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Evaluation of the Stability Constants for Alkaline-Earth Metal Complexes with Dodecaoxohexaphosphate(III) Using EDTA as a Complexation-Competing Agent

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The stability constants for complexes of a ring oxoanion of phosphorus dodecaoxohexaphosphate(III), with magnesium, calcium, and strontium were evaluated in aqueous solutions at an ionic strength of 0.1. A new spectroscopic equilibrium analysis for a system involving complexes of very high stability was accomplished by introducing EDTA as a complexation-competing agent to the system. The logarithmic stability constant values for the magnesium, calcium, and strontium complexes were found to be 8.4, 8.8, and 7.5, respectively, whose stability order was different from that of a simple one expected from their ionic radii.

A dodecaoxohexaphosphate(III) (DOHP) was first synthesized by Blaser and Worms.[1] The structure has been determined by X-ray analysis,[2] the dissociated form of which is Chart 1.

Its characteristic absorption spectrum and hydrolytic behavior have been investigated.[3–5] The linear hexamer produced by the cleavage of the ring chain has been studied spectroscopically.[6] The stability constants of some metal–DOHP complexes have also been reported.[7,8] In a previous study,[8] the stability constants of divalent metal–DOHP complexes were determined at high ionic strength by a spectroscopic method based on a measurement of the change in the absorbance ratio at two wavelengths through equimolar-dilution. For a more diluted system, such as $I = 0.1$, however, this technique is not applicable to such highly stable complexes, since a determination of the free DOHP anion concentration is difficult.

In this study, a modified spectroscopic method employing EDTA as a competing agent has been attempted.

Experimental

Materials and Solutions. The potassium salt of DOHP ($K_6P_6O_{12}\cdot xH_2O$) was synthesized according to a procedure of Blaser and Worms.[1] A tetramethylammonium salt solution of DOHP was prepared by passing the potassium salt solution through a column containing a cation exchanger (Dowex 50W-X2, 50—100 mesh) of tetramethylammonium form. All other chemicals used were of commercially available reagent grade.

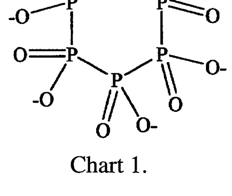

Chart 1.

Aqueous solutions containing alkaline earth metal ions and DOHP in equimolar amount were adjusted to $I = 0.1$ and pH 6.5 to 7.5 by adding the necessary amount of tetramethylammonium chloride and tetramethylammonium hydroxide. EDTA solutions of $I = 0.1$ were prepared at the same pH region, based on a calculation involving a set of known protonation constants.[9] The final EDTA concentrations were 0.0202 M (pH 6.5), 0.0180 M (pH 7.0) and 0.0171 M (pH 7.5), respectively ($1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$). Each EDTA solution was added to a metal–DOHP solution of the same pH to make the change in DOHP and the sample metal concentrations for the equilibrium analysis.

Spectral Measurement. The absorption spectrum of a sample solution was measured using a 5 cm quartz cell and a spectrophotometer Model U-best 30 (Japan Spectroscopic Co., Ltd.). At each dilution stage with the EDTA solution, the absorption spectrum was recorded and analyzed.

Results and Discussion

The molar absorption-coefficient curve of each metal DOHP complex was constructed under the condition where complete formation of the one-to-one complex is expected (Fig. 1). For a comparison, that of free DOHP anion is also shown in the figure. Their characteristic peak wavelengths and the corresponding molar absorption coefficients are given in Table 1. A metal ion of smaller ionic radius revealed a greater shift to longer wavelength (Mg > Ca > Sr > Ba). The remarkable decrease in the absorption coefficient at 355 nm for the complexes may indicate a lowering

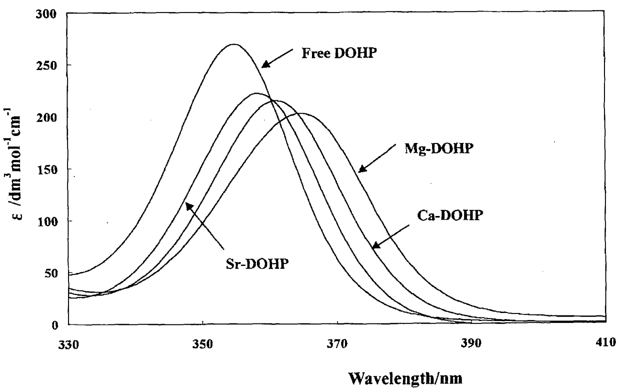

Fig. 1. Absorption spectra of one-to-one DOHP-alkaline earth metal complexes at pH 7.0 (without EDTA). Concentrations: M^{2+} = DOHP 3.51×10^{-3} M.

Table 1. Molar Absorption Coefficients (ε) of the Complex Peak and Free DOHP at Individual Peak Wavelength[a)]

	Peak wavelength nm	$\varepsilon_2^{MP^{4-}}$	$\varepsilon_1^{MP^{4-}}$	$\varepsilon_2^{P^{6-}}$	$\varepsilon_1^{P^{6-}}$
Mg–DOHP	365	203	93	89	—
Ca–DOHP	362	215	146	174	—
Sr–DOHP	359	222	181	230	—
Ba–DOHP	357	231	227	250	—
DOHP (free)	355	—	—	—	269

a) Subscription 1 : molar absorption coefficients of superscribed species at 355nm. Subscription 2 : molar absorption coefficients of superscribed species at the peak wavelength for individual metal complex.

in the ring property by metal-ion coordination.

When the free DOHP anion and its one-to-one alkaline earth metal complex coexist, the observed spectrum is generally not separated into two peaks, although the composite absorption peak shifts to longer wavelengths with increasing complexation. To analyze such a system, absorbance measurements at two wavelengths, which are characteristic of free DOHP and the metal complex, are essential. Furthermore, the addition of EDTA to this system may be effective to make a measurable change in the free DOHP concentration for the analysis. An example of the absorption spectrum of a solution containing these three components is given in Fig. 2. It has been confirmed that the presence of EDTA does not affect the spectral patterns of the species related to complexation.

We then obtain two absorbance values:

$$A_1 = \varepsilon_1^{P}[P^{6-}] + \varepsilon_1^{MP}[MP^{4-}], \tag{1}$$

$$A_2 = \varepsilon_2^{P}[P^{6-}] + \varepsilon_2^{MP}[MP^{4-}], \tag{2}$$

where P^{6-} and MP^{4-} refer to the free DOHP anion and the metal complex anion, and the ε_1's and ε_2's are the molar-absorption coefficients of superscribed species at 355 nm and at each characteristic peak wavelength for the complex. Since all of the ε's are already known (Table 1), $[P^{6-}]$ and $[MP^{4-}]$ can be determined using these equations based on spectral measurements of a solution containing these species in appropriate proportion.

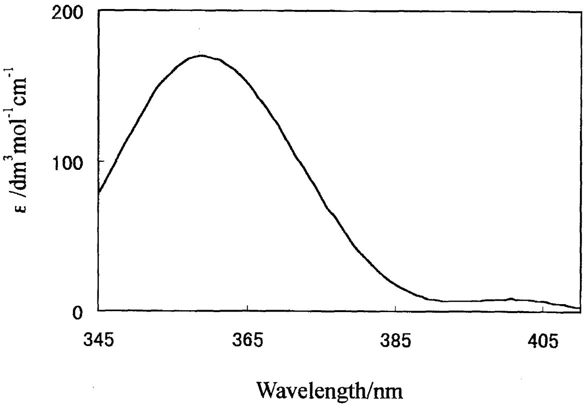

Fig. 2. Apparent absorption spectrum of free DOHP and Mg–DOHP complex in equilibrium in the presence of EDTA (pH 7.0, I = 0.1). Concentrations: Mg = DOHP 2.03×10^{-4} M. EDTA 0.0180 M.

When the free metal-ion concentration is negligible compared to other species concerned and C_L is approximately equal to the free-EDTA concentration in the region of large excess EDTA, the stability constant of the metal–DOHP complex can be expressed by

$$\begin{aligned}\beta_1 &= [MP^{4-}]/[M^{2+}][P^{6-}] \\ &= k\cdot C_L[MP^{4-}]/\{[P^{6-}]\cdot(C_M - [MP^{4-}])\},\end{aligned} \tag{3}$$

where C_M and C_L are the total concentrations of the metal ion and EDTA added as a competing agent, respectively, and k is the conditional stability constant of the metal–EDTA complex involving protonation equilibrium of EDTA, which can be calculated from the literature values.[9] Thus, the stability constant of the metal–DOHP complex can be evaluated from Eq. 1 to Eq. 3.

In Fig. 3 the stability constants determined in this way are plotted against the total DOHP concentration (C_P (C_M)) at different pH's. The values for the Ba complex are omitted because of its tendency toward precipitation. A change in

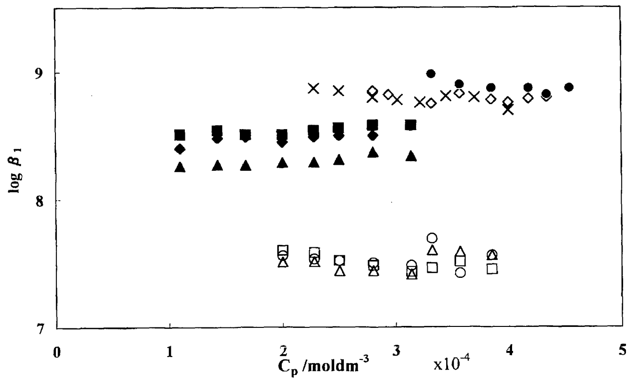

Fig. 3. The dependence of stability constants of Metal–DOHP complexes on dilution with addition of EDTA (C_p decreases with addition of EDTA diluent).
Mg–DOHP system (◆: pH 6.5, ■: pH 7.0, ▲: pH 7.5),
Ca–DOHP system (×: pH 6.5, ◇: pH 7.0, ●: pH 7.5),
Sr–DOHP system (○: pH 6.5, △: pH 7.0, □: pH 7.5).

Table 2. The Logarithmic Stability Constants of M–DOHP Complexes Measured at Different pH ($I = 0.1$)

	pH			
	6.5	7.0	7.5	Ave.
Mg	8.5	8.5	8.3	8.4
Ca	8.8	8.8	8.9	8.8
Sr	7.5	7.5	7.5	7.5

$$\begin{tikzcd}
M^{2+}\cdot\ aq \arrow[d] & + & P^{6-}\cdot\ aq \arrow[d] \arrow[l, phantom, "\mathrm{I}"] \arrow[rr] & & MP^{4-}\cdot\ aq \\
M^{2+} & + & P^{6-} \arrow[rr, "\mathrm{II}"'] & & MP^{4-} \arrow[u, "\mathrm{III}"']
\end{tikzcd}$$

Fig. 4. The complexation between M^{2+} and hexavalent DOHP anion written in the form of Born-Harber's cycle.

C_P has been made by adding an EDTA solution at constant ionic strength. It was confirmed that the ionic strength and the pH of the solution remained almost constant through this dilution. The average values are taken in the region of large EDTA excess for each pH series, and are tabulated in Table 2. The order of β_1 was Ca > Mg > Sr, which was different from that expected from their ionic radii. In the literatures there has also been reported a similar tendency for other chelating ligands, such as EDTA and DTPA.[9] This kind of irregularity in stability order may be understood in a qualitative sense, as described below.

The complex-formation process can be written by a Born–Harber's cycle, as shown in Fig. 4. The free energy of complexation is expressed as the summation of those for the composite three steps. Among the alkaline-earth metal–DOHP complexes, the hydration-energy term of the MP^{4-} complex may not be considerably different from each other; thus, the important steps that practically affect the complexibility order are considered to be the dehydration of the metal ion (step I) and complex formation in a vacuum (step II). Although the magnitude of the free-energy change at these two steps is in the ordinary order, Mg–Ca–Sr, the signs are opposite to each other. Therefore, the addition of these two terms can exhibit an irregular order, such as Ca > Mg > Sr, depending on each magnitude. An exceptionally large dehydration energy for Mg^{2+} may be responsible for producing such a stability reversal for magnesium and calcium complexes.

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