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The Chelate Formation of (*o*-Substituted Phenylazo)chromotropic Acids with Alkaline Earth Metals. II

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The acid dissociation constants of phenylazochromotropic acid and its *o*-substituted derivatives with -CH_3, -OCH_3, -$COCH_3$, -COOH, -CH_2COOH, -COCOOH, -OCH_2COOH, and -CH(OH)COOH in the *ortho* position to the azo group, and the stability constants of their 1 : 1 metal chelates with alkaline earth metals have been measured by potentiometric titation. The measurements have been carried out at 25°C and at $\mu=0.10$ with KNO_3. The effects of these substituents on the acid dissociation constants of the reagents and on the stability constants of these chelates were discussed. The pK_a value for the naphtholic proton of the *o*-substituted reagents was larger than that of phenylazochromotropic acid, and the stability constants of these chelates with alkaline earth metals decreased as follows: Mg>Ca>Sr>Ba, while for the chelates of the *o*-OCH_2COOH reagent the order was Ca>Mg>Sr>Ba, and for the *o*-CH(OH)COOH reagent it was Mg≈Ca>Sr>Ba. The plots of the stability constants, log K_1, against the sum of the acid dissociation constants, $pK_A(=pK_{a1}+pK_{a2})$, were approximately linear except for the above two reagents with calcium, strontium, and barium. From the results obtained, the *o*-OCH_2COOH reagent that behaves as a quadridentate ligand forms a more stable chelate with calcium, strontium, and barium, and the effect of the -OCH_2COOH group, especially that of the coordination of the -O- atom, is remarkable in its calcium chelate.

Many of the (*o*-substituted phenylazo)chromotropic acids are well known as colorimetric reagents and as metal indicators in chelatometry. In a previous paper,[1] the effects of various substituents on the acid dissociation of the reagents and also on the chelate formation with alkaline earth metals were discussed. The present authors have now extended the studies to alkaline earth metal chelates with the eight (*o*-substituted phenylazo)chromotropic acids shown in Fig. 1, and have investigated the effect of the substituents on the dissociation constants and the stability constants by means of the potentiometric-titration method.

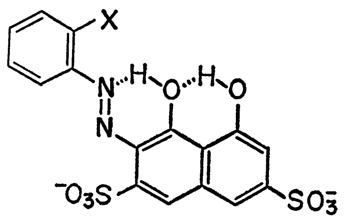

Fig. 1. Structure of reagents.
X: -H, -CH_3, -OCH_3, -$COCH_3$, -COOH, -CH_2COOH, -COCOOH, -OCH_2COOH, and -CH(OH)COOH

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[1] S. Nakashima, H. Miyata, and K. Tôei, This Bulletin, **41**, 2632 (1968).

Experimental

Reagents. The *o*-H reagent [phenylazochromotropic acid, 2-(phenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid],[2] the *o*-CH_3 reagent [2-(*o*-tolylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid], the *o*-OCH_3 reagent [2-(*o*-anisolazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid],[3] the *o*-$COCH_3$ reagent [2-(*o*-methylbenzoylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid,[4] the *o*-COOH reagent [2-(*o*-carboxyphenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid],[5] the *o*-CH_2COOH reagent[2-(*o*-phenylacetic acidazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid],[6] the *o*-COCOOH reagent [2-(*o*-oxalophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid],[7] the *o*-OCH_2COOH reagent [2-(*o*-phenoxyacetic acidazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid],[8] and the *o*-CH(OH)COOH reagent [2-(*o*-mandelic acidazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid][9] were synthesized by the coupling reaction of chromotropic acid with the corresponding diazonium compounds. The disodium salt of the reagents was obtained by the salting-out of purified azo sulfonic acids. These reagents are all fine crystals. They are dried at 60°C in a vacuum and stored in a calcium chloride desiccator. The stock solutions of these reagents were standardized by potentiometric titration with a standard 0.10 M potassium hydroxide solution.

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

Potentiometric titration. The apparatus and the procedure for the potentiometric titration were presented in a previous paper[1]; the temperature and ionic strength of a solution were maintained, respectively, at 25°C and at 0.10 with potassium nitrate.

Calculations of Acid Dissociation Constants and Stability Constants. The *o*-H, *o*-CH_3, *o*-OCH_3, and *o*-$COCH_3$ reagents are considered to be monobasic acids, while the *o*-COOH, *o*-CH_2COOH, *o*-COCOOH, *o*-OCH_2COOH, and *o*-CH(OH)COOH reagents are considered to be dibasic acids. The acid dissociation constants, K_{a_1} and K_{a_2}, and the stability constant, K_1, can be calculated by equations similar to those reported by Murakami *et al.*[10] K_{a_1}, K_{a_2} and K_1 are expressed as follows:

$$K_{a1} = \frac{[\mathrm{H}][\mathrm{HL}]}{[\mathrm{H_2L}]}, \quad K_{a2} = \frac{[\mathrm{H}][\mathrm{L}]}{[\mathrm{HL}]}$$

$$K_1 = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$

where the ionic charge was neglected for the sake of convenience

Results and Discussion

Titration Curves. The potentiometric titration curves for phenylazochromotropic acid (the *o*-H reagent) chelate system are illustrated in Fig. 2, while those for the *o*-COOH reagent chelate system are shown in Fig. 3. The clear inflection at $a=1$ in the titration curve of the ligand in Fig. 3 shows the dissociation of the carboxyl proton of the reagent. No inflection was observed at all on the neutralization of the naphtholic hydroxyl proton. The titration curves of the *o*-CH_3, *o*-OCH_3, and *o*-$COCH_3$ reagents were similar to that of the *o*-H reagent in Fig. 2, while those of the *o*-CH_2COOH, *o*-COCOOH, *o*-OCH_2COOH, and *o*-CH(OH)COOH reagents resemble the curve in Fig. 3.

Acid Dissociation Constants. The acid dissociation constants of the reagents were calculated from the titration curves and are summarized in Table 1.

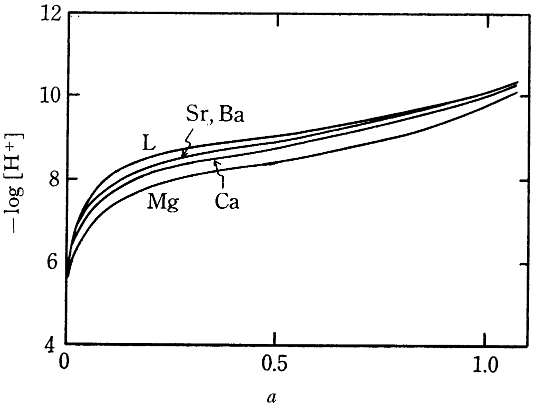

Fig. 2. Titration curves of phenylazochromotropic acid chelate system at 25°C, $\mu=0.10$.
L: ligand only
$[L]=[M]=1.188\times10^{-3}$ M
a: moles of base added per mole of ligand

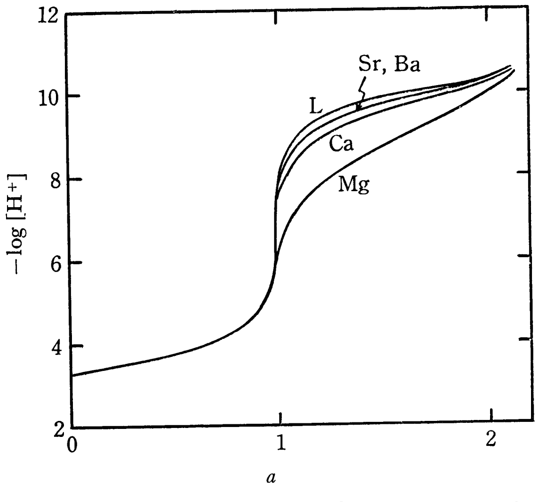

Fig. 3. Titration curves of the *o*-COOH reagent chelate system at 25°C, $\mu=0.10$.
$[L]=1.255\times10^{-3}$ M
$[Mg]=1.108\times10^{-3}$ M
$[Ca]=1.134\times10^{-3}$ M
$[Sr]=1.092\times10^{-3}$ M
$[Ba]=0.979\times10^{-3}$ M

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Table 1. Acid dissociation constants of (*o*-substituted phenylazo)chromotropic acids and stability constants of these chelates (t=25°C, μ=0.10; KNO_3)

Substituent X	Acid dissociation constant		Stability constant, log K_1			
	pK_{a1}	pK_{a2}	Mg	Ca	Sr	Ba
-H		9.19	3.64	2.70	2.08	1.84
-CH_3		9.60	3.47	2.56	—	—
-OCH_3		9.92	3.95	3.25	2.40	2.08
-$COCH_3$		9.65	3.66	2.95	2.35	
-COOH	3.60	10.00	4.53	3.37	2.82	2.81
-CH_2COOH	3.77	9.64	4.00	3.50	2.75	2.43
-COCOOH	3.54	9.96	4.55	3.41	2.88	2.73
-OCH_2COOH	2.84	9.83	4.31	5.13	3.65	3.00
-CH(OH)COOH	3.03	9.39	3.96	3.92	3.40	3.12

The pK_{a1} and pK_{a2} values correspond to the dissociation of the carboxyl group and one of the naphtholic hydroxyl groups respectively. The other naphtholic hydroxyl group is not dissociated under ordinary experimental conditions because of a strong hydrogen bridge between two oxygen atoms of chromotropic acid, as is shown in Fig. 1. The pK_a value of the *o*-H reagent is 9.19. It is suggested that pK_a values of the *o*-CH_3 and *o*-OCH_3 reagents are larger than that of the *o*-H reagent, because the methyl and methoxy groups are *ortho*- and *para*-directing and electron-donating. Because of the effects of these groups, the N···H hydrogen bond should become stronger, as is shown in Fig. 1; in fact, the pK_a values for the *o*-CH_3 and the *o*-OCH_3 reagents are 9.60 and 9.92 respectively. In the case of the *o*-$COCH_3$ reagent, the value is 9.65 in spite of its electron-withdrawing effect. However, the value of the *p*-$COCH_3$ reagent is 9.08 because of this effect. The same phenomenon appears in the case of the *o*- and the *p*-sulfophenylazochromotropic acids, where the pK_a of the *o*-reagent is 9.35, whereas that of the *p*-reagent is 8.95.[1] Thus, the introduction of such electron-withdrawing groups into the *para*-position results in a lowering of the pK_a value, while their introduction into the *ortho*-position leads to a rise in the value. This is due to the *ortho* effect which inhibits the dissociation of the naphtholic proton.

In the *o*-COOH reagent, the resonance of the carboxyl group is so inhibited by the six-membered ring, which contains the N···H hydrogen bond, that the carboxyl group and benzene ring cannot exist on the same plane. The carboxyl proton tends to be dissociated easily for this reason.

The pK_{a1} values of the five reagents which have a carboxyl group are compared with those of the aromatic acids in Table 2. The pK_{a1} values of all the reagents except the *o*-COCOOH reagent are smaller than those of the aromatic acids. This exception is also dependent on the *ortho* effect.

Table 2. The pK_a values of aromatic acids

Acid	pK_a
Benzoic acid	4.01[11]
Phenylacetic acid	4.31[12]
Phenylglyoxylic acid	1.32[13]
Phenoxyacetic acid	2.93[14]
Mandelic acid	3.41[15]

Stability Constants. The stability constants of their 1 : 1 chelates with alkaline earth metals are also tabulated in Table 1. The *o*-H, *o*-CH_3, *o*-OCH_3, and *o*-$COCH_3$ reagents are considered to form a bidentate ligand, the *o*-COOH, *o*-CH_2COOH, and *o*-COCOOH reagents are terdentate, and the *o*-OCH_2-COOH and the *o*-CH(OH)COOH reagents are quadridentate for alkaline earth metal ions.

The strontium and barium chelates of the *o*-CH_3 reagent were so unstable that their stability constants could not be determined. The barium chelate of the *o*-$COCH_3$ reagent also could not be obtained because of its precipitation.

The relation between the stability constants, log K_1, and the reciprocal of alkaline earth metal ionic radii,[16] $1/r$, is given in Fig. 4. The log K_1 values of most metal chelates decrease as follows: magnesium >calcium>strontium>barium, with an increase in

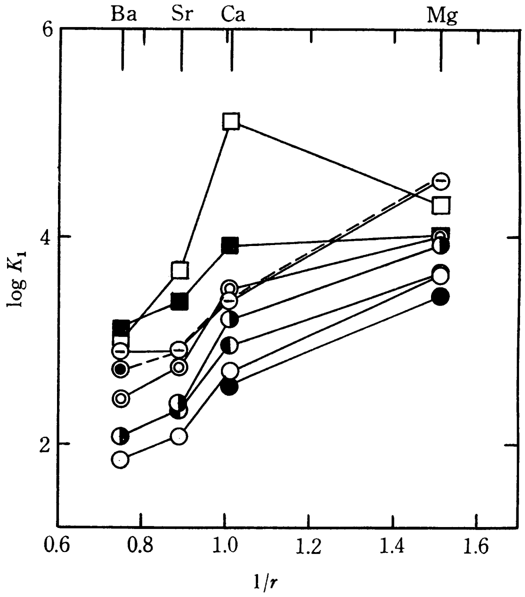

Fig. 4. Plot of log K_1 for (*o*-substituted phenylazo) chromotropic acid chelates against $1/r$ of metal ions.

○	-H	⊖	-COOH
●	-CH_3	◎	-CH_2COOH
◑	-OCH_3	⊙	-COCOOH
◐	-$COCH_3$	□	-OCH_2COOH
		■	-CH(OH)COOH

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the ionic crystal radii. However, in the *o*-OCH_2-COOH and the *o*-CH(OH)COOH chelates, the order of decreasing stability is calcium$\gtrsim$magnesium$>$strontium$>$barium. The values of the *o*-COOH chelates with strontium and barium are nearly equal, because the chelation in the *o*-COOH reagent is suitable for the barium ionic radius.

As the relation between metal ions and these ligands is regarded as a Lewis acid-base reaction, the log K_1 value is plotted against the sum of the dissociation constants, pK_A ($=pK_{a1}+pK_{a2}$), in Fig. 5. The log K_1 values are nearly proportional to the pK_A values. This implies that the stability of these chelates is mainly dependent upon the basicity, *i.e.*, the pK_A value, of the ligands, except for the calcium, strontium, and barium chelates of the *o*-OCH_2COOH and the *o*-CH(OH)COOH reagents.

As for the reagents behaving as monobasic acid, the plots of the log K_1 values of the *o*-H chelates against those of the *o*-OCH_3 or *o*-$COCH_3$ chelates are shown in Fig. 6(a). These reagents may form a bidentate ligand, and a good linear relation sphip is obtained among the reagents. This suggests that these chelate structures are similar to each other, as is shown in the structural formula (1). The chelate structure of the *o*-H reagent with an alkaline earth metal ion forms a stable six-membered ring. The bulky methyl group of the *o*-CH_3 reagent disturbs the chelate formation. Especially, these chelates with strontium and barium are very unstable because of these large ionic radii. The small stable deviation of the *o*-OCH_3 reagent with calcium is due to the coordination of the oxygen atom of the methoxy group, but those of the acetyl group scarcely coordinate at all with the metal ion.

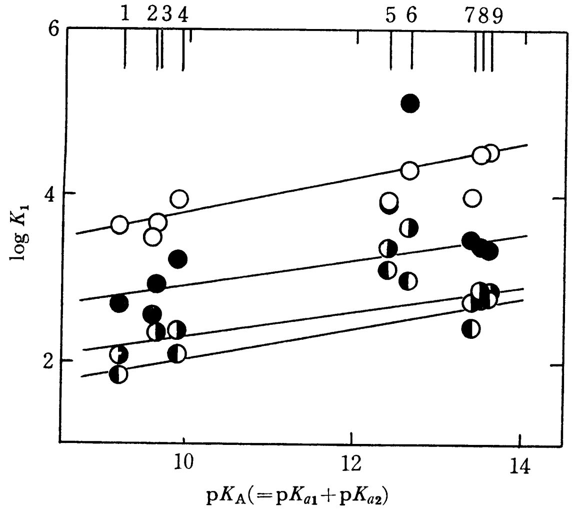
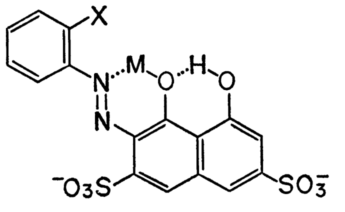


Fig. 5. Relation between pK_A of the reagents and log K_1 of their metal chelates.

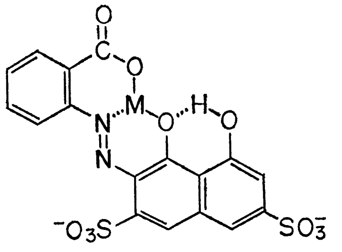
1 -H
2 $-CH_3$
3 $-COCH_3$
4 $-OCH_3$
5 -CH(OH)COOH
6 $-OCH_2COOH$
7 $-CH_2COOH$
8 -COCOOH
9 COOH

○ Mg, ● Ca, ◑ Sr, ◐ Ba



Structural formula 1
X: -H, $-CH_3$, $-OCH_3$

The same relationship is obtained for the dibasic acid system, as is shown in Fig. 6(b) and (c); these structures are shown in structural formulas (2), (3), and (4). That is to say, the structure of the *o*-COOH chelate has two chelate rings as a terdentate ligand, but those of the *o*-OCH_2COOH and the *o*-CH(OH)-COOH chelates probably have three chelate rings.



Structural formula 2

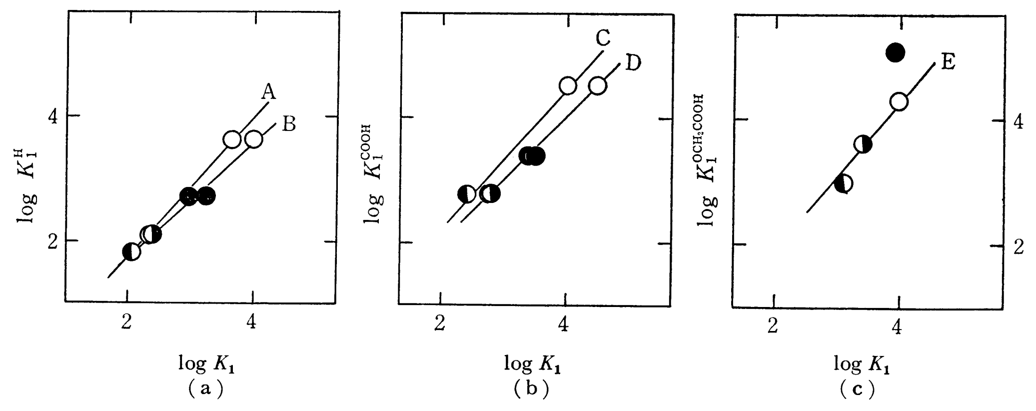
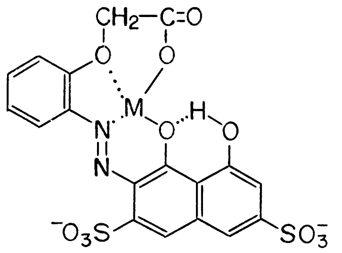


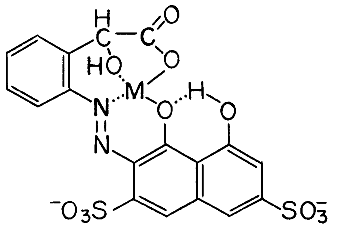
Fig. 6. Relation between log K_1's for pairs of ligands

A: $-H\sim-OCH_3$
B: $-H\sim-COCH_3$
C: $-COOH\sim-CH_2COOH$
D: $-COOH\sim-COCOOH$
E: $-OCH_2COOH\sim-CH(CH)COOH$

○ Mg, ● Ca, ◑ Sr, ◐ Ba



Structural formula 3



Structural formula 4

Thus, the reagents may behave as a quadridentate ligand. As is shown in Fig. 5, the positive deviation from the straight line for the log K_1 values of these calcium, strontium, and barium chelates is considered to result from this cause. This tendency is so remarkable in the *o*-OCH_2COOH chelate with calcium that the order of the stability is calcium>magnesium. On the other hand, on the magnesium chelates of these reagents, the plots in Fig. 5 lie on or under the straight line. This means that their oxygen atom (–O– or –OH) in the substituent scarcely contributes at all to the coordination, because the ionic radius of magnesium is much smaller than that of the other alkaline earth metals discussed before.

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