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A Study of Mercury Dissolution in Aqueous Solutions of Sodium Hypochlorite

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Abstract—Dissolution of mercury in aqueous solutions of sodium hypochlorite at pH 5.9–8.5, the corresponding reaction order, and the mechanism of this process were studied. The ratio of the rates of mercury oxidation and sodium hypochlorite decomposition was analyzed.

Salts of hypochlorous acid, hypochlorites, find wide application as strong oxidizing agents, their oxidizing power being largely determined by the acidity of the medium.

The aim of this study was to assess the possibility of using a sodium hypochlorite (NaClO) solution at pH 5.9–8.5 for oxidation of mercury and to determine the rate constants of mercury dissolution via its oxidation to Hg^{2+} ions in the above-mentioned acidity range.

EXPERIMENTAL

Mercury was oxidized with an aqueous solution of NaClO at pH 5.9, 6.5, 6.9, and 8.5 and temperatures of 25 and 50°C; the concentration in terms of active chlorine was 0.3–0.8 M. The required acidity was created with a buffer phosphate solution obtained by adding orthophosphoric acid, potassium dihydrophosphate, and sodium hydrophosphate to the NaClO solution. The pH value was monitored with an EV-74 ionometer with glass and silver chloride electrodes.

The NaClO solution was produced by passing chlorine through a carbonate-free solution of sodium hydroxide at a temperature of –5…0°C. The reaction vessel was cooled with a mixture of sodium chloride and ice. Chlorine was obtained by reacting chemically pure hydrochloric acid with potassium permanganate. The concentration of the hypochlorite was determined iodometricaly.

A mercury drop of mass 0.05–0.15 g was placed in a hermetically sealable glass jars thermostated at 25 and 50°C, and 50 ml of a sodium hypochlorite solution with certain acidity was added. The Hg^{2+} concentration was determined at regular intervals of time by a selective spectrophotometric technique with dithizone [1]. The optical density of the solutions was determined with a KFK-2 photoelectric colorimeter.

Mercury is a metal that is liquid at room temperature. The high surface tension allows even comparatively large mercury drops to take the shape of a sphere, the body with the smallest relative surface area. Dissolution of mercury is a heterogeneous process that occurs at the interface and depends on the area and state of the surface. Kinetic characteristics of the process of mercury dissolution in sodium hypochlorite solutions were determined using the formula established experimentally by A.N. Shchukarev for the rate of dissolution of a solid body in a liquid [2, 3]. This formula made it possible to calculate the rate constant k of mercury dissolution:

$$w = kS(c_s - c),$$

where w is the dissolution rate; S, area of contact between the solid and liquid; c, concentration of the substance being dissolved in the bulk of the liquid; c_s, concentration of a saturated solution; and k, constant for the given experimental conditions.

As the concentration of a saturated solution was taken the maximum possible concentration of Hg^{2+} ions. The latter was determined from the mass of the mercury drop and the volume of the hypochlorite solution in which it dissolved. The rate of mercury dissolution was found from the concentration of mercury(II) at certain instants of time. The contact area was calculated from the mass of a spherical drop of mercury and its density [4] at a given temperature.

The order of the dissolution reaction was determined for two mercury drops with different masses by the Van't Hoff formula

$$n = (\log w_1 - \log w_2)/(\log c_1 - \log c_2),$$

which includes reaction rates for two concentrations of the starting substance.

The parameters of the reaction of mercury dissolution at pH 5.9–8.5 are listed in the table. The kinetic curves plotted as the Hg^{2+} concentration c vs. time t (Fig. 1a) and $\log c$ vs. t (Fig. 1b) confirm the first reaction order obtained by calculation, because the time dependence of the concentration of Hg^{2+} ions is exponential, and that of $\log c$, linear (see Fig. 1). The activation energies were calculated using the Arrhenius equation from the dissolution rate constants for 25 and 50°C. The results obtained are listed in the table.

The dissolution of mercury is a heterogeneous process in which a kinetic region, with the process rate determined by the chemical reaction, and a diffusion region, with the process rate determined by diffusion, can be distinguished. As a rule, the reaction occurs in the kinetic mode at low temperatures. As the temperature is raised, the rate constant of the chemical process rapidly increases and, at a certain temperature at which the rate constant of the chemical reaction becomes higher than that of diffusion, the heterogeneous process passes from the kinetic to the diffusion region. It has been noted in the literature [2] that, if the activation energy is 5–20 kJ mol^{-1}, the process can be identified as occurring in the diffusion mode. If the activation energy is 50–200 kJ mol^{-1}, then the heterogeneous process occurs in the kinetic region. In the intermediate region, the rate of the heterogeneous process is determined both by diffusion and by the chemical process at the phase boundary. The calculated activation energies suggest that the dissolution of mercury proceeds in the intermediate region, with its rate determined both by the rate of the chemical reaction and by the diffusion process.

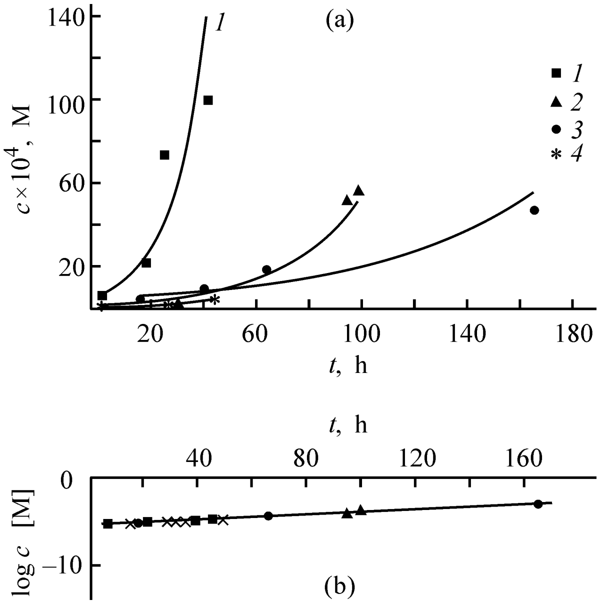

Fig. 1. Kinetic curves of mercury dissolution at 25°C. (c) Concentration of Hg^{2+} ions and (t) time. Variation of the Hg^{2+} concentration at pH: (*1*) 6.5, (*2*) 6.9, (*3*) 5.9, and (*4*) 8.5.

The temperature dependence of the reaction rate is characterized by the temperature coefficient defined as the amount by which the rate increases on raising the temperature by 10°C. The temperature coefficients are 2–4 for the rate of the chemical reaction, $\gamma_{ch} = (k_{ch})_{T+10}/(k_{ch})_T$, and 1.1–1.4 for that of the diffusion process, $\gamma_D = (k_D)_{T+10}/(k_D)_T$, [2]. According to this rule, an increase in the reaction rate by at least a factor of 6 would be observed on raising the temperature by 25°C if the dissolution of mercury preferentially occurred in the kinetic region. However, the reaction rate actually increases by only a factor of 2.6–4, which points to a substantial influence exerted by the diffusion process on the dissolution of mercury. The same is indicated by the temperature coefficients of mercury dissolution, calculated for different pH values. The range pH 6–7 corresponds to the maximum decomposition rate of hypochlorite and, as a result, to a high rate of mercury oxidation by active chlorine evolved in the decomposition. Therefore, the key role in the dissolution process is played in the given case by diffusion. On passing to the alkaline region, the rate of hypochlorite decomposition markedly decreases and the chemical reaction of oxidation starts to exert a noticeable influence on the process at pH 8.5. The observed increase in the dissolution rate on raising the temperature to 50°C is small as compared with that expected. This is probably accounted for by a rise in the instability of the hypochlorite solution with increasing temperature, which is accompanied by a decrease in the concentra-

Parameters of the reaction of mercury dissolution

pH	k, cm^{-1} h^{-1}		γ^*	E, kJ mol^{-1}	Reaction order
	25°C	50°C			
5.90	2.17×10^{-3}	–			1.003
6.50	1.18×10^{-3}	3.65×10^{-2}	1.24	36.15	1.008
6.90	2.07×10^{-2}	5.38×10^{-2}	1.04	30.58	1.010
8.50	6.75×10^{-3}	2.68×10^{-3}	4.00	44.15	–

[*] γ, temperature coefficient of the dissolution process.

tion of active chlorine and the resulting decline in the oxidizing power.

It was established experimentally that the reaction of self-decomposition of hypochlorite occurs at the maximum rate at pH 6 – 8.5 and is first-order with respect to the concentration of hydrogen ions, i.e., the self-decomposition rate changes by a factor of 10 upon a unity change in the pH value. Therefore, the self-decomposition rate increases at pH 6 – 8.5 by several orders of magnitude, to become comparable with the rate of fast reactions [5–7]. The maximum rate of mercury dissolution is observed at pH 6.5– 6.9, which correlates well with published data for the maximum rate of hypochlorite decomposition (pH ~7) [8]. The rate constant of mercury dissolution at pH 5.9 – 8.5 is $(0.2–2.0) \times 10^{-2}$, i.e., the decomposition rate of the hypochlorite is many times that of mercury oxidation. Therefore, in the authors' opinion, use of sodium hypochlorite for oxidation of mercury in this pH range is inadvisable because most part of active chlorine is wasted without having enough time for entering into the reaction.

CONCLUSIONS

(1) The rate constants of mercury dissolution in hypochlorite solutions at pH 5.9 – 8.5 were calculated. It was shown that the maximum rate of mercury dissolution is observed at pH 6.5– 6.9.

(2) It was established that the reaction of mercury dissolution is first-order. The apparent activation energies of 30 – 44 kJ mol^{-1} indicate that the heterogeneous dissolution occurs in the intermediate region, in which both the chemical reaction and diffusion affect this process.

(3) It was found that the rate of mercury oxidation by sodium hypochlorite at pH 5.9–8.5 is considerably lower than the decomposition rate of the hypochlorite itself.

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