Study on interactions in divalent ion complexes with L-tartaric acid and Cu(II) binary and ternary complexes

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ABSTRACT

The acidity and stability constants of M(TA) (TA:tartarate) and Cu(Phen)(TA) (Phen:1,10-phenanthroline) complexes, were determined by potentiometric pH titration. It is shown that the stability of the binary Cu(TA) and complexes is determined solely by the basicity of the carboxylate group. It is demonstrated that the equilibrium, $Cu(Phen)^{2+} + Cu(TA) \rightleftharpoons Cu(Phen)(TA) + Cu^{2+}$, is displacement due to the well known experience that mixed ligand complexes formed by a divalent 3d ion, a heteroaromatic N base and an O donor ligand possess increased stability. The other part of this displacement, which amount on average to an increased stability of the mixed ligand Cu(Phen)(TA) complexes of about 0.27 log unit. The stability constants of the 1:1 complexes formed between Cu^{2+} or $Cu(Phen)^{2+}$ and TA^{2-}, were determined by potentiometric pH titration in aqueous solution ($I = 0.1$ M, $NaNO_3$, 25°C). The order of the stability constants was reported.
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INTRODUCTION

The naturally occurring form of the acid is L(+)-tartaric acid (H_2TA) or dextrotartaric acid (Figure 1). Tartaric acid is found throughout nature, especially in many fruits and wine[1]. It is added to other foods to give a sour taste, and is used as an antioxidant. Salts of tartaric acid are known as tartarates. It is a dihydroxy derivative of dicarboxylic acid. Tartaric acid is a muscle toxin, which works by inhibiting the production of malic acid, and in high doses causes paralysis and death. The minimum recorded fatal doses for a human is 7.5 g/kg. In spite of that, it is included in many foods, especially sour-tasting sweets. As a food additive, tartaric acid is used as an antioxidant with E number E334, tartarates are other additives serving as antioxidants or emulsifiers. However, tartaric acid plays an important role chemically, lowering the pH of fermenting "must" to a level where many undesirable bacteria cannot live, acting as a preservative after fermentation[2]. Some researcher used identical methodology to show that antibodies also exhibited both stereoselective and stereospecific binding. To demonstrate this, they used sera derived form the separate immunizations of the three isomers of TA[2]. Tartaric acid in large doses is an unsafe agent, causing gastro-intestinal and death. Some researchers have measured the acidity and stability constants[3].

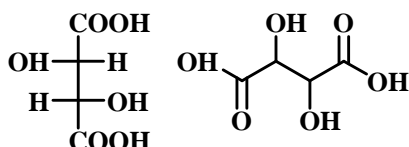**Figure 1 : Chemical structure of L-tartaric acid**

MATERIALS AND METHODS

Materials

Chemicals was purchased from Merck. Copper (II) nitrate trihydrate, sodium nitrate, potassium hydrogen phthalate and standard solutions of sodium hydroxide (titrisol), nitric acid, EDTA and of the buffer solutions of pH 4.0, 7.0 and 9.0 were from Merck. All the starting materials were pro analysis and used without further purification. Water was purified by Milil-Q water purification system, deionized and distillated.

pH titrations

Reagents: Carbonate-free sodium hydroxide 0.03 M was prepared and standardized against sodium hydrogen phthalate and a standard solution of nitric acid 0.5 mM. Copper (II) nitrate solution (0.03 M) was prepared by dissolving the above substance in water and was standardized with standard solution of EDTA 0.1 M (triplex).

Apparatus

All pH titrations was performed using a Metrohm 794 basic automatic titrator (Titrino), coupled with a Hero thermo stating bath at 25°C (±0.1°C) and a Metrohm combined glass electrode (Ag/AgCl). The pH meter was calibrated with Merck standard buffer solutions (4.0, 7.0 and 9.0).

Procedure

For the determination of acid dissociation constants of the ligand TA an aqueous solution (0.03 M) of the protonated ligand was titrated with 0.03 M NaOH at 25°C under nitrogen atmosphere and ionic strength of 0.1 M, $NaNO_3$. For the determination of binary (one ligand and Cu^{2+}) and ternary systems (Cu^{2+}, one of the other L ligand and TA), the ratios used were 1:1, 1:2 Cu(II) : Ligand and 1:1:1, Cu(II) : TA : Phen, 0.3 mM. This solution was titrated with 0.1 M NaOH under the same conditions mentioned above. Each titration was

repeated seven times in order to check the reproducibility of the data. The same experiments mentioned above carried out for other metal ions such as Co^{2+}, Mn^{2+}, and Zn^{2+}.

Calculation

The acid dissociation constants, $K_{H_2(TA)}^H$ and $K_{H(TA)}^H$ for $H_2(TA)$ were calculated by an algebraic method. The equilibrium involved in the formation of 1:1 complex of TA and a divalent metal ion may be expressed as equations (3) & (4).

RESULTS AND DISCUSSION

In this section we would discuss the resulted data.

Acidity constants

Tartarate (TA), $^-O_2CCH(OH)CH(OH)CO_2^-$, is a two-basic species and thus it can accept two protons, given $H_2(TA)$ for which the following deprotonation equilibria hold:

$$H_2(TA) \rightleftharpoons H^+ + H(TA)^- \tag{1a}$$

$$K_{H_2(TA)}^H = [H(TA)^-][H^+]/[H_2(TA)] \tag{1b}$$

$$H(TA)^- \rightleftharpoons H^+ + TA^{2-} \tag{2a}$$

$$K_{H(TA)}^H = [TA^{2-}][H^+]/[H(TA)^-] \tag{2b}$$

The two protons in $H_2(TA)$ are certainly bound at the terminal acetate groups, i.e., it is released from $HO_2CCH(OH)CH(OH)CO_2H$ according to equilibrium (1) & (2). These values are, as accepted, close to the pKa values of $H_3CCH(OH)CH(OH)CO_2H$ which is 4.7[4]. It is also closed to the deprotonation of acetate groups which occurs at the terminal acetate groups with TA.

Stability of binary and ternary complexes

If we abbreviate for simplicity Co^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+} and $Cu(Phen)^{2+}$ with M^{2+}, one may write the following two equilibriums (3) & (4):
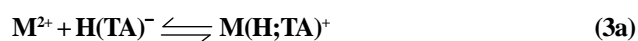
$$M^{2+} + H(TA)^- \rightleftharpoons M(H;TA)^+ \tag{3a}$$

$$K_{M(H;TA)}^M = [M(H;TA)^+]/[M^{2+}][H(TA)^-] \tag{3b}$$

$$M^{2+} + (TA)^{2-} \rightleftharpoons M(TA) \tag{4a}$$

$$K_{M(TA)}^M = [M(TA)]/[M^{2+}][TA^{2-}] \tag{4b}$$

The experimental data of the potentiometric pH ti-

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trations may be completely by considering the above mentioned equilibrium (1) through (4), if the evaluation is not carried into the pH range where hyrdoxo complex formation occurs.

The stability of ternary complexes may be evaluated by the following equlibrium:

$$mA + nB + qM + rH \rightleftharpoons A_mB_nM_qH_r \qquad (5a)$$

where M is the metal ion, H is the proton, A and B are the ligands. The global stability constant for the ternary complexes may be represented as following:

$$log\beta_{pqrs} = [A_mB_nM_qH_r]/[A]^m[B]^n[M]^q[H]^r \qquad (5b)$$

It is possible to define the stability constants for ternary complexes in relation to their binary ones[5], represented by the equilibrium (6) & (7).

$$M + L_1 \rightleftharpoons ML_1 \qquad (6a)$$

$$K^M_{M(L_1)} = [ML_1]/[M^{2+}][L_1] \qquad (6b)$$

$$ML_1 + L_2 \rightleftharpoons ML_1L_2 \qquad (7a)$$

$$K^M_{M(L_1L_2)} = [ML_1L_2]/[ML_1][L_2] \qquad (7b)$$

The difference between the stability constants of the ternary and binary complexes shows the tendency of the formation of ternary species[6]. This could be expected by Eq. (8):

$$\Delta log\ K = log\ K^{ML_1}_{M(L_1L_2)} - log\ K^M_{M(L_2)} \qquad (8)$$

$$= log\ K^{ML_2}_{M(L_1L_2)} - log\ K^M_{M(L_1)}$$

The difference between the constant refined from experimental data and those calculated statistically using Eq. (8) indicates the possibility of ligand-ligand interaction.

Potentiometric analyses

The model of species for this ternary system that was used in superquad program includes all the species of TABLE 1 as well as the hydrolysis of Cu^{2+}[7,8]. The stability constants of the binary complexes were refined separately using the titration data of this system in a 1:1 and 1:2 ligand:Cu^{2+} ratio in the same conditions of temperature and ionic strength. As they were in good agreement with reported value[9], they were fixed and, consequently, only ternary species were refined in ternary model of the species. The results are summarized in TABLE 1. The order of the resulted stability constants are $Mn^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$. The results show that

the stabilities of carboxyl-metal ion complexes in M(TA) do not strictly follow the Irving-Williams sequence[10-14]. Figure 2 shows Schematic structures of the species with interactions according to equilibrium (4) & (7) for Cu(Phen)(TA). The results of the acidity constants show good agreement with reported values[3,9]. The reported stability constant of Cu(TA) complex is similar to our results (TABLE 1). The difference between stability constants according eq. (8) show that mixed ligand complexes formed by a divalent 3d ion, a heteroaromatic N base and an O donor ligand possess increased stability.

TABLE 1 : Logarithm of the stability constants of binary and ternary complexes of M^{2+} at 25°C, 0.1 M, NaNO₃*.

	$pK^H_{H_2(TA)} = 3.09 \pm 0.07$		$pK^H_{H(TA)} = 4.19 \pm 0.05$	
No.	Species	logK^a	Δlog K^b	Ref.
1	Mn^{2+}	4.08±0.08		-
2	Co^{2+}	3.27±0.08		-
3	Zn^{2+}	2.69±0.07		[3]
4	Cu^{2+}	3.65±0.07		[3]
5	$Cu(Phen)^{2+}$	3.92±0.08	0.27±0.13	-

*The given errors are three times the standard error of the mean value or the sum of the propabable systematic errors. ^{a}according eq. (4). ^{b}according eq. (8).
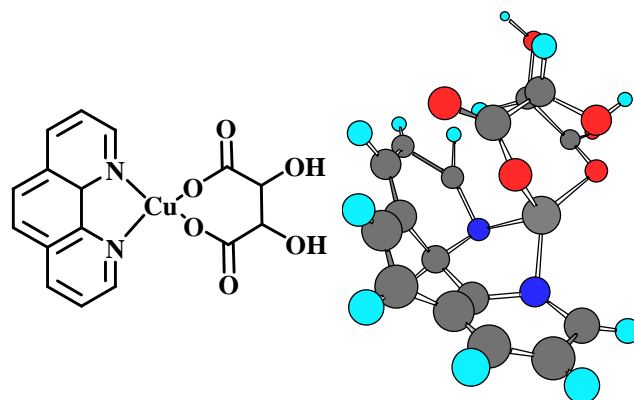

Figure 2 : Schematic structures of the species with interactions according to equilibrium (4) & (7) for Cu(Phen)(TA). The structure in the right part of the figure was drawn with the program CS Chem 3D, version 3.5, from Cambridge Software Corporation.

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