Stability Constants of Alkaline Earth Metals with *o*-Arsono-*o*′-hydroxy Azo Compounds

Kenyu KINA and Kyoji TÔEI
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama

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The acid dissociation constants of the *o*-arsono-*o*′-hydroxy azo compounds, and their chelate stability constants with alkaline earth metals, have been measured by the pH titration method at an ionic strength of 0.10 and at 25.0±0.1°C. These azo compounds were synthesized by the coupling reaction of diazotized *o*-aminophenylarsonic acid with naphthol sulfonates. As the coupling components, 1,8-dihydroxynaphthalene-3,6-disulfonic acid (chromotropic acid), 2-hydroxynaphthalene-3,6-disulfonic acid (R acid), and 1-hydroxynaphthalene-3,6-disulfonic acid were used. *o*-Arsonophenylazochromotropic acid (Neo-Thorin) formed the most stable chelates. It was concluded that the stabilization of the metal chelate ring of the Neo-Thorin was due to a quasi-aromaticity of the six-membered ring which was produced by the hydrogen bond between two naphtholic hydroxyl groups of chromotropic acid. The metal chelate stability order, Mg>Ca>Sr>Ba, is parallel to the reciprocal of the ionic radii of the metal ions.

According to Emi *et al.*,[1] the limit of the identification of the *o*-arsono-*o*′-hydroxy azo compounds depends of the coupling components rather than on the diazo components. Especially, the azo compounds of the chromotropic acid and the *R* acid, namely Neo-Thorin and thorin, are well-known as colorimetric reagents for Thorium. In general, the relation between the basicity of the coordinating site of the similar ligand and the metal chelate stability constants should present a good linearity from the standpoint of the Lewis acids and bases. The stability constants of the chelates which we have investigated, however, vary inversely with the basicity of the ligands. This result suggests the presence of a more significant factor than basicity. In this report, we will discuss these chelate systems from the electronic and structural points of view.

Experimental

Reagents. The azo compounds, 2-(2-arsonophenylazo)-1,8-dihydroxynapthalene-3,6-disulfonic acid disodium salt [Neo-Thorin], 1-(2-arsonophenylazo)-2-hydroxynaphthalene-3,6-disulfonic acid disodium salt [Thorin], and 2-(2-arsonophenylazo)-1-hydroxynapthalene-3,6-disulfonic acid disodium salt, were synthesized by the coupling reaction of diazotized *o*-aminophenylarsonic acid with the corresponding coupling components. These azo compounds were obtained as fine crystals.

In addition, a number of azo compounds for example, N.W. acid, and F acid, were obtained by the use of hydroxynaphthalene monosulfonic acid. These compounds, however, were not studied in this investigation because of their low solubility. A carbonate-free potassium hydroxide solution was prepared by the ion exchange method and was standardized titrimetrically against potassium hydrogen phthalate.

Reagent Solutions. The stock solutions of these ligands were standardized by potentiometric titration with standard 0.10 N potassium hydroxide. The stock solutions of magnesium, calcium, strontium, and barium were prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$, and $Ba(NO_3)_2$ of a guaranteed-reagent grade in distilled water. The concentration of the former two solutions was determined by chelatemetric titration,[2] while the concentration of the latter two was determined by the usual gravimetric method.

pH Titration Method. The measurements were carried out by the use of a micro-titration apparatus. The temperature was kept at 25.0±0.1°C throughout the titration by the circulation of water through a jacketed titration vessel with a capacity of 5 m*l*, and the ionic strength of the solutions was adjusted to 0.10 with potassium nitrate. Alkali was added from a calibrated 0.50 m*l* micrometer syringe to the solution in an atmosphere of nitrogen. The hydrogen-ion concentration was measured with an HRL-Model P pH meter (made by the Horiba Instruments Inc., Kyoto) equipped with a combined glass electrode (Metrohm, EA-125 U-type, Herisaw, Switzerland). The observed pH meter readings were converted into the actual hydrogen-ion concentrations by comparing them with the stoichiometric dissociation constant of acetic acid, which was obtained by titrating it before and after each measurement.[3] The pH ($-\log[H^+]$) region above 11.0 was calibrated by measurements of the KOH solution.[4]

Results and Discussion

Calculation of Acid Dissociation Constants and Chelate Stability Constants. The equilibria and the dissociation constants involved are:

$$H_3L \rightleftharpoons H_2L + H, \quad K_{a1} = [H][H_2L]/[H_3L],$$
$$H_2L \rightleftharpoons HL + H, \quad K_{a2} = [H][HL]/[H_2L],$$
$$HL \rightleftharpoons L + H, \quad K_{a3} = [H][L]/[HL],$$

where the ionic charge was neglected for the sake of convenience. The titration curve shows a well-defined inflection at $a=1$; therefore, the first dissociation step of this triprotic acid can be treated separately form the last two steps. The region before $a=1$ was treated as monoprotic acid, while after $a=1$ it was treated as diprotic acid. In general, the following relationship represents the step-by-step acid dissociation constant of the polyprotic acid:

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[1] K. Emi, K. Tôei, and K. Furukawa, *Nippon Kagaku Zasshi*, **79**, 681 (1957).

[2] K. Ueno, "Chelatemetric Titration" (in Japanese), Nankodo, Tokyo (1967).

[3] C. F. Richard, R. L. Gustafson, and A. E. Martell, *J. Amer. Chem. Soc.*, **81**, 1033 (1959).

[4] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd. Ed., Reinhold Publ. Corp., N. Y. (1958), p. 752.

$$\sum_{i=1}^{n}\frac{iT_{\mathrm{L}}-f}{f[\mathrm{H}]^i}K_{a1}\cdot K_{a2}\cdot\cdots\cdot K_{ai}=1,$$

$$f=(T_{\mathrm{OH}}+[\mathrm{H}]-[\mathrm{OH}]),$$

where T_{L} represents the total concentration of ligand species and where T_{OH} represents the total concentration of the base added to the system. In all the calculations, the concentrations were corrected for the volume change resulting from the addition of the potassium hydroxide solution; the calculation formula of the monoprotic acid is as follows:

$$\frac{T_{\mathrm{L}}-f}{f[\mathrm{H}]}K_{a1}=1,$$

while in the case of diprotic acid it is as follows:

$$\frac{2T_{\mathrm{L}}-f}{f[\mathrm{H}]^2}K_{a1}K_{a2}+\frac{T_{\mathrm{L}}-f}{f[\mathrm{H}]}K_{a1}=1.$$

From the above equation, the dissociation constants, $K_{a1}K_{a2}$ and K_{a1}, were calculated by solving the simultaneous equation from two points on the ligand-only titration curve.

The chelate stability constants were calculated by means of the following equations:

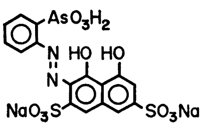
$$K_{\mathrm{ML}}=(T_{\mathrm{L}}-\mathrm{F})/[\mathrm{L}](\mathrm{F}+T_{\mathrm{M}}-T_{\mathrm{L}}).$$

where

$$\mathrm{L}=(3T_{\mathrm{L}}-T_{\mathrm{OH}}-[\mathrm{H}]+[\mathrm{OH}])/[\mathrm{H}]/K_{a3}+2[\mathrm{H}]^2/K_{a3}K_{a2}+3[\mathrm{H}]^3/K_{a3}K_{a2}K_{a1},$$

$$\mathrm{F}=[\mathrm{L}]\{1+[\mathrm{H}]/K_{a3}+[\mathrm{H}]^2/K_{a3}K_{a2}+[\mathrm{H}]^3/K_{a3}K_{a2}K_{a1}\},$$

and where T_{M} represents the total concentration of the metal species. All the calculations were carried out by using an NEAC-2203 computer (The Nippon Electric Co., Ltd.) of the Electronic Computer Center of Okayama University. The *o*-arsono-*o*′-hydroxy azo compounds are numbered as follows:



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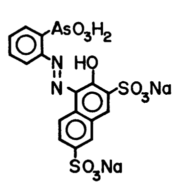

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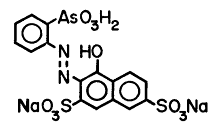

III

Titration Curves. The pH titration curves are illustrated in Figs. 1—3 for *o*-arsono-*o*′-hydroxy azo compounds, both on chelate systems and for each ligand alone. The dissociation constants, $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$, of phenylarsonic acid have been reported to be 3.39 and 8.25 respectively,[5] the clear inflections at $a=1$ and $a=2$, therefore, correspond to the dissociation of two arsonic protons. The $\mathrm{p}K_a$ value of an naphthlic proton is of an order of magnitude of 10, and this proton gives no inflection after $a=2$. The titration curve in the presence of a metal ion shows a lower pH value than in the presence of the ligand only. Such a depression of the titration curves indicates the formation of metal chelate species. The chelate stability order, Mg>Ca>Sr>Ba, can be readily

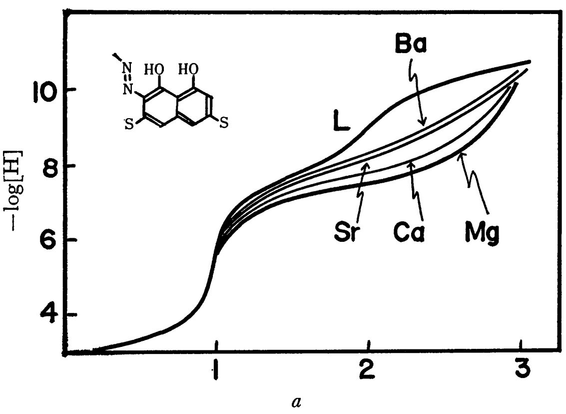

Fig. 1. Titration of 2-(2-arsonophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid disodium salt and its chelate system at 25°C, $\mu=0.10$.
L, Ligand only; a=moles of base added per mole of ligand. [Ligand]$=2.411\times10^{-3}$M, [Mg]$=2.216\times10^{-3}$M, [Ca]$=2.256\times10^{-3}$M, [Sr]$=2.078\times10^{-3}$M, [Ba]$=2.048\times10^{-3}$M.

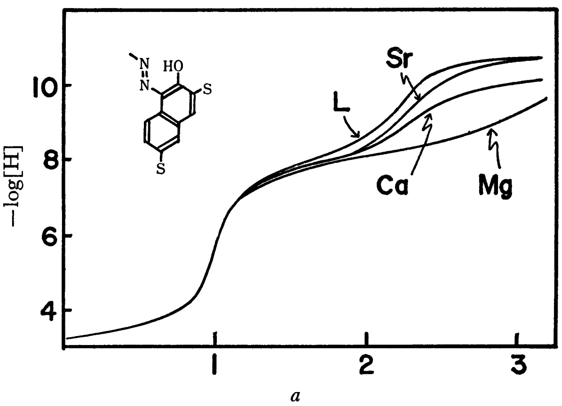

Fig. 2. Titration of 1-(2-arsonophenylazo)-2-hydroxynaphthalene-3,6-disulfonic and disodium salt and its chelate system at 25°C, $\mu=0.10$.
L, ligand only, [Ligand]$=1.734\times10^{-3}$M; a=moles of base added per mole of ligand.
The metal ions concentration are indentical to those described in Fig. 1.

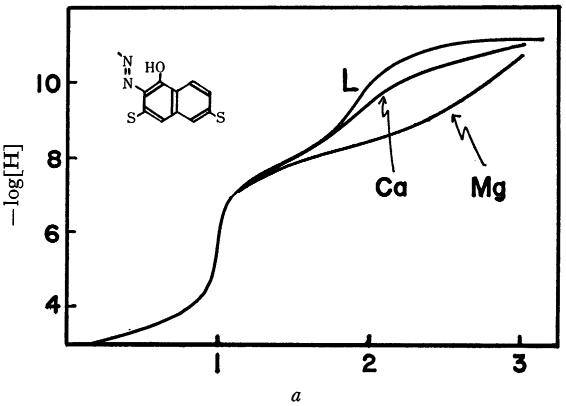

Fig. 3. Titration of 2-(2-arsonophenylazo)-1-hydroxynaphthalene-3,6-disulfonic acid disodium salt and its chelate system at 25°C, $\mu=0.10$.
L, Ligand only, [Ligand]$=2.452\times10^{-3}$M. The metal ions concentration are identical to those dercribed in Fig. 1. a=moles of base added per mole of ligand.

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

Table 1. Acid dissociation constants of *o*-arsono-*o*′-hydroxy azo compounds and stability constants of their chelates
(t=25.0±0.10°C; μ=0.10 by KNO_3)

Ligand	Acid dissociation constants				Stability constants, log K_{ML}			
	pK_{a1}	pK_{a2}	pK_{a3}	pK_A	Mg	Ca	Sr	Ba
I	2.93	7.65	10.15	20.73	5.57	5.20	4.39	4.22
II	3.44	7.86	10.80	22.10	5.20	4.17	2.87	—
III	3.09	8.05	11.40	22.54	5.35	3.50	2.0	1.8

where K_{a1}=[H][H_2L]/[H_3L], K_{a2}=[H][HL]/[H_2L], K_{a3}=[H][L]/[HL], K_{ML}=[ML]/[M][L].
— not measurable owing to precipitation

expected from the extent of the depression of pH. Evidently, Compound I formed a more stable chelate with Ca, Sr, and Ba than did the other two.

Acid Dissociation Constants. In Table 1, the pK_{a1} and the pK_{a2} values correspond to the dissociation of the arsonic group, while the pK_{a3} value corresponds to the dissociation of the naphtholic hydroxyl group. The overall acidity of the ligands is defined as the sum of the dissociation constants, pK_A=(pK_{a1}+pK_{a2}+pK_{a3}); therefore, the larger the pK_A value, the more basic the ligand. The basicity of the ligand increases as follows: Compound I<Compound II<Compound III. As Fig. 4 shows, there exists a strong hydrogen bond between the two oxygen atoms of the Compound I; this naphtholic hydroxyl group, therefore, does not dissociate under ordinary experimental conditions.[5] The pK_{a3} which corresponds to the dissociation of the first hydroxyl proton of Compound I is 10.15, a value lower than those of Compounds II and III. This higher acidity is also attributed to a strong intramolecular hydrogen bonding, which could stabilize the deprotonated anion. Actually, Compound II shows a higher basicity, because it can not form any hydrogen bond such as shown in Fig. 4.

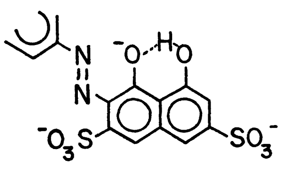


Fig. 4. Structure of hydrogen bonding.

Stability Constants. The chelate stability constants are also listed in Table 1. The stability constant of Compound II with the barium ion was not obtained because of precipitation. In general, the alkaline earth metals form an ionic coordination bond; the relation of the stability constants, log K_{ML}, to the reciprocal of the ionic radii, $1/r$, of alkaline earth metals is given in Fig. 5. The stability constants increase with a decrease in the ionic radii; that is, the decrease in the order of the metal chelate stability is as follows: Mg>Ca>Sr>Ba. The stability order relation to the ligands, except the Mg chelates, is as follows: Compound I>Compound II>Compound III. According to the concept of Lewis acids and bases, the strong basic ligand would form the more stable chelate compound. However, the metal chelate stability constants of these compounds vary inversely with the basicities of the ligands.

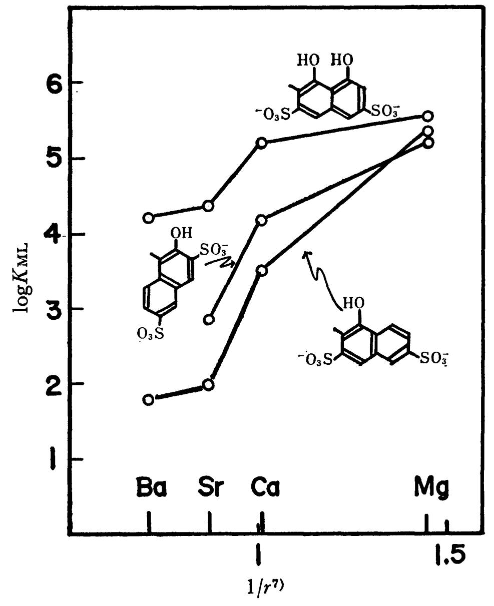
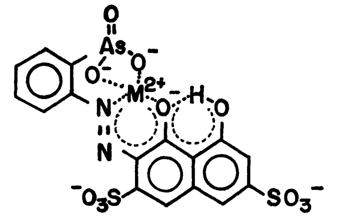


Fig. 5. Relation between logK_{ML} of the chelate of *o*-arsono-*o*′-hydroxy azo compounds and the reciprocal of the ionic radii.[7]

Such a difference depends largely on the nature of the naphtholic hydroxyl group. The chelate structure of Compound I may be as follows:



M^{2+}=Metal Ion

From the results of the measurement of the visible spectra of the free ligand, the λ_{max} values of Compounds I, II, and III are 505 mμ, 484 mμ, and 484 mμ, respectively; thus, Compound I indicates a bathochromic shift. This bathochromic effect of Compound I may be caused by the six-membered hydrogen bond ring acquiring a quasi-aromaticity which is similar to that of β-diketone derivatives.[6] As was shown in the above scheme, such a quasi-aromaticity is extremely advantageous for the stabilization of the six-membered chelate ring by means of the resonance effect.

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[6] K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Amer. Chem. Soc.*, **83**, 1272 (1961).

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

Table 2. Acid dissociation constants and stability constants of the metal chelates of the catechol derivatives[8]

Ligand	pK_a	pK_a	Zn		Cu	
			log K_1	log K_2	log K_1	log K_2
Catechol	9.13	11.59	8.46	6.78	12.52	9.66
Catechol-4-sulfonate	8.26	12.16	9.40	7.20	13.29	10.23
Tiron	7.54	12.23	10.19	8.33	13.99	11.17

where $K_1=[\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]$, $K_2=[\mathrm{ML_2}]/[\mathrm{L}][\mathrm{ML}]$

In the cases of Compounds II and III, they have lower logK_{ML} values than does Compound I because such an effect (the resonance effect) is absent. In the chelate system in which the resonance effect exerts a significant influence upon the chelate stability, the presence of a substituent group that increases the electron density of the donor atoms results in a decrease in the stability of the chelate ring. For example, the stability of the acetoacetic ester chelate is lower than that of the acetylacetone chelate. This has been explained on the basis of the electron-donating behavior of the ester group.[9] On the contrary, such a chelate system is stabilized by the presence of a electron-withdrawing group. A typical example of this can be seen in the Tiron. As Table 2 shows, the zinc or copper chelate of the Tiron is more stable than that of catechol or catechol-4-sulfonate, though the Tiron is less basic than the others. This phehomena shows that the localized electron on the oxygen atoms is dispersed by the sulfonate group; that is, such a stabilization may be due to the electron delocalization. From the structrural point of view, Compound II has a sulfonate group adjacent to the naphtholic hydroxyl group, as does the Tiron; therefore, Compound II forms a more stable chelate with Ca and Sr than does Compound III. This stabilization of the chelate ring may be the sulfonate group. As has been mentioned above, the main factor influencing the chelate stability is the nature of the naphtholic hydroxyl group with respect to calcium, strontium, and barium. On the other hand, the order of decrease in the stability constants of magnesium chelates is as follows: Compound I>Compound III>Compound II, although there is little difference among them. This order differs from the above-mentioned order. As is shown in Fig. 5, the magnesium ion has a much smaller ionic radius than those of calcium, strontium, and barium. Its chelating behavior, therefore, differs from that of the other alkaline earth metals. The stabilities of magnesium chelates are not greatly affected by the nature of the naphtholic hydroxyl group, but they are affected by its small ionic radius.

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8) Y. Murakami, K. Nakamura, and M. Tokunaga, This Bulletin, **36**, 669 (1963).

9) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," translated by M. Kobayashi, M. Fujimoto, and K. Mizumachi, lst. Ed., Kyoritsu Publ. Corp., Tokyo (1960), p. 136.