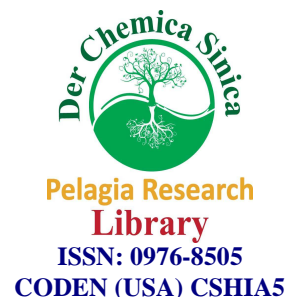




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Potentiometric study of vitamin E and vitamin D complexes with transition metals in acetonitrile- water medium

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ABSTRACT

Vitamin E and vitamin D complexes with transition metals in 92% (v/v) acetonitrile- water medium. The stability constants for the transition metals with α -tocopherol and cholecalciferol have been studied using pH-measurements in 92% (v/v) acetonitrile- water medium. The values of proton- ligand stability constant and metal- ligand stability constants were calculated. The overall stability constants were determined and are quoted.

Key words: Tocopherol, cholecalciferol, stability constants, binary complexes, transition metals.

INTRODUCTION

Vitamin E was discovered by Evans and Bishop more than 75 years ago as a lipid-soluble substance in lettuce and wheat necessary for the prevention of foetal death and resorption in rats fed a rancid lard diet [1]. This substance was designated as vitamin E following the recognition of vitaminD [2,3]. The term "Tocopherol" is used after the Greek words "tokos" (child birth), "phero" (to bring forth), and "ol" (alcohol). α -Tocopherol was isolated from wheat germ oil in 1936 [4]. It was first synthesized by Karrer [5] and its structure was determined by Fernholz [6] in 1938. The antioxidant properties of tocopherols were first reported by Olcott and Emerson in 1937 [7].

Vitamin E plays key role in human metabolism, specially as anticoagulant activity. The essentiality of vitamin E for humans was recognized in connection with studies on premature infants in which hemolytic anaemia was associated with vitamin E deficiency [8,9].

The vitamin D which occurs naturally in unfortified foods is generally derived from animal products. Saltwater fish, such as herring, salmon, sardine and fish liver oils are extremely rich sources. The two most prominent members of this group are ergocalciferol (vitamin D₂) and cholecalciferol (vitamin D₃). Cholecalciferol is the form of vitamin D obtained when radiant energy from the sun strikes the skin and converts the precursor 7-dehydrocholesterol into vitamin D₃. It is also important for phosphorus homeostasis [10,11]. Vitamin D is a powerful antirachitic agent; its primary effect on bone is the stimulation of bone resorption leading to an increase in serum calcium and phosphorus levels [12]. In this paper we describe the results of complexation of vitaminE and vitamin D₃ with transition metals in water –acetonitrile medium at 298K and at 0.1M ionic strength. The results obtained by potentiometric method are predicted. The complexes obtained by potentiometric method and their formation constants were calculated.

MATERIALS AND METHODS

Materials

All chemicals were of analytical grade and were used without purification. All solutions were prepared in double distilled, carbon dioxide-free water and acetonitrile from Merck, vitaminE (α -Tocopherol), vitaminD₃ (Cholecalciferol) from Himedia (France) was used. The solution of ligand was prepared half an hour prior to its use. Ferric (Loba chem.), copper, zinc (S.D.fine Chem.) Anala R grade quality in their nitrate form, cobalt (S.D.fine Chem.) in its chloride form were used. The sodium hydroxide (0.200M) was standardized against oxalic acid. The ionic strength (μ) was maintained at 0.100M by using KNO₃ (B.D.H.) as supporting electrolyte.

The ligand solution and acid solution were transferred into 100 ml beaker and titrated against NaOH solution. The titration was performed first without addition of metal and then in its presence.

Method

The potentiometric titrations were carried out under inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing the electrodes in order to prevent atmospheric oxidation using carbonate free NaOH. An Elico model LI-120 digital pH meter in conjunction with an Elico combined glass electrode consisting of glass and reference electrodes entity of the type CK-61/CN-91/CM-51 were used for the pH measurement. The combined glass electrode was activated by immersing 24 hours in 0.1N hydrochloric acid and then 12 hours immersed in glass distilled water. The precautions suggested by Bates [13], Albert and Sergeant [14] were adopted for smooth handling of the electrode. The combined glass electrode was connected to pH meter and by adopting standard procedure. The pH meter was switched on at least half an hour before to start titration. The buffer solution having the pH ranges 4.00, and 9.18 was used for the standardization of pH meter, before and after each titration. To obtain equilibrium and to avoid fluctuation in readings it was then immersed for 30 minutes in buffer. It was confirmed by titrating 0.2 M oxalic acid against standard sodium hydroxide.

The solution was stirred with every addition of NaOH by magnetic stirrer. The ligand solution of α -tocopherol and cholecalciferol was prepared in 100 ml acetonitrile and it was used for further titrations.

The pK value for α -tocopherol was determined pH metrically. Hence, proton–ligand stability constants of the ligand have been determined by Irving-Rossotti's pH metric titration technique [15]. For the determination of proton-ligand stability constants the stock solutions of nitric acid, vitamin and potassium nitrate were taken in 50 ml volumetric flask followed by acetonitrile to obtain desired concentration and percentage of acetonitrile. The content was diluted upto the mark. Aliquots of 50ml were transferred to the pH metric cell and titrated against standard NaOH solution. For the determination of metal ligand stability constants of vitamins with metal ions, suitable amount of metal ion, vitamin and nitric acid from stock solutions were taken into pH metric cell and titrated against NaOH solution until a precipitate was just observed in titration cell. The titration was stopped at this point. The ionic strength of solution during each titration was maintained 0.1M by adding 0.4M KNO₃. pH meter readings were taken after every fixed interval until stable readings were obtained.

RESULTS AND DISCUSSION

The metal ions and hydrogen ions act as Lewis acids. pH decreases, if a neutral metal ion is added to the ligand solution. The metal- ligand titration curve lie below the pure ligand titration curve. The potentiometric titration curves of α -tocopherol, and cholecalciferol with some transition metals are shown in fig.1, fig.2 and fig.3,fig.4. The pH of complex formation is much below than the pH of metal ion hydrolysis. These features of the pH metric studies confirm the formation of complexes by all the metal ions with vitamin.

The determination of proton – ligand stability constant of the ligand is a prerequisite for the evaluation of metal – ligand stability constant. The pK value of α tocopherol is lower indicating that more electronegative oxygen atom having loan pair of electron attached to benzene ring. The πA values range between 1.2 to 1.8 for α -tocopherol and cholecalciferol indicating the liberation of one proton from –OH attached to benzene ring.

The pK value of cholecalciferol is slightly greater than α -tocopherol. This can be explained on the basis of the strong + mesomeric effect [16] of oxygen atom with its loan pair of electrons. This trend in basicity can be attributed to the intrinsic nature of the basic site and inter molecular hydrogen bonding [17].

The values of \bar{n} ranges between 0.2 to 0.8 for metal- ligand formation curve data. This indicates that metal ion form 1:1 complex [18] with α -tocopherol and cholecalciferol

Initial concentration of ligand 2×10^{-3} M and metal 4×10^{-4} M were used to study the effect of stability constant. The concentration of ligand was higher to avoid the reproducibility of ligand.

The proton –ligand stability constants and metal – ligand stability constant of α -tocopherol with transition metal complexes in 92% (v/v) acetonitrile–water medium at 298K and ionic strength $\mu=0.1$ M (KNO_3).

Table 1

α - tocopherol $\text{pK}_1=2.02$								
Metal	V(II)	Mn(II)	Fe(III)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
logK	2.9263	3.0526	2.9897	2.7877	3.0209	2.9223	3.0701	3.1469

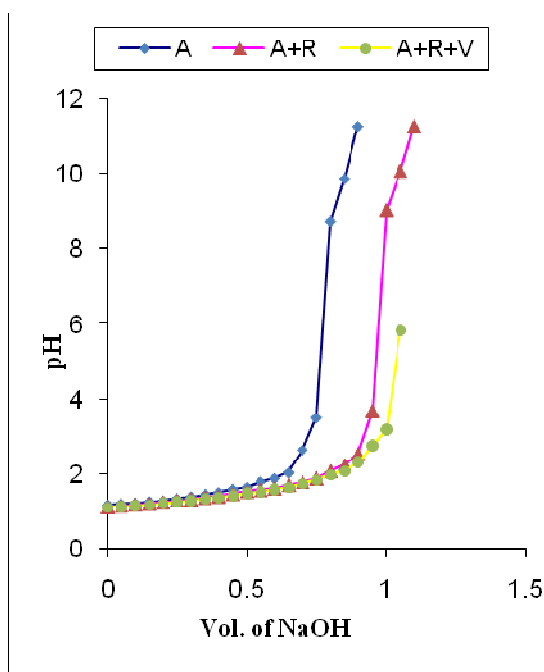
Potentiometric titration curve of α -Tocopherol with some transition metals

Fig. 1

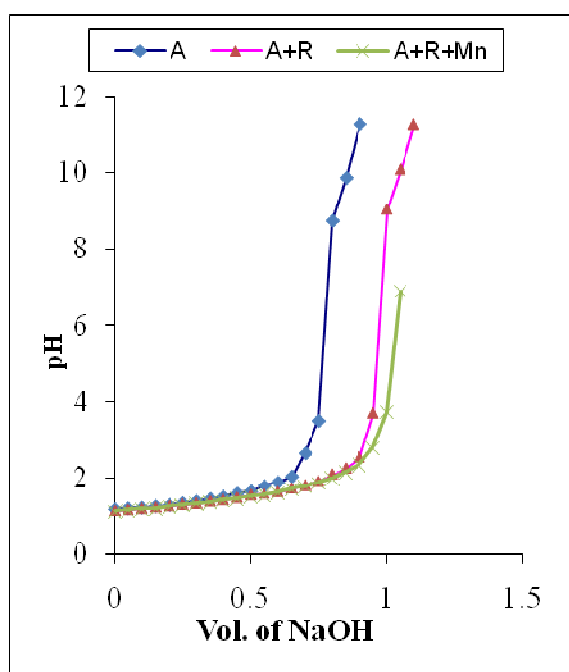


Fig. 2

The proton–ligand stability constant and metal–ligand stability constants of cholecalciferol with transition metal complexes in 92% (v/v) acetonitrile–water medium at 298K and ionic strength $\mu=0.1$ M (KNO_3).

Table 2

Cholecalciferol $\text{pK}_1=2.15$								
Metal	V(II)	Mn(II)	Fe(III)	Co(II)	Cu(II)	Zn(II)	Cd(II)	Pb(II)
logK	3.0898	2.9583	2.9856	2.9215	2.928	2.7524	3.002	3.1415

The basicity of the ligand have been measured in terms of their proton-ligand stability constant. The interaction of metal ion with a base is similar to the neutralization reaction involving hydrogen ion. J. Bjerrum [19] pointed out that the bases which have the strongest affinity for hydrogen ions form most stable complexes. This trend was observed in α -tocopherol and cholecalciferol. The more basic ligands form more stable complexes. Bjerrum, in his study on silver complexes with various amines showed a relationship between $\log K_{\text{Ag}^+}$ and $\log K_{\text{H}^+}$ for the ligands. Similar linear relationship was shown by several workers [20-34] between the $\log K$ of a series of metal complexes derived from one metal ion with a set of similar ligands and their pK values.

Potentiometric titration curve of cholecalciferol with some transition metals

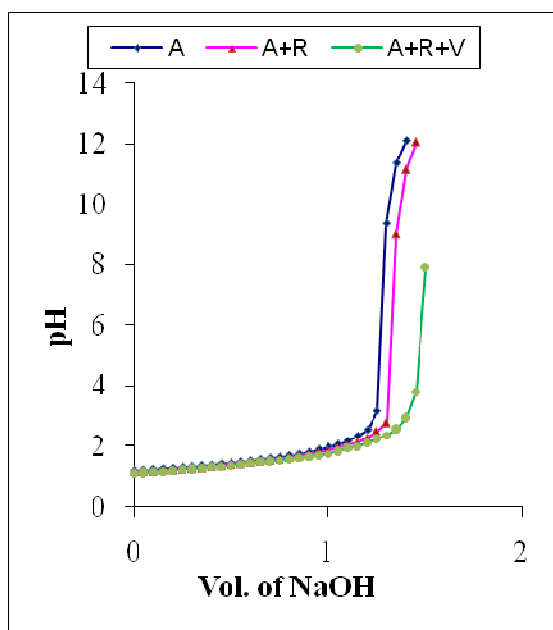


Fig. 3

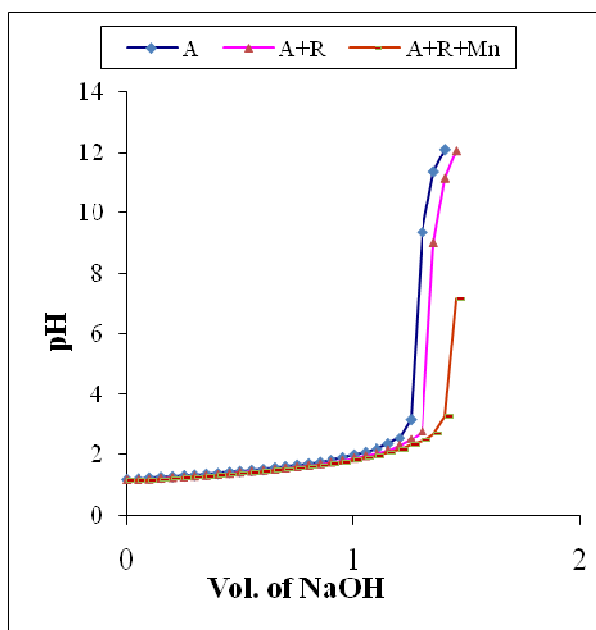


Fig. 4

CONCLUSION

In the present work, pH metric study was performed to determine stability constants and to assess binary species for α Tocopherol with transition metal ions in 92% acetonitrile-water medium. The following conclusions have been drawn: (1) α Tocopherol forms complexes with transition metal ions in the pH range 3.0-9.0. (2) The binary complexes are formed due to electrostatic interaction. (3) The concentration of ligand concentration of metal ions due to avoid reproducibility and more solubility of ligand.

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