ISSN 1070-4272, Russian Journal of Applied Chemistry, 2007, Vol. 80, No. 8, pp. 1316–1321. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © G.I. Medvedev, N.A. Makrushin, V. Khamun'ela, 2007, published in Zhurnal Prikladnoi Khimii, 2007, Vol. 80, No. 8, pp. 1276–1281.

APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Elecrodeposition of Lustrous Zinc Coatings from Sulfate Electrolyte

G. I. Medvedev, N. A. Makrushin, and V. Khamun'ela

*Novomoskovsk Institute, Mendeleev Russian University of Chemical Engineering, Novomoskovsk,
Tula oblast, Russia*

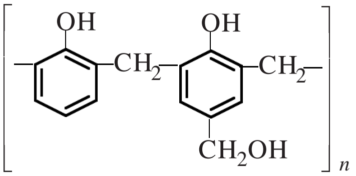
Received December 19, 2006; in final form, March 2007

Abstract—Electrodeposition of lustrous zinc coatings from a sulfate electrolyte containing $ZnSO_4$, Na_2SO_4, buffer additives, and fixers (products of phenol-formaldehyde condensation) was studied.

DOI: 10.1134/S1070427207080101

Lustrous zinc coatings on articles of simple configuration are deposited from sulfate electrolytes containing various brightening additives (aldehydes, ketones, sulfo compounds, and various condensation products of complex composition [1–4]).

In this study, we examined the electrodeposition of zinc from a sulfate electrolyte containing a fixer, product of phenol-formaldehyde condensation with the structural formula



The study was performed in an electrolyte containing (g l^{-1}): $ZnSO_4 \cdot 7H_2O$ 200–250, $Na_2SO_4 \cdot 10H_2O$ 50–100, $Al_2(SO_4)_3 \cdot 18H_2O$, H_3BO_3, aminoacetic acid 25–30, and fixer 0.5–5, at 18–25°C and pH 2–5. Zinc plates served as anodes. A 6–15-μm-thick zinc layer was deposited onto unpolished St.3 steel. Polarization curves were recorded with a P-5828 potentiostat. The luster was measured on a FB-2 photoelectric luster meter. The leveling power P of the electrolytes was determined by a direct profile measurement of the sample surface with a sinusoidal microprofile. P was calculated by the formula [5]

$$P = 2.3a/2\pi h_{av} \log(H_0/H_i),$$

where a is the sine wave amplitude of the microprofile; h_{av}, average thickness of the coating (10 μm); H_0 and H_i, initial and final amplitudes of the sinusoidal microprofile, respectively.

The capacitance of the electric double layer was measured in the course of electrolysis with a P-5021 ac bridge at a frequency of 30 kHz in a series equivalent circuit. A zinc-coated platinum wire placed at the center of a platinum-coated cylinder served as the working electrode. The pH value in the near-electrode layer was measured by the method described in [6]. The degree of surface filling with organic additives, Q, was estimated using the polarization curves [7] by the formula

$$Q = 1 - \exp(\Delta E/b),$$

where ΔE is the potential shift in cathodic polarization, and b is the Tafel constant found from the polarization curves plotted in the semilog scale.

The internal stresses and microhardness of the coatings were determined as described in [8].

The results obtained in a study of the influence exerted by the fixer concentration, nature of the buffer additive, and current density on the outward appearance of the coatings show that dark gray coatings with a rough surface are formed from an electrolyte containing $Al_2(SO_4)_3$ buffer additive and a fixer at $i_c = 1–11$ A dm^{-2}. At the same time, lustrous coatings are formed from an electrolyte containing H_3BO_3

Table 1. Effect of buffer additives, fixer concentration, and current density on the outward appearance of zinc coatings [electrolyte composition (g l^{-1}): $ZnSO_4 \cdot 7H_2O$ 200 and $Na_2SO_4 \cdot 10H_2O$ 50; pH 3–4, T = 20°C]

Buffer additive, g l^{-1}	Fixer concentration, g l^{-1}	Current density, A dm^{-2}	Coating appearance
HBO_3, 30	0.5	1–5	Silvery
		6–11	Silvery with burn-on
	1–2	1	Silvery
		2–10	Lustrous
		11	Lustrous with burn-on
	3–4	1	Silvery
		2–5	Lustrous
		6–8	Semilustrous
		9–11	Semilustrous with burn-on
	5	1–3	Lustrous
		4–6	Semilustrous
		7–11	Semilustrous with burn-on
Aminoacetic acid 30	0.5	1–5	Silvery
		6–8	Silvery with burn-on
	1–2	1–8	Lustrous
		9–11	Lustrous with burn-on
	3–4	1–4	Lustrous
		5–8	Semilustrous
		9–11	Semilustrous with burn-on
	5	1–2	Lustrous
		3–5	Semilustrous
		6–8	Silvery
		9–11	Silvery with burn-on

and aminoacetic acid. As can be seen in Table 1, the outward appearance of the coatings varies in this case with the fixer concentration and with the cathode current density.

The widest range of current densities at which lustrous coatings are formed is observed at fixer concentrations of 1–2 g l^{-1}. In this case, the current densities vary in the range from 2 to 10 A dm^{-2} in an electrolyte containing H_3BO_3, and from 1 to 8 A dm^{-2} in an electrolyte containing aminoacetic acid. At higher fixer concentrations (c = 3–5 g l^{-1}), the range of current densities at which lustrous coatings are deposited is markedly narrower.

In the electrolytes studied, the pH value should be within the range 3–4. At pH < 3, the i_c range providing deposition of lustrous coatings and the current efficiency decrease. At pH > 4 lustrous coatings are deposited, but the electrolyte exhibits an unstable behavior. The current efficiency by zinc in the electrolytes yielding lustrous coatings varies from 85 to 97%. In the electrolyte containing aminoacetic acid, the current efficiency is the highest (Fig. 1, curves *1*, *2*).

Cathodic polarization curves were measured in the zinc-plating electrolytes. As can be seen in Fig. 2, the presence of a fixer enhances the cathodic polarization (Fig. 2, curves *1*, *2*). The inhibition effect of the fixer on the electrodeposition of zinc is due to its

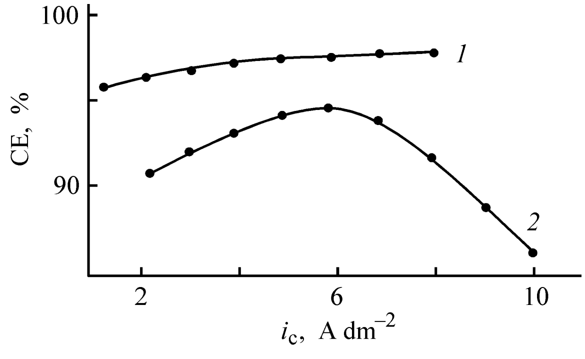


Fig. 1. Current efficiency CE by zinc vs. the current density i_c. Electrolyte composition (g l^{-1}): $ZnSO_4 \cdot 7H_2O$ 200, $Na_2SO_4 \cdot 10H_2O$ 50, fixer 1; pH 3.5. (*1*) Electrolyte + aminoacetic acid, 30 g l^{-1}; (*2*) electrolyte + H_3BO_3, 30 g l^{-1}.

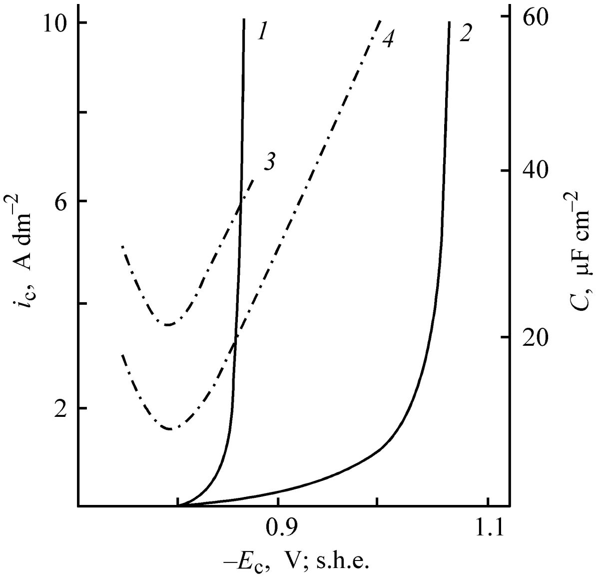


Fig. 2. Current density i_c and electric double layer capacitance C vs. the electrode potential E_c in a zinc-plating electrolyte. Electrolyte composition (g l^{-1}): $ZnSO_4 \cdot 7H_2O$ 200, $Na_2SO_4 \cdot 10H_2O$ 50, H_3BO_3 30, pH 3.5. (*1*), (*3*) Electrolyte, (*2*), (*4*) electrolyte + fixer, 1 g l^{-1}.

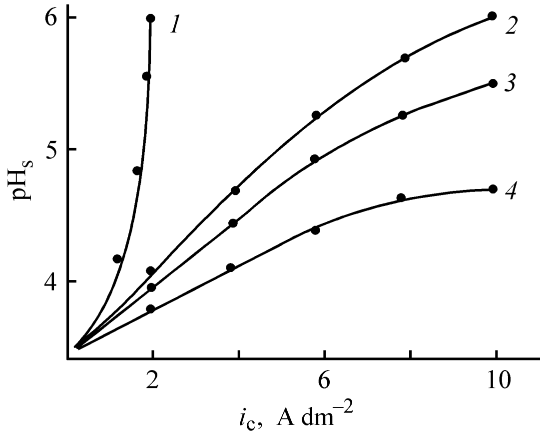


Fig. 3. Dependence of pH$_s$ in the near-cathode layer on the current density i_c in a zinc-plating electrolyte. Electrolyte composition (g l^{-1}): $ZnSO_4 \cdot 7H_2O$ 200, $Na_2SO_4 \cdot 10H_2O$ 50, fixer 1. (*1*) Electrolyte; (*2*) electrolyte + H_3BO_3, 30 g l^{-1}; (*3*) electrolyte + $Al_2(SO_4)_3 \cdot 18H_2O$, 30 g l^{-1}; (*4*) electrolyte + aminoacetic acid, 30 g l^{-1}.

adsorption on the cathode surface. This is confirmed by the results obtained in measuring the capacitance of the electric double layer. In the electrolyte containing no fixer, the capacity-vs.-potential dependence has a minimum (C = 20 μmF cm^{-2}) at a potential of –0.8 V (Fig. 2, curve *3*). Introduction of a fixer into the electrolyte lowers the double layer capacitance to 9 μmF cm^{-2} at E = –0.8 V (Fig. 2, curve *4*). An increase in the capacitance is observed at more negative potentials, which is due to partial desorption of the fixer from the electrode surface [9].

The electrolytes yielding lustrous zinc coatings exhibit the leveling effect. The leveling power varies from 0.2 to 0.4, depending on the cathode current density. The throwing power of the electrolytes is 8–12%. The microhardness of the zinc deposits varies within the range 80–100 kg mm^{-2}. The lustrous zinc coatings have small internal stresses (IS = 100–150 kg cm^{-2}).

As is known [3], the deposition of lustrous coatings is due to smoothing of the submicrometer surface roughness. For a dull coating to be formed, it suffices that an additive is adsorbed on the cathode surface and the electrocrystallization overpotential is raised, whereas formation of a lustrous coating, requires that an adsorption layer of a certain composition should be present on the cathode surface. Such layers can be formed from organic substances and products of secondary reactions in the near-cathode layer. In the case of a simultaneous metal deposition and hydrogen evolution, the adsorption layer may consist of hydroxides and other basic compounds [3].

The suggestion that zinc hydroxides are formed in the near-cathode space is confirmed by the results of pH measurements in the near-cathode layer (pH$_s$). As can be seen from Fig. 3, pH$_s$ varies at i_c = 1–10 A dm^{-2} from 4 to 6, depending on the nature of the buffer additive. In the electrolyte containing aminoacetic acid, the range of pH variation is the narrowest (curve *4*). It should be noted that the pH of hydrate formation in the zinc-plating electrolyte is 6.4. These results suggest that presence of zinc hydrates in the near-cathode layer is not necessary for lustrous coatings to be deposited. Apparently, lustrous coatings are deposited if a highly dispersed adsorption layer is formed on the surface [3].

Apparently, buffer additives control the dispersity of the adsorption layer. In their presence, the adsorption layer may change because of the formation of difficultly soluble zinc borates in the near-cathode space. It is not improbable that complex compounds of orthoboric and aminoacetic acids with zinc ions, as well as intracomplex (chelated) compounds of H_3BO_3 with the fixer, can be formed.

An important issue in elucidating the mechanism of formation of lustrous coatings, is determining the degree of filling of the cathode surface with the adsorbed additive. The dependences of the degrees of luster (curve *1*) and surface filling (curve *2*) on the current density are shown in Fig. 4. It can be seen that, as the cathode current density increases, the degree of luster of the coatings passes through a maximum, whereas the degree of filling decreases. At the current densities studied, the degree of surface filling varies from 24 to 10%. This shows that lustrous coatings are formed at a well-defined degree of surface filling.

To elucidate the mechanism by which the fixer affects the electrodeposition of zinc, we carried out a quantum-chemical study of a system constituted by hydrated ions present in the electrolyte and fixer molecules. To find the degree of polymerization, *n*, of the fixer molecule, its molecular weight was determined by the cryoscopic method. The results of these measurements demonstrated that $n = 1$. Consequently, the electrolyte also contains a monomeric product of phenol-formaldehyde (F) condensation.

The quantum-chemical calculation was performed by the semiempirical PM3 method [11, 12]. Compared with other semiempirical methods and ab initio calculations with different basis sets [13], this method describes rather well the parameters of intermolecular interactions. The energy of interaction between the particles constituting the system under consideration was calculated as the difference between the total electronic energy of the system and the sum of the total electronic energies of its constituents. For example, we calculated for the system Zn_{49}–$[ZnF]^{2+}$, first, the energy of interaction between a complex-forming ion and the ligand in the complex $[ZnF]^{2+}$ ion

$$\Delta E_c = E_{[ZnF]^{2+}} - (E_{Zn^{2+}} + E_F),$$

and then the energy of interaction of the complex ion with the cluster

$$\Delta E_{cl} = E_{Zn_{49}-[ZnF]^{2+}} - (E_{[ZnF]^{2+}} + E_{Zn_{49}}).$$

The results of the calculation show that, similarly to the case of 2-butyne-1,4 diol [14], the interaction of Zn^{2+} ions with the formaldehyde molecules is more energetically favorable than the formation of a hydrated shell of the ion. In a sulfate zinc-plating electrolyte, complex ions of composition $[Zn(H_2O)_x(F)_y]^{2+}$, where $x = 1–5$, $y = 1–3$, are most likely to exist in the electrolyte bulk.

In the near-cathode layer, mixed aqua hydroxo complexes of various compositions with formaldehyde molecules can be formed via alkalization. In view of the fact that formaldehyde molecules displace water molecules from the Zn^{2+} aqua complexes (Fig. 5), the formation of $Zn(OH)_2$, $Zn(OH)^+$, and $[ZnF]^{2+}$–$[Zn(OH)F]^+$ species is most likely in the near-cathode layer. Less probable is the formation of $[Zn(OH)_2F]$ species.

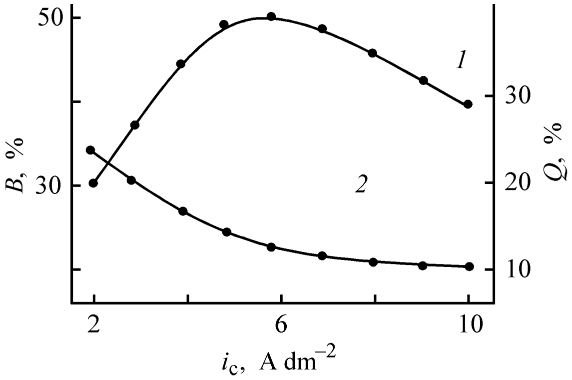


Fig. 4. Degree of luster *B* (*1*) and degree of the surface filling *Q* (*2*) vs. the current density i_c.

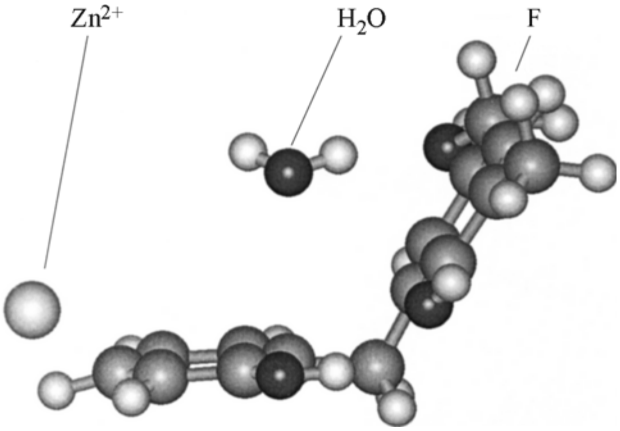


Fig. 5. Structure of a Zn^{2+} complex with a monomeric product of phenol-formaldehyde (F) condensation and a water molecule, according to the results of a quantum-chemical calculation Formaldehyde molecule: hydrogen atoms, white; carbon, gray; and oxygen, dark gray.

In the next stage, we carried out a quantum-chemical study of the structure of complexes with formaldehyde molecules at the electrode–solution interface. In doing so, we modeled the surface of the zinc electrode with a cluster formed by 49 atoms arranged in two layers having the hexagonal form. The clusters were chosen as recommended in [15].

To simulate the reduction of Zn^{2+} on the surface of the zinc electrode, the zinc cluster system Zn_{49}–Zn^{2+}–F was calculated. It was shown that the highest interaction energy with the Zn_{49} cluster is observed for $Zn(OH)^+$ species. The formaldehyde molecules in the complex constitute, as they approach the cluster, a stable system at a distance of 418 pm from the cluster. In this case, the interaction energy is 437 kJ mol^{-1}, which considerably exceeds the value for interaction of the cluster with

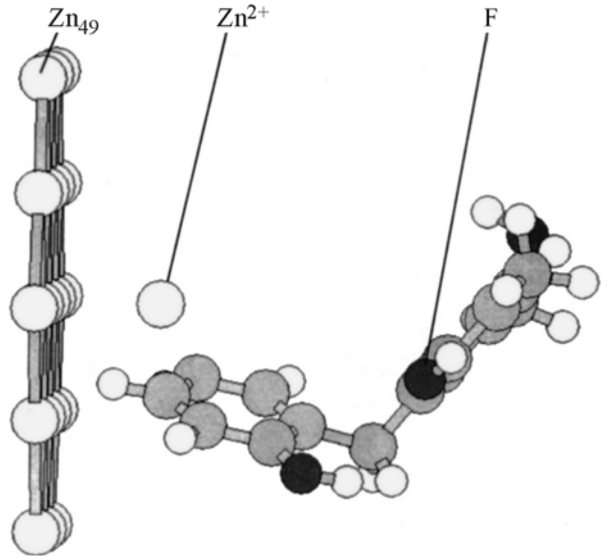


Fig. 6. Structure of a Zn^{2+} complex with a monomeric product of phenol-formaldehyde (F) condensation on the surface of the Zn_{49} cluster, according to the results of a quantum-chemical calculation.

a hydrated zinc ion (200 kJ mol^{-1}) and a $[Zn(OH)F]^+$ species. The presence of a formaldehyde molecule in the complex species makes distance between the zinc ion and the cluster surface considerably larger. This may result from the spatial structure of the forming complexes, which creates, owing to the large size of the formaldehyde molecule, steric hindrance to approach of zinc ions to the cluster (Fig. 6). It is noteworthy that, without Zn^{2+} ions, the formaldehyde molecule forms no stable system with the cluster.

The rather wide variety of complex species formed in the near-cathode layer suggest that their discharge can occur by different pathways. To assess the probabilities of these pathways, we calculated the change in the total energy of the reaction products (Table 2) in comparison with the total energy of the starting substances. In doing so, we took into account that the energy necessary for an electron to be involved in each of the above processes is constant. In the given case, the reactions involving and not involving formaldehyde molecules were considered.

Table 2. Changes in the total energy of the products in comparison with the total energy of starting substances

Reaction	Reaction equation	ΔE, kJ mol^{-1}
(1)	$Zn(OH)_2 + e = ZnOH + OH^-$	271
(2)	$ZnOH^+ + e = ZnOH$	–897
(3)	$[ZnF]^{2+} + e = Zn^+ + F$	–874
(4)	$[Zn(OH)F]^+ + e = ZnOH + F$	–662
(5)	$[Zn(OH)_2F] + e = ZnOH + OH^- + F$	173

It follows from the data in Table 2 that reactions (2)–(4) yielding ZnOH species and Zn^+ ions are the most probable from the energy standpoint. Presumably, of all three reactions, reaction (2) is the first to occur. The species forming in this case enter into the following electrochemical reactions:

$$ZnOH + e = Zn + OH^-,$$

$$Zn^+ + e \rightarrow Zn.$$

Thus, our quantum-chemical calculations demonstrated that, in a sulfate zinc-plating electrolyte containing formaldehyde molecules, the probability of existence of complex ions $[Zn(H_2O)_x(F)_y]^{2+}$ in the electrolyte bulk is the highest, whereas in the near-cathode space, $[Zn(OH)]^+$, $[ZnF]^{2+}$, and $[Zn(OH)F]^+$ are electrically active particles owing to alkalization.

The study we performed enabled us to develop a sulfate zinc-plating electrolyte of simple composition for deposition of lustrous coatings with smoothed surface. The electrolyte composition is as follows (g l^{-1}): $ZnSO_4 \cdot 7H_2O$ 200–250, $Na_2SO_4 \cdot 10H_2O$ 50–100, H_3BO_3 25–30, and fixer 1–2. The process is performed at i_c = 2–10 A dm^{-2}. The electrolyte temperature is 18–25°C, pH 3–4, and CE = 84–97%. The anodes are made of zinc. Aminoacetic acid (c = 25–30 g l^{-1}) can be taken instead of H_3BO_3. In this case, lustrous coatings are obtained at i_c = 1–8 A dm^{-2} with CE = 86–97%.

CONCLUSIONS

(1) A study of zinc electrodeposition from a sulfate electrolyte containing a fixer (product of phenol-formaldehyde condensation) and buffer additives demonstrated that the fixer taken together with H_3BO_3 or aminoacetic acid yields lustrous zinc coatings with smoothed surface at i_c = 1–10 A dm^{-2}.

(2) The system constituting hydrated zinc ions and fixer (formaldehyde) molecules was studied using the quantum-chemical method. It was shown that complexes of composition $[Zn(H_2O)_x(F)_y]^{2+}$ are most likely to be present in the electrolyte bulk. In the near-cathode layer, $[Zn(OH)]^+$, $[ZnF]^{2+}$, and $[Zn(OH)F]^+$ are electrically active species owing to alkalization.

(3) Sulfate electrolytes for deposition of lustrous zinc coatings with smoothed surface were developed.

REFERENCES

1. Kudryavtsev, N.G., *Elektroliticheskie pokrytiya metallami* (Metal Electroplating), Moscow: Khimiya, 1979.
2. Zhilienene, B.M., *Patentnaya literatura po elektroosazhdeniyu zinka iz netsianistykh rastvorov za 1960–1972 gody* (Patent Literature on Zinc Electrodeposition from Noncyanide Solutions, Published in 1960–1972), Vilnius: Inst. Khim. Khim. Tekhn., 1972.
3. *Blestyashchie elektroliticheskie pokrytiya* (Lustrous Electrolytic Coatings), Matulis, Yu.Yu., Ed., Vilnius: MINTIS, 1969.
4. Proskurin, E.V., Popovich, V.A., and Moroz, T.M., *Tsinkovanie: Spravochnoe izdanie* (Zinc Plating. Reference Book), Moscow: Metallurgiya, 1988.
5. Bakhchisarayunyan, N.G., Borisoglebskii, Yu.V., Burkat, G.K., et al., *Praktikum po prikladnoi elektrokhimii: Uchebnoe posobie dlya vuzov* (Laboratory Manual of Applied Electrochemistry: Textbook for Higher School Institutions), Voropaev, V.N. and Kudryavtsev, V.N., Eds., Leningrad: Khimiya, 1990, 3nd ed. revised.
6. Gershov, V.M., Purin, B.A., and Ozol'–Kalnin', G.A., *Elektrokhimiya*, 1972, vol. 8, no. 5, pp. 673–675.
7. Hangen, R., and Clampit, B., *J. Phys. Chem.*, 1954, vol. 58, no. 5, pp. 908–913.
8. Vyacheslavov, P.M., and Shmeleva, N.M., *Metody ispytanii elektroliticheskikh pokrytii* (Methods for Testing of Electrodeposited Coatings), Moscow: Mashinostroenie, 1977.
9. Damaskin, B.B., Petrii, O.A., and Batrakov, V.V., *Adsorbtsiya organicheskikh soedinenii na elektrodakh* (Adsorption of Organic Compounds on Electrodes), Moscow: Nauka, 1968.
10. Yakovlev, A.G., *Praktikum po fizicheskoi i kolloidnoi khimii* (Laboratory Manual of Physical and Colloid Chemistry), Moscow: Vysshaya Shkola, 1967.
11. Stewart, J.J.P., *J. Comput. Chem.*, 1989, vol. 10, no. 2, pp. 209–220.
12. Stewart, J.J.P., *J. Comput. Chem.*, 1991, vol. 12, no. 3, pp. 320–341.
13. Makrushin, N.A., Dubenkov, A.N., Ermakov, A.I., and Merkulov, A.E., *Izv. Tul'skogo Gos. Univ. Khimiya*, 2002, no. 3, pp. 24–31.
14. Larin, E.A., Makrushin, N.A., Dubenkov, A.N., et al., *Izv. Tul'skogo Gos. Univ., Khimiya*, 2004, no. 4, pp. 204–208.
15. Shapnik, M.S., *Elektrokhimiya*, 1994, vol. 30, no. 2, pp. 143–149.