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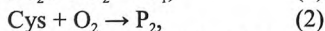
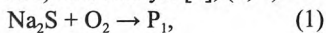
**CONNECTION BETWEEN THE NON-ADDITIVITY  
EFFECT SIGN AND THE RATIO OF MICHAELIS' CONSTANTS  
IN THE MODEL CATALYST SYSTEM**

*SUMMARY.* The non-additivity effects are widespread in the catalysis. In this paper, a non-additivity effect is referred to as a non-additive increase (or decrease) in activity, selectivity, stability, and other catalyst features that may occur when its component structure becomes more complex. However, the component structure of the catalytic system can also be made complex by introducing the additional substrates causing two and more reactions over a catalyst. Earlier, we have identified the non-additivity of the rates of joint oxidation of sodium sulfide and cysteine over Cu(II)-containing polyacrylamidic hydrogel as a catalyst. To understand the preconditions of the synergism emergence in this catalytic system, the components interactions are estimated by the Michaelis' constant. All the kinetic data obtained in the earlier work can be described by the hyperbolic dependence of the reaction rate on the concentration when changing from the initial value ( $v_0$ ) to maximum ( $v_{max}$ ). It corresponds to the conditions of applicability of the Michaelis-Menten's empirical equation. The positive effects are observed at the ratios of the substrates concentration close to  $K_{M Na_2S} / K_{M Cys}$ , the deviation from those results in negative effects.

**KEY WORDS.** Non-additivity effects, oxidation, sodium sulfide, cysteine.

The effects of non-additive increase in activity, selectivity and other features that may occur when the catalyst component structure becomes more complex are widely used in practice [1-8]. However, the component structure of the catalytic system can also be made complex by introducing additional substrates stimulating the occurrence of two or more reactions over a catalyst.

In our earlier works, we determined the non-additivity of the rates of joint oxidation of sodium sulfide and cysteine over Cu(II)-containing polyacrylamide hydrogel (PAAH) as a catalyst [9], (1, 2).



where  $P_1 = SO_3^{2-}$ ;  $S_2O_3^{2-}$ ;  $SO_4^{2-}$ , and  $P_2 = (Cys)_2$ .

$(Cys)_2 = HOOC-CH(NH_2)-CH_2-S-S-CH_2-CH(NH_2)-COOH$ .

The non-additive effect value was calculated from the reaction rates ( $\Xi$ ) for any specific time of the experiment, the following formula being used:

$$\Xi = (v_{mix} - v_{sum}) / v_{sum} = v_{mix} / v_{sum} - 1 = v_{mix} / (v_{Cys} + v_{Na_2S}) - 1,$$

where  $v_{\text{mix}}$  is the rate of the substrate mixture oxidation;  $v_{\text{sum}}$  is the sum of the rates of the separate substrate oxidation;  $v_{\text{Cys}}$  is the rate of the cysteine oxidation;  $v_{\text{Na}_2\text{S}}$  is the rate of the sodium sulfide oxidation.

Both sodium sulfide and cysteine, which can be considered a mercaptan model, are sulfur-containing compounds that occur in high concentrations in sulphur-alkaline wastewaters of oil-refining and pulp-and-paper industries [10]. The toxicity of such wastewaters does not permit them to be discharged into the water bodies or on the ground, even after significant dilution. Therefore, the problem of the sulfur-containing waste treatment is relevant, and their catalytic liquid-phase oxidation by oxygen as an environmentally friendly oxidizing agent is significant and promising.

To understand the preconditions of the emergence of the non-additive effects in this system, the components interactions were estimated by the Michaelis' constant:  $K_M = (k_2 + k_3)/k_1$ .

As Fig. 1 demonstrates, all the kinetic data obtained in [9] can be described by the hyperbolic dependence of the reaction rate on  $[C]$  when changing from the initial value ( $v_0$ ) to the maximum ( $v_{\text{max}}$ ). It corresponds to the conditions of applicability of the Michaelis-Menten's empirical equation

$$v_0 = v_{\text{max}} \frac{[C]}{K_M + [C]} \quad (1)$$

to process the obtained experimental data.

$K_M$  can also be used to evaluate the specificity of the catalyst effect on the substrate: the smaller the value  $K_M$ , the greater the specificity with this substrate.

The  $K_M$  values for Cys,  $(\text{Cys})_2$  and  $\text{Na}_2\text{S}$  were determined as being equal to 0.019, 0.034 and 0.083 M, respectively. This means that the amount of Cys required for 50% catalyst saturation is 1.8 times less than it is required for 50% cystine saturation.

Table 1

**The comparison of the Michaelis' constants ( $K_M$ ), the maximum oxygen consumption rates ( $v_{\text{max}}$ ), and the maximum absolute values of the catalytic activity of Cu(II)/PAAH ( $a_{\text{max}}$ ) with the air oxidation of cysteine, cystine, and sodium sulfide at 40 °C and pH = 11-12**

Kinetic parameters	Cysteine oxidation	Cystine oxidation	$\text{Na}_2\text{S}$ oxidation
$K_M$ , M	0.019	0.034	0.083
$v_{\text{max}}$ , mol $\text{O}_2$ /s	0.930	0.250	0.680
$a_{\text{max}}$ , act/s	0.520	0.140	0.380

Such a difference may be caused by more efficient binding of cysteine with the active catalyst centers and formation of the intermediate copper (II)-cysteinate complexes, or their more effective transformation into the reaction products. Perhaps, both stages progress more effectively. In this case, the fact of initial complete oxidation of cysteine and the subsequent oxidation of the accumulated cystine becomes evident. This correlates with the data presented in Table 1, which demonstrate that the transformation of the oxygen molecules should occur at the rate  $v_{\text{max}} = 0.93 \text{ molO}_2/\text{s}$  when cysteine is oxydated, and at the rate  $v_{\text{max}} = 0.25 \text{ molO}_2/\text{s}$  when cystine is oxydated, i.e. almost 4 times slower.

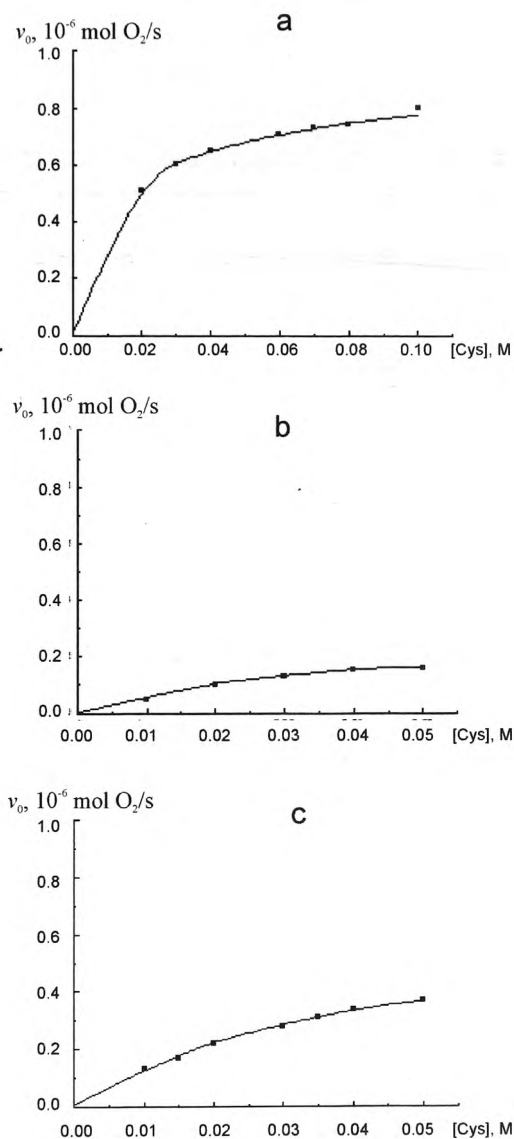


Fig. 1. The dependence of the initial rate of substrate oxidation on its concentration over Cu(II) / PAAH at 40 °C. pH = 11-12.  $V_{\text{sol}} = 5 \text{ mL}$ ;  $m_{\text{cat}} = 0.2087 \text{ g}$ ;  $[\text{Cu (II)}]_{\text{PAAH}} = 9.03 \cdot 10^{-6} \text{ M/g}_{\text{cat}}$ . a) – Cys; b) – (Cys)<sub>2</sub>; c) – Na<sub>2</sub>S

Table 2 demonstrates the initial rate values ( $v_0$ ) for the transformation of oxygen molecules and the absolute catalytic activity value ( $a_0$ ) in the  $\text{Na}_2\text{S}$ , Cys and  $(\text{Cys})_2$  oxidation with their solution concentrations varying. According to these data, the decrease in the concentration values also results in the decrease of  $v_0$  and  $a_0$  values in all the oxidative processes under study. However, these values are always higher in the oxidation of cysteine than in the oxidation of sodium sulfide and cystine, which also confirms the higher specificity of the catalyst to the cysteine oxidation.

Table 2

**The oxygen absorption rate in the oxidation of the  $\text{Na}_2\text{S}$  solutions, cysteine, and cystine depending on their concentrations**

$K_M, M$	$[\text{S}], M$	$v_0, 10^{-6} \text{ mol O}_2/\text{s}$	$a_0, \text{ molec. O}_2/\text{s}$
Sodium sulfide			
	0.1	0.37	0.21
0.083	0.08	0.34	0.19
	0.07	0.31	0.17
	0.06	0.28	0.16
	0.04	0.22	0.12
	0.03	0.17	0.09
	0.02	0.13	0.07
Cysteine			
	0.1	0.80	0.47
	0.08	0.74	0.41
	0.07	0.73	0.40
	0.06	0.71	0.39
	0.04	0.65	0.36
	0.03	0.60	0.33
0.019	0.02	0.51	0.28
Cystine			
	0.05	0.16	0.086
	0.04	0.15	0.083
0.034	0.03	0.13	0.074
	0.02	0.10	0.054
	0.01	0.05	0.027

Table 3

**The oxygen consumption rates ( $v_0$ ) at the joint and separate oxidation of the Cys and  $\text{Na}_2\text{S}$  solutions over  $\text{Cu(II)/PAAH}$  at 40 °C and pH=11-12 depending on the mixture compositions.  $V_{\text{sol}} = 5 \text{ mL}$ ;  $m_{\text{cat}} = 0.2087 \text{ g}$ ;  $[\text{Cu (II)}]_{\text{PAAH}} = 9.03 \times 10^{-6} \text{ M/g}_{\text{cat}}$**

$\text{H}_2\text{O}/$ 0.1M Cys	$v_0 = \text{tg}\alpha$	0.1M $\text{Na}_2\text{S}/$ 0.1M Cys	$v_0 = \text{tg}\alpha$	0.1M $\text{Na}_2\text{S}/$ $\text{H}_2\text{O}$	$v_0 = \text{tg}\alpha$
80/20	0.13	80/20	0.70	80/20	0.45
70/30	0.18	70/30	0.62	70/30	0.40
60/40	0.40	60/40	0.45	60/40	0.40
40/60	0.80	40/60	0.45	40/60	0.30
20/80	1.05	20/80	0.40	20/80	0.15

In this case, the addition of the second substrate ( $\text{Na}_2\text{S}$ ) should inhibit the cysteine oxidation and consequently result in the negative non-additivity effect ( $\Xi$ ) which increases when the content of the inhibitory substrate ( $\text{Na}_2\text{S}$ ) mixture increases. However, as it can be seen in Table 3, the increase in  $[\text{Na}_2\text{S}]$  in the Cys +  $\text{Na}_2\text{S}$  mixture to 70 and 80% does not inhibit the mixture oxidation, moreover, it even increases the oxygen consumption, i.e. results in positive  $\Xi$  values. To explain this fact, Table 2 should be considered again. These data suggest that the composition of the oxydated mixture is  $\text{Na}_2\text{S}/\text{Cys} = 80/20$  (vol.%) =  $0.08/0.02$  (M) =  $K_{M \text{Na}_2\text{S}}/K_{M \text{Cys}}$ , i.e. in this mixture, both  $\text{Na}_2\text{S}$ , and Cys are oxydated with the rate  $v_0 = \frac{1}{2} v_{\max}$ . This combination of rates correlates with the dynamics of non-additivity effect being in the area of positive values [9] (Fig. 2).

If the ratio is  $\text{Na}_2\text{S}/\text{CySH} = 70/30$  (vol%) =  $0.07 / 0.03$  (M), the slight shift (0.01 mol) from the  $K_M$  value occurs for both substrates. This is plotted in the position of the non-additivity curve for the  $\text{Na}_2\text{S}/\text{CySH} = 70/30$  ratio, it slightly moves down, and its segment falls into the area of negative  $\Xi$  values (we obtain the non-additivity with the sign variation). Further deviation from  $K_{M \text{Na}_2\text{S}}$  and  $K_{M \text{Cys}}$ , equal to 0.02 M, for  $\text{Na}_2\text{S}/\text{Cys} = 0,06/0,04$  results in the fact that a part of the non-additivity curve for this ratio entirely lies in the negative range of the  $\Xi$  values, etc.

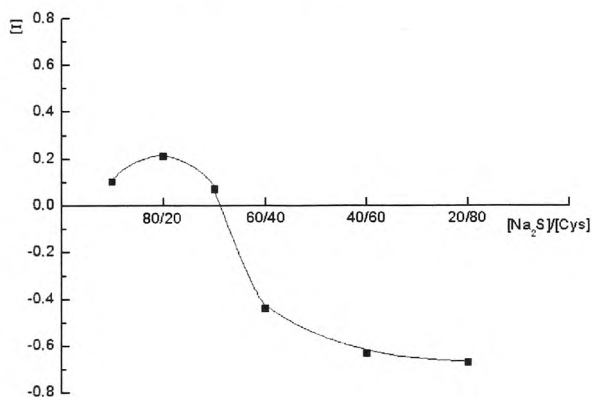


Fig. 2. The dependence of the non-additivity effect values ( $\Xi$ ) on the ratio of the initial  $\text{Na}_2\text{S}$  and Cys concentrations in the mixtures

Thus, the position of the curves representing the dynamics of the non-additivity variation for the mixtures of a certain composition depends on the ratio of the rates of the substrate oxidation in the mixture ( $v_{0 \text{Na}_2\text{S}}/v_{0 \text{Cys}}$ ). For the positive non-additivity at  $\text{Na}_2\text{S}/\text{Cys} = 0.08/0.02$  and  $70/30$ ,  $v_{0 \text{Na}_2\text{S}}/v_{0 \text{CySH}} = \frac{1}{2} v_{\max \text{Na}_2\text{S}} / \frac{1}{2} v_{\max \text{Cys}} = 0.68$  (molO<sub>2</sub>/c)/0.93 (molO<sub>2</sub>/c) = 0.73 and 0.50, respectively. The decrease in this value for the cases of  $\text{Na}_2\text{S}/\text{Cys} = 60/40$ ;  $40/60$ ;  $20/80$  to the corresponding values  $v_{0 \text{Na}_2\text{S}}/v_{0 \text{Cys}} = 0.50$ ; 0.44; 0.31, and 0.17 results in a gradual shift of the curves to the range of negative values for the non-additivity effect, see Fig. 2.

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