[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, UNIVERSITY OF MINNESOTA]

The Reduction of Sulfurous Acid (Sulfur Dioxide) at the Dropping Mercury Electrode

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In agreement with Gossman[2] the authors did not find reduction waves at the dropping mercury electrode with neutral or alkaline sulfite solutions, but well-defined waves were observed in acid medium. At *p*H values between 0 and 2 Gossman found a change of the reduction potential (45° tangent method) of 0.056/v. with a tenfold change of the total sulfur dioxide (dehydrated, hydrated and ionized) concentration and a change of 0.112/v. per unit change of *p*H at constant sulfur dioxide concentration. Referring to the electrochemical work of Roscoe and Jellinek,[3] Gossman postulates that sulfur dioxide in acid medium at the dropping electrode is reduced to hydrosulfurous acid.

$$2SO_2 + 2e \longrightarrow S_2O_4^{=}$$

In explaining the effect of *p*H upon the reduction potential he assumes that the reduction is accomplished by atomic hydrogen which is formed at the surface of the electrode. However, this assumption does not explain the fact that the potential changes by $2RT/F$ instead of RT/F with a unit change of the *p*H, because we would not have to consider the overpotential of hydrogen in this case. Gossman also assumes that sulfur dioxide or(and) sulfurous acid molecules are reducible and that the ions are not reducible. Working with unbuffered solutions of sodium sulfite and hydrochloric acid Gossman noticed two small waves at low acidities. The first wave is attributed by him to a reduction to hydrosulfite ions. According to Gossman the latter are not stable and decompose according to the equation

$$S_2O_4^{=} \longrightarrow SO_2^{=} + SO_2$$

The sulfur dioxide thus formed is then reduced to the sulfoxylate ion which occurs on the second wave. Gossman assumes that in more acid medium the hydrosulfurous acid is stable and that, therefore, in such a medium only one wave is found. This interpretation does not seem plausible and is not substantiated by our work. We have investigated the reduction of sulfurous acid in its various forms in buffer solutions of known *p*H. Quite generally, we could not confirm Gossman's conclusions.

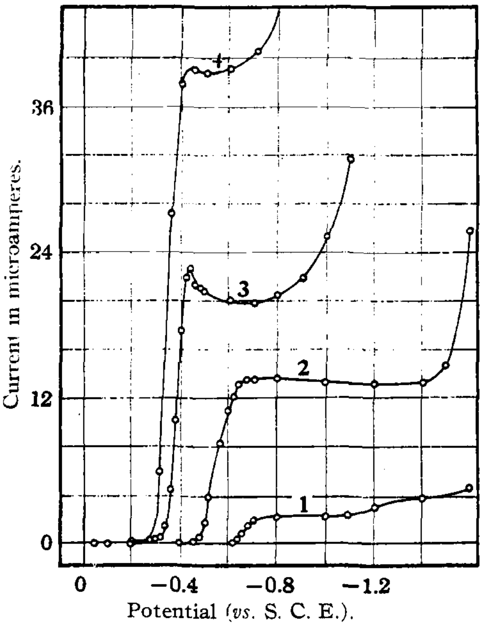

Fig. 1.—Sulfite waves at various *p*H: Curve 1, phosphate buffer, *p*H 6.0, Na_2SO_3 1.93 × 10^{-3} *M;* Curve 2, acetate buffer, *p*H 3.6, Na_2SO_3 1.98 × 10^{-3} *M;* Curve 3, HNO_3 0.1 *M*, *p*H 1, Na_2SO_3 1.54 × 10^{-3} *M;* Curve 4, HNO_3 1.0 *M*, *p*H 0, Na_2SO_3 2.75 × 10^{-3} *M*.

Experimental

The current–voltage curves were determined at 25.00 ± 0.05° in a thermostat using the manual apparatus.[4] After the measurements had been made in air-free solutions the total sulfite concentration was determined by pipetting 25 to 50-ml. volumes into an excess of standard iodine solutions and back-titrating with standard thiosulfate solution.

From Fig. 1 it is evident that keeping the total sulfite concentration constant, the diffusion currents increase with decreasing *p*H. At a *p*H of 6 two small waves were noticed but in buffer solutions with a *p*H of 3.6 or smaller only one wave was found. Figure 2 shows the two waves at a *p*H of 6 at different sulfite concentrations. Neither the first nor the second diffusion currents were found to be proportional to the concentration, their increase being less than linear with the concentration. In biphthalate buffer solutions with a *p*H of 3 only one wave was found. Although the diffusion current was markedly less than that at the same sulfite concentrations at *p*H values of 1 to 0, this diffusion current was found to be roughly proportional to the total sulfite concentration as shown in Fig. 3. In

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[1] From a thesis submitted by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the Doctor's degree (1940).

[2] B. Gossman, *Coll. Czechoslov. Chem. Commun.*, **2**, 185 (1930).

[3] H. Roscoe and K. Jellinek, *Z. Elektrochem.*, **10**, 266 (1903).

[4] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).

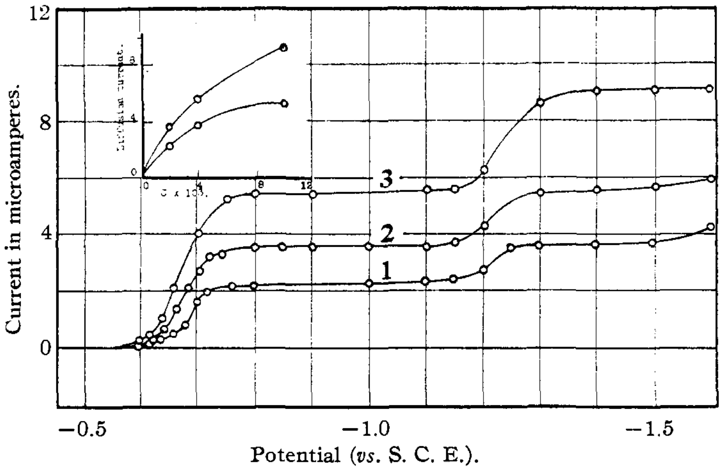

Fig. 2.—Sulfite waves in phosphate buffer of pH 6.0: KNO_3 0.1 N, buffer 0.05 M; Curve 1, Na_2SO_3 0.002 M; Curve 2, Na_2SO_3 0.004 M; Curve 3, Na_2SO_3 0.01 M.

0.1 N nitric acid the diffusion current was found to be strictly proportional to the concentration (see Fig. 4), and it remained practically constant when the acid concentration was increased to normal. The figures have been plotted without correcting for the iR drop. In the 0.1 N nitric acid solution the resistance was 1200 ohms.

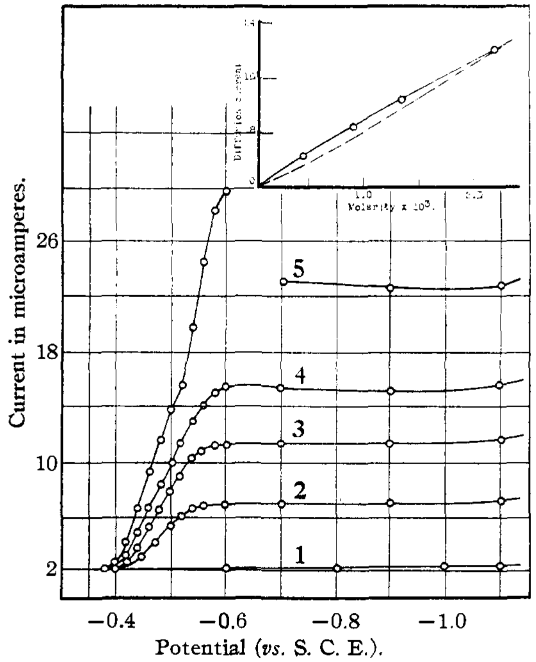

Fig. 3.—Sulfite waves in buffer of pH 3.0: (1) no sulfite; (2) 4.5 × 10^{-4} M sulfite; (3) 8.9 × 10^{-4} M sulfite; (4) 1.33 × 10^{-3} M sulfite; (5) 2.17 × 10^{-3} M sulfite.

Discussion

(1) In strongly acid medium (pH 1 to 0) all of the sulfur dioxide (in its various forms) is reduced when the diffusion current is reached. With the aid of the Ilkovic equation[5] the diffusion coefficient of sulfur dioxide was calculated assuming an electron transfer of one and of two per molecule. Assuming with Gossman an electron transfer of one, a diffusion coefficient at 25° of 8.2 × 10^{-5} cm.^{2}sec.$^{-1}$ is calculated, while a value of 2.04 × 10^{-5} cm.^{2}sec.$^{-1}$ is calculated for an electron transfer of two. In a previous paper[6] we calculated a diffusion coefficient of oxygen dissolved in water of 2.6 × 10^{-5} cm.^{2}sec.$^{-1}$ at 25°. Since the latter may be expected to be of the same order of magnitude as that of sulfur dioxide, it is quite evident that the reduction of sulfur dioxide in acid medium involves two electrons per molecule. Therefore, the net reaction in acid medium may be represented by the equation

$$SO_2 + 2H^+ + 2e \longrightarrow H_2SO_2 \quad (1)$$

or

$$H_2SO_3 + 2H^+ + 2e \longrightarrow H_2SO_2 + H_2O \quad (1a)$$

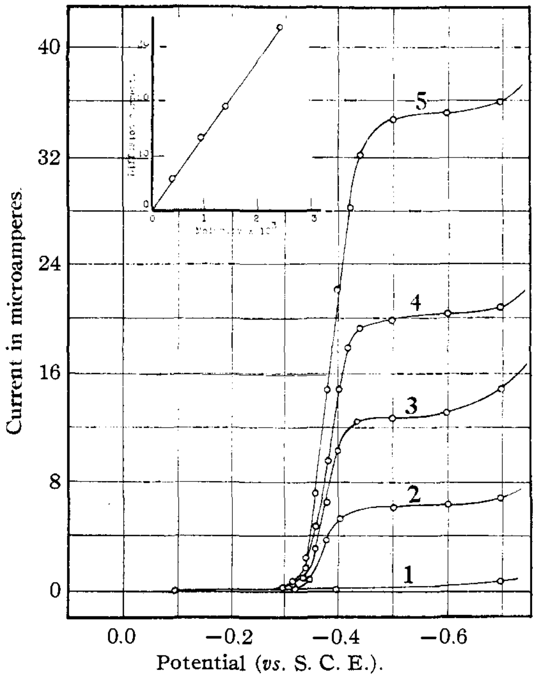

Fig. 4.—Sulfite waves in 0.092 N nitric acid: Curve 1 is the residual current; sodium sulfite concentration in curve (2) 4.85 × 10^{-4} M; (3) 8.6 × 10^{-4} M; (4) 7.43 × 10^{-3} M; (5) 2.33 × 10^{-3} M.

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[5] D. Ilkovic, *Coll. Czechoslov. Chem. Commun.*, **6**, 498 (1934); see also ref. 4.

[6] I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 1013 (1941).

If this reaction were reversible the potential π would be determined by the expression

$$\pi = \text{Const.} + \frac{RT}{2F} \ln \frac{[SO_2]_0[H^+]_0^2}{[H_2SO_2]_0} \qquad (2)$$

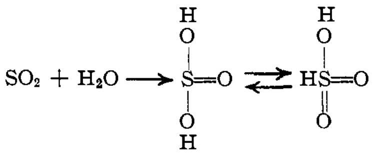
in which the subscript zero denotes the concentration at the surface of the electrode. Introducing the relations between the concentrations and current (see ref. 4) the equation of the polarographic wave at constant *p*H is given by

$$\pi = \pi_{1/2} + \frac{RT}{2F} \ln \frac{(i_d - i)}{i} \qquad (3)$$

A plot of the values of log $(i_d - i)/i$ *versus* the potential of the curves given in Fig. 4 after correction for the iR drop actually yielded a straight line with the theoretical slope of 0.030. Moreover, the half wave potential $\pi_{1/2}$ at a constant *p*H should be constant and independent of the sulfur dioxide concentration. This was found to be true in 0.1 *N* nitric acid, a value of $\pi_{1/2}$ of -0.37 v. (*vs.* S. C. E.) being found. The relation between $\pi_{1/2}$ and the *p*H is more involved than that indicated by equation (2), due to the changing degrees of dissociation of sulfurous and sulfoxylic acids with the *p*H. It should be pointed out that the agreement found between the experimental data and those calculated on the basis of equation (3) does not prove conclusively that reactions (1) or (1a) are reversible. It is even possible that intermediately other reduction products are formed.

(2) An explanation is in order for the fact that, keeping the total sulfite concentration constant, the diffusion current decreases with increasing *p*H. Gossman[2] assumes that H_2SO_3 is reduced and that the establishment of the equilibrium $H^+ + HSO_3^- \rightleftarrows H_2SO_3$ is relatively slow. Since, in the electrodeposition of hydrogen at the dropping electrode from solutions of weak acids, attainment of dissociation equilibrium is found to be faster than the speed of electroreduction, Gossman's explanation is not plausible. Assuming that H_2SO_3 is the reducible form we have to consider that this acid in some respects has similar properties to phosphorous and nitrous acids.[7] These acids exist in different tautomeric forms.

Assuming a similar equilibrium in solutions of sulfurous acid we have

 (4)

$$SO_2 + H_2O \longrightarrow \underset{\text{I}}{HO{-}\overset{}{S}(=O){-}OH} \rightleftarrows \underset{\text{II}}{HO{-}HS(=O)=O} \qquad (4)$$

Form I is the weaker acid of the two and is reducible, while the stronger acid form II with the hydrogen attached to the central atom is oxidizable. It is well known that sulfurous acid can act both as an oxidizing (I) and a reducing (II) agent. At an intermediate *p*H, say of 3, most of form II may be present in the ionized form and that of I in the un-ionized form. Hence, at such a *p*H only a small fraction of the total sulfur dioxide may be present as form I and the greatest part as form II (dissociated and undissociated). With decreasing *p*H the fraction present as form I increases and depending upon the equilibrium constant giving the ratio between I and II and the hydration constant of sulfur dioxide, most of the latter may be found in the form of I in strongly acid medium. If form I (ionized and un-ionized) is reducible at the dropping electrode and the speed of transformation of II into I is relatively small, it is evident that the height of the wave should become independent of the *p*H, unless the dehydration of sulfurous acid to sulfur dioxide is acid catalyzed.

(3) The occurrence of the two small waves at *p*H of 6 remains to be interpreted. From the literature[8] it is evident that the mechanism of the electro-reduction of sulfurous acid at various *p*H values is quite involved. Under certain conditions hydrosulfurous acid may be formed

$$HSO_3^- + 2H^+ + e \longrightarrow HSO_2 + H_2O \qquad (5)$$
$$2HSO_2 \longrightarrow H_2S_2O_4 \longrightarrow 2H^+ + S_2O_4^= \qquad (6)$$

The first small wave at a *p*H of 6 may correspond to a reduction to hydrosulfite. The hydrosulfite ion can be further reduced according to the equation

$$S_2O_4^= + 2H^+ + 2e \longrightarrow S_2O_3^= + H_2O \qquad (7)$$

This reduction may occur on the second wave at a *p*H of 6 (Fig. 2) with a half wave potential of -1.23 v. (*vs.* S. C. E.). The hydrosulfurous acid is not stable and decomposes

$$2H_2S_2O_4 + H_2O \longrightarrow H_2S_2O_5 + 2H_2SO_2 \qquad (8)$$

Apparently, a slow decomposition of the hydrosulfite formed on the first wave occurs already at a

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[7] See *e. g.*, J. H. Hildebrand, "Principles of Chemistry," The Macmillan Company, New York, N. Y., 1929.

[8] See J. W. Mellor, "Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green and Co., New York, N. Y., 1932, pp. 186 ff.

*p*H of 6, explaining why the height of the second wave is distinctly smaller than that of the first one. The rate of decomposition of hydrosulfurous acid increases with increasing hydrogen ion concentration, and also the $H_2S_2O_5$ formed (equation 8) decomposes with the formation of H_2SO_3

$$H_2S_2O_5 + H_2O \longrightarrow 2H_2SO_3 \qquad (9)$$

Therefore, the second wave disappears as the acidity increases. At *p*H values smaller than about 4 only one wave is found and the net reaction corresponds to a reduction to sulfoxylic acid (equations 5, 6, 8 and 9).

A polarographic investigation of various thionic acids at different acidities is planned in order to study the various involved reactions more in detail.

Summary

1. Sulfur dioxide in aqueous solutions can be determined polarographically in 0.1 to 1 *N* solutions of strong acids. The diffusion current is found proportional to the total sulfur dioxide concentration. The following reaction accounts quantitatively for the reduction: $SO_2 + 2H^+ + 2e \longrightarrow H_2SO_2$.

2. The diffusion coefficient of sulfur dioxide in aqueous medium was calculated to be 2.04×10^{-5} cm.,^{2} sec.$^{-1}$ at 25°.

3. Keeping the total sulfite concentration constant, the diffusion current decreases markedly when the *p*H becomes greater than 2. At a *p*H of 7 or greater than 7 no wave is found. This behavior is attributed to the facts that sulfurous acid exists in two tautomeric forms one of which is reducible, and that the speed of transformation of the oxidizible, strongly-acid form to the reducible, weakly-acid form is relatively small.

4. At a *p*H of 6 two small waves were found, the first one corresponding to a reduction to hydrosulfite, and the second to a reduction of the latter to thiosulfate.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 13, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Lead Amalgam–Lead Fluoride Electrode and Thermodynamic Properties of Aqueous Sodium Fluoride Solutions

BY REGINALD WILLIAM IVETT[1] AND THOMAS DE VRIES

The only use which has been made of electrodes whose reactions involve fluoride ions has been by Jahn-Held and Jellinek,[2] who measured the e. m. f. of the cells

Pb(5% amalgam), PbF_2 | HF(0.1 *N*) || KCl satd. || HF(1.0 *N*) | MF_2, M,

where M indicates copper, cadmium or zinc, as amalgams, or cobalt or nickel, as the powdered metal. They also measured the e. m. f. of the cell Pb(5% amalgam), PbF_2 | HF(1.0 *N*), H_2, Pt.

In this investigation further study was made of the reproducibility of the lead amalgam–lead fluoride electrode, using the cell Na(amalgam) | NaF(*m*) | PbF_2, Pb(amalgam). The free energy, heat content and entropy changes of the cell reaction, and the activity coefficients of the sodium fluoride were calculated from the e. m. f. measurements at 15, 25 and 35°, using 0.1 to 0.9 molal solutions. A saturated solution of sodium fluoride is 0.983*m* at 25°.

Materials

Sodium Amalgam.—Sodium amalgam was prepared by the electrolysis of a sodium carbonate solution using purified mercury as the cathode and a platinum foil as the anode. The sodium carbonate was recrystallized four times from conductivity water. The amalgam was washed repeatedly with water, then with acetone, and filtered through a small capillary into a flask filled with nitrogen.

Lead Amalgam.—Lead amalgam was prepared by using purified mercury as a cathode in a solution of Baker and Adamson reagent lead nitrate. The anode was a platinum foil in a solution of 1 *N* nitric acid, the two solutions being connected by means of an inverted glass U-tube filled with 1 *N* nitric acid. A current of about 0.2 ampere was passed until the concentration of the lead in the amalgam was about 5%. It was washed repeatedly with water, then with acetone, heated to 100° and filtered while hot through a small capillary into a container filled with nitrogen. A 5% amalgam consists of two phases at the highest temperature at which measurements were made, but can be changed to one phase by heating it to 100°.

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[1] Present address: Hercules Experiment Station, Wilmington, Del. This paper is an abstract of a thesis submitted by R. W. Ivett in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Jahn-Held and Jellinek, *Z. Elektrochem.*, **42**, 401 (1936).