[CONTRIBUTION NO. 125 FROM THE INSTITUTE OF ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

A Polarographic Investigation of Iron–Sulfosalicylate Complex Ions

BY CHARLES V. BANKS AND JAMES H. PATTERSON[1]

The yellow iron(III)–sulfosalicylate complex ion formed in neutral and alkaline solutions was studied by the half-wave potential method. It was found to contain three triply ionized sulfosalicylate ions for each iron(III) ion, and have a molar hydrolysis constant of approximately 10^{-43} at ionic strength 1. No evidence was found for complex ion formation between iron(II) and sulfosalicylate ions. The second molar dissociation constant, K'_{A2}, of sulfosalicylic acid was determined spectrophotometrically to be 3.23×10^{-3} at 25° and ionic strength 0.1.

Introduction

By applying Job's method of continuous variations to spectrophotometric data, Foley and Anderson[2] found that in acid solutions (to *p*H 2.4) iron(III) and sulfosalicylic acid react in a 1:1 ratio to form a violet complex ion. Above this *p*H their data seemed to indicate the formation of other complex ions having different mole ratios. Kennard and Johnson[3] found evidence for three complex ions having maximum stabilities at *p*H values of 1.5 (violet), 5.0 (red), and 8.2 (yellow) by studying the *p*H dependency of the absorption spectra of solutions containing iron(III) and sulfosalicylic acid. Babko[4] found complexes of iron(III) and salicylic acid that correspond well with these *p*H values and colors.

Although the yellow iron(III)–sulfosalicylate complex ion has been used extensively for the determination of iron, its composition and stability have not been carefully studied. Some[5] have actually considered the yellow color in alkaline solution to be caused by the dissociation of the complex ion to form colloidal hydrous iron(III) oxide.

Experimental

A Sargent model XXI polarograph was used for nearly all of the polarographic measurements. The cell was similar to the H-type cell described by Lingane and Laitinen[6] with a saturated calomel half-cell as anode. A large capacity cell of the type described by Meites[7] was used for the reversibility study. The temperature of the cell was kept at 25 ± 0.2° by a constant temperature bath. The dropping mercury electrode assembly was the conventional type supplied with the polarograph. All solutions were flushed for at least 15 minutes with nitrogen to remove dissolved oxygen before polarograms were made. The spectrophotometric data were obtained with a Beckman DU spectrophotometer with a hydrogen discharge ultraviolet source. One centimeter silica cells were used.

Data and Discussion

In the present research the half-wave potential method[8] was used for the investigation of the yellow iron(III)–sulfosalicylate complex ion. In Table I are listed the data for the variation of the half-wave potentials with *p*H at constant sulfosalicylate and iron(III) concentrations and constant ionic strength. Table II shows the variation of the half-wave potentials with sulfosalicylate concentration at constant *p*H, ionic strength and iron(III) concentration. All of the solutions were buffered with boric acid–sodium borate buffer, and the ionic strength was kept constant by adjusting the concentration of the sodium perchlorate supporting electrolyte. The reversibility of the iron(III) and iron(II) waves was tested by the criterion of Tomeš,[9] *i.e.*, $E_{1/4} - E_{3/4}$ should be 0.056/n volt at 25°. For all the iron(III) waves this value was between 60 and 87 millivolts. Only the waves for the highest *p*H had values over 80 millivolts, indicating a decrease in the reversibility with increasing *p*H. Waves for the reduction of iron(II) to metallic iron had values of 54 to 105

TABLE I

VARIATION OF HALF-WAVE POTENTIALS WITH *p*H[a]

*p*H	$E_{1/2}$, volts *vs.* S.C.E. Iron(III) wave	Iron(II) wave
8.38	−0.479	−1.404
8.51	− .488	−1.417
8.65	− .505	−1.422
8.88	− .540	−1.428
9.09	− .561	−1.446
9.26	− .561	−1.456
9.48	− .596	−1.463
9.70	− .624	−1.483
9.77	− .624	−1.490
10.05	− .639	−1.502
10.22	− .663	−1.502

[a] Solutions were 0.02 *M* in sulfosalicylate, 0.0001 *M* in iron(III) and 0.35 *M* in total borate. Ionic strength adjusted to 0.6 with sodium perchlorate.

TABLE II

VARIATION OF HALF-WAVE POTENTIAL WITH SULFOSALICYLATE CONCENTRATION[a]

*C*x mole/l.	log *C*x	$E_{1/2}$, volts *vs.* S.C.E. Iron(III) wave	Iron(II) wave
0.00486	−2.313	−0.520	−1.392
.01043	−1.982	− .568	−1.308
.0204	−1.689	− .586	−1.416
.0499	−1.302	− .647	−1.441
.1002	−0.999	− .764	−1.502
.2067	−0.685	− .830	−1.536

[a] Solutions were 0.5 *M* in total borate and 0.001 *M* in iron(III). Ionic strength was brought to 1.0 with sodium perchlorate, and *p*H was 9.0.

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(1) Abstracted from a dissertation submitted by James H. Patterson to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy. 1950.

(2) R. T. Foley and R. C. Anderson, THIS JOURNAL, **70**, 1195 (1948); **72**, 5609 (1950).

(3) M. Kennard and C. R. Johnson, *Proc. Trans. Texas Acad. Sci.*, **27**, 45 (1944).

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

(5) S. Lacroix and M. Labalade, *Anal. Chim. Acta*, **4**, 68 (1950).

(6) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(7) L. Meites, THIS JOURNAL, **71**, 3269 (1949).

(8) This polarographic method has been very adequately described by (a) M. v. Stackelberg and H. v. Freyhold. *Z. Elektrochem.*, **46**, 120 (1940); (b) I. M. Kolthoff and J. J. Lingane. "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 161–183; and (c) P. Souchay and J. Faucherre, *Bull. soc. chim. France*, 529 (1947).

(9) J. Tomeš, *Collection Czechoslov. Chem. Communs.*, **9**, 81 (1937).

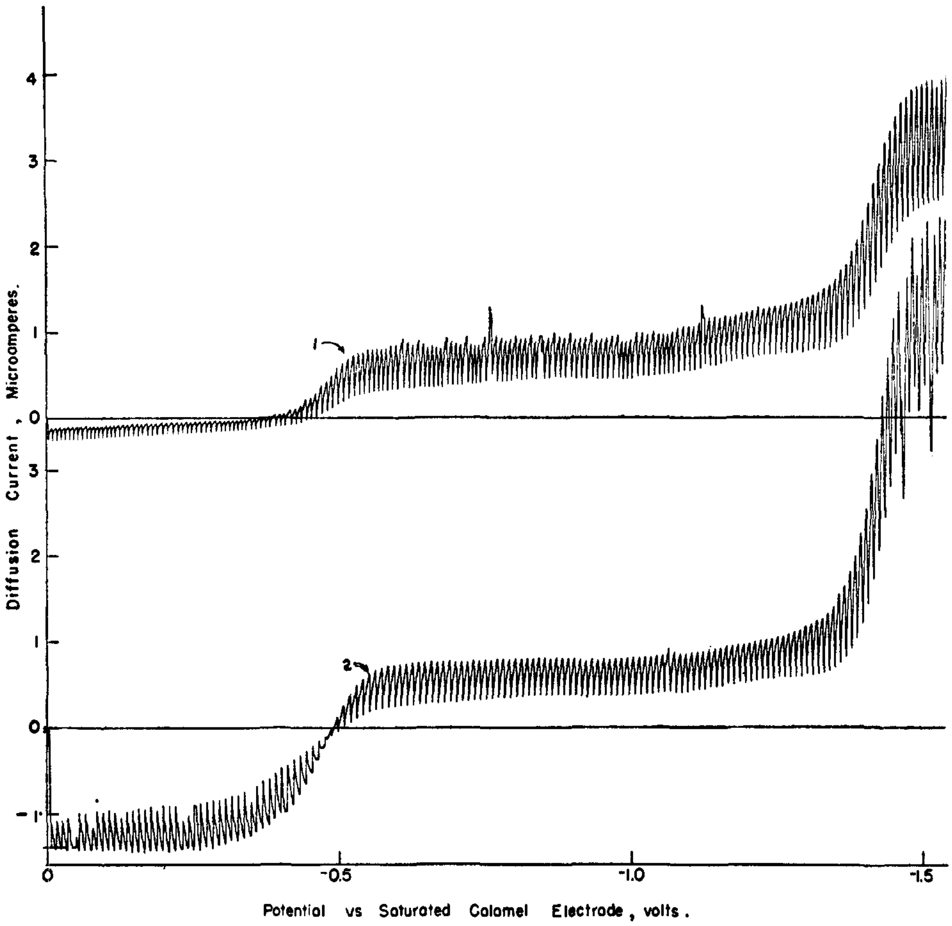

Fig. 1.—Proof of reversibility of iron(III)-iron(II) couple in alkaline solution: curve 1, polarogram of solution containing iron(III) ion, but negligible iron(II) ion; curve 2, polarogram of solution from curve 1 with iron(II) ion added.

millivolts for $E_{1/4} - E_{3/4}$ as compared to 28 millivolts expected for a two electron reduction, thus, this reduction must be irreversible. The reversibility of the iron(III) wave was also tested by obtaining a polarogram of a solution containing both iron(II) and iron(III) in the presence of sulfosalicylate at pH 9. Air oxidation of the iron(II) was prevented by the addition of iron(II) perchlorate solution by microburet into the large polarographic cell containing a solution of iron(III) and sulfosalicylate that had been flushed for 30 minutes. Figure 1 shows the polarograms obtained before and after addition of iron(II) solution. The smooth curve exhibiting only one point of inflection for the combined cathodic and anodic waves of the iron(III)–iron(II) oxidation–reduction system indicates that the reduction of iron(III) to iron(II) is essentially reversible.[8a]

The irreversibility of the wave for the reduction of the iron(II) ion to metallic iron makes the data for this wave useless for study by the half-wave potential method. It was assumed that the sulfosalicylate had negligible complexing action on iron(II) ions,[10] and that the principal iron(II) species in these solutions is $FeOH^+$. According to Lindstrand[11] the constant for the formation of this ion by the hydrolysis of ferrous ion is 1.2×10^{-6} at 20°.

The partial derivatives of the half-wave potential of the iron(III) complex ion wave with respect to pH and log C_X are, respectively, -0.0985 and -0.1660. Although these are somewhat less than the values of -0.1182 and -0.1773 theoretically expected, they indicate that three sulfosalicylate ions and two hydroxyl ions are required for the formation of the iron(III)–complex ion from $FeOH^+$ with which it is in equilibrium. From $K'_{A_3} = 3.23 \times 10^{-3}$ for sulfosalicylic acid and the fact that Meek[12] has shown that the third hydrogen of this acid is not appreciably ionized below pH 11, it is apparent that $^-O_3SC_6H_3(OH)COO^-$ is the only important sulfosalicylate species present in solution in the pH range used in this study. Therefore, it seems probable that the process of forming the iron(III)–sulfosalicylate complex ion involves the removal of the third hydrogen from the participating sulfosalicylate ions thus giving rise to a chelate structure like that ascribed by Babko[4] to the closely analogous iron(III)–salicylate complex ion.

The reaction for the dissociation of the iron(III)–sulfosalicylate complex ion may be written

$$Fe[O_3SC_6H_3(O)COO]_3^{-6} + 3H_2O \longrightarrow Fe^{+3} + 3[O_3SC_6H_3(OH)COO]^{-2} + 3OH^- \quad (1)$$

That three equivalents of hydroxyl ion are required for the formation of iron(III)–sulfosalicylate

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(10) A. Thiel and O. Peter, *Z. anal. Chem.*, **103**, 161 (1935).

(11) F. Lindstrand, *Svensk Kem. Tid.*, **56**, 282 (1944).

(12) H. V. Meek, Doctoral Dissertation, Iowa State College, 1950.

complex ion from iron(III) ion was confirmed by titrating a mixture of bis-(2,4-pentanediono)-iron-(III) and sulfosalicylic acid (100% excess) with sodium hydroxide solution. The vertical line in Fig. 2 is the calculated equivalence point for the reaction

$$\mathrm{Fe(C_5H_7O_2)_3 + 6HO_3SC_6H_3(OH)COOH + 12NaOH \longrightarrow Na_6Fe[O_3SC_6H_3(O)COO]_3 + 3C_5H_8O_2 + 3Na_2[O_3SC_6H_3(OH)COO]} \quad (2)$$

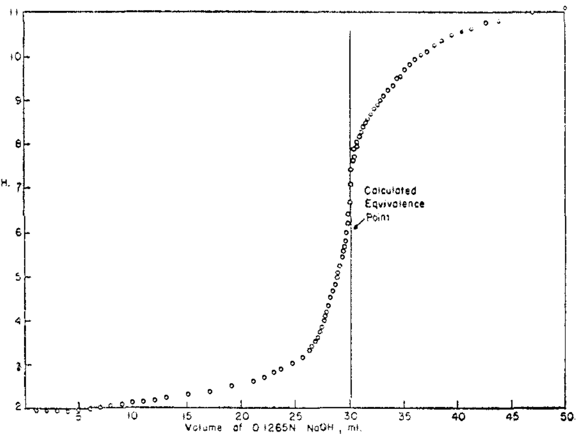

Fig. 2.—Titration of 0.316 millimole of bis-(2,4-pentanediono)-iron(III) plus 1.898 millimoles of sulfosalicylic acid.

The molar equilibrium constant, K'_1, for reaction (1) may be obtained from the approximate equation

$$(E_{1/2})_c - (E_{1/2})_s = (0.0591) \log K'_1/K'_2 - (0.1773) \log C_X - 0.1182(p\mathrm{H} - 14) \quad (3)$$

where $(E_{1/2})_c - (E_{1/2})_s$ is the difference of the half-wave potentials of the iron(III)–sulfosalicylate complex ion, $\mathrm{Fe[O_3SC_6H_3(O)COO]_3^{-6}}$, and the simple iron(III) ion, and K'_2 is the instability constant of $\mathrm{FeOH^+}$. The half-wave potential for the reduction of the simple iron(III) ion is at first approximation equal to the standard reduction potential (0.51 volt *vs.* S.C.E.) of this ion. From this reduction potential and the polarographic data in Tables I and II an average value of −33 is obtained for log K'_1/K'_2. From the data of Lindstrand[11] K'_2 is estimated to be about 10^{-9} at 25°, so that K'_1 is then 10^{-42}. In these K' values the activities of the hydroxyl ions and the molar concentrations of the other species are used.

The second molar dissociation constant, K'_{A_2}, of sulfosalicylic acid was determined by a spectrophotometric method[13] based on the fact that the molar absorbancy indexes, a_{M_1} and a_{M_2}, for $\mathrm{^-O_3SC_6H_3(OH)COOH}$ and $\mathrm{^-O_3SC_6H_3(OH)COO^-}$ are appreciably different at 317 mμ.[12] Figure 3 shows the results of this investigation. Under the experimental conditions, the values for a_{M_1} and a_{M_2} were found to be, respectively, 1568 and 708.

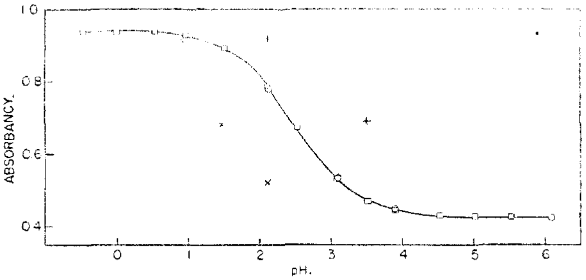

Fig. 3.—Absorbancy of sulfosalicylic acid with varying pH: sulfosalicylic acid, 6×10^{-4} *M*, $\mu = 0.10$, 0.1 *M* $\mathrm{HClO_4}$ adjusted to desired pH with NaOH, 25°. Absorbancies measured on Beckman DU spectrophotometer, $\lambda = 317.0$ mμ, band width 0.97 mμ: ○, observed points; □, calculated points for $K'_{A_2} = 3.23 \times 10^{-3}$ ($pK'_{A_2} = 2.49$); ×, points calculated for $K'_{A_2} = 3.23 \times 10^{-2}$; +, points calculated for $K'_{A_2} = 3.23 \times 10^{-4}$.

$$K'_{A_2} = \frac{a_{\mathrm{H}^+}[\mathrm{-O_3SC_6H_3(OH)COO-}]}{[\mathrm{-O_3SC_6H_3(OH)COOH}]}$$

Acknowledgments.—The authors wish to thank Mr. Richard E. Ewing and Miss Doris V. Stage for their translation of the very extensive article by Souchay and Faucherre from the French language.[8c] Acknowledgment is also made to the Ames Laboratory of the Atomic Energy Commission for underwriting the expenses for this investigation, and providing the necessary facilities for the conduct of the research.

AMES, IOWA RECEIVED OCTOBER 9, 1950

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(13) C. E. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, THIS JOURNAL, 71, 3031 (1949).