

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

## Spectrophotometric Studies on Complex Formation with Sulfosalicylic Acid. I. With Iron III

BY ROBERT T. FOLEY AND ROBBIN C. ANDERSON<sup>1</sup>

Sulfosalicylic acid has long been known as an analytical reagent for iron,<sup>2</sup> giving characteristic colors with iron(III) solutions, apparently because of complex formation. The color variations, shading from violet through deep red or rose in acid solutions to yellow in alkaline, suggest that more than one complex may be involved. The present investigations were undertaken to obtain information concerning the nature of the complex or complexes responsible for these effects.

## Experimental

**Materials.**—Standard iron(III) perchlorate solution was prepared by dissolving primary standard iron wire in hydrochloric and nitric acids. Perchloric acid was then added and the solution boiled slowly to drive off the more volatile acids.

C. P. sulfosalicylic acid (Eastman Kodak Co.) was dissolved in water, with sufficient perchloric acid to adjust to the same pH as that of the iron(III) perchlorate solution. The solution was standardized by titration with sodium hydroxide.

Sodium hydroxide solution for use in adjusting the pH was prepared from Merck Reagent grade sodium hydroxide. It was standardized with potassium acid phthalate. All solutions were prepared in calibrated apparatus at 25°.

**Apparatus.**—pH measurements were made with a Beckmann pH meter, Model G, with an accuracy of  $\pm 0.02$  pH unit.

Light absorption measurements were made with an Automatic Recording General Electric Spectrophotometer of the Hardy type<sup>3</sup> over a range of 400 to 700  $m\mu$  with slit adjustment to measure a 10  $m\mu$  band. Per cent. transmission values for solutions of equal concentration prepared independently varied not more than 0.3 per cent.

**Procedure.**—Calculated volumes of iron(III) perchlorate and sulfosalicylic acid were mixed. Sodium hydroxide was then added if needed to adjust the pH and the whole diluted to the proper volume and allowed to stand one hour. The transmittance curve was then recorded, the absorption cells being rinsed very carefully before filling with each sample.

Preliminary experiments showed that the solutions reached equilibrium within one hour and showed no measurable variation thereafter for periods of less than twenty-four hours.

The absorption cell was not thermostated, but all solutions were brought to constant temperature before measurements were made.

## Results

The composition of the complex was studied using Job's method of continuous variations,<sup>4</sup> the ratio of iron(III) to sulfosalicylic acid being var-

ied with the total molarity of the two kept constant. Several typical transmittance curves for solutions at a pH of 2.38 are shown in Fig. 1.

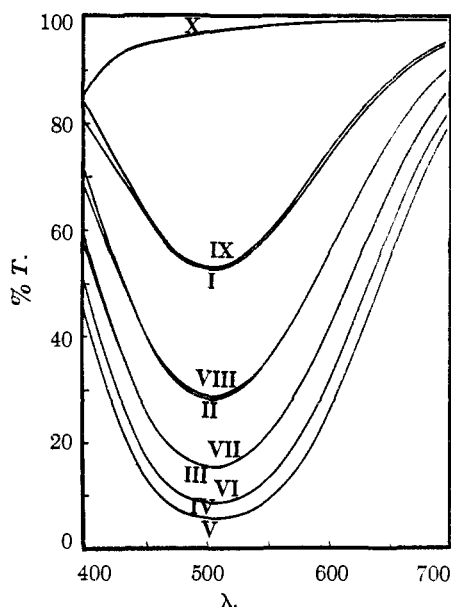


Fig. 1.—Method of continuous variations—absorption curves. The  $[\text{Fe}^{\text{II}}]/[\text{Fe}^{\text{III}}] + [\text{sulfosalicylic acid}]$  ratio varied as I, 0.1; II, 0.2; III, 0.3; IV, 0.4; V, 0.5; VI, 0.6; VII, 0.7; VIII, 0.8; IX, 0.9; X, 1.0.

From these curves values of the optical density ( $D = \log_{10} 1/T$  where  $T =$  transmittance) for a particular wave length were calculated for each solution. Sulfosalicylic acid and perchloric acid show no absorption at the wave lengths used. The absorption for a system with no reaction is determined therefore by subtracting the optical density of iron(III) perchlorate determined from curve X of Fig. 1. Subtraction of this absorption for a particular wave length, from the optical density of the solution gives  $\bar{D}$ , a quantity which is proportional to the concentration of the complex and which passes through a maximum when the ratio of iron(III) to total sulfosalicylic acid in the solution is the same as that in which they react to form the complex.<sup>4,5</sup>  $\bar{D}$  was plotted against the ratio

$$\frac{\text{concn. Fe(III) (moles/l.)}}{\text{concn. Fe(III) + concn. HO}_3\text{SC}_6\text{H}_3(\text{OH})\text{COOH}}$$

The results for wave lengths of 440, 500 and 540  $m\mu$  are shown in Fig. 2.

The occurrence of the maximum of  $\bar{D}$  in the curves of Fig. 2 at a ratio of 0.5 indicates that un-

(5) Moore and Anderson, *ibid.*, **67**, 167 (1945).

(1) Presented in part at Southwest Regional Meeting, American Chemical Society, Dallas, Texas, Dec. 12, 1946.

(2) Alten, Wieland and Hille, *Z. anorg. allgem. Chem.*, **215**, 81 (1933); Thiel and Peter, *Z. anal. Chem.*, **103**, 161 (1935); Kennard and Johnson, *Texas Acad. Sci. Proc. and Trans.*, **27**, 45 (1943).

(3) Hardy, *J. Opt. Soc. Am.*, **25**, 305 (1935); **28**, 360 (1938); U. S. Patent 1,987,441 (1935).

(4) Job, *Ann. chim.*, [10] **9**, 113 (1928); Vosburgh and Cooper, *This Journal*, **63**, 437 (1941).

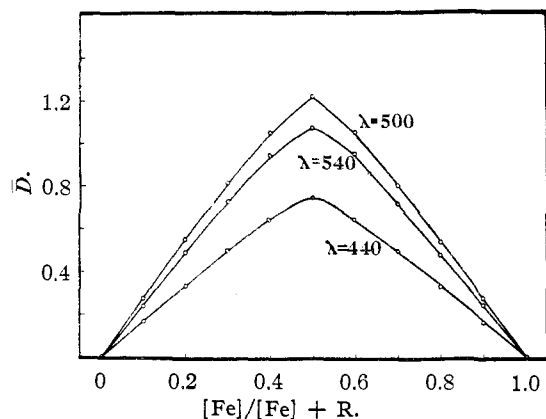


Fig. 2.—Method of continuous variations,  $pH$  2.38.

der these conditions the iron and sulfosalicylic acid react in a 1:1 ratio to form the complex.

It may be noted also that the absorption is essentially the same at the two extremes where the ratio of iron(III) to R (sulfosalicylate) is 9:1 and 1:9. Reasonable approximations for the extinction coefficients may be calculated by assuming that under such conditions essentially all of the reagent present in smaller proportion will react to form the complex. Correction can be made for absorption by excess iron(III). For the solution with ratio iron(III): R = 9:1, the value so obtained for the molar extinction coefficient of the complex was 753 at a wave length of 508  $m\mu$ . For solutions of ratios 1:9, 8:2, and 2:8, respectively, the corresponding values were 756, 761, 752. Thus there is no indication that in this  $pH$  range complex formation occurs with more than one iron (III) ion or R group. Similar agreement is obtained for absorption at other wave lengths.

With a change in  $pH$ , the results vary markedly. In more strongly acid solutions (*e. g.*,  $pH$  0.9)  $\bar{D}$  curves similar to those in Fig. 2 are obtained, except that the maximum tends to shift slightly to a concentration ratio of 0.46. Some variation is also apparent in solutions with excess sulfosalicylic acid as contrasted to excess iron; but, in general, solutions at  $pH$  values less than 2.5 show closely similar behavior.

From the curves of Fig. 1, values of the extinction coefficient may be calculated as indicated above. These can then be used to calculate the concentration of the complex in other solutions, *e. g.*, where equal concentrations of iron and sulfosalicylic acid are present. A better value for the extinction coefficient may then be calculated. By a series of successive approximations reasonably good values for the apparent dissociation constant (where R = sulfosalicylic acid concentration)  $K = \frac{[\text{Fe(III)}][\text{R}]}{[\text{FeR}]}$  may be determined. At  $pH$  2.38 and ionic strength of 0.061 a value of  $1.3 (\pm 0.2) \times 10^{-5}$  is obtained. At  $pH$  0.9 and ionic strength 0.153 the value is  $2.1 (\pm 0.4) \times 10^{-4}$ .

Earlier workers<sup>2</sup> have referred to red or orange or yellow "complexes" in less acid solutions, but

experiments at higher  $pH$  values in the present work indicate that information on such complexes based on ordinary color measurements alone is of doubtful significance. Typical results are shown in the curves of Fig. 3, for solutions of different  $pH$  and constant iron(III) and sulfosalicylic acid concentrations. The position of maximum absorption and thus the color of the solutions changes as well as the extent of absorption.

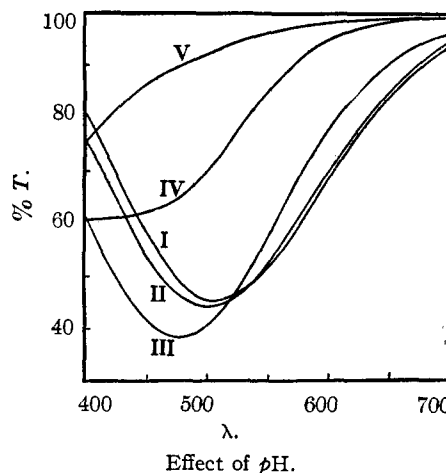


Fig. 3.— $[\text{Fe}^{\text{III}}] = 1.791 \times 10^{-4}$  mole/l. [sulfosalicylic acid] =  $2.292 \times 10^{-3}$  mole/l.: I,  $pH$  1.95; II,  $pH$  3.03; III,  $pH$  4.05; IV,  $pH$  5.72; V,  $pH$  9.38.

Graphs of  $\bar{D}$  against concentration ratios show maxima shifted toward values less than 0.5. For  $pH$  4.58, for example, the maximum  $\bar{D}$  occurs at a concentration ratio of 0.25–0.30 and for  $pH$  6.2 the maximum is between 0.1 and 0.2. These maxima might be taken as evidence of complexes with more R groups, but in some cases more than five sulfosalicylic acid molecules reacting per iron (III) ion would be indicated. It seems evident that other factors than complex formation are involved and that such maxima do not represent the compositions of real complexes.

It has been shown<sup>6</sup> that, even at  $pH$  2.38,  $\text{FeOH}^{++}$  is of major importance in iron(III) solutions; and, although dissociation constants for sulfosalicylic acid are not known exactly, experiments on buffers<sup>7</sup> have shown that the sulfonic acid group is highly ionized and that between  $pH$  1 and  $pH$  4 conversion in large measure to  $^-\text{O}_3\text{SCH}_2(\text{OH})\text{COO}^-$  should occur. These changes in ionic species might account in part for the effect of the hydrogen ion.

However, blank determinations show that in solutions of high  $pH$ , iron(III) perchlorate solutions absorb more strongly in the same regions as the iron(III)–sulfosalicylic acid mixtures, probably as a result of formation of hydrous iron(III) oxide sols. Where excess iron is present many of

(6) Rabinowitch and Stockmayer, *THIS JOURNAL*, **64**, 335 (1942); Bray and Hershey, *ibid.*, **56**, 1889 (1934).

(7) Private communication, U. S. Bur. Stds., Dr. R. G. Bates.

the mixtures form precipitates of hydrous iron (III) oxide on standing. The Job method may be applied successfully where other equilibria in solution are involved but any such sol formation makes uncertain the comparison and interpretation of absorption data for mixtures of varying concentrations.

Just recently, Babko's experiments on iron-salicylic acid systems, which might be expected to be closely analogous to the sulfosalicylic acid system, have been reported.<sup>8</sup> He found  $\text{FeR}^+$  (violet) in acid solution, then  $\text{FeR}_2^-$  (red), and finally  $\text{FeR}_3^{=}$  (yellow) at about  $\text{pH}$  10, but abstracts available do not indicate what corrections were made for hydrolysis or dissociation.

Experiments are now under way to extend transmittance measurements on the iron-sulfosalicylate systems to the ultraviolet region in an attempt to determine concentrations of the various species, especially  $\text{FeOH}^{++}$ , so that their effects may be measured.

**Effect of Temperature.**—The instrument used is such that accurate control of temperature is not possible, but approximate measurement of the temperature effect showed that increased

(8) Babko *J. Gen. Chem. (U. S. S. R.)*, **15**, 745 (1945); *C. A.*, **40**, 7042 (1947).

temperatures increase the extent of complex formation. The per cent. transmittance decreased about 7% on heating from 20 to 40°. A thermostated absorption cell has now been built so that the temperature effect may be measured more accurately in an attempt to determine the extent of dissociation of the complex.

The authors wish to express their appreciation to Mr. Leland L. Antes, Microscopy Specialist, Bureau Engineering Research, University of Texas, for his assistance in connection with use of the spectrophotometer.

### Summary

1. Spectrophotometric studies of complex formation between iron(III) and sulfosalicylic acid were made over a  $\text{pH}$  range of 1 to 9.

2. In strongly acid solutions (to  $\text{pH}$  2.4) iron (III) and sulfosalicylic acid react in a 1:1 ratio to form a violet complex. Stability of the complex is a function of the acidity.

3. Measurements at higher  $\text{pH}$  values indicate complexes of other mole ratios, but accurate formulas could not be determined from ordinary concentration measurements.

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## Some Reactions of Trisodium Monobismuthide in Liquid Ammonia<sup>1,2</sup>

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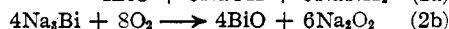
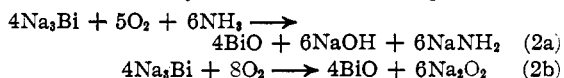
Although numerous intermetallic compounds of the alkali and alkaline earth metals have been prepared in liquid ammonia, the literature provides very little information concerning their reactions in this medium.<sup>4</sup> The present paper is concerned with the preparation of trisodium monobismuthide and the study of its properties as a reducing agent in liquid ammonia. Since there is no known method for the production of pure sodium bismuthate, it was of interest (particularly in view of the work of McCleary and Fernelius<sup>5</sup>) to determine whether trisodium monobismuthide could be oxidized to sodium bismuthate by treatment with molecular oxygen.

Trisodium monobismuthide was prepared by the reaction

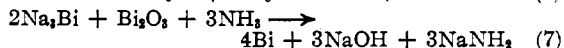
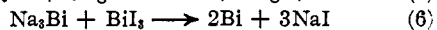
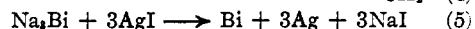
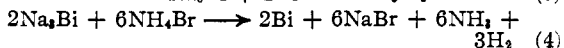
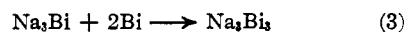


Treatment of the purified monobismuthide with molecular oxygen leads not to sodium bismuthate

but rather to an insoluble mixture of bismuth(II) oxide, sodium hydroxide and sodium peroxide



In addition, the following reactions of trisodium monobismuthide have been observed.



In the course of this work the conventional type of apparatus for the study of reactions in liquid ammonia at its boiling temperature has been modified extensively. The major improvements are concerned with techniques for filtration in a closed system.

### Experimental

**Apparatus.**—With the exceptions noted below, the over-all details of construction and mode of operation of the equipment shown in Fig. 1 are similar to those described by Johnson and Fernelius.<sup>6</sup> Both reactors A

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(2) Presented at the Second Southwestern Regional Meeting of the American Chemical Society, Dallas, Texas, Dec. 13, 1946.

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(4) Johnson and Fernelius, *J. Chem. Education*, **7**, 981-999 (1930).

(5) McCleary and Fernelius, *THIS JOURNAL*, **56**, 803 (1934).

(6) Johnson and Fernelius, *J. Chem. Education*, **6**, 445 (1929).