BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2110—2114 (1970)

Application of the AC Polarographic Method to the Microdetermination of the Sulfide Ion by the Methylene Blue Procedure*[1]

Kiyoshi HASEBE and Tomihito KAMBARA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received February 4, 1970)

A new AC polarographic method utilizing the methylene-blue procedure was used for the determination of the sulfide ion. By means of dimethyl-*p*-phenylenediamine sulfate and iron(III) alum, the sulfide ion is converted quantitatively into methylene blue in the sulfuric-acid milieu. The methylene blue thus formed shows a prominent and reproducible AC peak, which can be suitably utilized for the indirect microdetermination of the sulfide ion. Halide ions interfere with the determination, however.

The methylene blue method is very useful for the microdetermination of sulfur. The method[1-8] consists of the photometry of the methylene blue formed by the reaction of the sulfide ion with dimethyl-*p*-phenylenediamine in the presence of the ferric ion.

The present authors tried to apply the AC polarographic method to the microdetermination of the sulfide ion by methylene-blue procedure. Although this method is found to be a little inferior to spectrophotometry as to sensitivity, the AC polarographic peaks are very prominent and reproducible and are sufficient for use in the determination of microamounts of the sulfide ion.

Experimental

Apparatus. The polarograph used was a Yanagimoto pen recording polarograph, model PA-102. The capillary characteristics at an 80-cm mercury column height were: $m=1.10_6$ mg/sec in pure water and $t=4.90$ sec in the polarographic solution at 0.00 V *vs.* mercury pool. The polarographic cell was thermostated to 25±0.1°C.

All the absorbance measurements were carried out by the aid of a Shimadzu photoelectric spectrophotometer, model QV-50, using 1-cm glass cells. The measurement of pH was made with a Hitachi-Horiba, model D-5, glass electrode pH meter.

Reagents. The 10^{-2} M dimethyl-*p*-phenylenediamine solutions were prepared freshly for each use by dissolving its salts (Wako Chemicals Co.), namely, hydrochloride (special grade) and its sulfate (first grade), in a 0.1 M sulfuric acid milieu. Methylene blue (for microscopy, E. Merck AG), and all the other reagents used were of analytical-reagent quality. The sodium sulfide solution was prepared afresh each day and was stored in a stoppered brown bottle protected from light. The 10^{-2} M iron(II) solution was prepared by dissolving 3.921 g of Mohr's salt in 1 *l* of 0.1 M sulfuric acid. The 10^{-2} M iron(III) solution was prepared by dissolving iron alum in 1 *l* of 0.1 M sulfuric acid.

Results

Effect of Supporting Electrolyte. As is well known methylene blue gives an adsorption prewave in DC polarography and the corresponding AC peak is remarkably prominent, suggesting a very high analytical sensitivity. The methylene-blue method, which utilizes the formation of methylene blue by the reaction of the sulfide ion with dimethyl-*p*-phenylenediamine in the presence of the ferric ion, has been carried out mainly in hydrochloric acid milieus.[1,2,4-6] The methylene-blue reaction proceeds as follows:

$$2NH_2C_6H_4N(CH_3)_2 + 6Fe^{3+} + H_2S \longrightarrow$$
$$\text{Methylene blue}^+ + 6Fe^{2+} + NH_4^+ + 4H^+$$

First of all, the effects of the various supporting electrolytes were studied. It was found that hydrochloric acid is not suitable as a supporting electrolyte for the determination of methylene blue, because the anodic peak of chloride ion partially overlaps that of methylene blue. In a 0.1 M sulfuric acid milieu and also in a solution which is 0.1 M in sulfuric acid and 0.1 M in sodium acetate, well-defined AC peak of methylene blue was ob-

---

[*1] Part of the dissertation presented by Kiyoshi Hasebe to Hokkaido University, 1969.

1) J. K. Fogo and M. Popowsky, *Anal. Chem.*, **21**, 732 (1949).

2) S. Musha, *Nippon Kagaku Zasshi*, **71**, 572 (1950).

3) C. M. Johnson and H. Nishita, *Anal. Chem.*, **24**, 736 (1952).

4) Y. Oka and S. Matsuo, *Nippon Kagaku Zasshi*, **74**, 618 (1953).

5) H. Kitagawa and N. Shibata, *Bunseki Kagaku*, **7**, 181 (1958).

6) A. Kaya and Y. Kakita, *Nippon Kinzoku Gakkaishi*, **27**, 28 (1963).

7) Z. Marzenko and L. Chluj-Lenarczyk, *Chem. Anal.* (Warsaw), **10**, 729 (1965).

8) S. D. Yordanov and C. P. Ivanov, *C. R. Acad. Bulg. Sci.*, **21**, 451 (1968).

served.

Effect of Ferric and Ferrous Ions. For the conversion of the sulfide ion into methylene blue, the ferric ion is employed as the oxidizing agent. Hence, the effect of the excess ferric ion and the ferrous ion produced on the methylene-blue polarogram should be investigated. Figures 1 and 2 illustrate the DC and AC polarograms with the supporting electrolyte, that is, 0.1 M sulfuric acid and also in sodium acetate.

Curve (a) in Fig. 1 represents the DC polarogram of the blank solution, curve (b) was recorded after the addition of iron(III) in 5×10^{-4} M to the test solution, and curve (c) was recorded with a test solution containing the ferric ion and methylene blue in 5×10^{-5} M. When 0.1 M sulfuric acid alone is employed as the supporting electrolyte, the reduction wave of methylene blue in the DC polarogram appears *ca.* 0.3 V from the ferric ion wave, while in the AC polarography methylene blue shows a prominent peak which is not effected by the ferric ion. Therefore, the supporting electrolyte of 0.1 M sulfuric acid was employed, thereafter.

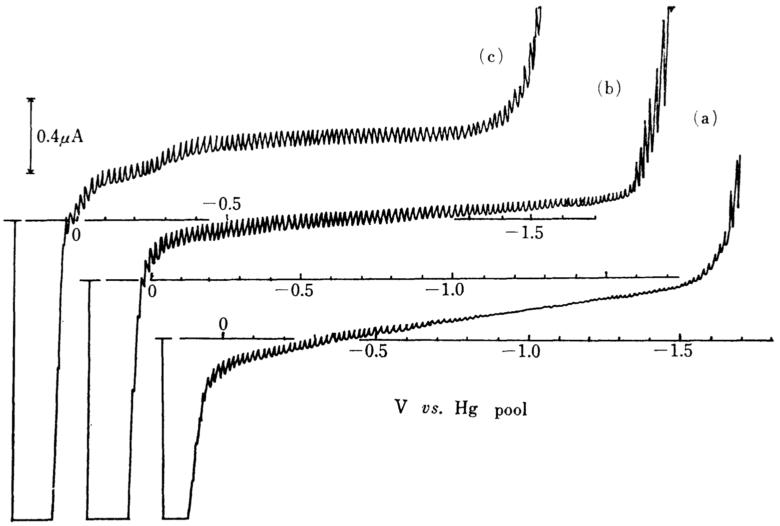

Fig. 1. Typical DC polarograms of methylene blue (Merck AG) and ferric ion.
Supporting electrolyte: (a) 0.1 M H_2SO_4+0.1 M NaOAc, (b) (a)+5×10^{-4} M Fe^{3+}, (c) (b)+5×10^{-5} M methylene blue. Parallel capacitance: 50 μF

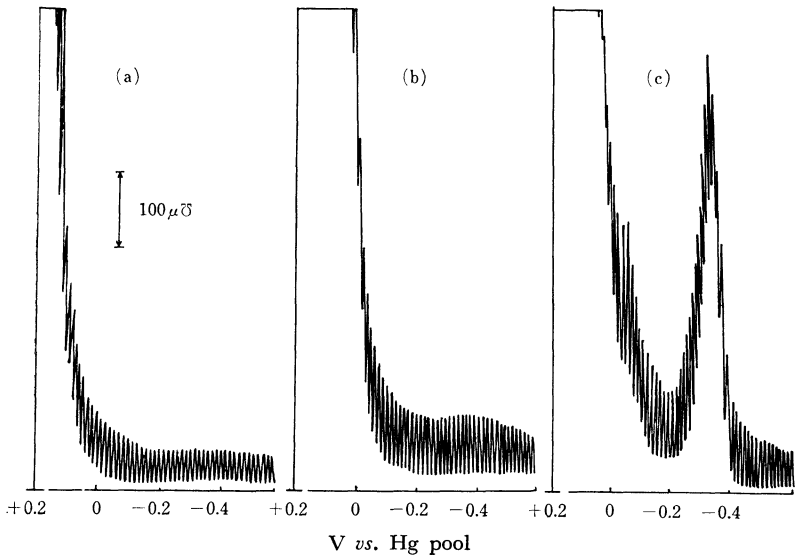

Fig. 2. The AC polarograms of methylene blue and ferric ion corresponding to Fig. 1.
Parallel capacitance: 0.05 μF.

Effect of Anions on the AC Peak of Methylene Blue. According to many authors,[2,6] the hydrochloride of dimethyl-*p*-phenylenediamine has widely been used for the color reaction forming methylene blue. When dimethyl-*p*-phenylenediamine was used, the anodic wave of the chloride ion interferes with the methylene-blue determination by the polarographic method. As the concentration of the chloride ion increases, the interference becomes especially remarkable.

Figure 3 compares polarograms of methylene blue as synthesized by dimethyl-*p*-phenylenediamine hydrochloride (a) and its sulfate (b). The prominent chloride peak appears near to the methylene blue wave. The use of sulfate is, needless to say, more advantageous than that of hydrochloride. As is well known, iodide reduces methylene blue to the leuco form, and chloride and, more strongly, the bromide ion suppress the methylene-blue peak height, as has been reported in our previous study.[9]

Effect of the Sulfuric Acid Concentration. The color development due to the formation of methylene blue from the sulfide ion and dimethyl-*p*-phenylenediamine in the presence of the ferric ion should be performed in a sulfuric acid milieu, because the chloride ion interferes with the polarographic determination of methylene blue.

The relationship between the concentration of sulfuric acid and absorbance of methylene blue, or the AC polarographic peak, was investigated. According to Rabinowitch and Epstein,[10] methylene blue exists in monomer and dimer forms in solution. On the other hand, Oka and Matsuo,[4] who discussed in detail the behavior of methylene blue in a hydrochloric acid milieu, reported the association of methylene blue with hydrochloric acid as indicated by the new absorption band at 735 mμ. Figure 4 shows the variation in the absorption spectrum of methylene blue with the sulfuric acid concentration. The new maximum in absorbance curves at 740 mμ *vs.* the reagent blank clearly shows another form of methylene blue in a sulfuric acid milieu. This maximum can be interpreted as resulting from the association of methylene blue with sulfuric acid. Thus, it is important to select a suitable acid concentration.

Figure 5 shows the relationship between the AC polarographic peak height and the sulfuric acid concentration. It can readily be seen that the optimum polarographic concentration of sulfuric acid is at 0.1—0.2 M.

Effect of the Ferric Ion Concentration and Deaeration on the AC Polarographic Peak. By applying the constant initial concentration of the sulfide ion of 4×10^{-4} M in the reaction mix-

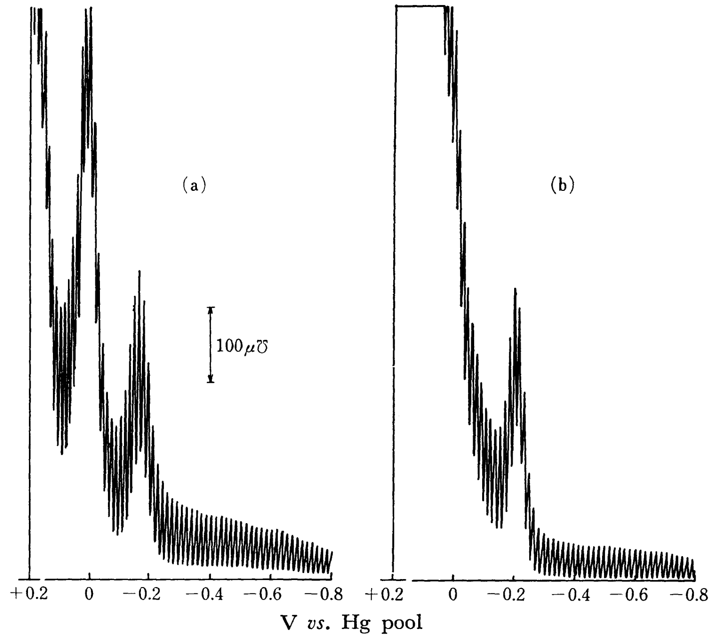

Fig. 3. The AC polarograms of methylene blue synthesized from sulfide ion by dimethyl-*p*-phenylenediamine hydrochloride (a) and its sulfate (b).

The final concentration of methylene blue: 5×10^{-5} M.
Parallel capacitance: 0.05 μF.

---

[9] K. Hasebe and T. Kambara, Preprint of the Discussion Meeting of the Polarographic Society of Japan, Hiroshima, October, 1968; *Rev. Polarog.* (Japan), manuscript in preparation.

[10] E. Rabinowitch and L. F. Epstein, *J. Amer. Chem. Soc.*, **63**, 69 (1941).

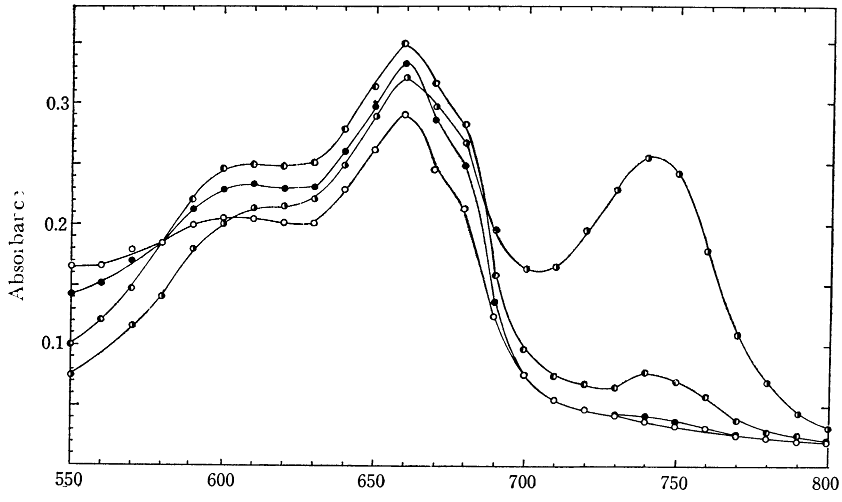

Fig. 4. Absorption spectra of synthesized methylene blue in various sulfuric acid concentrations (*vs.* reagent blank).

The concentrations of reactants in the reaction mixture is: 6×10^{-5} M S^{2-}, 5×10^{-3} M diamine, 5×10^{-4} M Fe^{3+}.

—○— 0.01 M H_2SO_4, —●— 0.05 M H_2SO_4, —◐— 0.2 M H_2SO_4, —◑— 1 M H_2SO_4.

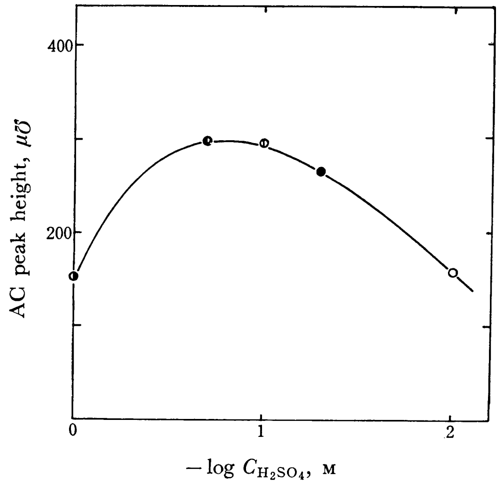

Fig. 5. Effect of the sulfuric acid concentration on the AC peak height of synthesized methylene blue corresponding to Fig. 4.

—◐— 0.1 M H_2SO_4.

ture, the effect of the ferric-ion concentration on the synthesis of methylene blue was studied.

Table 1 shows the relationship between the AC polarographic peak heights of methylene blue and the initial concentration of the ferric ion without deaeration. The optimum concentration of the ferric ion was found to be 5×10^{-4} M in the reaction mixture. With the ferric ion concentration of 5×10^{-4} M, the two means of obtaining the AC peak heights, with and without dissolved oxygen, were analyzed statistically. Consequently, it can be concluded that there is no significant difference between the AC peak heights obtained with and without deaeration.

TABLE 1. ANALYSIS OF MEANS

Relationship between the AC peak height of methylene blue and ferric ion concn. with and without deaeration.

Ferric ion concn., M	AC peak height, μ℧	
	With deaeration	Without deaeration
1×10^{-3}	132±15.6	133±15.6
5×10^{-4}	213±20.8 (208, 224, 208)*	205±26.0 (204, 196, 216)*
1×10^{-4}	113± 5.20	111±10.4

Confidence limits 95%; * Figures in parentheses represent individual values. Parallel capacitance 0.05 μF.

The initial concentration in the reaction mixture: 4×10^{-5} M S^{2-}, 5×10^{-3} M dimethyl-*p*-phenylenediamine.

F-test shows that there is no significant difference between two variances: $F(2, 2, 0.025)=39.0>F_0=1.18$, *t*-test shows that there is no significant difference between two means: $t(4, 0.05)=2.77>t_0=1.17$.

Effect of the Dimethyl-*p*-phenylenediamine Concentration. The dimethyl-*p*-phenylenediamine in the electrolysis solution showed no AC peak. The optimum concentration of dimethyl-*p*-phenylenediamine was determined by employing various concentrations of the diamine from 1×10^{-4} to 8×10^{-3} M. Figure 6 shows the change in the AC polarograms of methylene blue at various

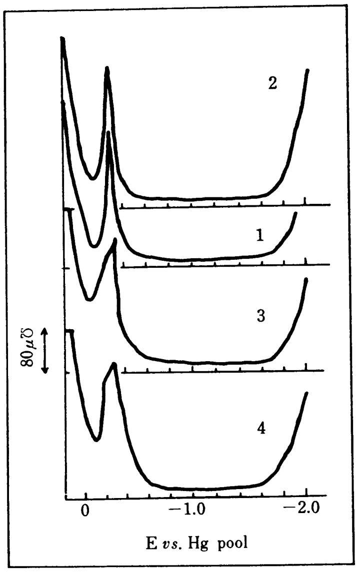

Fig. 6. Effect of dimethyl-*p*-phenylenediamine concentration on the AC polarographic peak.

Concentration in the reaction mixture is: 4×10^{-5} M S^{2-}; 5×10^{-4} M Fe^{3+}.
The diamine concentration is: (1) 5×10^{-4} M; (2) 1×10^{-3} M; (3) 5×10^{-3} M; (4) 8×10^{-3} M.

diamine concentrations.

It can be seen that 5×10^{-4} M or 1×10^{-3} M of dimethyl-*p*-phenylenediamine is most suitable for the determination of the sulfide ion. However, no peak of methylene blue appeared with 1×10^{-4} M diamine. The diamine in concentrations higher than 5×10^{-3} M interferes with the methylene blue peak, as Fig. 6 shows.

Effect of the Standing Time. At room temperature, no change in the AC polarographic peak height of methylene blue was observed over a period of 24 hr.

Established Procedure. The procedure for the sulfide determination has been established to be as follows:

To 0.5 m*l* of 2 M sulfuric acid in a 10-m*l* volumetric flask, add 0.5—1 m*l* of 10^{-2} M dimethyl-*p*-phenylenediamine in 0.1 M sulfuric acid and 0.5—0.6 m*l* of 10^{-2} M iron(III) ammonium sulfate. Add the sample solution containing the sulfide ion to the reagent mixture, shake, let stand for 15—20 min and then fill up to the mark with water. Record the AC polarogram without deaeration.

Calibration Curve. The relationship between the AC polarographic peak height of the synthesized methylene blue and the original amount of the sulfide ion was studied. The results are shown in Fig. 7.

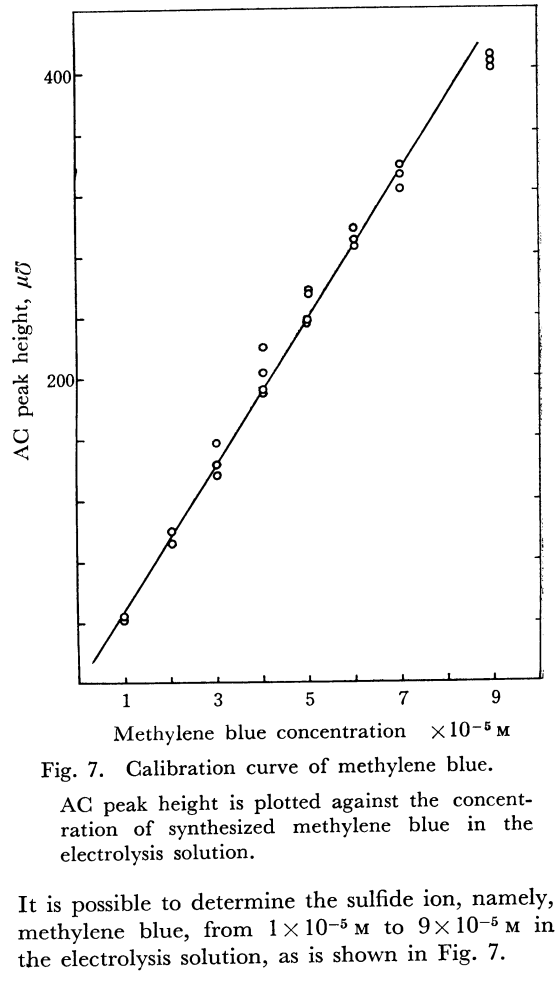

Fig. 7. Calibration curve of methylene blue.

AC peak height is plotted against the concentration of synthesized methylene blue in the electrolysis solution.

It is possible to determine the sulfide ion, namely, methylene blue, from 1×10^{-5} M to 9×10^{-5} M in the electrolysis solution, as is shown in Fig. 7.

Discussion

It has been said that the degree of methylene-blue color development changes slightly with the sequence of reagent addition.[2,4,5] In the AC polarography, however, no significant difference could be seen by any change in reagent addition.

Breyer and Hacobian[11,12] have reported that the sulfide ion gave a good AC polarographic peak in a supporting electrolyte of 1 M sodium hydroxide and that a linear calibration curve was obtained in the concentration range from 10^{-4} to 10^{-3} M. However, the direct determination of sulfide ion is much less sensitive than the present indirect method.

---

11) B. Breyer and S. Hacobian, *Aust. J. Sci. Res.*, **A4**, 610 (1951).

12) B. Breyer and H. H. Baur, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York, N. Y. (1963), p. 183.