Anderson,[9] to give more certain resolution of hydroxylysine from histidine.

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[9] P. B. Hamilton and R. A. Anderson, *J. Biol. Chem.*, **211**, 95 (1954).

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The Stability of Metal Chelates of 5-Sulfo-anthranilic Acid

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During an investigation of the analytical properties of derivatives of anthranilic acid, the stability constants of 5-sulfo-anthranilic acid with several transition metals were determined. The Bjerrum[1] titration method as modified by Calvin and Wilson[2] was adapted to the present work.

Experimental

Materials.—The 5-sulfo-anthranilic acid was prepared by a modification of the procedure suggested by Moser.[3] Thirty-four grams of anthranilic acid and 25 g. of sulfuric acid were thoroughly mixed in a beaker that was cooled in an ice-bath. The mixture was then ground in a mortar until it was a fine powder. The powder was heated in an oven at 150° for about 5 hours and was mixed. This was followed by heating at 180° for 9 hours. The product was crystallized 3 times from a 50% acetic acid solution, washed with acetone, and dried at 110°.

The metal solutions were prepared from the nitrate salts of the metals. The nickel, copper and zinc solutions were standardized by direct titration with a 0.015 *N* solution of disodium dihydrogen ethylenediaminetetraacetate. The cadmium and cobalt solutions were standardized by the addition of a known excess of a 0.015 *N* solution of disodium dihydrogen ethylenediaminetetraacetate and titration with a 0.015 *N* solution of zinc.

Procedure.—The titration vessel contained the metal ion in 100 ml. of aqueous solution. The 5-sulfo-anthranilic acid was added as a solid because it decomposed on standing in aqueous solution. The standard carbonate-free NaOH solution was added from a 10-ml. buret in which volume measurements could be estimated to within ±0.002 ml. After each addition of NaOH, the *p*H was measured with a Beckman model G *p*H meter that was standardized with Beckman buffer solutions at *p*H values of 4 and 7. During the titration the temperature was maintained at 35 ± 0.2°, carbon dioxide was excluded from the solution, and constant stirring was provided.

Calculation.—The calculations were made by adapting the method of Calvin–Bjerrum to the present situation.

H_2R represents the reagent, 5-sulfo-anthranilic acid

K represents the acid dissociation constant of the carboxyl group

T_M represents the total added metal concentration

T_{H_2R} represents the total added reagent concentration

From the equations for the conservation of species, charge balance and dissociation constant

$$T_M = [M^{++}] + [MR] + [MR_2^{=}]$$

$$T_{H_2R} = [HR^-] + [R^=] + 2[MR_2^=] + [MR]$$

$$[NO_3^-] = 2T_M$$

$$2T_{H_2R} + [OH^-] - [Na^+] = [H^+] + [HR^-]$$

$$K = [H^+][R^=]/[HR^-]$$

$$2[M^{++}] + [H^+] + [Na^+] = [NO_3^-] + 2[R^=] + [OH^-] + 2[MR_2^=] + [HR^-]$$

the following expressions for $\bar{n}$ and $R^=$ were obtained

$$\bar{n} = \left([H^+] + [Na^+] - T_{H_2R} - \frac{K}{[H^+]}\left(2T_{H_2R} - [Na^+] - [H^+]\right)\right)\Big/ T_M$$

$$[R^=] = \frac{K}{[H^+]}\left(2T_{H_2R} - [Na^+] - [H^+]\right)$$

The ionization of the sulfonic acid group was considered complete in all the calculations. Since a titration of the reagent with NaOH showed that the *pK* value of the protonated nitrogen is less than 2, a consideration of this ionization constant was omitted from the calculations. The treatment was further simplified by the fact that it was not necessary to add an excess of mineral acid to the solution prior to the titration.

Results and Discussion

The dissociation constant of 5-sulfo-anthranilic acid was found to be 2.00×10^{-5}. The chelate formation constants that were determined are given in Table I. The concentrations of metal salts and the concentrations of 5-sulfo-anthranilic acid in the table represent the total concentrations of each of these substances before the addition of NaOH.

TABLE I

CHELATE FORMATION CONSTANTS IN WATER AT 35°

Metal	Metal concn. $\times 10^3$ *M*	Reagent concn. $\times 10^3$ *M*	$k_1 \times 10^{-2}$	$k_2 \times 10^{-2}$	$K_{av} \times 10^{-2}$
Cu	1.01	6.84	2.45[a]	5.75	1.19[b]
	1.01	9.12	2.29[a]	5.75	1.15[b]
Zn	1.05	9.12	8.33	2.76	4.79
	1.05	13.68	7.58	2.28	4.16
Ni	1.02	6.84	7.58	2.24	4.12
	1.02	11.40	7.58	2.24	4.12
Cd	1.05	11.40	6.90	2.40	4.07
	1.05	13.68	7.09	2.51	4.22
Co	1.09	9.12	6.62	2.14	3.76
	1.09	11.40	6.62	2.14	3.76

[a] $k_1 \times 10^{-3}$. [b] $K_{av} \times 10^{-3}$.

The order of stability of the metals with 5-sulfo-anthranilic acid was found to be Cu, Zn, Ni, Cd and Co. This order agrees with that found for *o*-amino-phenol by Charles and Freiser,[4] with the exception that Cd was not included in their work and the positions of Zn and Ni were reversed. However, the values for the stability constants of these two metals are so nearly alike in the present work that their relative positions could have been reversed by experimental errors.

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[1] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[2] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[3] E. Moser, U. S. Patent 2,353,351.

[4] R. C. Charles and H. Freiser, THIS JOURNAL, **74**, 1385 (1952).

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Benzoylations of 2-Methoxylepidine and 4-Methoxyquinaldine by Means of Potassium Amide

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Although 2-methoxyquinoline has been shown to react with potassium amide in liquid ammonia at room temperature to form 2-aminoquinoline,[2] it seemed possible to benzoylate the methyl group of 2-methoxylepidine (I) with methyl benzoate by

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[1] Eli Lilly Fellow, 1952-1954.

[2] F. W. Bergstrom, *J. Org. Chem.*, **3**, 233 (1938).