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The Chelate Formation of *o*-Substituted Phenylazochromotropic Acids with Alkaline Earth Metals*[1]

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The acid dissociation constants of phenyl, *o*-, *m*-, and *p*-sulfophenyl-, *o*-carboxyphenyl-, *o*-phenol- and *o*-arsonophenylazochromotropic acid and the formation constants of their 1 : 1 metal chelates with alkaline earth metals have been measured by potentiometric titration. The measurements have been carried out at 25°C and $\mu=0.10$ (KNO_3). The influence of these substituents on the acid dissociation constants of the reagents, and on the chelate formation constants was discussed. The dissociation constants of the naphtholic protons of the *o*-substituted reagents increase as follows: *o*-OH < *o*-$AsO(OH)_2$ < *o*-COOH < *o*-SO_3Na < *o*-H. The metal chelate stabilities of *o*-phenol-, phenyl- and *o*-arsonophenylazochromotropic acids decrease as follows: Mg > Ca > Sr > Ba, while for chelates of *o*-carboxyphenyl- and *o*-sulfophenylazochromotorpic acids the order is Mg > Ca > Sr ≈ Ba. The sulfonic group in *o*-sulfophenylazochromotropic acid, in spite of its remarkable electron-withdrawing effect, depress the acid dissociation, and form more stable barium chelate than phenyl-, *m*- and *p*-sulfophenylazochromotropic acid do. The plot of the formation constants, log *K*, against the sum of the dissociation constants, pK_A $(=pk_{a_1}+pk_{a_2}+pk_{a_3})$, was approximately linear.

A variety of azo dyestuffs have found a wide application in analytical chemistry, especially many azo derivatives of chromotropic acid are well known as colorimetric reagents and as metal indicators in chelatometry.[1] In the authors' laboratory numerous azo compounds showing a high sensitivity for metal ions were synthesized, and the acid dissociation constants of these reagents and the formation constants of thorium chelates were measured spectrophotometrically.[2] The present authors have extended the studies to alkaline earth metal chelates with seven substituted phenylazochromotropic acids, namely phenyl-, *o*-, *m*-, and *p*-sulfophenyl-, *o*-carboxyphenyl-, *o*-phenol- and *o*-arsonophenylazochromotropic acid, and investigated the effect of substituents on the dissociation constants and the chelate formation constants by means of potentiometric titration method.

Experimental

Reagents. Phenylazochromotropic acid [2-(phenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt], *o*-sulfophenylazochromotropic acid [2-(2-sulfophenylazo)-1, 8-dihydroxynaphthalene - 3, 6 - disulfonic acid trisodium salt], *m*-sulfophenylazochromotropic acid ([2-(3-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid trisodium salt], *p*-sulfophenylazochromotropic acid [2-(4-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid trisodium salt], *o*-carboxyphenylazochromotropic acid [2-(2-carboxyphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt], *o*-phenylazochromotropic acid [Acid Chrome Blue K, 2-(2-hydroxyphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt] and *o*-arsonophenylazochromotropic acid [Neo-Thorin, Arsenazo, 2-(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt] were synthesized by the coupling reaction of chromotropic acid with diazobenzene, *o*-diazobenzenesulfonic acid, *m*-diazobenzenesulfonic acid, *p*-diazobenzenesulfonic acid, *o*-diazobenzoic acid, *o*-diazophenol and *o*-diazophenylarsonic acid, respectively. These reagents are all fine crystals. They were dried at 60°C *in vacuo*, and cooled in a phosphorus pentoxide desiccator. The

TABLE 1. ANALYSIS OF SODIUM CONTENT IN THE REAGENTS BY THE FLAME ANALYSIS

Substituent X	Calcd	Found
o-H	9.8%	9.7%
o-SO_3Na	12.1	12.3
o-COOH	9.0	8.8
o-OH	9.5	10.6
o-$AsO(OH)_2$	7.8	7.6
m-SO_3Na	12.1	12.7
p-SO_3Na	12.1	12.9

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1) J. S. Fritz, R. T. Oliver and D. J. Pietrzyk, *Anal. Chem.*, **30**, 1111 (1958); S. Shibata and T. Matsumae, This Bulletin, **31**, 377 (1958), *etc.*

2) H. Miyata, This Bulletin, **40**, 1875 (1967); H. Miyata, *ibid.*, **40**, 2815 (1967), *etc.*

analytical data of sodium content by the flame analysis are given in Table 1.

The stock solutions of these reagents were standardized by potentiometric titration with standard 0.10 M potassium hydroxide.

Analytical grade $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$ and $Ba(NO_3)_2$ are used to make stock solutions and the solutions are standardized by chelatometric titration.

Potentiometric Titration. The apparatus for potentiometric titration is presented in Fig. 1. The hydrogen ion concentration was measured by using a Metrohm pH meter E 388 [Metrohm A. G., Herisau, Switzerland] with a combined glass electrode. The pH meter was calibrated with an acetate buffer and with potassium hydroxide. Ten milliliters of solution were titrated by addition of 0.10 M potassium hydroxide from a calibrated 0.50 m*l* Agla micrometer syringe. All measurements were made at 25.0±0.1°C, and the ionic strength was maintained at 0.10 M with potassium nitrate. Solutions under titration were kept in a nitrogen atmosphere.

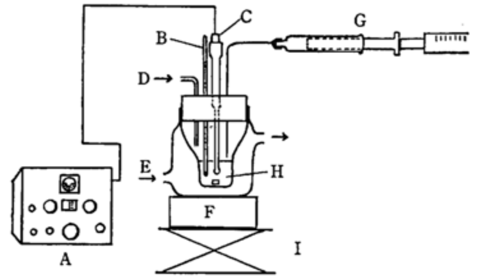

Fig. 1. Micro-titration apparatus.
A : "Metrohm" pH meter E-388
B : Thermometer
C : "Metrohm" combined glass electrode
D : N_2 gas
E : 25°C water
F : Magnetic stirrer
G : "Agla" micrometer syringe
total volume 0.5 m*l*
H : volume 10 m*l*
I : Laboratory jack

Calculations of Acid Dissociation Constants and Chelate Formation Constants. The dissociation constants, k_{a_1}, k_{a_2} and k_{a_3} and the formation constant, K, were evaluated by similar equations to those described elsewhere.³⁾

k_{a_1}, k_{a_2}, k_{a_3} and K are expressed as follows:

$$k_{a_1} = \frac{[H][HL]}{[H_2L]}, \quad k_{a_2} = \frac{[H][H_2L]}{[H_3L]},$$

$$k_{a_3} = \frac{[H][H_3L]}{[H_4L]}, \quad K = \frac{[MHL]}{[M][HL]}$$

where the ionic charge was neglected for the sake of convenience.

The formation constant of *o*-arsonophenylazochromotropic acid chelate was calculated by the following equations:

$$K = \frac{T_L - F}{[L^{5-}]\{F + T_M - T_L\}}$$

where

$$[L^{5-}] = \frac{3T_L - T_{OH} - [H^+] + [OH^-]}{\frac{[H^+]}{k_{a_1}} + \frac{2[H^+]^2}{k_{a_1}k_{a_2}} + \frac{3[H^+]^3}{k_{a_1}k_{a_2}k_{a_3}}}$$

$$F = [L^{5-}]\left\{1 + \frac{[H^+]}{k_{a_1}} + \frac{[H^+]^2}{k_{a_1}k_{a_2}} + \frac{[H^+]^3}{k_{a_1}k_{a_2}k_{a_3}}\right\}$$

where T_L, T_M and T_{OH} represent the total concentration of ligand, metal ion species and alkali added, respectively. These equations can be simplified for the calculations of the other chelate formation constants.

These constants were calculated by an NEAC-2203 computer (the Nippon Electric Co., Ltd) in the Electronic Computer Center of Okayama University.

Results and Discussion

Titration Curves. The potentiometric titration curves for *o*-substituted phenylazochromotropic acids with or without equivalent amounts of

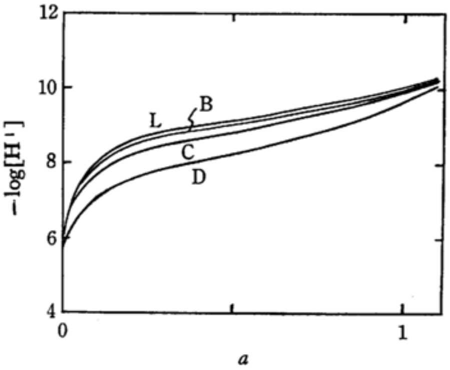

Fig. 2. Titration of phenylazochromotropic acid chelate system at 25°C, μ=0.10.
L, ligand only; B, Sr; C, Ca; D, Mg
[Ligand]=[Metal ion]=2.24×10^{-3} M
a=moles of base added per mole of ligand

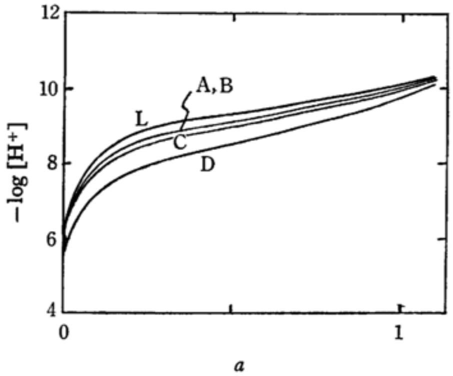

Fig. 3. Titration of *o*-sulfophenylazochromotropic acid chelate system at 25°C, μ=0.10.
L, ligand only; A, Ba; B, Sr; C, Ca; D, Mg
[Ligand]=[Metal ion]=2.20×10^{-3} M

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3) S. Nakashima, H. Miyata and K. Tôei, This Bulletin, **40**, 870 (1967).

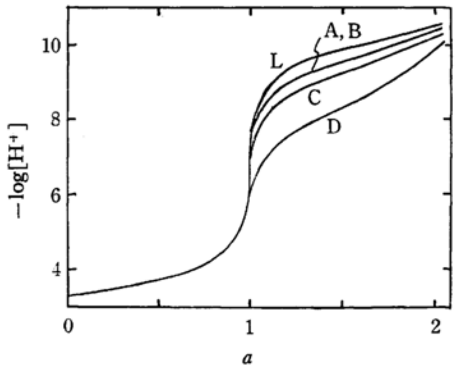


Fig. 4. Titration of *o*-carboxyphenylazochromotropic acid chelate system at 25°C, $\mu=0.10$.
L, ligand only; A, Ba; B, Sr; C, Ca; D, Mg
[Ligand]=[Metal ion]=2.39×10^{-3} M

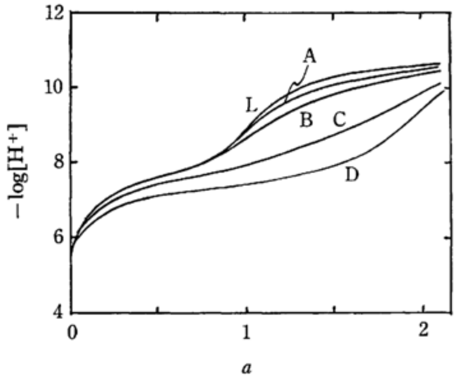


Fig. 5. Titration of *o*-phenolazochromotropic acid chelate system at 25°C, $\mu=0.10$.
L, ligand only; A, Ba; B, Sr; C, Ca; D, Mg
[Ligand]=[Metal ion]=1.56×10^{-3} M

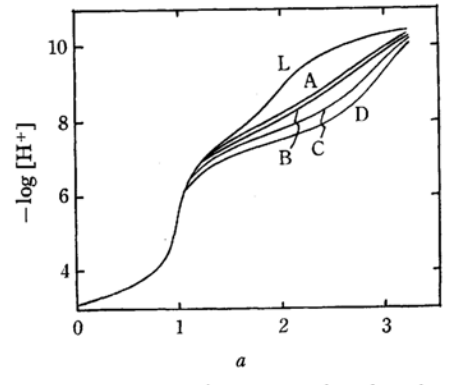
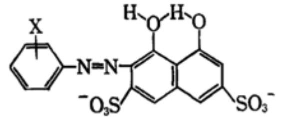


Fig. 6. Titration of *o*-arsonophenylazochromotropic acid chelate system at 25°C, $\mu=0.10$.
L, ligand only; A, Ba; B, Sr; C, Ca; D, Mg
[Ligand]=[Metal ion]=1.09×10^{-3} M

alkaline earth metal ions are illustrated in Figs. 2—6. The clear inflections at $a=1$ in the titration curves of the ligands in Figs. 4 and 5 show the dissociation of carboxyl and hydroxyl protons of the reagents, respectively, and similarly the inflections at $a=1$ and $a=2$ in Fig. 6 correspond to the dissociation of two arsonic protons. No inflection is observed at all on the neutralization of the napthalic protons of the above three reagents. Modification of the titration curves in the presence of metals is due to the chelate formation giving rise to free protons.

Acid Dissociation Constants. Substituted phenylazochromotropic acid is shown in the following structure:



X: *o*-H, *o*-SO_3^-, *o*-COOH, *o*-OH, *o*-$AsO(OH)_2$, *m*-SO_3^-, *p*-SO_3^-

The acid dissociation constants of the above seven derivatives are calculated from the titration curves and summarized in Table 2. As the pk_{a_3} value of *o*-arsonophenylazochromotropic acid is low, it is determined by titrating the reagent solution of 2.06×10^{-3} M. The constants obtained by this apparatus are in good agreement within experimental error with previous results³⁾ for the dissociation constants of *o*-phenolazochromotropic acid and the formation constants of its magnesium and calcium chelates.

In Table 2, the pk_{a_1} value corresponds to the dissociation of one of the naphtholic hydroxyl groups; the other napthalic hydroxyl group is not dissociated under ordinary experimental conditions, owing to a strong hydrogen bridge between two oxygen atoms of chromotropic acid as shown in the above structure. These ligands may be considered to be monobasic acids for phenyl-, *o*-, *m*-, and *p*-sulfophenylazochromotropic acids, dibasic acids for *o*-carboxyphenyl- and *o*-phenolazochromotropic acids and tribasic acid for *o*-arsonophenylazochromotropic acid.

The pk_a's of benzoic acid, phenol and phenylarsonic acid are 4.17,⁴⁾ 9.98⁵⁾ and 8.25 and 3.39 (obtained from potentiometric titration) respectively, whereas those of the corresponding azochromotropic acids are smaller. On the other hand, the pk_a's of the naphtholic hydroxyl groups in the azo compounds are much larger than that of chromotropic acid (5.44).⁶⁾ This implies that the formation of the intramolecular hydrogen bonding between the naphtholic hydroxyl group and the azo nitrogen atom adjacent to the phenyl group forms a stable six-membered ring.

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4) I. M. Kolthoff and W. Bosch, *J. Phys. Chem.*, **36**, 1695 (1932).

5) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **74**, 1058 (1952).

6) M. Sakaguchi, A. Mizote, H. Miyata and K. Tôei, This Bulletin, **36**, 885 (1963).

TABLE 2. ACID DISSOCIATION CONSTANTS OF SUBSTITUTED PHENYLAZOCHROMOTROPIC ACIDS AND FORMATION CONSTANTS OF THEIR CHELATES (t=25°C, μ=0.10; KNO_3)

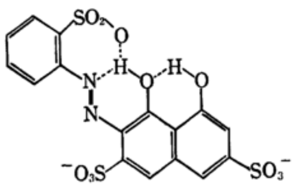
Substituent X	Acid dissociation constant			Formation constant, log *K*			
	pk_{a_1}	pk_{a_2}	pk_{a_3}	Mg	Ca	Sr	Ba
o-H	9.15			3.64	2.70	1.78	1.06
o-SO_3Na	9.35			3.58	2.91	2.58	2.66
o-COOH	9.94	3.71		4.55	3.40	2.81	2.81
o-OH	10.60	7.60		6.15	5.01	3.49	2.73
o-$AsO(OH)_2$	9.98	7.57	2.97	5.58	5.09	4.41	4.15
m-SO_3Na	8.85						1.44
p-SO_3Na	8.90						1.58

where $k_{a_1}=\frac{[H][HL]}{[H_2L]}$, $k_{a_2}=\frac{[H][H_2L]}{[H_3L]}$, $k_{a_3}=\frac{[H][H_3L]}{[H_4L]}$

Owing to the formation and the stabilization of the ring, the dissociation of the substituents in *o*-COOH, *o*-OH and *o*-$AsO(OH)_2$ compounds is easier than those of the corresponding phenyl compounds, meanwhile the dissociation of naphtholic hydroxyl groups is much more difficult than chromotropic acid.

Electron-withdrawing sulfonic group enhances the ligand acidity and thus the pk_a values of *m*- and *p*-sulfophenylazochromotropic acids are lower than that of phenylazochromotropic acid. However, the contribution of the sulfonic group in *o*-sulfophenylazochromotropic acid leads to the depression of the dissociation of the naphtholic proton as seen in Table 2.

This suggests that the sulfonic group in the ortho position for the azo group forms a hydrogen bond with the naphtholic proton in aqueous solution as the following structure shows:



Formation Constants. The formation constants of the 1 : 1 chelates of substituted phenylazochromotropic acids with alkaline earth metals are also tabulated in Table 2. The formation constant, log *K*, is plotted *versus* the sum of the disscoiation constants, pK_A ($=pk_{a_1}+pk_{a_2}+pk_{a_3}$), in Fig. 7. An approximately linear correlation between pK_A and log *K* is obtained for the chelates of a series of alkaline earth metals.

It is of interest that the log *K* values are nearly proportional to the pK_A values in spite of the complicated chelate structures and the differences of the numbers of the chelate ring formed. In barium chelates, however, a considerable deviation from the linearity is observed in comparison with the other metal chelate systems.

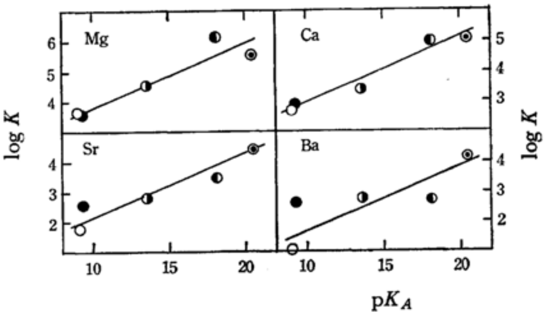


Fig. 7. Relation between pK_A of *o*-substituted phenylazochromotropic acids and log *K* of their metal chelates.
$pK_A = pk_{a_1} + pk_{a_2} + pk_{a_3}$
○ -H, ● $-SO_3^-$, ◑ -COOH, ◐ -OH, ⊙ $-AsO(OH)_2$

It should be noted that the formation constants of *o*-sulfophenylazochromotropic acid chelates are larger than those of phenylazochromotropic acid chelates except the magnesium chelate. It seems that the sulfonic group takes part in the chelate coordination. Particularly, its stability for barium chelate is much higher than that for *m*-, *p*-sulfophenyl- and phenylazochromotropic acid chelates. This result suggests that the sulfonic group at the ortho position has a strong coordination ability to barium ion. The order of decreasing stability of the metal chelates of phenyl-, *o*-phenol- and *o*-arsonophenylazochromotropic acid, magnesium> calcium> strontium> barium, agrees with the orders already reported for a large number of other ligands. However, in *o*-carboxyphenylazochromotropic acid chelate, the orders of decreasing stability is magnesium> calcium> strontium= barium and furthermore in *o*-sulfophenylazochromotropic acid it is magnesium> calcium> barium> strontium.

The relation of the formation constants, log *K*, of the chelates of *o*-substituted phenylazochromotropic acids to the reciprocal of the effective radii, $1/r$, for alkaline earth metal ions, which were calculated by Latimer,⁷⁾ is given in Fig. 8. Latimer suggests that these effective radii give a good estimate of ionic size in solution. Figure 8 shows two different trends on the chelates of the ligands investigated. The one is a straight line shown by a solid line on which lie chelates of phenyl-, *o*-phenol- and *o*-arsonophenylazochromotropic acid, but the log K values of the calcium chelates show a larger deviation from that line. The other includes *o*-sulfophenyl- and *o*-carboxyphenylazochromotropic acid, for which another linear relationship is observed from strontium to magnesium as shown by a dotted line, but the log K values of the barium chelates are equal to or larger than that of the strontium chelates.

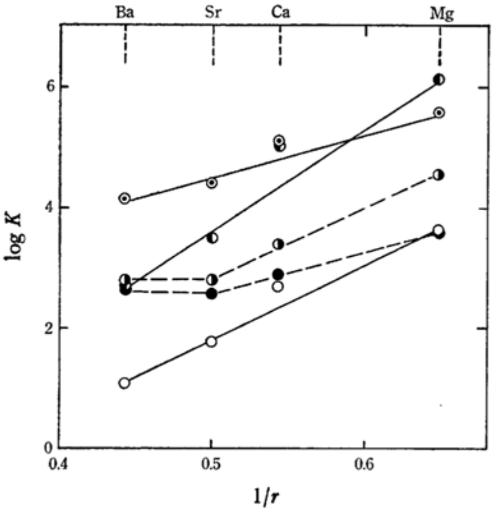


Fig. 8. Correlation of log K for *o*-substituted phenylazochromotropic acid chelates against $1/r$ of metal ions.
○ -H, ● $-SO_3^-$, ◑ -COOH, ◐ -OH, ⊙ $-AsO(OH)_2$

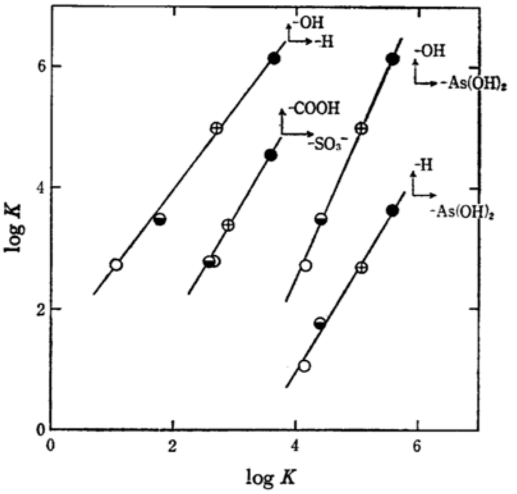


Fig. 9. Relation between log K's for pairs of ligands.
●: Mg, ⊕: Ca, ◒: Sr, ○: Ba

The plot of the log K value of one reagent against that of another reagent is given in Fig. 9. A good linear relationship is obtained among phenyl-, *o*-phenol- and *o*-arsonophenylazochromotropic acid chelate systems and between *o*-carboxyphenyl- and *o*-sulfophenylazochromotropic acid chelate systems.

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7) W. M. Latimer, *J. Chem. Phys.*, **23**, 90 (1955).