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ELECTROCHEMICAL VACANCY INJECTION INTO ELECTRODES

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Experimental data available in the literature concerning the kinetics of electrochemical incorporation of metals into electrodes are analyzed which indicate that the bulk diffusion coefficients are anomalously high in electrodes when they are cathodically polarized in electrolyte solutions. The concept of an electrochemical injection of vacancies into the electrodes is formulated; this injection leads to higher diffusion rates in the electrodes. Expressions are obtained which describe the laws of incorporation under conditions where the kinetics of the process is governed by vacancy injection. New experimental results concerning incorporation kinetics are reported which confirm these concepts.

Even in the first investigations of cathodic incorporation of alkali metals, research workers were aware of a striking mismatch between theoretical estimates of the largest possible rates and the high rates actually observed for the penetration of metals that are incorporated into electrodes of zinc, lead, cadmium, and a number of other metals. The observed incorporation currents are several (sometimes six to seven) orders of magnitude higher than those expected, and this has not found a satisfactory explanation for a long time.

For instance, the diffusion coefficient of potassium through zinc membranes at room temperature was found to be $5 \cdot 10^{-12}$ cm^2/sec [1] while on the basis of theoretical estimates, it should have a value of 10^{-18} to 10^{-17}. It has been concluded, therefore [2], that potassium penetration into zinc electrodes predominantly occurs along crystallite boundaries. In fact, the experimental diffusion coefficient is of the same order of magnitude as the boundary self-diffusion coefficient in zinc. It has been assumed from the results of this work and a number of further studies that diffusion of the incorporated metal at room temperature into the electrode only occurs along crystallite boundaries and dislocations [3], and that the bulk phase layer of incorporation products is a layer at the electrode surface not thicker than 5-10 nm.

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However, it was found when investigating sodium incorporation from aqueous NaOH solution into lead by x-ray analysis [4] that the incorporation product, a solid solution of sodium in lead, has a thickness of at least 3000 nm, and that diffusion occurs throughout the entire electrode volume, not merely along crystallite boundaries. The bulk diffusion coefficient of sodium in lead was found to be 10^{-13} cm^2/sec. But extrapolation of the results of conventional diffusion experiments carried out at 300°C [5] yields a value of about 10^{-20} cm^2/sec for room temperature, i.e., a value seven orders of magnitude lower.

The result obtained in [4] was confirmed in another work [6], where the same process was investigated by x-ray and chemical analysis. It was found in the same work when comparing the amounts, Q, of sodium incorporated into lead, tin, and cadmium under identical conditions that these differ by no more than a factor of two, despite the substantial differences (orders of magnitude) in the equilibrium solubilities of sodium in these metals. This implies that equilibrium solubility is not the decisive factor for the way in which the system "electrode/metal being incorporated" behaves during the incorporation process. Anomalously high diffusion rates in electrodes during cathodic incorporation have been observed in a number of further studies [7, 8].

Thus, a large number of experimental observations exist by now according to which the properties of certain metals where diffusion follows a vacancy mechanism are substantially altered during cathodic polarization. Their diffusional permeability increases by several orders of magnitude (up to seven), the diffusion mechanism changes, i.e., instead of the boundary diffusion expected at room temperature one finds bulk diffusion, and possibly the solubility of alkali metals in them increases to some extent. There are indications that these changes extend to a surface layer of considerable depth, of at least several micrometers.

In the present work we offer an explanation for the observations described above which is based on the concept that a direct connection exists between the surface and bulk properties of metals which becomes manifest in a dependence of vacancy concentration in the metal's crystal lattice on changes in the energy state of the metal surface.

It has been found that under diffusion control, changes in the incorporation rate with electrode potential, E, usually occur on account of changes in the diffusion coefficient [9-12]; the incorporation current density, i, or the amount of metal incorporated can be written as $i = K \cdot t^{-0.5}$ or $Q = K \cdot t^{0.5}$, and the incorporation rate constant, K, is related to potential by a power law of the form of

$$K = A \cdot \sqrt{(E^* - E)}. \quad (1)$$

Coefficient A is constant over the range of potentials where a given phase is formed but changes when a different phase is formed, and E* is the potential where this phase starts to form. This law holds for incorporation, both when it yields intermetallic compounds and when it yields solid solutions. In the present work we discuss the case where the incorporated metal is dissolved in the electrode metal and where the rate of compound formation can be neglected relative to the rate of solid-solution formation. Usually this is observed when alkali metals are incorporated from aqueous and nonaqueous electrolyte solutions into lead, tin, zinc, and certain other soft metals at temperatures close to ambient.

We shall write the diffusion coefficient, D, of one of the components in a nonideal solid solution as the product of its self-diffusion coefficient, D*, and a thermodynamic factor, $g = 1 + (\partial \ln \gamma / \partial \ln c)$, where γ is the activity coefficient of the diffusing component, and c is its concentration [13]:

$$D = D^* \cdot g. \quad (2)$$

Kinetic laws of the type of (1) are obeyed, provided the kinetic coefficient L in the equation for diffusion flux density, $j = L \cdot X$ (where j is the flux density and X is the driving force [9]) is independent of concentration or, at small relative concentration changes, D* is constant on account of the well-known relation [13]

$$L = \frac{D^* \cdot c}{kT}.$$

In this relation, k is the Boltzmann constant, and T is absolute temperature. It follows that the power-law dependence of the incorporation rate on potential is caused by the concentration dependence of the thermodynamic factor g(c).

For incorporation yielding a solid solution, the incorporation rate constant can be written as follows [12]:

$$K = \frac{c_0 \sqrt{D_{\text{eff}}}}{\sqrt{\pi}} \tag{3}$$

where c_0 is the concentration of the metal being incorporated at the electrode surface. The effective diffusion coefficient, D_{eff}, can be written as [14]

$$D_{\text{eff}} = \frac{1}{c_0} \int_0^{c_0} D(c)\, dc = \frac{D^*}{c_0} \int_0^{c_0} g(c)\, dc. \tag{4}$$

From (1), (3), and (4) we obtain

$$K = B \sqrt{D^* \gamma (E^* - E)}, \tag{5}$$

where B is a potential-independent coefficient.

Consider the effect of the electrode polarization on the self-diffusion coefficient. We know that in diffusion following the vacancy mechanism, the following relation can be written for the self-diffusion coefficient [13]:

$$D^* = N_V \cdot D_V, \tag{6}$$

where N_V and D_V are the relative concentration and diffusion coefficient of the vacancies. The equilibrium concentration of vacancies in the crystal is determined by their free energy of formation, G_V, via the relation $N_V = \exp(-G_V/kT)$ [13]. For estimates of calculations of vacancy concentration changes in a given crystal, G_V can be replaced by the formation enthalpy, H_V:

$$N_V \cong \exp\left(-\frac{H_V}{kT}\right). \tag{7}$$

Conditionally we shall visualize the formation of a vacancy in a crystal as the formation of a spherical cavity of radius r_V. In this case the crystal volume increases by the volume of the vacancy. Under these conditions the energy of vacancy formation can be written approximately as the work of formation of a surface equal in size to the surface of this cavity [15]:

$$H_V \cong 4\pi r_V^2 \cdot \sigma, \tag{8}$$

where σ is the reversible surface work for the crystal face.

Thus, the equilibrium concentration of vacancies in a solid according to Eq. (8) is found to depend on the surface energy of the solid. Sufficient justification appears to be lacking that this result should have arisen only from the simplifications made when deriving Eq. (8). In fact, if we regard the process of vacancy formation, in the customary way, as that of transfer of an atom from the bulk to the surface of the crystal, then the energy of vacancy formation — which is calculated as the difference in energies of the crystal in the initial and final state — is found to depend on the crystal's surface energy, and should vary with it. The physical meaning of this effect can be visualized when taking into account that as a result of surface-tension forces, the crystal as it were is subject to a compression acting from all sides. Because of the elastic properties of the crystal, this pressure is distributed throughout the crystal volume (for a flat electrode, this distribution is more uniform the thinner the electrode). When this pressure (i.e., σ) is increased, then vacancies are pushed out from the crystal, which leads to a reduction of their equilibrium concentration. When the pressure (i.e., σ) decreases, the opposite effect will result, viz., an increase in vacancy concentration. Theremodynamic relations exist which establish the dependence of equilibrium vacancy concentration in the crystal on the pressure that is acting from all sides (e.g., in [16]). For $\sigma \to 0$ one has $N_V \to 1$: The crystal ceases to exist.

When a crystalline metal is immersed into electrolyte solution, adsorption of the solution components together with the electric charge of the double layer gives rise to a change in the reversible surface work, which ought to lead to a change in equilibrium vacancy concentration in the metal.

We have used the term "electrochemical" injection of vacancies into electrodes for the effect where the vacancy concentration increases owing to the decrease in the metal's reversible surface work which occurs during the adsorption of solution components or during an increase in electric double-layer charge, and distinguish it from the "diffusional" injection of vacancies which is seen when one of the components is removed from an alloy (e.g., during anodic extraction of a metal from an electrode that previously had been incorporated into the electrode [3], or during the selective dissolution of binary alloys [17]). Electrochemical vacancy injection is the result of double-layer influence on the physical state of the electrode metal. It depends on the nature of the metal and on the experimental conditions whether this effect can be detected experimentally. With low vacancy diffusion rates such as should be found in metals with a relatively high melting point, changes in the energy state of the surface are unable within the time of the experiment to have an effect on the metal's bulk properties. However, in soft metals the vacancies diffuse rapidly, and a new vacancy concentration in the bulk of a sufficiently thin electrode will be established rapidly when the potential is changed. For lead, for instance, which is kept in an electrolyte solution at room temperature and the potential of zero charge, one can assume that $D^* = 10^{-16}$ cm^2/sec. If under these conditions one has $N_V = 10^{-9}$ [18], then from relation (6) we obtain $D_V = 10^{-7}$ cm^2/sec. This implies that in an electrode 0.01 cm thick, the time required to establish the new equilibrium vacancy concentration that corresponds to a new value of electrode potential is measured in minutes.

In electrodes that are nonuniformly polarized or that are in a nonequilibrium state on account of prior mechanical treatment, additional vacancy fluxes should arise which lead to mass transport by self-diffusion in the direction of lower deviations from the equilibrium state. Under these conditions a steady-state vacancy concentration can be established for a certain time in the electrode which is higher than the initial vacancy concentration.

Quantitative estimates of the effect of vacancy injection can be made by following the arguments used in [19] when calculating the energy of dislocation formation as a function of potential for an electrode subjected to deformation, or in [20] when calculating the effect of polarization on the activation energy of surface self-diffusion.

When the reversible surface work is reduced by an amount $\Delta\sigma$, then vacancies are injected into the electrode, and the self-diffusion coefficient assumes a new value D*. From (6), (7), and (8), we obtain

$$\frac{D^*}{D_0^*} = \exp\left(\frac{4\pi r_V^2 \Delta\sigma}{kT}\right), \qquad (9)$$

where D_0^* is the initial value of the self-diffusion coefficient. By calculating the relative change, D^*/D_0^*, of the self-diffusion coefficient via (9) we obtain the following results:

$\Delta\sigma$, kJ/cm^2	10	12,5	15	17,5
D^*/D_0^*	10^4	10^5	10^6	10^7

Using them we can explain the anomalously high mobility of atoms of the metal being incorporated into lead electrodes which had been found in the cathodic-incorporation experiments. Not only the size but even the sign of crystal-lattice relaxation is unknown for vacancy formation in polyvalent metals; we shall assume, therefore, that the vacancy radius in lead approximately equals the crystallographic radius of the atoms (1.75 Å [21]). The absolute σ-values are not exactly known for solid metals [22], but relation (9) only contains their change, $\Delta\sigma$. Lead is a metal resembling mercury in many properties. Its surface tension in the molten state is approximately the same as that of mercury at the same temperature [23]. We shall assume that the change in reversible surface work which occurs when lead is immersed into different solvents is approximately the same as that found for mercury, i.e., about 6 μJ/cm^2 for immersion into water and 12-15 μJ/cm^2 for immersion into dimethylformamide (DMF) or propylene carbonate (PC) [24]. In [4] and [6], cathodic incorporation occurred at potentials of -1.8 to -2.0 V vs nhe, so that the total change in reversible surface work (including immersion of the electrode into the aqueous solution and cathodic polarization) evidently was at least 15 μJ/cm^2. It follows for the above calculations of D^*/D_0^* that the self-diffusion coefficient should increase by six orders of magnitude for this $\Delta\sigma$-value. The diffusion coefficient of an impurity diffusing via a vacancy mechanism ought to increase by approximately the same factor [13], and this is what was found in the experiments. During in-

corporation from nonaqueous solutions, the effect of vacancy injection upon immersion of the electrode into the solution evidently is stronger than during incorporation from aqueous solutions, so that in nonaqueous solutions, low values of polarization during incorporation already lead to high diffusion rates [12]. One must add to what has been said above that the strong change in vacancy concentration which occurs in the metal should influence the energy state of the crystal lattice, which in turn may lead to higher solubility of other metals in the electrode metal.

By solving expression (5) for the incorporation rate constant one can show that vacancy injection will influence, not only the size of this constant but also the sort of potential dependence exhibited by it.

Let E_0 be the potential of the maximum in the σ vs E curve. Then quantity $\Delta\sigma$, which refers to potential E, can be written down as [25]

$$\Delta\sigma = \frac{C_{dl}}{2}(E-E_0)^2, \tag{10}$$

where C_{dl} is the electric double-layer capacity. One can assume that C_{dl} is independent of potential, since the experiments are done in the cathodic potential range at high electrolyte concentrations. From [9] and [10], we obtain

$$\frac{\sqrt{D^*}}{\sqrt{D_0^*}} = \exp\left[\frac{\pi r_v^2 C_{dl}(E-E_0)^2}{kT}\right]. \tag{11}$$

After substituting (11) into (5) we obtain an expression for the ratio of incorporation rate constants K and K_0 pertaining to potentials E and E_0:

$$\frac{K}{K_0} = \exp\left[\frac{\pi r_v^2 C_{dl}(E-E_0)^2}{kT}\right]\sqrt{\frac{(E^*-E)}{(E^*-E_0)}}. \tag{12}$$

Close to the maximum in the σ vs E curve, quantity σ and hence the self-diffusion coefficient as well change only slightly with potential, so that the thermodynamic factor (4) is mainly responsible for any change in the incorporation rate constant, and a power law holds for the relation between the rate constant and potential. Estimates show that for lead, the change in vacancy concentration in the region of the maximum in the σ vs E curve is no more than 15% for a potential change of ±0.25 V. Vacancy injection begins to have an ever larger effect on the incorporation rate as one moves away from the potential of the maximum, so that the incorporation rate constant begins to increase with increasing negative potential according to the exponential law (11). Owing to the high mobility of the vacancies, their concentration can be regarded as not changing across the diffusion layer of the metal that is incorporated [17], and hence its diffusion coefficient does not depend on the coordinates.

At more negative potentials (when a layer of the intermetallic compound has not yet been formed on the electrode), the effect of the thermodynamic factor can only become weaker, but the effect of vacancy injection increases. It follows from expression (12) that under conditions where the incorporation behavior is determined by electrochemical vacancy injection, plots of quantities $\sqrt{\log K}$ or $\sqrt{\log Q_t}$ (where Q_t is the amount of metal that has been incorporated after time t) against potential (as measured against a constant reference electrode) should be straight lines with a slope of $f = (2.3kT/\pi r_v^2 C_{dl})^{0.5}$.

Figure 1 shows results obtained when measuring, as functions of potential, the amounts of sodium incorporated into lead from concentrated aqueous NaOH solutions after 22 h. The amounts of sodium were determined by chemical analysis. The experimental conditions and measuring procedure have been outlined in [6]. One can see that the linear relation between E and $\sqrt{\log Q_t}$ derived above holds satisfactorily over the potential range of −1.6 to −2.0 V vs nhe.

Incorporation of sodium into lead was studied over a wider potential range from a saturated $NaNO_3$ solution in dimethylformamide. The experiments were done in an atmosphere of purified argon at 60°C. The solvent was twice distilled to remove water and other impurities. The trace water concentration in DMF was not over 0.01%. The sodium nitrate was twice re-

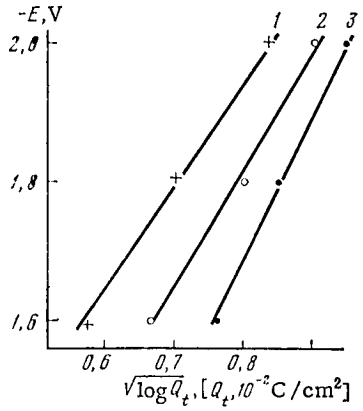

Fig. 1

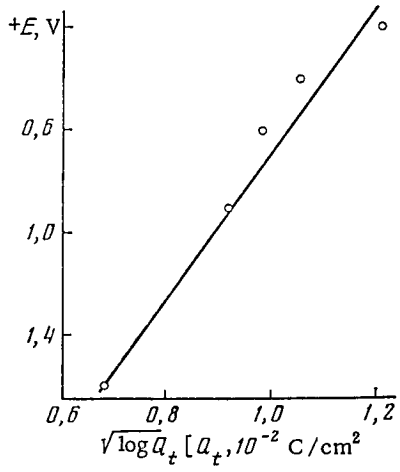

Fig. 2

Fig. 1. Plots of $\sqrt{\log Q_t}$ against potential (nhe) during the incorporation of sodium into lead from aqueous NaOH solutions with concentrations of: 1) 9.6 N, 2) 10.0 N, and 3) 11.0 N; t = 22 h.

Fig. 2. Plots of $\sqrt{\log Q_t}$ against potential (vs a sodium reference electrode) during the incorporation of sodium into lead from 0.5 N $NaNO_3$ in DMF at 60°C; t = 22 h.

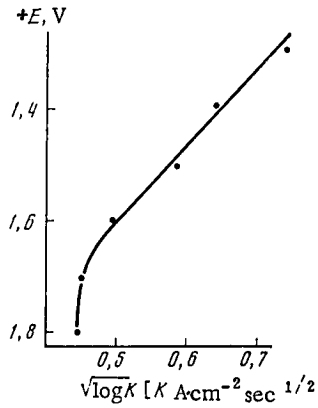

Fig. 3. A plot of $\sqrt{\log K}$ against potential (vs a lithium reference electrode) during lithium incorporation into lead from 0.5 N $LiClO_4$ in PC at 25°C.

crystallized and dried. The amount of sodium incorporated was determined by chemical analysis via the procedure outlined in [6], after washing the polarized electrode in heptane and in water. The phase composition of the incorporation products was determined by x-ray diffraction with a URS50-I instrument. The results of the measurements are presented in Fig. 2. Though less perfectly than in Fig. 1, the experimental points still fall onto a straight line, so that in this case too, the incorporation behavior is determined by electrochemical vacancy injection. A linear relation between $\sqrt{\log Q_t}$ and E that exists over a wide potential range indicates that any phases for which the potential of the maximum in the σ vs E curve would be markedly different from that for a saturated solid solution of sodium in lead are not formed at the electrode. This is in harmony with the data [26] obtained when measuring the electron work function of a solid solution of sodium in lead and of compounds of the lead–sodium system.

Lines of intermetallic compounds were not found in x-ray studies of electrodes that had been polarized for 22 h to a potential of 0.2 V against the sodium reference electrode, but

TABLE 1. Effect of Several Factors on Quantity f for Lead

Electrolyte composition	Polarization time	Temperature, °C	f, V
NaOH in H_2O 9,6–11 *N*	22 h	20	1,4÷2,2
$NaNO_3$ in DMF 0,5 *N*	22 h	60	2,9
$NaClO_4$ in PC 0,5 *N*	20 min	60	0,9
$LiClO_4$ in PC 0,5 *N*	2 min	25	1,3

strong lines of the compound $NaPb_3$ are present in the x-ray patterns obtained from electrodes that had been polarized under the same conditions for 68 h. But the x-ray patterns obtained from electrodes that were polarized under the same conditions for 3 h already display a decrease of 0.0036 ± 0.0004 Å in the crystal lattice parameters of lead, which indicates that a supersaturated solid solution of sodium in lead reaching a concentration of 8 atom % [27] is formed, and not merely a saturated solution as during incorporation from aqueous solutions [4]. These results confirm the earlier suggestion that crystallization of the intermetallic compounds at room temperature is slow [4, 6], and indicate that the compounds are formed at the electrode under the above experimental conditions in quantities so small as not to have any marked effect on vacancy injection.

In doing the above experiments we always checked the relation between the incorporation rate at constant potential and time, and found linearity between Q_t and $t^{0.5}$, which is evidence for diffusion control. Estimates of the effective diffusion coefficients yield values between 10^{-14} and 10^{-12} cm^2/sec.

A power-law relation between the incorporation rate constant and potential was found in [12] over the potential range from 2.2 to 1.8 V against a lithium reference electrode when lithium incorporation into lead was studied from 0.05 N $LiClO_4$ in PC at 25°C by chronoamperometry. This relation changes into a semilogarithmic one at less positive potentials for the same experimental conditions, as shown in Fig. 3; this indicates that electrochemical vacancy injection determines the kinetics of the process in the potential range stated.

Table 1 shows the slopes of the experimental plots of E against $E - \sqrt{\log Q_t}$ or $E - \sqrt{\log K}$, that were obtained under different conditions. The theoretical value of f for lead at 20°C is 0.7 V for C_{dl} = 20 μF/cm^2, and 1 V for C_{dl} = 10 μF/cm^2. One must admit that the agreement between experimental and theoretical slopes is satisfactory in view of the rough assumptions made in the calculations.

The time needed to establish a new vacancy concentration in the electrode may turn out to be comparable with the duration of the experiment at low incorporation times, e.g., in the experiments for which the results are shown in Fig. 3 (order of 100 sec). In this case the vacancy flux from the surface into the electrode which develops with increasing negative potential gives rise to a transient vacancy flux in the diffusion region which should depend on potential according to the same law as the equilibrium vacancy concentration. Despite the fact that it is in the same direction as the flux of atoms being incorporated, this vacancy flux also can give rise to accelerated transport of these atoms into the electrode, since mobile complexes may form between the atoms and vacancies [16]. Then the expression for the effective diffusion coefficient of the atoms being incorporated will contain the diffusion coefficient of the complexes and the equilibrium constant of complex formation as linear terms in addition to the vacancy concentration. To find the equilibrium constant one needs information about the energy of complex formation in the particular system [28]. In our case this quantity is unknown, and can only be used as an additional fitting parameter in the theoretical estimates, so that a more detailed discussion of this problem is not appropriate at the present time.

The research results outlined in the present paper have shown that despite their low relative concentration, vacancies of the crystal lattice of metals can importantly influence the diffusion processes occurring under the conditions of electrochemical experiments in electrodes. During adsorption and polarization, electrochemical injection of additional vacancies into the electrodes can substantially enhance the diffusion rate (by up to 6 or 7

orders of magnitude), and even become the major factor for the kinetics of reactions where diffusion in the electrode is the rate-determining step.

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INVESTIGATION OF THE ELECTRODE PROCESSES OF THE OXIDATION OF PHTHALOCYANINES IN SOLUTIONS

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The electrode processes of oxidation of phthalocyanine and its Co, Zn, and Cu-complexes were investigated. The influence of the concentration of the complex and the indifferent electrode on the one-electron oxidation of the investigated phthalocyanines in solution was considered. The kinetic parameters of the transfer of the first electron in the oxidation of zinc and cobalt complexes were determined. A change in the mechanism of the oxidation of Co phthalocyanine as a function of the coordinating ability of the solvent was detected.

As was shown earlier [1], in the anodic oxidation of cobalt and zinc phthalocyanines there is a step-by-step stripping of electrons with loss of the first electron by the macroligand, while in the presence of supplementary coordination of solvent molecules, in the case of the cobalt complex, it may be stripped from the central metal atom. The anodic oxidation of complexes of other metals has practiclaly not been studied [1, 3].

The purpose of the work was to investigate the electrode processes of oxidation of phthalocyanine and its complexes, differing in the nature of the central metal atom.

In the work we used the methods of cyclic volt-amperometry, differential polarography on solid electrodes and a rotating disk electrode (RDE). Measurements of the j versus E curves were performed in the usual three-electrode cells in deoxygenated medium in Au, Pt, pyrographite (PG), and an optically transparent electrode (OTE) of In_2O_3. The polarization curves on an RDE were recorded with scanning of the electrode potential 0.1 V/min and a controlled angular rate of rotation of the electrode (ω). The objects of the investigation were chromatographically individual metal-free tetra-4-tert-butyl phthalocyanine and its Co, Zn, and Cu-complexes – $Pc^t(H_2, Co, Zn, Cu)$. It must be noted that the introduction of tert-butyl groups into the phthalocyanine (Pc) molecule has no significant effect on the position of its electron levels [4]. The solvents 1,2-dichlorobenzene (DCB) and pyridine (PN), preliminarily dried over $CaCl_2$, were purified by double redistillation at reduced pressure. Directly before each experiment, DCB was passed through a column with Al_2O_3. Dimethyl sulfoxide (DMSO) was dried with molecular sieves and redistilled at reduced pressure over CaH_2 in an atmosphere of inert gas. The salt $N(C_4H_9)_4ClO_4$ (TBAP) was purified as in [1]. The potentials measured relative to a silver chloride electrode were converted to the normal hydrogen electrode. The polarization curves were measured with a P-5827 potentiostat and a PU-1 polarograph. The kinematic viscosity was determined with a VPZh-1 capillary viscosimeter.

In an investigation of the electrooxidation of Pc^tCo in DCB it was noted that the shape of the first reversible wave of the potentiodynamic curve [1] is preserved only up to a definite value of the concentrations of the supporting electrolyte and complex in solution, above which the wave is deformed. Such a nature of the wave was noted especially graphically on the differential polarograms. Curve 1 of Fig. 1, measured on an Au-electrode in a 10^{-4} M solution

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