In their paper Drenan and Hill[6] give two calculated values for M in the case of hydrogen iodide adsorbed on graphite at 81.33° K. M is equal to 16.99 if the adsorption is non-localized and 2.16 if it is localized. As both these values are greater than unity the entropy of adsorption to the standard $s_0 = s_1$ must be less than the entropy of liquefaction which is an interesting and unexpected result, especially in the case of localized adsorption.

Summary

Equations are derived showing that the BET constant a_1b_2/a_2b_1 is unity only when the differential entropy of adsorption to a standard state on the surface defined by $s_0 = s_1$ (the bare fraction of the surface being equal to the fraction covered by one layer of molecules) is equal to the entropy of liquefaction of the adsorbate. It is also shown from published results that the value of a_1b_2/a_2b_1 may range at least from 10^{-5} to 10, and that the single isotherm method of determining heats of adsorption can only be used when the entropy of adsorption is known.

CAMBRIDGE, ENGLAND RECEIVED MAY 8, 1950

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

A Spectrophotometric Study of the Hydrolysis Products, Some Possible Complexes and Metal Salts of Fluoroboric Acid[1]

BY EDWARD R. SCHEFFER[2] AND ELLWOOD M. HAMMAKER

In the course of an investigation of fluoroboric acid, spectrophotometric analysis was studied as a possible method of identification and analysis of the acid, its hydrolysis products, and its compounds. An attempt was made also to determine the extent of complex formation, if any, of the fluoroborate ion and some of its hydroxy acids. In certain cases, the method of continuous variations as developed by Job[3] and improved by Vosburgh and Cooper[4] was applied in the study of possible complexes. The characteristic spectra of two hydrolysis products of fluoroboric acid have been obtained, and the general lack of any complexing tendency has been demonstrated.

Experimental

Measurements.—Light absorption measurements were made with a Beckman model DU spectrophotometer. Quartz or corex cells (1-cm.) were used, and all readings were made at room temperature.

Materials.—C. P. samples of hydrated cobalt and nickel nitrates were dissolved to give 0.1 M solutions (1) in water, (2) in 7.7 M hydrochloric acid and (3) in 42% aqueous fluoroboric acid. A 0.2 M solution of cupric sulfate was prepared from the C. P. hydrate. C. P. chromium metal was treated with 60% perchloric acid, 42% fluoroboric acid, and anhydrous $H[BF_2(OH)_2]$ to give solutions 0.03, 0.07 and 0.02 M, respectively, in chromium(III) ion. $H[BF_2(OH)_2]$ was prepared by the method of Sowa, *et al.*,[5] and $BF_3\cdot2H_2O$ was prepared by the method of Meerwein and Pannwitz.[6] Saturated aqueous solutions were prepared from technical sodium, potassium and ammonium fluoroborates. A 1 M solution of zinc fluoroborate was prepared from the pure hexahydrate. Technical lead fluoroborate solution (50.7%), purified tin(II) fluoroborate solution (47.7%) and cadmium fluoroborate solution (50.8%) were used as received.

The fluoroborate salts and solutions were very kindly furnished by the General Chemical Division, Allied Chemical and Dye Corporation.

Procedure and Results.—To investigate the possible formation of complexes between fluoroboric acid and cobalt(II) or nickel(II), respectively, three solutions were prepared for each ion as described under Materials. The nitrate salts were used in each case, because in dilute aqueous solutions the absorption is attributed to the hydrated ion and not to any complex formation with the nitrate ions. According to Job,[7] a 1 to 1 complex with the chloride ion is formed in hydrochloric acid of the concentration used. The absorption spectrum for each solution was determined, and the results obtained for cobalt are shown in Fig. 1. Similar results were obtained with nickel; in this case, however, the characteristic absorption maxima appeared at 720 and 395 mμ for the hydrated ion, and at 740 and 425 mμ for the chloride complex.

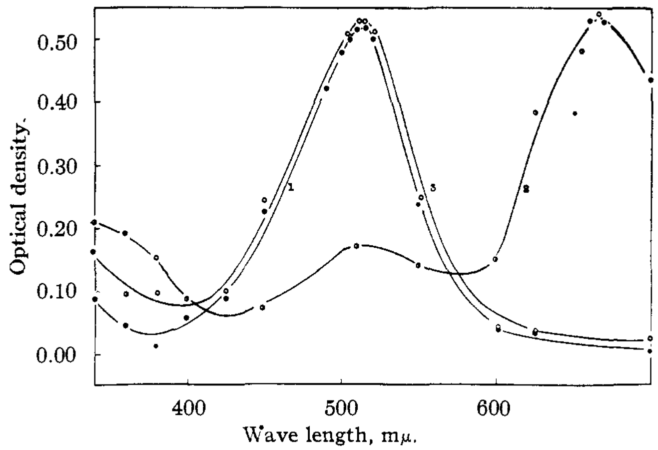

Fig. 1.—Absorption curves for cobalt(II) complexes: (1) aqueous solution, (2) hydrochloric acid solution, (3) fluoroboric acid solution.

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(1) Part of a thesis submitted by Edward R. Scheffer to Rutgers University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) National Lead Company, Titanium Division, Sayreville, N. J.

(3) Job, *Ann. chim.*, [10] **9**, 113 (1928).

(4) Vosburgh and Cooper, THIS JOURNAL, **63**, 437 (1941).

(5) Sowa, Kroeger and Nieuwland, *ibid.*, **57**, 454 (1935).

(6) Meerwein and Pannwitz, *J. prakt. Chem.*, N. F., **141**, 123 (1934).

(7) Job, *Ann. chim.*, [11] **6**, 97 (1936).

The method of continuous variations was applied to the study of a possible complex between copper and the fluoroborate ion. A series of eleven solutions was prepared from the 0.2 *M* copper sulfate and the saturated sodium fluoroborate solutions, ranging from 100% of the copper solution to 100% of the fluoroborate solution. The optical density of each solution was measured at 550 mμ, and the value *Y* was calculated for each concentration. This value represents the difference between the optical density found and the optical density that the solution would have had if there had been no reaction on mixing. The value of *Y* was the same for all of the mixtures, namely, 0.020 ± 0.003.

The method applied to copper cannot be used for chromium because of the formation of the CrF^{++} ion.[8] To study chromium, two solutions were prepared by dissolving the metal in perchloric and in fluoroboric acid. Both solutions were allowed to stand exposed to air for several days in order to ensure practically complete oxidation of chromium(II) to chromium(III). The spectrum of each solution was determined with the results shown in Fig. 2. The absorption maxima appear at the same wave lengths as found by Bose and Datta[9] for $Cr(H_2O)_6^{+++}$. Figure 2 illustrates also the data obtained from the solution of chromium(III) and $H[BF_2(OH)_2]$.

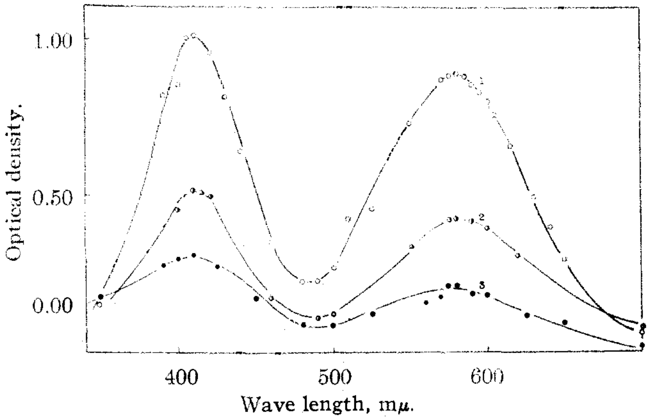

Fig. 2.—Absorption curves for chromium(III) in: (1) fluoroboric acid, (2) perchloric acid, (3) $H[BF_2(OH)_2]$.

The spectra of $H[BF_2(OH)_2]$ and of $BF_3 \cdot 2H_2O$ are shown in Fig. 3. These spectra are compared with that of concentrated fluoroboric acid. The two hydrolysis compounds had to be used as prepared because dilution with an oxy-solvent causes immediate precipitation.

In order to determine whether or not any complexing or identifying characteristics could be observed within the wave length region available, the spectra of several fluoroborates, namely, those of potassium, ammonium, zinc, lead, tin and cadmium, were measured at the concentrations indicated. None of these solutions showed a characteristic spectrum.

Discussion

No shift in absorption maxima is indicated when either cobalt or nickel is dissolved in concentrated fluoroboric acid. This observation is in contrast to the shift produced due to the formation of the chloride complex, and indicates that no complexing occurs between the fluoroborate ion and cobalt(II) or nickel(II), respectively.

According to the method of continuous variations, if a straight line with a slope of zero is obtained when the value *Y* is plotted against concentration, no formation of complexes is indicated. Hence the data for the copper sulfate–sodium fluoroborate series indicated that there is no complex formed between copper(II) and the fluoroborate ion or any of its possible hydrolysis products at these concentrations.

Similarly, no complexing of chromium(III) with fluoroborate ion is indicated. The absorption maxima for chromium in fluoroboric acid appear at the same wave lengths as those for chromium in perchloric acid, and perchlorate ions have been shown to have the least tendency to complex with tervalent ions. The same results were also obtained between chromium and $H[BF_2(OH)_2]$, and the behavior of the other hydrolysis products should be comparable because of the similarity in their structures.

Since, as shown in Fig. 3, all of the absorption by $H[BF_2(OH)_2]$ and by $BF_3 \cdot 2H_2O$ is very weak, the maxima which appear in these curves could not be detected in dilute fluoroboric acid solutions for the identification of the hydrolysis products. Fluoroboric acid shows some absorption in the ultraviolet region, but no maxima within the wave length region studied.

As in the case of the fluoroboric acid, each of the fluoroborate solutions absorbed to some extent in the ultraviolet region without reaching a maximum.

Acknowledgment.—The authors wish to thank the Rutgers Research Council which provided the fellowship that made this research possible.

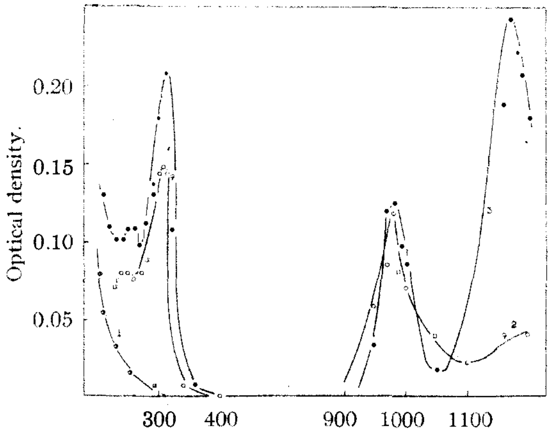

Fig. 3.—Absorption curves for (1) HBF_4, (2) $H[BF_2(OH)_2]$, (3) $BF_3 \cdot 2H_2O$.

Summary

No indication of complex formation between copper(II), nickel(II), cobalt(II) or chromium(III) with fluoroborate ion was obtained under the conditions studied. The spectral characteristics of two hydroxy-fluoroboric acids have been determined. The lack of spectral characteristics

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(8) Scheffer and Hammaker, THIS JOURNAL, **72**, 2575 (1950).

(9) Bose and Datta, *Z. Physik*, **80**, 376 (1933).

in the spectral range covered, (approximately the region from 215 to 1200 mμ), has been shown for fluoroboric acid and for several fluoroborates.

NEW BRUNSWICK, N. J. RECEIVED SEPTEMBER 3, 1949

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

Spectrophotometric Studies on Complex Formation with Sulfosalicylic Acid. IV. With Iron(III) at Higher *p*H Values

BY ROBERT T. FOLEY[1] AND ROBBIN C. ANDERSON

In an earlier article[2] it was shown that in solutions of *p*H values less than 2.4, iron(III) and sulfosalicylic acid react in a 1:1 ratio to form a violet complex. It was noted in this report and in earlier analytical studies[3] that, as the acidity decreases, the colors of the solutions shift from violet to orange, and eventually to yellow in basic solutions. This suggests formation of more than one complex, similar to those of the type FeR_2 and FeR_3 reported by Babko[4] in reaction with salicylic acid under similar conditions. The first measurements in higher *p*H ranges gave anomalous ratios of iron(III) to sulfosalicylic acid, so further investigations have now been made to obtain information on the nature of the complexes formed.

Experimental

Materials.—The iron(III) perchlorate, sulfosalicylic acid and sodium hydroxide solutions were prepared as described previously.[2]

The sodium acetate–acetic acid, ammonium acetate–acetic acid and potassium acid phthalate–potassium hydroxide buffers were prepared from reagent grade chemicals.

Apparatus and Procedure.—Measurements of *p*H were made with a Beckman *p*H meter, model G. Absorption data were taken with a Beckman model DU spectrophotometer, using a hydrogen lamp in the ultraviolet and a tungsten lamp in the visible region. This instrument was equipped with a thermostated cell holder.[5]

All measurements were at 25°. The procedure was the same as that described earlier.[2,5]

Results

Absorption in the Ultraviolet.—The absorption spectra of sulfosalicylic acid, iron(III) perchlorate and an iron(III) perchlorate–sulfosalicylic acid mixture were measured from 400 mμ down to 250 mμ. The mixture showed no distinctive bands. Its ultraviolet absorption was essentially a summation of the effects of the iron(III) perchlorate and sulfosalicylic acid. The various studies on the complex have therefore been continued using wave lengths in the visible range.

Solutions with Acetate Buffers.—To obtain further information on the ratio of iron(III) to sulfosalicylic acid in the orange and yellow solutions, the method of continuous variations[6] has been applied to measurements on solutions above *p*H 2.4. Equimolar solutions of iron(III) perchlorate and sulfosalicylic acid were mixed in varying proportions. A sodium acetate–acetic acid or ammonium acetate–acetic acid buffer solution was then added so that mixtures might be compared at the same *p*H value and also at essentially the same ionic strength.

The difference ($\bar{D}$) between the observed optical density of the iron–sulfosalicylic acid mixture in each case and that which would be shown by a solution containing the same concentration of iron(III), sulfosalicylic acid and buffer, without interaction, was then plotted against the ratio of iron(III) concentration to the total sum of iron(III) plus sulfosalicylic acid concentrations. (Correction for absorption by the acid is usually negligible.) The quantity ($\bar{D}$) is proportional to the concentration of complex formed and should show a maximum value for solutions containing iron(III) and sulfosalicylic acid in the same proportion as that in which they react to form the complex.

The location of the maxima observed for these and other types of mixtures are given in Table I.

TABLE I

METHOD OF CONTINUOUS VARIATIONS

Total molarity Fe(III) + $C_7H_6SO_6$	*p*H	Approx. ionic str., g. ions/l.	Buffer	Fe/Fe + R for max. abs.
0.0036	0.85	0.03	None	0.46–0.48
.0072	0.9	.15	None	.45– .48
.0036	2.38	.06	None	.5
.00287	4.5	.3	$NaC_2H_3O_2$	.25
.00072	4.58	.25	$NaC_2H_3O_2$	.3
.00072	6.2	.9	$NH_4C_2H_3O_2$	.1
.00144	6.35	.8	$NH_4C_2H_3O_2$	.12
.00240	5.30	.11	$KHC_8H_4O_4$	.45
.00150	7.75	.51	$NaHCO_3$	.45

Curve 3 of Fig. 1 is typical of the results with sodium acetate buffers. Curve 1 shows, for comparison, typical results for acid solution (*p*H 0.9) without buffer. In the presence of acetate buffers one could apparently obtain a

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[1] Metals Section of the Transformer and Allied Products Laboratory, General Electric Company, Pittsfield, Massachusetts.

[2] Foley and Anderson, THIS JOURNAL, **70**, 1195 (1948).

[3] *Cf.*, for example, Alten, Wieland and Hille, *Z. anorg. allgem. Chem.*, **215**, 81 (1932); Moser and Irany, *Monatsh.*, **43**, 679 (1923).

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

[5] Foley and Anderson, THIS JOURNAL, **71**, 909 (1949); *cf.* Bell and Stryker, *Science*, **105**, 415 (1947).

[6] Job, *Ann. chim.*, [10] **9**, 113 (1928).