Stability Order in Metal Chelate Compounds. II.[1]
*5-(p-Sulfophenylazo)-salicylate Complexes**

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In accordance with the work reported, up to the present time it is understood that the stability of metal chelate compounds and their stability order with respect to nuclear metal atoms are functions of the geometrical and electronic structures of a ligand molecule and of the character of the resultant coördinate bonds as well.

In continuation of an investigation which may contribute to the clarification of these relationships, 5-(*p*-sulfophenylazo)-salicylic acid has been used as a chelating agent in the present work. Recently, 5-(*p*-sulfophenylazo)-salicylic acid was employed as a reagent to detect the presence of magnesium,[2] aluminum, beryllium,[3] gallium and indium[4] for analytical purposes; nevertheless, no quantitative study of the interaction of this ligand with any metal ion has been reported up to the present time.

Since the stability constants of metal-salicylate and metal-5-sulfosalicylate complexes have been evaluated,[5-7] the substituent effect of the *p*-sulfophenylazo group, which is situated at the 5-position in the parent molecule, on the chelate formation may be compared with those of other substituents among the chelate derivatives.

Experimental

5-(*p*-Sulfophenylazo)-salicylic Acid.—The coupling reaction of the diazotized sulfanilic acid with salicylic acid in equimolar amounts was carried out in alkaline aqueous media. Acidification of the reaction mixture with hydrochloric acid resulted in the formation of a precipitate. This precipitate was then recrystallized several times from water or aqueous ethanol, giving a 90% yield of yellow-orange needles. These fine crystals were found to be the dihydrated monosodium salt of 5-(*p*-sulfophenylazo)-salicylic acid (I), which was dehydrated above 180°C and decomposed above 250°C. The estimated molecular weight was 380.7 by potentiometric titration (calcd. 380.3).

Found: C, 41.06; H, 3.55; N, 7.44. Calcd. for $C_{13}H_{13}N_2O_8SNa$(dihydrate): C, 41.05; H, 3.44; N, 7.36%.

The dihydrate form I was transformed to the corresponding monohydrate at 110°C under reduced pressure (5 mmHg); it was also identified by reductive cleavage to sulfanilic acid and 5-aminosalicylic acid.

The synthesized material I was used to prepare a stock solution for potentiometric titrations after the establishment of the purity by means of potentiometric titration with a standard base.

Metal Solutions.—The bivalent metal nitrates, $Zn(NO_3)_2\cdot 6H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$, $Ca(NO_3)_2\cdot 4H_2O$, and manganese sulfate, $MnSO_4\cdot nH_2O$, of analytical grade were purchased from the Wako Pure Chemical Industries, Ltd. The nona-hydrated ferric nitrate, $Fe(NO_3)_3\cdot 9H_2O$, was a pure grade reagent of the same company. Aqueous stock solutions of these metal salts were standardized for metal ion concentration by the usual procedures of chelatometric titration.

Potentiometric Measurements. — The apparatus and procedures for potentiometric measurements have been mentioned elsewhere.[8] In the present work, the temperature and ionic strength of a titrating solution were maintained, respectively, at 25.0 ±0.1°C and 0.10 M with potassium nitrate. Since the solubility of the ligand in aqueous media at $\mu=0.10$ M in potassium nitrate was observed to be very low, the ligand concentration for potentiometric measurements had to be maintained in a relatively low range (approximately 2×10^{-3} M or less). The measurement of each metal chelate system was checked by repeated titrations to avoid any significant error which might be caused by the low concentration of the system.

Calculation of Acid Dissociation Constants. — The dissociation constants of the dibasic acid I are defined as follows:

$$K_{H_2L}=\frac{[H^+][HL^{2-}]}{[H_2L^-]},\qquad K_{HL}=\frac{[H^+][L^{3-}]}{[HL^{2-}]}$$

These constants were evaluated in a manner similar to that mentioned in a previous paper.[1]

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[1] Part I: Y. Murakami, K. Nakamura and M. Tokunaga, This Bulletin, 36, 669 (1963).

[2] I. M. Korenman and E. I. Levina, *Uchenye Zapiski Gor'kovsk. Gosudarst. Univ. im. N. I. Labachevskogo, Ser. Khim.*, **1958**, No. 32, 149; *Chem. Abstr.*, **54**, 5339 (1960).

[3] N. Appala Raju and K. Neelakantam, *Current Sci.* (*India*), **29**, 52 (1960); *Chem. Abstr.*, **54**, 17152 (1960).

[4] M. Z. Yampol'skii, *Trudy Komissii Anal. Khim., Akad. Nauk S. S. S. R., Inst. Geokhim. i Anal Khim.*, **11**, 5 (1960); *Chem. Abstr.*, **55**, 11177 (1961).

[5] J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants, Part I, Organic Ligands," The Chemical Society, London (1957).

[6] D. D. Perrin, *Nature*, **182**, 741 (1958).

[7] C. V. Banks and R. S. Singh, *J. Inorg. Nucl. Chem.*, **15**, 125 (1960).

[8] Y. Murakami, This Bulletin, **35**, 52 (1962).

TABLE I. ACID DISSOCIATION CONSTANTS OF SALICYLIC ACID AND ITS DERIVATIVES

Ligand	5-(p-Sulfophenylazo)-salicylic acid	5-Sulfosalicylic acid[6,7]		Salicylic acid[6]
μ	0.10	0.1	0.15	0.15
t°C	25.0 ±0.1	25	20	20
pK_{H_2L}	2.38±0.02	2.49	2.62	2.98
pK_{HL}	11.04±0.02	12.00	11.95	13.61

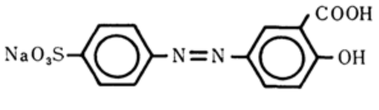
The Calculation of Stability Constants.—Because of the hydrolytic hehavior of the chlates of nickel(II), cobalt(II) and manganese(II), only potentiometric data of a limited range were used for the evaluation of the stability constants of these chelate systems. Such ranges were: 6~9.5, 6~9.5 and and 7~9.3 in $-\log[H^+]$; up to 1.35, 1.30 and 0.85 in $\bar{n}$-value* for nickel(II), cobalt(II) and manganese(II) respectively. No such limitations were required for alkaline earth metal chelates, even though an $\bar{n}$-value did not exceed 1.3 over the whole pH range studied. In these regions of $\bar{n}$-value, the main chelate species existing in the system were considered to be the 1 : 1 and 2 : 1 (lignd to metal) chelates. Therefore, the stability constants for each chelate system were evaluated in accordance either of two methods, namely, (1) the intersection method[1,8] or (2) the lineation method.[8] The two stability constants, K_1 and K_2, are defined as follows:

$$K_1=\frac{[ML]}{[M][L]},\qquad K_2=\frac{[ML_2]}{[ML][L]}$$

On the other hand, the $\bar{n}$-value already exceeded 1.2 at $a=0$** in the potentiometric titration of the iron(III) chelate system. Thus, the only stability constant evaluated was for the 2 : 1 chelate.

Results and Discussion

Acid Dissociation Constants. — A titration curve of the monosodium salt of 5-(p-sulfophenylazo)-salicylic acid (II) is shown in Fig. 3.



II

The titrating solution was pale yellow-orange below $a=1$ and became reddish in the region beyond $a=1$, where the reddish color deepened as the pH increased. The first dissociation process is clearly separated from the second; thus the carboxy-proton of the ligand is very acidic in comparison with the phenol-proton. The acid dissociation constants of ligand II evaluated in this work are shown in Table I, together with those of 5-sulfosalicylic acid[6,7] and of salicylic acid.[6] Both K_{H_2L} and K_{HL} values vary in a parallel manner among these ligands, and the acidity increases in the order: salicylic acid<5-sulfosalicylic acid<5-(p-sulfophenylazo)salicylic acid. Therefore, a p-sulfophenylazo group seems to be a more effective substituent in electron-withdrawing effect than a sulfonate group. Judging from these observations, a phenylazo group may transmit the electron-withdrawing effect of the para sulfonate group through resonance interaction and withdraw an electron from the salicylate group as well.

Interaction of Bivalent Metal Ions with 5-(*p*-Sulfophenylazo)-salicylate. — Titration curves are illustrated in Figs. 1 and 2 for the 5-(p-sulfophenylazo)-salicylate chelate systems of manganese(II), cobalt(II), nickel(II), zinc(II), magnesium(II) and calcium(II) for 10 : 1 and 4 : 1 molar ratios of ligand to metal ion.

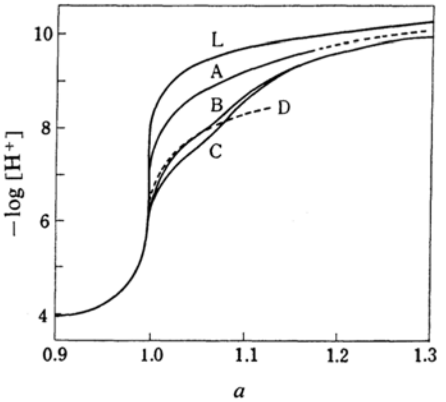


Fig. 1. Potentiometric titration of bivalent metal chelates of 5-(p-sulfophenylazo)-salicylate at total ligand concentration of 2.03×10^{-3} M with 10 : 1 molar ratio of ligand to metal ion: A, Mn; B, Co; C, Ni; D, Zn; L, ligand alone; a=moles of base added per mole of ligand; t=25°C; μ=0.10 M (KNO_3). Dotted lines represent non-equilibrated titration.

Since 5-(p-sulfophenylazo)-salicylate is considered to be a bidentate ligand, at most three moles of the ligand per mole of metal ion would be enough to satisfy the coördination sites of these bivalent metal ions. However, potentiometric titrations in the present work were carried out with an excess of the ligand

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* $\bar{n}$ is referred to the Bjerrum formation function.

** a stands for the amount of base added per mole of ligand.

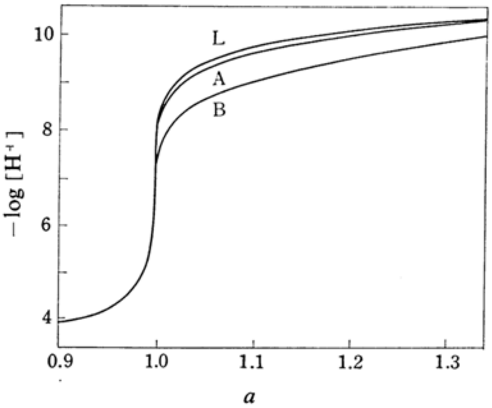

Fig. 2. Potentiometric titration of bivalent metal chelates of 5-(*p*-sulfophenylazo)-salicylate at total ligand concentration of 2.03×10^{-3} M with 4 : 1 molar ratio of ligand to metal ion: A, Ca; B, Mg; L, ligand alone; a=moles of base added per mole of ligand; t=25°C; μ=0.10 M (KNO_3).

in an attempt to avoid as much as possible both disproportionation and hydrolysis of metal chlates in a higher pH region.

Manganese(II), Cobalt(II), Nickel(II) and Zinc(II). — All the titration curves coincide well with that of the ligand alone in the lower buffer region, $a=0\sim1.0$, as is shown in Fig. 1. Thus, the only significant chemical process occurring in this region is the dissociation of a carboxyl-proton.

The depression of titration curves was observed beyond an a-value of 1.0 in comparison with the titration curve of the ligand alone. Such a depression became noticeable at pH 6.0 and above for cobalt(II) and nickel(II), and above pH 7.0 for manganese(II), as may be seen in Fig. 1. It is obvious that ligand II undergoes chelation with these bivalent metal ions in these higher pH regions. A small inflection region, which corresponds to the formation of a 1 : 1 chelate, was observed at $a=1.1$ for the nickel(II) chelate system and less significantly for the cobalt(II). Judging from the extent of the depression of titration curves among these bivalent metal chelate systems, the stability order with respect to metal ions is: manganese(II) < cobalt(II) < nickel(II). Meanwhile, the hydrolytic tendency of these metal chelates was found to be significant beyond $a=1.18$ for manganese(II) and beyond $a=1.3$ for cobalt(II) and nickel(II) in a manner similar to these observed for the salicylate and 5-sufosalicylate chelates of the same bivalent metals.[6,7)

Such hydrolytic behavior was much pronounced for the zinc(II) chelate system, and a pH drifting became significant in the region immediately beyond $a=1.0$. Further addition of a base resulted in the gradual formation of a precipitate. It seems, therefore, that the zinc chelate is much less stable than the corresponding cobalt and nickel chelates, since the hydrolytic tendency of zinc(II) was found to be comparable with these of cobalt(II) and nickel(II) ions.* On the other hand, the greater hydrolytic behavior** of the zinc(II) ion than that of the manganese(II) ion is responsible for the precipitation in the lower pH range, where the manganese chelate system did not form a precipitate.

Copper(II). — Titration of the copper(II) chelate system was carried out at various molar ratios of ligand to metal ion, ranging from 1 : 1 to 10 : 1 under the same experimental conditions as employed for other bivalent metal chelate systems. An appreciable pH-depression was observed, even in the a-range below 1.0. Equilibrium of the system was reached in a short period of time in a limited initial range of titration with a base; nevertheless, equilibrated potentiometric data were not obtained over most of the pH range studied due to the sluggish pH-drifting. Such a drifting tendency became increasingly pronounced as the pH was raised, even though no precipitate was noticed throughout the titration. Since the hydrolysis of copper ion alone is not significant in the lower pH region[9,10) the slow rate of the equilibration of the chelate system is conceivably due to the sluggish formation of chelate species. Because of such complex behavior of the copper chelate system, no quantitative interpretation of the data was possible.

Magnesium(II) and Calcium(II). — Neither drifting of pH nor precipitation was observed throughout the titration. These bivalent metal ions and the ligand undergo chelation in the region beyond $a=1.0$, as may be seen in Fig. 2. Both alkaline earth metal ions form much less stable chelates than the transition metal ions.

Interaction of Iron(III) with 5-(*p*-Sulfophenylazo)-salicylate. — Titration of a solution containing a 4 : 1 molar ratio of ligand to metal ion resulted in a large pH depression over the whole pH range and in two steep inflections, at 1.50 and 1.75, in a-value, as is shown in Fig. 3. No precipitate was observed at any time during the titration. The

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* The estimated hydrolysis constants for zinc(II), cobalt(II) and nickel(II) are 8.7, 8.9 and 9.4 respectively in pK unit, at 30°C and μ=0.1 (S. Chaberek, Jr., R. C. Courtney and A. E. Martell, *J. Am. Chem. Soc.*, **74**, 5057 (1952)).

** The thermodynamic hydrolysis constants for zinc(II) and manganese(II) ions were 8.96±0.03 and 10.59±0.04 respectively in pK unit, at 25°C (D. D. Perrin, *J. Chem. Soc.*, **1962**, 2197, 4500).

9) C. Berecki-Biedermann, *Arkiv. Kemi*, **9**, 175 (1956).

10) D. D. Perrin, *J. Chem. Soc.*, **1960**, 3189.

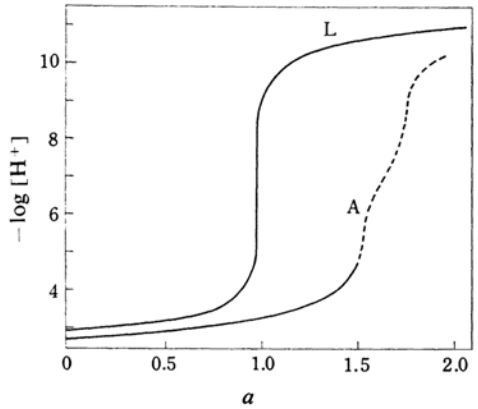

Fig. 3. Potentiometric titration of Fe(III)-5-(*p*-sulfophenylazo)-salicylate chelate system at total ligand concentration of 2.03×10^{-3} M with 4 : 1 molar ratio of ligand to metal ion: A, Fe; L, ligand alone; a=moles of base added per mole of ligand; t=25°C; μ=0.10 M (KNO_3). Dotted curve represents non-equilibrated titration.

former inflection corresponds to the formation of the 2 : 1 chelate, in addition to the liberation of a carboxy-proton of the uncoördinated ligand, while the latter most probably corresponds to the formation of the 3 : 1 chelate. Such a profound pH depression is to be ascribed to the greater stability of iron(III) chelates in comparison with that of other bivalent metal chelates. Similar results were obtained for the salicylate and 5-sulfosalicylate chelates.⁶⁾

On the other hand, the sluggish pH drifting in the region beyond a=1.5 precludes the quantitative analysis of the chelating behavior of the system. Since 5-(*p*-sulfophenylazo)-salicylate demonstrated a strong affinity to ferric ion, the slow rate of the chelate formation would be responsible for such a pH drifting, and neither a hydrolytic reaction nor other complex reactions of the chelates would be the significant account. A similar conclusion was reached concerning the sluggish equilibration of the 4-sulfocatechol-iron(II) chelate system.[11)]

The development of the deeper color for the ferric chelate system than for the ligand alone also provides evidence for the strong interaction of ferric ion with the ligand. The titrating solution was dark brownish in the lower buffer region (a<1.0). A reddish color gradually developed in the solution on approaching to the first inflection region, and this was further deepened as the pH was raised. However, the intensity of this reddish color gradually diminished in the second inflection region, and more apparently as the pH increased further. The hydrolysis of the chelate system, which may proceed extensively in this higher pH region, is most probably the cause of this color-fading.

Stability Constants.—The stability constants for the 5-(*p*-sulfophenylazo)-salicylate, as well as for the salicylate and 5-sulfosalicylate chelates, are listed in Table II. The stability order of these chelates in K_1 with respect to the ligands is shown in the increasing order: 5-(*p*-sulfophenylazo)-salicylate < 5-sulfosalicylate < salicylate. The decreased basicity of the donor group of the present ligand is responsible for the lower stability. The slightly greater

TABLE II. STABILITY CONSTANTS OF THE METAL SALICYLATES

Ligand		5-(*p*-Sulfophenylazo)-salicylic acid	5-Sulfosalicylic acid[6,7]		Salicylic acid[6]
μ		0.10	0.1～0.15	0.15	0.15
t°C		25.0±0.1	25	20	20
Mn(II)	$\log K_1$	4.94±0.02	5.24	5.10	5.90
	$\log K_2$	3.5 ±0.1	3.00	2.90	3.9
Fe(II)	$\log K_1$	—	—	5.90	6.55
	$\log K_2$	—	—	<4.0	4.7
Co(II)	$\log K_1$	5.84±0.02	6.13	6.00	6.75
	$\log K_2$	3.93±0.02	3.69	3.60	4.7
Ni(II)	$\log K_1$	6.17±0.02	6.42	6.30	6.95
	$\log K_2$	4.05±0.03	3.82	3.90	4.8
Cu(II)	$\log K_1$	—	9.52	9.50	10.60
	$\log K_2$	—	6.93	6.80	7.85
Zn(II)	$\log K_1$	—	—	6.05	6.85
	$\log K_2$	—	—	<4.6	—
Mg(II)	$\log K_1$	4.45±0.02			
	$\log K_2$	3.04±0.1			
Ca(II)	$\log K_1$	3.10±0.03			
Fe(III)	$\log K_1$	—	—	14.60	16.35
	$\log K_2$	10.70±0.02	—	10.55	11.90

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11) Y. Murakami and K. Nakamura, This Bulletin, **36**, 1408 (1963).

values of K_2 for the 5-(*p*-sulfophenylazo)-salicylate chelates than those for the corresponding 5-sulfosalcylate chelates are rather unexpected.

The stability order with respect to the bivalent metal ions in the present work may be put foward in an increasing manner as follows: calcium(II) < magnesium(II) < manganese(II) < (zinc(II)) < cobalt(II) < nickel(II) < (copper(II)). By referring to other analogous metal chelates listed in Table II, the following general stability order with respect to the bivalent transition metals may be afforded: manganese(II) < iron(II) < zinc(II) ~ cobalt(II) < nickel(II) < copper(II). Zinc(II) is placed below nickel(II) in stability, contrary to what was observed for the catechol chelates.

The pronounced color-deepening effect of the iron(III) chelate system indicates a strong electronic interaction among the ligand molecules and the metal atom through the coördinate bonds.

Summary

The interaction of 5-(*p*-sulfophenylazo)-salicylic acid with zinc(II), copper(II), nickel(II), cobalt(II), manganese(II), magnesium(II), calcium(II) and iron(III) has been investigated in aqueous media at 25.0±0.1°C and the ionic strength of 0.10 M. The stability constants for the 1 : 1 and 2 : 1 (ligand to metal) chelates of nickel, cobalt, manganese and magnesium, and for the 1 : 1 calcium chelate, as well as for the 2 : 1 ferric chelate, have been evaluated, and the resulting stability order with respect to the bivalent metals has been found to follow the sequence: calcium(II) < magnesium(II) < manganese(II) < (zinc(II)) < copper(II) < nickel(II) < copper(II). The stability sequence, zinc(II) < nickel(II), is contrary to that observed for the catechol chelates.

A *p*-sulfophenylazo group demonstrated an electron-withdrawing effect, the magnitude of which was slightly greater than that of a sulfonate group. However, the effect of the former group on the chelate-stability has been found to be comparable with that of the latter.

The present salicylate derivative is also a good chelating agent for iron(III) ion, even though the chelate system somehow becomes involved in a higher pH range.

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