

SPECTROPHOTOMETRIC DETERMINATION OF Cu (II) BY THE SYSTEM I⁻ - STARCH IN THE PRESENCE OF Fe (III)

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ABSTRACT

The conditions for the spectrophotometric Cu (II) determination by the system I⁻ - starch in the presence of Fe (III) are studied. The redox reaction between Cu(II) and I⁻ ions, and the reaction between I₃⁻ - complex and starch proceed in a medium of 0.08 mol l⁻¹ sodium acetate - acetic acid buffer with pH 4.9 in the presence of 0.34 mol l⁻¹ KI and 0.08 % starch. The absorbance of the I₃⁻ - starch compound is measured at λ 485 nm. Five hundred fold excess of fluoride ions against Fe (III) concentration is necessary to eliminate Fe (III) interference.

Keywords: copper, iodine, starch, spectrophotometry, glycerine.

INTRODUCTION

The redox reaction $2\text{Cu}^{2+} + 7\text{I}^- \rightleftharpoons 2\text{CuI}_2 + \text{I}_3^-$ [1-3] proceeds in water solutions of Cu (II) containing high concentration of iodide ions. The I₃⁻ complex possesses yellow colour and its absorption spectrum has a sharp maximum at a wavelength of 395 nm (Fig.1, [1]). By measuring the absorbance of the complex at 430 nm methods for the determination of Cu (II) and Cu (III) are developed [1-3]. As the absorbance is measured at the slope of the spectrum the methods provide results that are not enough precise. An additional reason for the larger dispersion of the results is the volatility of the iodine from the unstable I₃⁻ complex.

In the presence of starch the I₃⁻ complex forms intensive coloured compound used as an indicator in the iodometric titrations, which colour mainly depends on the structure and composition of the starch [5]. By measuring the absorbance of I₃⁻ - starch compound a spectrophotometric methods for the I₂ [6] and Tl (III) [7] determinations are developed.

In the present work the property of the I₃⁻ complex to form a stable compound with the starch is used and the conditions for the spectrophotometric determination of Cu (II) in the presence of Fe (III) are found.

EXPERIMENTAL

Solutions and apparatus

The following solutions were used: (1) 1.63 10⁻³ mol l⁻¹ Cu (II) prepared by dissolving CuO (p.a.) in 1 mol l⁻¹ sulfuric acid; (2) sodium acetate - acetic acid buffer; (3) 0.12, 0.32, 0.67, 1.2, 1.8, and 2.7 mol l⁻¹ KI prepared daily from KI (p.a., Merck); (4) 1% starch (Himsnab, Dimitrovgrad) in a mixture of water and glycerine (1:1) [7]; the solution is stable in a week; (5) 1% starch prepared daily by introducing 1g starch in 2 ml water and adding the mixture to 100 ml boiling water; (6) 0.01 mol l⁻¹ Fe (III) prepared by dissolving FeCl₃ in 1 mol l⁻¹ hydrochloric acid; (7) 0.1 mol l⁻¹ NaF.

A single-beam spectrophotometer Spekol 11 (Carl Zeiss; Jena) with cells of 1 cm was used to measure the

absorbance of the solutions. The spectra were recorded with a double-beam apparatus Cary (Varian) in cells of 1 cm.

Procedure

A proper volume of Cu (II) solution, 5 ml of buffer solution, and 7 ml of KI solution were introduced in a measuring flask of 25.00 ml. After a 10 or 20 min stay in a dark place, 2 ml of starch solution was added and the solution was diluted up to the mark. The starch solution and the distilled water were added drop by drop with continuously shaking of the flask. The absorbance was measured at λ 485 nm towards a blank solution. The spectra were recorded towards distilled water. When the influence of Fe (III) was studied, a volume of 0.6 ml Fe (III) solution and different volumes of NaF were added.

RESULTS AND DISCUSSIONS

The experiments were carried out in weak acid solutions to minimize the harmful reaction of an oxidation of iodide ions from the air oxygen [5] and to avoid the hydrolysis of the starch [8]. The sodium acetate-acetic acid buffer with $\text{pH} = 4.9 \pm 0.1$ was used to maintain the weak acid medium.

Two modes of preparation of the starch solution (water and water – glycerine [7]) were used, for which the concentrations of starch and the potassium iodide were varied. It was established that starch concentrations of 0.02; 0.04; and 0.08 % in the solutions for the absorbance measurement do not exert any effect on the absorption spectrum of the I_3^- -starch compound. The subsequent experiments were carried out with starch concentration of 0.08 %.

The concentrations of copper (II) studied were in the limits of $0.6 \times 10^{-5} - 6 \times 10^{-5} \text{ mol l}^{-1}$, and the potassium iodide concentrations were varied from 0.034 mol l^{-1} to 0.76 mol l^{-1} . At these high iodide concentrations Cu (II) forms with I^- ions the CuI_2^- complex, instead of the precipitate CuI, as seen from Fig. 1. The correlation between $C_{\text{Cu}^{2+}}$ and C_{KI} shown in Fig.1 was calculated from the equation $C_{\text{Cu}^{2+}} C_{\text{I}^-} = K_s (1 + \beta C_{\text{I}^-}^2)$, where K_s is the solubility constant of the CuI precipitate ($\text{p}K_s = 12$ [9]), and β is the formation constant of the complex CuI_2^- ($\lg \beta = 8.85$ [9]). The slight soluble compound CuI is not formed when the value of the left-hand side of the above equation is lower than that of the right-hand

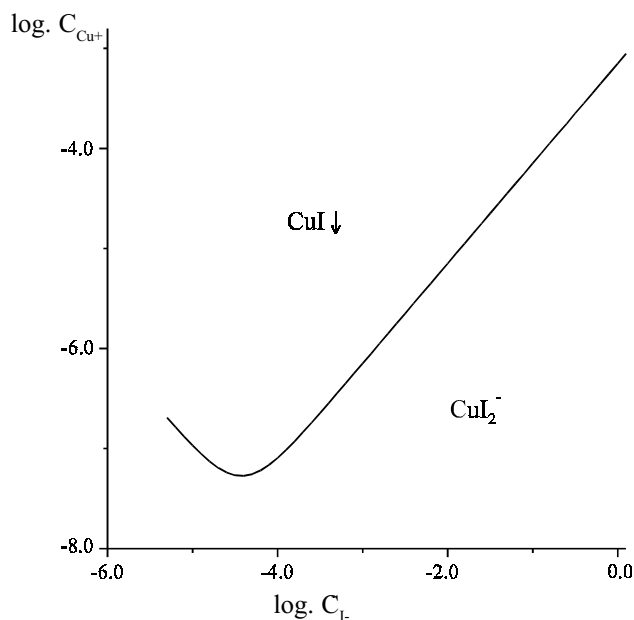


Fig. 1. Theoretical plot of the dependence $\log C_{\text{Cu}^{2+}} - \log C_{\text{I}^-}$.

side, and the area below the curve in Fig. 1 corresponds to concentrations of Cu (I) and KI at which the $[\text{CuI}_2^-]$ -complex is formed.

As the copper (II) concentration studied are low a stay of 10 and 20 min of the solutions after an introduction of the I^- ions was tested. It was found that a stay of 10 min is enough for the equilibrium of the reaction between Cu(II) and I^- to be reached. The equilibrium between I_3^- -complex and the starch is established five minutes after the dilution of the solutions, and the absorbance is invariable up to 20 minutes.

Experiments with water - glycerine solution of starch

The spectra of the I_3^- -starch compound towards water were recorded at six concentrations of KI (Fig. 2). Two maxima are observed, localized at wavelengths of 485 and 545 nm. Up to 0.19 mol l^{-1} KI inclusive the higher maximum is at 545 nm. From 0.34 to 0.76 mol l^{-1} KI the higher is the maximum at 485 nm. The larger change of the absorbances of the last two solutions with high KI concentrations is explained by the oxydation process of the iodide ions from the air oxygen. The absorbances of the blank solutions containing 0.50 and 0.76 mol l^{-1} KI measured towards water at λ 485nm are 0.060 and 0.130 , respectively.

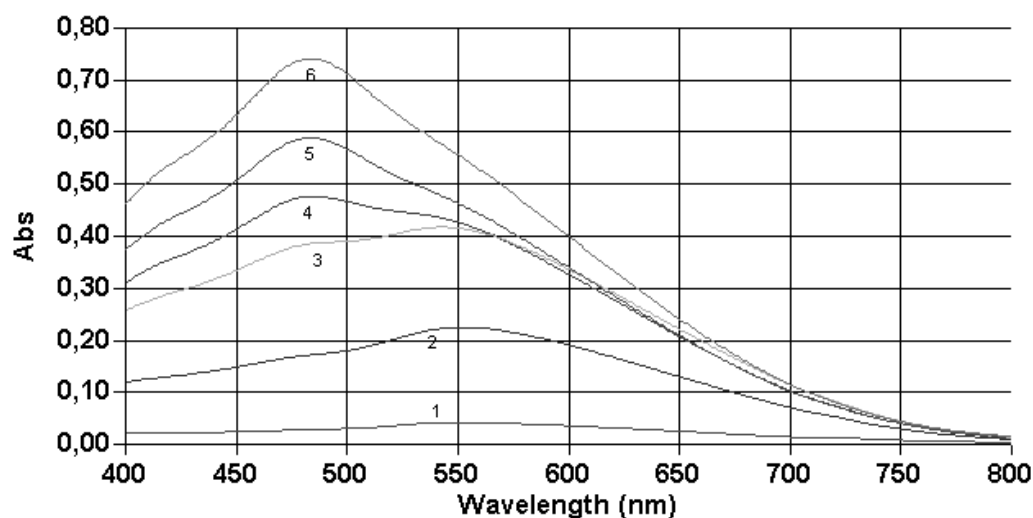


Fig. 2. Spectra of the I_3^- - starch compound at $C_{Cu} = 3.84 \cdot 10^{-5} \text{ mol l}^{-1}$, starch 0.16% (water – glycerine solution) and concentrations of KI in mol l^{-1} : (1)- 0.034; (2)- 0.090; (3)- 0.19; (4)- 0.34; (5)- 0.50 and (6)- 0.76.

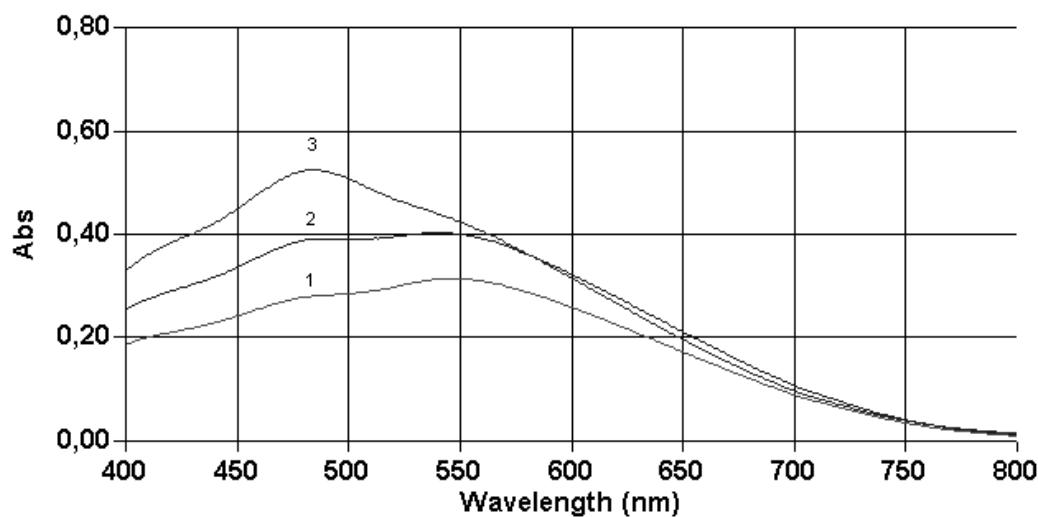


Fig. 3. Spectra of the I_3^- - starch compound at $C_{Cu} = 3.84 \cdot 10^{-5} \text{ mol l}^{-1}$, starch 0.16% (water solution) and KI concentrations in mol l^{-1} : (1)- 0.090; (2)- 0.19; (3)- 0.34.

To test the Beer's law a KI concentration of 0.34 mol l^{-1} was selected at which the sensitivity is high and the absorbance of the blank is still low ($A=0.010$). The absorbance of the solutions was measured at wavelength of 485 nm , corresponding to the higher maximum at this KI concentration. It was found that the dependence between the absorbance and the copper (II) concentration is a straight line. The Beer's law was tested analysing three parallel series each of them consisting of five solutions with different Cu (II) concentrations. A linear correlation between the absorbance of I_3^- starch com-

pound and the concentration of Cu (II) was found ($r=0.995$) and the regression equation at $P=95\%$ and $f=13$ is: $A = (1.29 \pm 0.02) 10^4 C_{Cu^{2+}}$.

Experiments with of starch aqueous solution

The spectra of the I_3^- starch compound at three KI concentrations were recorded (Fig. 3). Two maxima are observed at the same wavelengths as well as at the spectra given in Fig. 2. There is however slight difference between the absorbances of the compound in the presence and the absence of glycerine. The optimal value of the KI concentration - 0.34 mol l^{-1} and that of the

wavelength - 485 nm, picked out at the experiments with the water - glycerine solution of starch, are confirmed. Five solutions with different Cu (II) concentrations were analysed three times and the results were described by a regression analysis. The presence of a linear correlation between the absorbance and the copper (II) concentration is proved ($r=0.998$) and the equation of Beer's law at $P=95\%$ and $f=13$ is: $A = (1.22 \pm 0.03) \times 10^4 \cdot C_{\text{Cu}^{2+}}$.

Experiments for masking Fe (III)

Experiments with $2.4 \times 10^{-4} \text{ mol l}^{-1}$ Fe (III) in the solution for the absorbance measurement and different concentrations of NaF were made. It was proved that 500 fold excess of fluoride ions against Fe (III) concentration is necessary to eliminate the Fe (III) interference.

CONCLUSIONS

The experiments reported here show that Cu (II) in the presence of Fe (III) can be determined by measuring the absorbance of the I_3^- - starch compound formed between the I_3^- complex liberated by the reaction between Cu (II) and I⁻ ions and the starch added to the solution. The conditions for the Cu (II) determination are summarized as follows: a medium of 0.08 mol l^{-1} sodium acetate - acetic acid buffer with pH 4.9; KI concentration of

0.34 mol l^{-1} ; a starch concentration of 0.08 %; a 10 min stay in a dark place for the redox reaction to proceed; the absorbance measurement at wavelength of 485 nm; 500-fold excess of fluoride ions against Fe (III) concentration to eliminate Fe (III) interference; the more stable water-glycerine solution of starch is preferred.

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