The Dissociation Phenomena of o-Phenol- and m-Chloro-o-phenol-azochromotropic Acids and the Formation Constants of Magnesium and Calcium Chelates

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The acid dissociation constants of o-phenol-, m-chloro-o-phenol- and o-anisolazochromotropic acids have been measured by potentiometric titration. The measurements have been carried out at $25.0\pm0.1°C$ and $\mu=0.10$ (by KNO_3). From these constants, the dissociation of the hydroxyl groups in the reagents has been discussed. The phenolic hydroxyl group was first dissociated, and then one of the naphtholic hydroxyl groups; the other naphtholic group was not dissociated under ordinary experimental conditions. The pK_{a_1} and pK_{a_2} values were 7.60 and 10.60 for o-phenolazochromotropic acid, and 7.56 and 10.35 for m-chloro-o-phenolazochromotropic acid. o-Phenol- and m-chloro-o-phenolazochromotropic acids formed 1 : 1 chelates with calcium and magnesium. The formation constants were measured potentiometrically; the log K's for calcium were 5.01 and 5.22, and for magnesium, 6.15 and 6.22.

Many of the derivatives of chromotropic acid are sensitive colorimetric reagents to various metal ions. Especially o, o'-dihydroxyazo compounds of chromotropic acid are very sensitive to alkaline earths.[1] o-Phenol- and m-chloro-o-phenolazochromotropic acids are, therefore, widely used as colorimetric reagents[2] and as metal indicators[3] in chelatometry for the determination of alkaline earths. The present paper will describe the dissociation of the reagents and their chelation with calcium and magnesium.

Experimental

Reagents. m-Chloro-o-phenolazochromotropic acid [Eriochrome Blue SE, 2-(1-hydroxy-4-chloro-2-phenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonic acid disodium salt] obtained from the Sumitomo Dye Co., with the trade name Plasmocorinth B, was used for the studies without any further purification. o-Phenolazochromotropic acid [Acid Chrome Blue K, 2-(1-hydroxy-2-phenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonic acid disodium salt] and o-anisolazochromotropic acid [2-(1-methoxy-2-phenylazo)-1, 8-dihydroxynaphthalene-3, 6-disulfonic acid disodium salt] were synthesized by the coupling reaction of chromotropic acid with o-diazophenol and with o-diazoanisol respectively. These reagents were dried at 60°C in a vacuum, and cooled in a phosphorus pentoxide desiccator. The stock solutions of o-phenol- and m-chloro-o-phenolazochromotropic acids were *ca.* 5×10^{-3} M; they were standardized by potentiometric titration with standard 0.1 M

potassium hydroxide. Analytical grade $Mg(NO_3)_2\cdot6H_2O$ and $Ca(NO_3)_2\cdot4H_2O$ were used to make stock solutions and were standardized by the usual technique of chelatometric titration.

Potentiometric Titrations. The hydrogen ion concentration was measured by using an HRL Model P pH meter (made by the Horiba Instruments Inc., Kyoto), with glass and calomel electrodes. The pH meter was calibrated before and after the measurements with an acetate buffer and with potassium hydroxide. The measurements were carried out at $25.0\pm0.1°C$, while the ionic strength was maintained at approximately 0.10 M with potassium nitrate. Solutions under investigation were kept in a nitrogen atmosphere by the circulation of purified nitrogen through the jacketed titration cell.

Calculations of Acid Dissociation Constants and Chelate Formation Constants. The dissociation constants, K_{a_1} and K_{a_2}, and the formation constant, K, can be calculated by similar equations reported by Murakami *et al.*[4] K_{a_1}, K_{a_2} and K are there defined as follows:

$$K_{a_1} = \frac{[H^+][H_2L^{3-}]}{[H_3L^{2-}]}, \qquad K_{a_2} = \frac{[H^+][HL^{4-}]}{[H_2L^{3-}]}$$

$$K = \frac{[MHL^{2-}]}{[M^{2+}][HL^{4-}]}$$

The third dissociation constant, K_{a_3}, can not be determined by using a pH meter with a glass electrode, because the third hydrogen atom is strongly bridged between two oxygen atoms of chromotropic acid. In calculating the dissociation constants, an NEAC-2203 computer (made by the Nippon Electric Co., Ltd.), installed in the Electronic Computer Center of Okayama University, was utilized.

1) K. Emi, K. Tôei and H. Miyata, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **78**, 736 (1957).
2) J. S. Brush, *Anal. Chem.*, **33**, 798 (1961).
3) C. Spach and A. Erny, *Bull. Soc. Chim. Biol.*, **45**, 1191 (1963).
4) Y. Murakami, K. Nakamura and M. Tokunaga, This Bulletin, **36**, 669 (1963); **35**, 52 (1962).

Results and Discussion

The Dissociation Constants and the Dissociation Phenomena. The titration curves of o-phenol- and m-chloro-o-phenolazochromotropic acids are shown in Figs. 1 and 2. Both solutions were red purple below $a=1$ and became deep blue beyond $a=1$. The clear inflections, which were observed at $a=1$ in both titration curves, showed the first dissociation of these reagents, but no inflections which corresponded to the second dissociations were observed. On the other hand,
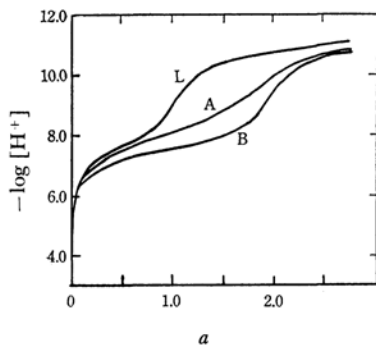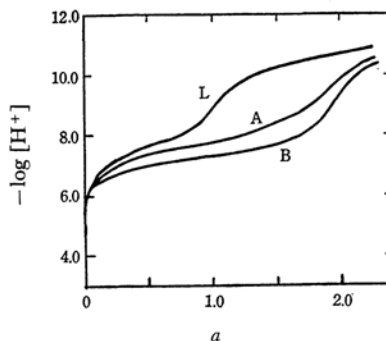

Fig. 1. Titration of 1 : 1 metal chelates of o-phenolazochromotropic acid at 25°C, $\mu=0.10$.
L, ligand only; A, Ca; B, Mg
[Ligand] = [Metal ion] = 1.70×10^{-3} M
a = moles of base added per mole of ligand

Fig. 2. Titration of 1 : 1 metal chelates of m-chloro-o-phenolazochromotropic acid at 25°C, $\mu=0.10$.
L, ligand only; A, Ca; B, Mg
[Ligand] = [Metal ion] = 2.12×10^{-3} M
a = moles of base added per mole of ligand

in the titration curve of o-anisolazochromotropic acid, no inflection could be found at $a=1$. Hence, it will be obvious that the dissociation corresponding to this inflection is not that of the naphtholic proton, but that of the phenolic proton. The acid dissociation constants of these agents were calculated from the titration curves and are summarized in Table 1. The acid dissociation of o-phenolazochromotropic acid may be represented by the following scheme:
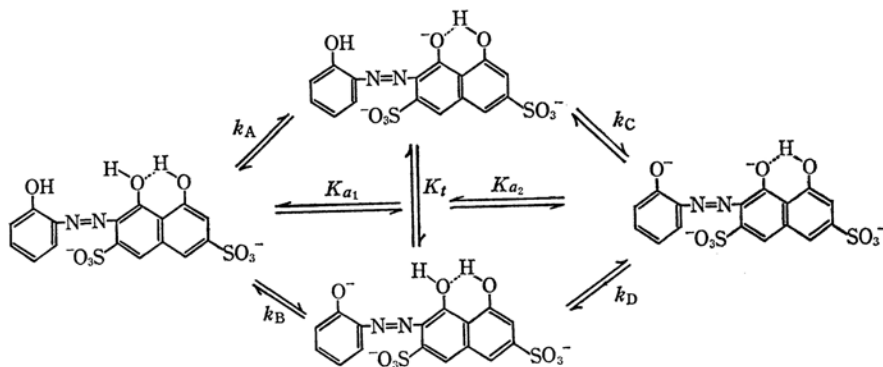

TABLE 1. ACID DISSOCIATION CONSTANTS OF o-PHENOL- AND m-CHLORO-o-PHENOLAZOCHROMOTROPIC ACIDS AND THEIR FORMATION CONSTANTS FOR Mg AND Ca

Ligand		pK_{a_1}	pK_{a_2}	pK_{a_3}	log K	
					Mg	Ca
o-Phenolazochromotropic acid	the authors	7.60	10.60		6.15	5.01
	Tolmachev et al.[5]	7.55	9.28	12.40		
m-Chloro-o-phenol-azochromotropic acid	the authors	7.56	10.35		6.22	5.22
	Miyata[6]	7.15	10.48			
	Brush[2]	8.0	10.5	11.9		

5) V. N. Tolmachev and G. G. Lomakina, *Zhur. Fiz. Khim.*, **31**, 1027 (1957); *Chem. Abstr.*, **52**, 50 (1958).

6) H. Miyata, This Bulletin, **37**, 426 (1964).

In the above scheme, K_{a_1} and K_{a_2} are the macroscopic dissociation constants, and k_A, k_B, k_C and k_D are the microscopic constants. The relationships among these various equilibrium constants are as follows:

$$K_{a_1} = k_A + k_B \tag{1}$$

$$\frac{1}{K_{a_2}} = \frac{1}{k_C} + \frac{1}{k_D} \tag{2}$$

$$K_t = \frac{k_A}{k_B} = \frac{k_D}{k_C} \tag{3}$$

The pK_{a_1} and pK_{a_2} values of o-phenolazochromotropic acid are 7.60 and 10.60 respectively, from Table 1.

On the other hand, in order to determine the microscopic constants, the pK_a value of o-anisolazochromotropic acid was measured by the same manner; it was 10.00. This pK_a value can be estimated to be equal to the value of pk_A in the above scheme. From the values of pk_A as well as of pK_{a_1} and pK_{a_2}, the other microscopic constants are obtained by using Eqs. (1) to (3); $pk_B = 7.60$, $pk_C = 8.20$, $pk_D = 10.60$ and $K_t = 0.004$.

With this information, it can be considered that first the phenolic proton is completely dissociated, and that afterwards the dissociation of the naphtholic proton occurs. The dissociation constants of phenol and chromotropic acid are 9.98[7] and 5.44[8] respectively; the pK_a value of the latter is, then, much smaller than that of the former. However, as is obvious from the results, in o-phenolazochromotropic acid the pK_a value of the phenolic proton is smaller than that of the naphtolic proton. A possible explanation of this is that o-phenolazochromotropic acid forms an intramolecular hydrogen bond in an aqueous solution, as is shown below:
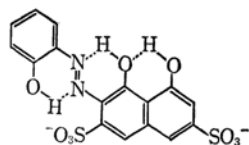
The remarkable electron-withdrawing effect of the sulfonic group at the ortho position of the azo group leads to the first dissociation of the phenolic proton. After the dissociation of the phenolic proton, the electron-donating effect of O^- at the ortho position of the azo group depresses the second dissociation of the naphtholic proton. The electron-donating effect of O^- is proved from the fact that the pK_{a_2} of o-phenolazochromotropic acid is 10.60, while the pK_a of phenylazochromotropic acid is 9.30.[9] The effect of the Cl group as the substituent for pK_a is almost not found at all in the first dissociation, but it decreases the second dissociation constant. This indicates an electron-withdrawing effect.

The Formation Constants. o-Phenol- and m-chloro-o-phenolazochromotropic acids may be considered to form the chelate of the following structure with some metal ions:
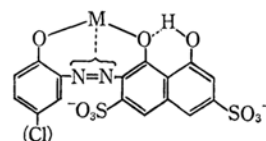
Titration curves are shown in Figs. 1 and 2 for the o-phenol- and m-chloro-o-phenolazochromotropic acid chelates of magnesium and calcium. An inflection at $a=2$ and a wide depression of hydrogen ion concentration corresponding to the formation of the 1 : 1 chelates are observed. The results of the evaluation of the formation constants are given in Table 1. There is generally a correlation between the dissociation constant, pK_a, of chelating reagents and the formation constant, $\log K$, of their metal chelates; that is, the value of $\log K$ generally becomes larger with an increase in the pK_a value. However, in both the reagents under investigation, a contrary relationship is observed; namely, the pK_a of o-phenolazochromotropic acid is larger than that of m-chloro-o-phenolazochromotropic acid, but the $\log K$ of the metal chelates of the latter is slightly larger than that of the former.

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8) M. Sakaguchi, A. Mizote, H. Miyata and K. Tôei, This Bulletin, **36**, 885 (1963).
9) H. Miyata, *ibid.*, **36**, 382 (1963).