;
Spectrophotometry;
Asmus method.

INTRODUCTION

The transition metals have tendency to form coordination compounds with Lewis bases with groups which are able to donate an electron pair. Many hydrazones and phenylhydrazones show physiological activity. These act as herbicides^[1], insecticides^[2], acaricides^[3], nematocides and plant growth regulators^[4]. They show spasmolytic activity, antibacterial activity^[5], hypertensive action and activity against leukemia, sarcomas and other malignant neoplasms^[4]. The physiological activity seems to be due to chelation. The metal complexes of GPPH reveal that the ligand can be used as potential analytical reagent^[6]. In order to investigate metal chelating ability of the ligand, stability constant determination is done in the present work. The stability constant depends on several parameters such as electronegativity, hardness

or softness of the donor atoms in ligand structure, topology of ligand and the ionic radial charge, hardness or softness of the metal ion and its atomic number^[7]. Gallacetophenone phenylhydrazone may behave as a poly dentate ligand and despite various metal – GPPH complexes are studied, no study has been made to determine their stability constants. In the present investigation, the stability constants of chelates of the above mentioned ligand with Fe(II), Ti(IV), Mo(VI) and Al(III) haven been determined spectrophotometrically at room temperature 30±1°C and 0.1M NaNO₃ ionic strength.

EXPERIMENTAL

Reagents

All the chemicals used were of Analytical Reagent

grade and their solutions were prepared in distilled water. Lower concentrations of the solutions were prepared by suitable dilution of the stock solutions. Gallacetophenone phenylhydrazone was prepared as per the standard procedure given by Blatt^[9] and Curmish et al.^[10]. The molecular formula of the compound is $C_{14}H_{14}N_2O_3$ and it melts at 146-147°C. An ethanolic solution of the reagent was employed.

Apparatus

Recording spectrophotometer model SHIMADZU UV-240 and Elico digital pH meter model LI-120 were used in the present investigation.

Procedure

Preparation of stock solution of metal salt

Fresh stock solutions of $2.5 \times 10^{-2} M$ of metal salt (Ti^{4+} , 8.87g/l; Al^{3+} , 11.336g/l; Mo^{6+} , 4.412g/l; Fe^{2+} , 9.8 g/l) were prepared by dissolving accurate amount of metal salts in appropriate volume of water or acid.

Buffer solutions

Buffer solutions of different pH ranges were prepared by mixing appropriate volumes of 0.5M sulphuric acid and 10% sodium acetate (pH 2.5), 0.5M formic acid and 0.5M sodium formate (pH 3.5) and 0.5M acetic acid and 0.5M sodium acetate (pH 4.5).

Preparation of stock solution of ligand

Fresh stock solution of $2.5 \times 10^{-2} M$ of GPPH was prepared by dissolving the accurately weighed amount of GPPH (6.45 g/l) in 95% ethanol.

Preparation of working solution

Dilute solutions of metal ions and ligand solution under study were obtained by appropriate dilution of the stock solution. These are freshly prepared just before use.

Determination of λ_{max} of the metal – ligand solution

A number of solutions were made by mixing different volumes of $2.5 \times 10^{-4} M$ solution of each of the metal salt and $2.5 \times 10^{-3} M$ of GPPH solution. In each measurement pH was adjusted suitably by adding appropriate buffer and ionic strength was maintained constant using 0.1M $NaNO_3$ at room temperature. The alcohol concentration was maintained at 25% v/v. Then

the absorption spectra of the complexes were recorded against the reagent blank.

The absorption maxima (λ_{max}) of the mixtures of the different metal ions and the ligand are shown in TABLE.

Determination of stoichiometry

Job's method of continuous variations^[11] was used to determine stoichiometry. $2.5 \times 10^{-4} M$ solutions of metal ions(m) and $2.5 \times 10^{-3} M$ of ligand were prepared and a series of mixtures containing 'x' ml metal ion solution and (50-x) ml of ligand solution were made upto 50 ml volumetric flask. The absorbance of solution was taken at λ_{max} as was determined previously.

A plot of absorbance versus concentration of metal ion / metal in plus ligand [(M) / (M) (L)] was drawn in each case. The composition of the complexes from Job's plot are shown in TABLE 1.

Determination of stability constant

The stability constant of metal ions (Ti^{4+} , Al^{3+} , Mo^{6+} and Fe^{2+}) with GPPH were determined spectrophotometrically using Asmus method. The method consists of determining the absorbances of solutions containing fixed volume of the metal in solution (V_0) of concentration (C_0) and increasing volumes (v) of the ligand solution of concentration (b_0), the total volume of solution (V) being kept constant. From the absorbance, the extinction modulus, 'm' is calculated by dividing absorbance by the cell width. Then graphs are drawn between $1/m$ and $1/V^n$ where $n=1,2,3$ etc. The value of 'n' corresponding to the linear plot gives the number of ligands attached to the metal ion.

The intercept of the straight line plot gives the stability constant

$$\text{Intercept} = -(b_0/V)^n \cdot 1/k$$

where K is instability constant.

The stability constants which are evaluated are shown in TABLE 1.

TABLE 1 : Stability constant data of metal – GPPH systems

Metal – GPPH system	λ_{max} (nm)	M : L	Stability constant (log k)
Fe (II) – GPPH	378	1:2	8.84
Ti(IV) – GPPH	375	1:2	8.44
Mo(VI) – GPPH	375	1:2	7.17
Al(III) – GPPH	375	1:1	3.50

Short Communication**RESULTS AND DISCUSSION**

Stoichiometry of the complexes were determined from the plot of absorbance versus $[M] / [M][L]$. Asmus method was used to confirm the composition of the complexes. The results from Asmus method showed that except for aluminium, the metal of ligand ratio is 1:2 and for Al and GPPH it is 1:1

Furthermore, the stability of the complexes were evaluated. The values of the stability constant, $\log k$ were calculated using Asmus method. From the results of stability constants, the order of stability constant and hence the reactivity of the ligand towards the metals follows the trend $Fe(II) > Ti(IV) > Mo(VI) > Al(III)$. From these studies, it is known that the transition complexes of GPPH namely $Fe(II) - GPPH$, $Ti(IV) - GPPH$ and $Mo(VI) - GPPH$ are relatively more stable, while the non-transition complex of $Al(III) - GPPH$ is less stable. Addition of fluoride ions to the less stable $Al(III) - GPPH$ complex resulted in a proportional decrease of absorbance. The bleaching action of fluoride has been utilized for its indirect spectrophotometric determination in water samples by the same author^[12].

Thus the complexes of GPPH have been studied to determine their stability. It is interesting because these data are useful to understand the role of metal ions in the analysis of water samples and the role of GPPH as an analytical reagent.

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