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Kinetic Studies of the Oxidation of L-Ascorbic Acid by Tris(Oxalate)Cobaltate in the Presence of CDTA Metal Ion Complexes

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Realizaram-se estudos cinéticos envolvendo a reação de redução de tris(oxalato)cobalto por L-ácido ascórbico, em diferentes valores de pH. A variação da concentração do complexo de Co(III) foi acompanhada pela absorbância em 600 nm, em condições de pseudo-primeira ordem: $[H_2A] = 3,0 \times 10^{-2}$ mol L^{-1}, $[Co(C_2O_4)_3]^{3-} = 3,0 \times 10^{-3}$ mol L^{-1}, na presença de CDTA ($3,0 \times 10^{-3}$ mol L^{-1}), em I = 1,0 mol L^{-1} (NaCl) e a 25,0±0,1 ºC. Foram investigadas as atividades catalíticas dos complexos de CDTA com Fe(III), Ni(II), Cu(II), Cr(III) e Mn(II). Para Fe(III)/CDTA, o melhor catalisador, os valores de constantes de velocidade observada de pseudo-primeira ordem foram proporcionais à concentração de ferro $(1-10) \times 10^{-5}$ mol L^{-1}.

It was investigated the kinetic of the reduction reaction of tris(oxalate)cobaltate by L-ascorbic acid, H_2A, at different acidity. The Co(III) complex was monitored at 600 nm, under pseudo-first-order conditions: $[H_2A] = 3.0 \times 10^{-2}$ mol L^{-1}, $[Co(C_2O_4)_3]^{3-} = 3.0 \times 10^{-3}$ mol L^{-1}, in the presence of CDTA (3.0×10^{-3} mol L^{-1}) and ionic strength 1.0 mol L^{-1}, (NaCl) at 25.0±0.1 ºC. The catalytic activity of CDTA metal ion complexes of Fe(III), Ni(II), Cu(II), Cr(III) and Mn(II) was also examined. The pseudo-first-order rate constant was proportional to the concentration of Fe(III)/CDTA, which is the best catalyst, in the range of $(1-10) \times 10^{-5}$ mol L^{-1}.

Keywords: ascorbic acid, tris(oxalate)cobaltate(III), CDTA, iron(III), kinetic study

Introduction

The redox reactions of L-ascorbic acid are of fundamental interest in chemistry, biochemistry, pharmacology and several areas of medicine, since it is necessary in human diet in order to synthesize collagen and epinephrine, besides preventing scurvy. L-Ascorbic acid, H_2A, has two acid protons ($pK_1 = 4.04$ and $pK_2 = 11.34$), and is a strong reducing agent (E^0 $D/H_2A = 0.390$ V *vs.* N.H.E.) in aqueous solution. This reduction potential depends on the medium acidity, and in some cases the HA^-, $HA^\bullet$, $A^{-\bullet}$ radicals may be formed as intermediate species.[1-4]

Redox studies of L-ascorbic acid by various metal ion complexes have proposed the formation of a protonated ascorbate free radicals as $H_2A^{+\bullet}$ or $HA^\bullet$ but not the radical $A^{-\bullet}$ in the rate-determining step.[3-9]

The oxidation studies of L-ascorbic acid by $[Co(C_2O_4)_3]^{3-}$ were already performed in basic and acid aqueous solutions, and it was pointed out that the redox process in acidic medium ($3.2 < pH < 4.7$) produced L-dehydroascorbic acid, D (equation 1). L-dehydroascorbic acid, D, also includes the hydration and cyclization of D form, with formation of the bicyclic-L-dehydro species.[8,9] These studies indicated an outer-sphere electron-transfer process and no evidence of stable intermediate species formation.

$$H_2A + 2\,[Co^{III}(C_2O_4)_3]^{3-} \longrightarrow D + 2\,H^+ + 2\,[Co^{II}(C_2O_4)_3]^{4-} \quad (1)$$

The redox reaction rate demonstrates a strong dependency on the pH and the oxidation of A^{2-} showed to be faster than HA^- or H_2A.[8,9]

It was found that iron(III) catalyzes the oxidation of L-ascorbic acid by dissolved oxygen, hydrogen peroxide, peroxide-bound chromium and $[Co(C_2O_4)_3]^{3-}$ in presence of EDTA.[10-14] This last study, performed in universal buffer medium, led to a linear relationship between the observed pseudo-first order constant and the iron(III)/EDTA complex concentration.[14]

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The catalytic effect of iron(III)/EDTA could be explained by the much faster reactions of iron(III)/EDTA, rather than $[Co(C_2O_4)_3]^{3-}$, with L-ascorbic acid.[14] The rate constants for the reduction of several iron(III)/complexes and $[Co(C_2O_4)_3]^{3-}$ by L-ascorbic acid are reported in the literature and showed the strong influence of acidity and also the effect of the ligand, L, coordinated to Fe(III) (L = H_2O, phen, EDTA, bipy, $C_2O_4^{2-}$).[5,6,8-10,14-17]

The reaction of Fe(II) with $[Co(C_2O_4)_3]^{3-}$, which was investigated by some authors, has also to be considered. By keeping $[Co(C_2O_4)_3]^{3-}$ at 5×10^{-2} mol L^{-1}, which is about ten times over iron(II) concentration, the k_{obs} value obtained for the redox reaction was 9.49 s^{-1} and k = 190 mol^{-1} L s^{-1}.[18-20]

In this work the catalytic effect of iron(III) on the oxidation of L-ascorbic acid by $[Co(C_2O_4)_3]^{3-}$ was studied in the presence of polyaminocarboxylic acid, CDTA (pK_1 = 2.42; pK_2 = 3.54; pK_3 = 5.84 and pK_4 = 9.22), in a universal buffer solution over a large pH region. This study provides information to improve an analytical method for iron(III) at pH = 7.0.[14,17] For comparative studies, the catalytic effect of others transitions metal ions such as: Ni(II), Cu(II), Cr(III) and Mn(II) was also investigated.

Experimental

Reagents and solutions

All reagents used were from AR or CP specification and all solutions were prepared using deionised water obtained from a Nanopure System. Sodium chloride (Merck), stock solution (2.0 mol L^{-1}), was prepared without further purification or standardization. Sodium hydroxide (Aldrich), 1.768 mol L^{-1} was standardized with potassium hydrogenphthalate.[21]

CDTA, trans-1,2-cyclohexyletilenedinitrilotetraacetic acid, $C_{14}H_{22}N_2O_8 \cdot H_2O$ (Merck), stock solution (1.5×10^{-2} mol L^{-1}, pH = 5.8) was prepared by dissolution in NaOH standard solution (pH= 5.8).

Phosphoric, acetic and boric acids (Merck) 1.80 mol L^{-1} stock solutions were diluted to 0.180 mol L^{-1} and then standardized with NaOH solution (0.1768 mol L^{-1}).

Iron(III) perchlorate (Aldrich) stock solution (6.0×10^{-2} mol L^{-1}) was standardized by complexometric method with EDTA.[21] The potassium tris(oxalate) cobaltate(III) salt was prepared as described elsewhere.[22] It was dissolved in buffer solution just before use in order to get a solution 6.0×10^{-3} mol L^{-1}. L-Ascorbic acid (Merck), L-$C_6H_8O_6$, was also dissolved in buffer solution, just before use, in order to obtain a solution 6.0×10^{-2} mol L^{-1}.

Working solutions and spectrophotometric measurements

Several universal buffers solutions were prepared containing H_3PO_4, H_3C-COOH and H_3BO_3 (0.18 mol L^{-1} of each). NaOH 1.768 mol L^{-1} standard solution was used to adjust the pH of the buffers solutions from 3 to 8.[23] NaCl 2.0 mol L^{-1} solution was use to make up the ionic strength 1.0 mol L^{-1} in all working solutions.

The working solutions were prepared by mixing equal volumes of the of L-$C_6H_8O_6$ 6.0×10^{-2} mol L^{-1} and $[Co(C_2O_4)_3]^{3-}$ 6.0×10^{-3} mol L^{-1} solutions containing CDTA 6.0×10^{-3} mol L^{-1}. In the catalytic studies iron(III) was added as Fe(III)/CDTA in the L-$C_6H_8O_6$ solution just before mixing, once Fe(III) is reduced by L-$C_6H_8O_6$.

The final solutions concentration of $[Co(C_2O_4)_3]^{3-}$, CDTA, L-$C_6H_8O_6$ and Fe(III)/CDTA, after mixture, were 3.0×10^{-3}, 3.0×10^{-3}, 3.0×10^{-2} and $(1-10) \times 10^{-5}$ mol L^{-1}, respectively.

A glass electrode, combined with an Ag/AgCl reference electrode, Metrohm AG Herisau, filled with 3.0 mol L^{-1} NaCl and a 654 pHMeter Metrohm instrument were used in the pH measurements at (25.0 ± 0.1) ℃.

Spectrophotometric measurements were performed in a Hewlett Packard 8452A diode-array spectrophotometer using a thermostated Tanden cell (optical path length = 0.875 cm).

Results and Discussion

Data treatment

The redox reaction was followed spectrophotometrically at 600 nm where the major absorbing species is the complex $[Co(C_2O_4)_3]^{3-}$ (molar absorptivity of 150 ± 10 mol^{-1} L cm^{-1}).[14]

A ten times excess of L-$C_6H_8O_6$ over $[Co(C_2O_4)_3]^{3-}$ was kept in all experiments in order to have pseudo first order conditions. As the reaction was not affected by dissolved oxygen it was not necessary to eliminate the dissolved air before the kinetic runs.

The kinetic curves were analysed with the OLIS KINFIT set of programs. All the observed rate constants values presented in this work are the mean of at least three determinations and have an average error smaller than 5%.[24]

The pH influence on the uncatalysed reaction

The variation of $[Co(C_2O_4)_3]^{3-}$ concentration with time from the reduction by L-$C_6H_8O_6$, in the absence of any CDTA metal ion complexes showed a pseudo-first-order behaviour.

These experiments were carried out over a large pH range in universal buffer solution containing CDTA, which was added to avoid precipitation of cobalt(II) and cobalt(III) oxalate at high pH. No experiments at pH lower than 3.0 were carried out, due to the $[Co(C_2O_4)_3]^{3-}$ decomposition and precipitation of CDTA.[25,26]

The dependence of k_{obs} with pH (Figure 1) suggests that the H_2A specie is much less reactive than the HA^- species. In the $6.0 < pH < 7.5$ range, where HA^- is the predominant species, the k_{obs} value is almost constant. It was observed that at pH higher than 10 the oxidised species, D, decomposes rapidly.[1,4,14]
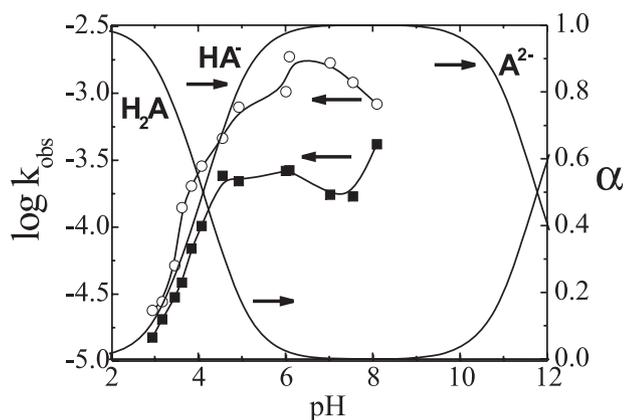
Figure 1. The diagram distribution (α *vs.* pH) for L-$C_6H_8O_6$ and the variation of k_{obs} in function of acidity (log k_{obs} *vs.* pH) for redox reaction between L-$C_6H_8O_6$ and $[Co(C_2O_4)_3]^{3-}$ without (■) and with [Fe(III)/CDTA] = $1.0x10^{-5}$ mol L^{-1} as catalyst (○). [L-$C_6H_8O_6$] = $3.0x10^{-2}$ mol L^{-1}; $[Co(C_2O_4)_3]^{3-}$ = $3.0x10^{-3}$ mol L^{-1}; [CDTA] = $3.0x10^{-3}$ mol L^{-1}; ionic strength = 1.0 mol L^{-1} kept with NaCl in universal buffer (25.0±0.1) °C.

The sequence of reactions represented below, may describe the mechanism.[8,9,14]

$$H_2A \rightleftharpoons HA^- + H^+ \qquad pK_1 = 4.04 \qquad (2)$$

$$HA^- \rightleftharpoons A^{2-} + H^+ \qquad pK_2 = 11.34 \qquad (3)$$

$$H_2A + [Co(C_2O_4)_3]^{3-} \longrightarrow H_2A^{+\bullet} + Co^{2+} + 3\ C_2O_4^{2-} \quad k_a \quad (4)$$

$$HA^- + [Co(C_2O_4)_3]^{3-} \longrightarrow HA\bullet + Co^{2+} + 3\ C_2O_4^{2-} \quad k_b \quad (5)$$

$$A^{2-} + [Co(C_2O_4)_3]^{3-} \longrightarrow A^{-\bullet} + [Co(C_2O_4)_3]^{4-} \quad k_c \quad (6)$$

$$H_2A^{+\bullet}/HA^\bullet/A^{-\bullet} + [Co(C_2O_4)_3]^{3-} \longrightarrow D + [Co(C_2O_4)_3]^{4-} + 2\ H^+$$
$$\textit{fast} \quad (7)$$
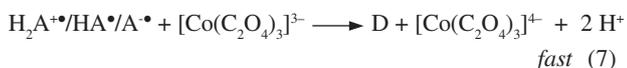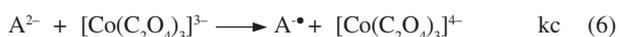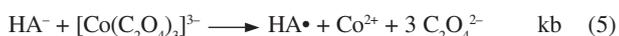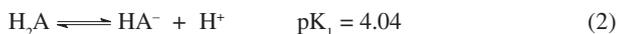
The reduction rate of the tris(oxalate)cobaltate(III) complex concentration is given by the rate law described in equation 8. Using the experimental data obtained at pH range from 3 to 5 the rate law under pseudo-first-order conditions can be written by equation 9, which results in

equation 10 (in all equations C_{H_2A} is the total concentration of ascorbic acid).

$$\frac{d[Co(C_2O_4)_3^{3-}]}{dt} = 2\left\{ k_a[H_2A] + k_b[HA^-] + k_c[A^{2-}] \right\}\left[Co(C_2O_4)_3^{3-} \right] \quad (8)$$

In this pH range the contribution A^{2-} is very small (see Figure 1) and the term $k_c[A^{2-}]$ can be ignored.

$$\frac{d[Co(C_2O_4)_3^{3-}]}{dt} = 2\left\{ \frac{k_a[H^+] + k_b K_1}{[H^+] + K_1} \right\} C_{H_2A}\left[Co(C_2O_4)_3^{3-} \right] \quad (9)$$

$$k_{obs} = \frac{2k_a[H^+] + 2k_b K_1}{[H^+] + K_1} \cdot C_{H_2A} \quad (10)$$

By working under limiting conditions, such as k_a is much smaller than k_b because H_2A (equation 4) reacts much slower than HA^- (equation 5), the term $2k_a[H^+]$ can be neglected and the equation 10 can be represented as equation 11, as follows:

$$\frac{1}{k_{obs}} = \frac{[H^+]}{2k_b K_1 C_{H_2A}} + \frac{1}{2k_b C_{H_2A}} \quad (11)$$

Taking the equation 11, in the pH region from 3 to 5, a plot of $1/k_{obs}$ *vs.* $[H^+]$ provides a linear relationship and from the slope and intercept the values of k_b and K_1 can be, respectively, obtained (Figure 2). The least squares regression (Y= 5465 + 6.382x10^6 X, r = 0.97) showed some dispersion of the experimental data in spite of the k_{obs} values have been obtained with the average error smaller than 5%. The values found were k_b = (3.2 ± 1.5) x10^{-3} mol^{-1} L s^{-1} and K_1 = (0.83 ± 0.09) x 10^{-4} mol L^{-1} and the order of magnitude of these data is in good agreement with the literature: k_b = 4.1x10^{-3} mol^{-1} L s^{-1}, K_1 = 1.12x10^{-4} mol L^{-1}, k_b = 7.0x10^{-3} mol^{-1} L s^{-1} and K_1 = 0.71x10^{-4} mol L^{-1}.[9,14]
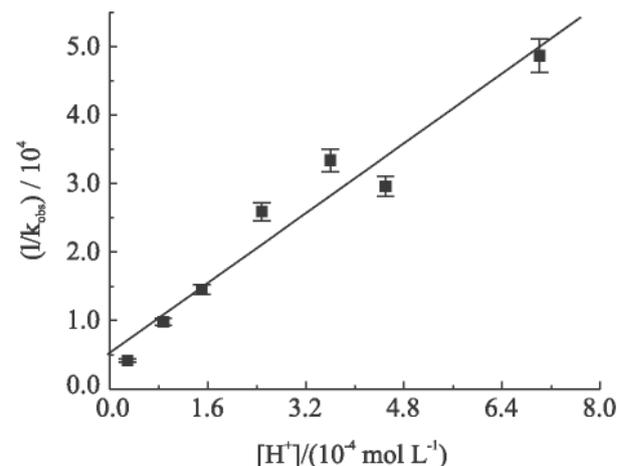

Figure 2. Determination of k_b considering the equation (11). K_1 and the k_{obs} calculated in the range of pH 3-5.

By using the experimental data, which were obtained in the pH range from 6.0 to 8.0, the rate law can be described according to the following equations:

$$\frac{d[Co(C_2O_4)_3^{3-}]}{dt} = 2 k_c [A^{2-}][Co(C_2O_4)_3^{3-}] = 2 k_c \frac{K_2 \cdot C_{H_2A}}{[H^+]} [Co(C_2O_4)_3^{3-}] \quad (12)$$

$$k_{obs} = 2 k_c \frac{K_2 \, C_{H_2A}}{[H^+]} \quad (13)$$

Taking into account the second ionisation step for ascorbic acid $K_2 = 4.6 \times 10^{-12}$ mol L^{-1}, the $k_c = 8.5$ mol^{-1} L s^{-1} was obtained from the slope of the k_{obs} vs. 1/[H$^+$] plot. The k_c values found in the literature were 20 mol^{-1} L s^{-1} and 10.8 mol^{-1} L s^{-1}, in universal buffer solution and in ionic strength kept with NaClO$_4$ and NaCl, respectively.[8,14,23]

The iron(III) catalytic effect

The variation of the $[Co(C_2O_4)_3]^{3-}$ concentration by the reduction with L-$C_6H_8O_6$, in the presence of Fe(III)/CDTA complex, also revealed a pseudo-first-order rate behaviour. The observed rate constant is proportional to the Fe(III) concentration and dependent of the pH medium (Figures 1 and 3).

It can be also noted that at pH lower than 5.0, where H$_2$A and HA$^-$ species are present, the reaction is slower even in the presence of Fe(III).

The k_{obs} values depend linearly on the iron concentration (Figure 3). According to equation 14, where the intercept, k_{unc}, is k_{obs} for the uncatalysed reaction and the slope, k_{spe}, is the specific rate constant for iron(III)

Figure 3. Influence of iron(III) concentration on the k_{obs} values. [L-$C_6H_8O_6$] = 3.0×10^{-2} mol L^{-1}; [Co(C$_2$O$_4$)$_3$]$^{3-}$ = 3.0×10^{-3} mol L^{-1}; [CDTA] = 3.0×10^{-3} mol L^{-1}; ionic strength = 1.0 mol L^{-1} kept with NaCl in universal buffer (25.0±0.1) $^\circ$C. (■) = pH 7.5 and (○) = pH 5.0.

catalysed reaction. At pH = 5.0 it was obtained k_{unc} = 2.2×10^{-4} s^{-1} and k_{spe} = 24 mol^{-1} L s^{-1} but at pH = 7.5, k_{unc} and k_{spe} were found to be 3.2×10^{-4} s^{-1} and 93 mol^{-1} L s^{-1}, respectively (Figure 3). In similar studies with Fe(III)/EDTA, at pH 7.0, it was obtained k_{spe} = 145 mol^{-1} L s^{-1}and the k_{obs} and k_{spe} had maximum values, where HA$^-$ is the predominant species in solution.[14]

$$k_{obs} = k_{unc} + k_{spe} [Fe(III)] \quad (14)$$

Likewise Fe(III)/EDTA, when Fe(III)/CDTA is acting as a catalyst, the mechanism can be described by the sequence of reactions from 15 to 19, where the electron transfer reaction involving Fe(II) is much faster than the reaction of Co(III) complex with ascorbic acid, as it was described in the literature.[5,6,9,14-17]

$$Fe(III)/(CDTA) + HA^- \rightleftharpoons Fe(III)/(CDTA)(HA)^- \quad (15)$$

$$Fe(III)/(CDTA)(HA)^- \longrightarrow Fe(II)/(CDTA) + HA^\bullet \quad (16)$$

$$Fe(II)/(CDTA) + [Co(C_2O_4)_3]^{3-} \longrightarrow Fe(III)/(CDTA) + Co^{2+} + 3\,C_2O_4^{2-} \quad (17)$$

$$HA^\bullet + [Co(C_2O_4)_3]^{3-} \longrightarrow D + Co^{2+} + 3\,C_2O_4^{2-} \quad (18)$$

$$Fe(III)/(CDTA) + HA^\bullet \longrightarrow Fe(II)/CDTA + D + H^+ \quad (19)$$
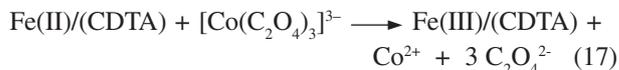
The catalytic effect of Fe(III)/CDTA (log β = 30.1, k_{spe} = 93 mol^{-1} L s^{-1}, pH = 7.5) is smaller than Fe(III)/EDTA (log β = 23.8, k_{spe} = 145 mol^{-1} L s^{-1}, pH = 7.5).[14,27] The Fe(III)/EDTA complex, which is seven coordinated with one coordination site occupied by a labile water molecule, will account for the efficient formation of a inner-sphere complex, represented by equation 15.[10,28] The catalyst activities order for Fe(III)/L (L = phen, bipy, H$_2$O, EDTA, CDTA) reaction with L-$C_6H_8O_6$ depends on the nature of ligand and is in agreement with the reduction potential values for the complexes involved.[5,6,9,14-17]

Influence of others transition metal ions

The catalytic effects of other CDTA metal ion complexes were also investigated. At pH = 7.5 (Universal buffer) the observed rate constant was 1.7×10^{-4} s^{-1} without catalyst ([Co(C$_2$O$_4$)$_3$]$^{3-}$, CDTA and L-$C_6H_8O_6$ were 3.0×10^{-3}, 3.0×10^{-3} and 3.0×10^{-2} mol L^{-1}, respectively). Cu(II)/CDTA (k_{obs} = 2.3×10^{-4} s^{-1}), Mn(II)/CDTA (k_{obs} = 2.4×10^{-4} s^{-1}) and Ni(II)/CDTA (k_{obs} = 2.4×10^{-4} s^{-1}) exhibit no significant catalytic effect. Cr(III)/CDTA showed some activity (k_{obs} = 3.8×10^{-4} s^{-1}) but ten times lower than the
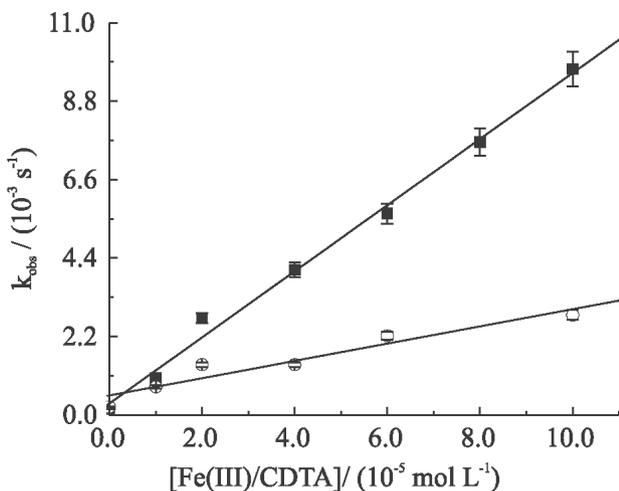
Fe(III)/CDTA (k_{obs} = 3.9x10^{-3} s^{-1}). For Cr(III)/CDTA it can be assume that Cr(III) is present as free ion due to the inertia in the Cr(III) complexes formation.

Conclusions

The reduction of iron(III) complexes and tris(oxalate) cobaltate by L-ascorbic acid depends on the pH and the nature of the ligand. Iron(III) complexes react much faster than [Co(C$_2$O$_4$)$_3$]$^{3-}$, which may explain the catalytic effect of iron(III) ion. Considering the dependence of k_{obs} with the pH, it was possible to calculate the rate constants of the reaction involving the species H$_2$A, HA$^-$ and A^{2-} (equations 4-6), the order of reactivity was H$_2$A < HA$^-$ < A^{2-}. The present studies showed that Fe(III)/CDTA increases the catalytic activity of iron(III). As suggested by the literature,[1-3] the addition of EDTA or CDTA to complex metal ions and stabilize ascorbic acid solutions from oxidation by oxygen may not work properly.

Acknowledgments

Supplementary Information

Supplementary data are available free of charge as PDF file at http://jbcs.sbq.org.br.

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