SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Effect of Ethanedioic Acid Additives on the Dissolution of Manganese Oxides in Sulfuric Acid Solutions¹

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Abstract—The effect of ethanedioic acid additives on the rate of manganese(IV) oxide dissolution in sulfuric acid solutions was studied by kinetic and electrochemical methods. Interaction modes were established, and some details of the studied process mechanism were elucidated. Interaction schemes corresponding to the observed kinetic dependences were proposed.

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The development of hydrochemical processes for the extraction of metals from oxide and sulfide ores requires the detailed study of mineral dissolution processes [1–11]. In this context, the search for reagents and the determination of kinetic parameters for MnO_2 dissolution processes and details for the mechanism of MnO_2 interaction with reagents are topical [10, 11]. It is of interest to study the kinetic processes of manganese(IV) oxide dissolution in sulfuric acid media with addition of ethanedioic acid as a reducing agent.

The literature data on the kinetic MnO_2 dissolution processes with the use of organic solvents is almost unavailable [6–8, 10]. This work is devoted to studying the MnO_2 dissolution kinetics in sulfuric acid media with addition of ethanedioic acid as a reducing agent by kinetic and electrochemical methods.

EXPERIMENTAL

Sulfuric acid (extra pure grade), ethanedioic acid $(H_2C_2O_4)$ (extra pure grade), and MnO_2 synthesized via the calcination of $Mn(NO_3)_2 \cdot 6H_2O$ in air at 400°C by the method [12] were used as reagents.

Kinetic methods. An experiment was performed in a temperature-controlled reactor at an agitator rotation speed of 700 rpm. The total concentration of manganese(II) ions that had passed into a solution was determined spectrophotometrically with the use of formaldoxime by the method [7, 13].

The dissolution of manganese(IV) oxide was studied in sulfuric acid solutions of ethanedioic acid within the range of 0.01 N $\leq c(H_2C_2O_4) \leq 0.8$ N and 293 K $\leq T \leq 353$ K at $\omega \approx 700$ rpm. The sulfuric acid concentration of 0.2 N was constant in all experiments.

Electrochemical methods of study. Electrochemical experiment was performed in an electrochemical cell on a Pt electrode in a temperature-controlled reactor with sulfuric acid solutions (at specified pH values) on an IPC PRO MF potentiostat at different sweep rates in the potentiodynamic mode.

CALCULATIONS

The obtained kinetic data were presented in the dissolved oxide content (α)-time (τ , min) coordinates, where $\alpha = D_{\tau}/D_{\infty}$ (D_{τ} and D_{∞} are the absorbances of a filtrate solution sample at a time moment τ and after the complete dissolution of an oxide portion (τ_{∞}), respectively) was determined by the spectrophotometric method [7, 13] with the use of formaldoxime. The kinetic parameters of dissolution were calculated by analyzing the obtained data in MathCad 11.0 to determine the dissolution rate (W, min⁻¹) by the equation of heterogeneous reaction kinetics [5, 14] (reversible first-order reaction equation) as

$$\alpha = \alpha_{\infty}(1 - \exp(-W\tau), \qquad (1)$$

where α is the dissolved oxide content, unit fractions, and α_{∞} is the equilibrium content of Mn^{2+} ions in a solution after the maximal dissolution of oxide.

The kinetic models reflecting the effect of the acid concentration (c, N), the temperature (T, K), and the electrochemical potential (E, V) on the dissolution

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Fig. 1. Dissolved MnO₂ content (α) versus time (τ) in a 0.2 N H_2SO_4 solution (353 K, pH 1.5) at $c(H_2C_2O_4)$ of (1) 0.01, (2) 0.015, (3) 0.02, (4) 0.04, (5) 0.06, and (6) 0.08 N. Points are experimental data, and lines are Eq. (1).

rate (W, \min^{-1}) were constructed by means of orthogonal factorial design of experiment: $\ln W$ was taken as a response function, and $\ln c$ and 1/T were used as control factors.

RESULTS AND DISCUSSION

The effect of the ethanedioic acid concentration on the MnO_2 dissolution rate is illustrated in Fig. 1 as an experimental dissolved oxide amount versus time plot.

The experimental data were used to calculate the MnO_2 dissolution rates (*W*) depending on the ethanedioic acid concentration by reversible first-order reaction equation (1) (Table 1).

The plot of the data from Table 1 in the logarithmic coordinates $\log W - \log c(H_2C_2O_4)$ (Fig. 2) has provided the possibility to describe the dissolution process by kinetic model (2), in which the reaction order for oxalate ions was 0.7, namely,

$$\log W = 0.56 + 0.7 \log c (C_2 H_2 O_4).$$
(2)

Table 1. Kinetic characteristics of the dissolution process $(c(H_2SO_4) = 0.2 \text{ mol/L}, \text{pH } 1.50, 353 \text{ K})$

$\frac{c(\mathrm{H}_{2}\mathrm{C}_{2}\mathrm{O}_{4}),}{\mathrm{N}}$	τ _{0.5} , min	W, min ⁻¹	$c(H_2C_2O_4),$ N	τ _{0.5} , min	W, min ⁻¹
0.01	108	0.03	0.04	12	0.09
0.015	30	0.04	0.06	8	0.14
0.02	18	0.05	0.08	5	0.22



Fig. 2. $\log W$ versus $\log c(H_2C_2O_4)$ for the dissolution of MnO₂.

Effect of solution pH. The effect of solution pH $(c(H_2SO_4) = 0.2 \text{ N}, c(H_2C_2O_4) = 0.01 \text{ N})$ on the MnO₂ dissolution process was also studied to determine the species that limits the dissolution rate. The results were shown in Fig. 3 and compared with the distribution diagrams (plotted by the method [15]) for various $H_2C_2O_4$ species at different solution pH values. The maximum dissolution rate (*W*) was found to occur at pH 1.6 \pm 0.2 corresponding to the species $HC_2O_4^-$, which determined the controlling oxide dissolution rate (*W*).

In this case, the dissolution rate W is described by the kinetic model

$$W = W^{0} \frac{[H^{+}]}{[H^{+}] + K_{1}} \frac{[\text{HC}_{2}\text{O}_{4}^{-}]}{[\text{HC}_{2}\text{O}_{4}^{-}] + K_{2}},$$
(3)

where W^0 is the reaction rate constant, min⁻¹, K_1 and K_2 are the adsorption equilibrium constants (for the adsorption of hydrogen ions H⁺ and hydrooxalate ions HC₂O₄⁻ on the surface of MnO₂, $K_1 = 0.02$ and $K_2 = 0.003$), and [H⁺] and [HC₂O₄⁻] are the concentrations of hydrogen and hydrooxalate ions, respectively.

Effect of the temperature. To estimate the character of kinetic or diffusion hindrances occurring in the MnO₂ dissolution process, the study was performed within a temperature range of 293–353 K. It has been established that the oxide dissolution rate (*W*) grows with increasing temperature. It is unreasonable to perform the studies at higher temperatures, as ethanedioic acid decomposes at 373–403 K. The activation energy was calculated by the Arrhenius equation [5, 10, 14, 16]. Based on the obtained experimental data and the analysis of the log*W*–1/*T* dependence, $E_a = 80 \pm 2$ kJ/mol was calculated.



Fig. 3. $\log W$ versus solution pH for the dissolution of MnO₂ in sulfuric acid solutions of H₂C₂O₄ in comparison with the distribution diagram of an aqueous H₂C₂O₄ solution (β is the content of ions in a solution). Points are experimental data log *W*-pH.

From our data it follows that MnO_2 dissolution kinetic model (3) taking into account the temperature has the form

$$W = W^{0} \frac{[H^{+}]}{[H^{+}] + K_{1}} \frac{[\text{HC}_{2}\text{O}_{4}^{-}]}{[\text{HC}_{2}\text{O}_{4}^{-}] + K_{2}} \exp\left(-\frac{E_{a}}{RT}\right), \quad (4)$$

where E_a is the activation energy, kJ/mol, R is the universal gas constant, and T is the temperature, K.

Electrochemical study of the oxidation of ethanedioic acid on a Pt electrode. To confirm the effect of the potential (*E*) on the $H_2C_2O_4$ oxidation rate and clarify the mechanism of the dissolution of manganese oxides in sulfuric acid solutions with ethanedioic acid additives, we studied the electrochemical features of the behavior of $H_2C_2O_4$ in the process of polarization on a Pt electrode.

The results of the experimental study of the anode voltage-current characteristics for the oxidation of ethanedioic acid on a Pt electrode (the dependence of the polarization potential on the $H_2C_2O_4$ concentration at a scanning rate of 0.05 V/s in the background electrolyte with $c(Na_2SO_4) = 0.2 \text{ N}$) are shown in Fig. 4.

The anode current (*I*) was found to increase with increasing $H_2C_2O_4$ concentration. To determine the reaction orders for the anode process, the obtained experimental data were replotted in the coordinates $\log I - \log c(H_2C_2O_4)$ (Fig. 5).

The analysis of the electrochemical oxidation of $H_2C_2O_4$ (Figs. 4 and 5) at solution pH of 6 has allowed us to establish that the process rate passes through a maximum at E = 1.4 V for a normal hydrogen electrode and is characterized by the following parameters (before its maximum):

$$\left(\frac{\partial E}{\partial \log I}\right)_{\text{pH},c(C,O_4^2)} = 0.07 \text{ V},$$
(5)



Fig. 4. Anodic voltage-current characteristics for the oxidation of $H_2C_2O_4$ at different concentrations of (1) 0.0000, (2) 0.0001, (3) 0.0002, (5) 0.0004, (6) 0.0005, (7) 0.0006, (8) 0.0007, (9) 0.0008, (10) 0.0009, and (11) 0.0010 mol/L on a Pt electrode depending on the electrode potential.



Fig. 5. Logarithmic plot of the current $\log I$ versus ethanedioic acid concentration $\log c(H_2C_2O_4)$.

$$\left(\frac{\partial \log I}{\partial \log c(C_2 O_4^{2^-})}\right)_{\text{pH},E} = 0.6 \pm 0.2 \text{ A}.$$
 (6)

The anode current order calculated for $H_2C_2O_4$ from the dependence $\log I - \log c(H_2C_2O_4)$ (Fig. 5) is 0.6 ± 0.2 .

$$\left(\frac{\partial \log I}{\partial pH}\right)_{c(C_2O_4^{2^-}),E} = 0.65 \text{ V } (pH < 2.5), \qquad (7)$$

$$\left(\frac{\partial \log I}{\partial pH}\right)_{c(C_2 O_4^{2^-}),E} = -0.50 \text{ V (pH > 2.5)}.$$
 (8)

Based on the results of experimental studies, it is possible to reveal that the mechanism of the anode oxidation of $HC_2O_4^-$ ions on Pt electrodes corresponds to the following stages:

Stage 1:
$$H_2C_2O_4 - \bar{e} \rightarrow HC_2O_{4,s} + H^+$$
, (9)

Stage 2:
$$HC_2O_{4,s} \rightarrow HCO_{2,s} + CO_2$$
, (10)

Stage 3:
$$HCO_{2,s} - \bar{e} \rightarrow CO_2 + H^+$$
. (11)

The stagewise oxidation of $H_2C_2O_4$ is confirmed by the data of potentiometric measurements (one-electron process) and the results of estimating the slope of the Tafel "overpotential–log *I*" dependence.

From the obtained data it follows that the rate of anodic $H_2C_2O_4$ oxidation on a Pt electrode depending on the stationary potential (E_{st}) is described by electrochemical model (12) coinciding with empirical equation (4)

$$I_{+} = k_{+} \frac{[\mathrm{H}^{+}]}{[\mathrm{H}^{+}] + K_{1}} \frac{[\mathrm{HC}_{2}\mathrm{O}_{4}^{-}]}{[\mathrm{HC}_{2}\mathrm{O}_{4}^{-}] + K_{2}}$$

$$\times \exp\left(-\frac{E_{a}}{RT}\right) \exp\left(\frac{\beta z F E_{\mathrm{st}}}{2RT}\right),$$
(12)

where $\beta z = 0.5$ (β is the transfer coefficient, and z is the number of electrons participating in the reduction of manganese oxide).

Analyzing the effect of different factors on the oxide dissolution rate, we have found that an essential part is played by the potential jump, the concentration of hydrogen ions and hydrooxalate ions of ethanedioic acid, as reflected in Eq. (12). Based on the analysis of the obtained kinetic and electrochemical data on the dissolution processes, kinetic model (13) of the MnO_2 dissolution rate in sulfuric acid solutions of ethanedioic acid has been proposed. It has been revealed that the cathode MnO_2 reduction current will be higher than the dissolution rate is determined by the rate of the transition of ions into a solution instead of the rate of their reduction, i.e.,

$$W = W^{0} \frac{[\mathrm{H}^{+}]}{[\mathrm{H}^{+}] + K_{1}} \frac{[\mathrm{HC}_{2}\mathrm{O}_{4}^{-}]}{[\mathrm{HC}_{2}\mathrm{O}_{4}^{-}] + K_{2}}$$

$$\times \exp\left(-\frac{E_{\mathrm{a}}}{RT}\right) \exp\left(\frac{\beta z F E_{\mathrm{st}}}{2RT}\right).$$
(13)

The proposed equation (13) characterizes the dependence of the dissolution rate on the concentration of hydrogen and hydrooxalate ions, E_{st} , and T, and it agrees with experimental data.

Clarification of the dissolution mechanism. The experimental data obtained in this work allow us to propose the following mechanism of MnO_2 dissolution in sulfuric acid solutions of ethanedioic acid with consideration for the theory of the structure of a double electrical layer [16]. The dissolution process can be described in the form of several intermediate stages

with consideration for the adsorption of $HC_2O_4^-$ ions on active sites as

$$\equiv Mn - OH_{s}^{0} + An^{-} + H^{+}$$

$$\xrightarrow{k_{1}} \equiv MnOH_{2}^{+}...An_{s}^{-} + HC_{2}O_{4}^{-}$$

$$\xrightarrow{k_{2}} \equiv MnOH_{2}^{+}...HC_{2}O_{4,s}^{-} + An^{-}$$

$$\xrightarrow{k_{3}} \text{ dissolution products,}$$

where θ_1 is the unfilled oxide surface degree, θ_2 and θ_3 the degree of oxide surface filling with complexes $\equiv MnOH_2^+...An_s^-$ and $\equiv MnOH_2^+...HC_2O_{4,s}^-$, respectively, and k_1 , k_{-1} , k_2 , k_{-2} , and k_3 are the equilibrium constants of the corresponding reactions.

CONCLUSIONS

The dependences of the MnO_2 dissolution rate on the ethanedioic acid concentration, pH, temperature, electrochemical potential, and process time have been studied. The kinetic model providing the calculation

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of the dissolution rate in the simultaneous presence of these parameters has been derived. The oxide dissolution process occurs in the kinetic modemode. The most probable rate-controlling stage is the diffusion of ions towards the oxide surface.

The kinetic and electrochemical characteristics obtained for the behavior of MnO_2 in sulfuric acid solutions of ethanedioic acid can be used for the optimization of existing technologies and the development of new technologies in hydrometallurgy.

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