
INVESTIGATION METHODS FOR PHYSICOCHEMICAL
SYSTEMS, STRUCTURES
AND PROPERTIES OF MATERIALS AND COATINGS

Applying a Theory of Generalized Variables to Electrochemical Kinetics: Interpreting the Results of Studying Chromium Deposition from Cr(III) Baths

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Abstract—By using the theory of generalized variables (the similarity theory and dimensional analysis), universal system of dimensionless complexes (the similarity criteria) is derived, which allows describing the kinetics of multistage reaction (metal electrodeposition at rotating disc electrode). The proposed mathematical apparatus can be flexibly adapted to describing the kinetics of virtually any complicated electrochemical system. The dimensionless complexes derived are used in interpreting the results of our studies on the chromium electrodeposition from Cr(III) oxalate and formate salt solutions at a rotating disc electrode. Possible mechanism of the electrodeposition from the oxalate and formate electrolytes is offered.

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INTRODUCTION

The reaction of chromium electrodeposition from aqueous solutions of its three-valent compounds is a complicated electrochemical process whose principal characteristic features are as follows [1, 2]:

—a stage character of the Cr(III) ion discharge accompanied with partial diffusion transfer of intermediates [Cr(II) ions] between the near-electrode layer and the bulk of the bath;

—diversity of the forms of different Cr(III) and Cr(II) complexes in the bulk of the bath and near-cathode layer; outstanding inertness of the Cr(III) complexes and low stability of the Cr(II) complexes;

—the hydrogen evolution which accompanies the Cr(III) and Cr(II) ion discharge and results in changing the convective mass transfer conditions near the cathode, an increase in pH in the near-electrode layer, and formation of chromium hydroxo compounds that affect significantly the kinetics of electrode processes.

The features listed make difficult adequately interpreting the kinetic data in terms of classic equations of electrochemical kinetics. For example, the voltammetric curves of chromium deposition on rotating disc electrode (RDE) have a complicated wave-like shape with current maxima [2] and cannot be expressed by simple equations [3].

A convenient method of theoretically and experimentally studying complicated systems and processes with diverse and not perfectly known inner connections

(and chromium electrodeposition, among them) is the similarity theory and the dimensional analysis (theory of generalized variables) [4–9]. The essence of the theories is in combining the independent variables and quantities sought for into dimensionless complexes (the similarity criteria) of certain structure, which are generalized variables and parameters of the problem; their quantitative interrelations are further revealed. This approach allows clarifying the relations between the system's variables and parameters, presenting the solution in simpler and compact form, and generalizing the obtained conclusions over the entire class of similar processes and phenomena.

Earlier we showed that the similarity theory and the dimensional analysis can be applied to the theoretical analysis of kinetics of some types of electrochemical reactions [8, 9].

In this work we attempt at using the mathematical apparatus of the theory of generalized variables when interpreting the results of kinetic studies in the chromium electrodeposition from Cr(III) complex ion solutions at RDE.

THEORY

Prior to analyzing the particular features of the chromium electrodeposition, let us discuss a general case of multistage deposition of a metal on a RDE from a bath containing the metal's complex ions.

Assume that the mathematical equations describing the kinetics of the analyzed electrochemical process are unknown. Then, we can reveal the structure of dimensionless complexes by using the approach of the theory of dimensional analysis [4–8].

Based on *a posteriori* data, we can choose the initial (that is, determinable directly from experiment) quantities that are essential in solving the problem, in particular.¹

Analytical concentrations of the depositing metal ions C_1 , intermediates (ions of the metal in its intermediate oxidation step) C_2 , ligand species C_3 , and hydroxonium ions C_4 in the bulk of the bath;

the electrodeposition current density (for the stage of the intermediate ion reduction to the metal) i ; the maximal electrodeposition current density (in the bath of a given composition at a given RDE velocity) i_{\max} ; and the current density of the electrochemical stage preceding the metal deposition stage (the intermediate formation reaction) i_{pr} ;

the absolute value of the electrode polarization η ;

the RT/F (R factor,² where R is the universal gas constant, T is the temperature, and F is the Faraday constant);

the electrochemical equivalent of the metal electrodeposition reaction ϵ ;

the disc rotation velocity f ;

the bath kinematic viscosity ν ;

the disc electrode radius r ;

the partial derivative of the deposition current density with respect to the polarization (the differential conductivity) $\frac{\partial i}{\partial \eta}$;

the partial derivatives (at $\eta = \text{const}$) of the deposition current density with respect to the bulk concentrations of the metal ion $\frac{\partial i}{\partial C_1}$, the intermediates $\frac{\partial i}{\partial C_2}$, the

ligand species $\frac{\partial i}{\partial C_3}$, and the hydroxonium ions $\frac{\partial i}{\partial C_4}$.

The particular forms of the dimensionless complex quantities were derived according to the procedure described at length in [7]; for the corresponding mathematical transformations and the expressions for thus obtainable dimensionless complexes, see Appendix.

The physical meaning of the obtained complex quantities $\pi_1, \pi_2, \dots, \pi_{14}$ can be presented as follows.

Complexes π_1, π_2 , and π_3 are the similarity simplexes (that is, the ratios of the like quantities); they represent the dimensionless concentrations of the intermediates, ligand species, and hydroxonium ions,

respectively. Here the metal ion concentration C_1 is taken as the conditional scale unit of the correlation.

In the structure of the complex π_4 the electrical work of transferring one mole of unit charges, caused by the electrode polarization (ηF), is correlated with the energy of the particles' thermal motion (RT). In its physical meaning, this similarity criterion is a dimensionless form of the electrode polarization (that is, the driving force of the electrode reaction).

According to [3], the Reynolds number for RDE is:

$$\text{Re} = \frac{r^2 \omega}{\nu}, \quad (1)$$

where $\omega = 2\pi f$ is the rotation electrode angular velocity.

The complex π_5 differs from Eq. (1) only in the constant factor $(2\pi)^{-1}$ and is here but a modified Reynolds number; the latter is known to be a merit of the ratio of the liquid motion inertia force and the inner friction force [4].

The meaning of the dimensionless simplexes π_6 and π_7 is simple: the former characterizes the metal deposition relative current density (it takes values from 0 to 1), the latter gives the rate ratio for the 2nd and 1st steps of the electrochemical reaction (it was shown [10] for multistage electrode reactions complicated by partial intermediates transfer between the near-electrode layer and the bulk that generally $i_{\text{pr}} \neq i$, hence, $\pi_7 \neq 1$).

The behavior of any electrochemical reaction always can be characterized by some polarization resistance

$\frac{\partial \eta}{\partial i}$ at the electrode/electrolyte interface, which varies depending on the current density (or polarization) value. Therefore, the interface can be thought of as a nonlinear resistive element in electrical circuit, for which the current density generally relates to the polarization according to the equation: $i = \text{const} \eta^m$, where $m = \text{const} = f(\eta)$.

For the complex π_8 we write:

$$\pi_8 = \frac{\frac{\partial i}{\partial \eta} \eta}{i} = \frac{\partial \ln i}{\partial \ln \eta} = m. \quad (2)$$

Obviously, the quantity π_8 is the merit of nonlinearity of given electrode reaction considered as an element of electrical circuit. The value $m = 1$ corresponds to linear current–voltage characteristic of electrode process (e.g., at small deviation from the equilibrium potential). At $m \neq 1$, the i vs. $f(\eta)$ dependence is nonlinear. For electrochemical reactions we may observe the cases of

$m = 0$ (the limiting current), and even $m < 0$ (the descending segments in voltammograms with negative value of $\frac{\partial i}{\partial \eta}$).

¹ The choice of these quantities is to a great extent arbitrary and based, among other, on intuitive considerations.

² The expediency of introducing of quantity will be evident from the derivation given below.

When more than one electrochemical reaction passes at an electrode, each of them is characterized by its intrinsic value of m , which changes on the varying of electrode potential.

The mathematical expression for the complex π_9 is:

$$\pi_9 = \frac{i\eta}{\left(\frac{i^3 \varepsilon^3}{C_1^2}\right)} \quad (3)$$

The numerator of the fraction characterizes the energy dissipated in unit time as a consequence of the electrode polarization. As to the physical meaning of the denominator in Eq. (3), we may *formally* consider electrochemical reaction (like any heterogeneous process) as the transfer of some mass across the interface. Obviously, in electrochemical reaction, a mass $\mu = i\varepsilon$ ($\text{kg m}^{-2} \text{s}^{-1}$) is transferred per unit surface per unit time; the linear velocity of the transfer is $V = \frac{i\varepsilon}{C_1}$ (m s^{-1}).

Hence, the conditional kinetic energy of the transferred particles is $\frac{1}{2}\mu V^2 = \frac{1}{2}\frac{i^3 \varepsilon^3}{C_1^2}$. Thus obtained expression coincides with the denominator of the fraction in Eq. (3), accurate within a constant factor. Thus, the complex π_9 allows correlating the electrical energy dissipated at the electrode with the conditional kinetic energy of the mass transferred across the electrode/electrolyte interface.

Even crude estimation of π_9 values for the values of i , η , ε , and C_1 (practically taking place in electrochemical systems) shows that the complex possesses giant ($\approx 10^{10}$ and higher) values and hence, is degenerated (that is, characterizes the interrelation between incomparable values); therefore, it should be mapped out of the analyzed parameters of the process [4].

According to [11], in a region well remote from the disc surface, the axial component of the convective velocity toward RDE (without taking into account the sign in the chosen frame of axes) is as follows:

$$v_c \approx 0.89\sqrt{v\omega} \quad (4)$$

Taking into account the approximate formula (4), one may conclude that the expression in the numerator of the complex π_{10} (the dimensionality of $\text{kg m}^{-2} \text{s}^{-1}$) allows estimating (accurate within a constant factor) the convective flux of metal ions toward the RDE surface. In the structure of the complex π_{10} this quantity is correlated with the full rate of electrochemical reaction ($i\varepsilon$).

It is easy to certain that π_{10} is a modified reciprocal Stanton diffusion criterion of similarity [12], which equals

$$St' = \frac{\beta}{\omega_n} = \frac{Nu'}{Pe'}, \quad (5)$$

where β is the mass transfer coefficient (actually, the rate constant for the heterogeneous process, m/s), ω_n is the average velocity of the liquid flow, m/s), Nu' is the Nusselt diffusion criterion, Pe' is the Peclet diffusion criterion.

The complex π_{10} , like $(St')^{-1}$, allows estimating the ratio of the intensity of flux of the substance transferred by convection and of the summary mass transfer in the heterogeneous process.

Expressions for the complexes π_{11} , π_{12} , π_{13} , and π_{14} can be written as follows:

$$\begin{aligned} \pi_{11} &= \frac{\partial \ln i}{\partial \ln C_1}, & \pi_{12} &= \frac{\partial \ln i}{\partial \ln C_2}, & \pi_{13} &= \frac{\partial \ln i}{\partial \ln C_3}, \\ \pi_{14} &= \frac{\partial \ln i}{\partial \ln C_4}. \end{aligned} \quad (6)$$

These formulas are similar to the equations determining the partial orders of electrochemical reaction with respect to the corresponding reagents. However, unlike the determination of true orders (where the derivatives are found at constant electrode potential $E = \text{const}$ [13]), these partial derivatives are determined at a constant polarization $\eta = \text{const}$.

Instead of the polarization η , it is often more convenient to use $\Delta E = |E - E^0|$ as initial quantity (here E^0 is the standard electrode potential of the electrode reaction; correspondingly, the partial derivatives $\frac{\partial i}{\partial C_j}$ are

determined at $E = \text{const}$. Such a substitution allows forming new system from the fourteen dimensionless complexes, which is a full analog of the above-described one (in the formulas of π_4 , π_8 , and π_9 , the quantity ΔE should be substituted for η). The complexes π_8 and π_9 lose the above-formulated physical meaning (for π_9 , however, this is not important because of its degeneration in electrochemical systems). In this case the quantities π_{11} , π_{12} , π_{13} , and π_{14} attain the meaning of true reaction orders with respect to the corresponding reagents. The fixing upon η or ΔE is determined by the specificity of particular kinetic problem.

The similarity simplexes π_1 , π_2 , and π_3 and the similarity criteria π_4 and π_5 are formed only from the process' independent parameters and hence are the determining complexes [6]. The rest of them are the determinable ones. For this reason, the functional interrelations between the quantities P_j , which characterize the electrochemical kinetics, can be presented as nine functional links (or criterial dependences) between the complexes constituted by these quantities:

$$\begin{aligned} \pi_j &= f_j(\pi_1, \pi_2, \pi_3, \pi_4, \pi_5), \\ \text{where } j &= 6, 7, \dots, 14. \end{aligned} \quad (7)$$

The theory of generalized variables rather states the existence of the dependences (7), than reveals their particular mathematical form. This should be done based on the results of independent analytical or experimental investigation.

Noteworthy is that the suggested mathematical model can be easily adapted to describing the kinetics of almost any electrochemical transformation at RDE. For instance, when considering one-stage processes, i_{pr} and C_2 should be excluded from the primary quantities, while π_1 and π_{12} , from the set of dimensionless complexes. Moreover if the bath contains several different ligands, rather than one ligand as we initially assumed, this results but in the appearance of additional complexes similar in their structure to the quantities π_2 and π_{13} .

Thus, applying the theory of generalized variables is a universal method of treating kinetic data, easily adaptable according to the specificity of a particular electrochemical system.

EXPERIMENT, CALCULATIONS, AND DISCUSSION

In this work we used our recent experimental data [2] on the chromium electrodeposition on RDE from formate and oxalate chromium-plating baths.

The kinematic viscosity of the formate and oxalate electrolytes (measured using a VPZh-3 glass capillary viscosimeter at $t = 25^\circ\text{C}$) equals 1.55×10^{-6} and 1.60×10^{-6} m²/s, respectively.

According to [3], when calculating the Reynolds number by formula (1), the full radius of the rotating cylinder (here the gold disc and its surrounding Teflon housing) is taken as the quantity r . In our experiments, this quantity is $r = 7 \times 10^{-3}$ m.

The equilibrium potential of the studied reaction $\text{Cr(II)} + 2e^- \rightarrow \text{Cr(0)}$ can hardly be determined experimentally. In its theoretical calculations by Nernst equation, the activity of chromium (II) complex ions in the near-electrode layer is required, which is unknown. Therefore, when calculating the complexes π_4 , π_8 , and π_9 , we substituted the quantity $\Delta E = |E - E_0|$ (where $E_0 = -0.913$ V) for the polarization η .

The values $\frac{\partial i}{\partial(|E - E^0|)} = \frac{\partial i}{\partial|E|}$ required in the calculating of π_8 were found by graphically differentiating i vs. E curves.

To decrease the amount of data to be analyzed, we shall restrict our consideration, like in [2], to the case when $C_1 = \text{const}$ (the chromium (III) ion concentration is 0.2 mol/dm³), $C_2 = \text{const} = 0$, $C_3 = \text{const}$ (the formic or oxalic acid concentration is 0.4 mol/dm³), and $C_4 = \text{const}$ (pH 3.0). This assumption means that the determining complexes π_1 , π_2 , and π_3 retain their constant values (0, 2, and 0.005, respectively), hence, they can be neglected in the kinetic analysis. We can also

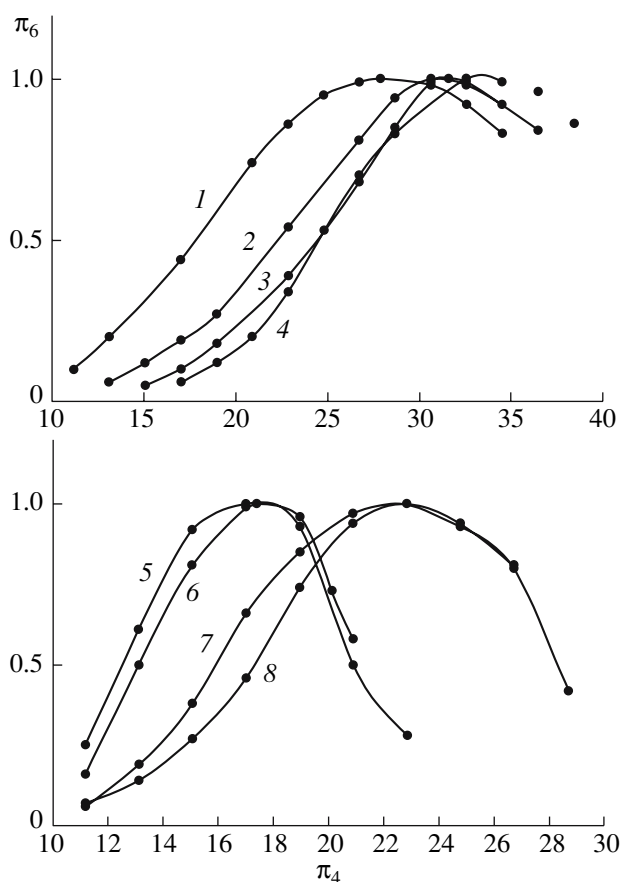


Fig. 1. Dependences $\pi_6 = f_6(\pi_4)$ for (1)–(4) formate and (5)–(8) oxalate chromium plating baths at different values of criterion π_5 : (1) 158; (2) 480; (3) 980; (4) 1607; (5) 153; (6) 465; (7) 949; and (8) 1557.

exclude from our consideration the quantities to be determined (π_{11} , π_{12} , π_{13} , and π_{14}), as well as the degenerated complex π_9 (see above). Additionally, we exclude from our consideration the simplex π_7 , because in [2] we did not determine the current density of the electrochemical stage $\text{Cr(III)} + e^- \rightarrow \text{Cr(II)}$, which precedes the metal deposition stage proper.

Thus, characterizing the kinetic peculiarities of the chromium electrodeposition on RDE from the Cr(III)-baths we restrict our consideration to a set of the following criterial dependences:

$$\pi_6 = f_6(\pi_4, \pi_5), \quad (8)$$

$$\pi_8 = f_8(\pi_4, \pi_5), \quad (9)$$

$$\pi_{10} = f_{10}(\pi_4, \pi_5). \quad (10)$$

In Fig. 1, we show the dependences of the relative current density π_6 of the chromium deposition on the dimensionless polarization π_4 .³ They represent voltam-

³ For convenience, in what follows, we shall use the term “dimensionless polarization” although in calculating π_4 we substituted the quantity ΔE for the polarization η , as shown above.

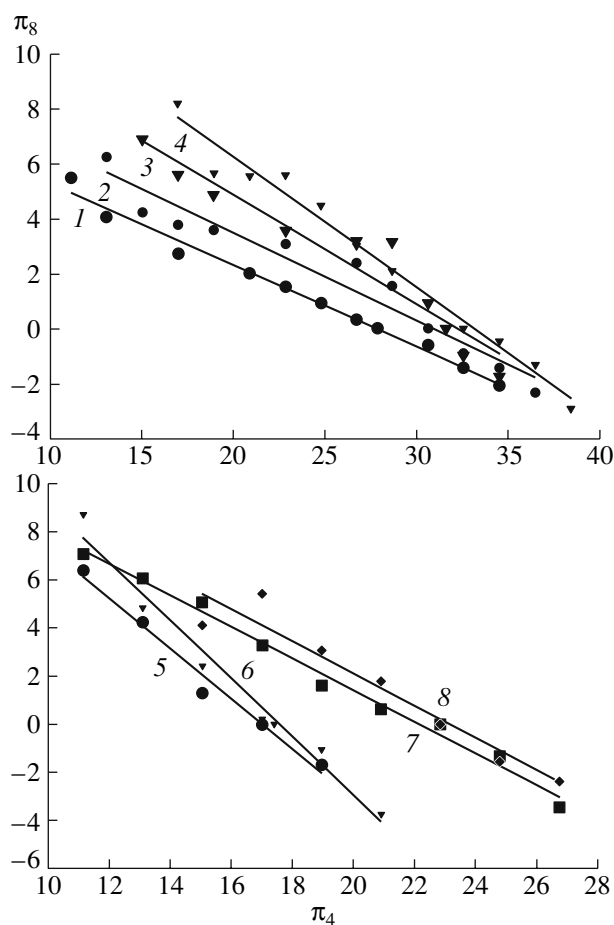


Fig. 2. Dependences $\pi_8 = f_8(\pi_4)$ for (1)–(4) formate and (5)–(8) oxalate chromium plating baths. Values of criterion π_5 the same as for the corresponding curves in Fig. 1.

metric curves for the reaction studied, in dimensionless complex coordinates. These dependences, like their corresponding i vs. E curves, show current waves with maxima [1, 2]. With an increase in the modified Reynolds criterion π_5 , these curves shift toward higher π_4 values, which points to the decrease in the metal deposition rate. This is apparently caused by an increase in the intermediates flux carried from the near-electrode layer to the bulk, thus making the Cr(II) ion surface concentration decrease [10]. We recall that this effect is clearly seen for both the baths in the complex coordinates π_6 vs. π_4 , but has never been observed in the common i vs. E curves recorded in oxalate bath [2].

It was shown [2] that the absolute values of the chromium electrodeposition current density in the formate and oxalate baths, all other factors being equal, differ virtually by an order of magnitude, which makes difficult correctly comparing the corresponding voltametric data. By contrast, when passing to the dimensionless coordinates π_6 vs. π_4 , it is possible to correlate the experiment results in the comparable scales of the

dimensionless relative current density, which undoubtedly is an advantage of the procedure.

All other factors being equal, the maximum deposition current ($\pi_6 = 1$) in the formate bath is achieved at much higher values of π_4 than in oxalate electrolyte (~28–35 and ~16–22, respectively). This may be an indirect evidence of some difference in the mechanism of the metal deposition from these baths.

To first approximation, the dependences of the criterion characterizing the nonlinearity of the electrode reaction (considered as an element in the electrical circuit) π_8 on the dimensionless polarization π_4 may be approximated by straight lines with negative tangent of their slope angles (Fig. 2). The scatter of the points is likely to be due to the inaccuracy of the graphical differentiation of i vs. E curves during the calculating of the complex π_8 . In the ascending segment of the i vs. E curves (up to the current maximum), the π_8 values are positive. When the dimensionless polarization π_4 reaches the value corresponding to $\pi_6 = 1$, the complex π_8 obviously equals zero. With a further increase in π_4 , the value of π_8 becomes even more negative. At any fixed π_4 value, the complex π_8 increases with an increase in the modified Reynolds criterion π_5 .

With an increase in the dimensionless polarization π_4 , the π_{10} complex characterizing the rate ratio of the electrolyte convective transfer to the rotating disc and the electrode reaction rate, decreases steeply in the domain of small π_4 (Fig. 3). This indicates that the mass transfer role in determining the metal deposition rate is ever increasing with an increase in the polarization rate.

In all cases, an increase in modified Reynolds criterion π_5 , at a fixed π_4 value, resulted in the increase in the complex π_{10} .

Worthy of noting is the fact that at equal values of π_4 and π_5 in the descending segment of the π_{10} vs. π_4 curve, the value of the complex π_{10} in the formate bath is by an order of magnitude lower than that in the oxalate bath. Taking into account the physical meaning of the similarity criterion π_{10} (see above), we concluded that the mass transfer regime affects the chromium electrodeposition reaction rate much less in the oxalate bath than in the formate bath.

With a further increase in π_4 , the complex π_{10} reaches its minimal value, then begins to increase; the ascending segment of the π_{10} vs. π_4 curve corresponds to descending segments of a polarization curve in the dimensionless coordinates π_6 vs. π_4 (see Fig. 1). The increase in π_{10} is most clearly visualized in the case of oxalate bath.

It is of interest to compare the calculated minimal values of π_{10} with a value this complex would possess in the case of the limiting diffusion current. On substituting the well-known expression for the RDE limiting diffusion current $i_{lim,dif}$ [3] in the equation for the complex π_{10} , we obtain (after simple transformations): $\pi_{10,dif} = 6.42 \times 10^{-3} D^{-2/3} \nu^{2/3}$, where D is the diffusivity.

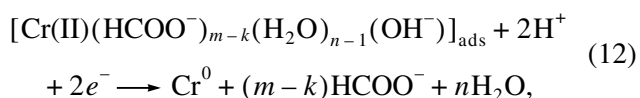
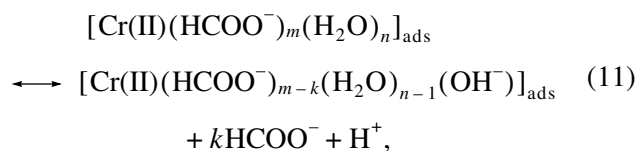
Assuming that $D = 2 \times 10^{-9}$ m²/s, we obtain $\pi_{10, \text{dif}} \approx 0.55$, which is rather close to the found minimal value of π_{10} for the formate bath; however, this value is significantly lower than that found for the oxalate bath. This fact corroborates the conclusion [2] that the current maxima on the voltammetric curves taken in these baths originate from different reasons. Unlike the formate bath, in the oxalate solution reaching the maximal current is not associated with any feature of the mass transfer stage but is due to the slowness of some chemical stage.

Thus, the analysis of the π_{10} vs. π_4 curves allows concluding that changes of conditions of the convective mass transfer affects the kinetics of chromium deposition from an oxalate bath much less than from the formate one.

We emphasize that a comparative analysis of the convective effects on the metal electrodeposition rate in the oxalate and formate baths may be correct only in the complex dimensionless coordinates that allow quantitatively comparing the mass transfer intensity and the electrode process rate, even without the corresponding kinetic equations of the type $i = \varphi(E, \varphi)$.

When generalizing the results of the analysis of kinetic data in terms of the theory of generalized variables, we conclude that at equal values of the similarity criteria, which are the problem's arguments (π_4, π_5), the character of the corresponding criterial dependences (π_6 and π_{10}), as well as their absolute values, differ significantly in the oxalate and formate baths. This corroborates the earlier conclusion [1, 2] that despite many common features, the kinetics and mechanism of chromium electrodeposition from the oxalate and formate baths are different.

These distinctions are likely to be caused by the different nature of the electrochemically active complexes participating in the discharge that yields the metal. It was shown earlier [2, 15] that the electrochemically active complexes in the formate bath are Cr(II) hydroxo complexes formed at the electrode surface as the products of the dissociation of inner-sphere-coordinated water molecules, which precedes the discharge. Then the mechanism of the chromium electrodeposition can be conditionally presented by the following reaction scheme:⁴



where $m = 1, 2; k = 0, 1, 2$.

⁴ No particular information on the composition of the reacting complexes is at hand.

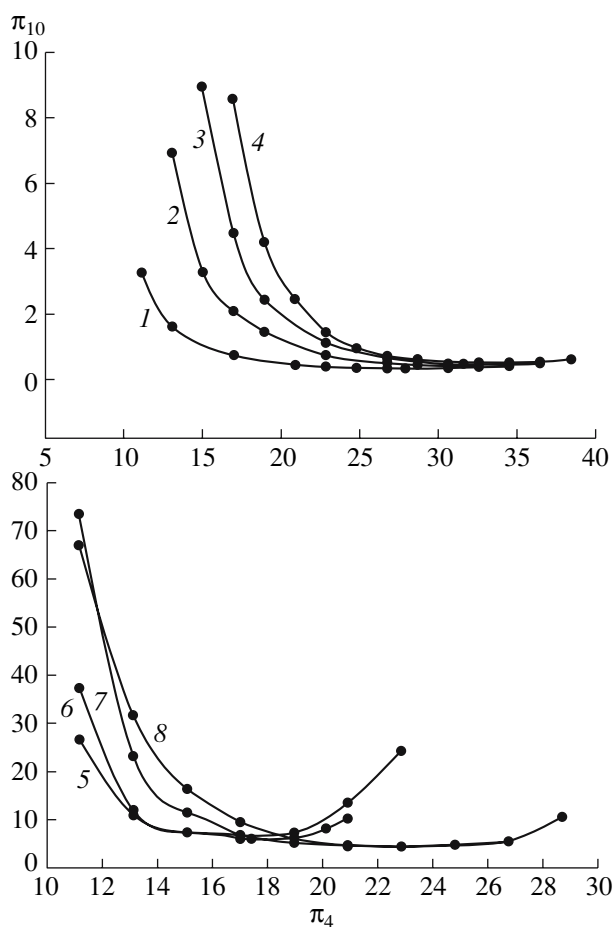


Fig. 3. Dependences $\pi_{10} = f_{10}(\pi_4)$ for (1)–(4) formate and (5)–(8) oxalate chromium plating baths. Values of criterion π_5 the same as for the corresponding curves in Fig. 1.

The slow step in the consecutive two-electron reaction (12) is likely to be the first electron transfer [15].

An increase in pH and a decrease in the formic acid concentration in the bath must result in the shift of the equilibrium (11) to the right, thus contributing to the increase in the electrochemically active complex concentration and hence, the electrode reaction rate. This agrees well with the earlier experimental data [1, 2, 15].

An increase in the disc electrode rotation velocity, along with the aforementioned intensifying the convective removal of the intermediates [Cr(II) ions] from the electrode surface, favors the lowering of pH.⁵ This naturally leads to the lowering of the electrochemically active complex concentration, thus, slowing down the electrode reaction (cf. the aforementioned π_6 vs. π_4 curves).

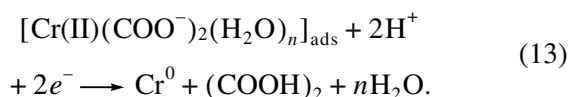
A thermodynamic stability of the Cr(II) oxalate complexes exceeds that of the corresponding formate complexes by several orders of magnitude [2], there-

⁵ During the chromium deposition, the electrolyte acidity in the near-electrode layer is always lower than that in the solution bulk because of the concurrent hydrogen evolution reaction.

Table 1. Dimensionalities of primary quantities

Quantity P_i and its designation		Dimensionality of the quantity	Powers of dimensionalities			
			[M], kg	[L], m	[T], s	[J], A
P_1	C_1	kg m^{-3}	1	-3	0	0
P_2	C_2	kg m^{-3}	1	-3	0	0
P_3	C_3	kg m^{-3}	1	-3	0	0
P_4	C_4	kg m^{-3}	1	-3	0	0
P_5	i	$\text{m}^{-2} \text{ A}$	0	-2	0	1
P_6	i_{\max}	$\text{m}^{-2} \text{ A}$	0	-2	0	1
P_7	i_{pr}	$\text{m}^{-2} \text{ A}$	0	-2	0	1
P_8	η	$\text{V} = \text{kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$	1	2	-3	-1
P_9	RT/F	$\text{V} = \text{kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$	1	2	-3	-1
P_{10}	$\frac{\partial i}{\partial \eta}$	$\text{A}/(\text{V m}^2) = \text{kg}^{-1} \text{ m}^{-4} \text{ s}^3 \text{ A}^2$	-1	-4	3	2
P_{11}	ε	$\text{kg s}^{-1} \text{ A}^{-1}$	1	0	-1	-1
P_{12}	f	s^{-1}	0	0	-1	0
P_{13}	v	$\text{m}^2 \text{ s}^{-1}$	0	2	-1	0
P_{14}	r	m	0	1	0	0
P_{15}	$\frac{\partial i}{\partial C_1}$	$\text{kg}^{-1} \text{ m A}$	-1	1	0	1
P_{16}	$\frac{\partial i}{\partial C_2}$	$\text{kg}^{-1} \text{ m A}$	-1	1	0	1
P_{17}	$\frac{\partial i}{\partial C_3}$	$\text{kg}^{-1} \text{ m A}$	-1	1	0	1
P_{18}	$\frac{\partial i}{\partial C_4}$	$\text{kg}^{-1} \text{ m A}$	-1	1	9	1

fore, the formation of a significant amount of the hydroxo complexes is questionable; we may assume that it is the oxalate complexes of two-valent chromium that directly discharge (involving hydrogen ions):



According to [16], oxalate ions represent a continuous system of conjugated π -bonds and thus can play the role of bridge-ligands, which assure fast electron transfer to the chromium atom.

The suggested reaction scheme agrees with the data of [17]: in particular, the rate of chromium deposition from oxalate bath increases with an increase in the solution acidity.

As mentioned above, the origin of the descendent segments in the i vs. E curves taken in the oxalate and

formate baths is due to different reasons. When chromium is deposited from a formate bath, this phenomenon is probably caused by blocking the electrode surface with slightly soluble Cr(III) hydroxide compounds [1, 2]. This is caused by the local increase in pH near the electrode, due to the passing of concurrent hydrogen evolution reaction. Obviously, such effects must be highly sensitive to changes in the convective mass transfer, which agrees well with our data.

Earlier we suggested [17] that the appearance of extrema in the i vs. E curves taken in oxalate baths is probably due to the desorption, of the adsorbed oxalate complex ions of two-valent chromium at sufficiently negative electrode potentials, rather than to the formation of Cr(III) hydroxide compounds. This phenomenon seems to weakly depend on hydrodynamic conditions, as was already mentioned above.

The described kinetic analysis of the chromium electrodeposition reaction illustrates a promising and

Table 2. Solutions of the set of equations (16) and their corresponding dimensionless complexes

Value z_{ij}	Number of the solutions for the system													
	$i = 1$	$i = 2$	$i = 3$	$i = 4$	$i = 5$	$i = 6$	$i = 7$	$i = 8$	$i = 9$	$i = 10$	$i = 11$	$i = 12$	$i = 13$	$i = 14$
z_{i1}	-1	-1	-1	0	0	0	0	0	2	1	1	0	0	0
z_{i2}	1	0	0	0	0	0	0	0	0	0	0	1	0	0
z_{i3}	0	1	0	0	0	0	0	0	0	0	0	0	1	0
z_{i4}	0	0	1	0	0	0	0	0	0	0	0	0	0	1
z_{i5}	0	0	0	0	0	1	1	-1	-2	-1	-1	-1	-1	-1
z_{i6}	0	0	0	0	0	-1	0	0	0	0	0	0	0	0
z_{i7}	0	0	0	0	0	0	-1	0	0	0	0	0	0	0
z_{i8}	0	0	0	1	0	0	0	1	1	0	0	0	0	0
z_{i9}	0	0	0	-1	0	0	0	0	0	0	0	0	0	0
z_{i10}	0	0	0	0	0	0	0	1	0	0	0	0	0	0
z_{i11}	0	0	0	0	0	0	0	0	-3	-1	0	0	0	0
z_{i12}	0	0	0	0	1	0	0	0	0	1/2	0	0	0	0
z_{i13}	0	0	0	0	-1	0	0	0	0	1/2	0	0	0	0
z_{i14}	0	0	0	0	2	0	0	0	0	0	0	0	0	0
z_{i15}	0	0	0	0	0	0	0	0	0	0	1	0	0	0
z_{i16}	0	0	0	0	0	0	0	0	0	0	0	1	0	0
z_{i17}	0	0	0	0	0	0	0	0	0	0	0	0	1	0
z_{i18}	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Complex π_j	$\pi_1 = \frac{C_2}{C_1}$	$\pi_2 = \frac{C_3}{C_1}$	$\pi_3 = \frac{C_4}{C_1}$	$\pi_4 = \frac{\eta F}{RT}$	$\pi_5 = \frac{r^2 f}{v}$	$\pi_6 = \frac{i}{i_{\max}}$	$\pi_7 = \frac{i}{i_{pr}}$	$\pi_8 = \frac{\partial i}{\partial \eta} \frac{\eta}{i}$	$\pi_9 = \frac{C_1^2 \eta}{i^2 \varepsilon^3}$	$\pi_{10} = \frac{C_1 \sqrt{v f}}{i \varepsilon}$	$\pi_{11} = \frac{\partial i}{\partial C_1} \frac{C_1}{i}$	$\pi_{12} = \frac{\partial i}{\partial C_2} \frac{C_2}{i}$	$\pi_{13} = \frac{\partial i}{\partial C_3} \frac{C_3}{i}$	$\pi_{14} = \frac{\partial i}{\partial C_4} \frac{C_4}{i}$

fruitful applying of the mathematical apparatus of the theory of generalized variables in the electrochemical kinetics. The advantage of the method is the possibility to obtain, from primary experimental data (i vs. E curves taken for different ω), a great deal of supplementary information in the form of manifold interdependences of dimensionless quantities, which have clear and straightforward physical meaning. Another important advantage of using the theory of generalized variables in interpreting the kinetic data is the decrease in the number of quantities to be analyzed and the possibility of the flexible adapting of the mathematical apparatus to describing the kinetics of practically any complicated electrochemical system.

It is particularly worth of noting that the methods of the theory of generalized variables allow not only decrease the number of parameters to be analyzed, as well as the problem's variables, but systematize them rationally. For example, it is clear from the above discussion that the effects of the RDE rotation velocity and

radius, as well as the solution kinematic viscosity, on the metal deposition kinetics cannot be analyzed separately and independently but only in aggregate, which is quantitatively expressed by the Reynolds criterion (this statement is but trivial in hydrodynamics, but not in the electrochemical kinetics). Thus, the methods of the theory of generalized variables open way to a theoretically substantiated and optimized approach to planning electrochemical experiment and then describing and interpreting the obtained data.

We conclude that presenting the kinetic data via the dimensionless complexes (similarity criteria) only supplements the traditional approach (with the use of voltammograms), rather than competes with it.

APPENDIX

Yet us summarize the dimensionalities of the initial quantities P_i in Table 1. From the powers of dimensionalities of the quantities P_i , given in Table 1, we formed

a rectangular matrix A consisting of 18 rows and 4 columns:

$$A = \begin{pmatrix} 1 & -3 & 0 & 0 \\ 1 & -3 & 0 & 0 \\ 1 & -3 & 0 & 0 \\ 1 & -3 & 0 & 0 \\ 0 & -2 & 0 & 1 \\ 0 & -2 & 0 & 1 \\ 0 & -2 & 0 & 1 \\ 1 & 2 & -3 & -1 \\ 1 & 2 & -3 & -1 \\ -1 & -4 & 3 & 2 \\ 1 & 0 & -1 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 1 & 0 & 1 \\ -1 & 1 & 0 & 1 \\ -1 & 1 & 0 & 1 \\ -1 & 1 & 0 & 1 \end{pmatrix}. \quad (14)$$

It is easy to show that the matrix A has the rank 4. Because the full number of the initial quantities is 18, from these quantities we can form $i = 18 - 4 = 14$ independent complexes of the following type:

$$\pi_i = \prod_{j=1}^{18} P_j^{z_{ij}}. \quad (15)$$

In formula (15) the powers z_{ij} are the solutions of the set of four linear equations, composed by using elements a_{xy} from the matrix A:

$$\begin{cases} \sum_{j=1}^{18} a_{j1} z_{ij} = 0, \\ \sum_{j=1}^{18} a_{j2} z_{ij} = 0, \\ \sum_{j=1}^{18} a_{j3} z_{ij} = 0, \\ \sum_{j=1}^{18} a_{j4} z_{ij} = 0. \end{cases} \quad (16)$$

The set of equations (16) combines up eighteen variables z_{ij} . As shown above, the rank of the coefficient matrix equals 4, hence, the system has $i = 18 - 4 = 14$ linearly independent solutions that can be easily found, e.g., by selection. The calculated values z_{ij} and their corresponding structures of dimensionless complexes are given in Table 2.

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