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

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[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*, **106**, 415 (1947).

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

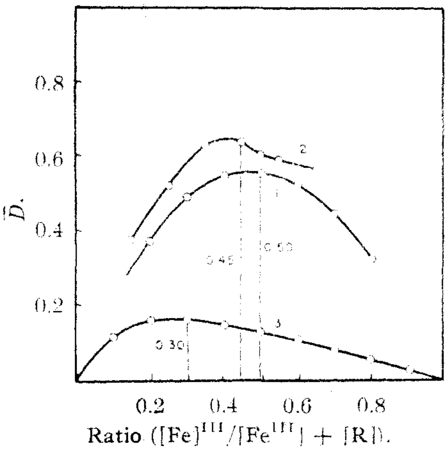

Fig. 1.

maximum at any ratio from 0.1 to 0.5 by adjusting the *p*H.

Maxima in the region of 0.25 to 0.33 could be interpreted as indicating complexes of types such as FeR_2 and FeR_3; but, as also shown in Table I, further studies at even higher *p*H values gave maxima as low as 0.1 or 0.12. These results would apparently require existence of complexes such as FeR_7 or FeR_8; but neither the chemical reactions of the ferric ion, its classical coördination number, nor its structure would indicate that such complexes might exist.

An alternative explanation of the observations might lie in the occurrence of mixtures of two or more complexes, but no mixture of FeR, FeR_2 and FeR_3 should give a maximum at a ratio as low as 0.12.

Typical absorption curves for various iron(III) and iron(III)-sulfosalicylate solutions, both in ordinary acid media (curves 1a and 1b) and in presence of sodium acetate are shown in Fig. 2. The effect of the acetate buffer itself was actually greater than that of the sulfosalicylate. This effect could introduce rather large errors into the calculated $\bar{D}$ values and might thus give rise to anomalies in the method of continuous variations.

Solutions with Other Buffers.—Tests were made with a number of other buffers to determine whether the anomalous results above were specific to solutions containing acetate. Oxalate, citrate and phosphate buffers were found to destroy the complex, but solutions containing phthalate and bicarbonate buffers showed the typical colors of iron(III)-sulfosalicylate mixtures. Phthalate buffer decreases the intensity of color of the iron(III)-sulfosalicylate complex but does not destroy it. Bicarbonate solutions became turbid by precipitation of iron(III) carbonate where iron(III) was present in relatively large excess; but such precipitation was slow enough so that absorption measurements could be made without interference.

Potassium acid phthalate-potassium hydroxide buffer was used for measurements at *p*H 5.3, with an orange complex of iron(III) and sulfosalicylate being formed. Sodium bicarbonate buffer was used at *p*H 7.75, with a yellow complex being formed. Figure 2 shows a comparison of the absorption curves of these mixtures with those for the violet complex at *p*H 2.38 and for solutions in acetate buffers.

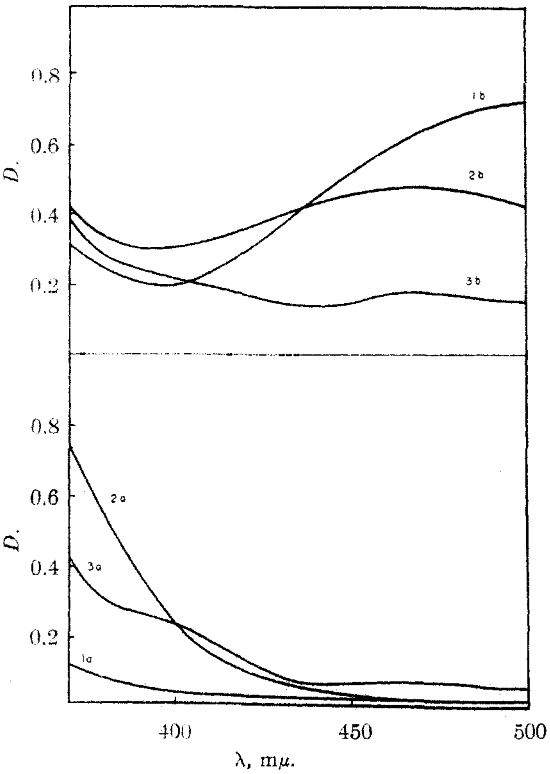

Fig. 2.—$Fe(ClO_4)_3$: 1a, 0.0072 *M*, *p*H 2.20; 2a, 0.00075 *M*, (phthalate buffer) *p*H 5.3; 3a, 0.00065 *M*, (acetate buffer) *p*H 4.63. Sulfosalicylic acid +: 1b, 0.00036 *M* Fe(III), *p*H 2.34; 2b, 0.00036 *M* Fe(III), (phthalate buffer) *p*H 5.3; 3b, 0.00072 *M* Fe(III), (acetate buffer), *p*H 4.66.

Visually these colors are the same as those in the unbuffered solutions of those using acetate buffers. Curve 2 of Fig. 1 and the data of Table I show, however, that the results from the method of continuous variations in the presence of phthalate and bicarbonate buffers resemble closely those for the acid solutions with no buffer and show no definite evidence for the existence of any other than a complex with iron(III) and sulfosalicylate in a 1:1 ratio.

This was tested further by calculations based on Job's general equation[7] for systems involving mixtures, in various proportions, of solutions of the reagents which are *not* equimolar. For a reaction

$$A + nB \rightleftharpoons AB_n$$

the equilibrium constant may be calculated from

$$K = \frac{T^n p^{n-1}[(p + n)x - n]^{n+1}}{(p - 1)^n[n - (n + 1)x]}$$

n in this equation is the same as in the formula AB_n. x is determined experimentally as the ratio of volumes of solutions of A and B which give maximum absorption when solutions of A of molarity T and of B of molarity pT are mixed. Thus if experimental values of x, p and T are known, n can be determined by assuming various values, calculating K and determining that value which will give most nearly constant values for K.

This was applied to iron(III)-sulfosalicylate mixtures in potassium acid phthalate buffer at pH 5.3, using sulfosalicylic acid solutions 3, 5 and 8 times as concentrated as the iron(III) perchlorate. The results at $p = 3$ were inconclusive because the observed x values were so close to 0.5 that calculations were impracticable. (It may be seen that if $n = 1$ and $x = 0.5$, the equation becomes indeterminate.) Results for the other solutions are given in Table II.

TABLE II

JOB'S GENERAL EQUATION

T, M	p	x	K		
			$n = 1$	$n = 2$	$n = 3$
0.0006	5	0.42	1.78×10^{-5}	9.61×10^{-8}	3.82×10^{-13}
	8	.39	2.45×10^{-5}	49.3×10^{-8}	7.95×10^{-11}

The value $n = 1$ clearly gives best results. Furthermore, it is notable that the values of the equilibrium constant calculated from these data are consistent with those reported previously[2] and with those based on use of approximate extinction coefficients (see below).

Extinction Coefficients and Equilibrium Constants.—Approximate extinction coefficients determined from the optical densities of solutions which contained a large excess of one reagent or the other, so that dissociation of the complex would be extremely small, are summarized in Table III. The values in acetate solutions are much higher than for other corresponding solutions, indicating again a specific effect of acetate.

TABLE III

EXTINCTION COEFFICIENTS

pH	Ionic str. (approx.), g. ions/l.	Buffer	Wave length for max. abs. mμ	Extinc. coeff. (approx.)
1.13	0.08		510	1440
2.38	.061		508	756
5.2	1.1	$NaC_2H_3O_2$	470	3205
5.3	0.11	$KHC_8H_4O_4$	470	1090
6.35	.8	$NH_4C_2H_3O_2$	454	3150
7.75	.51	$NaHCO_3$	430	1950

The apparent equilibrium constant

$$K = [Fe^{III}][R]/[FeR]$$

may be evaluated, using the extinction coefficient to determine the concentration of the complex. R is taken to be the total concentration of C_6H_3-$OHCOOHSO_3H$ without correction for ionization. K for the complex at pH 2.38 was found to be 1.3×10^{-5} and that for the complex at pH 5.3 in the presence of phthalate buffer was 2.2×10^{-5}. These results indicate further the similarity of the complexes in the two cases. It should be noted, of course, that the numerical values for K can at best be close approximations, because the data now available are insufficient to make accurate correction for effects of ionic strength and of possible competitive effects such as formation of undissociated acid or of ions such as $FeOH^{++}$.

Discussion

The anomalous maxima obtained in the method of continuous variations in the presence of acetate buffers are difficult to explain. However, since the acetate ion itself forms complexes with iron(III),[7] the "corrected" optical densities and the concentration ratios used are both of doubtful accuracy and the observed maxima are possibly only apparent maxima.

The results with other buffers do indicate definitely that the change, as pH is increased, from violet to orange to yellow in the color of iron(III)-sulfosalicylate mixtures—a type of change which indicates some change in the nature of the complex—does not necessarily involve in this case a change in the ratio of iron(III) to sulfosalicylate in the complex. The formation of the various sulfosalicylate ions by stepwise dissociation of the acid might give rise to complexes involving different internal structures. However, it is quite possible also that the observed changes may result from effects of still other reagents in the system, *e. g.*, OH^-. The pH ranges and colors involved, and the known tendencies of iron(III) to form $FeOH^{++}$ and similar ions, would indicate that the latter effect is a strong possibility.

For lack of sufficient details of Babko's methods of measurement and calculation of results, it is difficult to compare his results on salicylic acid complexes with those for sulfosalicylic acid. On the one hand it may be noted that the data on iron-sulfosalicylic acid solutions in acetate buffers might have led to the conclusion that complexes of the types FeR_2 and FeR_3 were formed—provided the pH range happened to be limited. On the other hand, the tendency of iron(III) ions to form sulfate complexes indicates that the introduction of the sulfonic acid might well alter the pattern of complex formation.

Acknowledgment.—The authors wish to express their appreciation to the Pan American Refining Corp. for their support of this work through a fellowship granted to one of us (R. T. F.).

Summary

Spectrophotometric studies on iron(III)-sulfosalicylate mixtures have been extended to pH values ranging up to 8. The effects of acetate,

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(7) *Cf.* Ricca and Faraone, *Gazz. chim. ital.*, **79**, 340 (1949), or *C. A.*, **43**, 8935^b (1949).

oxalate, citrate, phosphate, phthalate and bicarbonate buffers have been determined.

Attempts to determine the composition of the complex in acetate buffers gave anomalous results. Oxalate, citrate and phosphate destroyed the complex. Tests in phthalate and bicarbonate buffers indicated a 1:1 complex, up to *p*H 7.75.

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Mass Spectrometric Analysis of Low-molecular-weight Monodeutero-paraffins

BY D. P. STEVENSON AND C. D. WAGNER

The analysis of monodeutero-paraffins prepared in this Laboratory[1] (all eight of the monodeutero-alkanes, C_1–C_4) presents certain problems which have been solved successfully by the use of mass spectrometric techniques. The general applicability of these techniques has made it desirable to treat these aspects in a paper separate from that dealing with the preparation and purification of the compounds.

The mass spectrometer provides a sensitive means of detecting impurities in volatile substances, provided the impurities have molecular weights greater than the molecular weight of the substance under investigation or, more generally, are of such a nature that they produce ions not coincident in mass-charge ratio with those of the substance under investigation. In general for impurities of molecular weight less than the substance under investigation to be determinable by the ordinary mass spectrometric analytical methods, a "pure" or standard sample must be available for comparison purposes. Such standard samples of monodeuteroparaffins are not available and ordinary methods of standardization are not applicable. For the determination of olefin and ordinary (undeuterated) alkane in the deutero-hydrocarbons, special methods were devised. These methods and the results obtained are described below. No description of the detection of impurities of higher molecular weight by the mass spectrometric technique is given here since these are adequately described in the literature.[2]

Determination of Olefins.—As has been discussed in another recent paper,[1] a characteristic side reaction in the synthesis of a paraffin by hydrolysis of a Grignard reagent leads to the formation of equal amounts of olefin and undeuterated paraffin. Since certain reactions of paraffins are very sensitive to trace olefin impurities,[3] sensitive analytical methods are necessary to check the efficacy of chemical treatments employed to remove the olefins. In addition to having high sensitivity, the methods must consume a very small sample, or be non-destructive, since the deuteroalkanes are laboratory preparations prepared on small scale.

In principle, infrared absorption is applicable to this problem. Rasmussen and Brattain[4] have observed that monoölefins, in general, have very strong characteristic absorption bands in the region 10–12.5 μ where the corresponding paraffins have relatively very weak absorption. To the extent that monodeutero-paraffins do not differ significantly in their absorption in this region from that of the ordinary paraffins, infrared absorption measurements should afford considerable sensitivity to detection of olefins. However, for even the simple monodeutero-paraffins considered in this paper, it is found that characteristic absorption bands do appear in this region (10–12.5μ) which render the method inapplicable in the absence of authentic standards for comparison.[5]

Since the infrared method of olefin detection was found to be inapplicable, it was deemed desirable to develop a potentially absolute mass spectrometric method for olefin estimation in both paraffins and monodeutero-paraffins. This method is described in the following paragraphs.

Owing to the nature of the ionization process, the appearance potential of the ion-fragment, $C_nH_{2n}^+$, in the mass spectrum of the paraffin, C_nH_{2n+2}, or $C_nH_{2n+1}D$, is necessarily 1.1 to 1.4 ev. greater than the appearance potential of the ion, $C_nH_{2n}^+$, in the mass spectrum of the olefin, C_nH_{2n}. This follows from the fact that the appearance potential of $C_nH_{2n}^+$ in the mass spectrum of C_nH_{2n+2} or $C_nH_{2n+1}D$ is greater than or equal to the ionization potential of the olefin, C_nH_{2n}, plus the heat of dehydrogenation of the paraffin, C_nH_{2n+2} or $C_nH_{2n+1}D$, while the appearance potential of $C_nH_{2n}^+$ in the mass spectrum of the olefin C_nH_{2n} is approximately equal to the ionization potential of the olefin, C_nH_{2n}. The heats of dehydrogenation of the C_2–C_4 paraffin lie between +27 and +33 kcal./mole or 1.2–1.4 ev.[6] Thus, it should be possible to measure the

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[1] C. D. Wagner and D. P. Stevenson, THIS JOURNAL, **72**, 5784 (1950). The deuterium oxide used in the syntheses was supplied by Stuart Oxygen Company on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

[2] H. W. Washburn, H. F. Wiley and S. M. Rock, *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943).

[3] R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642, 2518 (1946).

[4] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1940).

[5] The authors are indebted to various colleagues, particularly Dr. F. S. Mortimer for infrared absorption measurements on the various C_1–C_4 monodeutero-paraffins. A detailed account of the infrared absorption of these substances will be published at a later date.

[6] Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 65, 876 (1935)