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THE INTERACTION OF 2-AMINO-2-HYDROXYMETHYL-1,3-PROPANEDIOL WITH COBALT(II) AND MANGANESE(II) IONS

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The stepwise complex formation between 2-amino-2-hydroxymethyl-1,3-propanediol (TRIS) with Co(II) and Mn(II) was studied by potentiometry at constant ionic strength 2.0 M (NaClO₄) and $T = (25.0 \pm 0.1)^\circ\text{C}$, from pH measurements. Data of average ligand number (Bjerrum's function) were obtained from such measurements followed by integration to obtain Leden's function, $F_0(L)$. Graphical treatment and matrix solution of simultaneous equations have shown two overall stability constants of mononuclear stepwise complexes for the Mn(II)/TRIS system ($\beta_1 = (5.04 \pm 0.02) \text{M}^{-1}$ and $\beta_2 = (5.4 \pm 0.5) \text{M}^{-2}$) and three for the Co(II)/TRIS system ($\beta_1 = (1.67 \pm 0.02) \times 10^2 \text{M}^{-1}$, $\beta_2 = (7.01 \pm 0.05) \times 10^3 \text{M}^{-2}$ and $\beta_3 = (2.4 \pm 0.4) \times 10^4 \text{M}^{-3}$). Slow spontaneous oxidation of Co(II) solutions by dissolved oxygen, accelerated by S(IV), occurs in a buffer solution TRIS/HTRIS⁺ 0.010/0.030 M, with a synergistic effect of Mn(II).

Keywords: Cobalt(II); manganese(II); TRIS; sulfite

INTRODUCTION

TRIS (2-amino-2-hydroxymethyl-1,3-propanediol) has been found to be an excellent stabilizer for S(IV) (SO_3^{2-} , HSO_3^- or SO_2 , according to the acidity) in solution, with some advantages to similar use with monoethanolamine.¹

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Some of our studies on the autoxidation of Co(II)/N₃⁻ and Co(II)/TRIS complexes, accelerated by S(IV) led to alternative methods for analytical determination of S(IV) in environmental analysis²⁻⁵ and determination of hydrolysis products of SF₄.⁶ The Co(II) complexes are slowly oxidized to Co(III) complexes. Mn(II) plays an important role in these processes by markedly accelerating the Co(III) formation.

These metal(III) ions, rapidly oxidize sulfite to SO₃^{•-} radical, which in turn initiates a series of free radical propagation reactions in which sulfite is oxidized by the dissolved oxygen to mainly sulfate.⁷⁻¹⁰

Studies of azide complex formation for several metal ions, such as Co(II),¹¹ Co(III),¹² Cu(II),¹³ Ni(II),¹⁴ Fe(III),¹⁵ U(VI),¹⁶ Mn(II),¹⁷ and Mn(III),¹⁸ have been done by our research group with special interest on determination of the stability constants which helped in elucidation of these mechanisms⁷⁻⁹ and for analysis.²⁻⁶

In the present work, a potentiometric study was performed on complex formation of TRIS with Mn(II) and Co(II). Determination of the stability constants of these complexes brought additional information about the distribution of complex species, according to the TRIS concentration, and more contributions to the elucidation of the synergistic effect of Mn(II).

EXPERIMENTAL

All reagents were from AR specification (Merck or Fluka Chemie A.G.). TRIS was used as a primary standard. Standard perchloric acid solution was used to prepare the TRIS/HTRIS⁺ buffers.

The manganese(II) and cobalt(II) perchlorate solutions were prepared by reaction of excess carbonate salts with 6.0 M perchloric acid. After filtering, a known amount of perchloric acid was added to avoid hydrolysis. The 1.0 M Mn(II) and Co(II) solutions were standardized by titration with EDTA¹⁹ and electrogravimetrically,¹⁹ respectively.

Sodium perchlorate solution, used for making up the ionic strength, was standardized by taking a small volume and dried in an oven at 120°C until constant weight.

A 0.05 M bisulfite stock solution was prepared by dissolving Na₂S₂O₅ in water previously purged with nitrogen. It was iodometrically standardized 24 h later by pipetting samples directly from the cold solution, in order to minimize oxidation or volatilization losses of SO₂. Nitrogen was always blown over the liquid surface for a few seconds when the stock flask was opened. Under such conditions, this standard solution is stable for 10 days

if maintained at 5°C. Diluted solutions, from the stock solution, were prepared daily before use.

Spectrophotometric Measurements

A Hewlett Packard 8452A diode array spectrophotometer and calibrated quartz cells of 1.0 cm optical pathlength were used for spectrophotometric measurements at 230 nm. All measurements were carried out at room temperature (about 25°C).

To 9.00 mL of solution containing TRIS and S(IV) in appropriated concentration, a 1 mL solution of Co(II), Mn(II) and HClO₄ were mixed by fast injection with an Eppendorf pipette.

In all figures the concentration of the final air saturated solutions just after mixing are indicated.

Potentiometric Measurements

A Metrohm 654 pH meter instrument connected to a glass electrode Metrohm AG Herisau combined with an Ag/AgCl reference electrode filled with NaCl 3.0 M, was used in the pH measurements at (25.0 ± 0.1)°C.

Calibration of the glass electrode was performed at 2.0 M ionic strength by titration with 0.01000 M HClO₄ in NaClO₄. The analysis of the linear plot of E vs. $-\log[H^+]$, from at least four titrations of the supporting electrode, led to an average working slope for the electrode. The estimated slope has been found to be about 1.4% higher than the theoretical value, 0.05916 V at 25°C.

The pH meter–electrode system was calibrated for hydrogen ion concentration, instead of activity, by using a buffer potassium phthalate 0.05 M solution (conditional pH = 3.826), at the same ionic strength (NaClO₄ 2.00 M) of the working solution. This conditional pH had been previously determined by comparison with one HClO₄ 0.01000 M solution at the same ionic strength.

The pH before and after the addition of Mn(II) or Co(II) to TRIS/HTRIS⁺ buffer, was followed potentiometrically.

Working Solutions

Several series of working solutions were prepared by adding small different volumes of 2.056 M Mn(ClO₄)₂ or 1.585 M Co(ClO₄)₂ solution to 10.0 mL of several TRIS/HTRIS⁺ buffer solutions in NaClO₄ to make up the ionic strength to 2.0 M. To each buffer solution, six different volumes of Mn(II)

or Co(II) solutions were added. The final solutions were $(5.00\text{--}30.0) \times 10^{-3}$ M for Co(II) or $(1.00\text{--}12.0) \times 10^{-2}$ M for Mn(II).

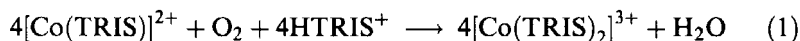
In order to keep such working solutions free from oxygen all metal ion and buffer solutions were bubbled with purified nitrogen just before mixing. During all measurements, N₂ flow was maintained at the surface of the working solutions.

All measurements were performed in a thermostated cell compartment $(25.0 \pm 0.1)^\circ\text{C}$.

RESULTS AND DISCUSSION

(a) Oxidation of Co(II)/TRIS Complexes by Dissolved Oxygen

The complexes of Co(II)/TRIS are easily oxidized by dissolved oxygen in a buffer TRIS/HTRIS⁺ (1). The Co(III)/TRIS complex formation can be followed by spectral changes at 230 nm.



The formation of Co(III) is strongly affected by the acidity and the TRIS/HTRIS⁺ concentrations.

Figure 1 shows that oxidation of Co(II)/TRIS complex, by the dissolved oxygen, is higher at higher TRIS and HTRIS⁺ concentrations (Figure 1, (a) and (b)) for the same pH.

The autoxidation of Co(II) complexes has been found to be markedly accelerated by the presence of S(IV) (Figure 1, (c)). Mn(II) ions accelerate the process (Figure 1, (d)) decreasing the induction period initially observed (Figure 1, (c)). This positive synergism is defined as an acceleration of the Co(II) catalyzed oxidation of sulfur(IV) oxides. It depends on the concentration ratio of the both metal ions and its catalytic activity. The transition metal ions act as individual catalysts which results in an oxidation rate that is not necessarily the sum of the individual rates.^{3,7,9,10}

The pH effect can be seen by comparing Figure 1, (d) and (e). At higher pH the oxidation is much more efficient.

The mechanism of the S(IV) induced autoxidation of Co(II) to Co(III) and simultaneous oxidation to S(IV), is based on radical formation as described elsewhere.⁸

Determination of the stability constants for Co(II) and Mn(II)/TRIS complexes brings additional information about the distribution of complex species, according to the TRIS concentration, and more contribution to the

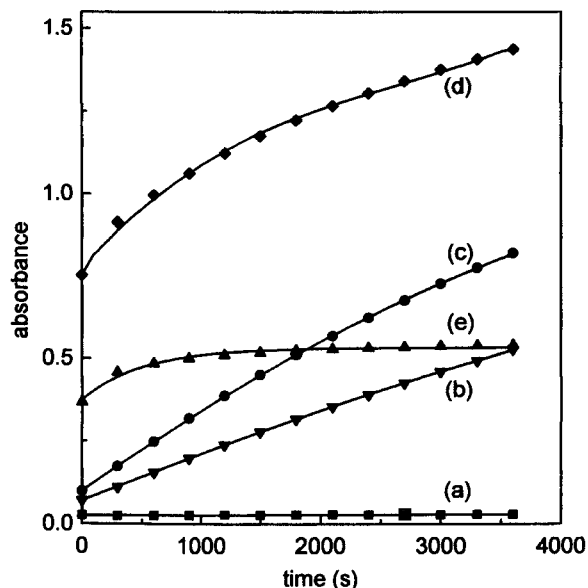


FIGURE 1 Absorbance changes at 230 nm due to Co(III)/TRIS complex formation as a function of S(IV) and Mn(II) addition. $[\text{Co(II)}] = 1.00 \times 10^{-3} \text{ M}$. (a) $[\text{TRIS}] = 5.00 \times 10^{-3}$, $[\text{HTRIS}^+] = 1.50 \times 10^{-2}$, $[\text{S(IV)}] = 0$, $[\text{Mn(II)}] = 0$. (b) $[\text{TRIS}] = 1.00 \times 10^{-2}$, $[\text{HTRIS}^+] = 3.00 \times 10^{-2}$, $[\text{S(IV)}] = 0$, $[\text{Mn(II)}] = 0$. (c) $[\text{TRIS}] = 1.00 \times 10^{-2}$, $[\text{HTRIS}^+] = 3.00 \times 10^{-2}$, $[\text{S(IV)}] = 1.00 \times 10^{-4}$, $[\text{Mn(II)}] = 0$. (d) $[\text{TRIS}] = 1.00 \times 10^{-2}$, $[\text{HTRIS}^+] = 3.00 \times 10^{-2}$, $[\text{S(IV)}] = 1.00 \times 10^{-4}$, $[\text{Mn(II)}] = 1.00 \times 10^{-3}$, $\text{pH} = 7.60$. (e) $[\text{TRIS}] = 5.00 \times 10^{-3}$, $[\text{HTRIS}^+] = 3.00 \times 10^{-2}$, $[\text{S(IV)}] = 1.00 \times 10^{-4}$, $[\text{Mn(II)}] = 1.00 \times 10^{-3}$, $\text{pH} = 7.15$. Optical length 1.0 cm, reference solution: buffer TRIS/HTRIS⁺. Concentrations are expressed as M.

elucidation of the synergistic effect of Mn(II), which still requires detailed kinetic study. The present paper is related to Ref. 5, where an alternative analytical method for S(IV) is described.

(b) Determination of the Stability Constants of Co(II) and Mn(II)/TRIS Complexes

The Henderson–Hasselbalch equation for buffer systems and mass balances was applied to the present system, where TRIS acts as both ligand for the metal cation and as a component of the buffer solution.²⁰

The experimental procedure to obtain \bar{n} data is based on a potentiometric titration (described in more detail in Ref. 17). Initially the conditional pH_1 was measured from TRIS/HTRIS⁺ buffer solution in NaClO₄ (ionic strength 2.0 M) which provides the equilibrium concentration of $[\text{TRIS}]_1$

and $[\text{HTRIS}^+]_1$. Subsequent addition of a volume of a metal cation solution, results in a new conditional equilibrium of pH_2 , $[\text{TRIS}]_2$ and $[\text{HTRIS}^+]_2$.

A conditional $\text{p}K_a$ of the HTRIS^+ , at ionic strength 2.00 M (NaClO_4) and $(25.0 \pm 0.1)^\circ\text{C}$, was determined. The use of $\text{p}K_a$, from each $\text{TRIS}/\text{HTRIS}^+$ buffer concentration, is a reliable procedure as it corrects any drift in junction potentials and eventual slope deviation of the glass electrode. The average $\text{p}K_a$ value of HTRIS^+ at this ionic strength was 8.4.

The average number of ligands, \bar{n} (Bjerrum's function) was obtained as described elsewhere.^{20,21}

Since the same curve of \bar{n} vs. $[\text{TRIS}]$ was obtained for six different Mn(II) and Co(II) concentrations (Figure 2), no significant polynuclear complexation is evident in these metal cations for the concentration range employed.

An appropriate computer program, elaborated in QuickBasic 4.50 – Microsoft, was used to obtain data of the Leden's function, $F_0(L)$,²⁰ by integration of the curve \bar{n} vs. $\log[\text{TRIS}]$ from several consecutive small increments of ligand concentration.²¹

The treatment of $F_0(L)$ data, to calculate the stability constants, was done by two different methods. The first one was the familiar graphical procedure, extrapolating the subsidiary $F_n(L)$ function to zero ligand concentration.²⁰ The graphical treatment has clearly shown the existence of two and

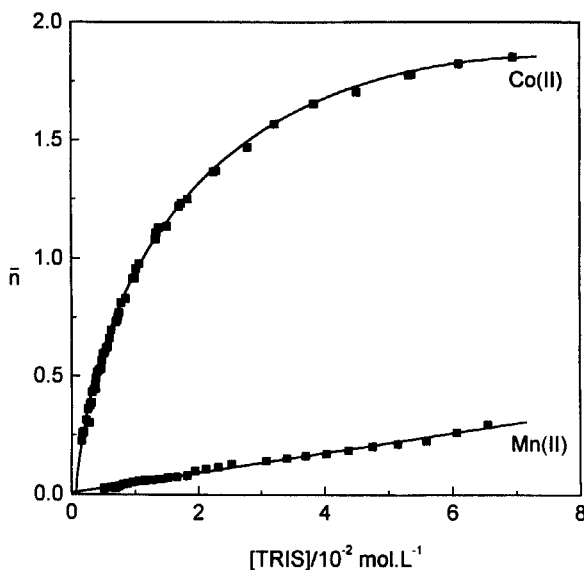


FIGURE 2 Formation curves for Mn(II) and $\text{Co(II)}/\text{TRIS}$ complexes.

three stepwise complexes for the Mn(II)/TRIS and Co(II)/TRIS system, respectively.

Computer methods of calculation, based on properly weighted simultaneous equations were also used for the final results.²¹ Both solutions gave very similar values, however, the best set of constants came from matrix calculations, by solving the system of equations.

The final result was Mn(II)/TRIS: $\beta_1 = (5.04 \pm 0.02) \text{M}^{-1}$ and $\beta_2 = (5.4 \pm 0.5) \text{M}^{-2}$ and Co(II)/TRIS: $\beta_1 = (1.67 \pm 0.02) \times 10^2 \text{M}^{-1}$, $\beta_2 = (7.01 \pm 0.05) \times 10^3 \text{M}^{-2}$ and $\beta_3 = (2.4 \pm 0.4) \times 10^4 \text{M}^{-3}$. Figures 3 and 4 show the distribution diagrams.

As can be inferred from the values of the constants for the Co(II)/TRIS system, $\beta_1 < \beta_2 < \beta_3$, a larger entropic factor favors the initial steps. The linear relationship of $\log K$ vs. $(n - 1)$, found for the Co(II)/TRIS system, indicates that the magnitude of the free energy involved in complex formation decreases linearly for each ligand introduced. On this basis, no change of configuration has been found to occur, as happens in the Co(II)/SCN⁻ system,²² where a change from octahedral to tetrahedral is observed.

As already pointed out, because of the synergistic effect of the manganese(II) ions on the induced autoxidation of metal ions by S(IV), it is important to compare the formation curve of Co(II) and Mn(II) complexes.

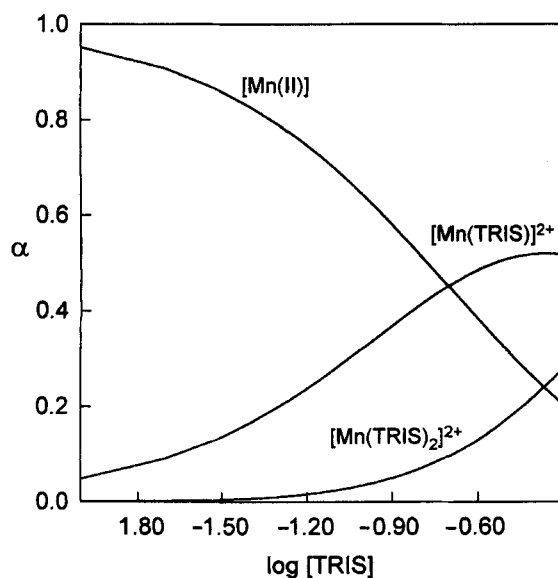


FIGURE 3 Distribution diagram of the species in the Mn(II)/TRIS system calculated from the equilibrium constants.

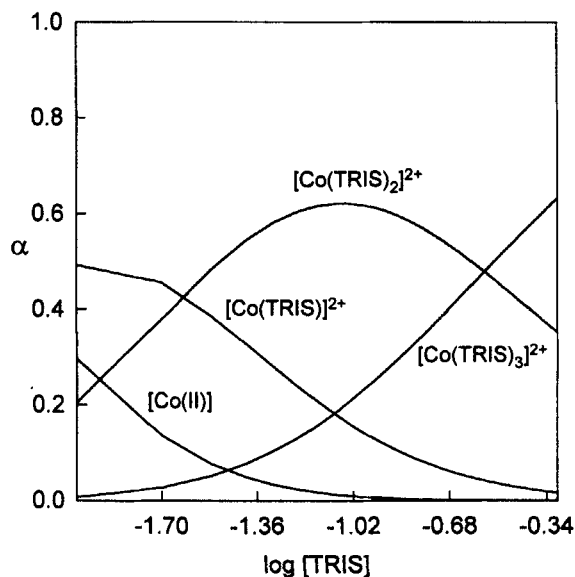


FIGURE 4 Distribution diagram of the species in the Co(II)/TRIS system calculated from the equilibrium constants.

It was found that the concentration 0.005/0.015 M [TRIS]/[HTRIS⁺] is the best experimental condition for analytical S(IV) determination.⁵ At this TRIS concentration the average numbers of ligands are 0.6 and 0.025 for Co(II) and Mn(II) complexes, respectively (Figure 2). The predominant species present is [Co(TRIS)]²⁺, while Mn(II) remains virtually uncomplexed, with a very small formation of [Mn(TRIS)]²⁺. As the Co(II)/SO₃²⁻ complexes²³ are fairly strong it is quite possible that sulfite could eventually displace the TRIS ligand.

Acknowledgments

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