

ON THE DETERMINATION OF TRIETHYLENETETRAMINE

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Methods are described for the determination of triethylenetetramine (TETA) by spectrophotometric way and by colorimetric titration based on formation its coloured cupric complex.

The reaction between TETA and KMnO_4 has been studied, and a method described for the determination of the change of amount of TETA in oxidation reaction.

Introduction

Recently, we studied the catalytic effect of ferrictriethylenetetramine complex. Namely, this complex is an extremely effective catalyst of the decomposition reaction of H_2O_2 [1].

It was observed that during the reaction the catalytic activity of the complex rapidly decreased [2]. We supposed that the reason of the decreasing of the catalytic activity is the oxidation of TETA by hydrogen peroxide. This process takes place simultaneously with the decomposition reaction. Consequently, it was necessary to determine the change in the concentration of TETA and to demonstrate the variation in its oxidation state during the decomposition reaction.

The pH-metric titration of TETA generally applied for the determination of polyethylene-poliamines was not suitable for our purposes, because the concentration of TETA in our experiments was 10^{-3} — $5 \cdot 10^{-3}$ mol/l only, and at such a low concentration the titration curves are inconvenient for further consideration.

We have attempted to develop a method for the determination of TETA based on the formation of its cupric complex.

Experimental

Reagents. Eastman Kodak TETA technical quality was distilled over sodium at reduced pressure. All other reagents used were c. p. grade.

Instruments. The spectrophotometric measurements were carried out with Beckman B spectrophotometer; for the colorimetric titrations Pulfrich photometer was applied.

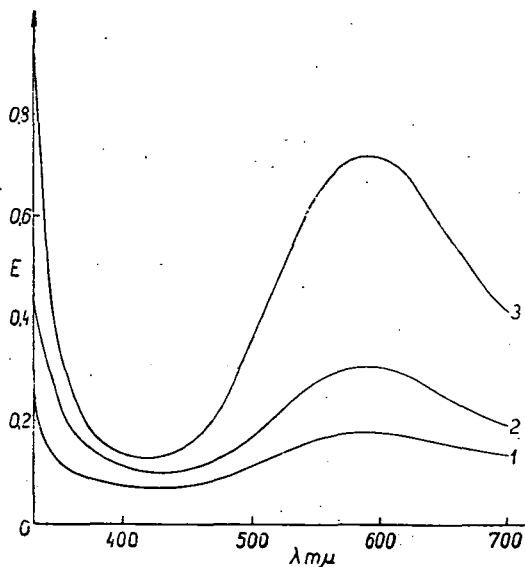


Fig. 1. The spectra of solutions of Cu(II)-TETA complex.

$$\begin{aligned}
 [\text{CuSO}_4] &= 5 \cdot 10^{-3} \text{ mol/l} \\
 [\text{TETA}] &= 1.) 10^{-3} \text{ mol/l} \\
 &2.) 2 \cdot 10^{-3} \text{ mol/l} \\
 &3.) 5 \cdot 10^{-3} \text{ mol/l}
 \end{aligned}$$

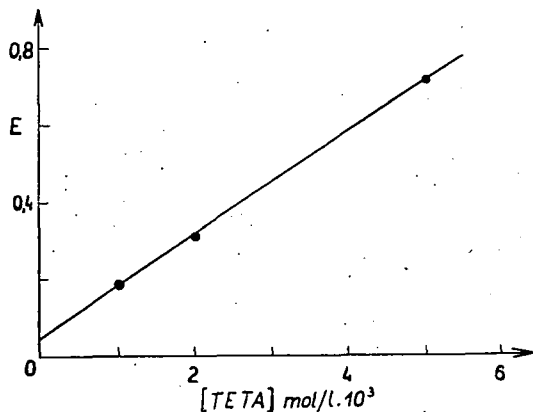


Fig. 2. The validity of the BEER'S law.

$$\begin{aligned}
 [\text{CuSO}_4] &= 5 \cdot 10^{-3} \text{ mol/l} \\
 \lambda &= 590 \text{ m}\mu
 \end{aligned}$$

Results and Discussion

The cupric ion forms a very stable ($pK = 20,1$), intensively blue coloured complex with TETA, in which the ratio of Cu and TETA is 1:1 [3]. On the Fig. 1 the spectra of solutions are depicted in which the concentration of cupric ion is constant and the amount of TETA is varied.

The absorbancy as a function of concentration of TETA is shown graphically in Fig. 2. The obeying of BEER'S law is evident, consequently the TETA can be determined colorimetrically.

Another possibility for the determination is the colorimetric titration of TETA by standard cupric sulphate solution. During the titration the absorbancy of the solution increases to the equivalent point. After the equivalent point the absorbancy remains constant, as the own colour of the cupric ion is negligible compared with the intensive colour of the complex.

In these experiments the stock solution of TETA was introduced to a cuvette. On the cuvette there was a mark at 100 ml. To the solution distilled water was added to 100 ml, and then was titrated with 0,01 mol/l CuSO_4 solution.

After the addition of each portions of titrant the absorbancy was measured with Pulfrich photometer using filter S-57.

It is necessary to correct the values of absorbancy measured owing to the dilution of solution during the titration. For that

purpose the values of absorbancy data were multiplied by a factor $\frac{100+x}{100}$ where x is the volume of titrant added.

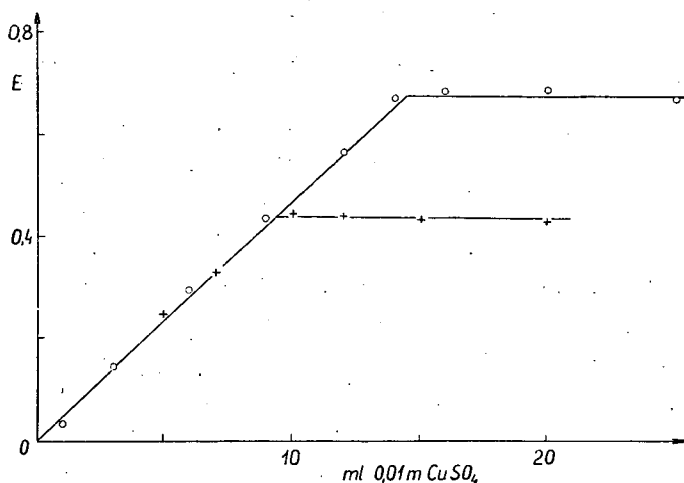


Fig. 3. Colorimetric titration of TETA (Filter: S-57)

Fig. 3 shows that the titration curves are very suitable for the determination of equivalent point. The maximum error is 2–3%. The lower limit of the determination is $5 \cdot 10^{-4}$ mol/l TETA.

In order to follow the change of concentration of TETA during the decomposition reaction some experiments were carried out by the above spectrophotometric method. The composition of reaction mixture was:

$$\begin{aligned}
 [\text{H}_2\text{O}_2] &\approx 10^{-1} \text{ mol/l} \\
 [\text{TETA}] &= 2,5 \cdot 10^{-2} \text{ mol/l} \\
 [\text{Fe}(\text{ClO}_4)_3] &= 7,9 \cdot 10^{-7} \text{ mol/l} \\
 \text{pH} &= 10,0.
 \end{aligned}$$

5 ml portions of this solution were pipetted in 0, 10, 30 minutes of the reaction and then introduced to a 50 ml measuring flask, containing 25 ml 0,01 molar CuSO_4 solution. Then the flask was filled up to the mark with water. The absorbancy of these solutions were determined between the wavelength 330–620 $\text{m}\mu$. The change was observable but not considerable. The reason of the absence of an essential change of the spectra is that the number of primer amine groups — according to the VAN SLYKE determination — did not decrease during the reaction¹. From the above experiments we cannot get quantitative data for the oxidation of TETA during the reaction.

In order to obtain quantitative data for the extent of oxidation of TETA, we studied the possibility of permanganometric determination. Reaction between the TETA and KMnO_4 in sulphuric acid medium is very slow. The time of complete reaction is 10–12 hours. During the reaction formation of

¹ The authors wish to express their gratitude to Mrs. É. FODOR for the VAN SLYKE determination.

MnO₂ precipitate was observed, Mn(II) can catalyse the reaction. In the presence of 2 ml 0,1 mol/l MnSO₄ in 60 ml volume the reaction takes place 3—4 hours. Firstly, we studied the permanganate consumption of different amounts of TETA. In these experiments fixed amounts of 4 N H₂SO₄ (20 ml), and 0,2 N KMnO₄ (20 ml) were mixed with varying amounts of TETA (up to 5 ml 0,005 M). Let stand it for about 12 hours KJ was added, then the J₂ was titrated by 0,2 N thiosulphate solution.

Fig. 4 shows that the amounts of KMnO₄ consumed are proportional to the TETA concentration. According to numerous experiments, under the above conditions one mole of TETA consumes 35 ± 1 equivalence of KMnO₄.

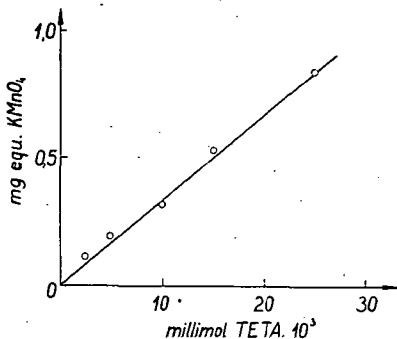


Fig. 4. The KMnO₄ consumption of TETA

In the following experiments a reaction mixture was composed:

$$\begin{aligned}
 [\text{H}_2\text{O}_2] &\approx 10^{-1} \text{ mol/l} \\
 [\text{TETA}] &= 4,8 \cdot 10^{-3} \text{ mol/l} \\
 [\text{Fe}(\text{ClO}_4)_3] &= \text{a) } 1,6 \cdot 10^{-7} \text{ mol/l}^2 \\
 &\quad \text{b) } 7,9 \cdot 10^{-7} \text{ mol/l} \\
 &\quad \text{c) } 1,1 \cdot 10^{-5} \text{ mol/l} \\
 \text{pH} &= 10,0.
 \end{aligned}$$

From time to time 5 ml portions of this solution were taken and the KMnO₄ consumptions were determined by the above method. Before the addition of measured amounts of KMnO₄ the excess of H₂O₂ was decomposed by dilute KMnO₄ solution. The permanganate consumption of portions decreases gradually. The difference between the original (35) and actual values (Δ) is characteristic of the extent of oxidation of TETA by the H₂O₂ in the decomposition reaction. The values of Δ as a function of time is graphically shown in Fig. 5.

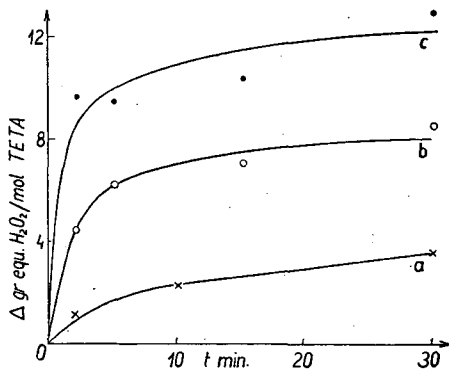


Fig. 5. The oxidation of TETA by H₂O₂ in the presence of different amounts of Fe(III)

With increasing concentration of Fe(III) the extent and velocity of oxidation of TETA increases, consequently the Fe(III)-TETA complex can catalyse both the decomposition of hydrogen peroxide and the oxidation of TETA by H₂O₂.

References

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- [3] Jonassen, H. B., A. W. Meibohm: J. Phys. Chem. **55**, 726 (1950).

² Blank, as impurity of the other reagents.