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COMPARISON OF THE RATE OF REDUCTION OF DIFFERENT SPECIES OF IRON GALLIC ACID AND IRON GALLIC ACID METHYL ESTER WITH ASCORBATE

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The rate constants for reduction of iron gallic acid and iron gallic acid methyl ester by ascorbate were studied at different pH (4-5.6). These values were found to be greater in case of iron gallic acid as compared to iron gallic acid methyl ester. It was also observed that there are more than one species present in the solution at these pH. Therefore the individual rate constant for each species were determined by linear regression method or by solving simultaneous equations. The decrease in rate constant of ML and ML2 in iron gallic acid methyl ester was found to be of same magnitude as in MHL and ML2 of iron gallic acid.

Key words: Iron gallic acid, Gallic acid methyl ester, Ascorbate.

Introduction

The basic requirement of a biologically important iron chelator is a high and selective affinity to bind iron firmly under physiological conditions [1]. The tripositive ferric ion is a hard acid and consequently is bound most strongly by hard bases. The most effective of these are oxyanions, such as hydroxide, phenoxide, carboxylate, hydroxamate and phosphonate [2,3].

Charge neutralization is an important factor and is optimum when the total charge of the six donor atoms is -3, as for the bidentate hydroximate and tropolonate ligands [4].

Gallic acid is a simple model of catechol type siderophore forming highly stable and intensely coloured complexes with iron (III). The stoichiometry and the spectral properties vary with pH [5].

From the biological point of view bioavailability of iron is maximum when it is in the reduced or ferrous form. It has been reported that at pH 2 as well as at pH 5.5, Fe(II) is more easily absorbed as compared to Fe(III) [6].

Ascorbic acid which is a biological reducing agent enhances iron absorption both by reducing iron to the more soluble ferrous ion and by the formation of soluble iron ascorbate chelates [7].

Reduction of many Fe(III)-siderophore complexes with ascorbic acid has been studied, i.e. ferrichrome A, ferrichrome, ferrioxamine B, ferrioxamine E and tris aceto hydroxamate [8-10]. In this study reduction of complex of gallic acid and methyl ester of gallic acid has been undertaken with the objectives outlined above [11].

Experimental

All reagents used were A.R. grade and all the solutions were made with double deionized water. Acetate buffers were used to make the solution at different pH (from 4-5.6) [13].

The absorption peak of the complex at each pH were located by scanning the spectra of these solutions in the region of 3500-700 nm on Beckman Model 25 Spectrophotometer. The peaks were noted to select the λmax.

The kinetics of reduction of the complexes were followed at the wave length of maximum absorbance. The concentration of the complexes were in the range of 1×10^{-4} M. The reductant concentration were kept in excess (about 100-fold) and spanned as wide a range as experimentally possible. At least three reproducible kinetic runs were performed with each reductant solution. A minimum of 30 mins. was allowed to attain temperature equilibration of the working solutions. The reaction was carried out under pseudo 1st order conditions with reductant concentration taken in excess over the complex concentration.

Results and Discussion

The reduction of the complexes with ascorbate was found to be first order in the complex concentration as was evident from the linear plot of $\ln(A-A\infty)$ versus t. Observed rate constants (kobs) were determined for different concentrations of ascorbic acid at constant temperature. Plot of kobs vs [ascorbate] at a given pH and constant temperature were also linear. The method have been described elsewhere [13,14].

The reduction for iron gallic acid were performed at pH 4.2, 4.4, 4.6, 4.8, 5.2 and 5.4 and for iron gallic acid methyl ester at pH 4.0, 4.6, 5.0 and 5.6. A plot of kobs vs concentration of ascorbate was found to be linear with zero intercept (Figs. 1,2). The slope of this plot gave k (rate constant). (Table 1). This rate constant may be called $k_{1,2}$ because at this pH range [ML] and [ML2] species are dominant [15]. therefore $k_{1,2} = k_1[ML] + k_2[ML2]$, selected pH range is that one in which for iron gallic acid methyl ester ML, ML2 and ML3 are present

at different stages and for iron gallic acid ML and ML2. For this complex, below pH 5, MHL species is also present (Figs. 3,4).

$$Fe(III) + H_2GA \xrightarrow{pH4} [Fe(III)(H_2GA)]$$

$$[Fe(III)(H_2GA)] \longrightarrow [Fe(III)(HGA)] + H^+$$

$$[Fe(III)(HGA)] + HGA \xrightarrow{pH6} [Fe(III)(HGA)_2]$$

$$[Fe(III)(HGA)_2] + HGA \xrightarrow{pH8} [Fe(III)(HGA)_3]$$

therefore at pH 4 k_{obs} may be called as k1, 11 and

$$k1,11 = (k1 + k11K[H])[ML]$$

$$= \frac{k1 + k11K[H]}{1 + K[H]}$$

or k1, 11 (1+K[H]) = k1 + k11 K[H]

The graph between k1, 11 (1+K[H]) and K[H] gave the slope equal to k11 and intercept equal to k1 (Fig. 5).

At those pH's where only ML and ML2 are present the following equation is used

$$k1,2/[ML2] = k1 \frac{[ML]}{[ML2]} + k2$$

and the graph was drawn between k1,2/[ML2] and [ML]/[ML2] with the slope equal to k1 and intercept equal to k2. (Fig. 6). From this graph it was found that k1 for iron gallic acid

TABLE 1. RATE CONSTANT OF COMPLEXES AT DIFFERENT pH.

pH	Fe(GA)	Fe(GAME)
4.0	—	0.95
4.2	40	—
4.4	36	—
4.6	30	0.013
4.8	22	—
5.0	10	0.0127
5.2	8	—
5.4	6	—
5.6	4	0.0126

TABLE 2. RATE CONSTANTS OF DIFFERENT SPECIES OF THE COMPLEXES.

	Fe (GA)	Fe(GAME)
K11	90	—
K1	13	0.09
K2	4	0.004
K3	—	0.0038

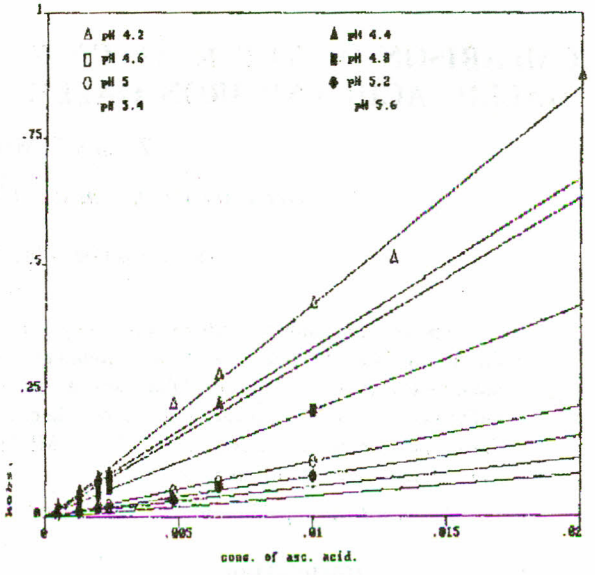

Fig. 1. Reduction of FeGA at different pH by ascorbate.

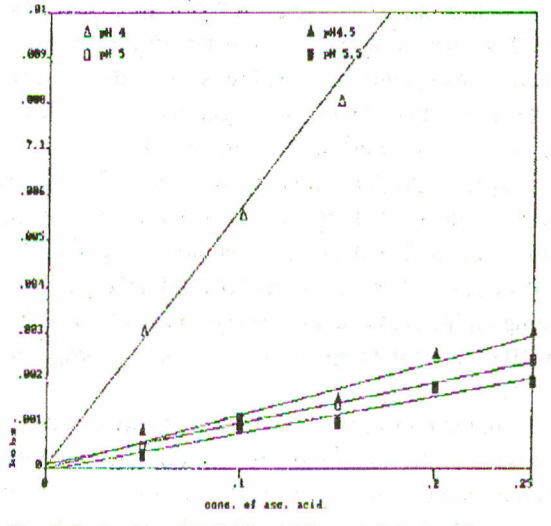

Fig. 2. Reduction of FeGAE at different pH by ascorbate

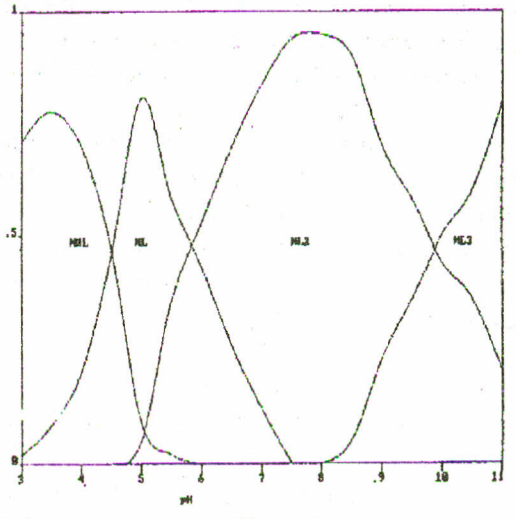

Fig. 3. Species distribution at different pH by computer program best.

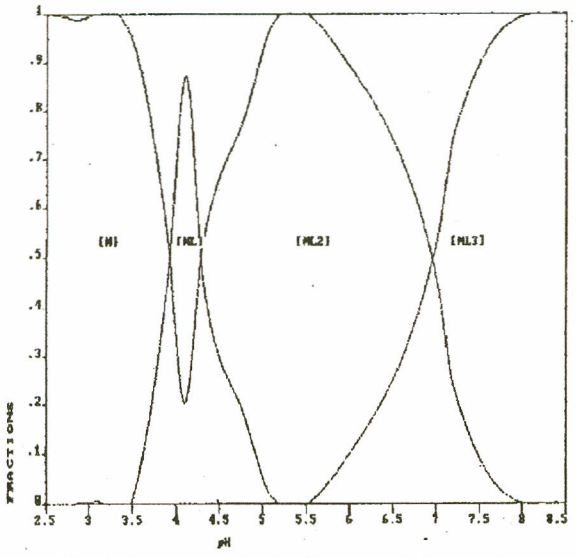

Fig. 4. Bjerrum species distribution at different pH

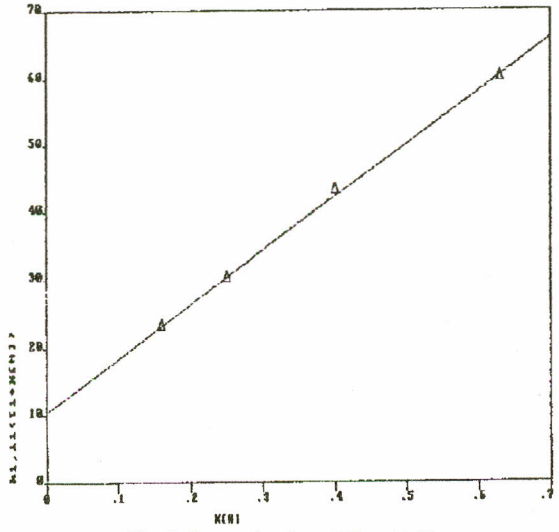

Fig. 5. Determination of kI and kII.

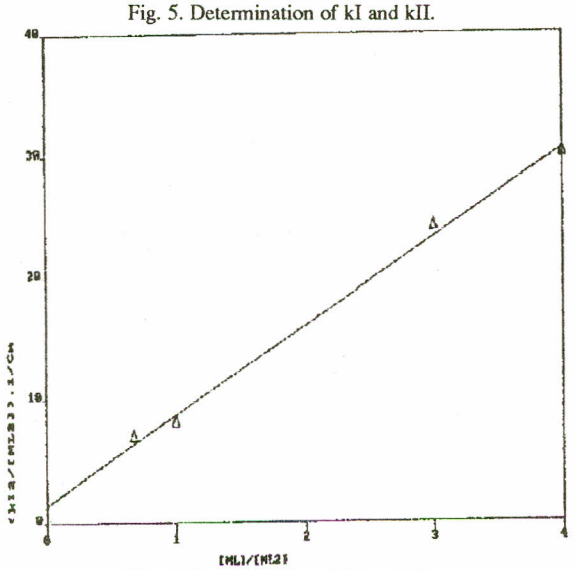

Fig. 6. Determination of k1 and k2.

is 13 ± 1.5 while k2 is about 4 ± 0.5 and for gallic acid methyl ester. It is .09 ± .01 and .04 ± .0006. k3 of this complex was found to be equal to k2. It shows that the hindrance in electron transfer due to geometry is same in both cases. 1:1 complex has four free corners for ascorbate to approach, which is not in 1:2 and 1:3 k11 of iron gallic acid was calculated the value found to be 90 (Table 2).

It may as concluded that reduction of iron gallic acid complex was much faster than that of its methyl ester analog.

Another interesting observation was that, the k11 of iron gallic acid is 22 times greater than k2 of iron gallic acid , while the reduction of 1:1 methyl gallic acid ester complexes is also 22 times faster than 1:2 complex of iron methyl gallic acid ester. So the decrease in rate of reduction from 1:1 to 1:2 is perhaps due to the complexation and the change in geometry of the complex.

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