Removal of Dissolved Oxygen by Sodium Sulfite. Application to the Polarographic Study

By Shinichi KIKUCHI, Kenichi HONDA and Seckchill KIM

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As is well known, in most cases of the polarographic study, the dissolved oxygen in the test solution must be removed before measuring because of its own waves which interfere with that of the substance being determined. Usually inactive gases as hydrogen or nitrogen are bubbled through the test solution for that purpose. But this is a rather time-consuming and elaborate procedure and as a result it influences the speed and efficiency of the determination. Against this physical method, the chemical method that is to adsorb the dissolved oxygen by the reducing agent, sodium sulfite, was reported by E. Varasova[1] and also was recommended by Heyrovsky[2] and Hohn[3]. Though this method seems rather simple if adequately effective, the quantitative investigation for the efficiency of sodium sulfite is not yet reported.

So there is little knowledge in the literature of the subject for the use of sodium sulfite. Of course, considering the change of the constitution of the solution which may affect the wave form of the substance being determined, its volume of addition should be as little as possible, providing it adsorbs the dissolved oxygen effectively.

From this standpoint, the effect of sodium sulfite upon the oxygen wave and its relation to the time after adding it to the test solutions were investigated. Effect to the *p*H, effect to the wave-height of the substance to be determined and effective *p*H range are also reported here.

Experimental

The concentration of dissolved oxygen was determined polarographically in the solutions of various kinds of supporting electrolyte, such as Sörensen's phosphate, glycocol–NaOH and borate-NaOH buffer solutions, 0.1M LiCl, KCl and NaOH solutions, their mixture with methanol and so on. All those solutions were made up from the reagents of "guaranteed" grade. To obtain the desired concentration of sodium sulfite, one of the freshly prepared 10, 5 and 1% solutions of it was added to the test solution. Gelatine was not used. Electrolysis was carried out in an open cell with the saturated calomel reference electrode on a liquid paraffine bath thermostatted at 25±0.1 °C. Polarographic apparatus used here was the d.c. amplification system recording polarograph which was constructed in this laboratory[4]. The capillary characteristics were 0.96 $mg^{2/3}$ $sec.^{-1/2}$ as $m^{2/3}$ $t^{1/6}$ in 0.1M KCl with no applied potential.

Results and Discussions

In order to show the concentration of dissolved oxygen, its wave-height is adopted. This is done because the object of the present study is not the direct determination of the dissolved oxygen; moreover the relative variation of dissolved oxygen corresponding to the volume of added sodium sulfite is more important. The wave-height is measured at the point of −0.5 V. vs. S.C.E. where it is accepted that there is the linear relation between the concentration and the wave-height[5].

(A) Effect in Neutral and Alkaline Solutions.

Concentration∼time relations are shown in Figs. 1∼7; solutions of each figure are 0.1M LiCl, KCl, phosphate buffer of *p*H 8.6, borate-NaOH buffer of *p*H 9.4.10,9,12.2 and 0.1N NaOH respectively. Each curve in the

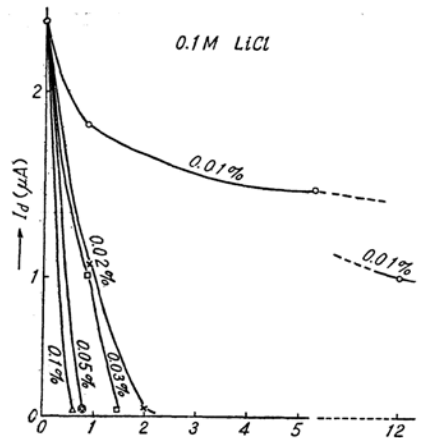

Fig. 1.

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[1] E. Varasova, *Collection Czech. Chem. Comms.*, **2**, 8 (1930).

[2] J. Heyrovsky "Polarographisches Praktikum", Springer-Verlag, Berlin, 1948, S. 55.

[3] H. Hohn, "Chemische Analysen mit dem Polarographen", Springer-Verlag, Berlin, 1937, S. 44.

[4] S. Kikuchi, Y. Sakaguchi and K. Honda, This Bulletin, **25**, 98 (1952).

[5] G. A. Marsh, *Anal. Chem.*, **23**, 1427 (1950).

figures represents the wave-height decrease with the time lapse after the addition of sodium sulfite; the value in percentage beside the curve shows its concentration. The wave-height at the point of time 0 indicates that of dissolved oxygen in blank solution.

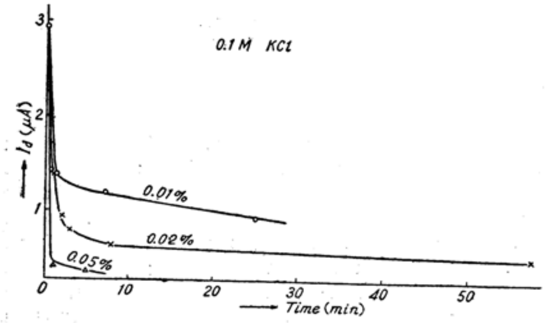

Fig. 2.

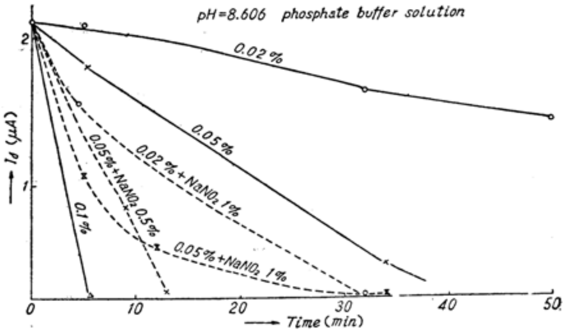

Fig. 3.

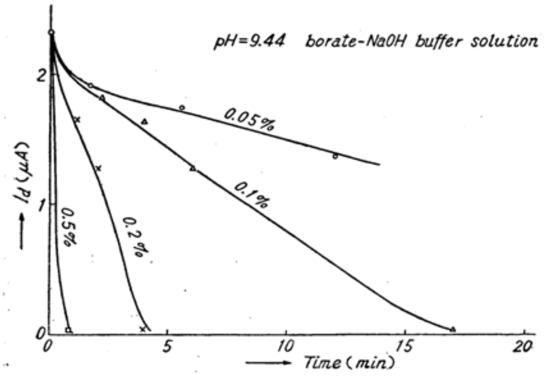

Fig. 4.

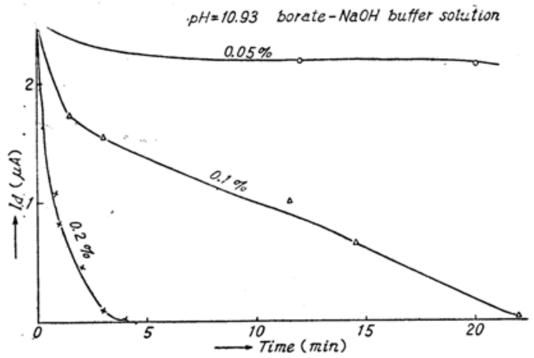

Fig. 5.

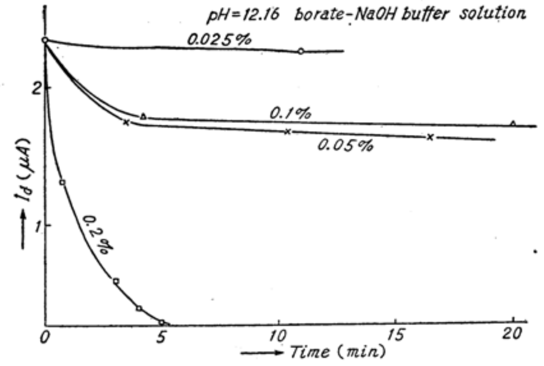

Fig. 6.

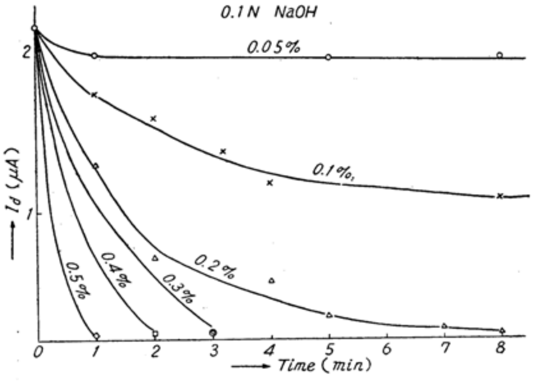

Fig. 7.

Of course, the necessary degree of removal of dissolved oxygen depends upon the magnitude of the wave to be interfered with, so minimum but adequate concentration of sodium sulfite can be determined from the figures according to the individual case. But from the practical standpoint, supposing that it is necessary that the height of the oxygen wave should decrease about one-fiftieth of ts original height within 5 minutes, the minimum concentration of sodium sulfite are as follows;

0.02% in 0.1M LiCl
0.05 ” 0.1M KCl
0.1 ” pH 8.6 buffer
0.2 ” pH 9.4 buffer
0.2 ” pH 10.9 buffer
0.2 ” pH 12.2 buffer
0.3 ” 0.1N NaOH

From the figures and values above, it is found that the reducing power of sodium sulfite is most efficient in a neutral solution and becomes less effective towards the alkaline side. The reducing reaction proceeds quickly in the first five minutes and after that proceeds more slowly.

(B) **Influence of Positive and Negative Catalyzer upon the Reducing Power of Sodium Sulfite.**

As to the reaction between oxygen and sodium sulfite, several positive and negative catalysts are described in the literature of the subject⁶⁾. Alcohol, glycocol, aldehyde, etc. which are often encountered in organic polarography are known as negative catalyzers. In the solutions which contain the substances mentioned above, the efficiency of of sodium sulfite is markedly diminished. Those appearances are shown in Figs. 8, 9 and 10, in which the constitutions of the solutions are glycocol-NaOH buffer of *p*H 19.0, 0.1M KCl-methanol (volume ratio 1:1) and phosphate buffer of *p*H 8, 6-methanol (9:1) respectively.

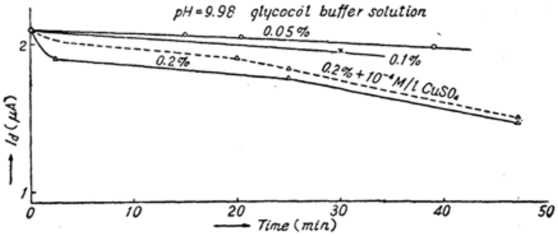

Fig. 8.

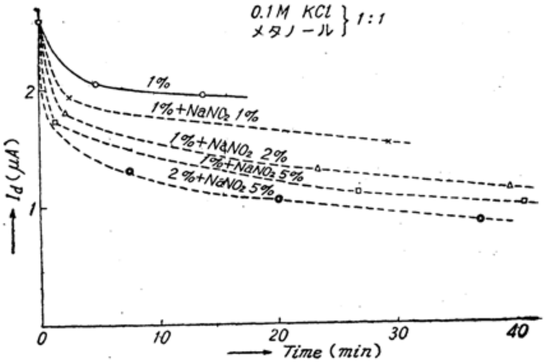

Fig. 9.

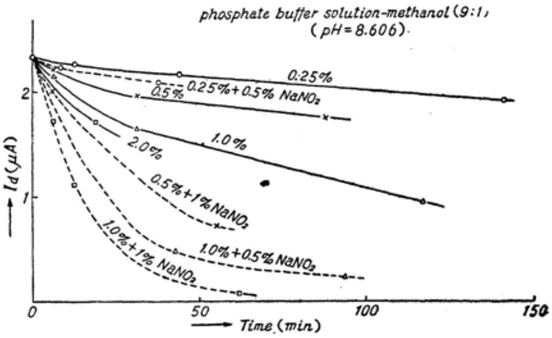

Fig. 10.

As shown in accompanying figures, the addition of sodium sulfite even up 0.2∼2% is not yet sufficient and it seems unsuitable for the practical use for it may cause some important change of the constitution of the solution. To supplement this deficiency, some positive catalysts are tested. As a matter of course, it is demanded that the catalysts itself produces no reducing waves polarographically. Nevertheless, cupric sulphate is first selected, because in spite of having a well-defined wave of cupric copper, it appears at comparatively noble potential and so it seems less likely to interfere with other waves, if used in a very dilute state. Its behavior is shown as a dotted line in Fig. 8. As shown, the addition in such a concentration of 10^{-4} M/l. does not bring any effective result. But it is assumed that in the case of determination of copper the effect of sodium sulfite would be accelerated. Secondly sodium nitrite which generally is not reduced at dropping mercury electrode before the discharge of sodium ion provided that there are no polyvalent cations such as La^{+++} and Ca^{++}, is tested. Its behavior is shown as the dotted lines in Figs. 3, 9 and 10. In Fig. 3, in the phosphate buffer solution, the addition of 0.5∼1% nitrite increased the removing effect somewhat more than threefold, but when the methanol content is half the volume as in Fig. 9, its effect is not so pronounced and the addition of 5% increases the power of sodium sulfite about twofold. In Fig. 10 when methanol is 10%, its catalytic effect is promoted more than before. 1% addition of nitrite promotes the reaction more than twofold.

In conclusion, when a hindering substance is contained, it is possible to remove oxygen by the addition of a promoting reagent, but from the fact of its being time-consuming, its utility still remains doubtful.

(C) **Influence to the *p*H of the Solution.**

By the addition of different substances, a change of the constitution of the solution is more or less inevitable. From the standpoint of organic polarography, the variation of *p*H value corresponding to the addition of sodium sulfite is measured roughly in the buffered solutions. The results are shown in Table 1.

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6) Mellor "Inorganic and Theoretical Chemistry".

TABLE I.

Na_3SO_3	Sõrensen's borate-NaOH Buffer	
%	pH	pH
0	9.29	12.12
0.05	9.3	12
0.1	9.3	"
0.5	9.5	"
1.0	9.5	"

As seen in this table, the addition causes little variation in strong alkaline solutions, but some increase of pH value in neutral and weak alkaline solutions and so will bring on a shift of half-wave potential of organic compounds. As a result, when the addition is more than 0.5% the calibration of pH is necessary even if the solution is buffered.

(D) Influence to the Wave-height of the Substance being Determined.

If the sodium sulfite which is known as the reducing reagent reduces the substance to be determined, its use would be nonsense. For the example of p-nitroanthranilic acid, this propriety is examined in the mixture of buffer solution and methanol. The wave-heights are compared in both the cases, wheh nitrogen is bubbled and when sodium sulfite in cooperation with sodium nitrite is added. The results are shown in Table II.

TABLE II. WAVE-HEIGHT OF p-NITROANTHRANILIC ACID

(A) 8×10^{-4} M/l. in pH 8.6 Buffer and Methanal (11:1)

	Nitrogen passed (10 min.)	0.8% Na_3SO_3+1.2% $NaNO_2$		
Time (min.)	—	41	84	200
Wave-height (μA.)	4.2_8	4.2_8	4.2_8	4.3_9

(B) $1+10^{-3}$ M/l. in pH 12.2 Buffer and Methanol (9:1)

	Nitrogen passed (10 min.)	0.5% Na_2SO_3+3% $NaNO_2$	
Time (min.)	—	35	77
Wave-height (μA.)	5.0_5	4.9_8	5.0_5

As shown in Table II, both wave-heights coincide within experimental error after the elapse of more than an hour. The results indicate that sodium sulfite will not affect the wave of organic compound.

(E) Effect in the Acidic Solution.

Hitherto it is acknowledged that the efficacy of sodium sulfite is restricted in neutral and alkaline range because on the acidic side the reduction wave of HSO^-_3 appears.[7] From the experimental result, in the buffer solution of pH 5.6 the oxygen wave reduces more than 90% of its original height within 10 min. Qualitatively it is found that its reducing action still proceeds in acidic solution.

As a result when the wave of the substance being determined appears at the nobler potential than that of HSO^-_3, it is possible to use this method.

Summary

(1) From the polarographic standpoint, the behavior of reducing the dissolved oxygen by sodium sulfite is investigated in various kinds of supporting electrolytes.

(2) The efficiency is most prominent in neutral solution and becomes less effective towards basic.

(3) Influence upon the pH of the solution by the addition should not be neglected.

(4) There would be no effect to the reducible substance.

(5) Its reducing action still proceeds in acidic solution.

(6) The stock solution of sodium sulfite should be as fresh as possible. But a too fresh solution in 5~10 min. after preparation does not show the effect. The reason is not yet clarified. Ten or more days after preparation, it becomes less effective.

Laboratory of Electro-and Photochemistry
Institute of Industrial Science,
University of Tokyo, Chiba

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[7] I. M. Kolthoff and C. S. Miller, *J. Am.Chem. Soc.*, **63**, 2818 (1944).

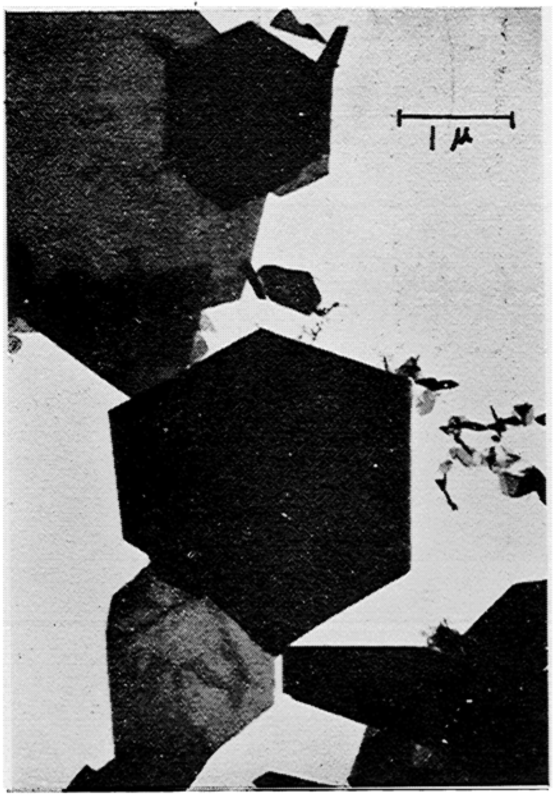

Fig. 1. Electron micrograph of the smoke of $CdCl_2$. ×15.000

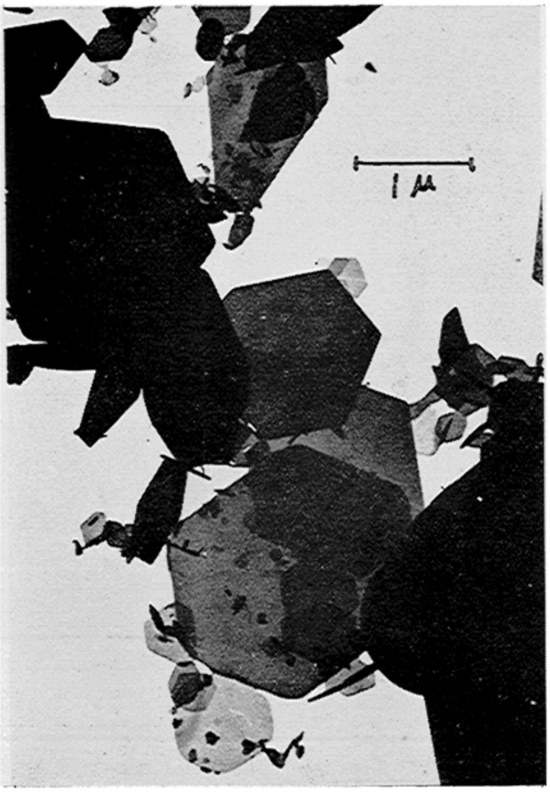

Fig. 2. Electron micrograph of the smoke of $CdBr_2$. ×15.000

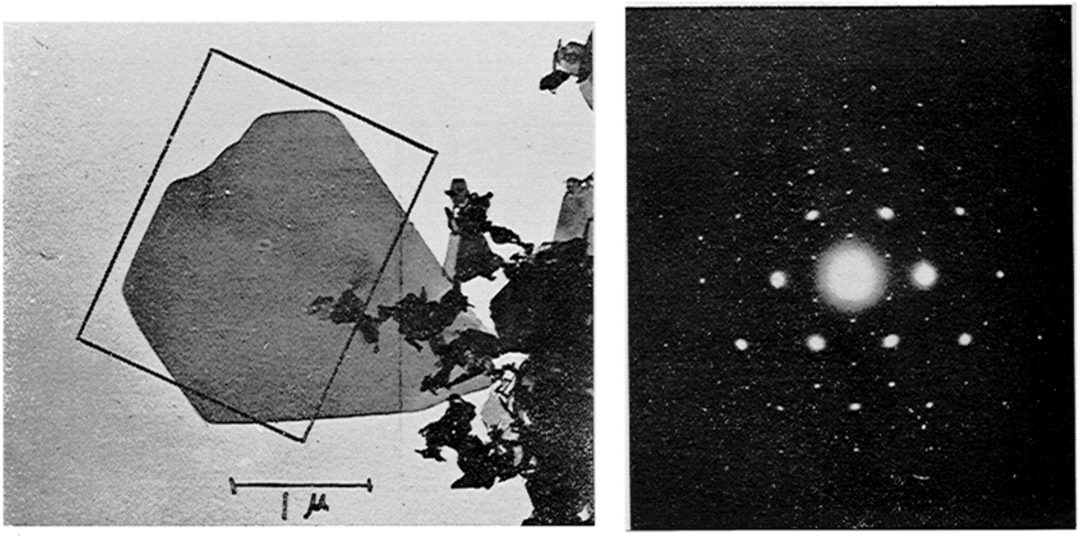

Fig. 3. (a) Electron micrograph of flakes of $CdCl_2$. ×18.000

(b) Diffraction pattern produced by transmission perpendicular to the portion indicated in the rectangle in (a).

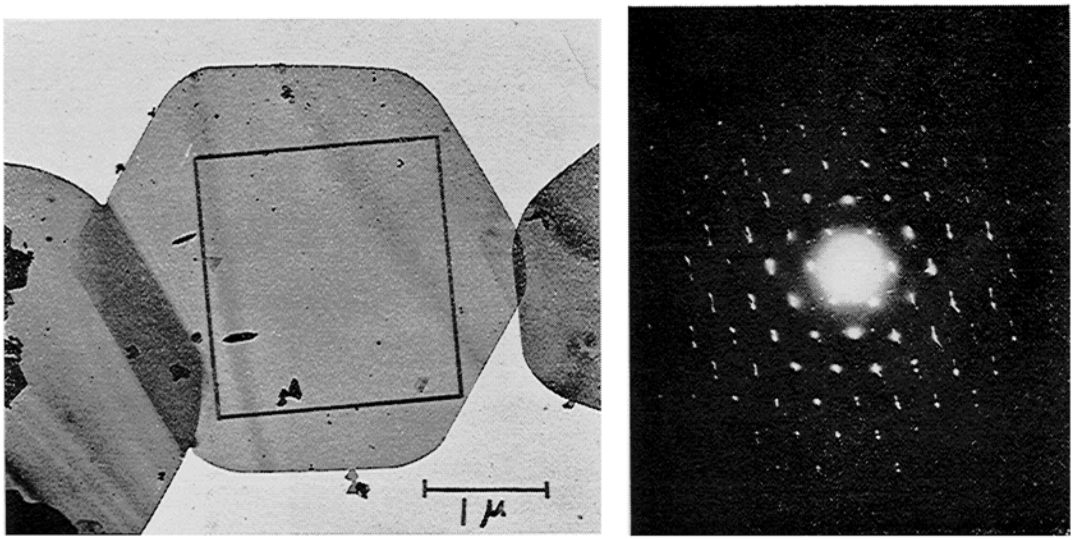

Fig. 4. (a) Electron micrograph of flakes of $CdBr_2$. ×18.000

(b) Diffraction pattern produced by transmission perpendicular to the portion indicated the rectangle in (a).