

Determination of Properties of Trace Copper Complex Solution by β -Correction Spectrophotometry

HONG WEN GAO*, GUI SHENG YE and MEI TAO

*School of Chemistry and Chemical Engineering
Anhui University, Hefei 230 039, P.R. China*

The reactions were sensitive between copper(II) and dibromo-*o*-carboxy-chlorophosphonazo (DBKCPA) and pH 7 and between copper(II) and *o*-sul-fobenzeneazo rhodanine (SBAR) at pH 9.5 in the presence of cetyl trimethylammonium bromide (CTMAB). Because of the serious interference of excess ligand the determination of properties of Cu complex solutions was carried out by β -correction theory instead of the single wavelength method. This investigation gave the simple determination of the complex ratio, stepwise real molar absorptivity (ϵ) and stepwise or cumulative stability constant (K).

INTRODUCTION

The two ligands, dibromo-*o*-carboxy-chlorophosphonazo (DBKCPA) and *o*-sul-fobenzeneazo rhodanine (SBAR) were ever applied to the determination of trace amounts of metals, for example strontium¹, palladium², etc. However, in this experiment, because of the serious interference of excess ligand the unacceptable errors were given by using ordinary spectrophotometry. The complexation between the above ligands and copper(II) has not been reported till date. This paper applied the β -correction spectrophotometry^{3, 4} to determine the properties of copper complex solutions, which was able to eliminate the above interference of excess ligand. The composition ratio, stepwise real molar absorptivity and stepwise stability constants of copper complexes were determined. Results were more acceptable than those by the conventional methods such as molar ratio⁵, continuous variation⁶ and equilibrium⁷.

The following expression is developed for the determination of the real absorbance (A_c) of metal (M) complex (ML_γ) produced with a ligand (L).

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta}$$

The symbols ΔA and $\Delta A'$ are the absorbances of the mixed solution of ML_γ and excess L measured at wavelengths λ_2 and λ_1 against the reagent blank, respectively. The coefficients α and β are named correction coefficients and they are able to be measured from only ML_γ solution and L solution and then computed as follows:

$$\alpha = \frac{\epsilon_{ML_\gamma}^{\lambda_1}}{\epsilon_{ML_\gamma}^{\lambda_2}} \quad \text{and} \quad \beta = \frac{\epsilon_L^{\lambda_2}}{\epsilon_L^{\lambda_1}}$$

where $\epsilon_{ML_\gamma}^{\lambda_1}$, $\epsilon_{ML_\gamma}^{\lambda_2}$, $\epsilon_L^{\lambda_1}$ and $\epsilon_L^{\lambda_2}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2 , respectively, whose ratio may be computed after the direct determination of L and ML_γ solutions.

The amount (γ') of L to coordinate M in reaction may be expressed as follows:

$$\gamma' = \eta \times C_L / C_M$$

where $\eta = (A_c - \Delta A) / A_0$. The symbol η indicates the reacted percentage of L and δ the cell thickness (cm). The factors C_M and C_L are the concentrations (mol/L) of M and L in the beginning. A_0 is the absorbance of the blank reagent measured at wavelength λ_2 . If γ' reaches maximum and remains constant, it was thought that $\gamma = \gamma'$ where γ is a natural number and it is named the composition ratio of the complex produced. In addition, the following expression was established for the stepwise stability constant (K_n) of complex ML_γ from the reaction $ML_{n-1} + L \rightleftharpoons ML_n$. For this purpose, such an M-L solution must be prepared to form the complex ratio γ' between $n-1$ and n and studied successively.

$$K_n = \frac{\gamma' + 1 - n}{(n - \gamma')(C_L - \gamma' C_M)}$$

From each K_n the cumulative constant (K) of complex ML_γ is able to be calculated from the following expression:

$$K = K_1 \times K_2 \times \dots \times K_n \dots \times K_\gamma$$

In addition, from such an M-L reaction the stepwise absorptivity (real $\epsilon_{ML_n}^{\lambda_2}$ not apparent $\epsilon_a^{\lambda_2}$, $n = 1, 2, \dots, \gamma$) of complex ML_γ may be expressed as follows:

$$\epsilon_{ML_n}^{\lambda_2} = \frac{A_c}{\delta C_M (\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \epsilon_{ML_{n-1}}^{\lambda_2}$$

In this equation all symbols have the same meanings as in the above.

EXPERIMENTAL

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai, China) in 10 mm glass cells. Standard Cu(II) solution, 1000 mg/L: prepared from 1.00 g high-purity copper. Standard Cu(II) working standard, 10.00 mg/L; ligand solutions, 1.00 mmol/L DBKCPA and 1.00 mmol/L SBAR both dissolved in water. They should be stored in dark bottles. The buffer solution pH 7.0 and 9.5 was prepared with sodium tetraborate. The cationic surfactant, cetyl trimethylammonium bromide (CTMAB) (Shanghai Organic) solution, all 2%, were prepared in order to raise the reaction sensitivity.

20 micrograms of Cu(II) were taken in a 25 mL volumetric flask. Added distilled water to about 10 mL. Then added 2.5 mL of buffer solution and 1 mL of 2% CTMAB (in Cu-SBAR reaction system). Added 2.5 mL of 1.00 mmol/L ligand. Diluted to required volume and mixed well. After the reaction came to an end, measured absorbances against a reagent blank at the selected wavelengths listed in Table-1, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of ligands and copper complex solutions: From curves 3 and 3', two wavelengths of each solution should be selected such that the difference in absorbances was a maximum. From curves 1, 1', 2 and 2', β and α of the two solutions were calculated. All results were listed in Table 1.

Figure 2 shows the effect of pH on absorbance of copper complex solutions.

Figure 3 gives the effect of the addition of DBKCPA and SBAR solutions on complexation ratio.

TABLE-1
WORKING WAVELENGTHS, CORRECTION COEFFICIENTS AND OTHER
OPERATION CONDITIONS FOR THE DETERMINATION OF PROPERTIES OF
COPPER COMPLEX SOLUTIONS WITH LIGANDS, DBKCPA AND SBAR

Ligand	DBKCPA	SBAR
λ_1 , nm	540	470
λ_2 , nm	630	560
β	0.185	0.134
α	0.864	1.17
A_c	1.190 (ΔA) - 0.185 ($\Delta A'$)	1.190 (ΔA) - 0.134 ($\Delta A'$)
pH	7	9.5
Surfactant	/	CTMAB
Reaction time, (min)	> 5	between 10-20

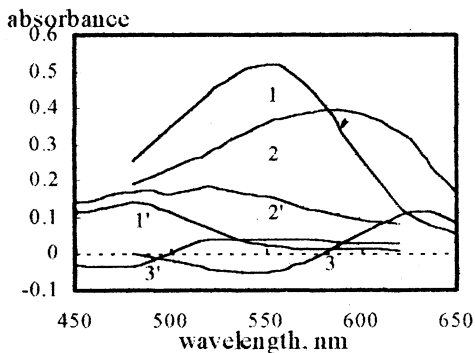


Fig. 1. Absorption spectra of ligands and their copper complex solutions: 1-DBKCPA and 1..SBAR; 2. only Cu-DBKCPA complex and 2'. only Cu-SBAR complex solution; 3. Cu-DBKCPA solution and 3'. Cu-SBAR solution against reagent blank.

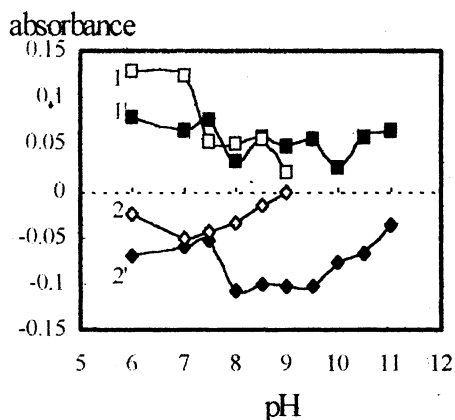


Fig. 2. Effect of pH on absorbance of copper complex solutions against reagent blank: 1. $\Delta\Delta$ (Cu-DBKCPA solution at 630 nm), 1'. $\Delta\Delta$ (Cu-SBAR solution at 560 nm); 2. $\Delta\Delta'$ (Cu-DBKCPA solution at 540 nm), 2'. $\Delta\Delta'$ (Cu-SBAR solution at 470 nm).

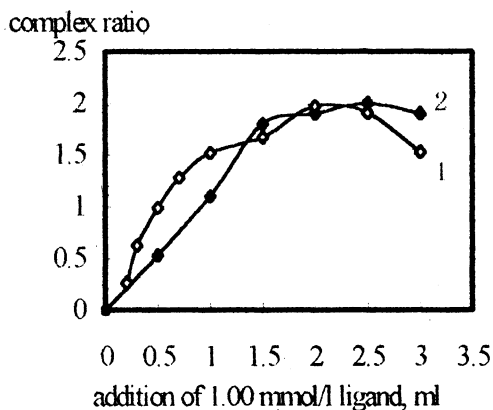


Fig. 3. Effect of the addition of 1.00 mmol/L ligands on composition ratio (γ') of copper complexes: 1. Cu(II) complex solution with DBKCPA, 2. Cu(II) complex solution with SBAR.

Effect of Operation Conditions and Determination of Composition Ratio

From curves in Figure 2, it was found that the sensitivity of Cu-DBKCPA reaction reached maximum when pH was between 6 and 7 and that of Cu-SBAR reaction came to maximum when pH was between 8.0 and 10.5. By varying the selection of anion and cation surfactants and their addition the reaction between Cu(II) and DBKCPA was not affected but the reaction between Cu(II) and SBAR became double sensitive in the presence of CTMAB. The effect of the reaction time indicated that the reaction between Cu(II) and DBKCPA was completed in 5 min and the reaction between Cu(II) and SBAR in 10 min but the fading of such a color solution was found after 20 min.

By varying the addition of two ligands the absorbances of copper complex solutions were measured. Both of the effective percentage of ligands and complexation ratio (γ') were calculated according to the above equations. The

results were shown in Figure 3. It was found that the complex ratio of each curve approached the maximal value 2 when the addition of 1.00 mmol/L ligand was more than 1.5 mL. Therefore the formed complexes were expressed as $\text{Cu}(\text{DBKCPA})_2$ and $\text{Cu}(\text{SBAR})_2$.

Determination of Stability Constant and Real Molar Absorptivity

The following solutions were prepared for the determination of stepwise stability constant and stepwise real molar absorptivity of complexes: 20.0 $\mu\text{g}/25$ mL Cu(II) with 0.30 and 0.70 $\mu\text{mol}/25$ mL DBKCPA and with 0.50 and 1.30 $\mu\text{mol}/25$ mL SBAR. Ten replicated determinations of each solution were carried out. The relative standard deviations of complexation ratios (γ') were equal to 2.5, 3.8, 7.8, 4.5%, respectively. The stepwise and cumulative stability constants K_n and K were as follows: $K_1 = 2.96 \times 10^5$, $K_2 = 2.90 \times 10^4$ and $K = 8.58 \times 10^9$ of $\text{Cu}(\text{DBKCPA})_2$; and $K_1 = 2.73 \times 10^5$, $K_2 = 5.39 \times 10^4$ and $K = 1.47 \times 10^{10}$ of $\text{Cu}(\text{SBAR})_2$. The stepwise real molar absorptivities, all $\epsilon_{\text{ML}_n}^{\lambda}$ of copper complexes with DBKCPA and SBAR were calculated according to the above equation. Results were listed as follows:

$$\epsilon_{\text{Cu}(\text{DBKCPA})}^{630} = 8.61 \times 10^3, \quad \epsilon_{\text{Cu}(\text{KBKCPA})_2}^{630} = 1.49 \times 10^4, \quad \epsilon_{\text{Cu}(\text{SBAR})}^{560} = 3.41 \times 10^3,$$

$$\epsilon_{\text{Cu}(\text{SBAR})_2}^{560} = 9.84 \times 10^3 \quad \text{and} \quad \text{L mol}^{-1} \text{ cm}^{-1}.$$

However, their apparent values were only

$$\epsilon_{\text{Cu}(\text{DBKCPA})}^{630} = 1.09 \times 10^4 \quad \text{and} \quad \epsilon_{\text{Cu}(\text{SBAR})_2}^{560} = 7.22 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}.$$

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