Eurasian ChemTech Journal 1(1999) 65-81

The kinetics and mechanism of the sulfur dioxide oxidation by the oxygen in the presence of the cobalt and nickel complexes, fixed on polymer matrix

V. S. Emelyanova*, K. A. Zhubanov, T. V. Shakieva, G. A.Yuldasheva.

Research institute of new chemical technologies and materials, Almaty

Abstract

Catalytic sulphur dioxide oxidation by oxygen on the cobalt and nickel complexes fixed on polyetheleneamine was investigated. On the base of kinetics study it was established that SO_2 and oxygen interact in inner sphere mechanism. UV-spectra and quantum-chemical calculations are presented, and on the base of them the ways of oxygen activation are discussed.

Introduction

In the solution of the problems of the clearing of emanating and technological gases from harmful admixtures, the large hopes are assigned also on catalytically active metallcomplexes, fixed on polymeric matrixes.

The sulfur dioxide is thrown out in air in the quantity 150 million tons annually and it has harmful effect on human organism, causing mostly the illness of organs of breathing.

The molecule of sulfur dioxide has biphele properties and can act as the σ-donor or as π-electron acceptor. And the donor-acceptor properties are exhibited to the same extent. Hence, the methods of gases clearing from sulfur dioxide are encompass reduction it to sulfur, or by oxidation to sulphate. The catalytic oxidation of sulfur dioxide to sulfuric acid by oxygen is more economic.

The features of oxygen as oxidant are instituted by the large stock of free energy released on reduction reaction $O_2 + 4e \rightarrow 2O^{2-}$, and kinetic inertness owing to biradical state and endothermality of the reaction of the joining the first electron confining the opportunity of involving O_2 in chemical processes without preliminary activation.

O_2 has two possible states - triplet and singlet, which are rather close on energy. In triplet (basic) state O_2 is more stable, as the electrons are on different p^{*1} orbitals with parallel spins. The reactions of activated O_2 are complicated on spin. The reactions of free O_2, going with conservation of a spin, lead to forming radicals.

At the co-ordination the degeneration - both *p*-orbitals is taken off and O_2 becomes singlet. There are three types of oxygenal complexes: *p*-complex (unstable superoxocomplex), *p-s*-complex (orbital) and *s*-complex (irreversible, strong complex). In the *p*-complexes only *p*-dative transition of electrons is exhibited, in the *p-s*-complexes *p*-dative and *s*-donor, in *s*-complexes covalent bonds.

The widely known fact is the involvement of natural complexes of transition metals with nitrogen containing macroligands in oxygen activation. Metallproteins (myoglobin, hemoglobin), metal porphyrins (cobalt, vanadium, nickel, iron), coopercontaining an oxygen carrier – hemocyanin and other are referred to them. The activity of natural immobilized of complexes exceeds activity of known catalysts of the reduction of oxygen by sulfur hydride on 6-8 orders. The attempts of modeling of natural compounds on the basis of Schiff bases [1] have shown that the basic structural and power characteristics of synthetic oxygen carriers depend both on structure of an organic matrix, and on nature of the transition metal, fixed on it. It is revealed, that nitrogen polymerVEMEA-N-VP, polyethyleneimine, and also oxygenated polymer polyacrylic acid are a convinent matrix for fixing of transition metals. Obtained immobilized catalysts exhibit high activity and stability in the reactions of low-temperature oxidation of sulfur dioxide by oxygen. The sulfur dioxide belongs to a number of well water soluble gases [2].

*Corresponding author.

Results and Discussion

At the dissolving in water depending on acidity and according to the constants of the applicable equilibriums [2] the sulfur dioxide is by way of sulphite, bisulphites-ions and non-dissociated molecules SO_2 (fig. 1).

The aqueous solutions of the studied systems have pH in the region 8 - 10. In this field according to the chart (fig. 1) SO_2 is in the form of SO_3^{2-}, therefore we used sulphite of sodium as the donor of the SO_2. The method of application of the kinetic's studying of SO_3^{2-} oxidation by oxygen is described in detail in [3]. The typical conversion and potentiometric curves in coordinates $W_{O_2} = f(Q_{O_2})$ are illustrated in fig. 1, where W_{O_2} – rate of oxygen absorption in $\text{mole} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$; Q_{O_2} – amount of the absorbed oxygen in $\text{mole} \cdot \text{l}^{-1}$, j – redox-potential of solution measured by the platinum electrode in relation to calomel-semielement and re-counted on the hydrogen scale.

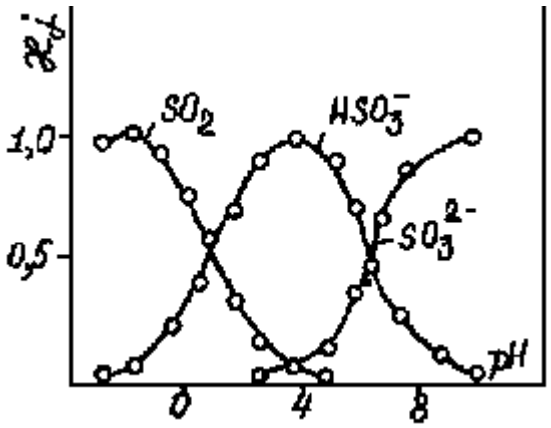


Fig. 1. The diagram of the oxygenous compounds of the sulphur on pH distribution

In all investigated conditions at $P_{O_2} > 0{,}7$ atm. Na_2SO_4 is the only product of Na_2SO_3 oxidation, the stoichiometric ratio of the amount of the absorbeded oxygen (Q_{O_2}) to the initial concentration of sodium sulphite is equal to 0,5 and corresponds to the stoichiometry of reaction (1):

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad (1)$$

The redox-potential of the system in the investigated conditions is situated in the interval 650 - 320 μV, and df /dCCoSO$_4$ > 0, df /dCCo < 0, df /dCNa$_2$SO$_3$ < 0, df /dPO$_2$ = 0. The function df /dC$_{PEI}$ passes through the minimum corresponding to the proportion Co : (R-CN), close to unit, df /dT > 0, all this allows to suppose, that the redox potential of system is described by the Nernst equation in the form:

$$\phi = \phi_0 + \frac{RT}{F} \ln \frac{[Co^{3+}]\beta_j \cdot C_{PEI} \cdot \alpha_j \cdot C_{SO_3^{2-}}}{[Co^{3+}]\beta_i \cdot C_{PEI} \cdot \alpha_i \cdot C_{SO_3^{2-}}} \quad (2)$$

Where b_j, b_j, a_i, a_i - constants of complexes formation of the cobalt(III) and cobalt(II) with polyethyleneimine and sulphite-ion respectively. According to the potentiometric data, the introducing Na_2SO_3 in system $CoSO_4$ - PEI - H_2O results to sharp fall of redox-potential approximately by 100 - 200 mV owing to reduction of a cobalt(III) to cobalt(II), thus there is discoloration of solution from pink to brownish depending on the proportion $C_{Co^{3+}} / C_{SO_3^{2-}}$. At the same time the absorption of the oxygen begins. With occurrence of the reduced form of the cobalt in the system the rate of absorption of oxygen rises and passes through maximum. The position of maximum on function $W_{O_2} = f(Q_{O_2})$ depends on the proportion $C_{Co(III)} / C_{Co(II)}$ and is instituted by constants of cobalt(III, II) formation with polyethyleneimine and sulphite - ion.

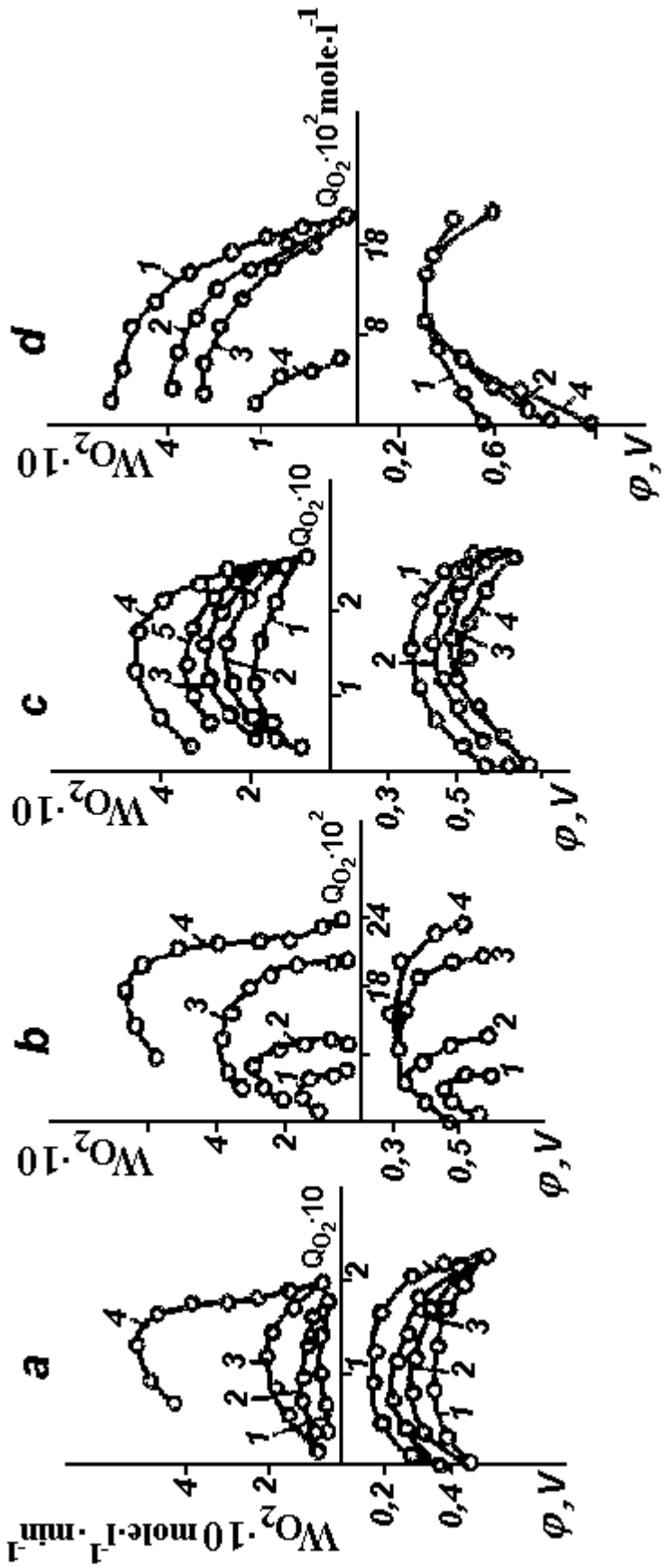


Fig. 2. The oxidation of the sulphur dioxide by oxygen in the presence of cobaltous complexes fixed on polyethileneimine P_{O_2} = 150 Pa , T = 296K.

a),f): $W_{O_2}(Q_{O_2}, \varphi, \chi_j) = f(C_{CoSO_4})$;
χ: 1. CoL; 2. Co-L-L.

b),g): $W_{O_2}(Q_{O_2}, \varphi, \chi_j) = f(C_{Na_2SO_3})$;
χ: 1.CoLCoP; Co-L-CoSO$_3$P; SO$_3$CoLCoSO$_3$P;

c),h): $W_{O_2}(Q_{O_2}, \varphi, \chi_j) = f(C_{PEI})$; χ: 1. CoL; 2. CoLCoP; 3.CoLCoP$_2$

d): $W_{O_2}(Q_{O_2}, \varphi) = f(C_{HClO_4})$; $C_{HClO_4} \cdot 10^2$ 1.-0; 2.-1,5; 3.-3; 4.-15 mole·l^{-1}

e): CoX: 1.-CoSO$_4$; 2.-CoCl$_2$; 3.-Co(NO$_3$)$_2$

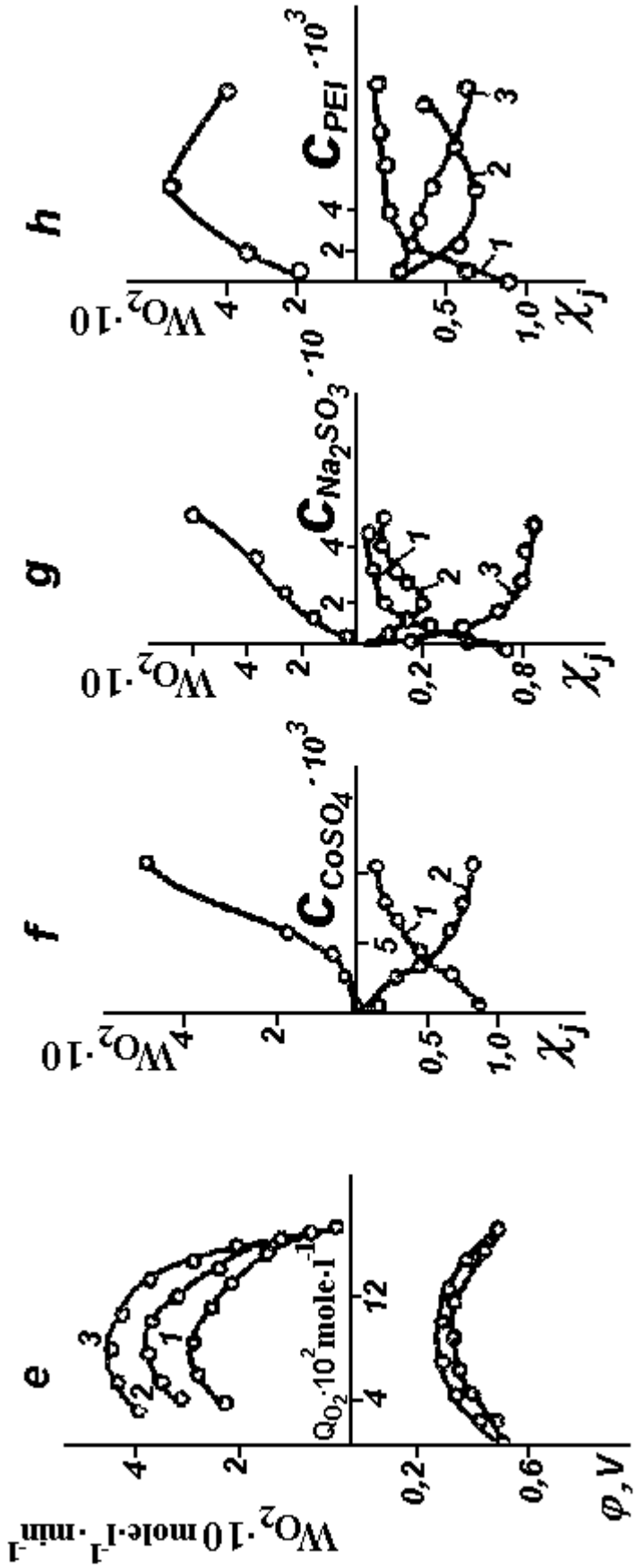


Fig. 2. The oxidation of the sulphur dioxide by oxygen in the presence of cobaltous complexes fixed on polyethileneimine P_{O_2} = 150 Pa , T = 296K.

a),f): $W_{O_2}(Q_{O_2},\varphi,\chi_j) = f(C_{CoSO_4})$; b),g): $W_{O_2}(Q_{O_2},\varphi,\chi_j) = f(C_{Na_2SO_3})$;
χ: 1. CoL; 2. Co-L-L. χ: 1.CoLCo·P; Co-L-CoSO$_2$·P; SO$_2$CoLCoSO$_2$·P;

c),h): $W_{O_2}(Q_{O_2},\varphi,\chi_j) = f(C_{PEI})$; χ: 1. CoL; 2. CoLCoP; 3.CoLCoP$_2$

d): $W_{O_2}(Q_{O_2},\varphi) = f(C_{HClO_4})$; $C_{HClO_4}\cdot10^2$ 1.-0; 2.-1,5; 3.-3; 4.-15 mole·l^{-1}

e): CoX: 1.-CoSO$_4$; 2.-CoCl$_2$; 3.-Co(NO$_3$)$_2$

During the experiment the redox-potential of system varies insignificantly and only at the end of the experiment, when $C_{SO_3^{2-}} \to 0$ and $W_{O_2} \to 0$, leaves for anodic field, reaching the reference value. Thus, the experimental results allow us to suppose, that the system Co(III) – Co(II) participates in the catalytic act. The additional evidences to this are presented in fig. 2a,f. The conversion curves differ by initial concentration of the cobalt in the system $CoSO_4$ – PEI – H_2O – Na_2SO_3.

The function $W_{O_2} = f(Q_{O_2})$ is described by the equation:

$$W_{O_2} = \frac{k_1 \cdot C_{Co(III)} \cdot \alpha \cdot C_{Co(III)}}{1 + \alpha \cdot C_{Co(III)}}, \qquad (3)$$

Where *a* - equilibrium constant:

$$Co(III)L + Co\ (III) \xleftrightarrow{\alpha} CoL - Co$$

$$k_1 = 7{,}4 \cdot 10^3\ mole^{-1} \cdot l \cdot min^{-1},$$

$$\alpha = 3{,}3 \cdot 10^2\ mole^{-1} \cdot l \quad \text{at } 303K$$

On the bottom of fig. 2a,f the chart of cobalt complexes distribution is presented. With the increasing of concentration $CoSO_4$ in solution the fraction of mononuclear complexes of cobalt decreases and the fraction of binuclear complexes increases. The comparsion of the functions $W_{O_2} = f(C_{CoSO_4})$ and $\chi_j = f(C_{CoSO_4})$ also results to the deduction, that the catalytic activity of system $CoSO_4$ - PEI - H_2O is conditioned by accumulating of cobalt complexes in solution:

$$W_{O_2} = k \cdot \chi_2$$

In all investigated interval of $C_{Na_2SO_3}$ the nature of kinetic curves does not inflect. In each case the redox potential of the system $CoSO_4$ – PEI – H_2O – Na_2SO_3 is reverted to the reference value (fig. 2b,g).

The dependence of the rate of oxygen absorption on initial concentration Na_2SO_3 in solution (fig. 2g) is described by the equation:

$$W_{O_2} = \frac{k_1\alpha_1 \cdot C_{SO_3^{2-}} + k_2\alpha_1\alpha_2 \cdot C^2_{SO_3^{2-}}}{1 + \alpha_1 \cdot C_{SO_3^{2-}} + \alpha_1\alpha_2 \cdot C^2_{SO_3^{2-}}} \qquad (4)$$

Where α_1 and α_2 - equilibrium constants of the systems:

$$Co - L - Co^{4+} + SO_3^{2-} = O_3S - Co - L - Co^{2+} \qquad (5)$$

$$O_3S{-}Co{-}L{-}Co^{2+} + SO_3^{2-} = O_3S - Co - L - SO_3 \qquad (6)$$

In fig. 2g the chart of distribution of cobalt complexes containing sulphite-ion depending on initial concentration of sulphite in solution $CoSO_4$ – PEI – H_2O is presented. Comparing the functions $W_{O_2} = f(C_{Na_2SO_3})$ and $\chi_j = f(C_{Na_2SO_3})$ it is also possible to suppose, that the intermediate complex of sodium sulphite oxidation has the active forms containing one and two sulphite groups in intermediate, and the greatest simbatness with the function $W_{O_2} = f(C_{Na_2SO_3})$ is observed for the second form of the complex.

The solution of the equation (4) by the method of least squares has allowed to determine the kinetics and thermodynamic constants (k_1, k_2, α_1 and α_2). They are presented below:

Complex	k, $mole^{-1} \cdot l \cdot min^{-1}$	α, $l \cdot mole^{-1}$
$O_3S - Co - L - Co^{2+}$	$3 \cdot 10^3$	$5 \cdot 10$
$O_3S - Co - L - Co - SO_3$	$7 \cdot 10^3$	$2 \cdot 10$

The interesting results are received at variation C_{PEI} in system $Co(II) - Co(I) - SO_3^{2-} - PEI - H_2O$. C_{PEI} varies in the interval from 0 to $10^{-3} mole \cdot l^{-1}$, the results are presented in fig. 2c,h. The function $W_{O_2} = f(C_{PEI})$ passes through maximum at $C_{Co(II)}/C_{RCN} = 1$, the further increasing of C_{PEI} has negative effect on the rate of sodium sulphite oxidation by oxygen. The function $W_{O_2} = f(C_{PEI})$ is described by the equation:

$$W_{O_2} = \frac{k_1\beta_1 \cdot C_{PEI}}{1 + \beta_1 \cdot C_{PEI} + \beta_1\beta_2 \cdot C^2_{PEI}} \qquad (7)$$

Where b_1 and b_2 - equilibrium constant:

$$O_3S - Co - Co - SO_3 + PEI = O_3S - Co - Co - SO_3PEI$$

$$O_3S - Co - Co - SO_3PEI + PEI = O_3S - Co - Co - SO_3PEI_2$$

In the bottom of fig. 2c,h the chart of accumulation of the polyethylene complexes of cobalt(II) is presented depending on initial concentration of the polyethyleneimine in solution. In the investigated interval, with increasing of C_{PEI} the fraction of the cobaltous without polyethyleneimine, falls, the fraction of complex containing one PEI in coordination sphere, passes through maximum, and for complex containing in the structure two groups PEI rises. The analysis of the results demonstrates, that between function $W_{O_2} = f(C_{PEI})$ and fraction of the complex containing one PEI simbatness is observed, that is the activity of polyethylene complex of cobalt during oxidation Na_2SO_3 by oxygen is connected with accumulation of this complex.

The solution of the equation (7) by the method of least square has allowed to determine kinetic (k_1) and thermodynamic (b_1 and b_2) constants. They are presented below:

Complex	k, $l \cdot mole^{-1} \cdot min^{-1}$	β, $l \cdot mole^{-1}$
$(PEI)SO_3 - Co - L - CoSO_3$	$7{,}2 \cdot 10^3$	1,2
$(PEI)_2O_3S - Co - L - CoSO_3$	$1{,}85 \cdot 10^3$	$1{,}62 \cdot 10^4$

In the interval of $CHClO_4$ from 0 to $3 \cdot 10^3 mole \cdot l^{-1}$ stoichiometry of reaction (1) is conserved, though with increasing of $CHClO_4$ the rate of oxygen absorption falls. At the $CHClO_4 > 10^{-1}$ quantity of the absorbed oxygen is sharply decreased, that is the stoichiometry of interaction SO_2 with oxygen varies (fig. 2d).

In the interval of $CHClO_4$ from 0 to $3 \cdot 10^{-2} mole \cdot l^{-1}$ the dependence of WO_2 upon the initial concentration of $HClO_4$ in system is described by the equation

$$W_{O_2} = \frac{k}{1 + \sigma \cdot C_{HClO_4}} \qquad (8)$$

The plot decision of the equation (8) has allowed to determine the value $s = 2{,}14 \cdot 10^{-2} l \cdot mole^{-1}$, this constant well coincides with the equilibrium constant, indicated in the literature [2]:

$$SO_3^{2-} + H^+ \longleftrightarrow HSO_3^- \qquad s = 4{,}3 \cdot 10^{-2}$$

That is protonisation of SO_3^{2-} results in decreasing of its donor properties and reactivity in relation to oxygen.

It was interesting to trace the influencing of the ligand nature, directly connected to cobalt, on activity of catalyst in reaction (1). Nitrate, sulphate and chloride of cobalt are chosen as the objects of the studying. The results are illustrated in fig. 2e.

The behavior of three systems is similar, however, they differ on activity. In fig. 3 three systems are compared in identical conditions. The magnitudes of WO_2 for the investigated complexes alongside with the values of the potentials of ligands oxidizing dimerization (j $x_2 \leftrightarrow 2x^-$) are presented below:

Complex	$W_{O_2} \cdot 10^2, mole \cdot l^{-1} \cdot min^{-1}$	lg W	j $x_2 \leftrightarrow 2x^-$, V
$CoSO_4$	$3 \cdot 10^{-2}$	-1,52	2,01
$CoCl_2$	$3{,}8 \cdot 10^{-2}$	-1,42	1,36
$Co(NO_3)_2$	$4{,}5 \cdot 10^{-2}$	-1,35	0,79

From the results it follows, that the increasing of the ligand donor capacity in the surrounding of cobalt, results the increasing of the complexes catalytic activity in reaction (1), and the linear dependence between lgW and magnitude j° is observed. It allows to suppose, that the investigated ligands execute the role of bridge for the conduction electrons between two atoms of cobalt in such complex system.

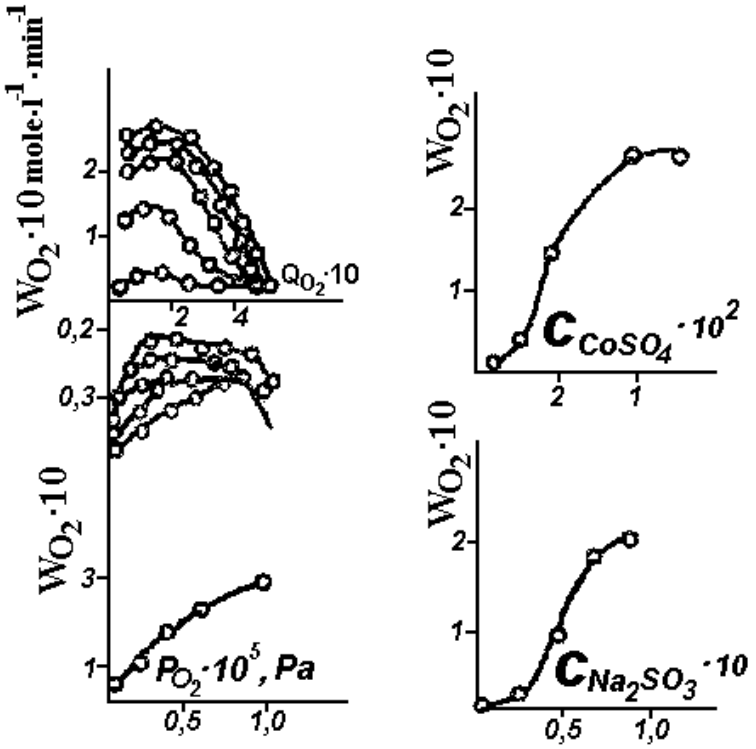


Fig. 3. Oxidation of the sulphur dioxide by the oxygen in the presence of the ammiakate of cobalt $P_{O_2} = 10^5$ Pa, T=303K

The similar results are received for nitrogencontaining monomeric ligands, as ammonia (fig. 3). The kinetic laws are described by the equations (3-8). The differences are: activity rate constants of cobalt complexes with NH_3 are more than on two orders below than complexes (tab. 1) and stability of work. At the end of the experiment, when $C_{SO_3^{2-}} \to 0$, the redox potential of the solution practically up to the end is not reverted; the less initial concentration of cobalt in solution, the more delayed returning redox potential to the initial state.

Table 1.
Oxidation of sulfur dioxide by oxygen in solution $CoSO_4$ - NH_4OH - H_2O
$C_{CoSO_4} = 2\cdot 10^{-2}$ mole·l^{-1} t = 296 K, P_{O_2} =1 atm,

Complex	k, l·mole^{-1}·min^{-1}	α, l·mole^{-1}
$NH_3 - Co - OH - CoSO_3NH_3$	5,1	4,3·10
$NH_3Co - OH - Co - NH_3$ (SO$_3$ SO$_3$)	1,2·10	1,2·10

The electronic spectra of the absorbing of the compounds in visible range (400 ÷ 800 ηm) and in ultraviolet (200 ÷ 400 nm) are investigated. The studies were carried out, using a spectrophotometer of the firm Jasca, model 78507. The spectra of aqueous solutions $CoSO_4$ and $CoCl_2$ are investigated at their concentration in aqueous solution equals to 10^{-2} mole $\cdot l^{-1}$. The color of solutions is pink, that according to the literature data [4] testifies to formation of octahedral complex compounds $[Co(H_2O)_6]SO_4$ and $Co(H_2O)_6 \cdot 2Cl$. For $[Co(H_2O)_6]SO_4$ the band with the maximum on 511 nm and the shoulder from the shortwave party is observed at 483 nm. In UV-interval from 225 to 300 nm at the given concentration of salt of cobalt the absorbing is not present.

$Co(H_2O)_6 \cdot 2Cl$ has similar picture: the band with the maximum 511 nm and shoulder from the shortwave party at 475 nm. Thus we have practically identical absorbing in the case of two cobalt salts ($CoSO_4$ and $CoCl_2$), that undoubtedly points that the absorbing is conditioned by d-d-transferring of cobalt(II) and the dependence from extrasphere ligand is little.

At addition the solution of polyethyleneimine ($C_{PEI} \sim 10^{-2}$ mole $\cdot l^{-1}$) to the solution $CoSO_4$ ($C_{CoSO_4} \sim 10^{-2}$ mole$\cdot l^{-1}$) decolourization from pink to orange was visually observed, that testifies to reagent interaction and formation of the complexes. A spectrum of the complex is presented with new band with maximum at 450 nm, and the doublet band of d-d-transferrings from the complex $Co(H_2O)_6^{2+}$ shifted to the shortwave part of the spectrum, and is observed by the way of well allowed doublet with maximum at 506 nm and 474 nm. On the other hand this doublet is possible to be considered as part of an electronic spectrum of the formed complex $Co^{2+} \cdot PEI$.

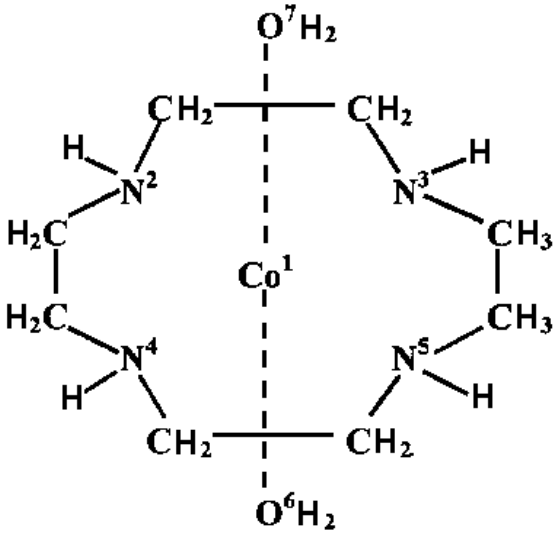
At the dilution of the complex (< 10^{-3} mole$\cdot l^{-1}$) the band with a maximum is observed at 232 nm in UV-range, and the band d – d-transferrings of the cobalt has come back in the initial position, characteristic for $Co(H_2O)_6^{2+}$ and is observed on length 503 nm with a shoulder at 486 nm. However, from the literature [5] it is known, that the complex PEI – Co^{2+} has characteristic band of absorbing at 313 nm.

Thus above described variations in electronic spectra of system PEI – Co^{2+} can be interpreted so: at strong watering there is a breaking down of the complex PEI – Co^{2+}, and the band 232 nm belongs to $-NH_2^+-$ groups PEI. As it was found out, the reason of breaking down of the complex is connected with using distilled water appeared to be acidic with pH=5,0. In [6] it is indicated, that the complex PEI – Co^{2+} is reshaped at pH > 5 and is stable at large pH. Accounting it, the distilled water with pH = 7,1 was prepared. And the dilution of a source complex PEI – Co^{2+} at $C_{Co} < 10^{-3}$ was without breaking down of the complex, it was characterized by absorption bands at 230 nm and 312 nm, and also very weak bands d – d-transferrings. It has doublet at 507 nm and 472 nm.

At addition the solution Na_2SO_3 to the solution of the complex PEI – Co^{2+} there is a variation of electronic spectrum of PEI – Co^{2+}. There is a band with maximum at 478 nm, which, apparently, covers weak band of d–d-transferrings. The strong absorption is lower 450 nm is conditioned by a very intensive band with maximum at 225 ÷ 230 nm. This spectrum is conditioned by formation of complexes in triple system $Co^{2+} - PEI - SO_3^{2-}$.

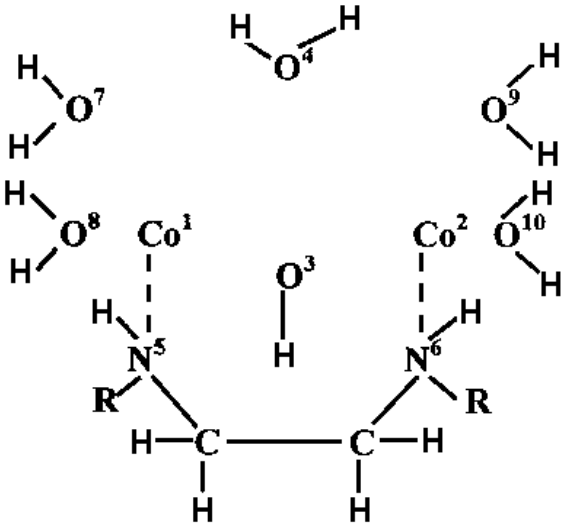
Thus experimentally in electronic absorption spectra at $C_{Co^{2+}} \sim 10^{-3}$ mole$\cdot l^{-1}$ an intensive (230 nm and 312 nm) and two very weak (507 nm and 472 nm) absorption bands are found out. At $C_{Co^{2+}} > 10^{-2}$ mole$\cdot l^{-1}$ the spectrum is introduced by a new band 450 nm and doublet of the bands at 506 and 474 nm. In the ternary system $CoSO_4$ – PEI – Na_2SO_3 the intensity of bands 230 nm and 313 nm sharply rises, thus there is one additional band 285 nm.

Calculation of electronic absorption spectra of sheaths of solvent molecules of following complexes (I - III) is held by Semiempirical method ZINDO/S [5] (fig. 4):

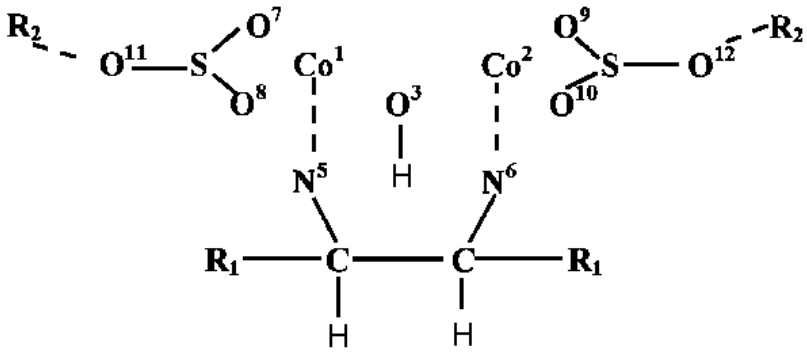


q (the system charge) = 3

I(a, b)



IIa R=H; q=5
IIb R=CH_2 - CH_2 - NH_2; q=5
IIc R=CH_2 - CH_2 - NH_3^+; q=7



IIIa R_1 =CH_2 - CH_2 - NH_2; R_2 - absent; q=-1
IIIb R_1 =CH_2 - CH_2 - NH_2; R_2 = H_2O; $r_{O^{11,12}-R^2} = 1{,}65\,\mathring{A}$, q = -1
IIIc R_1 =CH_2 - CH_2 - NH_2; R_2 = H_2O; $r_{O^{11,12}-R^2} = 1{,}85\,\mathring{A}$, q = -1
IIId R_1=CH_2-CH_2-NH_2; R_2=H_3O^+; $r_{O^{11,12}-R^2} = 1{,}08\,\mathring{A}$, q=+1

Fig. 4. Possible intermediate complexes in the reaction (1)

The calculations are held with allowance of only the first cover of the solvent molecules.

The dimensional constitution is established as a result of optimization of geometry by method ZINDO/1 [5]. The calculations have shown, that at coordination of an ion of cobalt by four atoms of nitrogen (complexes Ia, b) the formation of several structures with various position of the cobalt ion inside polymeric semiring is possible. The optimized lengths of coordinate linkages for complexes I-III (tab. 2) are in the good consent with the data of X-ray crystal analysis [5].

Calculation of electronic spectra and optimization of geometry are conducted with the help of a package HyperChem, Release 4.0 for Windows (HyperCube Inc., 1994).

One can see from tab. in system (a1) the band ~230 nm it is possible to interpret as

transferring with carrying of charge in the complexes such as Ia, b. Apparently, it is possible to attribute the bands ~ 486 nm and ~509 nm to highspin transferring $^4T_{1g}(d) \rightarrow {}^4T_{1g}.(d)$ in the complex $Co(H_2O)6^{2+}$.

In the system (a_2) the bands ~ 230 nm and ~ 313 nm can be attributed to transferrings with carrying of charge in the complex IIa. The influence of the polymeric chain was modelled by the introducing of the substitute R = $CH_2 - CH - NH_2$. The atoms of nitrogen are fixed in the trans-position in relation to N^5 and N^6, as the not valent interactions, arising in trans-fragments, can influence on donor activity of nitrogen atoms. The coordination of the secondary atoms of nitrogen replaced by process of protonisation (structure IIc), shifts the band ~ 330 nm in field ~ 380 nm, the proportion of the intensivity varies also, in this complex in field ~ 230 nm weak d – d transferring is located.

The comparsion of calculated and experimental data testifies that at the given concentration of cobalt ions ($C_{Co^{2+}} > 10^{-2} mole \cdot l^{-1}$) in the aqueous solution of a binary system $CoSO_4$ + PEI the formation of the structure such as IIb is the most probable. Apparently, in the polymeric chains binuclear complexes are formed through one not coordinated atom of nitrogen.

Thus, the quantum-chemical analysis of spectrofotometric data of the binary system $CoSO_4$ – PEI demonstrates, that the increasing of concentration of cobalt ions results to the conformation variations of polymeric complex, increasing of positive charge of the system transfers compact conformstion of the chain to the unwrapped.

The structures such as IIa forming constructs an opportunity of passing of the reaction of oxigenation on binuclear scheme. At addition of Na_2SO_3 in the solution the sulphite-ion forces out water molecules from coordination sphere, and it results to formation of complexes IIIa-d (fig. 4).

The calculations have shown that in the presence stronger than water, reducer SO_3^{2-} coordination number of the cobalt ion falls to four. The formation of strong hydrogen bridge between the not coordinated atom of oxygen SO_3^{2-} group and hydrogen atom of the molecule of water introduces the basic variation to electronic structure of the complex.

Comparison of calculated and experimental energies of transferrings for complexes IIIb-d demonstrates proximity of these magnitudes. As it is visible from the table 2 different energy values of hydrogen bond or involvement in coordination of hydroxonium ion cause small energy scattering in the field of ~230 nm and ~313 nm.

Thus, the quantum-chemical interpretation of the photometric data confirms made from kinetics (equation (3)) deduction about the opportunity of passing of oxigenation reaction on conjoint binuclear mechanism. The kinetic data testify that such structure of transitive state provides optimal conditions for oxidizing reaction SO_3^{2-} to SO_4^{2-}. At the variation of C_{PEI} in an interval from 0 to $10^{-2} mole \cdot l^{-1}$ function $WO_2 = f(C_{PEI})$ passes through maximum corresponding $C_{Co^{2+}}/C_{PEI} = 1$. Further C_{PEI} increasing has negative effect for reaction rate. Apparently, the SO_3^{2-} displacement from coordination sphere by nitrogen atoms of aminogroup results to deceleration of oxidation process.

Activation energies of oxigenation reaction on cobaltammine compounds are calculated by method EMH. Spacing interval between ions of metal and molecule of oxygen is chosen as coordinate of reaction. In transitive oxigenated complex r_{M-O} = 1,86Å corresponds to the data of rentgenostructural analysis for oxigenated complex of cobalt.

The calculations have shown, that at substitution of the hydrogen atoms on an ethylenic fragment the transfer of charge on cobalt ions sharply rises, and the activation energy of oxigenation process is decreased to ~16 kkal per mol. Probably, the more transferring of charge on ions of metal, the more easier it is to carry out dative carrying of electronic gravity on oxygen atoms.

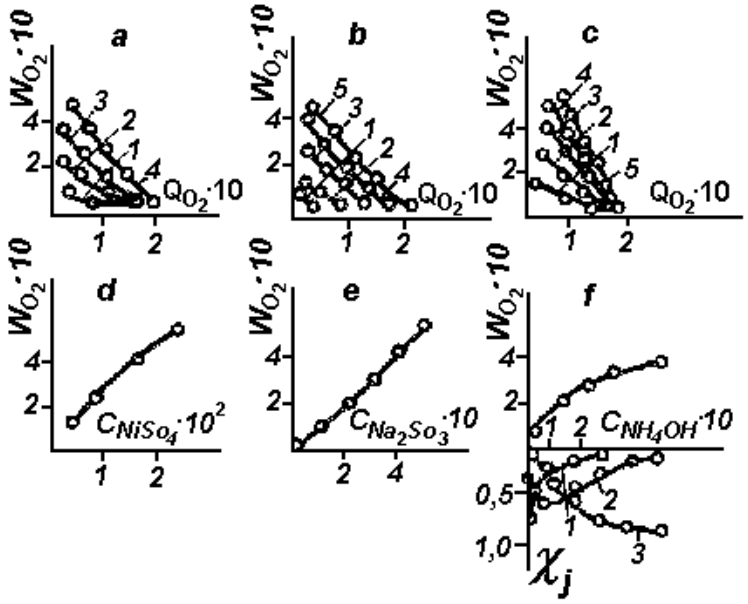
Table 2

Energy (λ, nm) and oscillator force (I) of electronic transferrings in solvate complexes I - III, calculated by a method ZINDO/S.

Pattern	Electronic transferring	λ	I
Ia	σ→ ((N) d)	248,7	0,2191
	σ→ ((N) d)	243,4	0,3329
Ib	σ→ ((N) d)	225,1	0,4738
IIa	σ→ ((N) d)	286,3	0,2272
IIb	→(dd)	312,4	0,0400
	→ (dd)	291,0	0,0760
	σ→ ((N) d)	241,3	0,0640
IIc	σ→((N) d)	384,7	0,1095
	σ→ ((N) d)	261,1	0,1605
	→ (dd)	234,2	0,0795
IIIa	σ→((O^8) +ds (Co))	375,6	0,1576
	σ→((O^7) +dd)	333,9	0,0822
	σ→σσ ((O^8) +d (Co) + (s))	216,3	0,2849
IIIb	σ→((O^9) d)	349,6	0,1581
	σ→ ((O^8) +dd)	345,5	0,1406
	→σ(d (Co) +d)	339,2	0,4885
	σ(d + (Co)))	288,2	0,1863
	→ (ds (Co))	247,2	0,4843
IIIc	→(d+s (Co) d+s (Co))	337,8	0,5401
	σ→ (d+s (Co) + (O^9) d+s (Co))	291,0	0,1967
	→ (d+s (Co) d+s (Co))	248,8	0,5346
IIId	→ (dd)	353,8	0,1201
	→(d+s (Co) d+s (Co))	322,3	0,7843
	σ→ (d+s (Co) + O^{10}) d+s (Co))	279,1	0,1894
	→σ (d (S+O^{10}))	245,9	0,4012

We have shown, that the nickelammine compounds are active and selective oxidation catalysts of sodium sulphite (SO_2 donor) by oxygen in low-temperature area in aqueous solution $NiSO_4$ - NH_4OH - H_2O (fig. 5).

The typical conversion curves in coordinates $WO_2 = f(QO_2)$ are presented in fig. 5. The conversion curves have falling nature, the quantity of the absorbed oxygen does not depend on initial $NiSO_4$ concentration in solution $NiSO_4$ - Na_2SO_3 - NH_4OH - H_2O and the proportion $C_{Na_2SO_3} / Q_{O_2}$ strictly corresponds to stoichiometry of the reaction.



a), d): $W_{O_2}(Q_{O_2}) = f(C_{NiSO_4})$; b), e): $W_{O_2}(Q_{O_2}) = f(C_{Na_2SO_3})$;

c), f): $W_{O_2}(Q_{O_2}) = f(C_{NH_4OH})$; χ_j: 1.-$Ni(NH_3)_2$; 2.- $Ni(NH_3)_3$; 3.- $Ni(NH_3)_4$.

Fig. 5. Oxidation of sulphur dioxide by oxygen in the presence of the nickelamine compounds. $P_{O_2} = 10^5$ Pa, T=313K

The dependence of the rate of oxygen absorption (WO_2 at $QO_2 \to 0$) upon initial concentration of nickel sulphite in solution $NiSO_4$ - Na_2SO_3 - H_2O (fig. 6d) is described by the equation of the first order: $WO_2 = k \cdot CNiSO_4$ at 30°C, k = 1,25 min^{-1}.

In all studied area of CNa_2SO_3 sodium sulfate is the only product of sodium sulphite oxidation, the proportion $C_{Na_2SO_3}/Q_{O_2}$ is conserved equal to two, applicable to stoichiometry of reaction (36) and directly proportional dependence between Na_2SO_3 oxidation rate (WO_2 at $QO_2 \to 0$) and initial Na_2SO_3concentration in solution is observed (fig. 6e).

$$WO_2 = k \cdot CNiSO_4 \text{ at } 30°C \; k = 1{,}25 \text{ min}^{-1}$$

In the researched interval of C_{NH_4OH} the rate of oxygen absorption in system $NiSO_4$ - Na_2SO_3 - NH_4OH is determined by accumulation of complex $Ni(NH_3)_4^{2+}$ fraction (fig. 5):

$$W_{O_2} = k \cdot \chi_{Ni(NH_3)_4^{2+}}$$

The solution of this equation on the data of function $WO_2 = f(CNH_4OH)$ has allowed to determine an equilibrium constant (9) and partial activity of the complex $Ni(NH_3)_4^{2+}$ in reaction.

$$Ni(NH_3)_3^{2+} + NH_3 \xleftrightarrow{\alpha_4} Ni(NH_3)_4^{2+} \quad (9)$$

The calculated magnitudes k and α_4 at 30°C are equal to: $1{,}16 \text{l} \cdot \text{mole}^{-1} \cdot \text{min}^{-1}$ and 5,4 $\text{l} \cdot \text{mole}^{-1}$ respectively. The value of stability constant for $Ni(NH_3)_4^{2+}$ is close to applicable magnitude cited in [6], that points correctness of the chosen fragment, responsible for catalysis of sodium sulphite oxidation by oxygen.

We have shown, that the nickel complexes fixed on polyethyleneimine are more active and more stable in reactoin (1), than nickel ammines.

The typical conversion and potentiometric curves in coordinates $WO_2 = f(QO_2)$ and $jO_2 = f(QO_2)$) are presented in fig. 6. $CNiSO_4$ changes in an interval from $2 \cdot 10^{-4}$ to $3 \cdot 10^{-2} \text{mole} \cdot \text{l}^{-1}$. Depending on initial concentration of $NiSO_4$ different forms of conversion curves $WO_2 = f(QO_2)$ are observed. Conversion curves have falling nature in the interval of $CNiSO_4$ from $0{,}2 \cdot 10^{-3}$ to $1{,}0 \cdot 10^{-3} \text{mole} \cdot \text{l}^{-1}$, at that condition directly proportional dependence between rate of the oxygen absorption (WO_2 at $QO_2 \to 0$) and initial concentration of $NiSO_4$ in solution is observed:

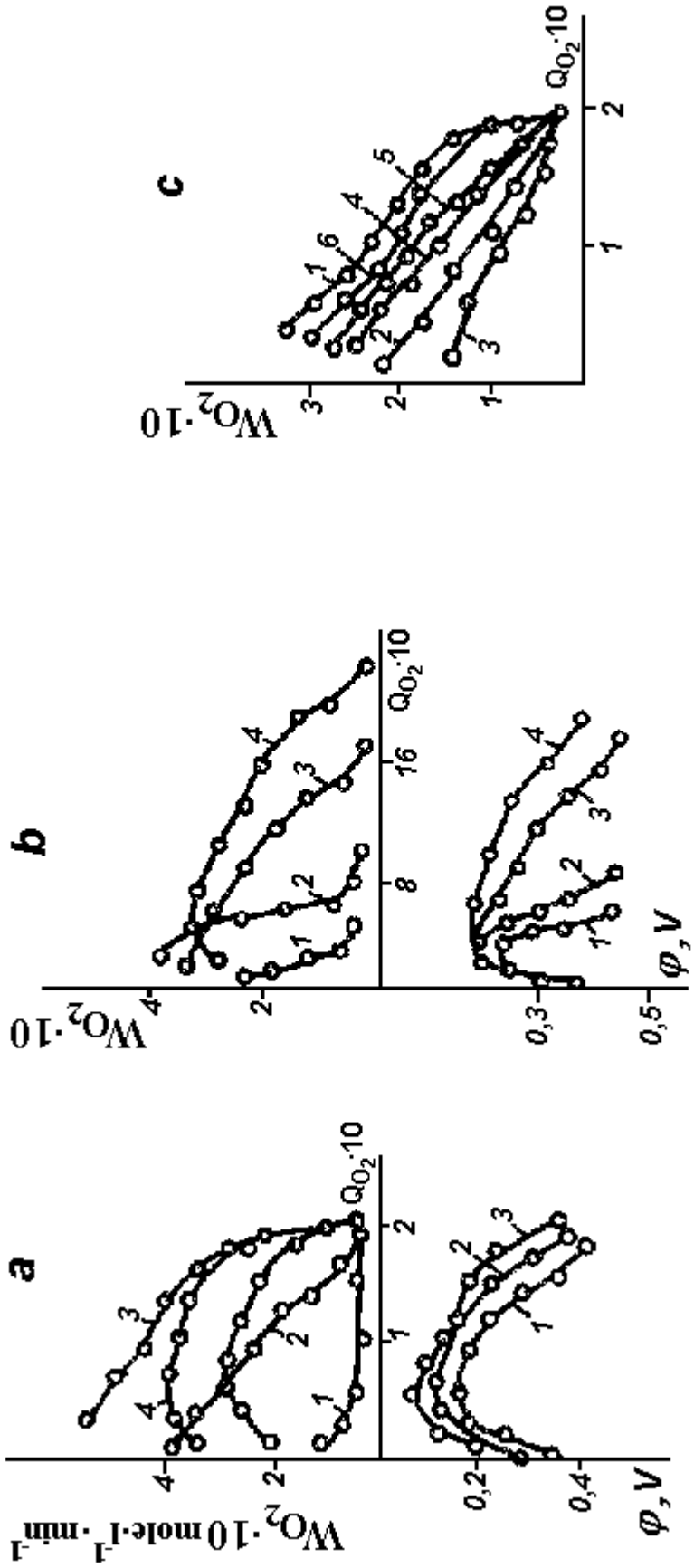


Fig. 6. Oxidation of sulphur dioxide by oxygen in the presence of the nickel complexes fixed on PEI P_{O_2} = 105Pa, T=303K;

a): $W_{O_2}(Q_{O_2}) = f(C_{NiSO_4})$; b): $W_{O_2}(Q_{O_2}) = f(C_{Na_2SO_3})$; c), e): $W_{O_2}(Q_{O_2}) = f(C_{HClO_4})$; d), f): $W_{O_2}(Q_{O_2}) = f(C_{PEI})$;

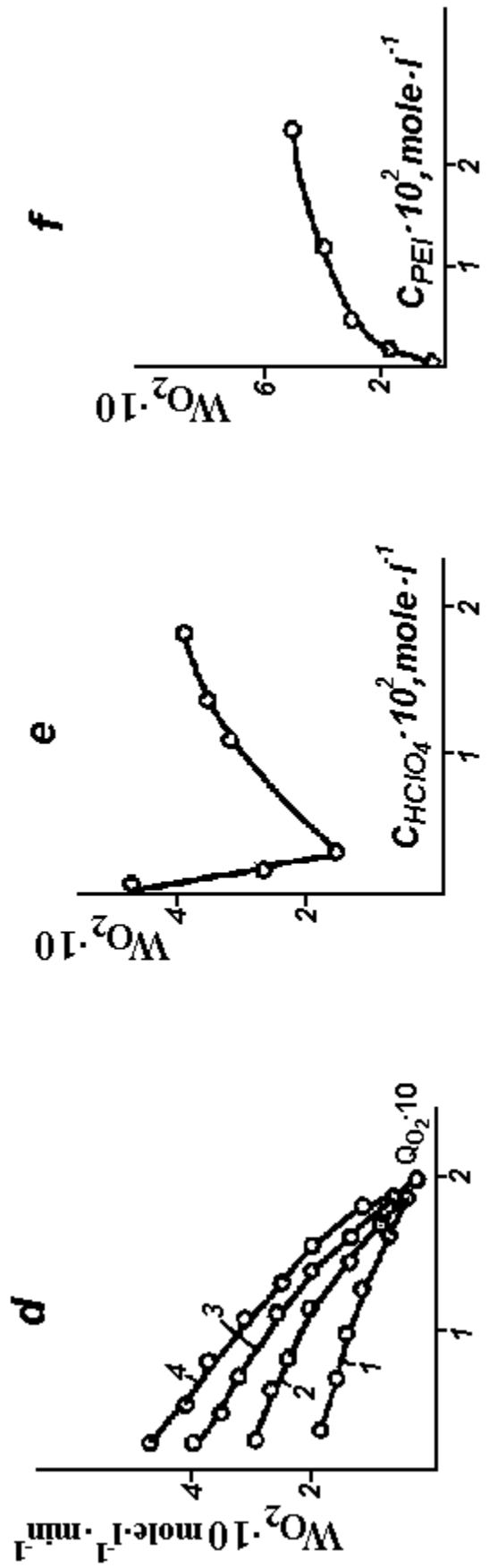


Fig. 6. Oxidation of sulphur dioxide by oxygen in the presence of the nickel complexes fixed on PEI P_{O_2} = 105Pa, T=303K;

a): $W_{O_2}(Q_{O_2}) = f(C_{NiSO_4})$; b): $W_{O_2}(Q_{O_2}) = f(C_{Na_2SO_3})$; c), e): $W_{O_2}(Q_{O_2}) = f(C_{HClO_4})$; d), f): $W_{O_2}(Q_{O_2}) = f(C_{PEI})$;

$WO_2 = k \cdot CNiSO_4$ at 30°C $k = 89\ min^{-1}$

In the interval of $CNiSO_4 \sim 10^{-2}\ mole \cdot l^{-1}$ the first order of reaction (1) on $CNiSO_4$ is broken, the functions $WO_2 = f(QO_2)$ become autocatalitical, similar of thouse, which are observed at catalysis of the reaction (1) by cobalt complexes fixed on polyethileneimine, and which suppose involvement of the binuclear complex containing metal in the initial and reduced form. In this case kinetic laws are described by equation (10):

$$WO_2 = k \cdot CNi^{3+} \cdot CNi^{2+}$$

at 30°C, $k = 2{,}8 \cdot 10^{1} l \cdot mole^{-1} \cdot min^{-1}$ (10)

Also the conversion curves depending on CNa_2SO_3 change the nature: at CNa_2SO_3 to $0{,}4\ mole \cdot l^{-1}$ the functions $WO_2 = f(QO_2)$ have falling nature, and at further increasing of CNa_2SO_3 the conversion curve obtain autocatalytical nature. The received results point that the increasing of electron-donor concentration in solution promotes formation of binuclear complexes.

The dependence of the rate of sodium sulphite oxidation by oxygen upon CNa_2SO_3 in the interval of CNa_2SO_3 to $0{,}4 mole \cdot l^{-1}$ described by equation (11):

$$W_{O_2} = \frac{k_1 \cdot C_{Na_2SO_3}}{1 + \beta_1 \cdot C_{Na_2SO_3} + \beta_1 \cdot \beta_2 \cdot C_{Na_2SO_3}} \qquad (11)$$

where b_1 è b_2 – equilibrium constants:

$$Ni^{2+}aq + SO_3^{2-} \xleftrightarrow{\beta_1} NiSO_3 aq + H_2O$$
$$NiSO_3 aq + SO_3^{2-} \xleftrightarrow{\beta_2} Ni(SO_3)_2 + H_2O$$

The solution of the equation (11) by the method of least squares has allowed to determine parameters of equation (11), they are compared at 30°C below:

b_1, $l \cdot mole^{-1}$	b_2, $l \cdot mole^{-1}$	k, min^{-1}
0,81	0,12	$5 \cdot 10^2$

The influence of polyethyleneimine concentration on the rate of oxygen absorption is investigated in the interval C_{PEI} from 0 to $23 mole \cdot l^{-1}$ (fig. 6b,d,f). Conversion curves $WO_2 = f(QO_2)$ in all investigated area PEI have falling nature, in each case the redox-potential of system is returned to the initial value at the end of experiment. The dependence of oxygen absorption rate (WO_2 at $QO_2 \rightarrow 0$) upon concentration of polyethyleneimine (fig. 6f) is described by equation (12)

$$W_{O_2} = \frac{k_1 \cdot \alpha_1 \cdot C_{PEI}}{1 + \alpha_1 \cdot C_{PEI}}, \qquad (12)$$

where α_1 - constant of following equilibrium:

$$NiSO_{3aq} + PEI \xleftrightarrow{\alpha_1} NiSO_3 \cdot PEI + H_2O$$

The magnitudes of α_1 and k_1 found from solution of equations (12) at 30°C are equal to $2{,}5 \cdot 10^3 mole$ and $3{,}5 \cdot 10^2\ min^{-1}$ respectively.

The results of influencing of oxygen partial pressure in O_2 - Ar gas mixture on rate of Na_2SO_3 oxidation in system $NiSO_4$ - PEI - Na_2SO_3 - H_2O are summarized in Tab. 3.

Table 3

Influence of oxygen partial pressure on reaction (36) rate in solution $NiSO_4$ - PEI - H_2O.
t = 303K, $CNiSO_4 = 2 \cdot 10^{-4} mole \cdot l^{-1}$, $CNa_2SO_3 = 0{,}4 \cdot 10 mole \cdot l^{-1}$

PO_2, atm	$WO_2 \cdot 10$, $mole \cdot l^{-1} \cdot min^{-1}$	ΣQO_2, $mole \cdot l^{-1}$	j_i, V	j_e, V
0,29	0,8	0,10	0,52	0,40
0,4	1,2	0,13	0,52	0,45
0,6	1,6	0,15	0,52	0,47
0,8	1,9	0,2	0,52	0,52
1,0	2,0	0,2	0,52	0,52

From the table data it follows that at PO_2 > 0,8 atm the stoichiometry of reaction is maintained, potential of system (j_e) is returned to the initial value (j_i). At smaller values of PO_2 the violation of stoichiometric ratio CNa_2SO_3 / QO_2, and consequently also violation of process selectivity in relation to natrium sulphate is observed. In solution beside with Na_2SO_4 the sodium dithionate accumulates. The dependence of oxygen absorption rate on its partial pressure in gas mixture is mathematically described by expression (13)

$$W_{O_2} = \frac{k \cdot \gamma \cdot P_{O_2}}{1 + \gamma \cdot P_{O_2}} \qquad (13)$$

The interesting results are received with the introducing $NiSO_4$ - PEI - Na_2SO_3 - H_2O acid in system and variation C_{H^+}. Chloric acid is chosen as proton-donor agent, as the chlorate - ion does not form strong complexes with nickel associations. $CHClO_4$ changes in the interval from 0 to $1{,}5 \cdot 10^{-2}\,mole \cdot l^{-1}$. The results are presented in fig. 6c,e. In the investigated area of $CHClO_4$ the absorbed oxygen quantity does not depend on acidity of environment and corresponds to the stoichiometry of reaction (1). In all investigated interval of C_{H^+} the conversion curves $WO_2 = f(QO_2)$ have falling nature indicating involvement of mononuclear complexes of nickel in limiting stage. The dependence of oxygen absorption rate (WO_2 at $QO_2 \rightarrow 0$) upon initial concentration of chloric acid (fig. 6e) has complex nature. In the interval of C_{H^+} from 0 to $4 \cdot 10^{-3} mole \cdot l^{-1}$ with further increasing of oxygen absorption rate in the area of $CHClO_4$ from $4 \cdot 10^{-3}$ to $1{,}5 \cdot 10^{-2} mole \cdot l^{-1}$ the fall of WO_2 is observed. Mathematically the function $WO_2 = f(CHClO_4)$ is described by the expression:

$$W_{O_2} = \frac{k_1 \cdot \sigma_1 \cdot \sigma_2 \cdot C^2_{H^+}}{1 + \sigma_1 \cdot C_{H^+} + \sigma_1 \cdot \sigma_2 \cdot C^2_{H^+}} \qquad (14)$$

The consideration of possible protolytic equilibriums in system $NiSO_4$ - Na_2SO_3 - O_2 - H_2O - PEI allows to suppose, that s_1 and s_2 are constants of the following equilibriums:

$$PEI \cdot Ni(SO_3)O_2 + H^+ \xleftrightarrow{\sigma_1} PEI \cdot Ni(HSO_3)O_2^+ \qquad (15)$$

$$PEI \cdot Ni(HSO_3)O_2^+ + H^+ \xleftrightarrow{\sigma_1} PEI \cdot Ni(HSO_3)HO_2^{2+} \qquad (16)$$

The negative influence of environment acidity on oxygen absorption rate is connected, in our opinion, with decreasing of donor activity of SO_3^{2-} as a result of it protonization with formation of less active electron-donor – SO_3^{2-} on stage (15). Apparently the positive effect C_{H^+} is conditioned by increasing of oxygen acceptor capacity as a result of it protonization on (16). The constants of reaction rate (k_1) and constants of equilibrium (15, 16) found by the solution of equation (14) are presented below:

s_1, $l \cdot mole^{-1}$	s_2, $l \cdot mole^{-1}$	k, min^{-1}
$8{,}4 \cdot 10^2$	0,19	$7{,}2 \cdot 10^2$

It is interesting to trace the influence of the ligand combined to nickel nature, on catalyst activity in reaction (1). Nickel nitrate, sulphate and chloride are chosen as objects of researching. The conversion curves are received in the field of nickel concentration, in the presence of binuclear complexes and the conversion curves have autocatalytical nature.

Behavior of three systems is similar, however, they differ on activity. Three systems are compared in identical conditions. The magnitudes of W_{O_2} (at $Q_{O_2} = 9 \cdot 10^{-2} mole \cdot l^{-1}$) for the studied complexes beside with value of oxidizing dimerization potential of ligands ($j^0 X_2 \leftrightarrow 2X$) are indicated below:

Complex	$W_{O_2} \cdot 10^{-2} mole \cdot l^{-1} min^{-1}$	lg W	$j^0 X_2 \leftrightarrow 2x^-$, V
$NiSO_4$	$2{,}7 \cdot 10^{-2}$	-1,52	2,01
$NiCl_2$	$3{,}7 \cdot 10^{-2}$	-1,42	1,36
$Ni(NO_3)_2$	$5{,}0 \cdot 10^{-2}$	-1,35	0,79

From results it follows, that the higher donor capacity of ligand in cobalt surrounding, the higher catalytic activity of complexes in reaction (1), linear dependence between lgW and $j^0X_2 \leftrightarrow 2X$ is observed at that. It allows to suppose, that the studied ligands play role of electrons bridge between two atoms of cobalt in such complicated system.

Thus, we studied the kinetics of the oxidation of sodium sulphite by oxygen in the presence of the cobalt and nickel complexes fixed on polyethyleneimine. The received results allow to suppose the following scheme of the mechanism:

$$(PEI)_3M^{2+} + SO_3^{2-} \leftrightarrow (PEI)_3MSO_3 \quad (17)$$

$$(PEI)_3MSO_3 + PEI \leftrightarrow (PEI)_4MSO_3 \quad (18)$$

$$(PEI)_4MSO_3 + PEI \leftrightarrow (PEI)_5MSO_3 \quad (19)$$

$$(PEI)_4MSO_3 + H^+ \leftrightarrow (PEI)_4MHSO_3^+ \quad (20)$$

$$(PEI)_4MHSO_3^+ + O_2 \leftrightarrow (PEI)_4M(O_2)HSO_3^+ \quad (21)$$

$$(PEI)_4M(O_2)HSO_3^+ + H^+ \leftrightarrow (PEI)_4M(HO_2)HSO_3^{2+} \quad (22)$$

$$(PEI)nM(H_2O)_2^+ + MCl_2 \leftrightarrow (PEI\text{-}M\text{-}Cl\text{-}M)^{4+} \quad (23)$$

$$(PEI)_4M(HO_2)HSO_3^{2+} \xrightarrow{k} M(PEI)_4^{2+} + H_2SO_4 \quad (24)$$

$$PEI\text{-}M\text{-}Cl\text{-}M\text{-}PEI + O_2 \leftrightarrow PEI\text{-}M\text{-}Cl\text{-}M\text{-}PEI \quad (25)$$

$$PEI\text{-}M(O_2)ClMPEI + jSO_3^{2-} \leftrightarrow PEI(SO_3)jM(O_2)ClMPEI \quad (26)$$

$$PEI(SO_3)jM(O_2)ClMPEI \rightarrow PEIM\text{-}Cl\text{-}MPEI + H_2SO_4 \quad (27)$$

On equilibrium stages (17) - (23) there is forming of the intermediate complex containing mononuclear metalcomplex with definite number macroligand: 3-5, the optimal number macroligand in internal sphere of metalcomplex is equal to four. The activation of oxygen occurs by formation of superoxocomplex on (21). In the limiting act (24) there is redox-disintegration of intermediate compound to emanating of metal complex fixed on PEI and product of reaction - sulfuric acid.

On equilibrium stages (25, 26) the dimeric metalcomplex, which is fixed on a polymeric matrix is formated, the oxygen joins in the form of μ-peroxocomplex of complex and in the limiting act (27) intrasphere oxidation of SO_3^{2-} by the activated oxygen with formation of reaction product occures.

Conclusion

It has been stated that cobalt and nickel complexes, fixed on polyethileneamine are the good catalysts for sulphur dioxide oxidation by oxygen. The kinetics of this process has shown that the SO_2 and O_2 interact in inner sphere mechanism, in the presence of this complex system. The oxygen activation has been carried on binuclear structures on cobalt complexes and on mononuclear and binuclear structures depending on nature of the ligands in inner sphere of the complexes. UV-spectra and the quantum-chemical accounts confirm this assumption.

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Received 30 October 1999