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Equilibrium studies on binary complex formation of lanthanide ions La(III), Pr(III), Sm(III), Gd(III) and Dy(III) with vitamin–U at constant temperature

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Abstract

The determination of formation constant of Binary Complexes(ML) , where M = La(III), Pr(III), Sm (III), Gd (III) And Dy (III) and L = Vitamin-U have been carried out using Irving-Rossotti titration technique in aqueous media at 25 ±0.1°C temperature . The ionic strength μ = 0.2M was held constant using sodium per chlorate as an electrolyte. The stability constant s of trivalent lanthanide vitamin-U complexes were calculated and explained. The mechanism, through which Protonation and complex formation takes place, has been suggested.

Key words: Vitamin-U, Stability constants, Lanthanides (III) Ions.

INTRODUCTION

The ligand vitamin-U is an α-amino acid. This compound containing both active $–NH_2$ group and an acidic group –COOH is capable of formation a chelate ring. It is very important in medicine, Biology and other fields of chemistry [1]. Metal complexes of vitamin-U have found useful applications in biological and pharmaceutical fields [2]. Methyl Methionine Sulfonium Chloride [M.M.S.C.] has protective effect against ethanol-induced injury in rats and the antiulcer effect of MMSC is related to its gastric mucin-increasing action [3].A previous study [4] showed that L-cysteine and MMSC inhibited ethanol-induced gastric mucosal damage and inceased the amount of surface mucin in rats. Vitamin-U is also used in antiradiation effect [5] cytoprotective effect of MMSC on necrotizing agent-induced gastric mucosal damage in rats have been carried out [6]. Akbarov et. Al. [7] demonstrated that the main factor in activation of Ca-dependent AT Pase by cobalt complexes with vitamin-U, Glycine, α-alanine etc. Invention provides a therapeutic composition for use in the treatment of mucosities and method for using such a therapeutic composition [8]. Experiments were made on the investigation of the effect of vitamin-U and nickel complex compound on the process of lipid per oxidation in rat liver [9]. Thermolysis studies of vitamin-U with some of its nickel (II) complexes have been carried out [10]. Scientists have focused considerable attention on lanthanides and their compounds.

MATERIALS AND METHODS

All the reagents used were of A.R.grade and metal per chlorate solutions of desired concentration were prepared from the higher molar stock solutions. Acid and metal contents of the solution under analysis were determined by acid – base [11] and complex metric method [12]. Ionic strength was maintained at 0.2 M using 0.1 M sodium per chlorate solution. Digital pH meter EQ-610 with a read ability of ± 0.01 was used for pH measure. It was calibrated with buffer solutions having pH 4.01, 7.0 and 9.18 at 25 ºC. The calibration was intermittently checked. Potentiometer titrations were carried out at 25 ± 0.1ºC using 0.2 M sodium hydroxide solution. Irving Rossotti technique [13] was used for the determination of binary formation constants. The values have been presented in the table-1

Table 1: Proton ligand and binary metal ligand formation constants of vitamin-U at 25±0.1ºC system

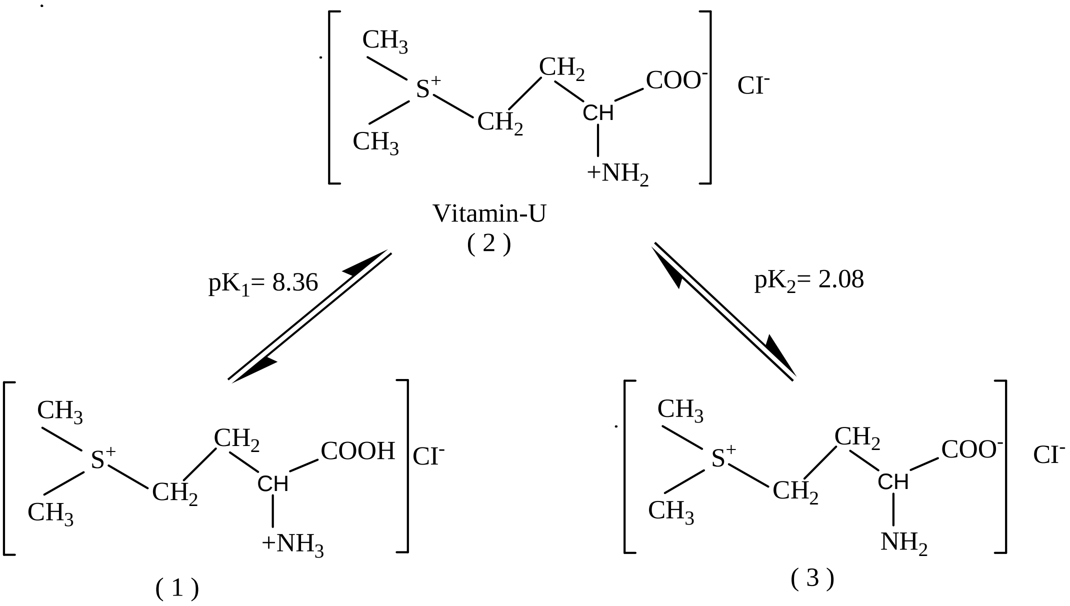
Ligand pK^H Values	Metal ligand Formation constants				
	La (III)	Pr(III)	Sm (III)	Gd (III)	Dy (III)
Vitamin-U	Log β =9.68±.14	Log β=9.85±.14	Log β=10.19±.17	Log β=9.85±.16	Log β=10± 0.18
Pk_1^H=8.36	Logk$_1$=6.68±.39	Logk$_1$=6.20±.16	Logk$_1$=6.25±.16	Logk$_1$=6.26±.17	Logk$_1$=6.38±.02
pK_2^H=2.08	Logk$_2$=3.0±.26	Logk$_2$=3.65±.02	Logk$_2$=9.68±.04	Logk$_2$=3.59±.04	Logk$_2$=3.64±.06

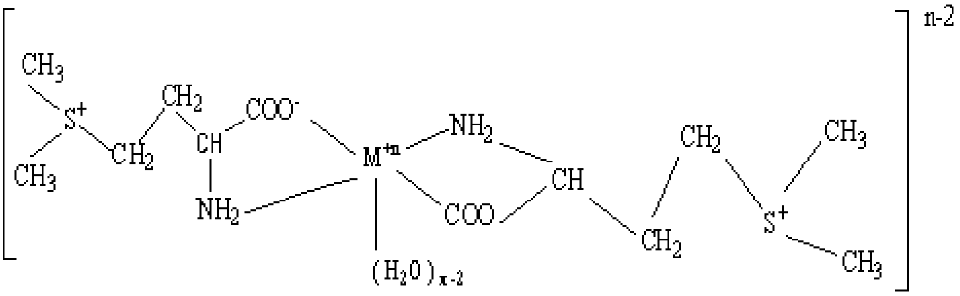
RESULTS AND DISCUSSION

The proton ligand and metal ligand formation constants of trivalent lanthanides (III) ions with vitamin-U were calculated by measuring the magnitude of the proton displacement during the titration of the ligand in absence and presence of metal ions titrated against sodium hydroxide solution respectively. The proton ligand and metal ligand stability constants have been presented in table [1].

Protonation of vitamin-U and mechanism of M – vitamin-U complex formation is as follows.

(I) Protonation of vitamin-U

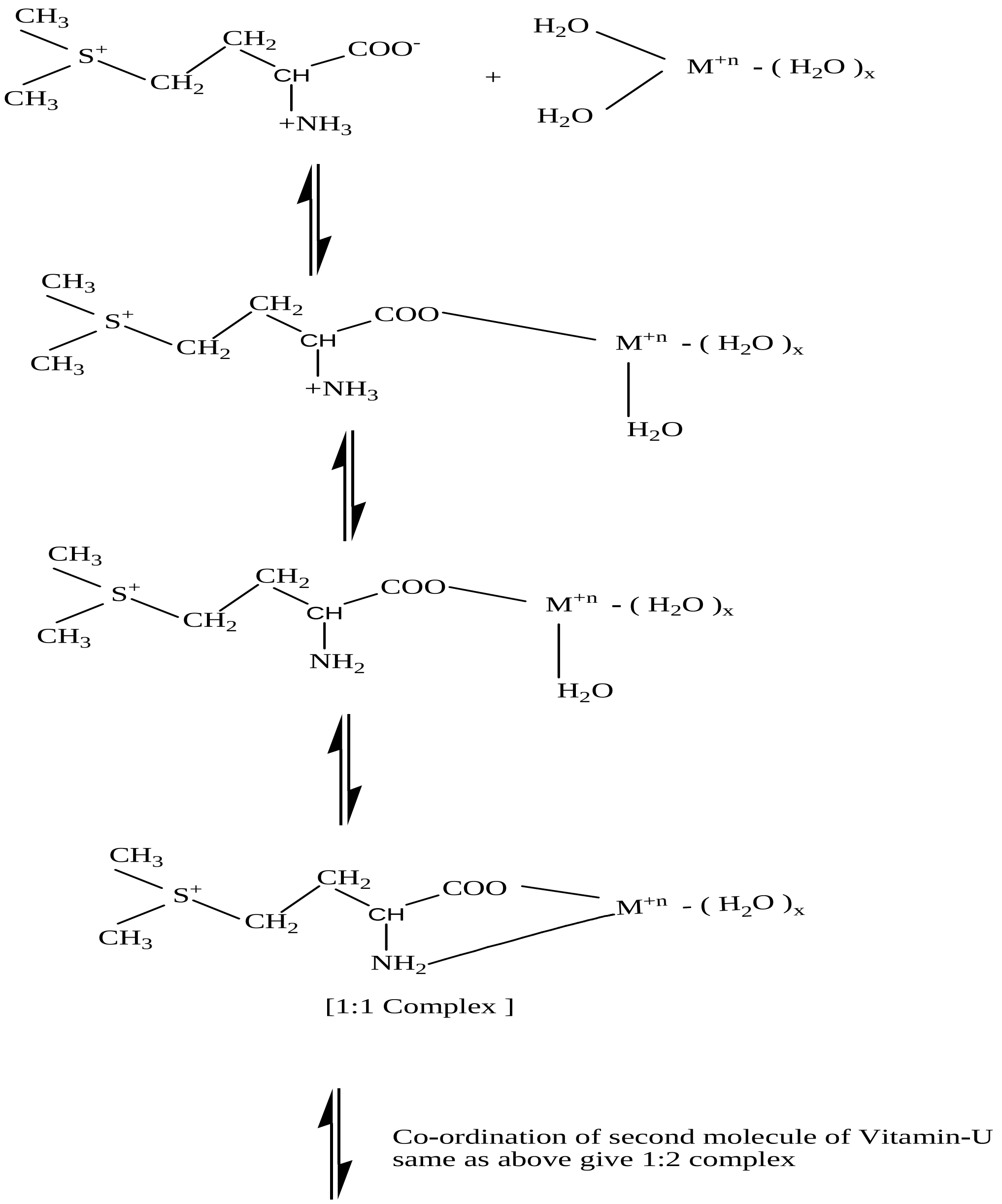




[1:2 Complex]

Lanthanide contraction occurs due to poor shielding of 4f electrons and a steady increase in effective nuclear charge is observed. The f orbital are split by an octahedral field into three levels t_{1g}, t_{2g} and a_{2g}–common coordination numbers shown by lanthanide ions are 6,7,8 and 9. Usual characteristics of lanthanide complex in solution being ionic and undergoing ligand exchange reactions easily compared by transition metal complexes. Lanthanides behave as typical hard acids and show preferred bonding with oxygen donor ligands. In the presence of water, complexes with nitrogen sulphur and halogens (except F) donor ligands are not stable. The 4f electrons are buried so deeply (compared to 5f) within the atom that they are unaffected by the environment to any great extent. The Values of ligand field stabilization energy (LFSE) is minimum due to absence of significant interaction with 4f orbital. La $^{3+}$ to Lu $^{3+}$ he ionic size decreases and partial molar volume decreases until crowding of ligands becomes intense. Stability of lanthanide complexes increases by means of chalets effect.

(2) Mechanism of M - Vitamin - U, complex formation



Co-ordination of second molecule of Vitamin-U same as above give 1:2 complex

Simple electrostatic or acid base concept of size and charge is not successful in characterization of the stability behavior of lanthanide complexes, and all lanthanides show discrepancies from the simple picture and often show change or even decrease in stability with increase in atomic number. As mentioned above, the fall in stability is observed in case of Gd - Vitamin-U chalets The highest stability of Sm-Vitamin-U chelate's may be due to the sudden increase in partial molal volume. The overall tendency in chelating- show a decrease in stability with increase in atomic number barring the exception of Sm-Vitamin-U.

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