[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Composition and Stability of 5-Sulfosalicylate Complexes of Beryllium and Copper[1]

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Spectrophotometric studies of the beryllium–5-sulfosalicylate system indicate the presence of two complexes: one predominating at *p*H 5.2 and another predominating at *p*H 8.0. Job's method of continuous variations showed that at *p*H 5.2 the ratio of beryllium to 5-sulfosalicylate in the predominant complex is 1:1. Evidence is presented that the phenolic proton of 5-sulfosalicylic acid is displaced upon formation of either the 1:1 or the 1:2 complex. The stability constants of the beryllium–5-sulfosalicylate complexes were calculated spectrophotometrically and by Bjerrum's method. The log k values were found to be $\log k_1 = 11.46$, $\log k_2 = 8.62$ and $\log k_1 = 11.50$, $\log k_2 = 8.84$, respectively. The stability constants of the two known copper–5-sulfosalicylate complexes were calculated by Bjerrum's method and the log k values were found to be $\log k_1 = 9.27$ and $\log k_2 = 6.64$.

Introduction

Although the metal complexes of 5-sulfosalicylic acid (H_3SSA) have been investigated by many authors, the stability constants of most of these complexes have not been reported.[2] Meek and Banks[3] have reported the formation of a 1:2 complex of beryllium with H_3SSA in the *p*H range 9–11 and have calculated its dissociation constant. The dissociation constants for some beryllium salicylates[4] have been reported.

The stability constants of some salicylate[5] and 5-sulfosalicylate[6] complexes of copper[7] also have been reported.

The present investigation was undertaken to calculate the step-wise stability constants for the 5-sulfosalicylate complexes of both beryllium and copper.

Experimental Work

Reagents.—All chemicals were of reagent-grade quality and were further purified where necessary. As iron[8] forms a colored complex with 5-sulfosalicylic acid, it was necessary to select only those lots of reagents in which the iron content was negligible.

Iron-free 5-sulfosalicylic acid was obtained by the method used by Ågren.[9] A solution of the monosodium 5-sulfosalicylate was passed through a cation-exchange resin (Dowex 50) in the hydrogen cycle to yield pure 5-sulfosalicylic acid. A stock solution of 5-sulfosalicylic acid was standardized by a potentiometric titration with standard sodium hydroxide solution.

Beryllium sulfate was prepared by adding an excess of concentrated sulfuric acid to triply sublimed beryllium basic acetate. Beryllium sulfate which separated out was washed with cold water and alcohol and recrystallized from water. The final product was $BeSO_4{\cdot}4H_2O$. Solutions of beryllium sulfate were made by direct weighing.

A stock solution of copper sulfate was standardized by titration with standard ethylenediaminetetraacetic acid (EDTA) solution with murexide as an indicator in ammoniacal solution.[10]

Apparatus and Procedure.—A Beckman model G *p*H meter with extension glass and calomel electrodes was used and was calibrated against standard Beckman buffers. All *p*H readings were corrected for changes in the volume of the solution during the potentiometric titrations.

A Leeds & Northrup model 4866 conductivity bridge was used for the conductivity measurements.

All titrations were carried out in a 250-ml. beaker equipped with a magnetic stirrer and in an atmosphere of nitrogen. Measurements were made at 25°. The ionic strength of all solutions was adjusted to 0.1 with sodium perchlorate, unless otherwise stated.

A Cary model 14 recording spectrophotometer and a Beckman model DU spectrophotometer and silica 1.0-cm. and 2-mm. slug cells were used for the spectrophotometric studies of the beryllium complexes.

The experimental method consisted of potentiometric titration of 5-sulfosalicylic acid in the absence and in the presence of the metal ions being investigated. The beryllium complexes were also investigated spectrophotometrically.

Beryllium–5-Sulfosalicylate Complexes

The Effect of *p*H.—Figure 1 shows the variation in absorbance with *p*H of solutions 1.0×10^{-3} M in H_3SSA (curve 1), 1.0×10^{-3} M in H_3SSA and 1.0×10^{-3} M in $BeSO_4$ (curve 2) and 1.0×10^{-3} M in H_3SSA and 0.5×10^{-3} M in $BeSO_4$ (curve 3), where H_3SSA is $HO_3S{-}C_6H_3OH{\cdot}COOH$. The absorbances were measured at the optimum wave length[8] of 317 mμ. The absorbance of 5-sulfosalicylic acid (curve 1) decreases as the *p*H is increased to about 4, is almost constant in the *p*H range 4.0–9.0 and increases at higher *p*H values. Complex formation begins after *p*H 2.0, as is indicated by a sharp rise in absorbance (curve 2) up to *p*H 6.0, after which it increases slowly, becoming almost constant beyond *p*H 8.0. In solutions of *p*H 7.1 and above, part of the beryllium precipitated as $Be(OH)_2$. As the ratio of beryllium to H_3SSA is 1:1, the complex formed in the *p*H range 2.0–6.0 may be a 1:1 complex

$$Be^{++} + HSSA^{-2} \rightleftharpoons BeSSA^{-} + H^{+} \qquad (1)$$

where $HSSA^{-2}$ is the $^{-}O_3S{\cdot}C_6H_3OHCOO^{-}$ ion. This complex then changes to a more stable 1:2 complex above *p*H 7.0, at which time half of the beryllium precipitates as $Be(OH)_2$.

$$2BeSSA^{-} + 2OH^{-} \rightleftharpoons Be(SSA)_2^{-4} + Be(OH)_2 \qquad (2)$$

A similar result was reported by Varma and Mehrotra[11] with beryllium–salicylate complexes in which case the precipitate was analyzed for beryllium. Martell, *et al.*,[12] also have observed that in

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[1] Contribution No. 764. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal–Ion Complexes, with Solubility Products of Inorganic Substances. Part I: Organic Ligands," Special Publication No. 6, The Chemical Society, London, 1957, Table 260, p. 56.

[3] H. V. Meek and C. V. Banks, THIS JOURNAL, **73**, 4108 (1951).

[4] V. K. Zolotukhin, *Dopovidi L'viv. Dershav. Univ. im. I. Franka*, **7**, No. 3, 209 (1957); *C. A.*, **52**, 19638*h* (1958).

[5] A. K. Babko, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 443 (1947) (in Russian).

[6] S. E. Turner and R. C. Anderson, THIS JOURNAL, **71**, 912 (1949).

[7] A. M. Vasil'ev and V. M. Gorokhovskiĭ, *Uchenye Zapiski Kazan. Univ.*, **113**, No. 8, 65 (1953); *C. A.*, **50**, 9925*d* (1956).

[8] R. T. Foley and R. C. Anderson, THIS JOURNAL, **70**, 1195 (1948).

[9] A. Ågren, *Acta Chem. Scand.*, **8**, 266 (1954).

[10] G. Schwarzenbach, "Complexometric Titrations," Interscience Publishers, Inc., New York, N. Y., 1957, p. 82.

[11] I. D. Varma and R. C. Mehrotra, *J. Indian Chem. Soc.*, **35**, 381 (1958).

[12] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, THIS JOURNAL, **79**, 3036 (1957).

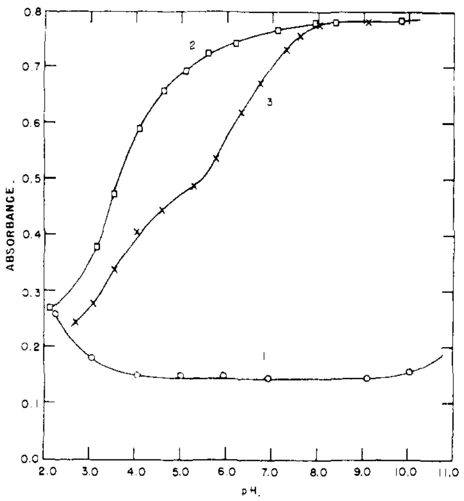

Fig. 1.—Effect of pH on absorbance at 317 mμ: curve 1, 1.00 × 10^{-3} M in H_3SSA; curve 2, 1.00 × 10^{-3} M in H_3SSA and 1.00 × 10^{-3} M in $BeSO_4$; curve 3, 1.00 × 10^{-3} M in H_3SSA and 0.50 × 10^{-3} M in $BeSO_4$.

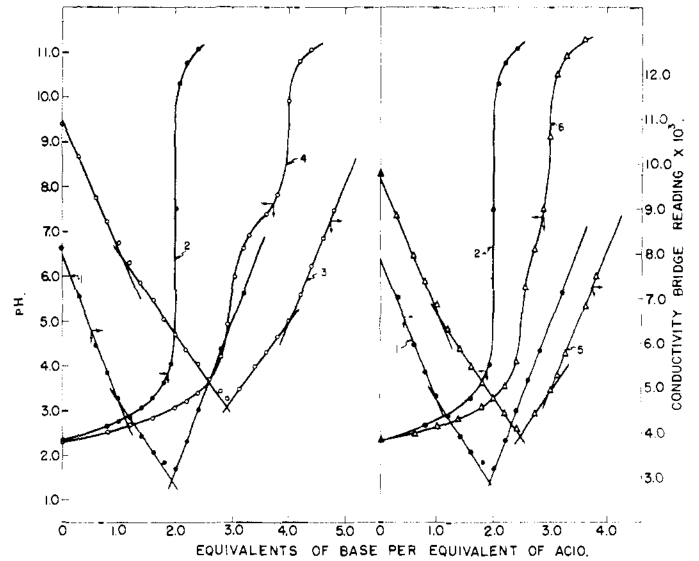

Fig. 2.—Conductometric and potentiometric titrations of 5-sulfosalicylic acid: curves 1 and 2, 3.33 × 10^{-3} M in H_3SSA; curves 3 and 4, 3.33 × 10^{-3} M in H_3SSA and 3.33 × 10^{-3} M in $BeSO_4$; curves 5 and 6, 3.33 × 10^{-3} M in H_3SSA and 1.66 × 10^{-3} M in $BeSO_4$.

certain cases the existence of a highly stable 1:2 chelate resulted from disproportionation of the 1:1 chelate, with simultaneous precipitation of half of the metal in the form of its hydroxide.

Curve 3 shows a break at about pH 5.5, which indicates the formation of a 1:1 complex, which then changes to a 1:2 complex as the pH is increased. The formation of the 1:2 complex is complete at pH 8.0 as evidenced by the fact that the absorbance remains constant above this pH. Curves 2 and 3 coincide above pH 8.0 because the same concentrations of the 1:2 complex are present.

Stoichiometry.—The Vosburgh and Cooper[13] extension of Job's[14] method of continuous variations was used to study the composition of the beryllium-5-sulfosalicylate complex at pH 5.15.

Solutions were prepared in which the sum of the concentrations of total beryllium and total 5-sulfosalicylate was 4.0 × 10^{-4} M. All of these solutions were 1.0 × 10^{-2} M in sodium acetate-acetic acid buffer and had pH values ranging from 5.12 to 5.17 as adjusted with sodium hydroxide. The solutions were then scanned on the Cary spectrophotometer and Job's plots were constructed at different wave lengths within the range 282 to 317 mμ. The average value of $[Be^{++}]/[Be^{++}] + [HSSA^{-2}]$, obtained from the maxima and minima was 0.49 ± 0.01, from which it was concluded that the complex formed at pH 5.15 has the mole ratio of beryllium to 5-sulfosalicylate of 1:1. It has been shown by Meek and Banks[3] that in the pH range 9–11 the mole ratio of beryllium to 5-sulfosalicylate is 1:2.

Displacement of Phenolic Proton.—To explain the effect of pH on the formation of beryllium-5-sulfosalicylate complexes, it was assumed that the phenolic proton of the 5-sulfosalicylic acid is displaced during the complex formation. The following experiments justify these assumptions.

Figure 2 represents the titration of solutions 3.33 × 10^{-3} M in H_3SSA (curves 1 and 2), 3.33 × 10^{-3} M in $BeSO_4$ and 3.33 × 10^{-3} M in H_3SSA (curves 3 and 4) and 1.66 × 10^{-3} M in $BeSO_4$ and 3.33 × 10^{-3} M in H_3SSA (curves 5 and 6) with sodium hydroxide. The titrations were followed by observing the change in conductivity (curves 1, 3 and 5) and pH (curves 2, 4 and 6) of the solutions. Curve 1, for 5-sulfosalicylic acid, shows two breaks at about a = 1 and a = 2, where a represents the equivalents of base per equivalent of acid. The third (phenolic) proton of 5-sulfosalicylic acid is not titrated under the experimental conditions. Curve 2 shows only one inflection at a = 2.

Curve 3, for a solution containing a 1:1 ratio of beryllium sulfate to 5-sulfosalicylic acid, shows three breaks at about a = 1, a = 3 and a = 4, which corresponds to the replacement of the sulfonic proton, the formation of $BeSSA^-$ and the formation of $Be(SSA)_2^{-4}$ and $Be(OH)_2$ above pH 7.0 (equation 2), respectively. Curve 4 shows only two inflections, the first at a = 3 and the second at a = 4, which can be explained by the same reactions as postulated for curve 3. Both conductivity and pH curves indicate that the phenolic proton is displaced during the formation of the 1:1 beryllium-5-sulfosalicylate complex in the pH range 4.0 to 5.5. Schubert, *et al.*,[15] have postulated that in the acidic region (pH 3.6) the uncharged complex BeHSSA is the predominant species. It can be seen from curve 4, Fig. 3, that at pH 3.6, about 82% of the phenolic proton of 5-sulfosalicylic acid has been displaced through complex formation.

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(13) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

(14) P. Job, *Ann. chim.* (*Paris*), [10] **9**, 113 (1928).

(15) J. Schubert, A. Lindenbaum and W. Westfall, *J. Phys. Chem.*, **62**, 390 (1958).

It is more probable that the complex, at that *p*H, is present as Be-SSA$^-$ species.

Curve 5, for a solution containing a 1:2 ratio of beryllium sulfate to 5-sulfosalicylic acid, shows three breaks at about $a = 1$, $a = 2.5$ and $a = 3$, which corresponds to the replacement of the sulfonic proton, formation of BeSSA$^-$ and the formation of Be(SSA)$_2^{-4}$, respectively. Curve 6 shows only two inflections, the first at $a = 2.5$ and the second at $a = 3$, which is in complete agreement with the reactions postulated for curve 5.

These results are similar to those obtained by spectrophotometric measurements demonstrating that at about *p*H 5.0, the 1:1 beryllium-5-sulfosalicylate complex is formed which changes to the 1:2 complex at *p*H values above 8.0.

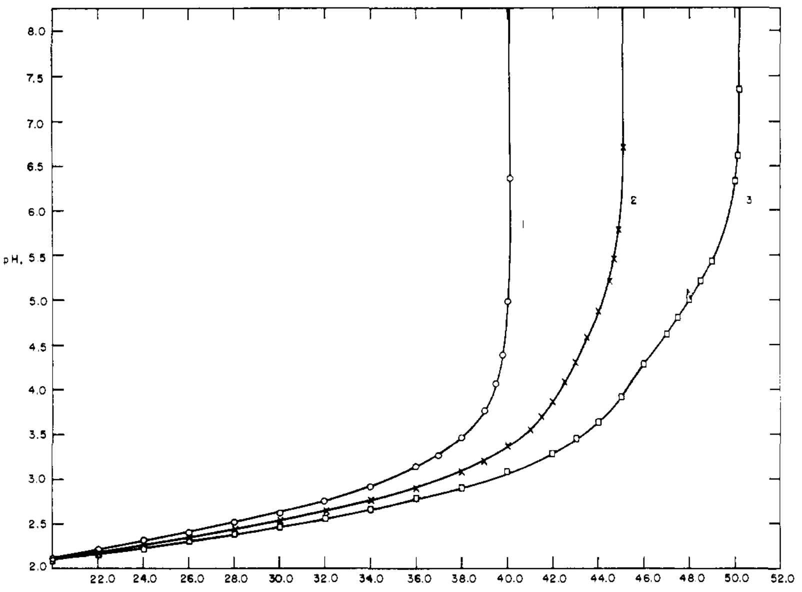

Fig. 3.—Potentiometric titration of 5-sulfosalicylic acid in presence of beryllium ions: curve 1, 2.005 × 10^{-2} *M* in H_3SSA; curve 2, 2.005 × 10^{-2} *M* in H_3SSA and 0.25 × 10^{-2} *M* in $BeSO_4$; curve 3, 2.005 × 10^{-2} *M* in H_3SSA and 0.50 × 10^{-2} *M* in $BeSO_4$.

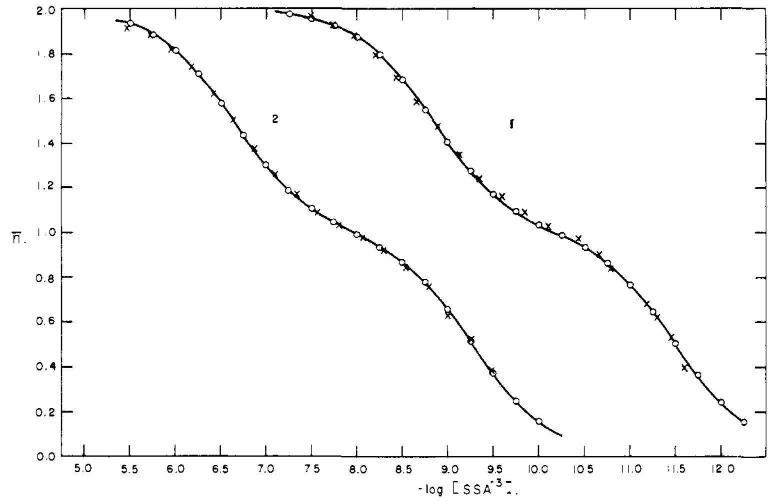

Fig. 4.—Degree of formation, $\bar{n}$, as a function of $-\log$-[SSA-3]: curve 1, beryllium-5-sulfosalicylate complex; curve 2, copper-5-sulfosalicylate complex; x-x-x-x-, experimental values; o-o-o-o-, calculated values.

Similar results were obtained for the copper-5-sulfosalicylate complex except that the complex formation starts at a higher *p*H (3.5) as is seen from Fig. 5.

To show further that the phenolic proton is displaced during complex formation, a series of solutions was prepared having the same concentration of disodium 5-sulfosalicylate but having various concentrations of beryllium sulfate. The *p*H of these solutions decreased with increasing concentration of beryllium ion and was almost constant after one equivalent of beryllium had been added. The *p*H of each solution was lower than that of a corresponding solution containing only beryllium sulfate. The absorbance of these solutions, measured at 317 mμ, showed an increase with increasing concentration of beryllium ions. These observations indicate clearly that the phenolic proton is displaced during complex formation, in accordance with equation 1. Similar results were obtained with disodium 5-sulfosalicylate and copper ions.

Stability Constant.—The stability constant for the 1:1 beryllium-5-sulfosalicylate complex was calculated by the method used by Meek and Banks.[3] At a constant *p*H (5.2), the formation of the 1:1 complex can best be represented by equation 1; from which it follows that

$$k_1'[H^+] = \frac{[BeSSA^-][H^+]}{[Be^{++}][HSSA^{-2}]} \qquad (3)$$

Substituting for [HSSA^{-2}] in terms of [SSA^{-3}], one may write

$$k_1'[H^+] = k_1K_{a3} = \frac{[BeSSA^-]K_{a3}}{[Be^{++}][SSA^{-3}]} \qquad (4)$$

where k_1 is the stability constant for the 1:1 complex, k_1' is a constant, which can be conveniently calculated from spectrophotometric data, and K_{a3} is the third dissociation constant of 5-sulfosalicylic acid.

At *p*H 5.2, it can be assumed that the absorbance, at 317 mμ, of a solution of beryllium sulfate and 5-sulfosalicylic acid is only due to the free HSSA^{-2}, the only 5-sulfosalicylate species predominantly present at that *p*H, and the 1:1 beryllium-5-sulfosalicylate complex. The absorbance of the solution is given by

$$A = l\{\epsilon_1[HSSA^{-2}] + \epsilon_2[BeSSA^-]\} \qquad (5)$$

where l is the path length of the cells (1.0 cm.), ϵ_1 and ϵ_2 are the molar absorptivities for HSSA^{-2} and the beryllium-5-sulfosalicylate complex, respectively. The molar absorptivity ϵ_1 for the HSSA^{-2} species was calculated to be 660 (317 mμ,

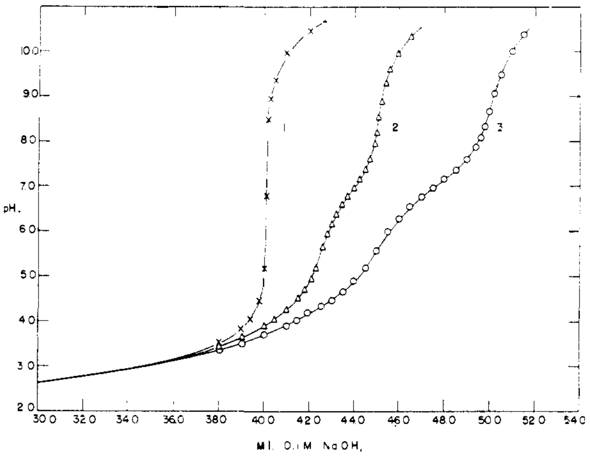

Fig. 5.—Potentiometric titration of 5-sulfosalicylic acid in presence of copper ions: curve 1, 2.005 × 10^{-2} *M* in H_3SSA; curve 2, 2.005 × 10^{-2} *M* in H_3SSA and 0.25 × 10^{-2} *M* in $CuSO_4$; curve 3, 2.005 × 10^{-2} *M* in H_3SSA and 0.50 × 10^{-2} *M* in $CuSO_4$.

*p*H 5.2) from the observed absorbance and known concentration of a solution containing only 5-sulfosalicylic acid. The molar absorptivity ϵ_2 of the 1:1 beryllium–5-sulfosalicylate complex was found to be 3.48 × 10^3 (317 mμ, *p*H 5.2) from the observed absorbances of solutions having known beryllium concentrations and relatively large known 5-sulfosalicylic acid concentrations.

For solutions containing a 1:1 mixture of beryllium and 5-sulfosalicylate in which the total beryllium concentration is *M* and [$HSSA^{-2}$] is *y*, we may write equations 3 and 5 as

$$k_1' = \frac{(M - y)}{y^2} \tag{6}$$

and

$$A = [(\epsilon_1 y + \epsilon_2 (M - y)] \tag{7}$$

The value of *y* was calculated as follows: A stock solution of the beryllium-5-sulfosalicylate complex, having the mole ratio of 1:1, was prepared and the *p*H adjusted to 5.2 by sodium hydroxide. Several dilutions, in the range (2.25 to 0.75) × 10^{-4} *M* in total beryllium, were prepared from this stock solution. Each solution was 1.0 × 10^{-2} *M* in sodium acetate–acetic acid buffer (*p*H 5.2) and 0.1 *M* in sodium perchlorate. From the absorbance of each of these solutions at 317 mμ, ϵ_1, ϵ_2 and the beryllium concentration, *y* (equation 7) was calculated. Upon substituting the value of *y* into equation 6, k_1' was found to be (8.38 ± 0.05) × 10^4. The value of K_{a3} (μ = 0.1) was determined by the method of Ågren,[9] and was found to be 1.81 × 10^{-12}. Knowing the values of K_{a3}, *p*H and k_1', k_1 (equation 4) was found to be (2.92 ± 0.02) × 10^{11}.

Schubert and Lindenbaum[16] have reported a value of 7.08 × 10^4 for the 1:1 beryllium-5-sulfosalicylate. In the opinion of the present authors, this value is probably for k_1'.

A similar procedure was used to calculate the stability constant for the 1:2 beryllium-5-sulfosalicylate complex, which forms at about *p*H 8.0. The formation reaction may be written as

$$BeSSA^- + HSSA^{-2} \rightleftarrows Be(SSA)_2^{-4} + H^+ \tag{8}$$

from which it follows that

$$k_2'[H^+] = \frac{[Be(SSA)_2^{-4}][H^+]}{[BeSSA^-][HSSA^{-2}]} \tag{9}$$

Substituting for [$HSSA^{-2}$] in terms of [SSA^{-3}] one may write

$$k_2'[H^+] = k_2K_{a3} = \frac{[Be(SSA)_2^{-4}]K_{a3}}{[BeSSA^-][SSA^{-3}]} \tag{10}$$

where k_2 is the stability constant for the 1:2 beryllium complex and k_2' is a constant, which is conveniently calculated from the spectrophotometric data.

At *p*H 8.0, the absorbance of a solution containing beryllium sulfate and 5-sulfosalicylate may be represented by

$$A = l\{\epsilon_1[HSSA^{-2}] + \epsilon_2[BeSSA^-] + \epsilon_3[Be(SSA)_2^{-4}]\} \tag{11}$$

where *l* is the path length of the cell (1.0 cm.), ϵ_1, ϵ_2 and ϵ_3 are the molar absorptivities of $HSSA^{-2}$ (the only uncomplexed 5-sulfosalicylate species predominantly present at *p*H 8.0), $BeSSA^-$ and $Be(SSA)_2^{-4}$, respectively.

For solutions containing a 1:2 mixture of beryllium and 5-sulfosalicylate in which the total beryllium concentration is *M* and that of [$HSSA^{-2}$] is *y*, we may write equations 9 and 11 as

$$k_2' = \frac{(M - y)}{y^2} \tag{12}$$

and

$$A = [\epsilon_1 y + \epsilon_2 y + \epsilon_3(M - y)] \tag{13}$$

The value of *y* was calculated as follows: A stock solution of beryllium-5-sulfosalicylate, having the mole ratio of 1:2, was prepared and the *p*H adjusted to 8.0 by sodium hydroxide. Several solutions varying in total beryllium content were prepared from this stock solution. Each of these solutions was 0.1 *M* in sodium perchlorate and at a *p*H of 8.0. The value of ϵ_3 was calculated from the observed absorbance at 317 mμ of solutions with known beryllium concentrations and relatively large known concentrations of 5-sulfosalicylic acid, all at *p*H 8.0, and was found to be 7.85 × 10^3. From the absorbances of the solutions and known ϵ_1, ϵ_2 and ϵ_3 and *M* in equation 13, *y* was calculated. Substituting the value for *y* into equation 12, k_2' was found to be (7.51 ± 0.36) × 10^4. Knowing k_2', *p*H and K_{a3}, k_2 (equation 10) was found to be (4.15 ± 0.2) × 10^5.

Meek and Banks[3] have reported *K'* = 3.84 × 10^9, for the over-all stability constant at μ = 0.1, where *K'* is $k_1'k_2'$ (equations 3 and 9). The value of $k_1'k_2'$ was found to be 6.29 × 10^9. The difference in the values might be due to the fact that *K'* was determined at *p*H range 10.3 to 10.5 and k_2' at *p*H 8.0.

Potentiometric Titration.—Figure 3 represents the titration of 100 ml. of solutions 2.005 × 10^{-2} *M* in H_3SSA (curve 1), 2.005 × 10^{-2} *M* in H_3SSA and 2.50 × 10^{-3} *M* in $BeSO_4$ (curve 2) and 2.005 × 10^{-2} *M* in H_3SSA and 5.00 × 10^{-3} *M* in $BeSO_4$ (curve 3) with 0.1 *M* sodium hydroxide. All solutions were 0.25 *M* in sodium perchlorate. Curve 1 indicates that only two protons of H_3SSA

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[16] J. Schubert and A. Lindenbaum, *J. Biol. Chem.*, **208**, 359 (1954).

are replaced by sodium. When H_3SSA is titrated in the presence of beryllium ions (curves 2 and 3), the phenolic proton also is replaced by sodium, as is indicated by the additional amount of base consumed by these solutions. This additional amount of base gives directly the amount of H_3SSA complexed with beryllium, according to the equations

$$H_3SSA + 2OH^- \rightleftarrows HSSA^{-2} + 2H_2O \quad (14)$$

$$Be^{++} + HSSA^{-2} + OH^- \rightleftarrows BeSSA^- + H_2O \quad (15)$$

$$BeSSA^- + HSSA^{-2} + OH^- \rightleftarrows Be(SSA)_2^{-4} + H_2O \quad (16)$$

No precipitation of beryllium was observed during any of these titrations.

Calculation of Stability Constants.—The Calvin and Melchior[17] extension of Bjerrum's[18] method was used to calculate the stability constants of the beryllium–5-sulfosalicylate complexes from potentiometric titration data. The two successive reactions for the complex formation may be represented by the equations

$$Be^{++} + SSA^{-3} \rightleftarrows BeSSA^- \quad (17)$$

$$BeSSA^- + SSA^{-3} \rightleftarrows Be(SSA)_2^{-4} \quad (18)$$

The over-all stability constant is given by

$$K = \frac{[Be(SSA)_2^{-4}]}{[Be^{++}][SSA^{-3}]^2} = k_1k_2 \quad (19)$$

where k_1 and k_2 are the formation constants for reactions 17 and 18.

The evaluation of $\bar{n}$ was made from Fig. 3. At any pH the horizontal distance between curve 1 and curve 2 or curve 3 measures quite accurately the additional base consumed by the reactions 15 and 16 or the total number of moles of SSA^{-3} complexed. This number divided by the total beryllium added is $\bar{n}$. At any pH the $[SSA^{-3}]$ was calculated as

$$[H_3SSA]_{total} = [H_2SSA^-] + [HSSA^{-2}] + [SSA^{-3}] + [BeSSA^-] + 2[Be(SSA)_2^{-4}] \quad (20)$$

from which

$$[SSA^{-3}] = \frac{[H_3SSA]_{total} - [BeSSA^-] - 2[Be(SSA)_2^{-4}]}{\frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]}{K_{a3}} + 1} \quad (21)$$

K_{a_2} (3.23×10^{-3})[19] and K_{a_3} (1.81×10^{-12}) being the second and third acid dissociation constants of 5-sulfosalicylic acid, respectively. All quantities in equation 21 are known. A series of values of $\bar{n}$ and $[SSA^{-3}]$ was obtained. Figure 4, curve 1, is a plot of $\bar{n}$ (calculated from curves 1 and 3, Fig. 3) against $-\log[SSA^{-3}]$. The $\bar{n}$ values calculated from curves 1 and 2, Fig. 3, were very similar to those calculated from curves 1 and 3 and hence were not plotted. The approximate values of $\log k_1$ and $\log k_2$ were read directly from the graph at $\bar{n} = 0.5$ and 1.5, respectively. The values of k_1 and k_2 then were used to calculate $\bar{n}$ for known values of $[SSA^{-3}]$. These calculated $\bar{n}$ values were also plotted against $-\log[SSA^{-3}]$ (Fig. 4). The values of k_1 and k_2 then were adjusted until the calculated $\bar{n}$ curve was in good agreement with the experimental curve. The final constants were $k_1 = 3.16 \times 10^{11}$ and $k_2 = 6.92 \times 10^8$. Considering the errors involved in the determination of k_1 and k_2 by the spectrophotometric and potentiometric methods, it is our opinion that the potentiometric method gives better results.

Copper–5-Sulfosalicylate Complex.—The procedure for the study of copper–5-sulfosalicylate complexes was similar to that used for the beryllium–5-sulfosalicylate system. Figure 5 represents the titrations of 100 ml. of solutions 2.005×10^{-2} *M* in H_3SSA (curve 1), 2.005×10^{-2} *M* in H_3SSA and 2.50×10^{-3} *M* in $CuSO_4$ (curve 2) and 2.005×10^{-2} *M* in H_3SSA and 5.00×10^{-3} *M* in $CuSO_4$ (curve 3), with 0.1 *M* sodium hydroxide solution.

It was observed that solutions containing copper sulfate and 5-sulfosalicylic acid in the ratios of 1:1 and 1:2 hydrolyze above pH 6.25 and 7.45, respectively. However, no hydrolysis occurred in solutions in which the ratio was 1:3. The titration reactions can be represented by equations 14, 15 and 16 by substituting Cu^{++} for Be^{++}. Curves 2 and 3, Fig. 5, each have two inflections, one at pH 5.50 and one at 8.50, indicating the formation of a 1:1 and a 1:2 complex (equations 15 and 16). No precipitation of copper was observed during the titrations. Turner and Anderson[6] have shown that copper forms a 1:1 and a 1:2 complex with 5-sulfosalicylic acid at pH 5.50 and 8.00, respectively.

Calculation of Stability Constants.—The procedure was the same as that used to calculate the stability constants for the beryllium–5-sulfosalicylate complexes. The values for $\bar{n}$, obtained from curves 1 and 3, Fig. 5, have been plotted against $-\log[SSA^{-3}]$ in Fig. 4, curve 2. Then $\bar{n}$ values obtained from curves 1 and 2 were very similar to those obtained above and hence were not plotted. The approximate values for $\log k_1$ and k_2 were read directly from the graph at $\bar{n} = 0.5$ and 1.5, respectively. The values for k_1 and k_2 then were used to calculate $\bar{n}$ for known $[SSA^{-3}]$. These calculated $\bar{n}$ values also were plotted against $-\log[SSA^{-3}]$ (Fig. 4, curve 2). As the calculated $\bar{n}$ curve was in good agreement with the experimental curve, it was not necessary to adjust the values of k_1 and k_2. The values are: $k_1 = 1.86 \times 10^9$, $k_2 = 4.36 \times 10^6$.

Turner and Anderson[6] have reported a value of 5.0×10^2 for the stability constant of the 1:1 copper–5-sulfosalicylate complex, at pH 5.0. This value is probably for k_1', hence substituting the values of $[H^+]$, k_1' and K_{a_3} in equation 4, k_1 was calculated to be 2.77×10^9 which is in good agreement with the value of k_1 obtained by the present authors.

Vasil'ev and Gorokhovskiĭ[7] have made a polarographic study of the copper–5-sulfosalicylate complexes. In the pH range 7–10 they have shown the existence of three complexes with coördination numbers 1, 2 and 3, their stability constants being 1.69×10^{15}, 7.69×10^{15} and 1.96×10^{16}, respectively. It seems more probable that the three values reported are for the over-all formation constant of the 1:2 complex.

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