

Electrolytic Formation of Metal Complex Nanoaggregates from Polymethine Dyes on Metallic Electrodes

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Abstract—An electrolytic method for the synthesis of metal complex aggregates from polymethine dyes on the surface of anodes from metals capable of electrolytic oxidation has been developed. It has been concluded that the electrochemical method for the synthesis of aggregates from polymethine dyes has technological prospects for the creation of photosensitive elements in organic nanoelectronics and photonics.

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INTRODUCTION

One of the topical problems of developing organic electronics is the creation of a reliable electrical contact between a metallic electrode and an organic semiconductor. The widely applied technology of the vacuum spraying of organic compounds onto a metal has some limitations for a number of thermally unstable organic compounds and saltlike components. At the present time, polymethine dyes differing from dyes of other classes by maximum light absorption and propensity to the formation of highly organized aggregate structures (J- and H-types) provoke considerable interest as materials of optoelectronic nanoelements. Polymethine dye aggregates are characterized by a maximum quantum yield of the generation of photoexcited charge carriers (Frenkel excitons) at a level of nearly unity [1]. These properties of polymethine dye aggregates alone have caused their practical application as highly efficient spectral sensitizers in classic photographic materials based on silver halides [2]. However, vacuum-spraying methods are hardly applicable to saltlike polymethine dyes due to their low volatility and insufficient thermal stability.

The study of aggregation processes for anionic polymethine dyes in aqueous solutions has shown that this process is stimulated by multicharged metal cations [3, 4]. Metal complexes are formed in this case. The thermodynamic studies [5] of the process of dye aggregate assembly under the action of multicharged cations indicates a decrease in the aggregate formation enthalpy and entropy, and this improves their thermal and photo stability.

The mentioned experiments have led to work on the electrolytic precipitation of polymethine dye

aggregates onto a metallic anode as a result of complexation between the cations formed in the oxidation of a metal and the anionic polymethine dyes dissolved in an aqueous electrolyte solution [6].

INSTRUMENTS AND MATERIALS

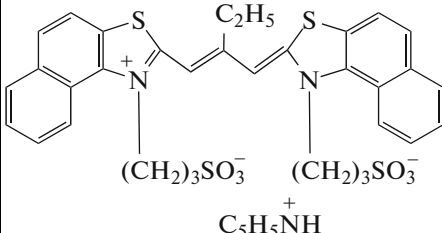
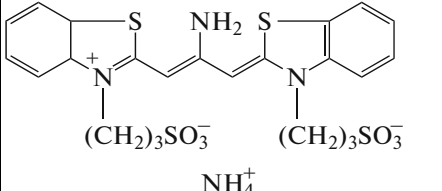
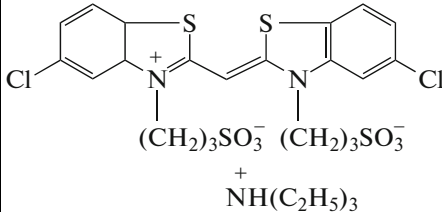
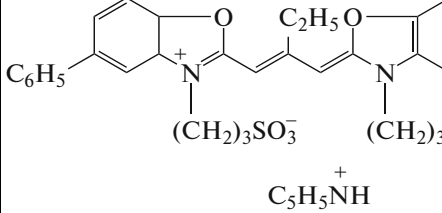
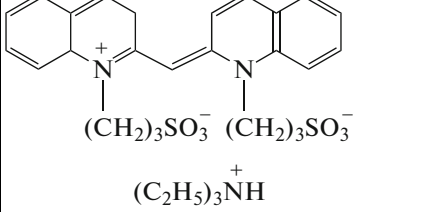
Five anionic polymethine dyes of different structures were studied. The structural formulas and spectral characteristics of the used dyes are given in Table 1. The dyes were synthesized in the State Research and Design Institute of Chemical Photographic Industry (GosNIKhIMFOTOPROEKT, Moscow) and characterized by elemental analysis and NMR spectra.

The optical absorption spectra of dye solutions were measured on an Ocean Optics USB2000+ and PerkinElmer Lambda UV-35 spectrophotometers (United States) within a range from 350 to 1100 nm. The solutions were prepared using deionized bidistilled water, which was treated with UV radiation and purified by reverse osmosis on a Milipore Milli-Q3 Direct UV water purification setup (France) with an electrical resistance of 18 M Ω cm. Portions of dyes and metal salts were weighed on a GR-202 A&D electronic microanalytical balance (Japan).

EXPERIMENTAL METHOD

The anodic electrolytic precipitation of dyes from aqueous solutions was performed in a two-electrode electrochemical cell with a metallic anode and an inert (platinum or graphite) cathode, which were spaced apart at a distance of 20 mm. The dye solution volume in the cell was 10 mL. The metals used as anodes were

Table 1. Structure and properties of the studied dyes*

Dye no.	Dye name and structural formula	Molecular weight, g	Molar extinction coefficient in alcohol, $\times 10^{-4}$, L/(mol cm)	λ_{\max} in water, nm
Dye1	3,3'-Di-(γ -sulfoethyl)-4,5,4',5'-dibenzo-9-ethylthiatrimethinecyanine betaine pyridinium salt 	759.9	11.2	535 (D)* 575 (M) 637 (J _{cis}) 660 (J _{trans})
Dye2	3,3'-Di-(γ -sulfoethyl)-9-aminothiatrimethinecyanine betaine ammonium salt 	611.8	5.0	418 (H) 450 (D) 475 (M)
Dye3	3,3'-Di-(γ -sulfoethyl)-5,5'-dichlorothiacyanine betaine triethylammonium salt 	696.1	7.8	408 (D) 428 (M) 464 (J)
Dye4	3,3'-Di-(γ -sulfoethyl)-5,5'-diphenyl-9-ethyloxatriethinecyanine betaine pyridinium salt 	779.1	10.6	507 (D) 520 (M) 545 (J)
Dye5	1,1'-Di-(γ -sulfoethyl)-2,2'-quinocyanine betaine triethylammonium salt 	615.9	7.6	490 (D) 523 (M) 570 (J _{cis}) 580 (J _{trans})

*D, M, J, and H stand for the dimeric and monomeric dye forms and J- and H-aggregates.

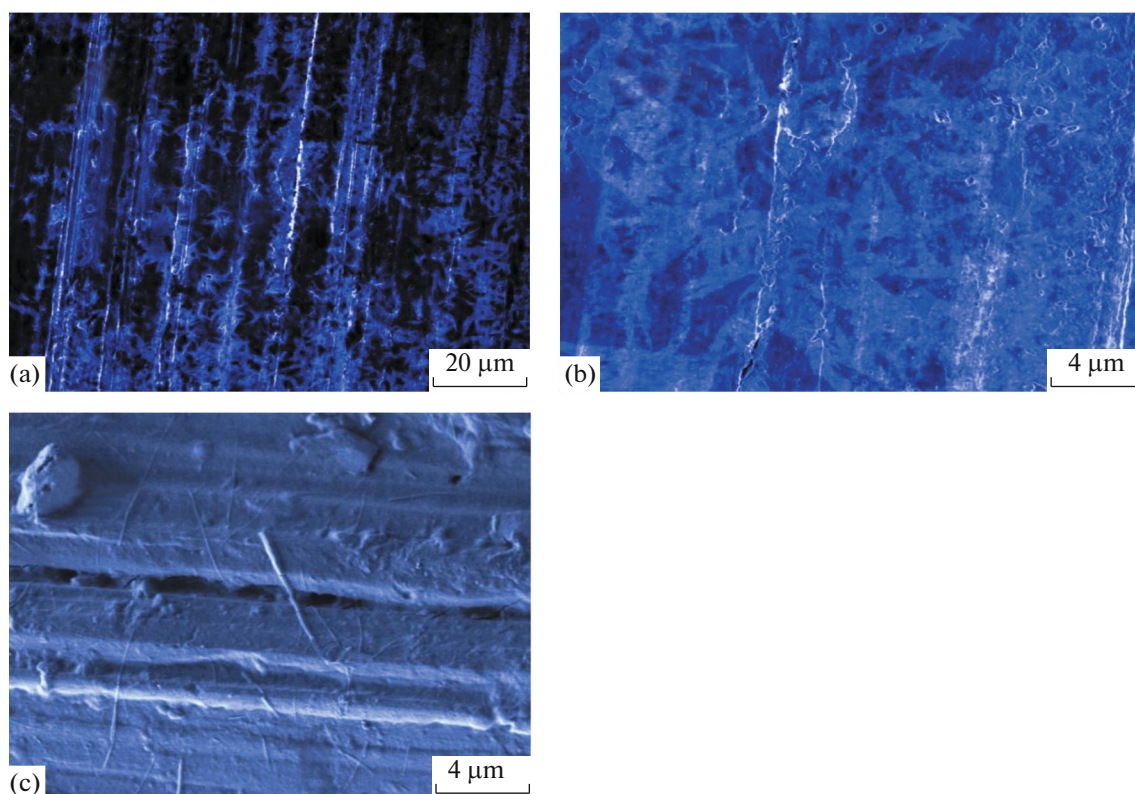


Fig. 1. (Color online) SEM-images of metal complex Dye1 layers on the copper electrode at $C_{\text{Dye1}} = 1.5 \times 10^{-5}$ M; voltage, 5.5 V; $T = 25^\circ\text{C}$; and precipitation time of (a) 5, (b) 10, and (c) 15 min.

Pt, Cu, Al, Ni, Fe, and Mn. The metals were applied in the form of plane specimens with a surface area of 20×40 mm. Moreover, copperclad fiberglass laminate with a copper-layer thickness of 0.2 mm on one side was used. Before electrolytic precipitation, the electrodes were carefully cleaned with GOI polishing paste no. 1 (Cr_2O_3 based) and then washed with 96% ethanol and bidistillate.

Electric power supply was provided by a Mastech HY-5002D stabilized laboratory power supply unit. The current and voltage during the hydrolysis of a dye solution were controlled with a Mastech digital multimeter. No additional electrolyte was applied in experiments to prevent the electrodes from the formation of gases hindering the uniform assembly of dye aggregate layers on the anode surface and avoid the formation of additional salts with metal cations from the anodes. Since, according to the “block” mechanism [7], metal complex dye aggregates are formed from dye dimers, the concentration of dyes in aqueous solutions was selected to be lower than the threshold aggregate formation concentration. To obtain the most uniform dye films on the anode surface at a temperature $T = 25^\circ\text{C}$, the optimal voltage range from 5.5 to 20.0 V was selected at an electrolysis time from 3 to 25 min, depending on the structure of a certain dye, its concentration, and the required thickness of a layer. The

concentrations of dye solutions were varied from 1.5×10^{-5} to 5×10^{-5} M depending on the structure of a dye. Dye layers with a thickness from 0.1 to 1.5 μm were obtained on the electrodes depending on the electrolysis time.

The obtained dye layers on the electrodes were studied on a JSM-7500F scanning electron microscope (JEOL, Japan). The reflectance spectra of metal complex aggregates on the metallic electrodes were recorded on an Avantes Avaspec-2048 spectrophotometer.

The composition of dye layers on the electrodes was determined by chemical analysis on an EMAL-2 mass analyzer and, in the case of paramagnetic cations, by electron paramagnetic resonance (EPR). The results were compared with the composition of salts, which were synthesized by the reaction between equimolar amounts of an aqueous dye solution and a metal (copper and manganese) salt and precipitated in the form of powders. Inorganic salts ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$) of chemically pure grade were used for the synthesis of metal complex dye aggregates.

Let us consider the synthesis of the metal complex of Dye3 and the Cu^{2+} cation as an example. The initial 4×10^{-5} M Dye3 solution free from J-aggregates was controlled spectrometrically. A portion of Dye3 with a

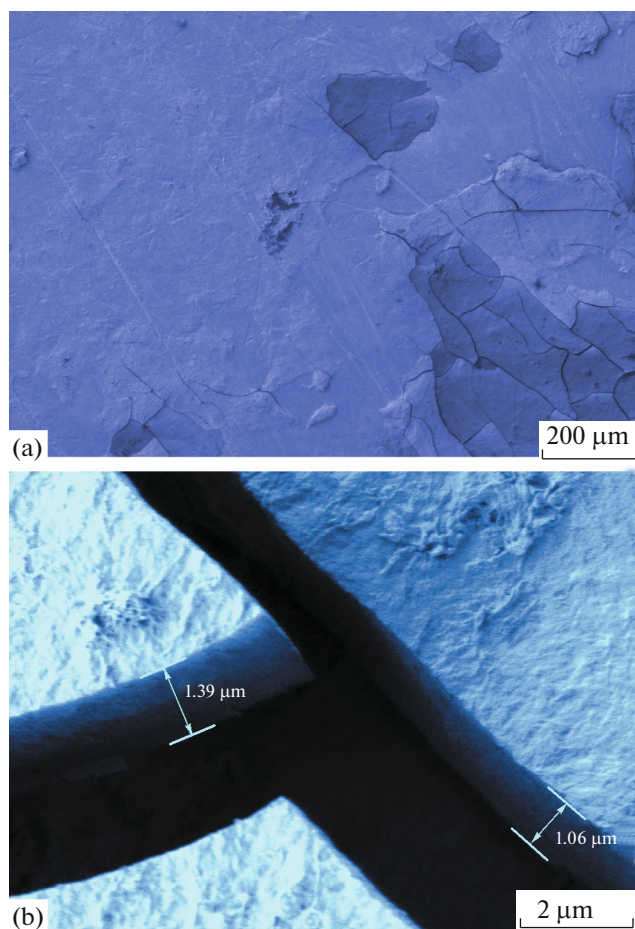


Fig. 2. (Color online) SEM-images of metal complex Dye1 layers on the copper electrode at different magnifications. $C_{\text{Dye1}} = 2.0 \times 10^{-5}$ M; voltage, 20.0 V; precipitation time, 20 min; and $T = 24^\circ\text{C}$.

mass of 34.8 mg was dissolved under vigorous stirring in 1000 mL of bidistillate in a glass 2 L in volume. To the resulting solution, a CuSO_4 solution with a concentration of 1.0×10^{-4} M was poured under vigorous stirring. The solution was vigorously stirred for 15 min and then allowed to stand for 30 min. Yellow-green flaky precipitate settled on the glass bottom. The supernatant was then decanted, and the precipitate suspended in the mother solution was filtered out. The precipitate was dried at 20°C for 5 days. The manganese complex with Dye3 was prepared in a similar way.

EPR spectra were measured on a Bruker E680X ELEXSYS EPR spectrometer.

RESULTS AND DISCUSSION

The formation of colored layers on anodes in the process of electrolysis was observed on all the metals studied as anodes except platinum. No dye layers were formed on the platinum anode, probably due to the

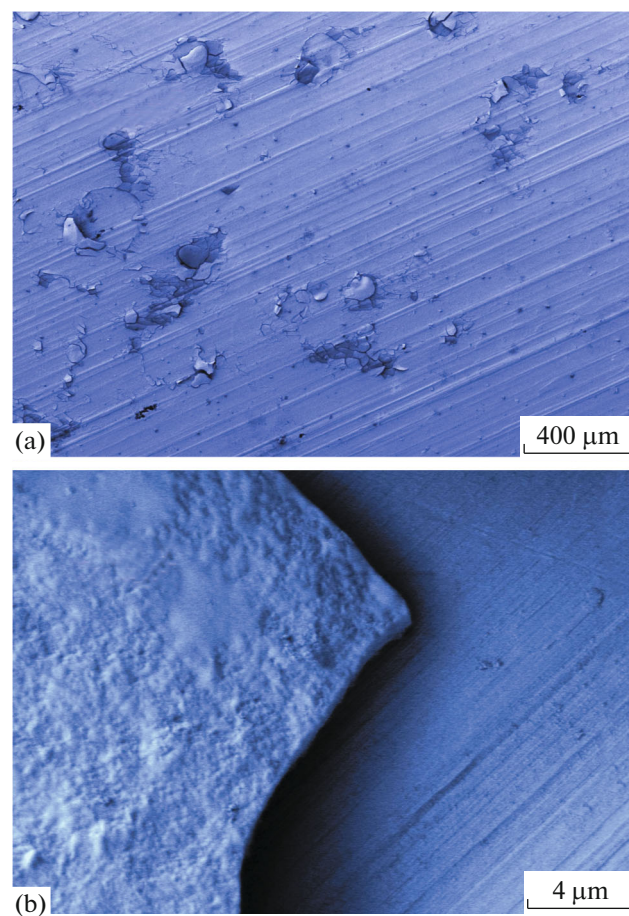


Fig. 3. (Color online) SEM-images of metal complex Dye1 layers on the aluminum electrode. $C_{\text{Dye1}} = 2.0 \times 10^{-5}$ M; voltage, 20 V; precipitation time, 20 min; and $T = 24^\circ\text{C}$.

absence of anodic oxidation for the noble metal. The electronic photos of Dye1 layers formed on the copper electrode surface are shown in Fig. 1 as an example at different magnifications. The images of layers in these electronic photos and the ones given below are painted by the authors in the same colors as for dye layers.

The appearance of individual crystalline formations (Fig. 1a) was first observed and, as the time of electrolysis increased, more coarse associates (Fig. 1b) were formed; thereupon, the electrode surface was coated with a continuous dye layer (Fig. 1c). In the case of longer electrolysis, cracks appeared in the formed layer (Figs. 2a, 2b), probably due to mechanical stresses in the thick layer of nearly $1 \mu\text{m}$. The photos of Dye1 layers formed on the aluminum electrode surface are shown in Figs. 3a and 3b as an example. The electronic photo of a Dye2 layer on the aluminum electrode is displayed in Fig. 4a. The structure of a dye layer is illustrated at a greater magnification in Fig. 4b. The electronic photo of a Dye3 layer, which was electrolytically formed on the aluminum electrode, is given in Fig. 5.

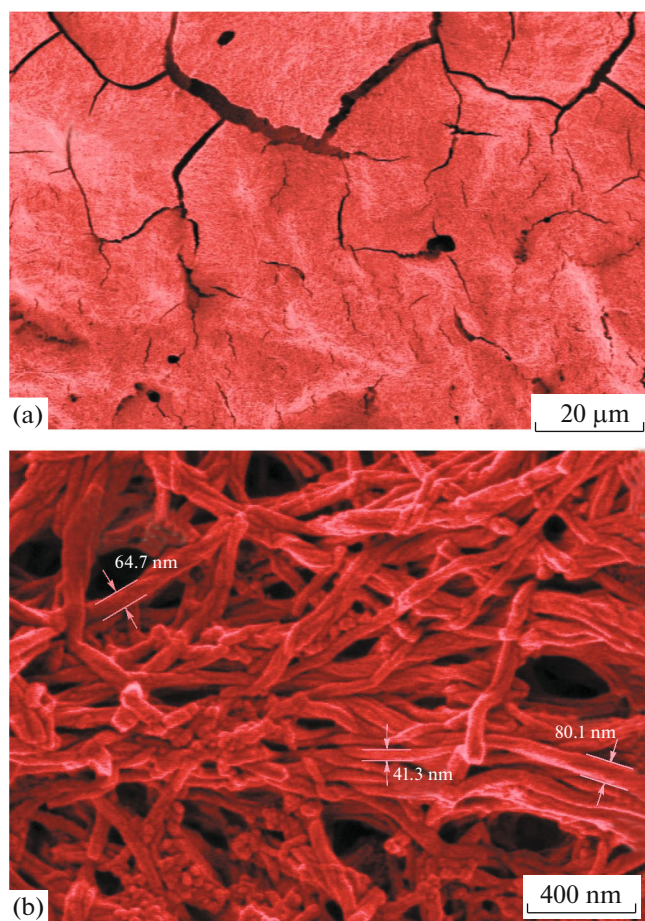


Fig. 4. (Color online) SEM-images of metal complex Dye2 layers on the aluminum electrode at different magnifications. $C_{\text{Dye2}} = 5 \times 10^{-5}$ M; voltage, 5.5 V; precipitation time, 20 min; and $T = 25^\circ\text{C}$.

It was established that Dye1–Dye3 layers were also formed on the Ni, Fe, and Mn anodes. Moreover, electrolytic Dye4 and Dye5 layers were obtained on different metallic anodes.

The measurements of reflectance spectra for the obtained layers of the studied dyes show that their absorption corresponds to the absorption of aggregates built of respective dyes. The reflectance spectra of Dye 1 layers on the copper and nickel anodes are given in Fig. 6 as an example. The minimum observed in the reflectance spectrum of the Dye1 layer obtained by the electrochemical method at ~ 660 nm coincides with the absorption maximum (λ_{max}) of J-aggregates of this dye in an aqueous solution [7]. It is noteworthy that J-aggregates are formed for Dye1 and Dye3–Dye5, while H-aggregates are formed on the electrode in the case of Dye 2.

The chemical analysis data for the Dye3 layers obtained by the electrochemical methods on the copper and manganese anodes and the Dye3 copper and manganese complexes synthesized by bulk crystalliza-

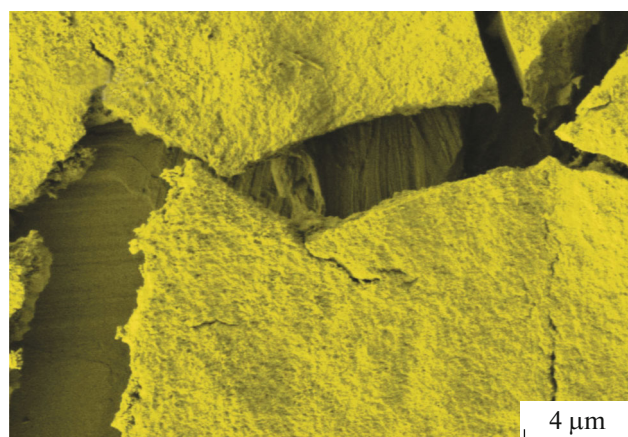


Fig. 5. (Color online) SEM-image of a metal complex Dye3 layer on the aluminum electrode. $C_{\text{Dye3}} = 4 \times 10^{-5}$ M; voltage, 5.5 V; electrolysis time, 20 min; and $T = 25^\circ\text{C}$.

tion from an aqueous solution are given in Table 2. According to chemical analysis data, the Cu and Mn contents in the electrolytic layers and the complexes synthesized by bulk crystallization are close to each other, thus arguing for the formation of metal complexes incorporating anode metal cations on the electrodes.

To prove the formation of the Dye3 metal complex with the paramagnetic Cu^{2+} cation on the copper electrode, the EPR spectrum of the layer formed in the process of electrolysis was measured (Fig. 7a). The results of the computer-aided modeling of this spec-

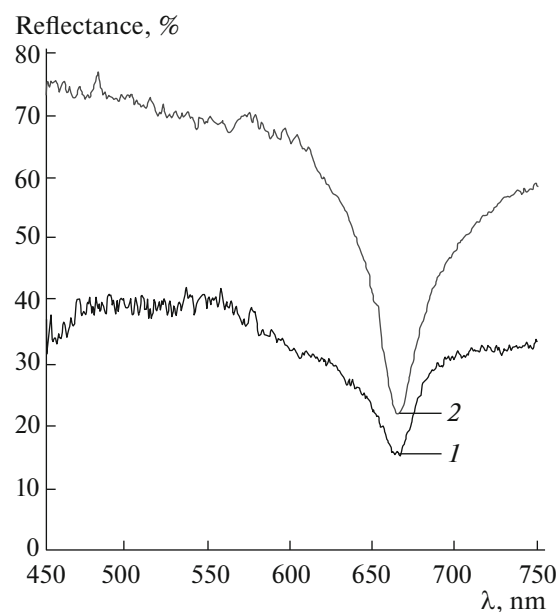


Fig. 6. Optical reflectance spectra of Dye1 layers formed on the surface of (1) aluminum and (2) nickel anodes.

Table 2. Chemical analysis data for the copper and manganese Dye 3 complexes

Element content, at %	Copper Dye3 complex synthesized by the electrochemical method on the copper electrode surface	Copper Dye3 complex synthesized by bulk crystallization	Manganese Dye3 complex synthesized by the electrochemical method on the manganese electrode surface	Manganese Dye3 complex synthesized by bulk crystallization
C	49.7	50.9	54.4	54.6
O	8.6	10.3	9.6	9.8
N	5.2	5.8	5.2	5.3
Cl	12.7	12.0	7.2	8.1
S	13.7	11.9	11.1	11.7
Mn	—	—	10.8	10.5
Cu	8.7	9.0	—	—

trum allow us to come to the following conclusions. The spin Hamiltonian parameters correspond to the Cu^{2+} ion coordinated to organic molecules, in this

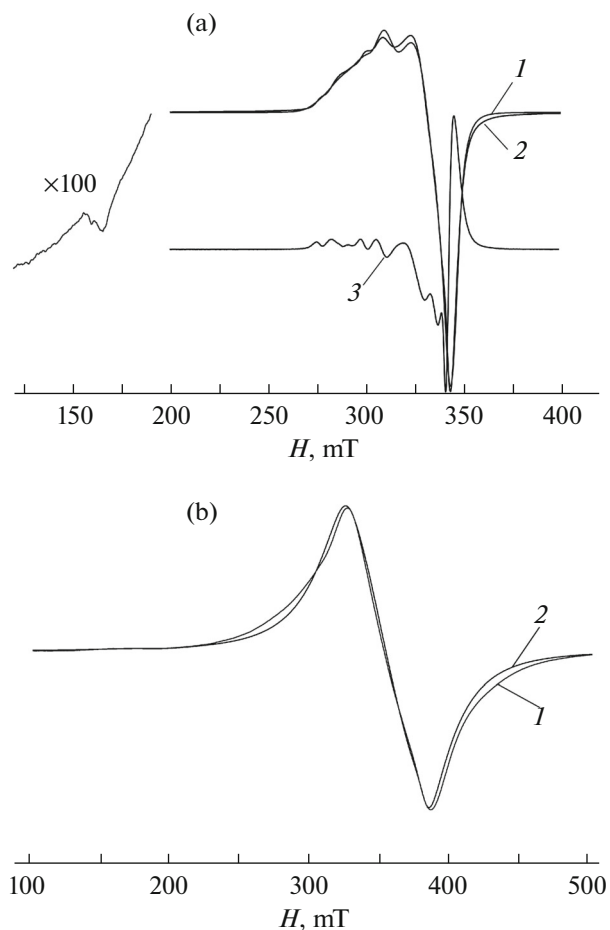


Fig. 7. EPR spectra of Dye3 electrolysis products at $T = 293$ K on (a) the copper and (b) manganese electrodes: (1) experiment, (2) theory, and (3) second derivative spectrum. The Forbidden transition is illustrated at the left of Fig. 7a.

case, dye molecules. The spectrum represents a superposition of the spectra of the mononuclear dye complex with the Cu^{2+} cation (I) and the binuclear associate (II), which is formed by Cu^{2+} metal complexes with dyes and incorporated into the structure of a J-aggregate. The existence of the latter spectrum is indicated by the half-field “forbidden” transition. The spin Hamiltonian parameters are as follows. For the mononuclear dye complex with the Cu^{2+} cation, the concentration $C_I = 0.60$, $g_z = 2.295$, $g_x = 2.079$, $g_y = 2.110$, $A = 4.32 \times 10^{-3} \text{ cm}^{-1}$, $B = 3.22 \times 10^{-3} \text{ cm}^{-1}$, and $C = 3.59 \times 10^{-3} \text{ cm}^{-1}$. For the binuclear associate, the concentration $C_{II} = 0.40$, $g_z = 2.300$, $g_x = 2.074$, $g_y = 2.104$, $A = 4.38 \times 10^{-3} \text{ cm}^{-1}$, $B = 3.38 \times 10^{-3} \text{ cm}^{-1}$, $C = 3.66 \times 10^{-3} \text{ cm}^{-1}$, $D = 1.641 \times 10^{-2} \text{ cm}^{-1}$, $E = 1.916 \times 10^{-2} \text{ cm}^{-1}$, where g_z , g_x , and g_y are the z , x , and y components of the g tensor; A , B , and C are the z , x , and y components of the HFS tensor; and D and E are the components of the fine structure (zero-field splitting and rhombic distortion, respectively) tensor.

The Mn^{2+} ion has a d^5 electron configuration, and the EPR spectrum is characterized by a g tensor of 2.000. The spectrum of the Mn^{2+} metal complex with Dye3 (Fig. 7b) is described by a rhombically distorted spin Hamiltonian with a spin $S = 5/2$ and Zeeman, hyperfine, and fine interactions. The spectrum parameters are as follows: $g_z = 2.00$, $g_x = 2.00$, $g_y = 2.00$, $A = 6.65 \times 10^{-3} \text{ cm}^{-1}$, $B = 3.40 \times 10^{-3} \text{ cm}^{-1}$, $C = 5.43 \times 10^{-3} \text{ cm}^{-1}$, $D = 9.39 \times 10^{-3} \text{ cm}^{-1}$, $E = 2.10 \times 10^{-3} \text{ cm}^{-1}$.

The spin Hamiltonian parameters of the complexes were found using the method of the best fitting between experimental and theoretical spectra by minimizing the error functional

$$F = \sum_i (Y_i^T - Y_i^E)^2 / N,$$

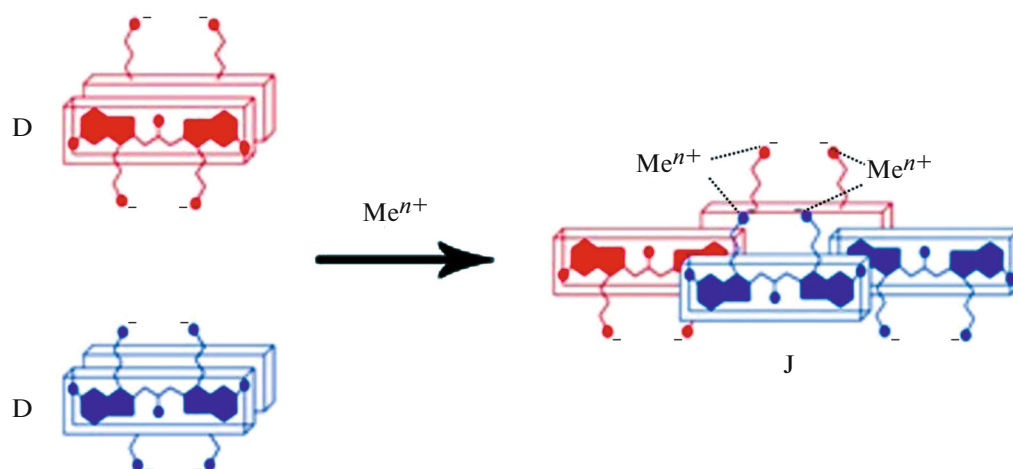


Fig. 8. (Color online) Scheme of the formation of a metal complex J-aggregate.

where Y_i^E is the array of experimental EPR signal intensities with a constant magnetic field step, Y_i^T are their theoretical intensities at the same field values, and N is the number of points. Theoretical spectra were plotted as described in [8]. The sum of Lorentzian and Gaussian functions was used as a line shape function [9]. According to the relaxation theory [10], the width of lines was specified by the expression

$$\Delta H = \alpha + \beta m_i + \gamma m_i^2.$$

Hence, the formed electrolytic coatings really represent metal complexes appearing due to the interaction between dye molecules and Cu^{2+} or Mn^{2+} ions.

Based on the entirety of data obtained in this work, it is possible to firmly conclude that metal complex aggregates of polymethine dyes with anode metal cations are formed on metallic anodes.

It has earlier been mentioned that the formation of metal complex J-aggregates of polymethine dyes occurs by the block mechanism from dimers [7]. The possible mechanism of the formation of metal complex aggregates on the surface of metallic anodes may be schematized, as is shown in Fig. 8. According to this scheme, multicharged cations formed in the oxidation of metallic anodes are coordinated to the sulfo groups of neighboring dye molecules, thus stabilizing the structure of an aggregate consisting of a great number of molecules.

CONCLUSIONS

An electrochemical method for the synthesis of metal complex aggregates of polymethine dyes on the surface of anodes manufactured of metals capable of

electrolytic oxidation has been developed. Dye layers are formed due to the complexation between anionic dyes and anode metal cations. It has been established that metal complex dye J- and H-aggregates are synthesized in this case on the surface of electrodes. It has been concluded that the electrochemical method of the synthesis of polymethine dye aggregates has technological prospects for the creation photosensitive elements in organic nanoelectronics and photonics.

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