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THE POTENTIOMETRIC STUDY OF Co(II) COMPLEXES WITH MERCAPTOCARBOXYLIC ACIDS*

The interaction between Co(II) ions and thiolactic acid TLA or thioglycolic acid TGA in aqueous 0.1 M $NaClO_4$ has been studied potentiometrically at 20°. The formation of complexes of the type Co(SRCOO) and $Co(SRCOO)_2^{2-}$ (where R = CH_2 or CH_3CH) has been found. The stability constants of these complexes have been determined as well as the acid dissociation constants of TLA and TGA.

Thiolactic acid and thioglycolic acid, belong to a physiologically important class of compounds. As they behave as strong complexing agents, it seemed to be interesting to comparise the stabilities of Co(II) complexes with these acids.

Experimental

Stock solution were prepared from reagent grade chemicals. Merck TGA and Fluka TLA were purified by vacuum distillation. Approximately 0.1 M solutions of them were prepared by diluting a known weight of the distilled acids with air-free water. These solutions were standarised by alkalimetric titration using potentiometric and-point detection.

A cobaltous perchlorate solution, approximately 1.00 M was prepared by dissolving a weighed amount of cobaltous carbonate in a known volume of standard perchloric acid and diluting obtained solution with a water. The solution was standarized using desodium dihydrogen etylendiaminetetraacetate (EDTA).

A 0.100 M potassium hydroxide solution was prepared from

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Polish Chemical Reagents Concentrated Volumetric Solution. The solution was found to contain less than 0.2% carbonate by potentiometric titration.

The ionisation and stability constants were determined using the pH-titration method [1]. The pH of all solutions was measured with a Precision Digital Radelkis pH-meter. A glass electrode of 0-14 pH range calibrated frequently against buffers of different pH-values was used in conjunction with saturated calomel electrode. Potentiometric titrations were performed under nitrogen in a water-jacketed beaker, and the temperature of the solution was kept constant 20 ± 0.2°C during the titrations and it was controled by an electrically maintained thermostat (UT-1 type German). Effective stirring was obtained with a magnetic stirrer. All the pH-titrations were carried out in medium composed of 0.1 M $NaClO_4$, with the standard 0.100 M potassium hydroxide.

The ionisation constants of TGA and TLA were determined by titrating TGA and TLA solutions. The titration curves were drawn, from which the dissociation constants were calculated using the Bjerrum's method.

The experimental procedure used to determine stoichiometry of the reactions between Co(II) and TGA or TLA as well as determining of stability constants of the complexes formed, consisted in performing of series pH-titrations TGA and TLA solutions, in absence or presence of Co^{2+} ions at various ligand to metal ratios.

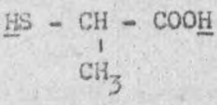
The stability constants were calculated using Calvin and Melchior's method [2].

Results and discussion

Both TGA (I) and TLA (II) have two replacable hydrogen ions as stressed in the formulae below:

$\underline{H}S - CH_2 - COO\underline{H}$

(I)



$$\underline{H}S - \underset{\displaystyle CH_3}{\underset{|}{CH}} - COO\underline{H}$$

(II)

The equilibrias involved are:

$$H_2A = HA^- + H^+; \qquad K_1 = \frac{[H^+][HA^-]}{[H_2A]}$$

$$HA^- = A^{2-} + H^+; \qquad K_2 = \frac{[H^+][A^{2-}]}{[HA^-]}$$

where H_2A represents the TGA or TLA.

It is obvious, that K_1 and K_2 correspond to dissociation of carboxylic and sulphydryl group, resp.

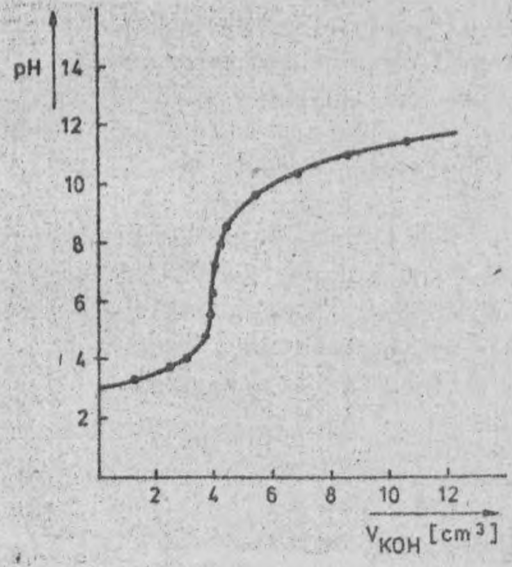


Fig. 1. Potentiometric titration of $4.3 \cdot 10^{-4}$ M TGA with 0.1 M KOH

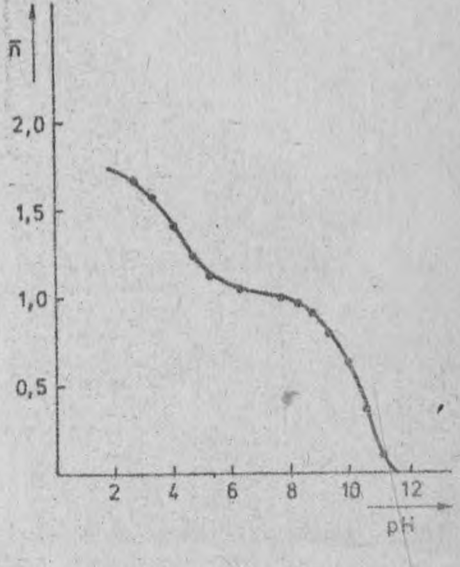


Fig. 2. Plot of $\bar{n}$ as a function of pH for titration of $4.3 \cdot 10^{-4}$ M TGA with 0.1 M KOH

The absence of inflecion after adding two moles of base (Fig. 1), indicates that the proton of sulphydryl group is not titratable under the experimental conditions.

The curve for titration of $4.5 \cdot 10^{-4}$ M TLA with 0.1 M KOH was analogous.

pK_1 values have been found (from Fig. 2) to be 3.25 and 3.63, pK_2 values as 10.35 and 9.85 for TGA and TLA resp.

The stoichiometry of complex formations were determined from titration curves in the presence of the Co^{2+} ions (Fig. 3). There is no indication of complex formation during the titration of carboxylic hydrogen of TLA ov TGA (the curves for TLA were analogous). Strong complex formation was evident during the titration of the mercaptan hydrogen.

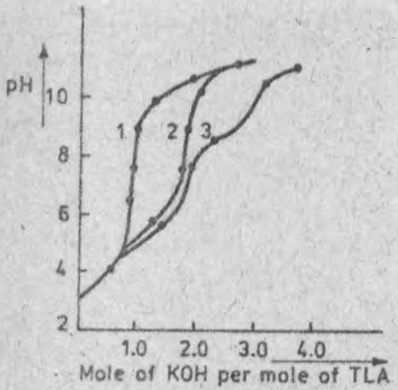


Fig. 3. Potentiometric titrations of 10^{-3} M TLA (curve 1), 10^{-3} M TLA + 10^{-3} M $Co(ClO_4)_2$ (curve 2), and 10^{-3} M TLA + + $5 \cdot 10^{-4}$ M $Co(ClO_4)_2$ (curve 3)

The addition equimolar of Co^{2+} greatly alters the shape of free ligand titration curves as a result of complex formation (curve 2 on Fig. 3).

The reaction between 'a' interval of 0-1 may be represented by the equotion:

$$H_2A + OH^- = HA^- + H_2O \qquad (1)$$

Two inflections have apeared at 2 and 3 moles of KOH per mole of acid. The inflection at a = 2 suggests the formation of CoA according to equotion:

$$Co^{2+} + H_2A + 2OH^- = CoA + 2H_2O \qquad (2)$$

The inflection at a = 3 suggests the formation of CoA_2^{2-}. Since it is accompanied with precipitation of half of the metal ion in the form of $Co(OH)_2$, we can presume a disproportionation of CoA, in accordance with the following equotion:

$$2CoA + 2OH^- = CoA_2^{2-} + Co(OH)_2 \qquad (3)$$

The inflection at two moles of KOH per mole of ligand when the molar retio TLA and Co(II) is 2 : 1 (curve 3 on Fig. 3) corresponds to the formation of CoA_2^{2-} represented by the equotion:

$$Co^{2+} + 2H_2A + 4OH^- = CoA_2^{2-} + 4H_2O \qquad (4)$$

The absence of the inflection at 1.5 moles of KOH per mole of acid, points out, that 1 : 1 and 1 : 2 complexes are formed simultaneously during the titration.

The stoichiometry of complex formation between TGA and Co(II) was the same.

In order to calculate the formation constants K_1 and K_2 of complexes CoA and CoA_2^{2-} resp., we have used Calvin and Melchior's method. The evaluation of $\bar{n}$ values were made from data of potentiometric titrations of TGA (or TLA) with standard alkali in the absence and presence of Co^{2+} (Fig. 4).

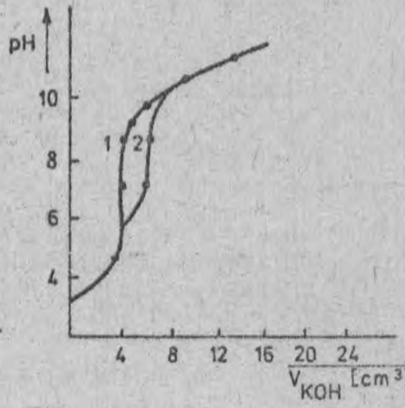


Fig. 4. Potentiometric titration of $4.3 \cdot 10^{-4}$ M TGA (curve 1) and $4.3 \cdot 10^{-4}$ M TGA + 10^{-4} M $Co(ClO_4)_2$ (curve 2)

At any pH, the horizontal distances between curves 1-2 measures the additional base consumed or the total number of $[A^{2-}]$ complexed. A series of $\bar{n}$ and $[A^{2-}]$ values at various pH were calculated and formation curves were plotted. The values of log K_1 and log K_2 were read from graph at $\bar{n}$ values of 0.5 and 1.5 resp. and were refined by relaxation method [3]. The calculated values of log K_1 were 6.24 and 6.15, values of log K_2 were 7.40 and 6.63 for TLA and TGA, respectively.

References

[1] J. Bjerrum, Metal amine formation in aqueous solutions, Copenhagen 1941.

[2] M. Calvin, N. O. Melchior, J. Am. Soc., 70, 3270 (1948).

[3] K. O. Watkins, M. M. Jones, J. Inorg. Nuclear Chem., 16, 187 (1961).

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POTENCJOMETRYCZNE BADANIA KOMPLEKSÓW Co(II) Z KWASAMI MERKAPTOKARBOKSYLOWYMI

Badano przy użyciu metod potencjometrycznych powstawanie kompleksów pomiędzy jonami Co(II) i kwasem tiomlekowym (TLA) oraz tioglikolowym (TGA) w roztworze wodnym, 0,1 M względem $NaClO_4$ w temperaturze 20°C. Stwierdzono powstawanie kompleksów typu Co(SRCOO) i $Co(SRCOO)_2^{2-}$ (gdzie $R = CH_2$ lub CH_3CH). Wyznaczono stałe trwałości tych kompleksów jak również stałe dysocjacji TLA i TGA.

Kwas tiomlekowy oraz tioglikolowy należą do grupy związków bardzo ważnych z punktu fizjologicznego. Ponieważ wykazują one silne własności kompleksujące wydało się nam interesujące porównanie trwałości kompleksów tych kwasów z jonami Co(II).

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ПОТЕНЦИОМЕТРИЧЕСКОЕ ИССЛЕДОВАНИЕ КОМПЛЕКСОВ Co(II) С МЕРКАПТОКАРБОНОВЫМИ КИСЛОТАМИ

При помощи потенциометрического метода исследовано образование комплексов Co(II) с тиомолочной (TLA) и тиогликолевой (TGA) кислотами в водном, 0.1 молевом ($NaClO_4$) растворе, при 20°C. Установлено образование комплексов типа Co(SRCOO) и $Co(SRCOO)_2^{2-}$. ($R = CH_2$ или CH_3CH). Определено константы диссоциации TLA и TGA.