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NOTE

Equilibrium Studies on Binary Chelate Formation of Vitamin-U with Some Alkaline Earth Metal Ions

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The present paper describes pH-metric study on formation constant of binary complexes of alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}), with vitamin-U carried out at constant temperature 25 ± 0.1°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: Vitamin-U, Chelate, Alkaline earth metals.

Vitamin-U (methyl methionine sulfonium chloride, MMSC) has two sites available for coordination from nitrogen of NH_2 group and oxygen of COOH group capable of forming a chelate ring. It is very important for antiulcer, mucosa and hairgrowth[1, 2] etc. Studies on some chelates derived from antiulcer vitamin have been carried out[3]. Effect of chelate formation on the activity of Ca-ATPase Co(II) bio-complexes with vitamin-U, glutamic and α-ketoglutanic acids is studied[4]. In present work, we describe pH-metric study on formation constant of binary complexes of alkaline earth metal ions with Vitamin-U.

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].

Ionic strength was maintained at 0.2 M dm^{-3} using sodium perchlorate. Systronics pH system 361 with readability of ± 0.01 was used for potentiometric studies. The temperature was maintained at 25 ± 0.1°C for the entire pH range from 0–14. It was calibrated with buffer solution and calibration was checked intermittently. Irving-Rossotti technique[7] was employed for the determination of proton ligand and metal ligand formation constants in aqueous solution. Irving-

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Rossotti technique[8, 9] was used for the determination of binary formation constants.

The proton ligand and metal ligand formation constants of ligands and bivalent alkaline earth metals with vitamin-U were calculated by measuring the magnitude of the proton displacement during titration of ligand in the absence and presence of metal ion respectively. The proton ligand and binary metal ligand formation constants are presented in Table-1.

The proton ligand formation constants are the same as reported earlier[10].

TABLE-1
BINARY METAL LIGAND FORMATION CONSTANTS OF VITAMIN-U AT TEMPERATURE 25 ± 0.1°C AND IONIC STRENGTH $\mu = 0.2$ M dm^{-3} ($NaClO_4$)

Ligand (Vitamin-U)		Alkaline earth metals			
		Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
$pK_1^H = 8.36 \pm 0.03$	log K_1	6.42	7.74	6.62	6.09
	log K_2	3.46	2.96	3.13	3.76
$pK_2^H = 2.08 \pm 0.03$	log K_3	9.88	10.44	9.76	9.85

The solution chemistry of alkaline earth metals is very interesting and biologically very important. The following factors explain satisfactorily the overall characteristics of stability and other aspects like ionzation enthalpies of metal ions, ionic radius, electronic structure of metal ions, nature of ligands involved in d_π-p_π interactions, nature of solvents, etc. In general, the stability of alkaline earth metal chelates with ligands having 'N' is slightly lower than that with oxygen.

Following are the three important types in general to understand the stability of alkaline earth metal ions:

1. For small and highly charged anions, their stability constants decrease with increase in crystal radii; thus $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$.
2. For anions (*e.g.*, NO_3^-, SO_4^{2-}, IO_4^- etc.), the order is $Mg^{2+} < Ca^{2+} < Sr^{2+} < Ba^{2+}$.
3. For hydroxy acids and amino carboxylic acids, the stability order is $Mg^{2+} < Ca^{2+} > Sr^{2+} > Ba^{2+}$.

In the present investigation the stability constant is highest for Ca^{2+} ion as expected (log β_2 and log K_1). The log K_1 values also follow the expected order $Ca^{2+} > Sr^{2+} > Ba^{2+}$ of anion Cl^-, the possible reason for the change is stability of K_2 and hence β.

Conclusion

The binary $ML(H_2O)_n$ complexes ($M = Mg^{2+}$, Ca^{2+}, Sr^{2+} and Ba^{2+} and L = vitamin-U) have been studied to determine their stability. The order of the stability is governed by various factors including stereochemistry. These data are very useful to understand the nature of various biological reactions.

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