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

Spectrophotometric Studies on Complex Formation with Sulfosalicylic Acid. V. With Aluminum(III) and Nickel(II)

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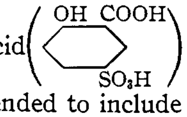
The reaction between aluminum(III) and sulfosalicylate ions has been studied by use of the 1:1 copper(II) complex with sulfosalicylate as an indicator. In the *p*H range in which such measurements can be made, aluminum(III) and sulfosalicylate were found to react in a 1:1 ratio. Spectrophotometric measurements show that nickel(II) and sulfosalicylate ions react in a 1:1 ratio between *p*H 5 and 9 to form a complex. There are some indications of one or more different complexes forming above *p*H 7, but evidence for these is not conclusive from the spectrophotometric data.

A series of experimental studies of the colored complexes formed by sulfosalicylic acid



with metal ions[1] has now been extended to include reactions with aluminum(III) ions and nickel(II) ions.

The aluminum(III) does not form a visibly colored complex, but was chosen for study because Moser and Irany[2] have used sulfosalicylic acid to prevent precipitation of aluminum(III). Furthermore, aluminum is known to form complexes similar to those of iron(III) with malic,[3] tartaric[3,4] and salicylic[5] acids and with 2,3-dihydroxynaphthalene.[6] Complex formation between aluminum and ions such as Cl^-, $SO_4^=$ and $C_2O_4^=$ has been reported recently.[7] Reaction of aluminum with 8-hydroxyquinoline-5-sulfonic acid has been studied by measuring the disappearance of color of the complex of iron(III) with this compound.[8]

Nickel(II) is of interest in these studies as a member of the same transition series as iron and copper.

Experimental

Materials.—Aluminum^{III} perchlorate was prepared by dissolving hydrated aluminum(III) chloride in perchloric acid solution and boiling until the solution no longer gave a positive test for chloride ion.

Nickel(II) sulfate was prepared by recrystallizing the salt (J. T. Baker Analyzed).

The sulfosalicylic acid, copper(II) sulfate and iron(III) perchlorate were prepared as described earlier.[1] Reagent grade sodium hydroxide was used where needed to adjust to a desired *p*H.

Apparatus and Procedure.—The apparatus and procedures were the same as those already described.[1] Spectrophotometric measurements were made with a Beckman model DU spectrophotometer which was equipped with a thermostated cell holder. *p*H determinations were made with a Beckman model G *p*H meter.

Results

Reaction with Al(III). Qualitative Tests.—Tests with aluminum(III) perchlorate solution and with solutions containing aluminum(III) perchlorate and sulfosalicylic acid showed that precipitation of aluminum(III) hydroxide occurs at definitely higher *p*H values in the presence of sulfosalicylic acid than with aluminum(III) perchlorate alone.

Aluminum(III) perchlorate was found to decrease the color from the complex in mixtures containing the copper(II) sulfosalicylate complex of type CuR. Tests against the CuR_2 complex could not be made satisfactorily because of the strong tendency toward precipitation of aluminum(III) hydroxide in the high *p*H ranges (above 8) involved. Figure 1 shows typical absorption curves for copper(II) sulfate; for copper(II) sulfate and sulfosalicylic acid at *p*H 4.01; and for a copper(II) sulfate, sulfosalicylic acid and aluminum perchlorate mixture at *p*H 3.97. All reagents were 0.036 *M* in concentration.

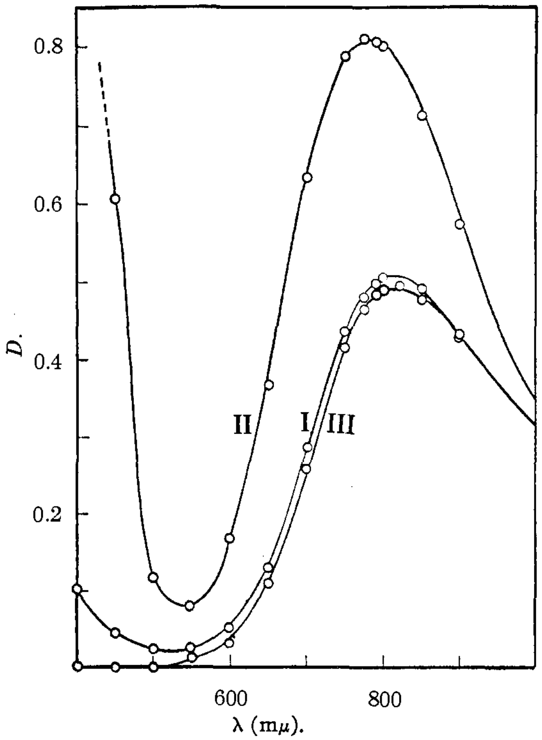


Fig. 1.—All components 0.0036 *M*, *p*H 4: I, copper(II)-sulfosalicylate + aluminum(III); II, copper(II)–sulfosalicylate; III, copper(II).

Tests with nickel(II) sulfate–sulfosalicylic acid mixtures gave no conclusive evidence of an aluminum(III) complex; but the *p*H range (about 4) necessary to avoid precipitation of aluminum(III) hydroxide was low enough so that the nickel(II) sulfosalicylate complex was probably largely dissociated (see below).

Addition of aluminum(III) perchlorate to the violet iron(III)–sulfosalicylate complex also gave no appreciable effect. However, later results showed that the aluminum(III) complex is weak enough so that the aluminum cannot compete successfully with the iron at comparable concentrations.

Determination of Nature of the Complex.—To determine the nature of the complex formed, a

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[1] R. T. Foley and R. C. Anderson, THIS JOURNAL, **70**, 1195 (1948); **71**, 909 (1949); **72**, 5609 (1950); S. E. Turner and R. C. Anderson, *ibid.*, **71**, 912 (1949).

[2] L. Moser and E. P. Irany, *Monatsh.*, **43**, 679 (1922).

[3] J. L. Delsal, *Compt. rend.*, **202**, 1589 (1936); J. L. Delsal, *J. chim. phys.*, **35**, 350 (1938); O. Quadrat and J. Korecky, *Collection Czech. Chem. Commun.*, **2**, 169 (1930).

[4] G. Spacu and E. Popper, *Kolloid Z.*, **103**, 19 (1943).

[5] G. N. Burrows and I. W. Wark, *J. Chem. Soc.*, 222 (1928).

[6] R. Weinland and H. Seuffert, *Arch. Pharm.*, **266**, 455 (1928).

[7] S. Lacroix, *Ann. chim.*, [12] **4**, 5 (1949).

[8] J. Molland, *Ayhandl. Norske Videnskaps.-Akad. i. Oslo I, Mat.-Naturv. Klasse*, **6**, 3 (1941); *cf. Chem. Zentr.*, **113**, I, 1338 (1942).

series of quantitative measurements were made of the effect of aluminum(III) on the copper(II) sulfosalicylate.

The Job method of Continuous Variations[9] was applied by mixing in varying proportions equimolar solutions of aluminum(III) perchlorate and of sulfosalicyclic acid—the latter containing an equal concentration of copper(II) as an "indicator" ion. The difference $[\bar{D}]$ between the observed optical densities of each mixture and the value which would have been obtained had no reaction with the aluminum(III) occurred was calculated. This was plotted against the ratio of the aluminum concentration to the total concentration of aluminum and sulfosalicylic acid. The presence of copper(II) causes these $\bar{D}$ values to be negative, but should not interfere with the method itself. Results for solutions with total molarity of 0.01 for aluminum(III) plus sulfosalicylic acid at *p*H 4.1, and temperature of 30° are shown in Fig. 2. The maxima all indicate that a complex containing aluminum and sulfosalicylate in a 1:1 ratio is formed. For solutions of total molarity 0.02, the maxima for curves plotted as in Fig. 2 were shifted slightly to the left, but there is no definite evidence of any other complex.

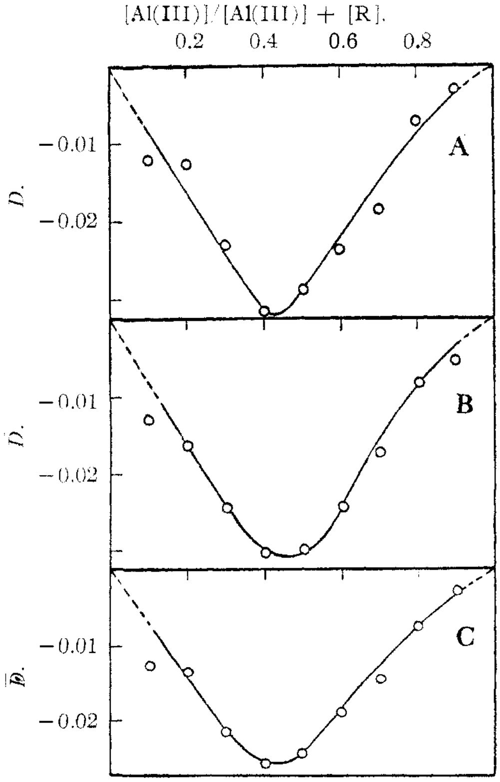

Fig. 2.—[Al(III)]/[Al(III)] + [R] *vs.* *D*: A, 700 mμ; B, 775 mμ; C, 820 mμ.

The ratio indicated above was checked by calculations of the concentrations of the various species in the mixtures. If the aluminum(III) sulfosalicylate complex is taken to be colorless, the optical density of any mixture for a 1-cm. light path can be expressed as

$$D = \epsilon_1 c_1 + \epsilon_2 c_2$$

where the ϵ_1 and ϵ_2 designate extinction coefficients of copper(II) and the copper(II) sulfosalicylate complex, respectively, and the c_1 and c_2, concentrations.

The extinction coefficients for copper(II) sulfate can readily be measured, and, by successive approximations, the extinction coefficients and equilibrium constant for the complex can be determined. Table I shows the results of such calculations. These are in good agreement with the values reported previously.

TABLE I

EXTINCTION COEFFICIENTS AND EQUILIBRIUM CONSTANT FOR COPPER(II) SULFOSALICYLATE COMPLEX

λ, mμ	ε	K_1, moles/l.
700	14.7	$2.1 \pm 0.25 \times 10^{-3}$
775	20.0	$2.4 \pm .8$
820	18.5	$2.2 \pm .2$
		Best av. $= 2.2 \times 10^{-3}$

These values may then be used for mixtures with or without aluminum(III) perchlorate as well as copper(II) and sulfosalicylate, where

$$D = \epsilon_1[m - x] + \epsilon_2 x$$

Here x is the concentration of the complex CuR and m is the original concentration of copper(II) and of sulfosalicylic acid. Then $[m - x]$ denotes the actual concentration of copper(II) ions in a given mixture. Since equal concentrations of copper(II) and sulfosalicylic acid are used, the difference between $[m - x]$ values in the presence and in the absence of aluminum(III) is a measure of the amount of sulfosalicylic acid reacting to form the complex. Table II shows the results of these calculations.

TABLE II

REACTION WITH Al^{III}

x, mole/l.	$(m - x)$, mole/l. Without Al(III)	With Al(III)	$C_6H_6SO_6$ in AlR_n	$\frac{Al(III)}{Al(III) + C_7H_6SO_6}$
0.0055	0.0025	0.0040	0.0015	0.2
.0038	.0032	.0050	.0018	.3
.0033	.0027	.0050	.0023	.4
.0027	.0023	.0049	.0026	.5
.0017	.0023	.0040	.0017	.6

These results also show that maximum reaction occurs at equal concentrations of aluminum(III) and sulfosalicylic acid and that the complex is of the type AlR. For ratios above 0.6, no consistent results could be obtained. (The reason for this is discussed below.) For the *p*H ranges used here, R is probably $^{-}SO_3C_6H_3OHCOO^{-}$; but data were not obtainable on reaction at low *p*H, so the possibility of reaction with $^{-}SO_3C_6H_3OHCOOH$ cannot be excluded.

Equilibrium Constant.—The apparent equilibrium constant

$$K_2 = \frac{[Al(III)][R]}{[AlR]}$$

can be evaluated from the data of Tables III and IV and the equations below. R designates simply the total concentration of sulfosalicylic acid, without correction for ionization. (The relatively small amounts of free sulfosalicylic acid present in

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(9) P. Job, *Ann. chim.*, **11**, 97 (1936).

such mixtures will be almost completely dissociated to $^{-}SO_3C_6H_3OHCOO^{-}$.)

$$c_3 = \frac{K_1x}{[m - x]}$$

$$y = m - x - c_3$$

$$K_2 = \frac{[n - y]c_3}{y}$$

where K_1K_2, x and $m - x$ are as designated above; c_3 = equilibrium concentration of sulfosalicylic acid in the mixture; n = original concentration of aluminum(III); and y = concentration of complex AlR.

It is evident that the effects of experimental errors will be cumulative in such calculations and the results cannot be highly accurate and precise; but they do give an approximate value of 5×10^{-4} for the constant.

This value is consistent with experimental results in that it can be used to show that, when the ratio in Table IV exceeds 0.6, the concentration of copper complex becomes so low that its effect is within experimental error, and the calculations no longer have significance.

Furthermore, calculations made with this equilibrium constant for the aluminum complex show that the effects of added aluminum(III) perchlorate on the violet iron(III) sulfosalicylate complex would be so small as to be within experimental error of the absorption measurements. This explains the lack of any observed effect in the tests with iron(III) solutions.

Reaction with Ni^{II}

Qualitative Tests.—The visible color of solutions changes to yellow-green when sulfosalicylic acid is added to neutral solutions of nickel(II) sulfate. Figure 3 shows a comparison of typical absorption curves for nickel(II) sulfate (0.07 *M*) alone and in the presence of sulfosalicylic acid (0.07 *M*). Tests with mixtures containing sulfuric acid in place of the sulfosalicylic acid gave the same results as curve 2, within experimental error—showing that the color effect observed is caused by the sulfosalicylic acid.

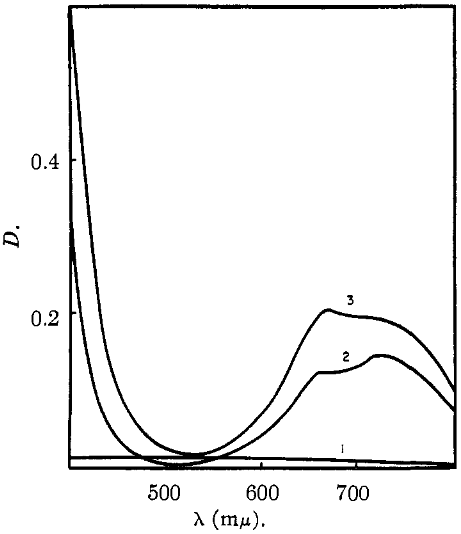

Fig. 3.—1, 0.07 *M* $C_7H_6SO_6$; 2, 0.07 *M* $NiSO_4$; 3, 0.07 *M* $NiSO_4$ + 0.07 *M* $C_7H_6SO_6$.

The complex formed readily, essentially within two minutes, but with a little increase in color being detectable up to 50 minutes. Thereafter, no appreciable change was observed in several hours. Temperature changes within ordinary ranges had relatively little effect. Measurements over a range of 28–34° showed a slight increase in optical density, but the increase was almost within the range of experimental error.

The color of the solutions was sensitive to *p*H. Below *p*H 5 no appreciable variation from the color of Ni(II) was detectable. Above that *p*H, with equivalent concentrations of nickel and sulfosalicylate ions (0.035 *M*), the color increased until *p*H 7 was reached and then stayed essentially the same until precipitation of the nickel occurred. With excess sulfosalicylic acid present, the optical density continued to increase beyond *p*H 7 and even to some extent beyond *p*H 9.

These solutions are clear and show no precipitate on centrifuging; but it should be noted that with slightly greater Ni(II) concentrations, in the range 0.04–0.05 *M*, similar solutions could be obtained at high *p*H values whose color was not highly reproducible and which on occasion formed precipitates on standing. At the higher *p*H values—especially above *p*H 8—it is difficult, therefore, to eliminate the possibility of formation of clear colloidal suspensions of $Ni(OH)_2$, perhaps stabilized by sulfosalicylate.

Nature of the Complex.—The Job method of Continuous Variations was used to study the nature of the complex. Optical densities were determined for a series of solutions of constant total molarity containing varying proportions of nickel(II) and sulfosalicylate. The difference $[\bar{D}]$ between these values and those which would have been obtained if no reaction occurred is plotted against the ratio of nickel(II) concentration to the total molarity. Figure 4 (curves I and II) shows typical results at 400 mμ for solutions of total molarity 0.096 at *p*H 6.6 and for solutions of total molarity 0.080, at *p*H 7.5. In the latter case precipitation occurs in mixtures at ratios above 0.6. Similar indications of complex formation were obtained at 725 mμ, as shown in curve III, although the variation in absorption is less.

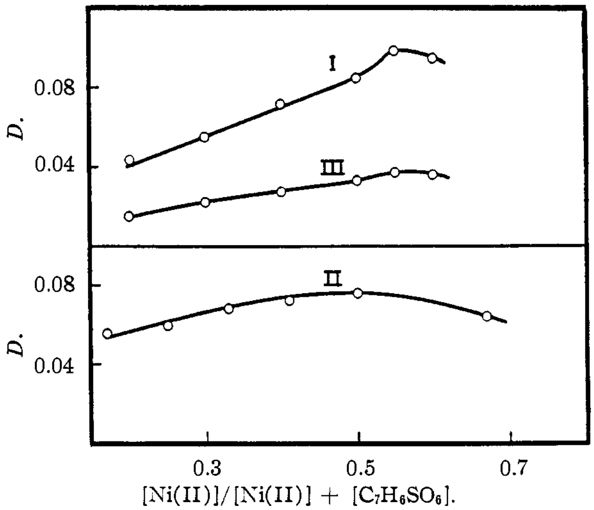

Fig. 4.—I, $[Ni(II)] + [C_7H_6SO_6] = 0.080$, *p*H 7.5, λ = 400 mμ; II, $[Ni(II)] + [C_7H_6SO_6] = 0.096$, *p*H 6.6, λ = 400 mμ; III $[Ni(II)] + [C_7H_6SO_6] = 0.080$, *p*H 7.5, λ = 725 mμ.

These curves indicate that maximum reaction occurs at a ratio of 0.50–0.55 and thus that the complex contains nickel(II) and sulfosalicylate in a 1:1 ratio and is of the type NiR or $[NiR]_n$.

In addition to the complex formation indicated by the above results, this system may involve stepwise dissociation equilibria of the sulfosalicyclic acid; and other reactions of the nickel ion, particularly with OH^-. Data are available for determining the relative importance of these equilibria in various solutions, although it is not practicable to make from these any accurate calculation of final *equilibrium* concentrations of the various ionic species in a mixture of a nickel salt and sulfosalicylic acid.

The first ionization constant for the acid is close to that for the acid sulfate ion, about 10^{-2}, and that for the second step has been found to be 1.07×10^{-3} in the range of ionic strengths used here.[10] The constant for ionization of the phenolic group may be taken to be about 10^{-13}, as in the second dissociation for salicylic acid. Vesterberg,[11] Kullgren[12] and Denham[13] have reported various data on the hydrolysis of nickel salts, indicating values ranging from 4×10^{-10} to 3×10^{-6} for K for formation of $NiOH^+$. Calculations from the above data at different *p*H values show that the first dissociation of the acid is almost complete at *p*H 2 and the second dissociation at *p*H 4. Dissociation of the phenolic group is not likely below *p*H 10, and $NiOH^+$ is a minor factor below *p*H 8. Thus the variation of color with *p*H for mixtures containing equal molar concentrations of nickel and sulfosalicylate is consistent with formation of a complex by reaction of Ni^{++} and $^-SO_3C_6H_3[OH]COO^-$ ions. These data do not, of course, show the actual structure of that complex.

The increasing color above *p*H 7 in the presence of excess sulfosalicylic acid suggests further reaction to form a complex with a sulfosalicylate: nickel ratio of 2:1 or higher. However, reactions involving hydroxide or a different linkage must also be considered. When excess nickel(II) was added to a fixed amount of sulfosalicylic acid solution which had been adjusted to various initial *p*H values and the mixtures were diluted to constant volume, a larger drop in *p*H was caused by the added Ni(II) in the higher *p*H ranges than in the lower. Since a large excess of Ni(II) was used, no complex above a 1:1 ratio should be expected. The pronounced effect of the Ni^{++} in the later solutions might involve reaction with the phenolic group. However, the magnitude of the effect and the general behavior of the complex and of sulfosalicylic acid indicate that a nickel–hydroxide complex or the formation of colloidal nickel hydroxide are also likely, and these could occur in the same region as the color changes with *p*H.

Extinction Coefficient and Dissociation Constant.—The relatively low extinction coefficient for the complex indicated in Fig. 4 and the difficulties resulting from precipitation of nickel(II) hydroxide introduce sufficient experimental error into the optical density measurements so that accurate evaluation of the extinction coefficient and equilibrium constant is not practicable.

For solutions of varying nickel(II) content, D was found to be essentially proportional to the concentration. This suggests that reaction is almost complete; and that the optical density is essentially that of the complex. Data for such solutions indicated a value of 9.5 as a reasonable average for the extinction coefficient. Using this extinction coefficient, one can calculate the dissociation constant for the complex. For solutions in the *p*H range 7.5–7.6, where the sulfosalicylic acid may reasonably be considered to be in the form of $R^{=}$ and hydrogen ions, values in the region of 4×10^{-5} were obtained.

Using these values of the extinction coefficient and equilibrium constant, optical density values were calculated and found to be in reasonable agreement with observed values; but it must be noted that the range of experimental error was large enough so that other constants in the same general range might have been used to get similar results. Conclusive determination of the constants is, therefore, not yet possible.

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