

Potentiometric study of vitamin K₃ complexes with transition metals in methanol- water and acetonitrile-water medium

Milind N. Gaikwad¹, Suresh T. Gaikwad², Anjali S. Rajbhoj*

¹Department of Chemistry, Arts, Commerce and Science College Kille-Dharur, 431124, Maharashtra, India

^{2,*}Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University Aurangabad, 431005, Maharashtra, India

*Corres. author: milind.g894@gmail.com
Phone No. & Fax No.: +91-02445-274129

Abstract: Vitamin K₃ complexes with transition metal ions in 25%(v/v) methanol-water and 20%(v/v) acetonitrile-water medium. The dissociation constant and stability constants were determined at 298K and at 0.1M ionic strength using potentiometric method. The dissociation constant and stability constants were determined.

Key words: Menadione, transition metals, stability constant, binary complexes.

INTRODUCTION

The compound 2-methyl-3-phytyl-1,4-naphthoquinone (II) is generally called vitamin K₁ but is preferably called phylloquinone¹. The compound was first isolated from putrified fish meal and was called at that time vitaminK₂² is one of a series of vitamin K compounds with unsaturated side chains called multiprenyl-menaquinones that are found in animal tissues and bacteria. The parent compound of the vitamin K series, 2-methyl-1,4-naphthoquinone, has often been called vitamin K₃ but is more commonly and correctly designated as menadione. Although green leafy vegetables have been known for some time to be the major source of vitamin K in the diet, it is now apparent that cooking oils, particularly soyabean oil and rapeseed oil are major contributors³. Green leafy vegetables, cauliflower and dairy products are the sources of vitamin K. The major use of vitamin K in the

animal industry is in poultry diets. Low blood levels of vitamin K can lead to very serious bleeding.

It has also been shown that hypothyroidism in human results in a decrease in both the rate of synthesis and destruction of the vitamin K dependent clotting factors⁴. Significant amounts of fat soluble vitamins can be stored in adipose tissue and the liver.

In the recent years science literature is receiving numerous reports on the study of metal complexes which describe their importance applicability in the field of scientific interest like , biochemistry, medicine, pathology, agriculture industries. It will not be exaggeration to say that metal complexes have vital role in modern scientific age to achieve advancement in any chosen field of sciences. Therefore in the present work, attempts have been made to report in the complex formation of menadione with transition metal complexes in 25% (v/v) methanol-water

20% (v/v) acetonitrile-water medium at 298K and at fixed ionic strength 0.1M KNO₃.

EXPERIMENTAL

Vitamin sample of menadione in pure form was obtained from Himedia. Methanol was used was AnalaR grade. Double distilled water was used for the preparation of metal ion solutions, acid solution, NaOH solution and KNO₃ solution. The conductivity and pH of this distilled water was found to be 1.60×10^{-6} mhos and 6.8 respectively. NaOH was standardized with oxalic acid solution and it was used for further potentiometric titrations. The concentration of metal ions in solutions was estimated by standard procedures⁵⁻⁷. Borosil quality glasswares were used in the experiments. The micro burette with graduation of 0.02 ml was calibrated by the method of Vogel⁸. 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 precautions suggested by Bates⁹, Albert and Sergeant¹⁰ were adopted for smooth handling of the electrode.

The experimental procedure for binary metal complexes involves following titrations-

- 1) Free HNO₃
- 2) Free HNO₃ + menadione
- 3) Free HNO₃ + menadione+ metal ion solution

These solutions were titrated against standard solution of sodium hydroxide. The ionic strength of the solutions was maintained constant i.e 0.1M by adding an appropriate amount of 4M potassium nitrate solution. The titrations were carried out at 298K in an inert atmosphere by bubbling free nitrogen gas through an assembly containing electrode to expel out carbon dioxide gas. The readings on pH meter in 25% (v/v) methanol-water and 20% (v/v) acetonitrile-water medium were recorded at every addition of sodium hydroxide in order to evaluate dissociation constant and stability constants. The method for the determination of the formation functions was described by Irving and Rossotti¹¹ and Hearon and Gilbert¹². The potentiometric titration techniques has been used by Irving and Rossotti, which was used earlier by Calvin and Melchior¹³ and now known as Calvin-Bjerrum titration technique.

Table 1-The dissociation constant of menadione in 25%(v/v) methanol-water and 20%(v/v) acetonitrile-water medium at 298K and at $\mu= 0.1M$ KNO₃

Menadione	pK ₁
25% (v/v) methanol-water	2.38
20% (v/v) acetonitrile-water	2.96

Table 2-The metal ligand stability constants of menadione with transition metal ions in 25%(v/v) methanol- water medium at 298K and at 0.1M KNO₃

Metal	V(II)	Mn(II)	Fe(III)	Co(II)	Cu(II)	Zn (II)	Cd(II)	Pb(II)
logK ₁	2.9201	2.8468	3.0221	2.8131	2.8146	2.9254	2.9324	2.9668

Table 3-The metal ligand stability constants of menadione with transition metal ions in 20%(v/v) acetonitrile-water medium at 298K and at $\mu= 0.1M$ KNO₃

Metal	V(II)	Mn(II)	Fe(III)	Co(II)	Cu(II)	Zn (II)	Cd(II)	Pb(II)
logK ₁	3.0958	3.1178	3.0695	2.7565	3.1742	2.7547	3.2794	2.7833

Potentiometric curve of menadione-Cu in 25%(v/v) methanol- water medium at 298K and at $\mu= 0.1M KNO_3$

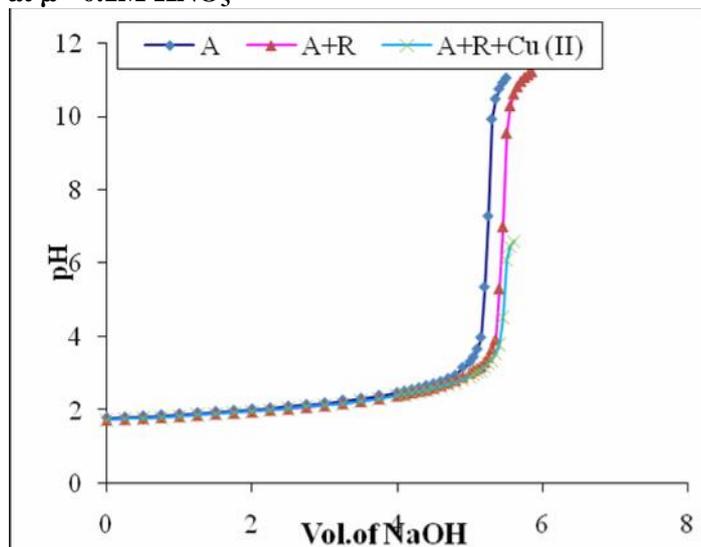


Fig. 1

Potentiometric curve of menadione-Cu in 20%(v/v) Acetonitrile - water medium at 298K and at $\mu= 0.1M KNO_3$

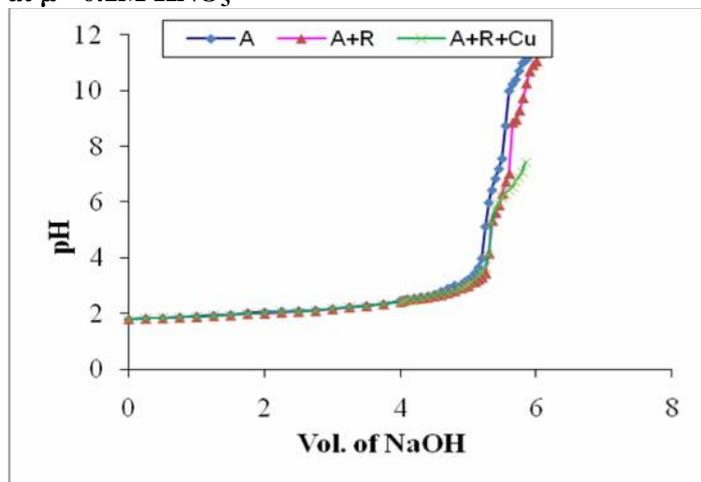


Fig. 2

RESULTS AND DISCUSSION

Binary metal complexes

The proton ligand stability constant and metal ligand stability constants of menadione in 25% (v/v) methanol-water and 20% (v/v) acetonitrile-water medium at 298K and at $\mu= 0.1M KNO_3$ are depicted in **Table 1**.

In menadione only one pK value is obtained. In protic solvents more dissociation takes place due to solvation process. In menadione two ketone groups are present and keto-enol tautomerism is possible. If enol form of menadione is considered, it is observed that only

one OH group gets dissociated. In the present ligand only one pK value is obtained at lower pH value.

The most important difference is that methanol is a protic solvent, while acetonitrile is aprotic. Because of the protic nature of methanol, negative ions (and lone pairs) are more strongly solvated in methanol than acetonitrile, meaning that the protonated (neutral) form of the vitamin should be favored in acetonitrile and the deprotonated form in methanol.

The pK value of menadione in 20% (v/v) acetonitrile-water is higher than 25% (v/v) methanol-water mixtures. In fact, the methanol solvent has a relatively lower polarity than water, so decreasing the polarity of solvent will lead to the increase of the bonding force between the ions with different charge. The lower pK value of menadione is explained on the basis of more electronegative oxygen atom attached to benzene ring having lone pair of electron, increases the electron density of other oxygen atom.

The effect of solvent is not only because of acidity or basicity but also because of its dielectric constant and its ability to solvate and stabilize certain in acid-base equilibria. Solvent having highest polarity or dielectric constant stabilizes the ionized species, higher will be the

pKa value and more stable will be in solution. The cis enol form predominates in solvents of low polarity. The intramolecular hydrogen bond formed in the cis enol form is more pronounced. Therefore the second pK is not observed in menadione. The metal-ligand stability constant values determined are in good agreement with Sahadev et al^{14,15}.

The metal ligand formation curve data for menadione in 25% (v/v) methanol-water and 20% (v/v) acetonitrile-water medium with transition metals indicates that the n values range between 0.2 to 0.8. This suggests that metal ions form 1:1 complexes¹⁵ with vitamin in solution. The log K values evaluated are in good agreement with Pfeiffer et al¹⁶.

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