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CHEMICAL KINETICS AND CATALYSIS

Kinetics of the Reduction of Cadmium Sulfate by Thiourea Dioxide in an Aqueous Ammonia Solution upon the Metallization of Carbon Fiber

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Abstract—The kinetics of the decomposition of thiourea dioxide and the reduction of cadmium cations by thiourea dioxide in an aqueous ammonia solution are studied. The kinetic parameters of these reactions are calculated using experimental data, allowing us to adjust conditions for the synthesis of cadmium coatings on carbon fiber of grade UKN-M-12K. The presence of the metal crystalline phase on the fiber is confirmed by means of X-ray diffraction, and its amount is measured via atomic absorption spectroscopy.

Keywords: thiourea dioxide, cadmium, carbon fiber, kinetic model, chemical metallization
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INTRODUCTION

The reduction of salts of metals from solutions by chemical reducing agents is one way of preparing dispersions of metals and metal coatings on dielectric materials. Such compounds as hypophosphite, sodium borohydride, sodium dithionite, and rongalite, which allow us to reduce cations of copper, silver, palladium, nickel [1–4], and other metals whose redox potentials are more positive than those of the reducing agents are traditionally used for these purposes. However, the reduction of cadmium cations, the redox potential of which in an aqueous medium is −0.4, cannot be accomplished with any of the above reagents.

Thiourea dioxide (TUDO) in an aqueous solution of ammonia at a concentration of 3 mol/L was used in [5] to synthesize a powder of high-purity metallic cadmium. As is well known, the ammonia complex of cadmium has a redox potential of −0.66 V [6]; i.e., the reduction of its ions is more difficult than that of neat Cd^{2+} ions. However, the increase in the activity of TUDO due to the formation of products of its decomposition (anions of sulfoxylic acid) in this case plays a key role [7]. As was shown in [8–10], the reduction of nickel and palladium ions by thiourea dioxide in an aqueous ammonia solution also proceeds because of the presence of SO_2^{2-} anions.

The aim of this work was to determine the kinetic parameters of the reduction of cadmium cations by thiourea dioxide and identify the stoichiometric mechanism of the reductive action of the latter under conditions of the metallization of carbon fiber (CF).

We initially studied the kinetics of the decomposition of thiourea dioxide in an aqueous ammonia solution to obtain a kinetic description of the reduction of cadmium cations. The conditions for applying cadmium coatings onto carbon fiber were selected on the basis of the resulting kinetic data.

EXPERIMENTAL

Solid thiourea dioxide $(NH_2)_2CSO_2$, synthesized from analytical purity grade thiourea and superior grade mark B hydrogen peroxide according to the procedure in [11], was used in the present work. The content of the main substance in the final product, determined by means of iodometric titration [11], was no less than 96%.

In our experimental studies of the kinetics of the decomposition of TUDO in an aqueous ammonia solution, the reaction mixture was sampled at regular time intervals and analyzed to determine the content of thiourea dioxide via iodometric titration [11].

For our experimental studies of the kinetics of the reduction of cadmium sulfate, aqueous solutions of TUDO and cadmium sulfate (chemically pure grade $3CdSO_4 \cdot 8H_2O$ was used) were prepared and held for 5 min in a thermostat. The solutions were then mixed, and an ammonia solution was added to the mixture.

The reaction mixture was sampled at specific time intervals, and the concentration of cadmium ions was analyzed by means of complexometric titration [12].

Table 1. Calculated rate constants of the decomposition of thiourea dioxide at different temperatures (pH 11.0; *R* is the linear correlation coefficient)

T, K	$k \times 10^2$, min^{-1}	*R*
299	2.0 ± 0.2	0.992
313	2.9 ± 0.2	0.988

High-strength carbon fiber of UKN-M-12K grade (OOO Argon, Balakovo, Saratov oblast) was used in our experiments on metallization. A bundle composed of 12000 elementary fibers (filaments) with diameters of 7 μm was used. Before metallization, each fiber sample was preconditioned according to the method described in [2].

The metallizing solution contained 70 g/L $3CdSO_4 \cdot 8H_2O$, 8.5 g/L thiourea dioxide, and 57 g/L ammonia. The reducing agent was added in the form of an aqueous solution after preliminarily exposing each fiber sample with a weight of 40 mg to a cadmium sulfate ammonia solution at a specified temperature.

The amounts of metallic cadmium deposited on the surfaces of carbon fibers was determined using a Carl Zeiss AAS-3 unit (Jena, Germany) by means of atomic-absorption spectroscopy after dissolving the coatings in aqua regia.

RESULTS AND DISCUSSION

The results from our experiments on the decay of TUDO in an aqueous solution with additions of ammonia, the amount of which ensured a constant pH value of 11, showed that the reaction was of the first order with respect to the TUDO concentration. The semilogarithmic anamorhosis of the kinetic curves obtained at an ammonia concentration of 3 mol/L is described by the linear equations $\ln C_{TUDO} = -2.33-0.038\tau$ with a linear correlation coefficient of 0.997 for $T = 313$ K and $\ln C_{TUDO} = -2.89-0.0199\tau$ with a linear correlation coefficient of 0.998 for $T = 299$ K, where τ is the length of the reaction. The rate constant values, calculated on the basis of experimental data for two temperatures, are given in Table 1. The activation energy calculated using the Arrhenius equation was 19.4 ± 0.1 kJ/mol. A comparison of the calculated rate constants and the literature data [13] shows the values conform with an accuracy of up to one order of magnitude.

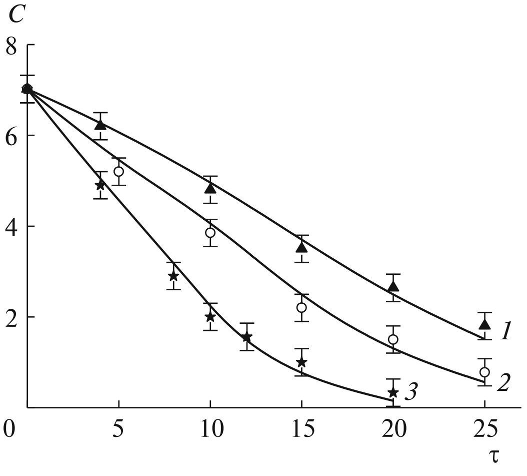

Fig. 1. Dependences of the concentration of cadmium ions (mmol/L) on the reaction time (min) at temperatures of (*1*) 328, (*2*) 338, and (*3*) 343 K; C^0_{TUDO} = 0.059 mol/L and C_{NH_3} = 3.0 mol/L. Lines correspond to theoretical dependences; points to experimental data.

As is known from the literature data, the rate of TUDO decomposition grows along with the pH of an aqueous solution, and a change in the reaction mechanism is observed [11]. Along with the heterolytic decay of TUDO molecules producing sulfoxilate anions HSO_2^- according to the reaction

$$NH_2NHCSO_2^- \rightarrow HSO_2^- + C(NH)_2, \quad (1)$$

homolytic decay with the formation of sulfur- and nitrogen-containing radicals [14] is also possible:

$$NH_2NHCSO_2^- + OH^- \rightarrow NH_2NHCOH^- + SO_2^{\cdot}. \quad (2)$$

The first-order reaction with respect to the TUDO concentration suggests that the step of the decay of its molecules under these conditions is irreversible.

Since sulfoxylate anions are registered directly by the polarography [15], reaction (1) can be considered as the one most plausible. The kinetic dependences of the concentration of cadmium cations on time (points correspond to experimental data) are shown in Fig. 1.

The mechanism of the reduction of cadmium cations in an aqueous ammonia solution can be generally be described schematically:

$$NH_2NHCSO_2^- \xrightarrow{k_1} C(NH)_2 + HSO_2^-, \quad (3)$$

$$HSO_2^- \rightarrow H^+ + SO_2^{2-}, \quad (4)$$

$$Cd(NH_3)_x^{2+} + SO_2^{2-} \xrightarrow{k_2} Cd + SO_2 + xNH_3. \quad (5)$$

Sulfoxylic acid anions are reducing intermediates, since sulfoxylic acid and its anions are fairly stable in an alkaline solution. According to the literature data [16], the rate constant of the decomposition of sulfoxylic acid anions at a temperature of 298 K and a pH of 9.04 is thus 25.2×10^{-4} min^{-1}, and it falls as the pH value rises. The given value is two orders of magnitude lower than the rate constant of the decomposition of TUDO molecules (Table 1), so we did not consider the step of the decay of sulfoxylic acid molecules in determining the rate constant of the reduction of cadmium ions. Deprotonation step (4) proceeds rapidly in an alkaline medium and was also not considered in our calculations.

Table 2. Rate constants of individual steps in the reduction of cadmium ions by thiourea dioxide at different temperatures

Rate constant	328 K	338 K	343 K
$k_1 \times 10^2$, min^{-1}	4.0 ± 0.2	5 ± 0.2	5.5 ± 0.2
k_2, L/(mol min)	3.2 ± 0.1	4.6 ± 0.1	6.6 ± 0.2

$C^0_{\mathrm{TUDO}} = 0.059$ mol/L; $C_{\mathrm{NH_3}} = 3.0$ mol/L.

Table 3. Relative weight of cadmium on carbon fiber under different experimental conditions

T, K	t, min	$m_{\mathrm{Cd}}/m_{\mathrm{CF}}$
297	350	0.036
323	200	0.038
358	100	0.030

t is the length of exposure of CF in a metallizing solution.

Preliminary approximations of the rate constant k_2 of the reduction of complex cadmium cations with sulfoxylic acid anions using Eq. (5) were estimated from the initial parts of the experimental kinetic curves. Rate constants k_1 for different temperatures of the reduction of cadmium ions in an aqueous ammonia solution were calculated with the Arrhenius equation from the activation energy of the step of the decay of thiourea dioxide molecule according to Eq. (1), using the numerical values of the rate constants given in Table 1. To solve the reverse kinetic problem, rate constant values k_1 were not varied and only the optimum constant values k_2 for step (5) corresponding to the reduction of cadmium cations with sulfoxylate anions were sought. The initial concentrations of sulfoxylic acid anions and urea were taken equal to zero.

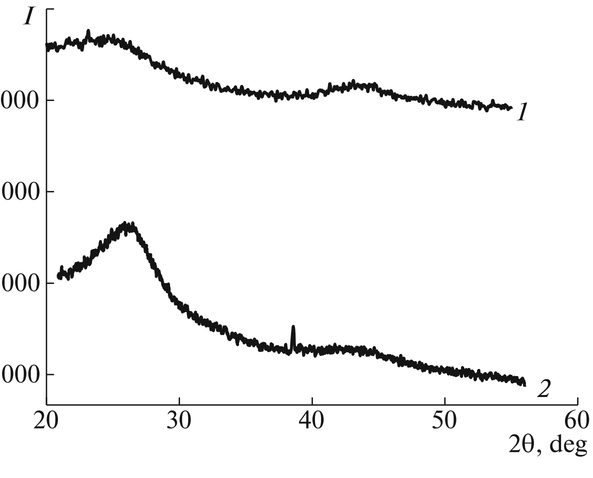

Fig. 2. X-ray difractogram of carbon fiber with (*1*) no c and (*2*) coated with cadmium; *I* is the intensity, and 2θ is the Bragg angle (deg).

The optimum values of the kinetic parameters were found using the WKINET computer program developed at the Faculty of Chemistry of Moscow State University using the Windows platform for numerically simulating the kinetics of complex reactions.

In light of Eqs. (3) and (5), the mathematical model can be described by the differential equations

$$-\frac{dC_{\mathrm{(NH_2)_2CSO_2}}}{d\tau} = k_1 C_{\mathrm{(NH_2)_2CSO_2}}, \tag{6}$$

$$-\frac{dC_{\mathrm{Cd^{2+}}}}{d\tau} = k_2 C_{\mathrm{Cd^{2+}}} C_{\mathrm{SO_2^{2-}}}, \tag{7}$$

$$\frac{dC_{\mathrm{SO_2^{2-}}}}{d\tau} = k_1 C_{\mathrm{(NH_2)_2CSO_2}} - k_2 C_{\mathrm{Cd^{2+}}} C_{\mathrm{SO_2^{2-}}}. \tag{8}$$

The dependences of the concentration of cadmium ions on time for different temperatures are shown in Fig. 1, and the rate constant values for the individual steps of the process are given in Table 2. Absolute values of the error in the rate constant determinations were calculated according to [17].

The activation energy calculated from the temperature dependence of the rate constant k_2 was 46 ± 7 kJ/mol. The good agreement between the experimental and calculated concentrations (Fig. 1) within the error shows that the proposed model of the reduction of cadmium ions by thiourea dioxide adequately describes the experimental data.

Our kinetic data were used to select the conditions for the synthesis of cadmium coatings on carbon fiber. It was found in preliminary experiments that a large part of the metal produced upon the reduction of cadmium cations remains in solution when the reaction is conducted with carbon fiber. The concentration of cadmium sulfate must therefore be increased by 1000% to obtain metallic cadmium directly on CF in amounts sufficient for its identification. At the same time, the concentrations of ammonia and thiourea dioxide are the same as in kinetic experiments. The direct problem is solved to select the length of the exposure of carbon fiber to a metallizing solution; i.e., the kinetic curves are calculated based on the obtained rate constants (Tables 1 and 2) and activation energies.

The experimental conditions and amounts of metallic cadmium produced on carbon fiber per unit weight of CF are given in Table 3. The X-ray difractograms of carbon fiber before and after the deposition of cadmium coating are shown in Fig. 2. The data show that the experimental temperature has a slight effect on the amount of metal, and the reaction can be conducted at room temperature with a sufficiently long exposure time. A signal at a 38° angle of reflection is observed in the X-ray difractogram after metallization; according to the crystallographic database www-mincryst (http://database.iem.ac.ru/mincryst/), this corresponds to a reflection from basal plane (101) of the crystal lattice of cadmium.

CONCLUSIONS

A kinetic model of the reduction of cadmium cations by thiourea dioxide in an aqueous ammonia solution was proposed, and the rate constants and activation energies of the process's steps were calculated. The possibility of synthesizing cadmium coatings on carbon fiber prepared from polyacrylonitrile (PAN) precursor using thiourea dioxide as a reducing agent was demonstrated.

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