The effectiveness of degenerate branching of the chains upon catalyzed decomposition of ROOH can be estimated from the parameter

$$\gamma = W_b/2W_i,$$

where W_b is the rate of the degenerate branching of the chains. The value of W_b was determined from the consumption rate of the effective acceptor of the free N-phenyl-β-naphthylamine radicals under the condition that all of the free radicals formed react with the acceptor (Table 1).

From the data in Table 1, $\gamma = 1.5 \cdot 10^{-2}$ (70°C), $1.1 \cdot 10^{-2}$ (80°C), and $7.7 \cdot 10^{-3}$ (90°C), i.e., $\gamma \ll 1$ and approaches zero at further increases in temperature. Contrary to that, for the familiar metallocomplex catalysts of hydroperoxide decomposition $\gamma < 1$ at about 90°C, differing from 1 but very little, and at temperatures above 90°C γ approaches unity [7, 8]. Apparently all the features of CoL_2O_2 investigated by us are associated with the presence of coordinated =NOH groups, which are capable of reacting not only with $RO_2^{\cdot}$ generated in bulk, but also with the radicals formed as a result of ROOH decomposition in the internal coordination sphere.

Thus, the high antioxidative effectiveness of CoL_2O_2 in autoxidation of RH is explained by the manifestation of the double mechanism of its action: one-time chain termination through the reaction with the peroxide radicals and simultaneous catalytic decomposition of the hydroperoxide predominantly into molecular products.

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STUDY OF ADSORPTION EFFECTS USING ELECTRICAL RESISTANCE MEASUREMENTS OF THIN FILM ELECTRODES

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The method of studying adsorption and catalytic processes through resistance changes of thin metallic films or wires in gaseous phase is well known [1]. For a long time this method was used in electrochemical investigations merely to study the processes accompanied by changes in the volumetric properties of the electrode, for example, saturation of a palladium electrode with hydrogen [2]. It has been shown in recent years that changes in resistance ρ of thin metallic films in contact with the electrolyte also enable one to obtain information on the adsorption effects at the boundary line electrode/solution [3-9]. The interest in such measurements was aroused by the fact that they can characterize the structure of the metal coating of the electric double layer. Until now, however, no systematic studies have been carried out regarding the effect of the composition of solution on the re-

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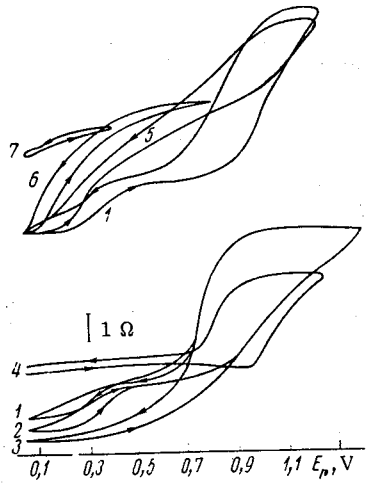

Fig. 1

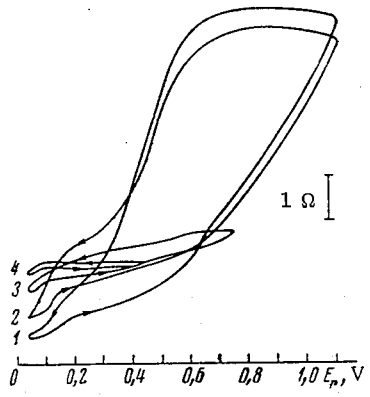

Fig. 2

Fig. 1. Dependence of Pt film resistance on potential in $5 \cdot 10^{-3}$ N H_2SO_4 (1), and with additions of $5 \cdot 10^{-3}$ N $ZnSO_4$ (2), $CdSO_4$ (3), Tl_2SO_4 (4), KCl (5), KBr (6), KI (7).

Fig. 2. Dependence of Rh film resistance on potential in $5 \cdot 10^{-3}$ N H_2SO_4 (1), and with additions of $5 \cdot 10^{-3}$ N KCl (2), KBr (3), KI (4).

sistance of thin film electrodes, and also for the comparison of the obtained data with the results of independent straight lines of the adsorption measurements.

We determined the dependence of resistance of Pt and Rh films on potential in acidic solutions containing various surface-active ions. The measurements of film resistance ρ changes were carried out using direct and alternating currents. In the latter case, the apparatus described in [10] was used. When measuring with alternating current, $5 \cdot 10^{-3}$ N H_2SO_4 was used as the supporting electrolyte. At such low electrolyte concentrations and low frequency of alternating current used (20-40 Hz), conductivity through the solution does not influence the results of the measurements of ρ. This is confirmed by the comparison of data obtained with the direct and the alternating currents. The measurements with direct current were carried out in 1 N H_2SO_4. Taking into account the effect of pH on the adsorption of the ions of solution, hydrogen and oxygen, the data in $5 \cdot 10^{-3}$ N H_2SO_4 are in satisfactory agreement with the data obtained in 1 N H_2SO_4.

Platinum and Rh films 120-150 Å thick were applied to devitrified glass by the method of cathodic vaporization in argon atmosphere at 10^{-2} mm Hg. Before measuring, the films were washed with bidistillate and subsequently subjected to electrochemical treatment in electrolyte solution by means of a cyclic variation of potential in E_r interval of 0.05-1.4 V (according to the reversible hydrogen electrode in the same solution) at a rate of 0.5-0.6 V/sec until a reproducible potentiodynamic I vs E_r curve had been obtained. After this, the electrode was maintained at $E_r = 0.05$ V until the establishment of a constant ρ value, and the triangular sweep of the potential was switched on at a speed of 1.4 V/sec during the operation of which $\Delta\rho$ vs E_r and I vs E_r curves were recorded on the double coordinate potentiometers LKD 4-003. It must be noted that after the cycling the shape of the I vs E_r curves on Pt and Rh films coincided with the curves for massive electrodes presented in the literature. Additions of the surface-active electrolytes were introduced into the supporting-electrolyte solution at $E_r = 0.05$ V, which enabled us to record the changing of ρ at a constant E_r. Solutions were freed of air oxygen by spectrally pure argon; the experiments were conducted at 20 ± 2°C.

Figures 1 and 2 present $\Delta\rho$ vs E_r curves in the studied systems (direction of the potential change during the recording of the curves is indicated by the arrows). On curves 1 (same as on I vs E_r curves), which pertain to the supporting-electrolyte solution, three characteristic regions can be distinguished for both metals: the hydrogen, the "double-layer," and the oxygen regions. In the "double-layer" region the film resistance increases

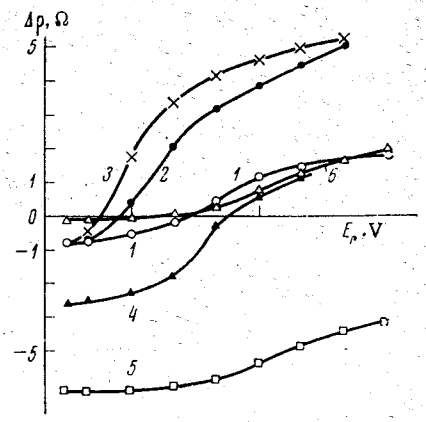

Fig. 3. The Δρ vs E_r curves calculated from Eq. (1) for Pt films in the following solutions: 1) 10^{-3} N H_2SO_4 + $3 \cdot 10^{-2}$ N Na_2SO_4; 2) 0.1 N KCl, pH = 2.3; 3) 10^{-3} N HBr + $3 \cdot 10^{-3}$ N NaBr; 4) 10^{-2} N H_2SO_4 + $3 \cdot 10^{-3}$ N $ZnSO_4$; 5, 6) 10^{-3} N H_2SO_4 + $3 \cdot 10^{-3}$ N Na_2SO_4 + Tl_2SO_4, whereby Γ_{Tl+} = 53 μl/cm².

with the displacement of the potential toward the positive side. It should be emphasized that Pt and Rh have no ideal "double-layer" region in sulfuric acid solutions but a rather gradual transition from the predominantly hydrogen adsorption to the predominantly oxygen adsorption takes place [11], even though the surface coverage with hydrogen and oxygen atoms in the potential region usually called the "double-layer" is not large. The "double-layer" region on rhodium is narrower than on platinum. Upon transition from the "double-layer" to the hydrogen regions, initially the lowering of film resistance takes place, but in the region of medium and heavy coverage of the surface with hydrogen ρ changes but little with E_r, whereupon a tendency toward an increase in resistance is observed as E_r approaches 0.05 V. The adsorption of oxygen leads to a sharp rise in Pt and Rh film resistances. In the oxygen region considerable hysteresis is observed between the anodic and the cathodic Δρ vs E_r curves. Let us note that Δρ vs E_r curves in $5 \cdot 10^{-3}$ N and 1 N H_2SO_4 solutions obtained by us are in agreement with an analogous curve in 1 M H_2SO_4 given in [9].

In the presence of $5 \cdot 10^{-3}$ N KCl and KBr the film resistance of Pt at E_r = 0.05 V does not change (Fig. 1, curves 5 and 6); however, at more anodic E_r the values of Δρ increase. The introduction of $5 \cdot 10^{-3}$ N KI at E_r = 0.05 V brings about a sharp increase in resistance (Fig. 1, curve 7). In the case of Rh films, the increase of resistance in the presence of all surface-active anions already takes place at E_r = 0.05 V (Fig. 2, curves 2-4) in accordance with the anion adsorption data on rhodium [12]. If anodic Δρ vs E_r curves are compared, it can be seen that the effectiveness of anion action increases in the series $Cl^- < Br < I^-$ in conformity with the increase of the surface activity in this series.

Zinc and Cd^{2+} cations, unlike the halogen anions, bring about a decrease of resistance of Pt (Fig. 1, curves 2 and 3) and Rh films. The interval of potentials in which this effect is detected fully coincides with the interval of the adsorption potentials of Zn^{2+} and Cd^{2+} on Pt and Rh, determined using the labeled atom method [13]. Adsorption of Tl^+ ions leads to an increase of the Pt film resistance at E_r = 0.05-0.70 V (Fig. 1, curve 4), and of Rh film resistance at E_r = 0.05-0.25 V.

The following basic factors, which determine the dependence of thin film electrode resistance ρ on the potential and the composition of solution are specified in [8, 11]: 1) the field of the electric double layer (the field effect); 2) the diffusion dispersion of free electrons by the adsorbed particles (the dispersion effect); 3) localization of the conductance electrons as a result of the chemical bond formation and the decrease of the thickness of the conducting layer upon strong chemisorption; 4) the emergence of new surface conditions upon adsorption of the solution components. The phenomena effected by the ad-

sorption of the hydrogen atoms on the surface of the metal should apparently be segregated into a special group [14]. The quantitative appraisal is thus far available only for the first two effects [6, 9]. According to [9]

$$\Delta\rho/\rho = -\alpha\Delta\varepsilon/q, \quad (1)$$

where α in principle can be either less or more than unity, $\Delta\varepsilon$ is the change of the electric double layer charge, q is the full free electron charge in the film per unit of surface area. Equation (1) was used [9] to analyze the conductivity data of the Pt films in H_2SO_4 and $HClO_4$ solutions. However, to calculate $\Delta\varepsilon$ the authors used the capacity values of the double Pt layer determined by the impulse methods. Actually, it is necessary to use the values of the free surface charges ε obtained under equilibrium conditions [11]. We carried out the calculation using such values, and its results are presented in Fig. 3.

Due to the absence of suitable data for Pt films, values for the platinized Pt electrode [12, 13, 15] in solutions were taken, differing somewhat in concentration from those used above. Therefore, only those conclusions from the comparison between the calculated and experimental data are presented further which cannot be substantially affected by the indicated circumstances.

The standardization of the calculated $\Delta\rho$ vs E_r curve in an acidified KCl solution was conducted over the section of the experimental $\Delta\rho$ vs E_r curve in the interval E_r = 0.5-0.7 V. A given solution was selected on the basis of its ability to exhibit an ideal double-layer region on Pt. The obtained value of the $\rho\alpha/q$ coefficient was used further to calculate $\Delta\rho$ vs E_r curves in other systems.

From the comparison of experimental (Fig. 1) and calculated (Fig. 3) curves it can be seen that in solutions containing SO_4^{2-}, Cl^-, Br^-, and Zn^{2+} ions, the field effect enables one to explain not only the sign but, in the first approximation, also the values of the resistance change of Pt films. It is difficult to expect a quantitative concurrence between the calculation and the experiment primarily due to a fact that in the calculations ε vs E_r curves for a platinized Pt electrode were used. The texture of the film surface may differ from the texture of the platinized Pt surface, which may lead to differences in the structure of the electric double layer on these Pt specimens.

If the adsorbed Tl^+ ions are directed to the ionic coating of the double layer, then one should expect a strong lowering of ρ in their presence (Fig. 3, curve 5). If the Tl^+ ions are directed to the metallic coating, a slight increase in ρ in accordance with the field effect in the hydrogen region, and a certain lowering of ρ compared to the sulfate ion solution at more anodic E_r must be observed (Fig. 3, curve 6). The strong increase of ρ in the presence of Tl^+ observed experimentally clearly points to a significant transfer of the charge when this ion is adsorbed on Pt. Besides, the effects of the 2)-4) type are probably beginning to enter into play.

Thus, in the case of weakly adsorbed ions the change of the film resistance is caused mainly by the field change effect, while in the presence of strong chemisorption, the dispersion effect, localization of the conductivity electrons, and the lessening of the conducting layer thickness should be taken into account.

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KINETIC POLYMERIZATION AND COPOLYMERIZATION CHARACTERISTICS OF SODIUM p-STYRENESULFONATE AND ACRYLAMIDE IN BINARY DIMETHYL SULFOXIDE—WATER MIXTURES

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As is known, the correct selection of the binary solvent mixture components permits variation not only in the kinetic and the statistic parameters [1, 2], but also the topology of the polymerization process [3] in the desired direction. This article examines the kinetic mechanisms of the homogeneous phase radical polymerization and copolymerization of sodium p-styrenesulfonate (SSS) and acrylamide (AA) in the mixed dimethyl sulfoxide (DMSO)—water media. The process rate was controlled by means of the polarographic method data [4]. In selecting the monomers and the components of the binary solvent mixture, we were guided by the following considerations.

1. In the working region of the degrees of conversion ψ ($\psi < 0.5$) the polymerization and copolymerization processes must be homogeneous for all compositions of the initial monomeric mixtures and of the binary solvents.

2. The physicochemical properties of the monomers to be investigated must be substantially different since this is precisely the case in which maximum differences in their behavior during polymerization and copolymerization can be expected. Therefore, one of the monomers to be investigated (AA) was nonionogenic, and the other (SSS) a strong electrolyte.

3. The initiator system must ensure a constant rate of free radical generation in all binary media under investigation. Preliminary measurements showed that the decomposition rate constant of azobis(isobutyronitrile) (ABI) does not depend on the composition of the binary solvents DMSO—water for all values of γ in the interval $0 \leqslant \gamma \leqslant 0.8$ (γ is the mass fraction of water in the DMSO—water mixture).

Initially, the homopolymerization kinetics of both monomers were investigated. Figure 1 presents in log—log coordinates the dependence of the homopolymerization rate on (SSS) and (AA) concentrations. The initial polymerization rates (V_1 and V_2) were calculated from the tangent of the inclination angle of tangents to the kinetic curves for $\psi \to 0$ [5]. As for the system dioxane—water investigated earlier [6, 7], the initial polymerization rate of (SSS) increases with the increasing γ, while the order of reaction with respect to monomer (n_1) changes inversely to the change in (V_1) (Fig. 1, curves 1-3). The values of n_1 were found to be equal to 1.35, 1.4, and 1.5 for γ values equal to 0.75, 0.25, and 0, respectively. The presence of a functional bond between V_1 and n_1 on the one hand and the composition of the binary solvent on the other can be explained by the dependence of the elementary rate constants of propagation k_p and termination k_t on the character of interactions in the system macroion—counterions—ionized monomer form [8]. It is clear that with the changes in the

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