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Spectrophotometric Study of Metal Chelates of Eriochrom Black T (BT). II. Solution Equilibria between BT and Lead(II)-Nitrilotriacetate (NTA) or Cadmium(II)-*N'*-(Hydroxyethyl)-ethylenediamine-*N*, *N*, *N'*-triacetate (EDTA-OH)

Mutsuo KODAMA and Chifumi SASAKI

Department of Chemistry, Ibaraki University, Mito, Ibaraki

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The solution equilibria between BT and lead(II)-NTA or cadmium(II)-EDTA-OH chelates were studied spectrophotometrically, and the composition and the stability constants of the BT chelates of these metal ions were determined. In the presence of an excess amount of NTA or EDTA-OH, lead(II) and cadmium(II) ions join with BT to form a chelate with a 1-to-1 composition. The magnitude of the stability constants ($10^{13.19}$ and $10^{12.74}$ respectively, $\mu=0.30$) can explain satisfactorily the well-known experimental fact that BT can be used as a metallochromic indicator in Pb(II)- and Cd(II)-EDTA titrations.

In a previous paper,1) the stability constants of the zinc(II)- and copper(II)-BT chelates with a 1-to-1 composition were determined by measuring spectrophotometrically the concentration of uncomplexed and complexed BT, which are in equilibrium with the chelon (NTA or EDTA-OH) and its metal chelates in the solution.

In this paper, the results of a spectrophotometric study of the solution equilibria between BT and the lead(II)-nitrilotriacetate or cadmium-(II)-EDTA-OH chelate and of a determination of the compositions and the stability constants of the BT chelates of these metal ions will be presented.

From the viewpoint of the chemical equilibrium, a theoretical consideration of the use of BT as a metallochromic indicator in the EDTA titrations of lead(II)2) and cadmium(II)3) will also be presented.

Lead(II) and cadmium(II) ions were found to form exclusively chelates with a 1-to-1 composition with BT in the presence of an excess of NTA or EDTA-OH, the magnitude of their stability constants can successfully explain the well-known fact that BT dye is a useful indicator in the EDTA titrations of lead(II) and cadmium(II) and fulfills the titrimetric requirements theoretically expected.

Experimental

Apparatus and Procedure. The apparatus (spectrophotometer and pH meter) and the experimental procedure employed were the same as have been described previously.1)

Reagents. Commercial Eriochrom Black T (BT) was purified by the procedure proposed by Diehl and Lindstrom.4) The way of preparing the standard solution of cadmium(II) perchlorate was described in the previous paper.1) The concentration of the cadmium-(II) solution was determined by EDTA titration, using BT as an indicator.3) A standard solution of lead(II) was prepared by dissolving a known amount of pure lead(II) nitrate (analytical-reagent grade) into redistilled water. The concentration was standardized against a standard CyDTA solution.5) The preparation and the standardization of nitrilotriacetic acid (NTA) have been described previously.1) Reagent grade *N'*-(hydroxyethyl)ethylenediamine-*N*, *N*, *N'*-triacetic acid (EDTA-OH) recrystallized from water was used. The concentration of its solution was standardized against a standard copper(II) solution by titration using murexide as an indicator.

All the other chemicals used were of an analytical-reagent grade, and all the absorption and pH measurements were conducted on solution with an ionic strength of 0.30 with sodium perchlorate.

Results and Discussion

Determination of Stability Constants of Lead(II)- and Cadmium(II) Chelates of BT. The solution equilibria between BT and the lead(II)-NTA or cadmium(II)-EDTA-OH chelate were studied over the pH range from 8.50 to 10.50. In this pH range, the solution containing free NTA or EDTA-OH is considered to have a buffer capacity sufficient to keep the pH value

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1) M. Kodama and H. Ebine, This Bulletin, **40**, 1857 (1967).

2) H. Flaschka and F. Huditz, *Z. anal. Chem.*, **137**, 172 (1952).

3) W. Biedermann and G. Schwarzenbach, *Chimia (Switz.)*, **2**, 56 (1948).

4) H. Diehl and F. Lindstrom, *Anal. Chem.*, **31**, 414 (1959).

5) C. A. Geotz and F. J. Debbrecht, *ibid.*, **27**, 1972 (1955).

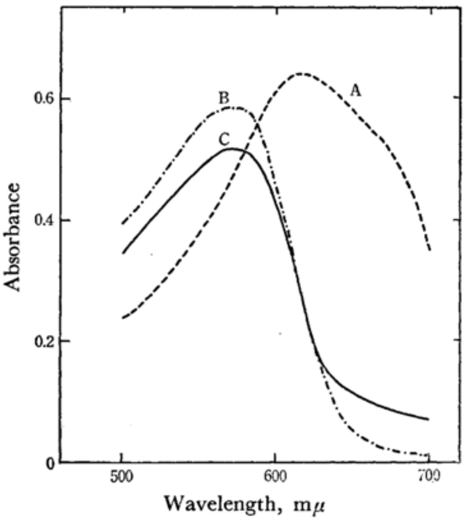

Fig. 1. Absorption curves.

A) 2.00×10^{-5} M BT, 10.0 mM EDTA, $\mu=0.30$ pH=9.50

B)**2.00×10^{-5} M BT, 30 mM NTA, 30 mM Cd(II), $\mu=0.30$, pH=10.0

C) 2.00×10^{-5} M BT, 30 mM NTA, 25 mM Pb(II), $\mu=0.30$, pH=9.65

** The complete displacement of NTA from its chelate by BT and the formation of CdD^- were confirmed by the present authors.

of the solution constant. For this reason, no other buffer reagent was used in this study.

The absorption spectra of uncomplexed and complexed BT were given in Fig. 1. These absorption spectra clearly suggest that the concentrations of BT and its chelates can be determined successfully by measuring the absorbancy at the wavelength of either 630 or 640 mμ.

Lead(II) ion has been reported to form only a 1-to-1 chelate, PbZ^-, with NTA under usual experimental conditions.[6] The cadmium(II) ion also forms exclusively chelate with a 1-to-1 composition with EDTA-OH.[7] Therefore, under the present pH conditions, the chemical equilibrium between BT and lead(II)-NTA or cadmium(II)-EDTA-OH can be written as follows:

$$HD^{2-} + MZ^{2-n} = MD^- + Z^{n-} + H^+ \quad (1)$$

where Z^{n-} refers to completely-dissociated chelon species.

For this equilibrium, thermodynamically Eq. (2) can be derived as in the case of the Cu(II)-CyDTA-BT system.[1]

$$\log\frac{A_D - A}{A - A_{MD}} = \log\frac{K_{MD}\cdot(\alpha_H)_z}{K_{MZ}\cdot(\alpha_H)_{BT}} + \log\frac{[MZ]_t}{[Z]_f} \quad (2)$$

The symbols used in Eq. (2) have the same meanings as those used in the previous paper.[1]

When the following equilibrium becomes important;

$$HD^{2-} + MZ^{2-n} = MDZ^{2-(n+3)} + H^+ \quad (3)$$

the (4) relation can be assumed in place of (2).

$$\log\frac{A_D - A}{A - A_{MD}} = \log\frac{K^{MZ}_{MDZ}}{(\alpha_H)_{BT}} + \log[MZ]_t \quad (4)$$

The above relations indicate that when MD^- is formed, only the plot of $\log(A_D-A)/(A-A_{MD})$ against $\log([MZ]_t/[Z]_f)$ can give a straight line with a slope of unity, but when the chemical equilibrium (3) becomes important, the plot of $\log(A_D-A)/(A-A_{MD})$ *vs.* $\log[MZ]_t$ yields a straight line with a slope of unity.

The experimental data obtained for lead(II)-NTA and cadmium(II)-EDTA-OH systems under the conditions where uncomplexed and complexed chelons are present in a large excess over BT were analyzed with the aid of Eqs. (2) and (4). Typical examples are shown in Figs. 2 and 3. In both systems, under the experimental conditions employed, only the plot of $\log(A_D-A)/(A-A_{MD})$ against $\log([MZ]_t/[Z]_f)$ gave a straight line with a slope of unity, indicating the formation of the normal chelate, MD^-.

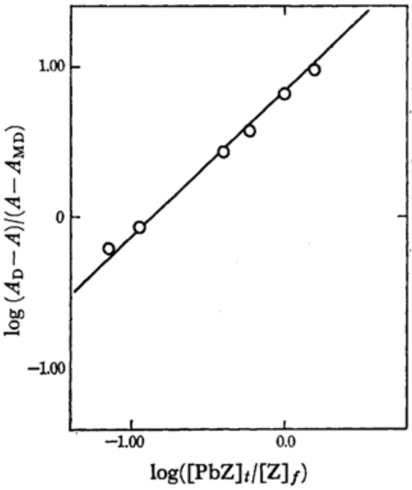

Fig. 2. The plot of $\log(A_D-A)/(A-A_{MD})$ *vs.* $\log([PbZ]_t/[Z]_f)$ for determining the equilibrium constant.
$\lambda=640$ mμ, pH=9.65, $\mu=0.30$
Total concentration of NTA=30.0 mM
Total concentration of BT=2.5×10^{-5} M
Concentration of Pb(II) ranges from 2.0 mM to 20.0 mM

The stability constants for lead(II)- and cadmium(II)-BT chelates were calculated from the $\log(A_D-A)/(A-A_{MD})$ value obtained when $\log([MZ]_t/$

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[6] G. Schwarzenbach and R. Gut, *Helv. Chim. Acta*, **39**, 1589 (1956).

[7] S. Chaberek, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 1477 (1955).

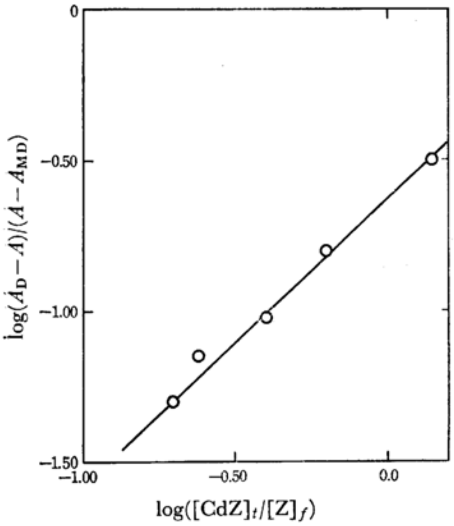

Fig. 3. The plot of $\log(A_D-A)/(A-A_{MD})$ *vs.* $\log([CdZ]_t/[Z]_f)$ for determining the equilibrium constant.
$\lambda=630$ mμ, pH=10.50, $\mu=0.30$
Total concentration of Cd(II)=2.32 mM
Total concentration of BT=2.50×10^{-5}M
Concentration of EDTA-OH ranges from 4.0 mM to 14.0 mM

TABLE 1

i) Dissociation constants of EDTA-OH and BT (mixed constants, $\mu=0.30$)
  a) EDTA-OH[8] $pK_1=1.98$, $pK_2=5.14$, $pK_3=9.53$
  b) BT $pK_1=6.80$, $pK_2=11.31$
ii) Formation constants of chelates ($\mu=0.30$)
  $K^{6)}{}_{Pb\text{-}NTA}=10^{10.94}$ $K^{7)}{}_{Cd\text{-}EDTA\text{-}OH}=10^{12.55}$
  $K^*{}_{PbD}=10^{13.19}$ $K^*{}_{CdD}=10^{12.74}$
* Obtained by the present authors

$[Z]_f$) is zero. The numerical values for EDTA-OH,[8] its cadmium(II) chelate,[7] and the lead(II)-NTA chelate[6] used in the calclations are listed in Table 1, along with the dissociation constants of BT.[9] These values were calculated in ways which have been described previously.[1] The dissociation constants of NTA used in the calculation have also been given previously.[1]

Theoretical Considerations of the Use of BT as an Indicator in the Lead(II)- and Cadmium(II)-EDTA Titrations. Reilley and Schmid[10] have proposed a simple but quantitative method for the rapid prediction of the optimum titration conditions. Provided that the concentration of the indicator is negligibly small and the degree of contrast between the colors of the indicator before and after the end point is large enough, the sharpness of an end point can be characterized simply by two numbers, Δ_1 and Δ_2, defined as follows.

$$\Delta_1{}^{10)} = \log K_{MD} - \log(\alpha_H)_{BT} + \log C_M - \log\beta_{MX} \qquad (5)$$

$$\Delta_2{}^{10)} = \log K_{MY} + \log(\alpha_H)_{BT} - \log K_{MD} - \log(\alpha_H)_Y \qquad (6)$$

Here, Δ_1 is a measure of the tightness of the metal-indicator complex and Δ_2, of the extent to which the chelon displaces the indicator from the metal-indicator complex.

To obtain the end point exactly, it is necessary that both Δ_1 and Δ_2 are greater than 3.0. Here, however, Δ values larger than 4.0 gives no practical improvement.

BT has been reported to have been used successfully as an indicator in the EDTA titrations of lead(II) ion in solutions of tartrate[2] and of cadmium(II) ions in an ammonia buffer[3] at pH values from 8.0 to 10.0. In the EDTA titration of lead(II), when the initial concentration of lead(II) is 1.00×10^{-2} M, the Δ_1 and Δ_2 values defined by Eqs. (5) and (6) were calculated to be 7.07 and 5.28 respectively, using the K_{PbD} value, the dissociation constants of BT[4] and tartaric acid,[11] and the stability constants of lead(II)-tartrate[12] and of the lead(II)-EDTA chelate.[13] Although the

TABLE 2

i) Dissociation constants
  a) Tartaric acid[11]
    $pK_1=2.88$, $pK_2=3.94$
  b) Alanine[14]
    $pK_1=2.34$, $pK_2=9.87$
  c) Ammonia[15]
    $pK=9.27$
ii) Stability constants of metal complexes
  a) Pb(II)-tartarate complex[12]
    $K_1=10^{3.78}$
  b) Pb(II)-alanine complexes[14]
    $K_1=10^{5.00}$, $K_2=10^{3.24}$
  c) Cd(II)-NH_3 complexes[15]
    $K_1=10^{2.74}$, $K_2=10^{2.21}$, $K_3=10^{1.37}$
    $K_4=10^{1.13}$
  d) Pb(II)-EDTA chelate[13] ($\mu=0.30$)
    $K_{PbY}=10^{17.44}$
  e) Cd(II)-EDTA chelate[13] ($\mu=0.30$)
    $K_{CdY}=10^{15.86}$

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8) H. Kroll, AEC Contract (30-1)-2096 Annual Report, 1959.

9) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 678 (1948).

10) C. N. Reilley and R. W. Schmid, *Anal. Chem.*, **31**, 887 (1959).

11) R. K. Cannan and A. Kibrik, *J. Am. Chem. Soc.*, **60**, 2314 (1938).

12) V. E. Panova, *Zhur. neorg. Khim.*, **1**, 422 (1956).

13) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).

14) C. B. Monk, *Trans. Faraday Soc.*, **47**, 292 (1951).

15) C. G. Spike, Thesis, Univ. of Michigan, Univ. Microfilms 5098 (1953).

TABLE 3. THE TITRATION OF Pb(II) ION IN THE ALANINE SOLUTION OF pH 8.50 WITH EDTA

The concentration of alanine is 0.10 M.

i) The concentrations of EDTA and Pb(II) are 10.0 mM.

V_{Pb}, m*l*	V_{EDTA} added, m*l*
5.00	5.02
10.00	10.00

ii) The concentrations of EDTA and Pb(II) are 1.00 mM.

V_{Pb}, m*l*	V_{EDTA} added, m*l*
5.00	4.96
10.00	9.90

stability and dissociation constants under varying titration conditions differ by several tenths of the p*K* unit from the literature values, the above results of the calculations can satisfactorily explain the well-known observations reported by Flaschka *et al.*2)

For 1.00×10^{-2} M Pb(II) ions in a 0.10 M alanine solution of pH 8.50, the Δ_1 and Δ_2 values can be calculated as 4.82 and 5.55 respectively, using the numerical values for alanine and its complexes14) given in Table 2. This clearly suggests that Pb(II) ions in a 0.10 M alanine solution of pH 8.50 can be successfully titrated with EDTA, using BT as a metallochromic indicator. The demonstrative results of the titrations shown in Table 3 can be regarded as satisfactory.

In the case of Cd(II)-EDTA titration, the Δ_1 and Δ_2 values (5.87 and 4.15 respectively) calculated for 1.00×10^{-2} M cadmium(II) and 0.10 M ammonia by using the above-determined K_{CdD} value and the numerical values13,16) given in Table 2 can be considered to have a magnitude which can explain well the facts given by Schwarzenbach *et al.*13)

From the facts obtained and the theoretical discussion given above, it can be safely concluded that reasonable K_{PbD} and K_{CdD} values have been determined.

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16) H. Lunden, *J. Chim. Phys.*, **5**, 574 (1907).