Spectrochemical Investigations of the Interaction between Simple Salt Anions and Transition Metal Cations. III. Association between Cupric Alaninate Complex and Sulphite Anion

By Hayami YONEDA

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Introduction

In the previous report⁽¹⁾ the author studied the absorption due to association between bisethylenediamine cupric complex and several anions, which had strong reducing power against cupric aquo ion, and concluded from comparison of the equilibrium constants of association that the special polarising power of the central cupric ion and the large polarisability of anions played an important role in association. If such a conclusion is appropriate, we can expect that there should exist the similar absorption due to association between the electrically neutral complex and the very easily polarisable anion and that we could determine the equilibrium constant of association by analyzing the absorption data.

In the present investigation, marked absorption due to association was found between cupric alaninate complex and sulphite and thiosulphate anions, and the estimation of the equilibrium constant was performed in the case of sulphite anion.

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1) This Bulletin, **29**, 68 (1956).

Experimental

Cupric alaninate $Cu(CH_3CHNH_2\cdot COO)_2\cdot H_2O$ was prepared by dissolving freshly precipitated cupric hydroxide into the boiling solution containing an equivalent amount of alanine and was recrystallized twice from hot water.

Optical densities were measured by means of Shimadzu the spectrophotometer using tungsten and hydrogen lamps and 1 cm. quartz cells. All measurement was done at room temperature 20°C.

Results

In the preliminary experiment the following measurement was made. Na_2SO_3 and $Na_2S_2O_3$, were dissolved to make 1 M solutions. In each solution cupric alaninate complex was dissolved to the concentration of 0.01 M. Such solutions of the complex were measured in their optical densities. In order to cancel the absorption due to the unassociated free anions, the corresponding salt solution was used as a standard. The results are shown in Fig. 1 with the results obtained in the ethylenediamine complex. It is interesting to find that the absorption due to association appears more distinctly here than in the case of the cupric ethylenediamine complex. In the present case too, the characteristic absorption band proper to the complex remains constant.

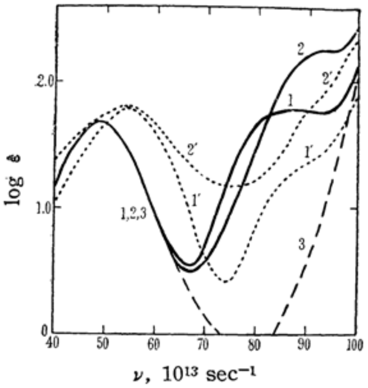

Fig. 1.

1. ——— [Cu alanine$_2$] in 1 mol./l. Na_2SO_3
2. ——— [Cu alanine$_2$] in 1 mol./l. $Na_2S_2O_3$
3. - - - - [Cu alanine$_2$] in water

1′. ----- [Cu en$_2$]$(ClO_4)_2$ in 1 mol./l. Na_2SO_3

2′. ----- [Cu en$_2$]$(ClO_4)_2$ in 1 mol./l. $Na_2S_2O_2$

(Curves 1′ and 2′ were cited from the previous work.)

In addition, it is noteworthy that the solution was photosensitive in the case of thiosulphate and that the reduction of cupric ion to cuprous ion proceeded at a measurable rate during measurment, and that the characteristic blue color of the complex faded gradually. In the sulphite solution such reduction was not observed during measurement. Accordingly, the determination of the equilibrium constant was done only in the case of sulphite. In order to estimate the equilibrium constant, optical densities of the following solutions were measured in the wavelength regions 400–320 mμ.

1) The solution which contains both [Cu alanine$_2$] and Na_2SO_3 at 0.01 M concentration.

2) The solution which contains both the complex and sulphite at 0.0075 M concentration.

3) The solution which contains both the complex and sulphite at 0.0050 M concentration.

4) The solution which contains only the complex at 0.01 M concentration.

The slight absorption which originated from Na_2SO_3 was canceled by taking the sulphite solutions of the corresponding concentration as a standard in the measurement. The results are shown in Fig. 2. In the figure, the full lines 1, 2, 3 correspond to the absorption of 0.01, 0.0075, 0.0050 M solutions and a broken line 4 to that of the complex only solution. The dotted lines 1′, 2′, 3′ are the results of subtraction from the absorption 1, 2, 3 by the absorption of the complex of the corresponding concentrations.

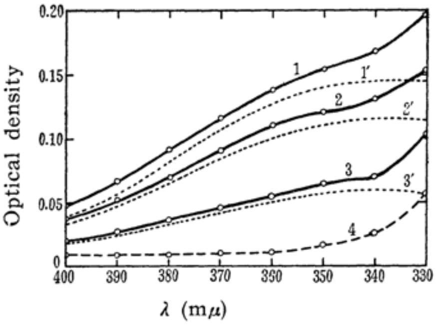

Fig. 2.

Determination of the Equilibrium Constant.—In the following equilibrium

$$\text{Cu alanine}_2+SO^{2}_{3}\rightleftarrows(\text{Cu alanine}_2\cdot SO_3)$$

the equilibrium constant of association is represented by

$$K=\frac{[(\text{Cu alanine}_2\cdot SO_3)]}{[\text{Cu alanine}_2]\cdot[SO_3^{2-}]}$$

As the total concentrations of the complex and the anion in the solution are always the same in the present case, we put them as u. If we represent the concentration of the association product in equilibrium with x, then the concentrations of the complex and the anion in equilibrium are both represented with $u-x$, and the equilibrium constant K is expressed by

$$K=\frac{x}{(u-x)^2} \tag{1}$$

where u takes the values of 0.01, 0.0075, and 0.0050. If we represent x corresponding to u=0.01, 0.0075, 0.0050 with x_1, x_2, x_3, and then these x_1, x_2, and x_3 take the definite values against the definite value of K. Consequently, x_2/x_1 and x_3/x_1 are also definite against the definite value of K. The values of x_2/x_1 and x_3/x_1 against K were calculated and plotted in Fig. 3.

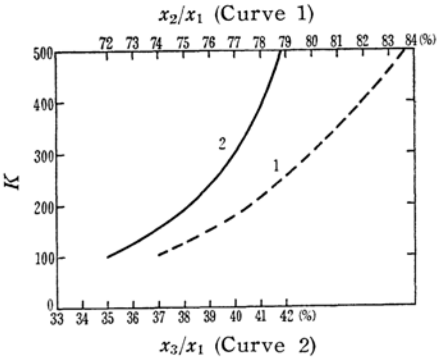

Fig. 3.

On the other hand, the measured optical density D is represented by

$$D=\varepsilon_c(u-x)+\varepsilon_a x \tag{2}$$

This relation is modified to

$$D-\varepsilon_c u=(\varepsilon_a-\varepsilon_c)x=y \tag{3}$$

where ϵ_c and ϵ_a are the molar extinction coefficients of the complex and the association product, and y represents the absorption due to association. If we represent y in the cases of x_1, x_2, x_3 with y_1, y_2, y_3 respectively, then $x_2/x_1=y_2/y_1$ and $x_3/x_1=y_3/y_1$. The values of y_2/y_1 and y_3/y_1 in each wave-length were calculated from the observed values of D, and the corresponding values of K were read from the graph. The results thus obtained are listed in Table I.

Discussion

We have obtained K=240 as the value of the equilibrium constant of association between [Cu alanine$_2$] and SO_3^{2-}. This value is almost ten times as large as that between [Cu en$_2$]$^{2+}$ and SO_3^{2-}(K=25). This surprising fact can be interpreted only by assuming that the electronic configuration of the central cupric ion plays an important role in association. In other words, in the ethylenediamine complex the charge of the central cupric ion is considerably neutralized by the lone pair electrons of the coordinating N atoms of the ethylenediamine molecules and as the result it has only the small polarising power against the outer anion. In contrast to this, in the alanine complex, though the charge neutralization as a whole complex radical is complete, the charge of the cupric ion is incompletely canceled, so that the cupric ion has enough polarising power against the outer anion.

As reported previously, $S_2O_3^{2-}$ associates much more firmly with [Cu en$_2$]$^{2+}$ than SO_3^{2-}. This fact suggests the much greater polarisation of $S_2O_3^{2-}$. Such polarisation is to be strengthened in the association with [Cu alanine$_2$]. As the result $S_2O_3^{2-}$ excited by a photon easily transfers its electron to the central cupric ion. The photochemical reduction of [Cu alanine$_2$] in the thiosulphate solution can be thus explained.

Conclution

Marked association absorption was found between electrically neutral [Cu alanine$_2$] and SO_3^{2-}, and $S_2O_3^{2-}$ and the equilibrium constant of association was determined spectrophotometrically in the case of [Cu alanine$_2$] and SO_3^{2-}. The value of K was found to be 240.

This value is much larger than that obtained in the corresponding case of [Cu en$_2$]$^{2+}$ and SO_3^{2-} (K=25). This result can be explained by assuming that the central

TABLE I

VALUES OF y AND K

λ(mμ)	y_1	y_2	y_3	y_2/y_1	K	y_3/y_1	K
390	0.058	0.045	0.023	77.5%	200	39.7%	285
380	.084	.065	.033	77.4%	195	39.8%	290
370	.106	.083	.042	78.5%	235	39.6%	280
360	.127	.099	.049	77.8%	210	39.0%	245
350	.141	.109	.057	77.7%	205	39.0%	245
340	.145	.113	.057	78.0%	215	39.3%	260
330	.143	.112	.056	78.7%	245	39.2%	255
320	.145	.114	.056	78.6%	240	39.0%	245
				Mean	218	Mean	263

Probable value of K=240

cupric ion in [Cu alanine$_2$] has much stronger polarising power than in [Cu en$_2$]$^{2+}$. The assumption of such strong polarising power can explain the photochemical reduction of Cu alanine$_2$·S$_2$O$_3$ system.

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Chemistry Department, Wakayama University, Wakayama