Spectrophotometric Determination of the Stability Constants of Mixed Ligand Complexes of Mercury(II)-Ethylenediaminetetraacetate with Thiocyanate and Bromide

Toshiaki NOMURA

Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto

(Received April 25, 1968)

Mercury(II) reacts with ethylenediaminetetraacetate (EDTA or H_2Y^{2-}) to form mercury(II)-ethylenediaminetetraacetate (Hg-EDTA or HgY^{2-}). Thiocyanate,[1] cyanide,[2] iodide and bromide[3] (X^-) react with Hg-EDTA to form a mixed ligand complex $[HgY(X)]^{3-}$. The degrees of the dissociation (α) of the mixed ligand complexes were determined by measuring its absorption. Then, the apparent stability constants of the thiocyanato or bromo mixed ligand complexes of these ions could be calculated by the molar ratio method.[4]

The $[HgY(X)]^{3-}$ mixed ligand complex dissociated to HgY^{2-} and X^-:

$$\underset{C(1-\alpha)}{[HgY(X)]^{3-}} \rightleftharpoons \underset{\alpha C}{HgY^{2-}} + \underset{\alpha C}{X^-} \qquad (1)$$

where C is the molar concentration of the mixed ligand complex assumed to have no dissociation and α, the degree of dissociation for the mixed ligand complex. The apparent stability constant (K) for this reaction may be expressed by:

$$K = \frac{[[HgY(X)]^{3-}]}{[HgY^{2-}][X^-]} = \frac{1-\alpha}{\alpha^2 C} \qquad (2)$$

The degree of dissociation is given by:

$$\alpha = \frac{E_{max} - E_s}{E_{max}} \qquad (3)$$

where E_{max} is the assumed absorbance of the mixed ligand complex, to which all HgY^{2-} should be reacted with X^-, and where E_s is the measured absorbance of the mixed ligand complex, at the equivalent point C. However, HgY^{2-} and X^- had appreciable absorptions in the ultraviolet region. Therefore, if the absorbances of HgY^{2-} and X^- at the equivalent point are given as E_R and E_T respectively, the measured absorbance ($E_{s'}$) is the sum of the absorbances of the mixed ligand complex (E_s), E_R and E_T:

$$E_{s'} = E_s + E_R + E_T$$
$$E_s = E_{s'} - E_R - E_T \qquad (4)$$

Since E_R and E_T are the α times of the absorbances of HgY^{2-} and X^- at the concentration of C (abbreviated as E_r and E_t respectively), Eq. (4) is given as follows:

$$E_s = E_{s'} - \alpha(E_r + E_t) \qquad (5)$$

When we substitute Eq. (5) into Eq. (3), the expression for the degree of dissociation becomes:

$$\alpha = \frac{E_{max} - E_{s'}}{E_{max} - E_r - E_t} \qquad (6)$$

Experimental

Reagents. All the analytical-grade reagents employed in this experiment were used without any further purification.

The stock Hg-EDTA solution of 1×10^{-2} M was prepared by dissolving 6.07 g of Doctite Hg-EDTA and diluting it to a volume of exactly 1 *l* with water. The working solution was prepared by diluting this stock solution with water.

The exact concentrations of stock solutions of thiocyanate and bromide prepared by dissolving potassium salts in water were standardized according to Volhard's method. The working thiocyanate solution of 5×10^{-4} M (F=0.977) and bromide solution of 1×10^{-3} M (F=0.998) were prepared by diluting this stock solution with water.

The pH and ionic strength were adjusted to the desired values with 0.1 M potassium perchlorate, 0.1 M disodium hydrogen phosphate, and 0.2 M sodium dihydrogen phosphate solutions.

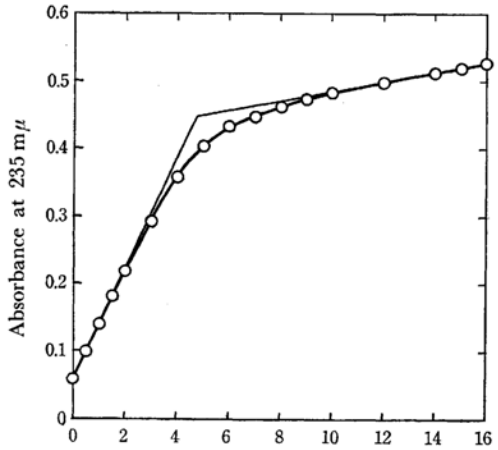
Apparatus. The absorption measurements were made with a Hitachi Perkin Elmer 139-type spectrophotometer with 10.0 mm quartz cells. A Hitachi-Horiba M-4-type pH meter was used to measure the pH.

Procedure. According to the molar ratio method, the solutions containing 5 m*l* of 5×10^{-4} M (thiocyanate) or 1×10^{-3} M (bromide) Hg-EDTA solutions were adjusted to pH 6.1 and an ionic strength, μ of 0.10; a thiocyanate or bromide solution and then water were added to make the volume exactly 50 m*l*. After these solutions had stood for a few minutes, these absorbances were measured at a fixed wavelength against water.

Results and Discussion

Thiocyanato Mixed Ligand Complex. The thiocyanate ion reacts with Hg-EDTA to form a $[HgY(SCN)]^{3-}$ complex at pH 3—8.3, and the mixed ligand complex has a considerable absorption at 235 mμ.[1] Therefore, the molar ratio method for the thiocyanato mixed ligand complex

1) S. Komatsu and T. Nomura, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 841 (1966).
2) S. Komatsu and T. Nomura, *ibid.*, **87**, 845 (1966).
3) S. Komatsu and T. Nomura, *ibid.*, **88**, 63 (1967).
4) A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).

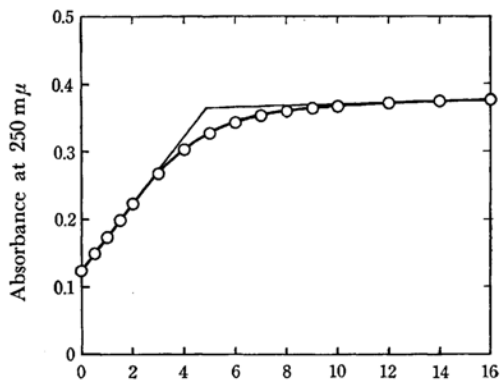


5×10^{-4} M Thiocyanate solution (F=0.977), m*l*

Fig. 1. The apparent stability constant of thiocyanato mixed ligand complex (molar ratio method) 5 m*l* of 5×10^{-4} M Hg-EDTA solution. pH 6.1, μ=0.10

was performed at pH 6.1 and 235 mμ using the previous procedure. The results for this method are shown in Fig. 1. In this figure E_{max}=0.448, $E_{s'}$=0.394, E_r=0.059, and E_t=0.033; therefore, the degree of the dissociation of this mixed ligand complex was calculated as α=0.152 using Eq. (6). Further, C, which could be determined as the section point of this method, was 4.64×10^{-5} mol. By putting these results into Eq. (2), the apparent stability constant of the complex was calculated as $K_{SCN}=7.9\times10^5$, or $\log K_{SCN}$=5.9.

Bromo Mixed Ligand Complex. Similarly, the bromide ion also reacts with Hg-EDTA to form the $[HgY(Br)]^{3-}$ complex at pH 3.5—7.7; this complex has a considerable absorption at 250 mμ.[3] Therefore, the molar ratio method was



1×10^{-3} M Bromide solution (F=0.998), m*l*

Fig. 2. The apparent stability constant of bromo mixed ligand complex (molar ratio method). 5 m*l* of 1×10^{-3} M Hg-EDTA solution. pH 6.1, μ=0.10

performed at pH 6.1 and 250 mμ. The results are shown in Fig. 2. The degree of the dissociation of the bromo mixed ligand complex was calculated as was that for the thiocyanate ion. Here, E_{max}=0.366, $E_{s'}$=0.326, E_r=0.124, E_t=0.006, and $C=9.82\times10^{-5}$ mol. Using these values, the following values were obtained: α=0.169, and $K_{Br}=3.0\times10^5$ or $\log K_{Br}$=5.5.

The apparent stability constants of cyano and iodo mixed ligand complexes can not, however, be calculated with this method, because these mixed ligand complexes dissociate to mercury(II) salts and EDTA by means of the reaction between the complexes and the excess cyanide or iodide ions.[2,3]

The author wishes to thank Professor S. Komatsu for many helpful discussions and suggestions during this work.