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ELECTROLYTIC OXIDATION OF SODIUM THIOSULFATE SOLUTION

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The electrolysis of a sodium thiosulfate solution was done with platinum electrodes. In neutral solution the thiosulfate was first converted into sulfate, sulfite, di-, tri-, and tetrathionates. The sulfite, tri-, and tetrathionates were finally oxidized to sulfate. In alkaline solution sulfite and trithionate formed as intermediates, and were completely oxidized to sulfate.

The electrolytic oxidation of sodium thiosulfate was studied by Thatcher[1,2)] Glasstone and Hickling[3)], and Bancroft[4)] in the 1900-1930's. In these reports, the chemical behavior of low polythionates such as di-, and trithionates was not described. The oxidation reactions of thiosulfate are so complicated due to the formation of several kinds of polythionate as intermediates that the mechanism of the electrolytic oxidation can not be fully discussed without the elucidation of the behavior of the intermediates. The present authors have studied the electrolytic oxidation of sodium thiosulfate solution as one of a series of investigations of the chemical behavior of low valence sulfur compounds.[5)] The oxidation process may be useful for the treatment of a waste water containing thiosulfate and sulfite.

Experimental

Sodium thiosulfate solution(0.1 mol/l) was put into an electrolytic cell of 500 ml and electrolysed at constant current of 1.67-7.50 A/dm^2 by using a Yanagimoto V$_E$-3 controlled potential electrolyser. A standard cylindrical platinum plate with the surface area of 60 cm^2 was used as anode and a spiral platinum wire as cathode.[6)] A Toyo filter paper, No.5C, was employed as a diaphragm. An alkaline sodium thiosulfate solution was made by the addition of sodium hydroxide, the amount of which was six times as much as that of the acid to be produced by the complete oxidation.

The products were analysed by the same method as described in the previous paper.[5)]

Results and Discussion

Some simultaneous and consecutive reactions occured both in neutral and alkaline solutions. The oxidation of sodium thiosulfate in neutral solution took place especially in a complicated manner as shown in Fig.1. The thiosulfate was at first converted into sulfate, sulfite, dithionate, trithionate, and tetrathionate. Then,

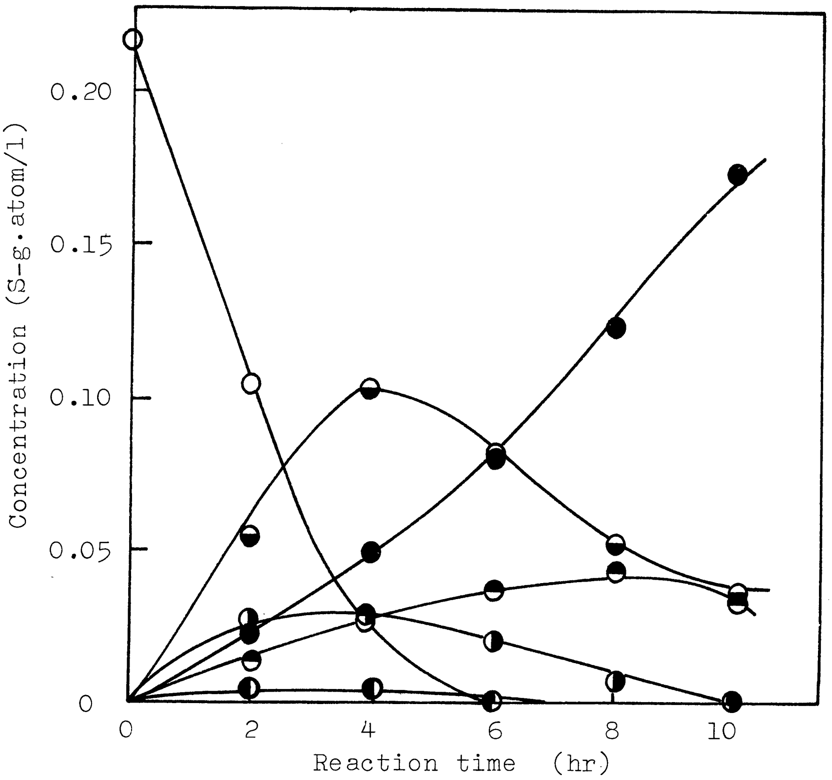

Fig.1. The electrolytic oxidation of sodium thiosulfate in neutral solution
Current density: 1.67 A/dm^2, Voltage: 5.0-6.0 V, Temperature: 16-18 °C
—○— $S_2O_3^{2-}$, —◑— $S_4O_6^{2-}$, —◒— $S_3O_6^{2-}$, —◓— $S_2O_6^{2-}$, —◐— SO_3^{2-}, —●— SO_4^{2-}

the sulfite and polythionates were further oxidized to sulfate leaving dithionate.

The pH of the solution increased first to 12.8, decreased gradually to 12, and then rapidly to 1.5 as shown in Fig.2. This change is explained as follows. At the beginning, the dithionate and polythionates are formed preferentially on the anode, as indicated by Eqs.(3)-(5); hydroxide ions are liberated with evolution of hydrogen gas on the cathode, causing the rise of the pH of the solution. Successively,

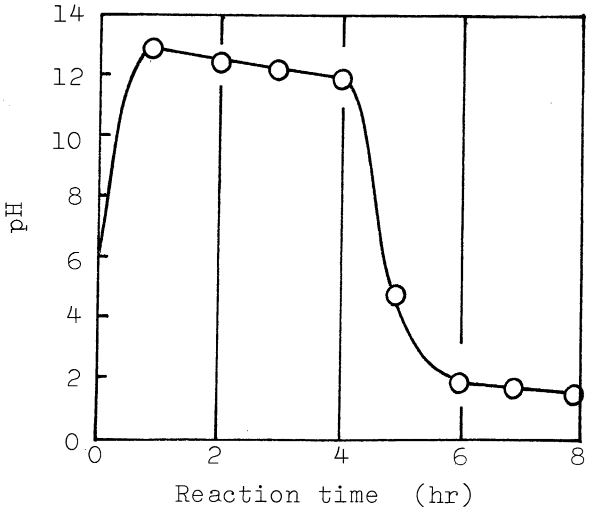

Fig.2. The pH change in the electrolytic oxidation of sodium thiosulfate solution

$$S_2O_3^{2-} + 3H_2O = 2SO_3^{2-} + 6H^+ + 4e \qquad (1)$$

$$SO_3^{2-} + H_2O = SO_4^{2-} + 2H^+ + 2e \qquad (2)$$

$$2SO_3^{2-} = S_2O_6^{2-} + 2e \qquad (3)$$

$$S_2O_3^{2-} + SO_3^{2-} = S_3O_6^{2-} + 2e \qquad (4)$$

$$S_2O_3^{2-} = S_4O_6^{2-} + 2e \qquad (5)$$

$$S_3O_6^{2-} + 6H_2O = 3SO_4^{2-} + 12H^+ + 8e \qquad (6)$$

$$S_4O_6^{2-} + 10H_2O = 4SO_4^{2-} + 20H^+ + 14e \qquad (7)$$

the oxidation of the polythionates occurs resulting in the formation of a large amount of hydrogen ions as Eqs.(6) and (7) indicate.

In alkaline solution, sulfite and trithionate were formed as intermediate, and were then completely oxidized to sulfate as shown in Fig.3. Dithionate and tetrathionate were not detected different from the test in neutral solution. Further, the concentration of trithionate was lower than in neutral solution. The oxidation rate of sodium thiosulfate was lower in alkaline solution than in neutral solution. This may be ascribed to the following two reasons: (1) The current efficiency decreases due to the oxygen evolution, the potential of which is lower in alkaline side. (2) The effective conversion of thiosulfate to sulfate in neutral solution

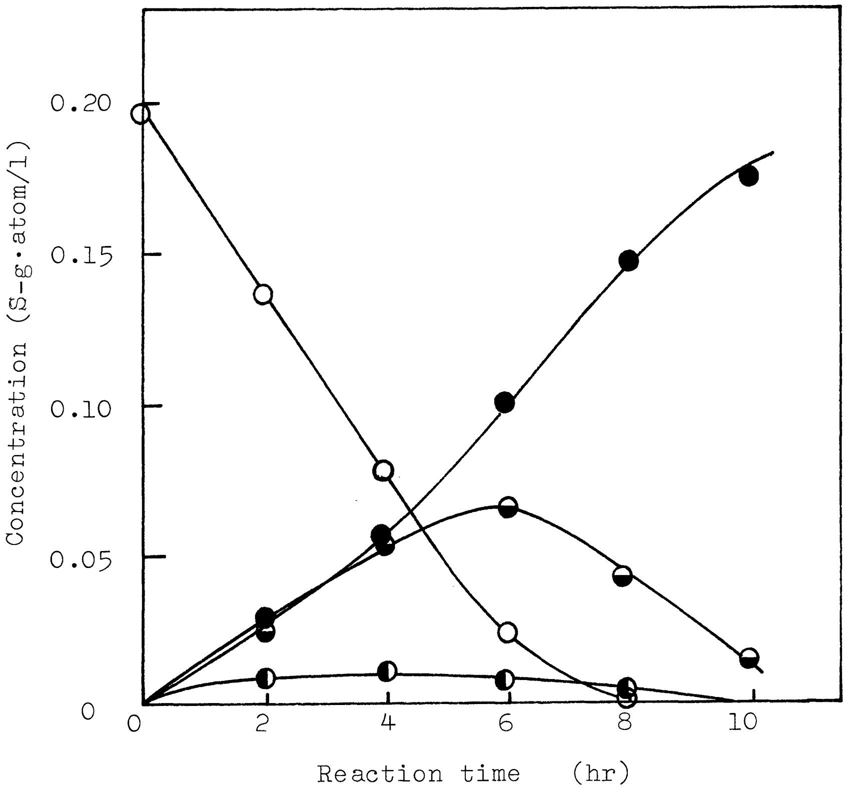

Fig.3. The electrolytic oxidation of sodium thiosulfate in alkaline solution Current density· 1.67 A/dm^2, Volatge: 4.5-5.0 V, Temperature 16-18 °C

—○— $S_2O_3^{2-}$, —◒— $S_3O_6^{2-}$, —◐— SO_3^{2-}, —●— SO_4^{2-}

due to the low concentration of polythionate. It was confirmed by other test that dithionate is stable in the electrolytic oxidation and even in the ozone oxidation, but in oxidizing thiosulfate, the concentration of dithionate tends to decrease after reaching its maximum as shown in Fig.1. The behavior of dithionate must be investigated in more detail to elucidate the mechanism of the electrolytic oxidation of thiosulfate. The electrolytic oxidations of thiosulfate, tri- and tetrathionate solution at constant potential are now under investigation.

Although the initial current efficiency was a little lower in alkaline solution than in neutral solution, the electrolytic oxidation in alkaline solution would be useful in waste water treatment because the complete oxidation of thiosulfate to sulfate can be reached. The dependency of current efficiency on current density is shown in Table 1. The lower the current density, the higher the current efficiency.

Table 1 The dependency of current efficiency on current density

Voltage (V)	4.5-5.0	4.5-5.5	5.5-6.5	6.0-7.0	7.0-10.0	8.0-10.5
Current density (A/dm^2)	1.67	2.50	3.33	5.01	6.67	7.50
Temperature (°C)	16-18	16-21	16-26	16-30	16-55	16-62
Current efficiency (%)	91	88	86	81	68	62
Electrolysis time (hr)	10	7.5	6.0	4.5	4.0	3.0

The density of 3 to 5 A/dm^2 may be applicable to a practical operation. At the current densities of 6.67 and 7.50 A/dm^2, the electrolysis of water took place rapidly, and the temperature of the solution rised to 55 and 62 °c respectively. The platinum electrode was slightly corroded at the density of 7.50 A/dm^2.

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