

# DETERMINATION OF COMPLEX STABILITY CONSTANT FROM CATALYTIC ACTIVITY I

## (Stability Constant of Iron(III)-Triethylenetetramine Complex)

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The catalytic effect of Fe(III)TETA complex on the decomposition of  $H_2O_2$  was inhibited by EDTA. From the extent of inhibition — from the initial velocity as a function of concentration of EDTA — the stability constant of Fe(III)TETA could be calculated.

The stability constant was also determined from the increasing of solubility of  $Fe(OH)_3$  in the presence of TETA.

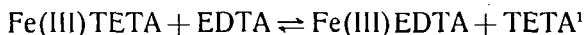
The two values are in good agreement.

### Introduction

In connection with our recent investigations [1] on the catalytic effect of iron(III)-triethylenetetramine (Fe(III)TETA) complex on the decomposition of hydrogen peroxide [2] it was necessary to know the stability constant of this complex. The experiments were carried out at relatively high  $p_H$  thus the existence of the complex in a reliable concentration requires a very great stability constant for the complex. The generally applied  $p_H$  metric method was not suitable for the determination of stability constant of this complex because these measurements have to be carried out at very low  $p_H$  due to the very small solubility product of  $Fe(OH)_3$ . Consequently, these measurements can not give reliable data for relations at about  $p_H$  10, where the kinetic experiments were carried out.

### Principle of method

It was observed that the ethylenediaminetetraacetic acid (EDTA) inhibits the decomposition reaction owing to the following displacement reaction:



The Fe(III)EDTA complex has no catalytic activity: the velocity of decomposition of hydrogen peroxide in the presence of even a relatively great

<sup>1</sup> For sake of simplicity the electric charge of complexes is not signed.

amount of Fe(III)EDTA is equal to the velocity of non-catalytic reaction at the same  $p_H$ . This phenomenon makes possible the determination of stability constant of Fe(III)TETA complex, since the velocity of decomposition reaction is a function of concentration of Fe(III)TETA. Thus the concentration of the complex can be calculated from the initial velocity. According to WANG the catalytic decomposition is bimolecular:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k[\text{Fe(III)TETA}][\text{H}_2\text{O}_2].$$

In our recent work it was shown that this expression is not correct: the bimolecular velocity constant increases with the concentration of Fe(III)TETA while the total concentration of TETA is constant. The variation of initial velocity constant with the concentration of Fe(III)TETA complex is shown in Table 1.

Table 1

[Fe(III)TETA] · 10 <sup>7</sup> mol. lit <sup>-1</sup>	$k \cdot 10^{-3}$ sec <sup>-1</sup> mol <sup>-1</sup>
2,9	1,8
4,7	1,9
6,0	2,1
7,9	2,6
11,0	3,3
14,0	3,5

Using the data of Table 1 the calculation of concentration of Fe(III)TETA complex is possible on the basis of bimolecular velocity relationship.

The equilibrium constant of the above displacement reaction is

$$K = \frac{[\text{Fe(III)EDTA}][\text{TETA}]}{[\text{Fe(III)TETA}][\text{EDTA}]}$$

Further, the stability constants of the Fe(III)TETA and Fe(III)EDTA complexes are defined by the following expressions:

$$K_1 = \frac{[\text{Fe(III)TETA}]}{[\text{Fe(III)}][\text{TETA}]}$$

and

$$K_2 = \frac{[\text{Fe(III)EDTA}]}{[\text{Fe(III)}][\text{EDTA}]}$$

Hence

$$K = \frac{K_2}{K_1}$$

Knowing the stability constant of Fe(III)EDTA complex ( $K_2$ ), the acidic dissociation constants of EDTA ( $K_n^E$ ) and TETA ( $K_n^T$ ), as well as the concentrations of EDTA, TETA and Fe(III)TETA, the stability constant of Fe(III)TETA

complex can be calculated. These concentrations can be calculated from the initial velocity of reaction, knowing the total concentrations.

$$K_1 = \frac{K_2}{K} = \frac{K_2[\text{Fe(III)TETA}]\alpha_E(c_{\text{EDTA}} - [\text{Fe(III)EDTA}])}{[\text{Fe(III)EDTA}]\alpha_T c_{\text{TETA}}}$$

where  $\alpha_T$  and  $\alpha_E$  are the fraction of TETA and EDTA in acid base system present as free TETA and EDTA<sup>4-</sup>.

$$\alpha_T = \frac{K_1^T K_2^T K_3^T K_4^T}{K_1^T K_2^T K_3^T K_4^T + K_1^T K_2^T K_3^T [\text{H}^+] + K_1^T K_2^T [\text{H}^+]^2 + K_1^T [\text{H}^+]^3 + [\text{H}^+]^4}$$

$$\alpha_E = \frac{K_1^E K_2^E K_3^E K_4^E}{K_1^E K_2^E K_3^E K_4^E + K_1^E K_2^E K_3^E [\text{H}^+] + K_1^E K_2^E [\text{H}^+]^2 + K_1^E [\text{H}^+]^3 + [\text{H}^+]^4}$$

Another possibility for determination of stability constant of Fe(III)TETA complex is the measurement of increasing of solubility of the ferric iron in the presence of TETA at a given  $p_H$ . The concentration of free Fe(III) is determined by the solubility product of ferric hydroxide:

$$[\text{Fe}^{3+}] = \frac{L}{[\text{OH}^-]^3}$$

The solubility of Fe(III) in alkaline medium does increase in the presence of TETA, owing to the formation of Fe(III)TETA complex. The concentration of the later is given by a kinetic measurement thus the stability constant can be calculated.

### Experimental

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

*Procedure.* The reaction was followed by permanganometric determination of non-decomposed hydrogen peroxide. Details of method are described in our paper [1].

### Results and discussion

The effect of EDTA on the velocity of decomposition was measured at two different concentrations of TETA at  $p_H$  10. Fig. 1 and Fig. 2 shows the results of kinetic experiments. The initial velocity ( $v_0$ ) was obtained from the kinetic curves by graphical differentiation. The actual concentrations of Fe(III)TETA were calculated from the initial velocity on the basis of bimolecular rate relationship using the data of Table 1. The concentration of Fe(III)EDTA is the difference between total Fe(III) and actual Fe(III)TETA concentrations. The concentration of TETA is practically constant owing to the great excess of it, the concentration of free EDTA was obtained as the difference of total EDTA and Fe(III)EDTA. The results of calculations are given in Table 2. and Table 3. The following numerical values of acidic dissociation constants of TETA and EDTA as well as the stability constant of Fe(III)EDTA were used for calculations:

Table 2

$$c_{\text{Fe(III)}} = 12,1 \cdot 10^{-7}; \quad c_{\text{TETA}} = 5 \cdot 10^{-3}; \quad c_{\text{H}_2\text{O}_2} = 0,098; \quad p_{\text{H}} = 10$$

No.	$c_{\text{EDTA}} \cdot 10^7$	$v_0 \cdot 10^4$ mol. lit <sup>-1</sup> sec <sup>-1</sup>	$[\text{Fe(III)TETA}] \cdot 10^7$	$[\text{Fe(III)EDTA}] \cdot 10^7$	$[\text{EDTA}^{4-}] \cdot 10^7$	$K_1 \cdot 10^{-21}$
1	0	4,0	12,1	0	0	—
2	5	4,0	≈ 12,1	≈ 0	≈ 1,8	—
3	10	2,9	10,2	1,9	2,9	8,6
4	20	2,4	9,0	3,1	6,0	9,7
5	50	1,5	6,6	5,5	15,8	10,5
6	80	1,1	5,3	6,8	26,0	11,2
7	100	0,5	2,8	9,3	32,2	5,4
8	200	—	≈ 0	≈ 12,1	≈ 66,7	—
					average:	9,1

All concentrations are given in mol. lit<sup>-1</sup>

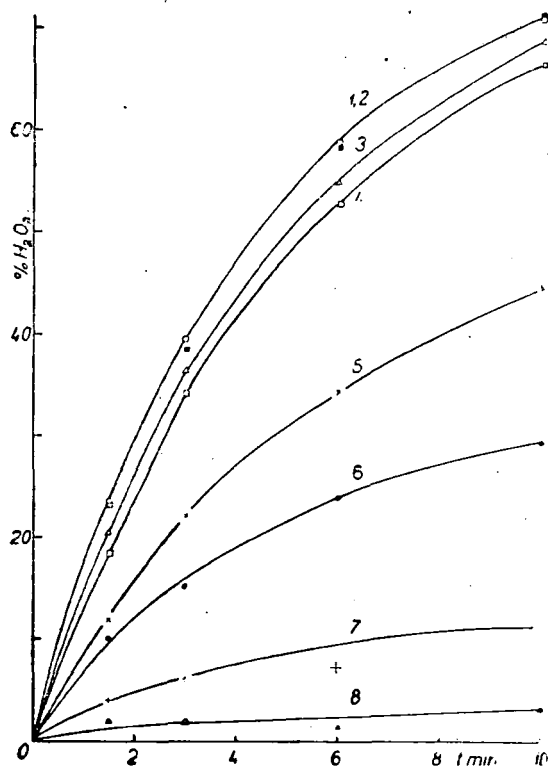


Fig. 1. Effect of EDTA on the decomposition of  $\text{H}_2\text{O}_2$  catalysed by  $\text{Fe(III)TETA}$ . Data are given in Table 2

Table 3

$c_{\text{Fe(III)}} = 13,3 \cdot 10^{-7}$ ;  $c_{\text{TETA}} = 10^{-2}$ ;  $c_{\text{H}_2\text{O}_2} = 0,105$ ;  $p_{\text{H}} = 10$ .

No.	$c_{\text{EDTA}} \cdot 10^7$	$v_0 \cdot 10^4$ mol. lit <sup>-1</sup> sec <sup>-1</sup>	$[\text{Fe(III)TETA}] \cdot 10^7$	$[\text{Fe(III)EDTA}] \cdot 10^7$	$[\text{EDTA}^{4-}] \cdot 10^7$	$K_1 \cdot 10^{-21}$
1	0	4,9	13,3	0	0	—
2	10	4,9	≈ 13,3	≈ 0	≈ 3,4	—
3	30	3,5	11,1	2,2	9,9	13,9
4	50	2,7	9,2	4,1	16,3	10,2
5	70	1,5	6,2	7,1	22,3	5,4
6	100	0,9	4,3	9,0	32,3	4,3
7	200	—	≈ 0	≈ 13,3	≈ 66,3	—
					average:	8,5

All concentrations are given in mol. lit<sup>-1</sup>.

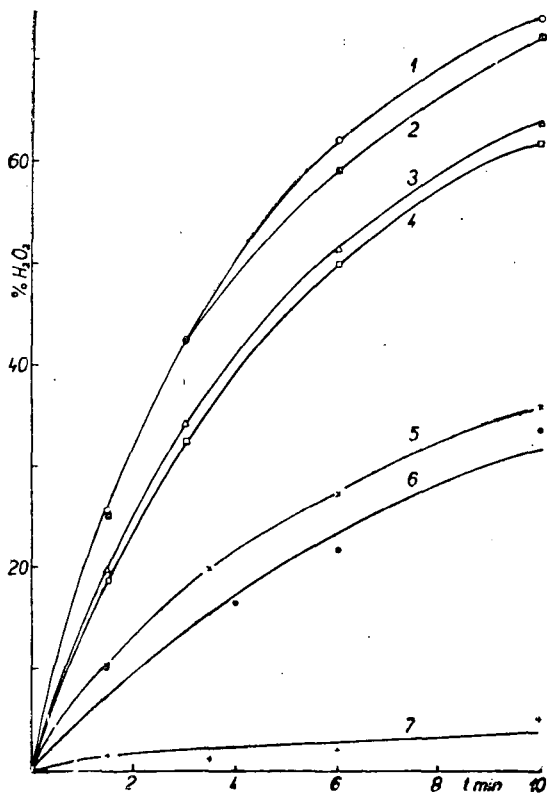


Fig. 2. Effect of EDTA on the decomposition of H<sub>2</sub>O<sub>2</sub> catalysed by Fe(III)TETA. Data are given in Table 3

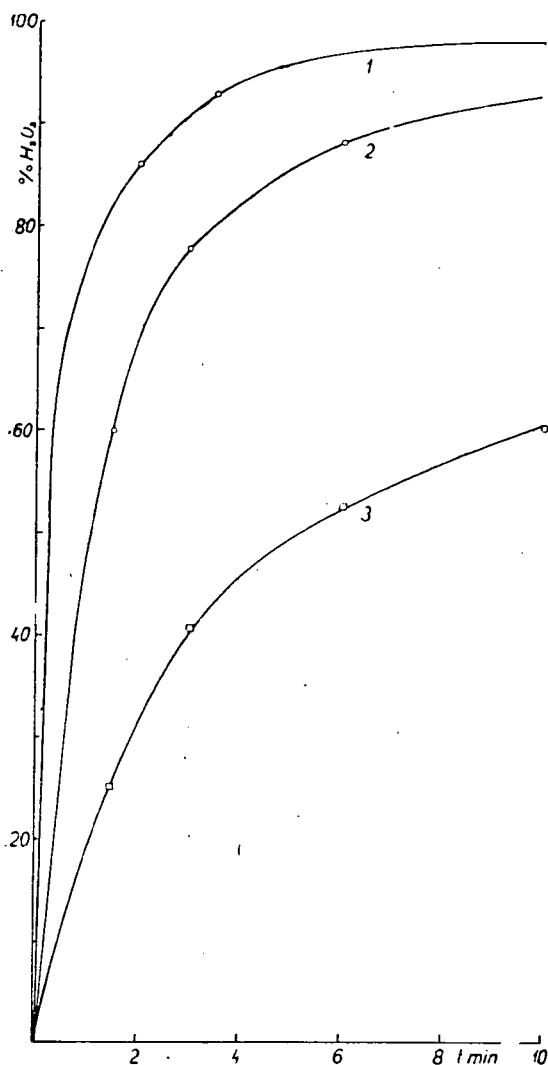


Fig. 3. Data are given in Table 4

In the case of greatest TETA concentration the velocity of decomposition reaction was too great for exact calculation. In these calculations two

Acidic dissociation constants of TETA [3]:

$pK_1^T$	3,89
$pK_1^T$	7,01
$pK_2^T$	9,36
$pK_4^T$	9,99

Acidic dissociation constants of EDTA [4]:

$pK_1^E$	1,99
$pK_2^E$	2,67
$pK_3^E$	6,16
$pK_4^E$	10,26

The values of  $\alpha_T$  and  $\alpha_E$  at  $p_H$  10 calculated from the above constants are:  $\alpha_T = 0,454$ ;  $\alpha_E = 0,355$ .

Stability constant of Fe(III)EDTA complex [5]:

$$pK_2 = 25,1.$$

The average value of stability constant of Fe(III)TETA complex from the two series is  $8,8 \cdot 10^{21}$ .<sup>2</sup>

*Solubility measurements.* Measured amount of TETA solution was added to an acidic  $Fe(ClO_4)_3$  solution, the  $p_H$  of the solution was adjusted to values of 10, the solution was vigorously shaken and then was filtered from the  $Fe(OH)_3$  precipitate. The kinetic experiments were carried out with these solutions. Fig. 3 shows the results of these experiments.

<sup>2</sup> It must be noted that the Fe(III)EDTA forms a mixed complex with hydrogen peroxide (RINGBOM A., S. SITONEN and B. SAXÉN: Anal. Chim. Acta 16, 541 (1957)). The influence of this fact was neglected because the error due to it may be only one order of magnitude, and the uncertainty of stability constant of Fe(III)EDTA complex is the same.

Table 4  
 $c_{\text{H}_2\text{O}_2} = 0,10$ ;  $p_{\text{H}} = 10$

No.	$c_{\text{TETA}} 10^3$ .	$v_0 \cdot 10^4$ mol. lit <sup>-1</sup> sec <sup>-1</sup>	[Fe(III)TETA] · 10 <sup>7</sup>	$K_1 \cdot 10^{-21}$ calculated from	
				$L = 1,1 \cdot 10^{-36}$	$L = 4,0 \cdot 10^{-38}$
1	10,8	—	—	—	—
2	5,4	8,3	26,3	1,0	26,8
3	2,7	3,7	12,4	0,9	25,3

All concentrations are given in mol. lit<sup>-1</sup>

different values of solubility product of iron(III) hydroxide were used [6], [7]. The data are given in Table 4. It must be noted that the concentrations are corrected considering the dilution of solution by adding hydrogen peroxide.

It can be seen that the stability constant obtained from the inhibition experiments is in a very good agreement with the value from the solubility experiments.

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#### References

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