Int. J. Chem. Sci. : 1 (2), 2003, 155–158

EQUILIBRIUM STUDIES ON BINARY CHELATE FORMATION OF VITAMIN–U WITH SOME TRANSITION METAL IONS

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ABSTRACT

The present paper describes a pH metric study on formation constant of binary complexes of transition metal ions V^{+5}, Cr^{+3}, Fe^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2} with Vitamin–U carried out at constant temperature $25 \pm 0.1^{\circ}C$ and ionic strength $\mu = 0.2\ M\ dm^{-3}$ ($NaClO_4$). Various factors influencing the formation and stabilities of binary complexes have been discussed.

Key words : Binary chelate, Vitamin–U, Transition metal ions

INTRODUCTION

The transition metals have tendency to form coordination compounds with Lewis bases, with groups which are able to donate an electron pair.

The ligand Vitamin–U (Methyl Methionine Sulfonium Chloride) (M.M.S.C.) has two sites available for coordination, one from nitrogen of $-NH_2$ group and other is oxygen of $-COOH$ group. Vitamin–U is very important for hair growth, mucoso and as an antiulcer[1,2] Thermal analysis of Vitamin–U and some of its Ni^{+2} complexes has been studied[3]. Polarographic determination of stoichiometry and stability constants of complexes of Vitamin–U with metal ions have also been carried out[4].

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EXPERIMENTAL

Vitamin–U was obtained from Fluka (AR Grade). Other reagents used were sodium perchlorate, perchloric acid, sodium hydroxide (BDH AR Grade). Acid and metal contents of the solution under analysis were determined by acid–base[5] and complexometric titrations[6,7]. Ionic strength was maintained at 0.2 M dm^{-3} with the use of sodium perchlorate. Systronics pH meter Model 361 (with readability ± 0.01) was used for potentiometric studies. μ pH meter was calibrated with buffer solutions and calibration was checked intermittently. All potentiometric titrations were carried out at 25 ± 0.1°C using carbonate free NaOH following the procedure[8–9]. Irving – Rossotti titration technique[9–10] was used for determination of binary formation constants.

The protein ligand and metal ligand formation constants of ligands and bivalent transition metal ions with Vitamin–U were calculated by measuring the magnitude of the proton displacement during titration of ligand in absence and in presence of metal ion, respectively. The proton ligand and binary metal ligand formation constants are presented in Table–1.

The proton ligand formation constant values are same as reported earlier[11].

Table 1. Binary metal ligand formation constant of Vitamin–U at temperature 25 ± 0.1°C and ionic strength $\mu = 0.2$ M dm^{-3} ($NaClO_4$)

LIGAND		METAL						
Vitamin–U		V^{+5}	Cr^{+3}	Mn^{+2}	Fe^{+3}	Co^{+2}	Ni^{+2}	Cu^{+2}
$pK_1H = 8.36 \pm 0.03$	log K_1	6.32	6.98	6.30	7.03	6.23	5.54	6.65
	log K_2	4.68	4.22	3.16	3.19	3.27	3.92	3.06
$pK_1H = 2.08 \pm 0.03$	Log β	11.00	11.20	9.46	11.22	9.50	9.46	9.71

RESULTS AND DISCUSSION

The solution chemistry of first transition series is very interesting. The following factors explain satisfactorily the overall characteristics of stability and other aspects : ionization enthalpies of metal atoms, ionic radius, electronic structure of metal ions, nature of ligands involved in dπ–pπ interactions, nature of solvent, etc.

In the present investigation, the V^{+5} is undergoing chelation in two steps. The overall stability is higher, especially due to the +5 charge of the metal ion. The metal–ligand interaction would be significant. The stability constant of Cr^{+3} – Vitamin–U complex is greater than that of Mn^{+2}, because of higher charge on the metal ion and small size. Manganese tripositive state is less stable than dipositive. The stability shown by Mn^{+2}, with Vitamin–U is the lowest in the selected ions. This is due to the lower charge and specific behaviour of metal ion. The overall stability constant values of Fe^{+3} and Cr^{+3} is similar.

Co^{+2}, Ni^{+2}, Cu^{+2}; all metal ions were selected for equilibrium study in water with Vitamin–U which coordinates through N and O of $-NH_2$ and $-COOH$, respectively. Copper has single s electron outside the filled 3d shell. The filled 'd' electrons are involved in metallic bonding. This factor contributes to much more noble character of copper, the effects to make compounds more covalent, Cu^{+2} has greater lattice and solvation energies, hence higher formation constant for complexes of Cu^{+2} ions is observed amongst three, Cu^{2+} shows higher stability as expected. Co^{2+} complexes with Vitamin–U is more stable than corresponding Ni^{+2} – Vitamin–U complex (Ni^{+2}; $\log K_1 = 5.54$ whereas Co^{2+}; $\log K_1 = 6.23$). This is attributed to the size of the metal ions.

CONCLUSION

The binary ML (xH_2O) complexes of V^{+5}, Cr^{+3}, Mn^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2} and Cu^{+2} with Vitamin–U ligand have been studied to determine their stability. It is interesting, because the order of the stability is governed by various factors like stereochemistry, charge on metal ion, electronegativity, nature of the metal ion and ligand. The first transition series is selected by nature in various biochemical processes. Hence, these data are very useful to study the various biochemical reactions.

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Accepted 27.5.2003