THE BEHAVIOUR OF PLATINIZED-PLATINUM AND PLATINUM–RUTHENIUM ELECTRODES IN METHANOL SOLUTIONS

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There has been an increase in interest, recently, in the problems of (i) the nature of the platinum electrode potentials set up in solutions of organic substances and (ii) the adsorption of organic compounds and the mechanism of their electro-oxidation.

A systematic study of the potentials set up in solutions of alcohols and aldehydes at open circuit was first made by MÜLLER et al.[1]. Considerable experimental work on the investigation of the behaviour of a platinized-platinum (Pt/Pt) electrode in solutions of organic substances was carried out in the U.S.S.R. (for review of this work see ref. 2) and the nature of the potentials is discussed in a number of recently published papers[3-9]. There are two basic approaches to the solution of this problem: some authors[10-12] assume that the potentials set up are more or less determined by the oriented adsorption of organic substances, others[1,3,4,8,13]—by the adsorbed hydrogen, which appears on the electrode surface as the result of dehydrogenation of the original substances.

Layers of strongly adsorbed substances are formed on the surface of a Pt/Pt electrode in solutions of organic compounds[10,13]. As far as can be judged from the interpretation of the experimental results, most authors assume physically-adsorbed or reversibly chemisorbed molecules of the initial substances to be present on the surface. However, recent experimental data[14-16] show an irreversible chemisorption to occur, at least partially, on platinum in solutions of organic compounds; this is accompanied by a far-reaching dissociation of the original molecules. In this connection, it should be noted that the dissociative nature of the chemisorption of hydrocarbons and alcohols from the gaseous phase on the surfaces of the catalysts is a well-known phenomenon and has been studied in detail in a number of works on catalysis (*e.g.*, refs. 17 and 18).

The mechanism of electro-oxidation* of alcohols and aldehydes has been discussed[1,13,15,19-24]. Some investigators assume the electron transfer to be the rate-determining step of the process[19,20,15]; according to others it is a chemical reaction—dehydrogenation or interaction with OH radicals[1,21-24].

A number of investigations[1,25,26] have been made to compare the catalytic activity of different metals and their alloys in electro-oxidation reactions of organic substances.

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* We consider here the mechanism of electro-oxidation of alcohols and aldehydes at low φ_r (below ~ 0.8 V). The kinetic characteristics of the processes at higher potentials have been studied much less comprehensively.

The present paper is concerned with the principal results in the investigations, carried out in our laboratory, of the behaviour of a Pt/Pt electrode in solutions of saturated alcohols and aldehydes and the methanol electro-oxidation on composite electrolytic deposits of platinum and ruthenium and palladium and ruthenium.

EXPERIMENTAL TECHNIQUE

The processes occurring after the introduction of the electrode into solutions of organic substances were investigated by means of the method suggested in refs. 10 and 13 and elaborated in more detail in ref. 8. JOHNSON AND KUHN[37] quote PAVELA as the only author of this method, although in reality it was proposed for the first time by SHLYGIN[10]. The substance under investigation was introduced into the electrolyte solution in which the electrode, polarized to the desired potential, was immersed and the change in the potential with time was measured. After the establishment of a steady potential, the solution with the substance under investigation was drained off and the electrode washed with a number of consecutive portions of the oxygen-free electrolyte. In the last portion, the charging curves or the potentiostatic curves, designated in the present paper as the $Pt(X_{ads})$ curves where X is the substance under investigation, were measured.

Kinetic measurements were performed on rotating platinized-platinum electrodes. During the measurements of the steady-state polarization curves, the electrode was polarized with a current of constant strength until the change in its potential became less than 0.1 mV/min.

The electrodes were platinized in 2% H_2PtCl_6 solution at current densities of 2–4 mA/cm² (Pt/Pt electrode). The true surface of the electrodes was determined from the length of the hydrogen arrest in 0.1 N H_2SO_4[8] and for different electrodes was equal to 150–1600 cm² per cm² of apparent surface.

Composite deposits of platinum and ruthenium were obtained by electro-deposition from 1% $(H_2PtCl_6 + K_2RuNOCl_5)$ with a varying Pt : Ru ratio at a current density of 2 mA/cm². Palladium–ruthenium catalysts were deposited on a platinum plate from 1% $(PdCl_2 + K_2RuNOCl_5)$ at a current density of 6 mA/cm². Usually, the weight of the deposits was 3.5–5 mg/cm². Their composition was determined using $K_2RuNOCl_5$ tagged with ^{106}Ru.

Commercial-grade organic compounds purified by distillation in a rectifying column were used in the experiments.

The values of the potentials measured against the reversible hydrogen electrode in the same solution are denoted by φ_r and those measured against N.H.E.—by φ. The measurements were performed at room temperature, $20 \pm 2°$.

EXPERIMENTAL RESULTS AND DISCUSSION

We have studied the behaviour of a platinized-platinum electrode in solutions of saturated alcohols from methyl to butyl alcohol, their aldehydes and formic acid. Since the processes determining the behaviour of a Pt/Pt electrode in methanol solutions proved to be simpler in some respects than those for higher alcohols and aldehydes, the discussion of the experimental material is divided into two parts. The first part is concerned with the data on methanol.

1. The nature of the potentials of a Pt/Pt electrode in methanol solutions[27]

Figure 1 shows the curves of the shift in φ_r of a Pt/Pt electrode after the introduction of methanol, at different initial potentials, $\varphi_r{}^0$. It is clear from the figure that the value of $\varphi_r{}^1$, which is set up after the introduction of methanol, depends only slightly on $\varphi_r{}^0$ as long as the latter is confined to the double-layer region (350–750 mV).
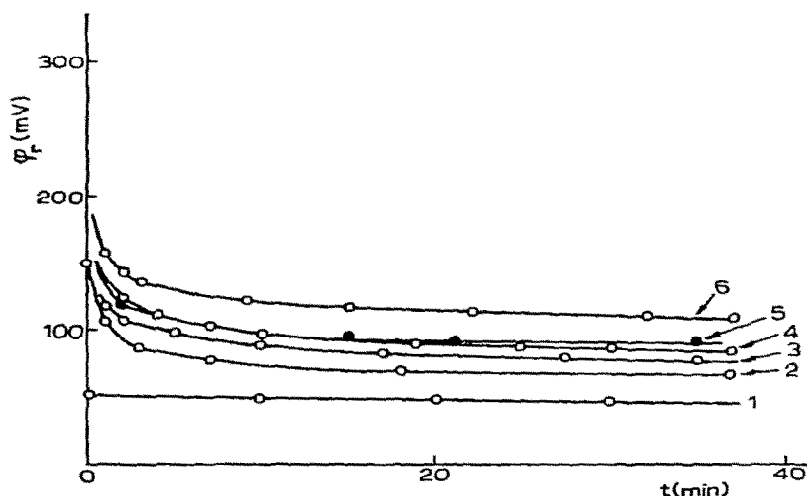

Fig. 1. Dependence of the curves of the potential shift on a Pt/Pt electrode after introduction of CH₃OH. (0.7 *M* CH₃OH + 0.1 *N* H₂SO₄), upon the initial potential: (1), 53; (2), 151; (3), 425; (4), 492; (5), 745; (6), 992 mV.

At low $\varphi_r{}^0$ the difference in $\varphi_r{}^1$ becomes appreciable. The value of $\varphi_r{}^1$ changes only slightly with changing pH of the solution. Thus, 45 min after the introduction of methanol at $\varphi_r{}^0 = 500$ mV, the Pt/Pt electrode showed the following potential values: 0.3 *N* H₂SO₄ (pH 0.75), 100 mV; 0.3 *N* (KH₂PO₄+KOH) (pH 5.3; 7.7; 11.3), 111, 114 and 117 mV, respectively; 0.1 *N* KOH (pH 13), 112 mV.

This slow establishment of the potential is characteristic of methanol solutions. Thus, 40–60 min (the usual time) after the introduction of the alcohol at φ_r in the double-layer region, $\partial\varphi_r/\partial t$ still amounts to 0.1–0.2 mV/min. Regardless of its concentration, when methanol is introduced at $\varphi_r{}^0$ close to zero, the potential of the Pt/Pt electrode shifts only in the direction of more negative values and no gas is evolved. To explain this behaviour, it should be assumed that, unlike other alcohols of the fatty series[9,28], methanol is not hydrogenized at an appreciable rate on a Pt/Pt electrode at $\varphi_r > 0$. However, as it was found by us recently, the hydrogenation of methanol occurs at 80° already with a measurable velocity.

After the Pt/Pt electrode is washed free of methanol, the charging curve (curve 2, Fig. 2) shows two arrests, one of which, (a), corresponds to the oxidation of the adsorbed hydrogen and the other, (b), to the oxidation of a strongly chemisorbed substance.

As the adsorption measurements were performed on electrodes with different true-surface values, the following quantities will be used henceforth in the analysis of the charging curves of Pt(X_{ads}): the adsorption coefficient, K, equal to the ratio of the quantity of chemisorbed substance to that of hydrogen $Q_H{}^0$, which is adsorbed in the supporting electrolyte solution at $\varphi_r = 0$ (all adsorption values are expressed in

terms of the amount of electricity expended in the oxidation of the adsorbed substance); the coefficient, m', equal to the ratio of the quantity of hydrogen adsorbed on the Pt/Pt electrode surface in the solution of the organic substance at φ_r^1, to Q_H^0; the coefficient, m, calculated in the same way as m', the only difference being that in this case the hydrogen section of the charging curve is extrapolated to $\varphi_r = 0$. A graphical calculation of the adsorption coefficients is shown in Fig. 2· $K = l_2/l_1$, $m' = l_3/l_1$, $m = l_4/l_1$.

When the electrode true-surface decreases with time, the adsorption coefficients, as the experiment showed, remain constant within experimental errors ($\pm 10\%$).

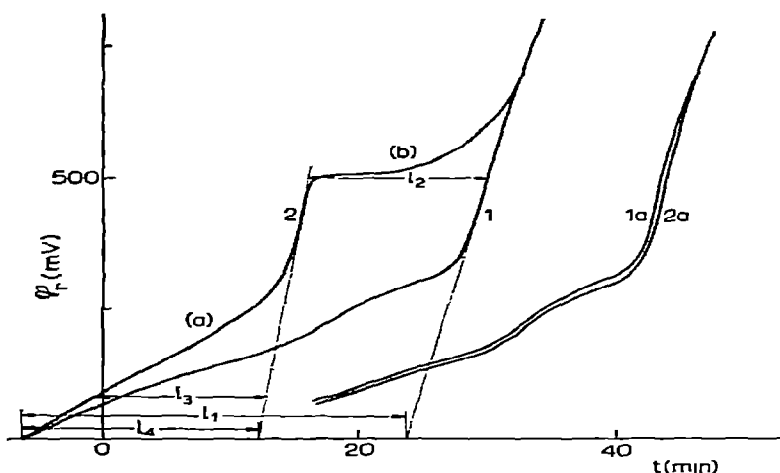The potentiostatic curve of Pt(CH$_3$OH$_{ads}$) (curve 2, Fig. 3) shows two waves.

Fig. 2. (1, 1a), Anodic and cathodic charging curves in a 0.1 N H$_2$SO$_4$ supporting electrolyte soln.; (2, 2a), anodic and cathodic charging curves after washing the Pt/Pt electrode free of CH$_3$OH. Concn. CH$_3$OH, 0.5 M; $\varphi_r^0 = 500$ mV; $i = 1 \cdot 10^{-4}$ A/cm^2.
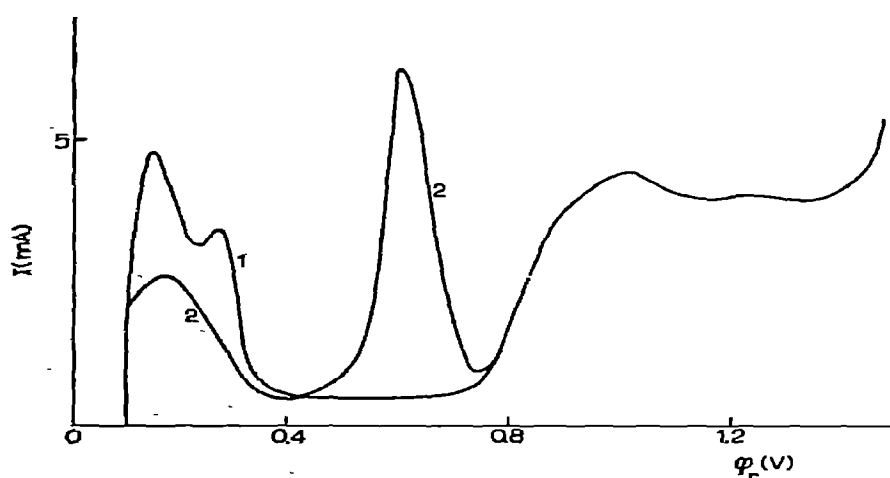

Fig. 3. (1). Potentiostatic curve in 0.1 N H$_2$SO$_4$ supporting electrolyte soln.; (2), potentiostatic curve of electro-oxidation of the substance chemisorbed in a CH$_3$OH soln. at open circuit. Concn. CH$_3$OH, 0.5 M; $\varphi_r^0 = 400$ mV; visible electrode surface, 1.78 cm^2; rate of potential increase, 5 mV/sec.

the first corresponding to the oxidation of the adsorbed hydrogen and the second to the oxidation of the chemisorbed alcohol. The calculation of the adsorption coefficient, K, on the basis of the curves in Fig. 3 is in good agreement with the results of galvanostatic measurements.

It follows from galvanostatic and potentiostatic measurements in 0.1 N H_2SO_4 that after the introduction of methanol at φ_r in the double-layer region, more than 40% of the electrode surface ($m' \approx 0.45$) is covered with adsorbed hydrogen. The charging curves of $Pt(CH_3OH_{ads})$ measured in phosphate buffer solutions and in 0.1 N KOH also show the presence of large amounts of hydrogen.

On the basis of the experimental data obtained, it can be concluded that in the presence of methanol, the shift of the potential of a Pt/Pt electrode is determined by the dehydrogenation reaction, and its final value by the following reactions:

$$H^+ + \bar{e} \rightleftarrows H_{ads} \tag{1}$$

or

$$H_2O + \bar{e} \rightleftarrows H_{ads} + OH^- \tag{1a}$$

Because of the large value of the exchange current of reactions (1) and (1a), the potential that is established should be close to the equilibrium potential of reaction (1) in acid solutions or to that of reaction (1a) in alkaline solutions.

2. The nature of the substance chemisorbed on a Pt/Pt electrode from methanol solutions at open circuit

The experimental results in ref. 14 and those obtained by us[29] show that on the surface of a Pt/Pt electrode in methanol solutions, the products of the decomposition of the methanol are chemisorbed. The conclusions concerning the nature of these particles[29] were drawn on the basis of the measurements in dilute methanol solutions.

After the introduction of methanol, there is a large decrease in the rate of the shift in φ_r as the concentration decreases. In sufficiently dilute methanol solutions, the electrode could be washed at different φ_r after the introduction of the alcohol so that the change in φ_r in the process of washing was insignificant. Regardless of methanol concentration and the potentials at which the electrode was washed, the quantities of the adsorbed substance and hydrogen always proved to be approximately proportional, with the factor of proportionality close to 1 ($K \approx m'$). Actually, the values of the coefficients K and m' are determined only by those of φ_r of the washing, these values being the greater the smaller φ_r. The experimental data obtained can be explained by assuming that it is particles of the composition HCO, which are formed as the result of the methanol molecule losing three hydrogen atoms, which are predominantly chemisorbed on the surface.

The adsorption measurements at open circuit, corresponding to the methanol introduction at different φ_r^0 before oxygen deposition (~ 800 mV), show that the sum of the coefficients K and m is always close to 1. Therefore, it can be supposed that a chemisorbed particle occupies as many sites for hydrogen adsorption (platinum atoms) as it gives off electrons (n) during oxidation. Assuming $n = 3$, we find that the chemisorbed particle occupies ~ 23 Å^2.

On the basis of the analysis of the hydrogen sections of the charging and potentiostatic curves after washing the Pt/Pt electrode free of methanol solution, it is concluded in ref. 30 that the reduction in the number of hydrogen sites as a result of

methanol chemisorption occurs for the most part uniformly, regardless of the energy of the Pt–H_{ads} bond. In the case of a partial removal of the chemisorbed product in the course of an anodic potentiostatic sweep, the number of the adsorption sites corresponding to different energies of the Pt–H_{ads} bond also increases by approximately the same fraction.

3. The mechanism of methanol oxidation on platinum

In accordance with the concepts of the mechanism of the potential establishment in a methanol solution, the kinetics of the shift in φ_r after the introduction of methanol should be determined by its oxidation rate. In this case, the oxidation rate of methanol, i, is equal to:

$$i = \frac{\partial Q}{\partial t} = \frac{\partial Q}{\partial \varphi_r} \frac{\partial \varphi_r}{\partial t} \tag{2}$$

where $\partial Q/\partial \varphi_r$ is the electrode capacity and $\partial \varphi_r/\partial t$ the rate of potential shift after the introduction of methanol. The value of $\partial Q/\partial \varphi_r$ for the potentials of the hydrogen region can be estimated approximately from the slope of the hydrogen section of the charging curve of $Pt(CH_3OH_{ads})$ The calculation of the methanol oxidation rate from eqn. (2) for $\varphi_r = 100$ mV leads to values exceeding, approximately, by six orders of magnitude those of the reaction rate obtained by extrapolating the stationary curves of methanol oxidation to these values of φ_r (curve 7, Fig. 4). Such a large difference cannot be accounted for by an inaccurate extrapolation of the steady-state curve and shows that under the conditions of the measurements of the potential-shift curves, the methanol oxidation rate at open circuit is much higher than in the case of the electro-oxidation under steady-state conditions. This conclusion is supported by the measurements of the current–time dependence after the moment of methanol coming into contact with the Pt/Pt electrode, the potential of which was kept constant at definite values (0.1–0.8 V) by means of a potentiostat[30a]. At all potentials studied, a decrease in the current of the organic substance oxidation is observed; this has also been observed in a number of other works[15,10,12,5]. Figure 4 shows polarization curves plotted on the basis of the i–t curves, each of them corresponding to a definite time interval after the introduction of methanol. It is clear from the figure that the effect of the process inhibition in time decreases with increasing φ_r of the electrode. At $\varphi_r = 0.4$ V, the ratio of the initial current (curve 1) to the current under steady-state conditions (curve 7) still amounts to ∼ 10^4. Under steady-state conditions, the rate of methanol oxidation at the potentials of the hydrogen region, which is considerable at the first moment of time, drops practically to zero (Fig. 4).

A detailed study leads to the conclusion that it is necessary to differentiate between the mechanism of methanol oxidation on a bare surface (or on that only slightly covered with the chemisorbed substance) and the mechanism of oxidation under steady-state conditions.

We assume that on a bare platinum surface, methanol oxidation at the potentials of the hydrogen and the double-layer regions of the charging curve (below $\varphi_r \sim 700$ mV) is determined by the dehydrogenation rate. This is supported by measurements of the dependence of the process rate upon the pH of the solution. Thus, in spite of the difference in the shape of the polarization curves in acid and in alkali at φ_r in the hydrogen region, the difference in the oxidation rates at the same

φ_r is as small as ~3–4 times (curves 8 and 9, Fig. 4). Near-values of the currents, measured after the introduction of methanol at 500 mV, were obtained in 0.1 N H_2SO_4 and 0.1 N KOH.

At φ_r in the hydrogen region, the dehydrogenation rate depends greatly upon the potential. In acid, in the region of φ_r equal to 100–300 mV, the slope of the polarization curve is ~130 mV (greatly decreasing at lower φ_r), in alkali it is ~40–50 mV. In the double-layer region, the slope of the polarization curve is ~350–400 mV (curve 1, Fig. 4). As shown in ref. 8, the Tafel dependence of the dehydrogenation rate
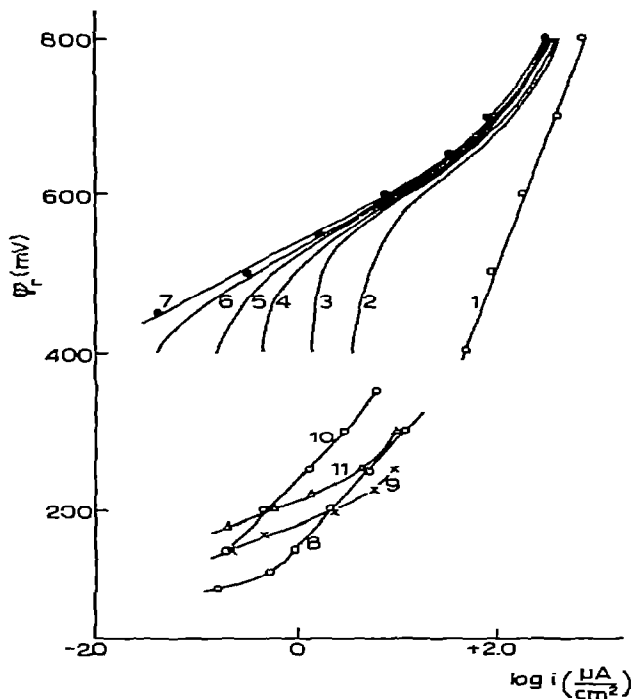

Fig. 4. Dependence of the rate of electro-oxidation of CH_3OH upon the potential measured at different time intervals after the introduction of CH_3OH: (1), initial curve; (2), 15 sec; (3), 30 sec; (4), 1 min; (5), 2 min; (6), 5 min; (7), steady-state curve. Concn. CH_3OH, 0.5 M; supporting electrolyte, 0.1 N H_2SO_4. Curves plotted from the currents measured at the first moment after CH_3OH introduction, in solns.: (8), 1 N H_2SO_4 + 0.5 M CH_3OH; (9), 1 N KOH + 0.5 M CH_3OH; (10), 1 N H_2SO_4 + 0.1 M CH_3OH; (11), 1 N KOH + 0.1 M CH_3OH. i referred to 1 cm^2 of true surface.

upon the potential can be explained on the basis of the kinetics of reactions on inhomogenous surfaces. At the present time, it is difficult to account for the changes of the slopes of the Tafel lines. It may be supposed, however, that the change observed upon transition from the hydrogen region to the double-layer region is due to the large change in the surface coverage with hydrogen. On the whole, the picture is more complicated than would follow from the assumption of a uniform inhomogeneity of the surface.

When methanol oxidation occurs under steady-state conditions, a pronounced dependence of the process characteristics upon pH of the solution is observed (Fig. 5). In alkaline solutions the overvoltage, η, of the process is smaller than in acid solutions

and decreases with increasing pH so that, for instance, at $i = 1$ mA/cm^2, $\partial\eta/\partial$pH $\approx$ -60 mV. The slope of the Tafel line rises from 55–65 mV in acid solutions to 85–105 mV in alkaline solutions

A galvanostatic curve showing the establishment of the steady potential during the electrode polarization in a methanol solution and the charging curve in the
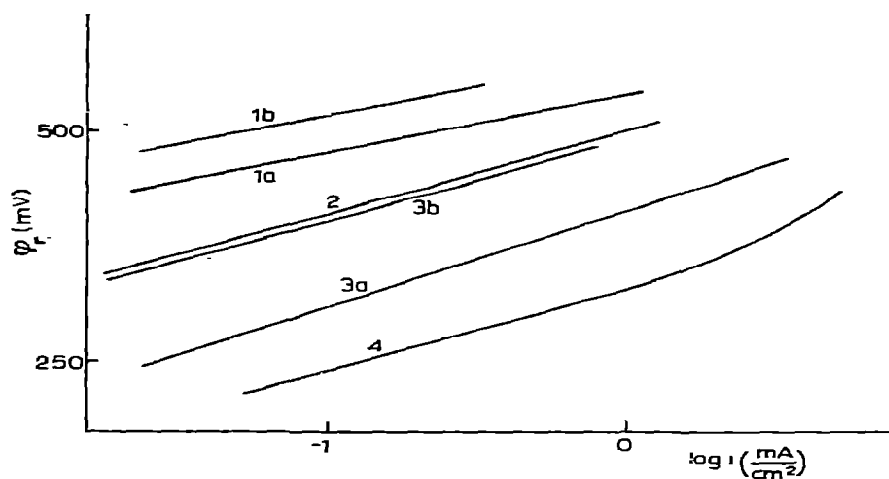

Fig. 5. Dependence of the rate of electro-oxidation of CH$_3$OH under steady-state conditions upon pH of the soln.: (1a), 1 N H$_2$SO$_4$; (2), 0.1 N KOH; (3a), 1 N KOH (pH = 13.95); (4), 10.7 N KOH (pH = 16.4). Concn. CH$_3$OH, 0.5 M. (1b, 3b), Polarization curves of oxidation of the substances chemisorbed during polarization in 1 N H$_2$SO$_4$ and 1 N KOH, respectively.
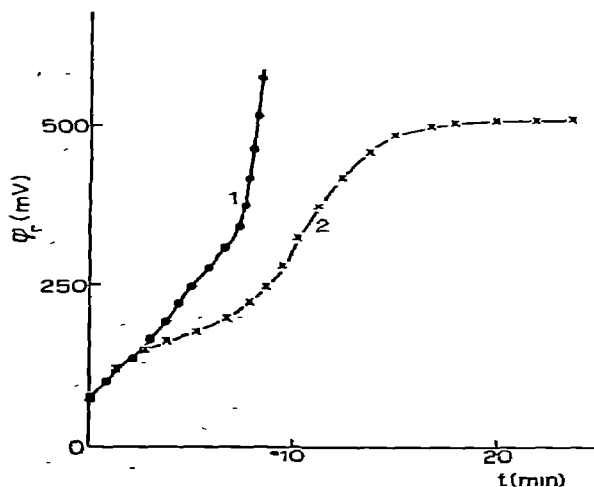

Fig. 6. Anodic charging curves: (1), 0.1 N H$_2$SO$_4$; (2), 0.5 M CH$_3$OH + 0.1 N H$_2$SO$_4$; $i = 5 \cdot 10^{-4}$ A/cm^2.

supporting electrolyte solution, measured by the current of the same density are compared in Fig. 6. The initial point of curve 2 corresponds to φ_r^1 established at open circuit after the introduction of methanol. As the quantity of hydrogen at φ_r^1 is about half that corresponding to curve 1 in Fig. 6, the shape of curve 2, the initial section of which coincides with curve 1, indicates that methanol is oxidized over the whole

range of φ_r, including the hydrogen adsorption potentials. After the steady state has been attained at a certain current density, the other steady potentials are reached within several minutes. The measurements of the surface coverage of platinum under the conditions of the measurement of the steady-state curve made in ref. 30a show that the coverage in the Tafel-line region is practically constant. Thus, in the establishment of the steady state a certain quantity of electricity is expended in the formation of a nearly stationary surface coverage with the chemisorbed substance.

The galvanostatic and the potentiostatic curves showing the oxidation of the products chemisorbed after the polarization of the electrode in a sulfate solution, are presented in Figs. 7a and 8a. A coefficient, K, equal to 0.8–0.9 corresponds to these
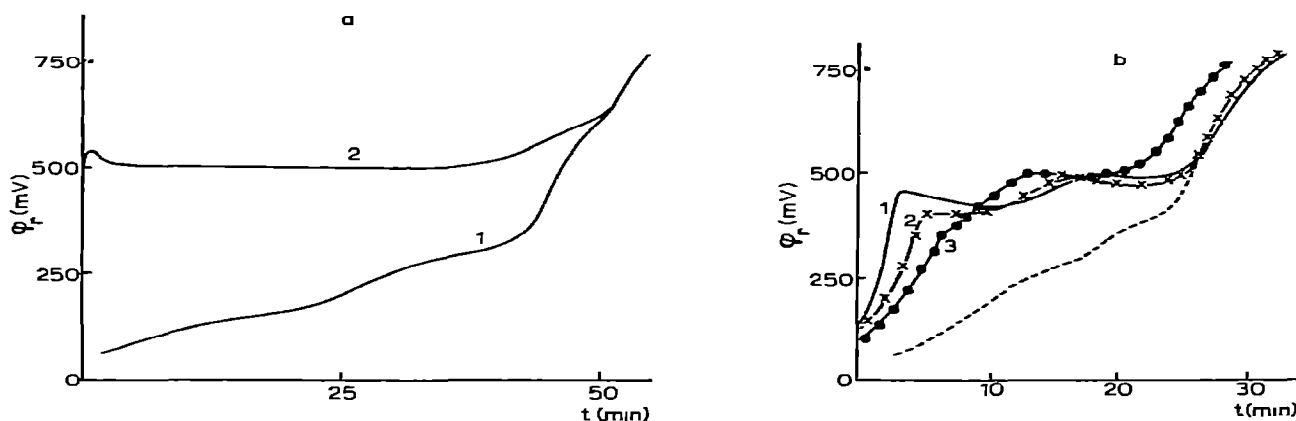

Fig. 7. (1a), Anodic charging curve in 0.1 N H_2SO_4; (2a), galvanostatic curve of electro-oxidation in the substance chemisorbed on a Pt/Pt electrode during polarization in 0.1 N H_2SO_4 + 0.5 M CH_3OH until the establishment of a steady state at $i = 5 \cdot 10^{-4}$ A/cm^2; (b), galvanostatic curves of electro-oxidation of the substance chemisorbed on a Pt/Pt electrode during polarization in alkaline solns. (0.5 M CH_3OH) until the establishment of a steady state at $i = 1 \cdot 10^{-4}$ A/cm^2. (1), 0.1 N KOH; (2), 1 N KOH; (3), 10.7 N KOH; ----, charging curve in 1 N KOH; $i = 1 \cdot 10^{-4}$ A/cm^2.

curves. Before the plateau of the oxidation of the chemisorbed substance under the galvanostatic conditions is reached, a maximum is observed, just as in the case of substances chemisorbed at open circuit in aldehyde solutions (the reasons for this phenomenon are discussed in the second part of this paper).

Two arrests are observed on the charging curves in the case of oxidation of chemisorbed products in alkaline solutions (Fig. 7b). In potentiostatic measurements there is a pre-wave corresponding to the first arrest (Fig. 8b, curve 2). In alkaline solutions as in acid solutions, the increase in the amount of chemisorbed substance with the polarization of the electrode is approximately twice the increase in the amount chemisorbed at open circuit. Thus, the polarization of the electrode in methanol solutions causes an additional accumulation of the chemisorbed substance, and, possibly, a change in its composition.

If, after the polarization of the electrode in 1 N H_2SO_4, the system is washed first with water and then with 1 N KOH, the charging curve measured in 1 N KOH coincides with the curve obtained after the polarization and washing of the electrode
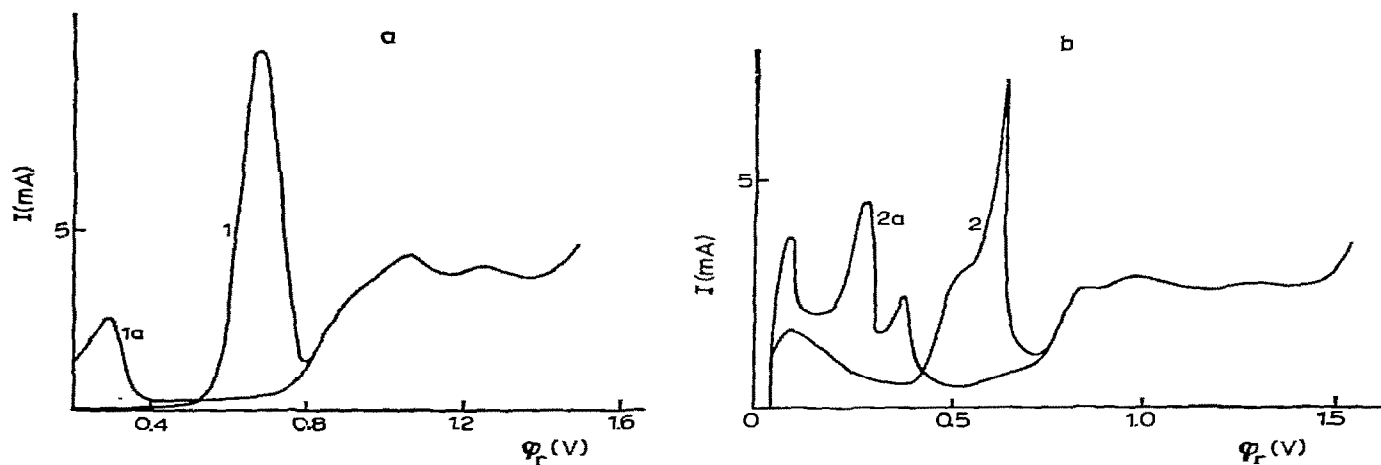
Fig. 8. Potentiostatic curves of electro-oxidation of the substance chemisorbed after polarization in CH3OH solns. (0.5 M CH3OH) in 0.1 N H2SO4 (1) and 0.1 N KOH (2); (1a, 2a), curves obtained in 0.1 N H2SO4 and 0.1 N KOH supporting electrolyte solns. Rate of potential change, 5.4 mV/sec; apparent electrode surface, 1.78 cm².

in 1 N KOH (Fig. 7b). A similar result is obtained if the electrode is polarized in alkali and then washed in acid and the charging curve measured in an acid solution. Thus, the substances chemisorbed in acids and alkalis can change reversibly one into the other.

Tafel plots of the electro-oxidation of the chemisorbed products were drawn, based on the measurements of the charging curves of Pt(CH3OH$_{ads}$) at different current densities, and the potentiostatic curves. The initial sections of the potentiostatic curves and the potential values of the plateaux on the charging curves of Pt(CH3OH$_{ads}$) in 1 N H2SO4, as well as the potentials of the beginning of the first arrest in 1 N KOH, were used for this purpose. In Fig. 5, the curves thus obtained are compared with the steady-state polarization curves of methanol electro-oxidation. The slopes of the curves coincide, but the overvoltage of electro-oxidation of the chemisorbed products is higher than that of the process occurring in the presence of methanol in the solution, although it is close to it. Thus, in 1 N H2SO4 the difference is ~40 mV, and in 1 N KOH—~85 mV. If the $i-\varphi_r$ curves of electro-oxidation of the chemisorbed substance are plotted from the potentials of the maxima on the charging curves in 1 N H2SO4, the difference in the overvoltages increases, so that the process rate of the oxidation of the chemisorbed substance and that observed in the presence of methanol in the solution will differ by more than one order of magnitude.

It is clear from Fig. 7b, that an increase in pH results in a decrease in the overvoltage of the beginning of oxidation of the chemisorbed substance, the dependence being approximately the same as for the same process in the presence of methanol in the solution. With increasing pH, the maximum on the first arrest disappears and the length of this arrest is somewhat reduced. However, the potentials and the length of the second arrest remain in this case practically unchanged.

From the similarity in the characteristics of electro-oxidation of the chemisorbed substance retained on the electrode after washing and those of the process occurring in the presence of methanol in the solution (see above) it can be concluded

that electro-oxidation of methanol under steady-state conditions is determined by oxidation of the products of its chemisorption. A marked difference is observed, however, in the rates of these two processes, which in the second part of the present paper will be shown to reach even higher values in the case of other electrode reactions. Some of the particles, less strongly bound to the electrode surface and more readily oxidized, seem to be removed in the electrode washing process. Further investigation is required in order to establish the nature of the adsorption of these particles.

Since in acid solutions the overvoltage of oxidation of methanol when it is present in the solution, and of oxidation of the chemisorbed substance depend only slightly upon pH, it is most likely that the slow step of the process is the interaction between the chemisorbed particles and the OH radicals, occurring, for instance, according to the scheme:

$$H_2O - \bar{e} \ \rightleftarrows \ OH_{ads} + H^+$$

$$OH_{ads} + RH \xrightarrow{slow} R \cdot + H_2O \tag{3}$$

where RH is the chemisorbed particle participating in the rate-determining step*. The deduction of the kinetic equation, corresponding to such an assumption is considered in ref. 6 for the case of acetylene oxidation.

The considerable dependence of the methanol oxidation rate in alkaline solutions upon pH (at $\varphi_r = $ const.) and the increase in the slope of the Tafel line can be due to a change in the mechanism of the process in passing from acid to alkaline solutions. At present it is difficult to suggest a mechanism which could give a quantitative coincidence with the experimental data in alkaline solutions. Some of the simplest schemes giving an approximate explanation of the kinetics observed, are as follows:

$$OH^- - \bar{e} \xrightarrow{slow} OH_{ads}$$

$$OH_{ads} + RH \xrightarrow{fast} R \cdot + H_2O \tag{4}$$

or

$$OH^- + RH - \bar{e} \xrightarrow{slow} R \cdot + H_2O \tag{5}$$

The equations corresponding to scheme (4) are considered in ref. 5. If it is assumed that the electrode coverage with the reacting chemisorbed particles as well as the part of the surface on which the discharge of the OH^- anions occurs, does not depend upon φ_r and pH in the Tafel region, and the inhomogeneity of the surface is not taken into consideration, in accordance with the schemes (4) and (5) we obtain:

$$i = k \exp\left(\frac{\beta F \varphi_r}{RT}\right) \cdot 10^{(1-\beta)pH} \tag{6}$$

$$\left(\frac{\partial \varphi_r}{\partial \log i}\right)_{pH} = 2.3 \frac{RT}{\beta F} \tag{6a}$$

$$\left(\frac{\partial \log i}{\partial pH}\right)_{\varphi_r} = 1 - \beta \tag{6b}$$

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* The designation RH for the chemisorbed particle (R = radical of any composition) has been chosen for convenience in writing equations and will be used in different schemes. In reality, the chemisorbed particle may contain, for instance, no hydrogen atoms at all.

According to the experimental data, within the pH range 11.5–14.0, $\beta \sim 0.68$–0.55 and $(\partial \log i/\partial \text{pH})_{400\text{mv}} \approx 0.5$–0.7. Thus, in alkaline solutions, β changes within appreciable limits and the values of $(\partial \log i/\partial \text{pH})_{\varphi_r}$ differ essentially from those expected from eqn. (6b). These deviations can be due to different reasons, such as the approximate character of the assumptions made in the deduction of eqn. (6) or the simultaneous occurrence of a process in accordance with scheme (3).

The change in the mechanism of methanol oxidation in alkaline solutions can be explained by changes in the conditions at the electrode surface state and in the nature of the chemisorbed particle. One of the probable reasons of the change in the nature of the reacting particle in alkaline solutions may be a readier oxidation of the particle R^- formed according to the reaction:

$$RH + OH^- \rightarrow R^- + H_2O \tag{7}$$

A similar hypothesis was advanced also by other writers (*e.g.* ref. 22), but no account was taken, in earlier works, of the fact that the particle participating in the limiting step is a chemisorbed one with a dissociation constant possibly differing from the pK of the original compound investigated. Evidently, the change in the mechanism should occur near the pK of the chemisorbed particle. It should be noted that the occurrence of reaction (7) with mechanism (3) remaining unchanged, may lead by itself to a decrease in the process overvoltage within the pH range close to pK. By taking into consideration only reaction (7), it is difficult, however, to explain without additional assumptions the experimental value of $(\partial \log i/\partial \text{pH})_{\varphi_r}$, the change in the oxidation rate of the chemisorbed substance with pH, and the fact that the dependence of the overvoltage upon pH is observed within a wide range of pH values (~ 11.5–~ 16.5). On the whole it is hardly possible, at the present time, to give a complete account of the oxidation mechanism of methanol, especially in the case of alkaline solutions.

4. Electro-oxidation of methanol at potentiostatic sweeps

Rapid rates of methanol electro-oxidation on a surface free of the chemisorbed substance can be observed on potentiostatic curves under definite scanning conditions, as shown in ref. 31. For this purpose, the organic substance was brought into contact with a Pt/Pt electrode, the potential of which was maintained at $+50$ mV. Then the potentiostatic curve was recorded during the first sweep from 50 mV in the anodic direction, as well as the curves at subsequent anodic pulses after the potential had been brought back to the initial value, 0.05 V, jump-wise or by changing the direction of the pulse. The results are presented in Fig. 9. The potentiostatic curve measured during the first sweep lies not only higher than the curves recorded during subsequent pulses, but also higher than the curves in the supporting electrolyte solutions; this is due to methanol dehydrogenation.

As shown by earlier measurements[31], the differences between the curve measured during the first anodic sweep and the curves measured during subsequent saw-toothed pulses from $\varphi_r = 50$ mV to $\varphi_r \leqslant 800$ mV or by the triangular pulse method, are due to the accumulation of the methanol chemisorption products on the electrode surface at low anodic potentials (in the case of the triangular pulse—on the cathodic branch of the curve). The first pulse occurs in the absence of the chemisorption
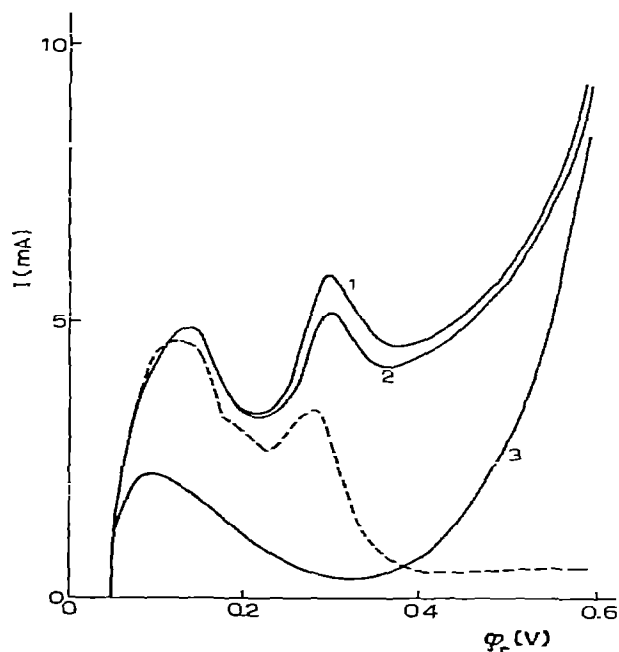
Fig. 9 Potentiostatic curves in 0.1 N H_2SO_4 ÷ 0.05 M CH_3OH solns · (1), first sweep; (2), saw-toothed pulse from 0.05–1.5 V; (3), anodic curve of the triangular pulse; – – – –, curve obtained in the supporting electrolyte. Rate of potential change, 5.4 mV/sec; apparent electrode surface, 1.78 cm².

products on the electrode surface since, as shown above, methanol is not chemisorbed at φ_r close to zero.

The analysis of the first potentiostatic pulses in solutions with different pH values, shows that at φ_r in the hydrogen region, the current of methanol oxidation depends to only a small extent on the pH of the solution; this is particularly easily observed in acid solutions.

It is clear from the curves in Fig. 9, that methanol electro-oxidation at low anodic potentials is characterized by the presence of current maxima, which seem to result from the appearance of the chemisorbed substance on the surface during the sweep. At the same time, it is necessary to take into consideration the increase in the anion adsorption with the potential shift in the direction of positive values[32].

5. Electro-oxidation of methanol on composite electrolytic deposits (c.e.d.) of platinum and palladium with ruthenium

In many cases, the catalytic activity of c.e.d. is known to be much higher than of each of the metals taken separately (see, *e.g.* ref. 2). Some interesting results were obtained by us in the investigation of platinum–ruthenium catalysts[33]. We undertook a detailed study because it has been pointed out in the literature that platinum–ruthenium alloys with a small percentage of ruthenium show a high catalytic activity in some processes[34,35]. Recently BOCKRIS *et al.*[26] reported the high catalytic activity of platinum–ruthenium alloys in the methanol electro-oxidation reaction. The adsorption and catalytic properties of a ruthenium electrode were studied by electrochemical methods in ref. 36.

We have measured the curves of the φ_r shift after the introduction of methanol, the steady-state polarization curves and those of electro-oxidation of the chemisorbed products, on electrodes of c.e.d. of platinum and ruthenium with 5, 10, 23 and 30% of the latter. According to these measurements, the activity of c.e.d. in the reaction of methanol electro-oxidation passes through a maximum and exceeds the activity of platinized platinum. The highest activity is obtained when the ruthenium content is from 5–10%. On an electrode with 10% ruthenium one hour after the introduction of methanol at 500 mV ($t = 20°$), φ_r reaches the value 30–40 mV and continues to shift in the cathodic direction at the rate of about 0.1 mV/min, whereas on a Pt/Pt electrode under similar conditions φ_r reaches only ~ 80–100 mV. At a temperature of 60°, on the same c.e.d. electrode in concentrated methanol solutions, the potential becomes more negative than the reversible hydrogen potential*.

With an increase in the ruthenium content in the deposit up to 30%, the rate of the potential shift decreases so that after 1 h φ_r reaches only a value ~ 200 mV. On a ruthenium electrode only a small potential shift is observed after the introduction of methanol in acid or in alkaline solutions, i.e., within the potential range studied (below 800 mV) methanol is practically unoxidized on ruthenium. The measurements of the polarization curves on a ruthenium electrode lead to the same conclusion.

In Fig. 10, the polarization curves of methanol electro-oxidation under steady-state conditions on c.e.d. of platinum and ruthenium at Pt : Ru = 9 : 1, are compared with those of a platinized-platinum electrode. In 1 N H₂SO₄, the overvoltage of the process on c.e.d. is approximately lower by 150 mV than on a Pt/Pt electrode. The slope of the Tafel lines is ~ 60 mV in the case of Pt and ~ 50 mV on c.e.d. In 1 N KOH, the overvoltage of methanol oxidation on c.e.d. is 60–70 mV lower than on Pt/Pt at a current density of 2.5 mA/cm². The polarization curves on c.e.d. in acid and alkaline solutions practically coincide, whereas on platinized platinum they diverge greatly. It is of interest to note that on c.e.d. the charging curves in acids and alkalis also differ only slightly (Fig. 11).

A comparison of the curves of electro-oxidation of substances chemisorbed during the polarization of electrodes of Pt and c.e.d. at Pt : Ru = 9 : 1 (Fig. 11), shows that marked differences are observed in the potentials of the beginning of oxidation and in those of complete oxidation of the chemisorbed substances on these electrodes. In the case of c.e.d., the overvoltage of oxidation in 1 N H₂SO₄ is ~ 200 mV lower than on a Pt/Pt electrode. The curves of electro-oxidation on c.e.d. in acids and alkaline solutions are similar. It is characteristic that in the case of c.e.d. the overvoltage of oxidation of the chemisorbed substance and that of the oxidation process under steady-state conditions, in the presence of methanol in the solution, practically coincide.

It can be concluded on the basis of the data obtained, that electro-oxidation of methanol on c.e.d. of platinum and ruthenium at Pt : Ru = 9 : 1 obeys simpler kinetic laws than on platinized platinum.

Measurements of the polarization curves on c.e.d. of palladium and ruthenium, show that a maximum of catalytic activity is also observed in this case at a low weight % content of ruthenium (20–30%). The palladium–ruthenium deposits prove to be somewhat less active in the electro-oxidation of methanol in acid solutions than the

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* In this case, the electrode surface is covered with gas bubbles, which probably consist of hydrogen.
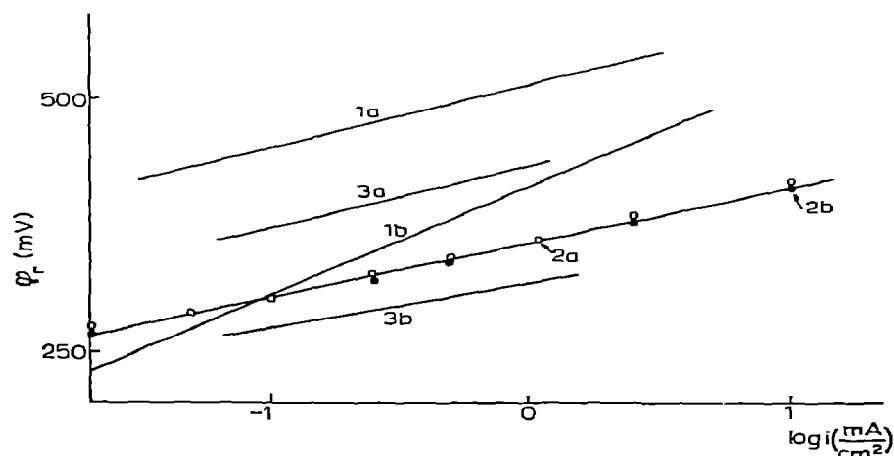
Fig. 10. Polarization curves of CH$_3$OH electro-oxidation (0.5 M) under steady-state conditions: (1), platinized platinum; (2) c.e.d. of platinum and ruthenium, Pt · Ru = 9 : 1; (3), c.e.d of palladium and ruthenium, Pd : Ru = 39 : 11. Supporting electrolyte: (a), 1 N H$_2$SO$_4$; (b), 1 N KOH.
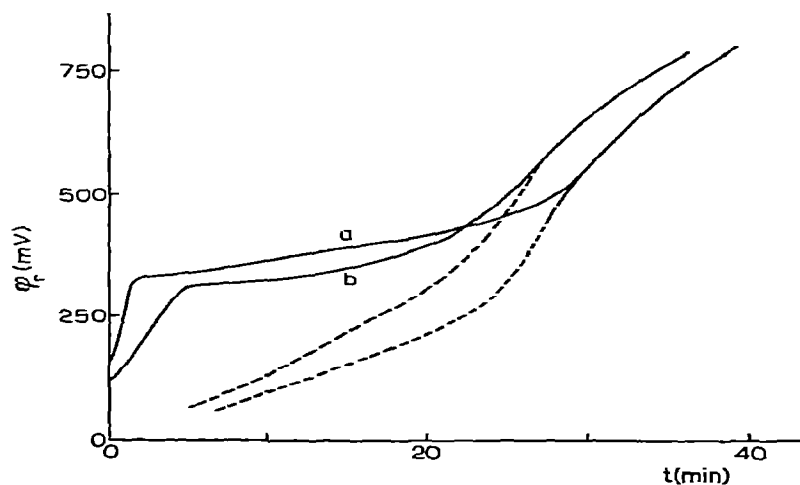

Fig. 11. Galvanostatic curves of electro-oxidation of the substances chemisorbed during polarization of a c.e.d. of platinum and ruthenium, Pt : Ru = 9 : 1: (a), 1 N H$_2$SO$_4$; (b), 1 N KOH; i = 1 · 10^{-4} A/cm^2; - - - -, anodic charging curves of the supporting electrolyte solns.

platinum–ruthenium alloys, but more active than platinized platinum in the same reaction (Figs. 10 and 12).

SUMMARY

Measurements of the curves showing the dependence of the shift in the Pt/Pt electrode potential, after the introduction of methanol, upon pH of the solution and the potential at the moment of introduction of methanol, lead to the conclusion that the potentials of a Pt/Pt electrode, in methanol solutions, are determined by the adsorbed hydrogen. The presence of adsorbed hydrogen has been established from the charging curves and the potentiostatic curves of a platinum electrode measured after its contact with methanol. The analysis of these curves shows, also, that under definite
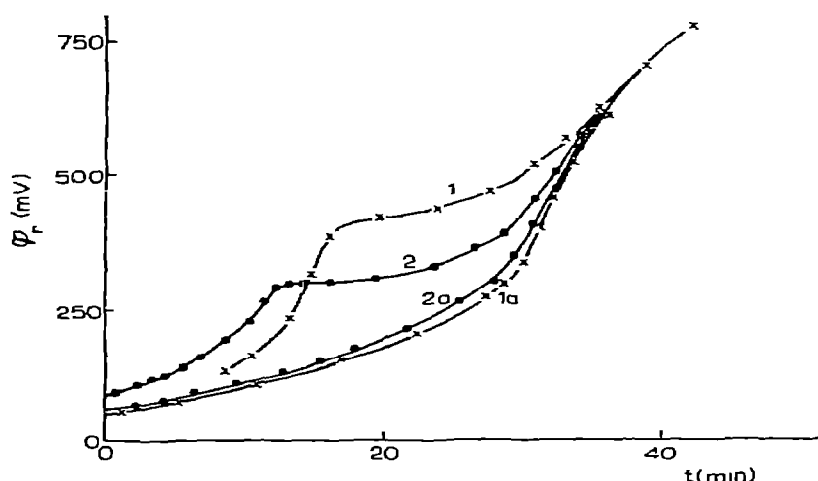
Fig. 12. Galvanostatic curves of electro-oxidation of the substances chemisorbed during polarization of a c.e.d. of palladium and ruthenium with 22% Ru: (1), 0.1 N H_2SO_4; (2), 1 N KOH; $i = 2 \cdot 10^{-4}$ A/cm²; (1a, 2a), anodic charging curves in 0.1 N H_2SO_4 and 1 N KOH, respectively.

conditions a predominant chemisorption of particles with the composition HCO occurs on platinized platinum in methanol solutions.

The kinetics of methanol oxidation under non-steady-state and steady-state conditions have been studied and the difference in the mechanisms of the process on the bare platinum surface and on that covered with a stationary layer of chemisorbed substance, shown. The influence of pH of the solution, the dependence of the rate upon the potential and the kinetic characteristics of electro-oxidation of the chemisorption products, are used as possible criteria for the elucidation of the mechanism of the process.

A hypothesis has been advanced, that on a bare surface the rate of the process is determined by dehydrogenation of the original alcohol molecules and under steady-state conditions—by the oxidation of the products of their chemisorption. In acid solutions the latter process may proceed by way of interaction with OH radicals. Some possible schemes of the oxidation process in alkaline solutions have been discussed.

Composite electrolytic deposits of platinum and ruthenium, and of palladium and ruthenium with a small percentage of ruthenium, have been found to be extremely catalytically active in the reaction of methanol electro-oxidation.

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