

THEORY OF POLAROGRAPHIC CURRENTS

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INTRODUCTION

Since the invention of the polarographic method in 1922 attention has been paid primarily to theoretical aspects of the method. Heyrovský and coworkers were interested in the problems of hydrogen evolution at the dropping mercury electrode (DME), in the reduction of oxygen-containing anions, in anodic reactions of anions connected with insoluble salt formation, etc. Shikata, Tachi and coworkers investigated mainly electrode processes of organic compounds with particular reference to the structural aspects.

At present the theory of classical d.c. polarography is in many ways a closed subject. Rapid developments are taking place only with regard to processes influenced in some part by adsorption, either of electro-inactive species or reactants and products of electrode reactions. With this in mind I intend to present first a brief review of those fields. Later I shall be concerned in more detail with the adsorption processes in polarography.

DIFFUSION CURRENTS

The most important contribution of the pre-war of the development of polarography seems to be the theory of the diffusion current at the DME. The original solution by Ilkovič¹ (1934) was only intuitive: the concentration gradient obtained for linear diffusion in a semi-infinite space towards a plane electrode was multiplied by $\sqrt{(7/3)}$. In this way the Ilkovič equation of instantaneous limiting diffusion current was obtained:

$$i_{\text{ilk}}^{\text{d}} = 0.732 \times 10^{-3} nFD_{\text{A}}^{\frac{1}{2}} m^{\frac{2}{3}} t^{\frac{1}{3}} C \quad (1)$$

where n is the number of electrons consumed in the overall electrode reaction, F is the faraday, D_{A} is the diffusion coefficient in $\text{cm}^2 \text{sec}^{-1}$, m is the outflow rate of mercury in g cm^{-1} , t is the time following the drop and C is the concentration in mole l^{-1} .

The differential equation of convective diffusion transport to an expanding sphere was formulated by MacGillavry and Rideal². Using rather extensive simplifications they obtained the solution identical with Eq. (1). In 1938 Ilkovič deduced a partial differential equation based on the model of the "expanding plane". Its surface increases like DME, and the diffusion and convection transport occurs only in the direction perpendicular to this surface. This equation reads

$$\frac{\partial c}{\partial t} = D_{\text{A}} \frac{\partial^2 c}{\partial x^2} + \frac{2}{3} \frac{x}{t} \frac{\partial c}{\partial x} \quad (2)$$

where x is the distance from the surface of the electrode. The solution of this equation with appropriate boundary conditions is again given by Eq. (1).

This solution, which neglects the spherical character of the transport to the electrode, has not been fully satisfactory. Lingane and Loveridge⁴ adopted a similar procedure to that adopted by Ilkovič in 1934. They used the expression for the concentration gradient due to diffusion to a spherical stationary electrode and multiplied it by $\sqrt{7/3}$. Finally, in 1952 an exact solution was obtained by Koutecký⁵, and by Kambara and Tachi⁶. Koutecký solved the original MacGillavry-Rideal partial differential equation and obtained the solution in the form

$$i_d = i_{1lk}^d (1 \pm 3.97 D_A^{1/2} t^{1/2} m^{-1/2}) \quad (3)$$

where the plus or minus sign applies if the original substance is present in the solution or in the electrode, respectively.

This result differs from that obtained by Lingane and Loveridge only in the numerical constant in the correction term. Matsuda⁷ took account also of the screening influence of the capillary tip; this is reflected in the value of the constant in the correction term 2.4.

At first, experiments with electroactive substances dissolved in the solution did not confirm the exact theory of the diffusion current, because of the surprising effect connected with the functioning of the DME. Previously it was generally assumed that the polarographic current measured on successive drops is not influenced by the transfer of exhausted solution from one drop to the next one, as it is (so it was supposed) carried down with the falling drop. Actually, as shown by Hans and coworkers⁸, a part of the exhausted solution remains at the orifice of the capillary and lowers the current at the beginning of the next drop. A similar, earlier observation of Airey and Smales⁹ and of Gierst¹⁰ escaped general attention. This "impoverishment effect" could be avoided by recording the instantaneous current at the first drop obtained by switching on the applied voltage at the start of drop formation⁸ (Figure 1; cf. ref. 11).

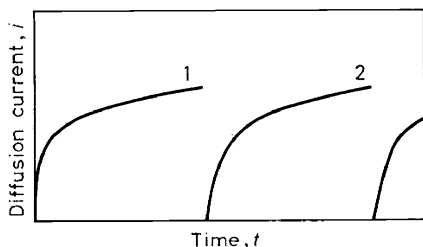


Figure 1. Diffusion current-time curves for the first drop (1) and second drop (2) using 2×10^{-3} M cadmium chloride in 0.1 M potassium chloride

The equation of the reversible polarographic current-potential curve was deduced in 1935 by Heyrovský and Ilkovič¹² (cf. also ref. 13). The equation of instantaneous current for a deliberate electrode potential with regard to the radial transport to DME was deduced by Koutecký⁵ (see also ref. 13).

It reads

$$i = i_{\text{Ik}} (1 + 3.97 D_A^{\frac{1}{2}} t^{\frac{1}{2}} m^{-\frac{1}{2}} \theta) \quad (4)^\dagger$$

Here

$$i_{\text{Ik}} = i_{\text{Ik}}^d [1 + \lambda \sqrt{(D_A/D_B)}]^{-1} \quad (5)$$

where D_A and D_B are the diffusion coefficients of the oxidized and reduced forms, respectively,

$$\lambda = \exp [nF (E - E^\circ)/RT] \quad (6)$$

and

$$\theta = \frac{1 \pm \lambda}{1 + \sqrt{(D_A/D_B)} \lambda} \quad (7)$$

The plus sign applies if the original substance and the product of the electrode reaction are able to exist in the solution, and the minus sign refers to the case where one of these substances is soluble in the solution and the other in the electrode.

CURRENTS CONTROLLED BY THE RATE OF ELECTRODE REACTION AND DIFFUSION

In the earliest approach to this problem the average diffusion flux to the electrode was expressed by the Ilkovič equation. In this way Tomeš¹⁴ deduced the equation of the irreversible polarographic wave; a similar procedure was adopted by Tanaka and Tamamushi¹⁵, Eyring, Marker and Kwoh¹⁶, and, for the general oxidation-reduction case, by Goto and Tachi¹⁷ and Tockstein¹⁸.

The exact solution based on Eq. (2) for description of the transport to DME was obtained by Meiman¹⁹ and for the general oxidation-reduction case by Koutecký²⁰. This solution is expressed by the approximate relation²¹

$$\frac{\bar{i}}{\bar{i}_\infty - \bar{i}} = 0.886 \left(\frac{k_r}{D_A^{\frac{1}{2}}} + \frac{k_o}{D_B^{\frac{1}{2}}} \right) t_1^{\frac{1}{2}} \quad (8)$$

where \bar{i} denotes the average current at DME, \bar{i}_∞ the average current in the reversible case, k_r and k_o the reduction and oxidation electrode reaction rate constants and t_1 the drop-time. An important discussion of this case by Delahay²² should also be mentioned.

The appropriate procedures for determination of the parameters of an electrode reaction in the general oxidation-reduction case were developed by Matsuda and Ayabe²³ and Koryta²⁴.

The elements of the theoretical solution of the polarographic current controlled by electrode reaction and diffusion have been presented by Koutecký and Čížek²⁵; an evaluation of the rate constants from their results is, however, very difficult.

The methods of analysis of irreversible polarographic curves influenced by equilibria between the complexes and the complex-forming agent were worked out by Badoz-Lambling and Gauguin²⁶, Matsuda and Ayabe²⁷ and Koryta²⁸ and analogous procedures for irreversible processes of organic

† Eq. (4) was verified by Kůta and Smoler¹¹.

substances with acid-base equilibria by Badoz-Lambling and Gauguin²⁶, Laviron²⁹, and Turyan³⁰. In the latter case the pH-dependence of the half-wave potential of reduction of a protonized form is given by Eq. (9)

$$E_{\frac{1}{2}} = RT/(\alpha \nu F) \ln 0.886 k^{\circ} i_{\frac{1}{2}}^{-1} D_A^{-\frac{1}{2}} + RT/(\alpha \nu F) \ln [H^+]/([H^+] + K) \quad (9)$$

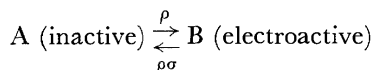
where K is the ionization constant, α is the charge transfer coefficient, ν the number of electrons transferred in the electrode reaction and k° the standard electrode-reaction rate constant.

CURRENTS CONTROLLED BY THE RATE OF CHEMICAL VOLUME REACTIONS

More than 50 years ago Eucken³¹ drew attention to the possibility that a volume chemical reaction may determine the rate of an electrode process. But Brdička and Wiesner³²⁻³⁴ were the first to prove the existence of this phenomenon using the polarographic method. The phenomenon is observed whenever the chemical equilibrium in the neighbourhood of DME is disturbed by the electrode reaction. The basic ideas developed from the concept of a reaction layer with a thickness of molecular dimensions at the surface of the electrode^{33,34} (the process would be, in fact, a surface reaction) to the statistical interpretation of this thickness³⁵ and, finally, to the exact solution of the partial differential equation of diffusion to a plane electrode and chemical reduction by Koutecký and Brdička³⁶ in 1947 and to Koutecký's papers on kinetic currents at DME^{37,38}.

If the chemical reaction leading to the re-establishment of the equilibrium proceeds with a sufficiently high rate, a steady state is set up between diffusion and chemical reaction of the original electroactive substance or the immediate product of the electrode reaction. The consequence of this is a fixed distribution of concentration of this substance in the surroundings of the electrode, the reaction layer. The establishment of such a steady state is subject to the condition that the relaxation time of the chemical reaction may be essentially shorter than the drop-time. An equivalent condition is that the effective thickness of the reaction layer must be considerably smaller than the thickness of the diffusion layer that would be formed if the chemical reaction did not take place.

In the case of a simple preceding reaction



the steady state concentration distribution of B is given by the equation (for $\rho\sigma \gg 1/t_1$)

$$C_B = C_A [1 - \exp(-x/\mu)] \quad (10)$$

where the reaction-layer thickness μ is

$$\mu = \sqrt{[D/\rho(1 + \sigma)]} \quad (11)$$

while x is the distance from the electrode.

In general the chemical reactions are classified according to their position with respect to the electrode reaction. In the simple case of one electrode and one chemical reaction we distinguish three cases: By a chemical reaction

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an electroactive substance is formed from an inactive species (preceding reaction), or a product of an electrode reaction deactivated (subsequent reaction), or the initial electroactive substance regenerated either totally or partially from a product of the electrode reaction (parallel reaction). (For examples and systematic treatment of various types of these processes see, for instance, refs. 39–44).

ELECTRICAL DOUBLE-LAYER EFFECTS

Charging current

The theory of the charging current at DME was worked out by Philpot⁴⁵ and Ilkovič⁴⁶. Philpot also used the charging current for determination of the integral capacity of the mercury electrode. Heyrovský, Šorm and Forejt⁴⁷ described the change of the charging current due to the adsorption of pyridine.

At present practically all capacity measurements connected with adsorption at mercury electrodes are based on the a.c. method^{47a}.

Only recently Mairanovskii⁴⁸ and Vavříčka, Němec and Koryta⁴⁹ determined the charge of the electrode q ($C\text{ cm}^{-2}$) using the polarographic charging current at DME in the presence of strongly adsorbing substances (see Figure 2) and attempted the determination of their adsorption isotherms.

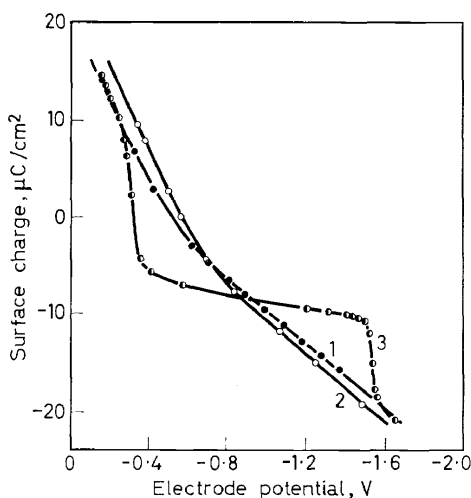


Figure 2. Dependence of the surface charge of a mercury electrode on electrode potential. (1) 0.1 M KCl. (2) 1 M KCl: full line, data of Parsons; circles: experimental values determined from charging currents. (3) 0.25 M KCl, 3×10^{-4} M tetrabutylammonium ion.

If charging currents are measured in the presence of low concentration of a surface active substance its diffusion to the electrode must be taken into account (see page 213).

Polarographic maxima

Polarographic maxima are caused by the tangential motion of the interface mercury–electrolyte^{50,51}. This stirring is caused either by a gradient of interfacial tension at the surface of DME (maxima of the 1st kind⁵²) or by the

flow of mercury out of the capillary (maxima of the 2nd kind⁵²). "Pure" maxima of the first kind are observed in dilute solutions of supporting electrolyte while typical maxima of the 2nd kind require rather high concentrations of supporting electrolyte. There are, of course, various intermediate cases. After less⁵³ or more⁵⁴ successful attempts of other authors Frumkin and Levich (for review see ref. 55) gave a satisfactory semi-quantitative interpretation of the whole group of these phenomena. This interpretation is based on such well-known concepts of electrochemistry and mechanics as interfacial tension, diffuse double-layer theory and the theory of motion of fluids. These investigations also enabled the above authors to detect new electro-kinetic phenomena. In general, the polarographic maxima themselves do not supply new data on electrode processes or properties of the interface and may thus be considered as an unwelcome parasitic phenomenon. There is, however, one exception connected with the acceleration of the transport to the electrode by this kind of stirring. According to Saraby-Reintjes and Overbeek⁵⁶ it enables measurement of higher electrode reaction rates than in absence of stirring.

Influence of the diffuse double-layer structure on the electrode processes

On the basis of their polarographic experiments Herasamenko and Šlěndyk⁵⁷ found that the hydrogen overvoltage at a mercury electrode depends strongly on the concentration of electrolyte. This finding inspired Frumkin⁵⁸ to work out the theory of diffuse double-layer influence on the rate of an electrode reaction. The dependence of an electrode reaction rate constant at standard potential k on the electrical potential difference in the diffuse double-layer ϕ_2 is given by the relation

$$k = k^0 \exp [-(z_A - \nu a) F\phi_2/RT] \quad (12)$$

For interpretation of processes at DME this equation was first used by Bagotsky⁵⁹ for hydrogen ion discharge reactions. The increase of the absolute value of a negative ϕ_2 accelerates the cation reduction. This was shown also in the case of electrode reactions of europium ions by Gierst⁶⁰ and of zinc ions by Koryta⁶¹. Among non-charged particles Eq. (12) applies to the reduction of oxygen as shown by Bagotsky and coworkers^{62,63} and Kůta and Koryta⁶⁴.

The double-layer influence is displayed in a rather peculiar way in the case of reduction of easily reducible anions⁶⁵ like persulphate, ferricyanide, etc. In contrast to cation reductions, anions are repelled by the negatively charged diffuse double-layer. At low electrolyte concentrations this repulsion effect increases more rapidly with increasing negative potential than the rate of the electrode reaction itself, i.e.

$$-(z_A - \nu a) \frac{\partial \phi_2}{\partial E} > \nu a \quad (12a)$$

Here the electrode reaction rate decreases with increasing negative potential. In consequence of this, current dips are formed on the polarographic curve (see *Figure 3*) which disappear if the concentration of supporting electrolyte is increased. The whole scope of numerous effects observed with anion reduction has been described by Frumkin and Nikolaeva-Fedorovich⁶⁶.

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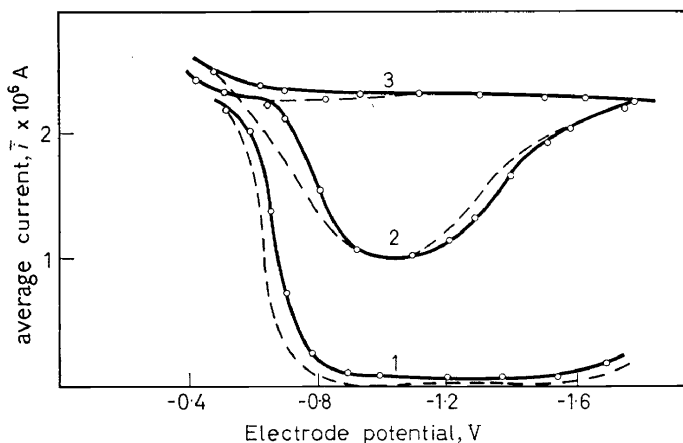


Figure 3. Effect of addition of potassium chloride on the average current for persulphate reduction. Persulphate solution used, 10^{-3} M potassium persulphate. (1) 10^{-3} M KCl added. (2) 10^{-2} M KCl added. (3) 0.1 M KCl added. Dashed curves computed theoretically.

The adsorption of thallium atoms at a thallium amalgam electrode has a profound effect on the kinetics of electrode reactions⁶⁷ which is caused by the change of ϕ_2 .

Among double-layer effects, the nature of which has not been cleared yet, belongs the variation of electrode reaction rates if the supporting electrolyte contains successively alkali metal cations in the series from lithium to cesium. In this series the electrode reaction rates of cations decrease⁵⁷ while those of anions are accelerated⁶⁶. In the field of organic electrode reactions a pronounced effect of this kind has been shown in the reduction of the anion formed by one-electron reduction of benzophenone⁶⁸.

In case of kinetic currents controlled by very rapid chemical reactions the reaction layer thickness may be comparable with the thickness of the diffuse double-layer. In such circumstances the reacting species should be transported to the electrode in part by migration; the dissociation rates of species formed by loosely bound ions should be influenced also by the electrical field in the diffuse double-layer (see e.g. ref. 69). The first of these influences was accounted for in the theoretical investigations of Gierst and Hurwitz⁷⁰ and Matsuda⁷¹.

PROCESSES INFLUENCED BY ADSORPTION

Kinetics of adsorption at DME

Let us assume that the adsorption process proper is very rapid and that the adsorption is strong so that for a high degree of coverage the concentration is sufficient, that is considerably smaller than that in the bulk of the solution. Under these conditions the adsorption is controlled by diffusion. The surface concentration of the surfactant at DME is given by the equation⁷²

$$\Gamma = 2\sqrt{(3D_s t / 7\pi)} C_s \quad (13)$$

where C_s and D_s are the concentration and diffusion coefficient of the

surfactant. If under conditions mentioned the maximum surface concentration is reached in practice, then the "time of coverage" ϑ is defined by the equation

$$\vartheta = 1.82 \times 10^6 \Gamma_m^2 D_s^{-1} C_s^{-2} \quad (14)$$

In spite of rather specialized assumptions this equation holds surprisingly well as will be seen in the next paragraph.

The relative coverage θ is then easily obtained as⁷³

$$\theta = \Gamma/\Gamma_m = \sqrt{t/\vartheta} \quad (15)$$

The adsorption at a stationary plane electrode under assumption of the linear adsorption isotherm

$$\theta = \beta C \quad (16)$$

is described according to Delahay and Trachtenberg⁷⁴ by Eq. (17)

$$\theta_t/\theta_e = 1 - \exp(-T) \operatorname{erfc}(T^{1/2}) \quad (17)$$

where θ_t is the coverage at the time t , θ_e is the equilibrium coverage and $T = Dt/(\beta\Gamma_m)^2$.

The same problem was solved for DME by Levich, Khaikin and Belokolos⁷⁵ using an approximate mathematical method for a deliberate adsorption isotherm

$$\beta C = f(\theta) \quad (18)$$

and, in part, by application of a digital computer for the case of the linear Langmuir isotherm. An approximate solution is given by the equation

$$(t/\vartheta)^{1/2} = \theta \cdot \frac{f(\theta_e)}{f(\theta_e) - f(\theta)} \quad (19)$$

The same problem with a linear adsorption isotherm was solved by

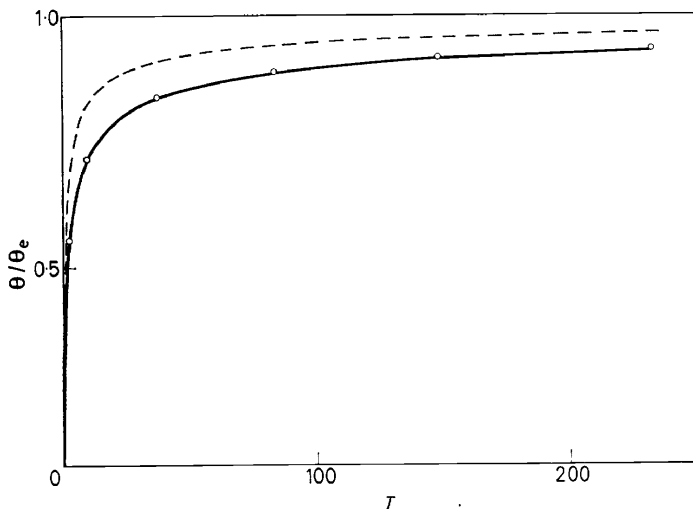


Figure 4. Establishment of adsorption equilibrium. $\phi = \theta_t/\theta_e$ (---) plane⁷⁴, (—) DME⁷⁶, points DME⁷⁷. $T = Dt/(\beta\Gamma_m)^2$.

Holub⁷⁶ using a digital computer and by Němec and Holub⁷⁷ by means of the analogue computer described in ref. 78. *Figure 4* shows the comparison between the establishment of adsorption equilibrium at a plane electrode and DME⁷⁷.

Influence of electro-inactive surfactants on electrode reactions

In 1958 Schmid and Reilly⁷⁹ put forward the idea that at a partially covered surface the electrode reaction rate may be expressed as a sum of two terms, one proportional to the free area and the other to the area covered by the surfactant, i.e.

$$k_e = k_e^0 (1 - \theta) + k_e^1 \theta \quad (20)$$

(the "blocking effect").

Weber, Koutecký and Koryta⁷³ solved the problem of the transport of the electro-active substance to DME in the case where the electrode reaction rate constant is given by Eq. (20) and θ by Eq. (15) (see *Figure 5*). This

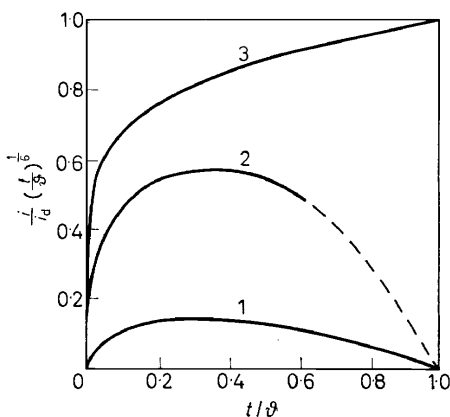


Figure 5. Blocking effect. Theoretical $i-t$ dependence for different $\beta = \sqrt{(7D/12\theta)}k_e^{0-1}$. (1) $\beta = 1$; (2) 0.1; (3) 0.

theory applied well to non-charged surfactants as shown by Kůta and Smoler⁸⁰. The experimental verification is shown in *Figure 6*. For ionic surfactants, though, large discrepancies were found. The attempt to remove discrepancies was made by Kůta, Weber and Koutecký⁸¹ who assumed that the rate constant of the process at the non-covered fraction of the surface is given by Eq. (12) while the potential difference in the diffuse double-layer depends on θ according to the equation

$$\phi_2 = \phi_2^0 + \theta \Delta \phi_2 \quad (21)$$

("electrostatic effect")

In this way a fair coincidence of the theory with the experiments was obtained in the case of inhibition (see *Figure 7*). On the same basis Gokhstein⁸² worked out a theory for acceleration of an electrode reaction by adsorption of ionic surfactants (without blocking the surface) and Kůta and Weber⁸³ for simultaneous acceleration and blocking by a surfactant. These theories were verified in the case of the influence of adsorption of tetrabutylammonium

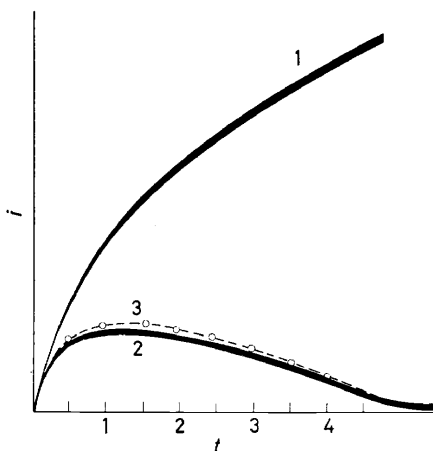


Figure 6. $i-t$ curves for 0.08 M $\text{Co}/\text{NH}_3/6 \text{Cl}_3$, 0.1 M sulphuric acid and 0.5 M potassium sulphate for the foot of the curve (1). Curve (2) 0.008 per cent polyvinyl alcohol added. Curve (3) Theoretical

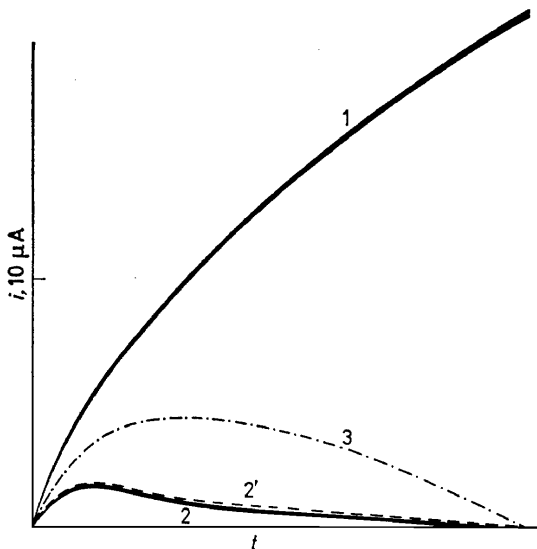


Figure 7. Electrostatic and blocking effect. $i-t$ curves for vanadyl ion 0.06 M in the presence of tribenzylammonium cation at the foot of the wave. (1) vanadyl ion in 0.1 M sulphuric acid; (2) 6.8×10^{-5} M tribenzylamine added; (2') theoretical curve; (3) theoretical curve neglecting the electrostatic effect

cation on persulphate anion reduction⁸² and of dodecylsulphonate anion on vanadyl cation reduction⁸³. The effect of inhibition is seen at high values of θ . A change from an acceleration to an inhibition effect of a surfactant by changing the electrode potential was described by Nikolaeva-Fedorovich, Fokina and Petrii⁸⁴ (see Figure 8).

Koryta and Holub⁸⁵ attempted a physical interpretation of Eq. (21) using the Grahame-Parsons⁸⁶ theory of electrical potential difference in the

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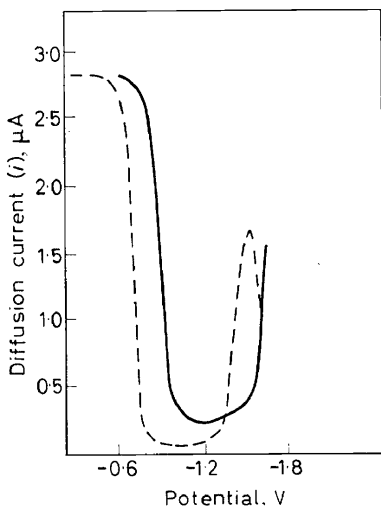


Figure 8. Effect of tetrabutylammonium ion on the reduction of PtCl_4^{2-} [(---) 10^{-3} M K_2PtCl_4 in 0.1 N Na_2SO_4 (—) after addition of 10^{-3} M TBA]

compact double layer under the influence of the specific adsorption of ions. This potential difference consists of two terms, one due to adsorbed ions, and the other due to the charge of the electrode. Thus, the basic equation⁸² reads

$$E - \phi_2 = \frac{zF \Gamma_m \theta}{K_1} + \frac{q}{K_0^0 (1 - \theta) + K_1^0 \theta} + \text{constant} \quad (22)$$

where K_1 is a constant value characteristic for each adsorbed ion, K_0^0 the original integral capacity of the electrode without adsorbed ions, K_1^0 the integral capacity of an electrode completely covered by adsorbed ions, z the charge of an adsorbed ion and q the charge of the electrode (C/cm^2).

Aramata and Delahay⁸⁷ and Sathyanarayana⁸⁸ found with weakly adsorbing neutral substances deviations from the linear dependence of the electrode reaction rate on coverage [according to Eq. (20)].

Adsorption of the electroactive substances

Reversible electrode reaction

The adsorption of the products of the electrode reaction or of original electroactive substances is manifested in Brdička's prewaves or postwaves⁸⁹, respectively. In the former case the adsorption of the product of the electrode reaction decreases its concentration at the surface of the electrode. In consequence of this the concentration of the original electroactive substance at the electrode decreases also to preserve the concentration ratio according to the Nernst equation and the current increases above its value in absence of adsorption. This rise of current is at last limited by the rate of growth of the electrode. The limiting current of Brdička's prewave obeys the equation

$$i_a = nF \Gamma_m \frac{\partial A}{\partial t} \quad (23)$$

where A is the area of DME.

Processes controlled by the rate of electrode reaction of adsorbed substances

This section includes the phenomena connected with formation of maxima at polarographic curves which can be explained neither by tangential movement of the interface, nor by simple double layer effects. For the case of a substance which is brought to the electrode by diffusion, and after a rapid adsorption undergoes some kind of a first order surface process the general boundary condition to the diffusion equation reads^{44,75,90,76}

$$x = 0: D \frac{\partial C_A}{\partial x} = \frac{\partial \Gamma_A}{\partial t} + \rho \Gamma_A \quad (24a)$$

eventually for DME

$$x = 0: D \frac{\partial C_A}{\partial x} = \frac{\partial}{\partial t} (A \Gamma_A) + \rho \Gamma_A \quad (24b)$$

Here ρ is either an electrode reaction rate constant or a function of an electrode reaction and chemical reaction rate constants. This boundary problem was solved for both a plane electrode^{44, 75, 76} and DME^{75, 76} in the case of the linear adsorption isotherm (see *Figure 9*). For short periods of time

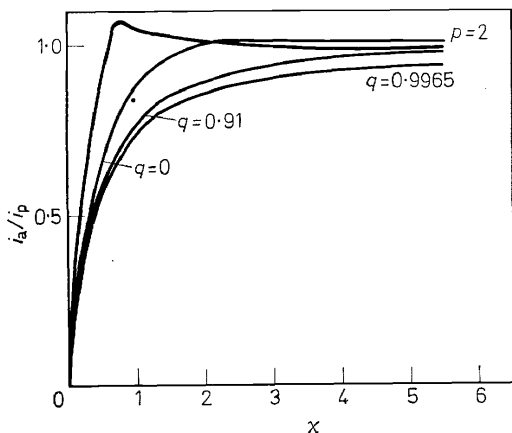
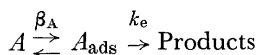


Figure 9. Dependence of i_a/i_p i.e. of the ratio of current corresponding to the surface reaction to that corresponding to the slow electrode reaction with the effective rate constant (Eq. 25) on $x = \sqrt{Dt}(2\beta\Gamma_m)^{-1}$; $\rho = \sqrt{4\beta^2\Gamma_m^2\rho/D - 1}$; $q = \sqrt{1 - 4\beta^2\Gamma_m^2\rho/D}$

the first term on the right hand side of Eq. (24a) is much larger than the second one. The current is proportional to Γ_A according to Eq. (13) or to an analogous expression for a plane electrode. For longer periods of time ($\partial\Gamma_A/\partial t$) becomes negligible and the current is given by the equation of a process controlled by diffusion and an irreversible electrode reaction with rate constant

$$k_{\text{eff}} = \beta\Gamma_m\rho \quad (25)$$

If the surface process is the electrode reaction only, i.e. if it follows reaction scheme



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then

$$k_{\text{eff}} = \beta_A \Gamma_{m,A} k_e \quad (28)$$

Let us assume that the adsorption coefficient β is given by the Frumkin-Butler equation^{91,92}

$$\beta = \beta_0 \exp [-a (E - E_m)^2] \quad (27)$$

where a is a constant and E_m is the electrode potential of maximum adsorption. Then at a definite potential the decrease of adsorption will overcompensate the increase of electrode reaction rate with increasing electrode potential and the polarographic curve will attain the shape of a peak^{41,93}, since

$$k_{\text{eff}} \sim \exp \left[-E^2 + \left(2a E_m - \frac{\alpha vF}{RT} \right) E \right] \quad (28)$$

(see Figure 10).

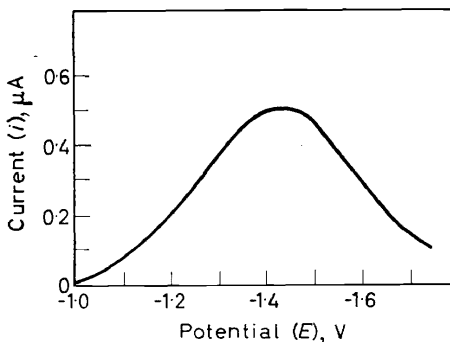
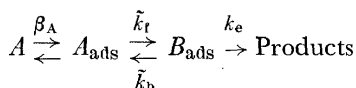


Figure 10. Polarogram of benzyl chloride electroreduction in the presence of sodium ions. Solution composition: 60% ethanol, 0.5 M sodium acetate.

For the reaction scheme



(the adsorbed product B_{ads} of a surface chemical reaction is electroactive, \tilde{k}_f and \tilde{k}_b are surface reaction rate constants)

$$k_{\text{eff}} = \frac{\tilde{k}_f k_e}{k_e + \tilde{k}_b} \beta_A \Gamma_{m,A} \quad (29)$$

If $k_e \ll \tilde{k}_b$ Eq. (28) simplifies to

$$k_{\text{eff}} = \sigma^{-1} k_e \beta_B \Gamma_{m,B} \quad (30)$$

where β_B is the adsorption coefficient and $\Gamma_{m,B}$ the maximum surface concentration of B , σ is the constant of the equilibrium between A and B in the solution since

$$\tilde{k}_b / \tilde{k}_f = \Gamma_A / \Gamma_B = \sigma \beta_A \Gamma_{m,A} / (\beta_B \Gamma_{m,B}) \quad (31)$$

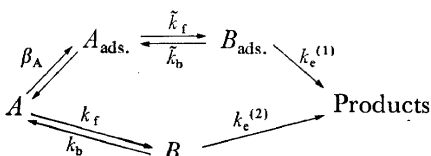
Equation (30) shows that k_{eff} may have an analogous potential dependence as in the first case but it depends also on σ which may be, for instance, pH-dependent.

If $\tilde{k}_b \ll k_e$ then the limiting surface current (cf. ref. 94) is reached with

$$k_{\text{eff}} = \tilde{k}_t \beta_A \Gamma_{m,A} \quad (32)$$

If \tilde{k}_t is potential independent (which is not safeguarded in view of possible loosening of a rigid orientation with increasing potential) the polarographic curve should have a plateau with a dip starting at a certain electrode potential.

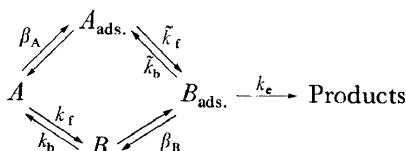
Parallel surface and volume transformation of A to B with an adsorbed product of the surface reaction and with an non-adsorbed product of the volume reaction is described by the scheme



and

$$k_{\text{eff}} = \frac{\tilde{k}_t k_e^{(1)}}{k_e^{(1)} + \tilde{k}_b} + \frac{k_e^{(2)} \sigma^{-1}}{1 + (k_e^{(2)} \mu/D)} \quad (33)$$

where $\mu = \sqrt{D/k_b}$, k_b and k_t are volume reaction rate constants. If the species B is electroactive only after adsorption (cf. ref. 95) the following scheme applies



The constant k_{eff} is given by the equation

$$k_{\text{eff}} = \frac{\tilde{k}_t + D/(\beta_A \sigma \mu)}{\tilde{k}_b + k_e + D/(\beta_B \mu)} \beta_A k_e \quad (34)$$

This effect is supposed in the reduction of some weak organic acids⁹⁵ (cf. also ref. 96) but this problem does not seem to have been solved yet.

The potential-dependent adsorption may also be the cause of an unexpected pH-dependence of half-wave potentials⁹⁷.

Inhibition by adsorption of the electroactive substance

This phenomenon described by Laviron⁹⁸ is caused by unsuitable orientation of the electroactive molecule in the adsorbed state. It is characterized by rather abrupt increase of current at the potential of desorption. The steepness of this step is connected with the dependence of adsorption energy on electrode potential. This phenomenon was observed in the case of the reduction of dipyrindylethylenes (cf. ref. 99) and of the Reinecke salt¹⁰⁰.

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At a highly covered surface of the electrode an electrode reaction may be inhibited if the molecule in transition state occupies a larger area than in initial state of the process¹⁰¹. This "effect of high coverage" is observed in the catalytic hydrogen evolution in the presence of diphenylammonium ions¹⁰² (see *Figure 11*).

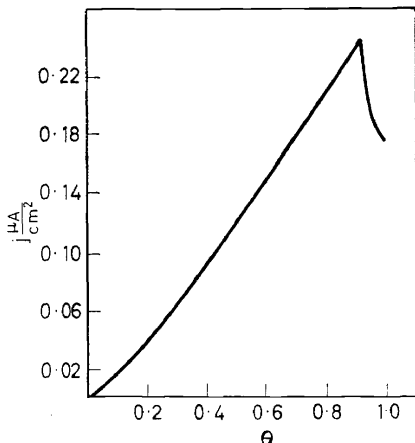


Figure 11. Dependence of catalytic current of hydrogen evolution in 0.2 M HCl in the presence of diphenylamine on coverage of the electrode at -0.8 V vs. N.C.E.

Inhibition by adsorbed electrode reaction products

For the case where the product of an electrode reaction is strongly adsorbed, while the rate of the electrode reaction is a linear function of coverage, Laviron and Degrand¹⁰³ deduced the equation for the foot of the polarographic curve

$$i = 0.57nFk_e \Gamma_m^{\frac{2}{3}} C^{\frac{1}{3}} e^{-s} \int_0^s x^{-\frac{1}{3}} e^x dx \quad (35)$$

where $s = ct k_e \Gamma_m^{-1}$ (see *Figure 12*) and c is the concentration of electroactive substance in mole cm^{-3} . This equation was verified in the case of reduction of triiodoimidazole.

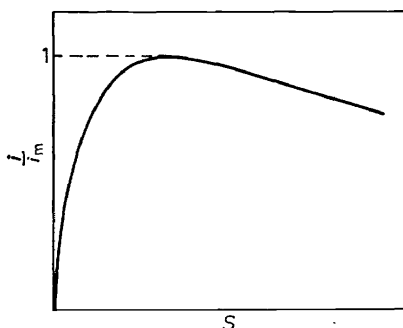


Figure 12. Inhibition by electrode reaction products (see Eq. 35)

An inhibition of this kind was found in processes connected with insoluble mercury salt formation^{104, 105, 106}. As shown by means of potentiostatic investigations these phenomena are caused by electrocrystallization of a monomolecular film by the growth of two-dimensional centres¹⁰⁷.

Inhibition of electrode reactions of adsorbed substances by electro-inactive surfactants

These phenomena which were investigated to a large extent by Holleck, Kastening and coworkers (e.g. ref. 108) do not obey Eq. (20). For large coverages by the inhibitor ($\theta_i \approx 1$) Kastening^{109, 110} has shown that the electrode reaction rate is proportional to a small fraction of the surface covered by the electroactive substance θ_A which depends on both the concentration of the electroactive substance C_A and of the inhibitor C_i in the following way

$$\theta_A \approx \text{const. } C_A/C_i^\kappa \quad (36)$$

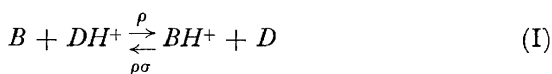
Here κ is a quantity characterizing the requirement of interfacial area by the inhibitor and by the electroactive substance; it is not given directly by $\kappa = \Gamma_{m,i}/\Gamma_{m,A}$ because of the influence of the inhibitor on the orientation of the electroactive substance.

Catalyzed hydrogen evolution

Catalysis by organic bases

This effect detected by Pech¹¹¹ in 1934 was ascribed by Frumkin and Andreyeva¹¹² to diffuse double-layer effects caused by adsorption of the catalyst and to the lowering of the activation energy of proton transfer to the electrode from an organic cation in comparison with the hydroxonium ion. Stackelberg and coworkers^{113, 114} and Nürnberg¹¹⁵ introduced also into the proposed mechanism the rate of chemical reaction of proton transfer to the basic form of catalyst and the desorption of the catalyst at negative potentials.

Mairanovskii (for review see ref. 116) proposed the following reaction scheme



where B denotes the basic form of catalyst and DH^+ the acid form of the proton-donor and vice versa. (I) may be a volume reaction and (II) a reversible electrode reaction as observed for some derivatives of pyridine or a surface reaction with (II) as an irreversible electrode (a more frequent case).

Catalysis by deposited platinum metals

Herasymenko and Šlendyk¹¹⁷ found that in acid media in the presence of platinum group metals in the solution the hydrogen overvoltage is lowered

considerably (by about 250 mV). They ascribed this phenomenon to the deposits of these metals on the surface of DME where the hydrogen evolution reaction should be faster than at a mercury surface. Fleischmann, Koryta and Thirsk¹¹⁸ have shown by potentiostatic experiments that in the case of ruthenium the metal is deposited by the growth of two-dimensional centres and the hydrogen evolution reaction proceeds very rapidly at the edges of these centres while their surfaces show very low catalytic activity.

CONCLUSION

The present review could not attempt to cover all theoretical aspects of polarography. However, in my opinion, it shows how strongly—and in spite of comments to the contrary, how favourably the whole field of electrode kinetics was influenced by the invention of electrolysis with the DME. I do not think that it is necessary to stress that at the present stage classical polarography represents only one of the methods of electrochemical research. It is certainly convenient and speedy, but for really effective kinetic investigations several methods have to be applied even at mercury electrodes.

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