3. N.N.Semenov, "Tsepnye Reaktsii" (Chain Reactions), Goskhimizdat, 1934.
4. D.A.Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat Transfer in Chemical Kinetics), Izd.Akad.Nauk SSSR, Moscow–Leningrad, 1947.
5. G.Greber, S.Erk, and U.Grigoulle, "Die Grundgesetze der Wärmeübertragung" (Translated into Russian), Inostr. Lit., 1958.
6. L.G.Loitsyanskii, "Laminarnyi Pogranichnyi Sloi" (The Laminar Boundary Layer), Fizmatgiz, Moscow, 1962.
7. V.G.Levich, "Fiziko-Khimicheskaya Gidrodinamika" (Physicochemical Hydrodynamics), Fizmatgiz, Moscow, 1959.
8. H.Shlichting, "Boundary Layer Theory" (Translated into Russian), Inostr.Lit., Moscow, 1956.
9. G.A.Aksel'rud, Zhur.Fiz.Khim., 27, 10 (1953).
10. V.G.Levich, Zhur.Fiz.Khim., 22, 575 (1948).
11. A.Acrivos and P.Chambré, Ind.Eng.Chem., 49, 1025 (1957).
12. D.Rosner, Jet Propulsion, 28, 555 (1958).
13. D.Rosner, Amer.Inst.Chem.Engineers J., 9, 321 (1963).
14. V.G.Levich and N.N.Meiman, Dokl.Akad.Nauk SSSR, 79, 97 (1951).
15. D.Rosner, ARS J., 29, 215 (1959).
16. G.Bopp and D.Mason, Electrochem.Technol., 2, 129 (1964).
17. M.Leveque, Ann.Mines, 13, 201 (1928).
18. P.Chambré, Appl.Sci.Res., A 6, 97 (1958).
19. S.Katz, Chem.Eng.Sci., 10, 202 (1959).
20. I.Tinkler and A.Metzner, "Heat Transfer — A Symposium", Univ.Michigan Press, 1953, p.211.
21. A.N.Frumkin and E.A.Aikazyan, Dokl.Akad.Nauk SSSR, 100, 135 (1955).
22. A.N.Frumkin and L.N.Nekrasov, Dokl.Akad.Nauk SSSR, 126, 117 (1959).
23. A.N.Frumkin, L.N.Nekrasov, V.G.Levich, and Yu.B.Ivanov, Electrochim.Acta, 1, 84 (1960).
24. V.S.Bagotskii, Zhur.Fiz.Khim., 22, 1466 (1948).
25. B.N.Kabanov and Yu.G.Siver, Zhur.Fiz.Khim., 22, 53 (1948).
26. L.Bircumshaw and A.Riddiford, Quart.Rev., 6, 157 (1962).
27. A.Riddiford, "The Rotating Disk Electrode" in "Advances in Electrochemistry and Electrochemical Engineering", Vol.5, No.4, London, 1965.
28. Ya.V.Durdin and Z.U.Dukhnyakova, "Sbornik Statei po Obshchei Khimii" (Collected Papers on General Chemistry), Vol.1, Leningrad, 1953, p.157.
29. L.Bircumshaw and A.Riddiford, J.Chem.Soc., 598, 1490 (1951); 698, 701 (1952).
30. M.Litt and G.Serad, Chem.Eng.Sci., 19, 853 (1964).
31. M.Litt and G.Serad, Amer.Inst.Chem.Engineers J., 51st National Meeting, September–October, 1963.
32. P.Delahay, "New Instrumental Methods in Electrochemistry" (Translated into Russian), Inostr.Lit., Moscow, 1957.
33. R.Bird, W.Stewart, and E.Lightfoot, "Transport Phenomena", Wiley, New York, 1960.
34. S.Goldstein (Editor), "Current Aspects of the Hydroaerodynamics of a Viscous Fluid" (Translated into Russian), Inostr.Lit., Moscow, 1948.
35. V.G.Levich, Yu.A.Chizmadzhev, and Yu.Kharkats, Dokl. Akad.Nauk SSSR, 166, No.1 (1965).
36. R.Weisz, Chem.Eng.Sci., 17, 265 (1962).
37. D.Ilkovič, Coll.Czech.Chem.Comm., 6, 498 (1934).
38. D.MacGillavry and E.Rideal, Rec.Trav.chim., 56, 1013 (1937).
39. V.P.Vorotilin, V.S.Krylov, and V.G.Levich, Prikl.Matem. i Mekhan., 29, 343 (1965).
40. V.P.Vorotilin, V.S.Krylov, and V.G.Levich, Dokl.Akad. Nauk SSSR, 160, 1358 (1965); 161, 874 (1965).
41. V.S.Krylov, Dokl.Akad.Nauk SSSR (in the press).
42. R.Highbie, Trans.Amer.Inst.Chem.Eng., 31, 365 (1935).
43. P.A.Semenov, Inzh.-Fiz.Zhur., Akad.Nauk Beloruss.SSR, 7, 294 (1965).
44. P.R.Owen and W.R.Thomson, J.Fluid Mech., 15, 321 (1963).
45. P.Danckwerts, Trans.Faraday Soc., 46, 300, 701 (1950).
46. M.Kh.Kishenevskii and A.P.Pamfilov, Zhur.Prikl.Khim., 22, 1173 (1949).
47. A.Gill, Amer.Inst.Chem.Engineers J., 8, No.2 (1964).
48. P.Chung and S.Lin, AIAA J., 1, 929 (1963).
49. V.G.Levich and A.M.Brodskii, Dokl.Akad.Nauk SSSR, 165, No.3, 4, 5 (1965).
50. A.M.Golovin, V.G.Levich, and V.V.Tolmachev (in the press).
51. V.G.Levich, V.S.Markin, and Yu.A.Chizmadzhev, Dokl. Akad.Nauk SSSR, 166, No.1 (1965).
52. P.Saffman, J.Fluid Mech., 6, 321 (1959); 7, 194 (1960).
53. O.Levenspiel and K.Bischoff, Ind.Eng.Chem., 58, 97 (1959).
54. Chem Min Heng, Sci.Sinica, No.12 (1955).
55. R.Aris and N.R.Amundson, Amer.Inst.Chem.Engineers J., 3, 280 (1957).

Institute of Electrochemistry,
Academy of Sciences of the USSR

U.D.C. 541.135.5-183

THE ELECTROCHEMICAL EFFECT OF HIGH COVERAGE

G.A.Tedoradze and A.B.Ershler

The inhibition of electrochemical reactions by adsorbed extraneous substances or reaction products is well recognised[1-8]. The basic causes underlying this phenomenon include blocking of the surface by an adsorption film, and the generation of an energy barrier opposing the reduction, through the adsorption of ions or polar molecules. In recent years, the inhibition of an electrochemical reaction by adsorbed reactant has been demonstrated by refined experimental techniques. This effect has been termed[9,10] the high-coverage effect.

Frumkin et al.[9] and Tedoradze and Dzhaparidze[10,11] were the first to compare the degree of coverage of the electrode surface by reactants, determined experimentally, with the rate of the electrochemical process, measured at the same potentials. They reported a decrease in current density with increase in coverage for the catalytic evolution of hydrogen from diphenylamine solutions. A qualitative explanation of the inhibition of the reduction of diphenylammonium ions at coverages of the electrode approaching unity has been given[9].

This article will describe the outward experimental symptoms of the high-coverage effect, and some possible causes. The reduction of organic substances at a mercury electrode, being the simplest case, will be treated in detail.

As long as the coverage of the surface by molecules of a reducible substance is not large, and interactions between these molecules (as well as the effect of adsorbed molecules of the product) can be ignored, the rate i of an

electrochemical reaction is proportional to the surface concentration of the reducible substance (Γ), and is given to a first approximation by the expression

$$i = nF\Gamma k \exp\left[-\frac{\alpha nF}{RT}(\varphi - \psi_1)\right]. \quad (1)$$

where φ is the potential of the electrode, ψ_1 is the potential at the point in the electrical double layer occupied by the reacting site of the reducible substance, and k is the value of the rate constant at $\varphi - \psi_1 = 0$. However, as Frumkin pointed out[12,13] in 1962, when the surface is largely covered with the reactant entirely different expressions should apply: formula (1), which assumes proportionality between the concentration of the activated complex and that of the reducible substance in its initial adsorbed state, is correct only for low and intermediate coverages of a uniform surface. At high coverages we can expect steric hindrance to oppose transition to the activated complex state, and the variation of the rate of the process with surface concentration may no longer be monotonic. Thus, the orientation of the adsorbate molecules on the surface may vary when the degree of coverage increases[14,15]. If this results in the reactive site of the molecule taking up a position remote from the electrode, we can assume that the formation of the activated complex will involve rotation of the adsorbed molecule on the electrode surface. At high coverages this reorientation can be impeded by neighbouring adsorbate molecules, and the probability of transition of a reacting molecule to the activated state is thereby decreased. However, this explanation of the high-coverage effect is not applicable to some substances. For example, the system of conjugated π-bonds allows motion of an electron along a molecule of dipyridylethylene, and it is impossible to choose an orientation of the reducible molecule on the electrode surface for which the steric hindrance effect is operative.

Transition to the activated complex state will also be hindered at high coverages if the activated complex occupies a greater area on the electrode surface than the molecule in its original adsorbed state[12,13]. The high-coverage effect observed[16-18] in the reduction of dipyridylethylene on mercury at pH values not far from neutrality appears to be a case in point.

It should be noted that a similar phenomenon has been reported[19-28] in the study of the reactions of organic substances in solution at high pressures: in some cases, formation of the activated complex involves an increase in the volume of the molecule (this is called the negative activation volume), and under these conditions increase in pressure inhibits the reaction. Cases are also known in which the activated complex is formed with a decrease in molecular volume (positive activation volume): the rate constant now increases with increase of pressure. One of the commonest causes of a change in volume by the molecule is identified, in the literature dealing with high-pressure chemistry, with unequal solvation of the initial state and the transition state. A difference in solvation can always be expected if the charge of the activated complex is different from that of the original molecule. In the examples which we shall consider, the volume of the activated complex may be greater than the volume of the adsorbed molecule in the initial state for yet other reasons, such as bond labilisation preceding bond rupture; replacement of a double bond by a single bond also causes an increase in volume, because double bonds are shorter than single bonds.

Phenomena reminiscent of the high-coverage effect can occur when two adsorbed species are involved[29] in the formation of the activated complex. If the difference in the adsorption energy of the two species is large, the surface concentration of the second component will be small at high coverages, and this will decrease the surface concentration of the activated complex and therefore also the rate of the electrochemical process.

The study of the variation of current density with surface concentration of (or coverage of the electrode by) the reducible substance is a direct and reliable method of observing high-coverage effects. To use this method, however, some serious experimental difficulties have to be overcome, because at least two surface-active substances are present on the electrode surface during the passage of Faradaic current, and their relative amounts depend on the duration of electrolysis. The method of differential capacity measurements, which is fairly accurate, gives only the total coverage of the electrode surface in this case. The electrocapillary curve method suffers from the same disadvantage, whereas the charging curve method, by which the surface concentration of reactant can be evaluated, is not accurate enough.

To measure the coverage of the surface by the reactant under conditions of Faradaic current flow through the cell, the differential electrode capacity method can be used if the product of the electrochemical reaction is not adsorbed on the electrode. The catalytic evolution of hydrogen on mercury is a reaction of this type. On the plot of the rate of reduction of the diphenylammonium ion against coverage, the high-coverage effect is shown by a current density maximum[9,11] at a Θ value close to 0.85. It should be noted that, if the current density–coverage curve goes through a maximum, the current density must also go through a maximum as a function of bulk concentration of the reducible substance. Bagotskii and Vasil'ev[30] have observed this type of variation. However, their maximum could be associated with inhibition of the electrode reaction by preferential adsorption of the reaction product on the electrode surface.

The influence of the reaction product on the rate of the electrode reaction will be minimal if the electrolysis is restricted to very short times and low current densities, so that the amount of product formed is insufficient to cause appreciable blocking of the surface. By constructing a family of plots of current density against surface coverage (or against bulk concentration of the reducible substance) at constant time, the inhibition caused by the reaction product can be separated from the high-coverage effect. These plots are most conveniently made on the basis of experimental $I-t$ curves.

Furthermore, the form of the $I-t$ curves can itself reveal the presence of a high-coverage effect. Thus, if the bulk concentration of the organic material is not very large (in practice, less than 10^{-3} M), the degree of coverage of the surface by the reactant reaches a value of the order of unity in a measurable time interval, determined by the diffusion of the organic molecules to the electrode surface [provided of course that the product Bc in the adsorption isotherm equation $Bc = f(\Theta)$, where B is a function of potential only, c is the bulk concentration, and Θ is the coverage, is large enough to induce such a high coverage]. Therefore, we can expect to find that the reduction will proceed without high-coverage effects at short times, when the coverage is still low. As the lifetime of the drop increases, the surface coverage by the reactant will also

increase, and after a definite time the coverage may be sufficient to display the high-coverage effect. When this happens, the current must begin to fall off (because of the sharp decrease in the rate constant), and a maximum appears on the $I-t$ curve.

However, a maximum on the $I-t$ curve could have quite a different explanation: for example, adsorption of the reaction product, which blocks part of the surface. As shown by Koutecký and by Koryta[31,32], the $I-t$ curves begin to fall off due to this blocking effect at surface coverages of the order of 0.8–1 if the rate constant is large enough. If the fall of the $I-t$ curve due to adsorption of the reaction product is assumed to set in at that exact coverage of the electrode surface, the quantity of electricity q_{max} which passes through the electrode up to the moment when the curve begins to fall off must be constant. The value of q_{max} should be approximately equal to $nF\Gamma_\infty$, or larger than this quantity, since formation of the reaction product is invariably accompanied by desorption of the product into the solution: this is because the concentration of the product in the region adjacent to the electrode is close to zero.

If we increase the bulk concentration of the organic compound, the current at constant potential and constant time increases. Therefore the time corresponding to the maximum on the $I-t$ curve (τ_{max}) will decrease, but q_{max} will be practically unaffected by the bulk concentration of the reactant. The changes in potential of the electrode at constant bulk concentration lead to the same result. In this case an increase in potential causes an increase in current, but the value of q_{max} remains independent of potential. However, the latter (and experimentally simpler) method is applicable only over a narrow range of potentials close to the potential of maximum adsorption of the reaction product. As we approach the potential of the desorption peak, q_{max} and τ_{max} begin to increase rapidly because of the faster desorption of the products from the electrode. Thus, in order to eliminate the effect of the reaction product on the rate of the electrode process, it is enough to arrange for the measurements to be completed in times much shorter than τ_{max}. The approximate constancy of q_{max} with change of potential, for the fall in the curve induced by reaction products, was demonstrated by Levinson in her investigation of the reduction of $\alpha\alpha\alpha\omega$-tetrachloroalkanes (Fig. 1).

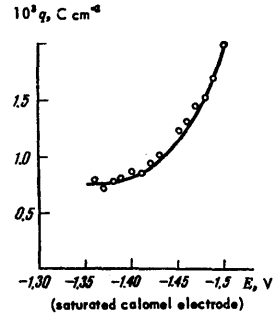


Fig. 1. Potential variation of the quantity of electricity passing through the electrode up to the onset of the fall of current in the reduction of $\alpha\alpha\alpha\omega$-tetrachlorononane; solution composition: 0.0031 M $CCl_3(CH_2)_7CH_2Cl$ + 70% CH_3OH + + 0.25 M Cs_2CO_3; from data of I. M. Levison.

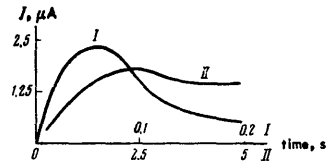


Fig. 2. Variation of the current with time in the reduction of dipyridylethylene; potential -0.83 V (s.c.e.); pH 5; concentration of reactant 2×10^{-3} M; from Ref. 18.

In the high-coverage effect, on the other hand, if concentration polarisation is small, the instant when the current begins to fall off (at constant bulk concentration and near the potential of the adsorption maximum of the reactant) is independent of the current, since it is determined by entirely different factors. Provided Bc is large enough, τ_{max} is independent of potential, and the value of q_{max} increases as the electrode potential increases, but if the currents are much smaller than the limiting diffusion current q_{max} can be significantly lower than $nF\Gamma_\infty$. Current falls of this type are found in the reduction of dipyridylethylene on mercury in aqueous solutions[17,18]. Curve *1* of Fig. 2 shows that 4×10^{-5} C cm^{-2} (including the charging current) have passed through the electrode up to the onset of current fall. Therefore, the whole of the reaction product can block no more than one-half of the electrode surface (assuming that the product takes up 46 Å^2 of the surface, i.e. the same area as the reducible compound[18]). We conclude that the current fall on the $I-t$ curve arises from the high-coverage effect.

In the case of the high-coverage effect, the value of q_{max} should decrease with increase in the concentration of reactant. If the rate of adsorption of the organic compound is determined by the rate of diffusion to the dropping mercury electrode[33,34], the following equation will apply

$$0.74c\frac{\sqrt{D\tau_{max}}}{\Gamma_\infty}\left(1+3.4\frac{\sqrt{D\tau^{1/6}_{max}}}{\sqrt[3]{m}}\right)\geqslant 1,$$

where D is the diffusion coefficient, and m is the mercury flow rate, derived from the well-known Koutecký equation[35].

The polarograms and polarisation curves of systems showing the high-coverage effect have a characteristic asymmetric shape, with an abrupt transition to the limiting diffusion current (Fig. 3). Thus, in the reduction of

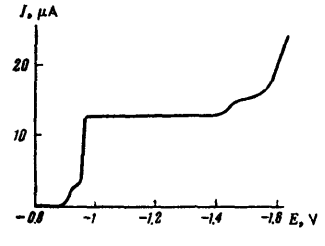


Fig. 3. Polarogram for the reduction of dipyridylethylene in aqueous solution of pH 6.7; concentration of reactant 2×10^{-3} M; from Ref. 18.

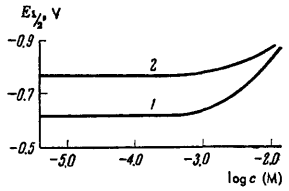


Fig. 4. Variation of the half-wave potential for the reduction of di(methoxycarbonylmethyl)mercury [$Hg(CH_2COOCH_3)_2$] with the logarithm of bulk concentration in 50% methanol.
1) 0.1 *N* KNO_3; 2) 0.1 *N* $NaOCOC_6H_5$; temperature 25°; from Ref. 37.

dipyridylethylene, the current increases by a factor of 4 over a range of 7 mV. If the surface concentration is decreased by making the solution more dilute with respect to the reducible substance or by adding an organic solvent, the wave reverts to the normal, symmetrical shape, and the half-wave potential shifts in the positive direction. In the reduction of di(methoxycarbonylmethyl)mercury, Butin et al.[37] observed a rather large (about 200 mV) positive displacement of the half-wave potential upon lowering the bulk concentration of the reducible compound from 0.02 to 0.001 M. At still lower bulk concentrations the half-wave potential becomes insensitive to concentration (Fig. 4).

However, we must stress that neither an asymmetric polarogram nor an increase in rate with dilution of the solution can be taken as sufficient criteria for the recognition of the high-coverage effect. According to Feoktistov, if the coverage of the electrode surface by the reactant is high at the half-wave potential, this potential for the reduction reaction suffers a negative shift even in the absence of the high-coverage effect. The maximum value of this shift is given by the formula

$$\Delta\varphi_{1/2} = \frac{RT}{\alpha nF} \ln c,$$

where c is the bulk concentration of the organic substance. The reaction products can also give rise to similar effects.

Thus, Laviron† [16] suggested, from the shape of the polarogram and of the $I-t$ curves, that auto-inhibition of the electrode process by the reducible substance occurs in the reduction of dipyridylethylene, but he did not discuss the physical significance of this term. A more detailed examination of this process[17,18] showed that if the time of electrolysis on each drop exceeds 1 sec, as was the case in the work of Laviron[16], inhibition of the reduction of dipyridylethylene by the reaction product takes place (Fig. 3). Adsorption of the reaction products is responsible for the preliminary wave in the reduction of dipyridylethylene[18]. The genuine high-coverage effect is observed on the polarisation curves measured[17,18] with shorter electrolysis times (Fig. 11, see below).

The high-coverage effect is most clearly revealed by galvanostatic measurements. If the bulk concentration of reducible material is not large, but the density of polarising current is appreciable, we can ignore the diffusion of reactant from the bulk during the measurement, and the shape of the potential–time curve (ignoring the double-layer charging current) is described by Eqn. (1). For galvanostatic measurements, this equation is conveniently written in the form

$$\varphi = \psi_1 - \frac{RT}{\alpha nF} \ln i + \frac{RT}{\alpha nF} \ln nF k\Gamma = \varphi_0 + \frac{2{,}3\,RT}{\alpha nF} \log k \frac{\tau - t}{\tau_1}, \qquad (2)$$

where t is the electrolysis time, τ is the transition time, τ_1 is the value of the transition time when $\Gamma = \Gamma_\infty$, i is the polarising current density, and φ_0 is a constant depending on i. If the reduction is preceded by chemical reaction, e.g. protonation of the reducible substance in the adsorbed state, the variation of potential with time becomes more complicated[17], but in any case the potential of the electrode (in the absence of the high-coverage effect) drifts monotonically towards more negative values as the surface concentration decreases during the course of electrolysis. As was stated at the beginning of this article, the high-coverage effect can be so large that the product $k\Gamma$ increases as Γ decreases at high coverages. In the galvanostatic regime this causes a drop of potential with time at short times, thus explaining the appearance of a maximum on the potential–time curve. Curves of this type were first reported and discussed by Zolotovitskii and the present writers[17].

The phenomenon was described mathematically[17] by assuming, as a first approximation, that over a given range of surface concentrations the rate of electron transfer decreases linearly with increasing coverage. This type of variation of current density with coverage corresponds to the following empirical formula for the electron transfer rate constant[9,11]:

$$nF\Gamma_\infty k = \frac{k'}{\theta} - k''. \qquad (3)$$

Here k' and k'' are constants. Fig. 5 shows theoretical curves of electrode potential against electrolysis time calculated on the assumption that over a range of coverages the rate constant varies as required by Eqn. (3), but at low enough coverages this quantity becomes truly constant.

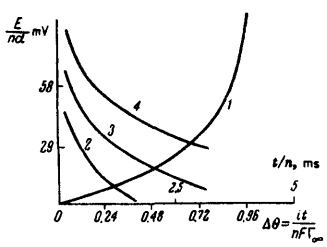


Fig. 5. Variation of electrode potential (relative to $\varphi = -\frac{0{,}058}{\alpha n} \log i$) with normalised time $\Delta\theta = \frac{it}{nF\Gamma_\infty}$ at $i = 3 \times 10^{-4}$ A cm^{-2}, $\alpha n = 1$, $\Gamma_\infty = 5 \times 10^{-10}$ mole cm^{-2}:
1) no high-coverage effect, $nF\Gamma_\infty k = 10^{-5}$ A cm^{-2}; [2)–4) under the conditions of the high-coverage effect the rate constant varies with coverage according to formula (3)] 2) $k' = 2.24 \times 10^{-5}$, $k'' = 2.17 \times 10^{-5}$; 3) $k' = 1 \times 10^{-5}$, $k'' = 0.97 \times 10^{-5}$; 4) $k' = 4.45 \times 10^{-6}$, $k'' = 4.31 \times 10^{-6}$ A cm^{-2}; from Ref. 17.

† Presumably this work is described by Tedoradze in Ref. 16, since Laviron is not mentioned in Ref. 16 (Ed. of Translation).

The disappearance of the high-coverage effect coincides with the transition from curves *2–4* to curve *1*. Irrespective of how accurately the high-coverage effect is described by the empirical formula (3), a minimum on the potential–time curve is a sufficient criterion for the existence of this effect.

In order to demonstrate the high-coverage effect with the aid of charging curves, the measurements must be made under conditions such that diffusion of the reactant to the electrode can be ignored. Otherwise, a potential minimum could arise from a trivial cause: the tangential motion of the mercury surface. We have observed this phenomenon in practically every system examined.

Charging curves with a potential minimum due to the high-coverage effect have been observed in the reduction at a mercury electrode of dipyridylethylene[17,18] (Fig. 6), ethyl bromoacetate and bromobutyrate, and di(methoxycarbonylmethyl)mercury[38].

We have found in the literature a number of charging curves showing a potential minimum, but nowhere was the cause of the phenomenon discussed[39-41].

A paper by Lorenz and Schmalz[39] describes the charging curves of eosin. Fig. 7 shows that the charging curve obtained for prepolarisation at a potential corresponding to a coverage close to the limiting value has a clear minimum, which disappears (as in the reduction of dipyridylethylene discussed above) if the electrode is previously held at a potential for which the coverage is less than unity. The transition times are so small in this case that the potential minimum cannot possibly be associated with the polarographic maximum.

Similar effects have been observed in the reduction at a mercury electrode of developers for colour photography[40] and in the reduction of hydroxylamine at a platinum electrode[41] previously activated at a potential of +0.1 V (normal calomel electrode). It should be noted that the adsorption of hydroxylamine on anodically oxidised platinum is insignificant. The potential minimum on the charging curve also disappears if the electrode is passive.

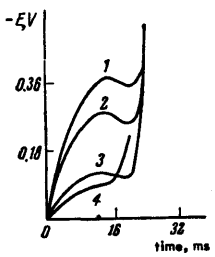


Fig. 6. Charging curves for dipyridylethylene after holding the electrode at various potentials (the zero of each curve is taken as the previous holding potential). Holding potentials: 1) -0.6; 2) -0.7; 3) -0.9; 4) -0.92 V (s.c.e.); polarising current density 10 mA cm^{-2}; from Ref. 18. Prior polarisation at the potential of incipient desorption of dipyridylethylene shortens the transition time and removes the fall of potential on the charging curve.

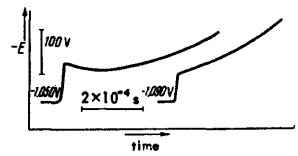


Fig. 7. Cathodic charging curve for eosin at a current density of 40 mA cm^{-2}; the numerals denote the prior polarisation potential; potential of incipient desorption of eosin -1.05 V; from Ref. 39.

We shall now briefly describe the electrochemical behaviour of various systems in which the high-coverage effect has been observed.

Diphenylamine[9-11]. When mercury is cathodically polarised in acid solutions of diphenylamine, the diphenylammonium cations formed by protonation of diphenylamine (B) are reduced:

$$B + H^+ \rightarrow BH^+; \quad BH^+ + e \rightarrow BH.$$

The unstable BH radicals decompose with formation of diphenylamine and molecular hydrogen:

$$2BH \rightarrow 2B + H_2.$$

Thus, the only product of the electrolysis of diphenylamine solutions is molecular hydrogen, which has no effect on the differential capacity of the mercury electrode[42]. The coverage of the electrode surface by diphenylamine was therefore measured from the change in differential capacity of the mercury electrode in the presence of a surface-active material. Polarisation curves for the discharge of diphenylammonium ions at various concentrations of diphenylamine are shown in Fig. 8, whence it can be seen that the overvoltage for hydrogen evolution at low current densities at first decreases and then increases with increase of catalyst concentration. The variation of current density with electrode coverage is different in 0.2 *N* and 1 *N* HCl solutions of diphenylamine. In 0.2 *N* HCl and at coverages below 0.9 (curve *b* of Fig. 9) the current density varies approximately linearly with the coverage of the electrode surface by the catalyst. At still higher coverages the rate of the reduction process falls off.

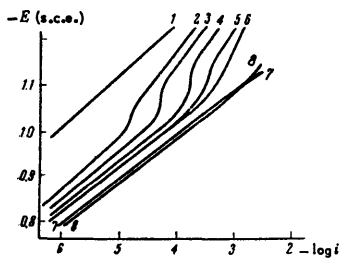


Fig. 8. Polarisation curves for the solutions 1 M HCl + x M $(C_6H_5)_2NH$: 1) $x = 0$; 2) $x = 4.85 \times 10^{-5}$; 3) $x = 9.6 \times 10^{-5}$; 4) $x = 1.33 \times 10^{-4}$; 5) $x = 2.66 \times 10^{-4}$; 6) $x = 3.6 \times 10^{-4}$; 7) $x = 1.48 \times 10^{-3}$; 8) $x = 1.9 \times 10^{-3}$; from Ref. 9.

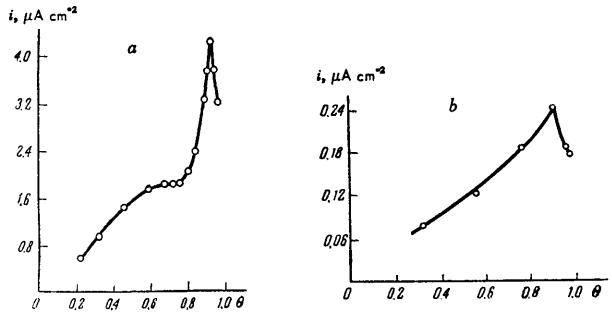


Fig. 9. Variation of the rate of electrochemical reaction with coverage of the mercury surface by an equilibrium mixture of diphenylamine and diphenylammonium ions at a potential of -0.8 V (s.c.e.); curve *a* was obtained in 1 M HCl, curve *b* in 0.2 M HCl; from Ref. 11.

In 1 *N* HCl the approximately linear variation of current density for reduction of the diphenylammonium ion with coverage of the electrode surface by catalyst holds only up to $\Theta < 0.5$. At higher coverages the current density is at first independent of coverage and then shows a steep rise. For Θ values close to 0.9 the current density (as in the case of 0.2 *N* HCl) suffers an appreciable drop with increase of surface coverage of the electrode by diphenylamine. The complicated shape of this plot has been qualitatively explained by invoking blocking of the electrode surface by electrochemically inactive diphenylamine molecules. However, it is impossible to explain the fall in current at high coverages, whether in 0.2 *N* or in 1 *N* HCl, in terms of blocking. The reasons are as follows.

Measurements of the differential capacity of the electrical double layer give only the degree of coverage of the electrode by the equilibrium mixture of diphenylamine and diphenylammonium. In 0.2 *N* HCl the adsorption layer consists almost entirely of molecules of diphenylamine. In 1 *N* HCl the proportion of diphenylammonium in the adsorption layer becomes much greater. Therefore, inhibition of the process through surface blocking by diphenylamine molecules should be less pronounced in the latter case, or else it should set in at higher coverages, but neither of these effects is found in practice (see Fig. 9).

Dipyridylethylene in water-alcohol mixtures is reduced reversibly, according to Volke and Holubek's polarographic data[43], by addition of two electrons and two protons:

$$\text{Py—CH=CH—Py} + 2e + 2H^+ \longrightarrow \text{Py—CH}_2\text{—CH}_2\text{—Py},$$

where Py is a pyridine ring.

Measurements of Faradaic impedance[18] show that in aqueous solution at pH ≤ 2 the reduction is likewise reversible. Essentially, at pH ≤ 2 dipyridylethylene exists in solution and is reduced in a weakly adsorbed protonated form, whereas at pH > 9 it exists in solution and on the surface exclusively as readily adsorbed, unprotonated molecules, and protonation is not one of the potential-determining stages. Between pH 4 and pH 9 both the protonated and the unprotonated forms exist in solution, but the mercury surface is covered only with unprotonated molecules, owing to the large difference in adsorbability between the two forms. However, despite the fact that under these conditions the dipyridylethylene is adsorbed mostly in the unprotonated form, it is the protonated species which undergo reduction (the half-wave potential is a function of pH). This is the region of pH in which the high-coverage effect can be observed on the polarograms, on the current-time curves, and on the charging curves (Figs. 3 and 6) if the surface concentration of reducible material exceeds 3×10^{-10} mole cm^{-2}. On decreasing the surface concentration by diluting the solution or by adding ethanol (up to 50 wt.%), the high-coverage effect was removed (Fig. 10).

It should be noted that a similar phenomenon is observed also in the reduction of diphenylammonium ions in 0.2 *N* HCl: a negative shift of the potential causes partial desorption of diphenylamine molecules and makes the relation between $\log i$ and the potential deviate from linearity in the sense of accelerating the process[44].

Ethyl bromoacetate and α-bromobutyrate are reduced irreversibly without prior protonation by addition of two electrons and one proton and splitting off a molecule of bromine. The high-coverage effect was detected in both compounds by the charging-curve method at $\Gamma > 2 \times 10^{-10}$ mole × × cm^{-2}; for the second compound the effect disappears at $\Gamma < 1 \times 10^{-10}$ mole cm^{-2}. However, studies of the variation of current (at constant potential and electrolysis time) with bulk concentration have made it clear, in both cases, that, when the charging curve indicates a surface concentration of reactant close to the limiting value, and the high-coverage effect operates, the current density remains proportional to the bulk concentration of reactant. Further increase in bulk concentration causes some deviation from linearity in the relation between current density and bulk concentration, but no maximum has been observed on this curve. We have concluded[38] that under conditions of constant-potential electrolysis (before plotting the charging curve) there is an accumulation of an intermediate (or side-product) of the reduction of bromoalkanoic acids at the electrode, this product being highly surface-active. Therefore the shape of the charging curve is determined by the adsorption of this intermediate. Since these products could be the corresponding organomercury compounds, we examined the charging curve of di(methoxycarbonylmethyl)mercury and methoxycarbonylmethylmercury bromide under conditions similar to those used for the esters of the bromoalkanoic acids. Clearly defined minima, indicative of the high-coverage effect, were observed on the charging curves of the symmetrical organomercury compound at $\Gamma = 2.5 \times 10^{-10}$ mole cm^{-2}.

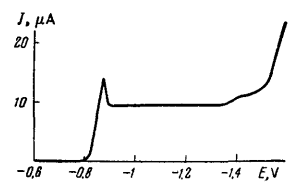


Fig. 10. Polarogram for the reduction of dipyridylethylene in 50 wt.% ethanol; pH 6.7; concentration of dipyridylethylene 2×10^{-3} M; from Ref. 18.

Zhdanov and Pozdeeva[45] found a high-coverage effect in the reduction of the 1,2-diphenyl-3-hydroxycyclopropenyl cation, which undergoes one-electron reduction in the first wave. The radicals formed by the electrode reaction disappear from the solution by two competing reactions: dimerisation, or decomposition to diphenylcyclopropenone and hydrogen. The half-wave potential of this wave moves towards more negative potentials upon increasing the concentration of diphenylcyclopropenone in solution. The shift can amount to 400 mV in 5 : 30 ethanol for concentrations between 10^{-5} and 10^{-4} M. Solutions which are dilute in ethanol show a sudden increase in current before the limiting current is reached. On the current–time curves corresponding to the first wave we find a falling off of the current before a quantity of electricity sufficient to give rise to surface blocking has passed through the electrode: therefore, the fall of current can only be ascribed to the high-coverage effect[45].

Phenomena interpreted as high-coverage effects have been observed also in the study of anodic reactions on platinum by Bagotskii and Vasil'ev[30], Hira Lal et al.[46], Podlovchenko and Iofa[47], Petrii et al.[48], Podlovchenko et al.[49], and Khazova et al.[50] (see Fig. 11). Some other results[29,51] also justify the conclusion that the high-coverage effect was operative.

Lastly, it may not be out of place to mention the results of a study[52] of the electrochemical behaviour of cobalt complexes on platinum. Anson found[52] that the oxidation process is accelerated when chloride, bromide, and iodide ions, and also pentanol (which is readily adsorbed on platinum[53]), are added to an aqueous solution of a divalent cobalt complex (CoY^{2-}, where Y is ethylenediamine tetraacetic acid). Special experiments having shown that chemical reaction between the reactant and the additives could not account for this effect, the author[53] suggested that the cause lay in adsorption of the additive, and consequent desorption of the reactant from the electrode.

In fact, if we plot the product $i\tau$ against $1/i$ from Anson's experimental results[52] (Fig. 12), we find that, when iodide ions are present in a solution of CoY^-, the graph goes through the origin, which shows that the cobalt complex is not adsorbed. If iodide ions are not added to the solution of CoY^-, the graph yields an intercept on the ordinate axis corresponding to the quantity of electricity needed to remove the adsorbed chelate. However, the surface concentration of the complex cannot be calculated in this way because the true surface area of the electrode is not quoted in the original paper[52]. The plots of $i\tau$ against $1/i$ for

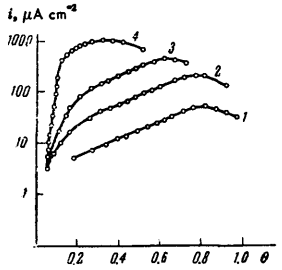


Fig. 11. Variation of the rate of oxidation of methanol on platinum with degree of coverage; from Ref. 50.

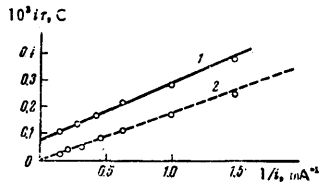


Fig. 12. Variation of the product $i\tau$ (where τ is the transition time) with $1/i$ for the reduction of cobalt(III) ethylenediaminetetraacetate on platinum:
1) in the absence of iodide ions; 2) in the presence of 10^{-4} M KI; concentration of complex 13.3×10^{-3} M; phosphate buffer (pH 7); from Ref. 52.

the oxidation of CoY^{2-} in the presence and in the absence of surface-active additives are similar to those for CoY^-.

Although this paper does not give the short-time charging curves for cobalt chelates, it would appear that high-coverage effects are present, and are neutralised by surface-active additives.

We may conclude that the study of the high-coverage effect is still in its early stages. In some cases, a choice between the various possible causes of the effect can be made on the basis of the structure of the reacting molecule. The most important requirements now are additional experimental information on the high-coverage effect and new criteria on which to base an unambiguous choice between possible alternative mechanisms. Studies of the influence of temperature and of the nature of the metal are a promising long-term approach.

1. A.N. Frumkin, Dokl. Akad. Nauk SSSR, 85, 373 (1952).
2. A.N. Frumkin, Uspekhi Khim., 24, 933 (1955).
3. A. Frumkin, Nova Acta Leopoldina, 19, No. 132, 1 (1957).
4. W.H. Reinmuth, "Advances in Analytical Chemistry and Instrumentation", Vol. 1, Interscience, New York, 1960, p. 241.
5. H.W. Nurberg and M. von Stackelberg, J. Electroanalyt. Chem., 4, 1 (1962).
6. B.E. Conway, Chem. in Canada, 12, No. 4, 39 (1960).
7. C.N. Reilley and W. Stumm, "Progress in Polarography", Vol. 1, Wiley, New York–London, 1962, p. 81.
8. J. Kuta and J. Smoler, *ibid.*, p. 43.
9. A.N. Frumkin, D.I. Dzhaparidze, and G.A. Tedoradze, Dokl. Akad. Nauk SSSR, 152, 164 (1963).
10. G.A. Tedoradze and D.I. Dzhaparidze, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 402 (1963).
11. G.A. Tedoradze and D.I. Dzhaparidze, Elektrokhimiya, 1, 910 (1965).
12. A.B. Ershler, G.A. Tedoradze, and S.G. Mairanovskii, Dokl. Akad. Nauk SSSR, 145, 1325 (1962).
13. A. Frumkin, Electrochim. Acta, 9, 465 (1964).
14. A.N. Frumkin, Trudy Inst. im. L. Ya. Karpova, No. 5, 3 (1926).
15. A. Frumkin, Z. Physik, 35, 792 (1926).
16. G.A. Tedoradze, Doctoral Thesis, Institute of Electrochemistry of the Academy of Sciences of the USSR, 1965.
17. Ya.M. Zolotovitskii, G.A. Tedoradze, and A.B. Ershler, Elektrokhimiya, 1, 828 (1965).
18. G.A. Tedoradze, Ya.M. Zolotovitskii, and A.B. Ershler, Elektrokhimiya, 1, 1272 (1965).

19. M.G.Gonikberg, Dokl.Akad.Nauk SSSR, 102, 117 (1955).
20. S.Glasstone, K.J.Laidler, and H.Eyring, "Theory of Rate Processes" (Translated into Russian), Inostr.Lit., Moscow, 1948, p.447.
21. S.D.Hamann, Austral.J.Chem., 9, 533 (1956).
22. D.W.Coillet and S.D.Hamann, Trans.Faraday Soc., 57, 2231 (1961).
23. M.G.Evans and M.Polanyi, Trans.Faraday Soc., 31, 875 (1935).
24. S.D.Hamann and D.K.Teplitzky, Discuss.Faraday Soc., No.114 (1956).
25. A.H.Ewald and S.D.Hamann, Austral.J.Chem., 9, 54 (1956).
26. J.Buchanen and S.D.Hamann, Trans.Faraday Soc., 49, 1425 (1953).
27. A.E.Stearn and H.Eyring, J.Chem.Phys., 5, 113 (1937).
28. K.J.Laidler, Discuss.Faraday Soc., No.88 (1956).
29. S.Gilman, J.Phys.Chem., 68, 70 (1964).
30. V.S.Bagotskii and Yu.B.Vasil'ev, Electrochim.Acta, 9, 869 (1964).
31. J.Koryta, Coll.Czech.Chem.Comm., 18, 206 (1953).
32. J.Koutecký and J.Weber, Coll.Czech.Chem.Comm., 25, 1423 (1960).
33. P.Delahay and P.Trachtenberg, J.Amer.Chem.Soc., 79, 2355 (1957).
34. P.Delahay and P.Trachtenberg, J.Amer.Chem.Soc., 80, 2094 (1958).
35. B.B.Damaskin, S.Vavrzhichka, and N.B.Grigor'ev, Zhur. Fiz.Khim., 36, 2530 (1962) [Russ.J.Phys.Chem., 1376 (1962)].
36. J.Koutecký, Czech.J.Phys., 2, 50 (1953).
37. K.P.Butin, I.P.Beletskaya, and O.A.Reutov, Zhur.Org. Khim. (in the press).
38. A.B.Ershler, G.A.Tedoradze, M.Fakhmi, and K.P.Butin, Elektrokhimiya, 2, No.3 (1966).
39. W.Lorenz and E.O.Schmalz, Z.Elektrochem., 62, 301 (1958).
40. W.Jaenicke and H.Hoffman, Z.Elektrochem., 66, 803 (1962).
41. D.G.Davis, Analyt.Chem., 35, 764 (1963).
42. A.N.Frumkin, O.A.Petrii, and N.V.Nikolaeva-Fedorovich, Dokl.Akad.Nauk SSSR, 137, 896 (1961).
43. J.Volke and J.Holubek, Coll.Czech.Chem.Comm., 27, 1777 (1962).
44. D.I.Dzhaparidze, Candidate's Thesis, Institute of Electrochemistry of the Academy of Sciences of the USSR, Moscow, 1963.
45. S.I.Zhdanov and A.A.Pozdeeva, Elektrokhimiya (in the press).
46. Hira Lal, O.A.Petrii, and B.I.Podlovchenko, Electrokhimiya, 1, 316 (1965).
47. B.I.Podlovchenko and Z.A.Iofa, Zhur.Fiz.Khim., 38, 211 (1964) [Russ.J.Phys.Chem., 112 (1964)].
48. O.A.Petrii, B.I.Podlovchenko, A.N.Frumkin, and Hira Lal, Zhur.Fiz.Khim. (in the press).
49. B.I.Podlovchenko, O.A.Petrii, A.N.Frumkin, and Hira Lal, Electrochim.Acta (in the press).
50. O.A.Khazova, Yu.B.Vasil'ev, and V.S.Bagotskii, Elektrokhimiya (in the press).
51. S.Gilman, J.Phys.Chem., 66, 2657 (1962).
52. F.C.Anson, Analyt.Chem., 36, 520 (1964).
53. M.Breiter, J.Electrochem.Soc., 109, 42 (1964).

Institute of Electrochemistry,
Academy of Sciences of the
USSR