

## Updated Spectrophotometric Investigation of Copper Complexes with Thiomicher's Ketone and Bromopyrogallol Red

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The novel investigation of the copper complexes with thiomicher's ketone (TMK) and bromopyrogallol red (BPR) was carried out at pH 7 by spectral correction technique. The characteristic factors were calculated, for example, complex ratio and stability constant. The results have shown that the  $\text{Cu}(\text{TMK})_2$  and  $\text{Cu}(\text{BPR})_2$  were formed and their real stepwise molar absorptivities were determined simply at pH 7. Their cumulative stability constants are  $5.08 \times 10^{11}$  and  $5.02 \times 10^{11}$  respectively.

**Key words:** spectral correction technique, copper complex, thiomicher's ketone, bromo-pyrogallol red.

### INTRODUCTION

A number of colour reactions of copper are reported, *e.g.*, with azo compounds<sup>1, 2</sup>, hydrazone reagents<sup>3, 4</sup>, nitroso- compounds<sup>5</sup> etc.. Some of their highly sensitive reactions have been playing important roles in the spectrophotometric determination of trace amounts of copper<sup>6, 7</sup>. The two ligands, thiomicher's ketone (TMK) and bromo-pyrogallol red (BPR) are also sensitive for chelating copper(II). They have ever been used for the determination of trace silver<sup>8, 9</sup>, but the formation and the characteristic factors of their complexes have never been studied in detail. Here, two such complex reactions have been used to determine the characteristic factors of two complexes, which include complex ratio, stepwise real molar absorptivity, stepwise and cumulative stability constant. The spectral correction technique<sup>10, 11</sup> was applied to the determination of the above factors. This method is simpler and more acceptable than the other classical ways, *e.g.*, molar ratios<sup>12</sup>, continuous variations<sup>13</sup>, equilibrium movement<sup>14</sup> and Yatzimirsky factor<sup>15</sup> because it can eliminate the interference of the excess of TMK or BPR and give the accurate absorbance of the Cu complexes. On the contrary, the traditional methods are often limited because of the excess of ligand in its complex solution.

### Principle

The following expression<sup>10</sup> is developed for the determination of the real absorbance ( $A_c$ ) of metal (M) complex ( $\text{ML}_\gamma$ ) with a ligand (L).

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

The terms,  $\Delta A$  and  $\Delta A'$  are the absorbances of the mixed solution of  $\text{ML}_\gamma$  and

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excess L measured at wavelengths  $\lambda_2$  and  $\lambda_1$  against the reagent blank, respectively. The coefficients,  $\alpha$  and  $\beta$  are correction factors and they are able to be measured from only  $ML_\gamma$  solution and L solution is then computed as follows.

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

The terms  $\epsilon_{ML_\gamma}^{\lambda_1}$ ,  $\epsilon_{ML_\gamma}^{\lambda_2}$ ,  $\epsilon_L^{\lambda_1}$  and  $\epsilon_L^{\lambda_2}$  are the molar absorptivities of  $ML_\gamma$  and L at wavelengths  $\lambda_1$  and  $\lambda_2$ , respectively. The molar ratio  $\lambda_2(\gamma)$  of the effective L to M is calculated by the relation:

$$\gamma' = \eta \times \frac{C_L}{C_M} \quad \text{and} \quad \eta = \frac{A_c - \Delta A}{A_0}$$

The term  $\eta$  indicates the reacted percentage of L and both  $C_M$  and  $C_L$  are the molar concentrations of M and L at the beginning.  $A_0$  is the absorbance of the L solution measured at wavelength  $\lambda_2$ . If  $\gamma'$  reaches maximum and remains constant, it was thought that  $\gamma = \gamma'$  where  $\gamma$  is a natural number and it is named the stoichiometric ratio of the complex. In addition, the following expression was established for the stepwise stability constant ( $K_n$ ) of complex  $ML_\gamma$

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

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

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

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

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

where  $\delta$  is the cell thickness (cm) and the other symbols have the same meanings as the above.

## EXPERIMENTAL

Absorbances were measured on a TU1901 spectrophotometer (P General, Beijing) with 1.0-cm cells.

TMK solution (0.50 mmol/L) was prepared by dissolving 0.1421 g of TMK (Shanghai Third Reagent) in 1000 mL of acetone and BPR solution (1.00 mmol/L) was prepared by dissolving 0.582 g of BPR (Shanghai Third Reagent) in 1000 mL of deionized water. Cu(II) standard solution, 100.0 mg/L, was prepared with copper sulfate (AR, Shanghai Reagent) and 10.0 mg/L Cu use solution was prepared daily by diluting the solution. The buffer solution pH 5 was prepared with acetic acid and sodium acetate and the anionic surfactant 5% SDBS was used in the Cu-BPR solution.

### Recommended Procedure

20  $\mu\text{g}$  copper was taken in a 25-mL calibrated flask. Added 2 mL of the buffer solution, TMK or BPR solution and in addition 1 mL of 5% SDBS in the Cu-TMK solution. Diluted to the mark with deionized water and well-mixed. Between 20 and 30 min, measured the absorbances of the Cu-TMK solution at 440 and 620 nm and those of the Cu-BPR solution at 560 and 620 nm, respectively.  $A_c$  of the complexes has been calculated by the above equation.

### RESULTS AND DISCUSSION

**Absorption spectra:** The reaction between copper and BPR is sensitive in the absence of surfactant but the reaction between copper and TMK gave a high sensitivity only in the presence of anionic surfactant, *e.g.*, SDBS. Their absorption spectra are shown in Fig. 1. We find that the peak and valley absorptions of the Cu-BPR solution are located at wavelengths  $\lambda_1 = 440$  and  $\lambda_2 = 620$  nm from curve

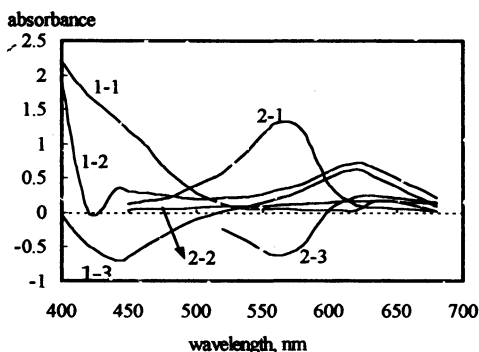


Fig. 1. Absorption spectra of reagent blank and copper complex solutions: 1-1, TMK solution in presence of SDBS at pH 7 against water; 1-2, only Cu-TMK complex solution in presence of SDBS at pH 7 against water; 1-3, Cu-TMK reaction solution in presence of SDBS at pH 7 against reagent blank; 2-1, BPR solution at pH 7 against water; 2-2, only Cu-BPR complex solution at pH 7 against water; 2-3, Cu-BPR reaction solution at pH 7 against reagent blank.

1-3 and those of the Cu-TMK solution at  $\lambda_1 = 560$  and  $\lambda_2 = 620$  nm from curve 2-3. From curves x-1 and x-2,  $\beta$  and  $\alpha$  are calculated. So the following equations were used:  $A_c = 1.01(\Delta A - 0.022\Delta A')$  for calculation of the real absorbance of the Cu-TMK complex and  $A_c = 1.06(\Delta A - 0.086\Delta A')$  for that of the Cu-BPR complex.

**Effect of TMK and BPR concentration:** By varying the addition of the TMK and BPR solutions, the absorbances of their Cu (0.80 mg/L) complexes are shown in Fig. 2. Both the positive and negative absorbances approach maximum from curves 1-1 and 2-1, when the concentration of TMK and BPR is more than 0.040 mmol/L. We have calculated the real absorbance ( $A_c$ ) and complex ratio ( $\gamma'$ ) and the results are shown in Fig. 3. From curves x-2, we observed that  $\gamma'$  approaches 2. Therefore, the formed complexes are expressed as  $\text{Cu}(\text{TMK})_2$  and  $\text{Cu}(\text{BPR})_2$  at pH 7.

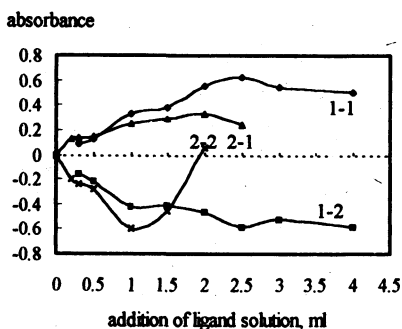


Fig. 2. Effect of ligand concentration on the measured absorbances: 1-1, reagent blank (TMK) in the presence of SDBS at pH 7 against water at 440 nm; 1-2, Cu(0.8 mg/L)-TMK-SDBS system at pH 7 against reagent blank at 620 nm; 1-3, same as 1-2 but at 440 nm; 2-1, reagent blank (BPR) at pH 7 against water at 560 nm; 1-2, Cu (0.8 mg/L)-BPR system at pH 7 against reagent blank at 620 nm; 1-3, same as 1-2 but at 560 nm.

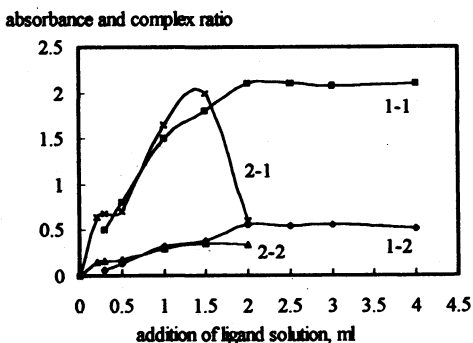


Fig. 3. Effect of ligand concentration on real absorbance  $A_c$  and the complex ratio,  $\gamma$ : 1-1,  $A_c$  of Cu-TMK complex in the presence of SDBS at pH 7 at 620 nm; 1-2,  $\gamma$  of Cu-TMK-SDBS reaction system; 2-1,  $A_c$  of Cu-BPR complex at pH 7 at 620 nm; 2-2,  $\gamma$  of Cu-BPR reaction system

**Effect of pH and time:** By varying pH of the solutions containing 20  $\mu\text{g}$  of copper, the absorbance change is shown in Fig. 4. Both the reactions approach maximum at pH 7. So pH 7 was selected in this study. The absorbances of the Cu (0.80 mg/L) complexes with TMK and BPR were measured at various reaction times and the effect is shown in Fig. 5. We see that the absolute absorbances reach maximum between 20 and 30 min. The absorbances begin to fall down when the reaction is over 30 min.

**Determination of stepwise absorptivity and stability constant of the complexes:** The following solutions was prepared and measured for the determination of the stepwise absorptivity and stability constants of complexes: 0.10  $\mu\text{mol}$  of Cu(II) plus 0.20  $\mu\text{mol}$  of TMK, 0.10  $\mu\text{mol}$  of Cu(II) plus 0.30  $\mu\text{mol}$  of TMK, 0.10  $\mu\text{mol}$  of Cu(II) plus 0.20  $\mu\text{mol}$  of BPR and 0.10  $\mu\text{mol}$  of Cu(II) plus 0.30  $\mu\text{mol}$  of BPR. The measurement results are shown in Table 1. The stepwise absorptivities and stability constants of the complexes all were calculated and presented in Table 1.

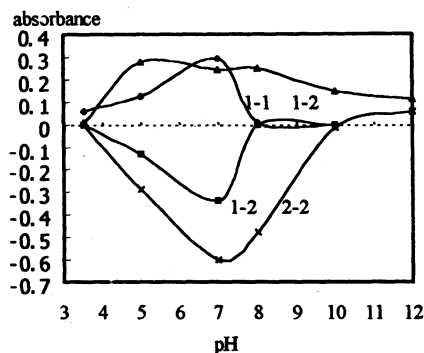


Fig. 4. Effect of pH on measurement of copper complex solution containing  $20 \mu\text{g Cu(II)}$ : 1-1, Cu-TMK-SDBS system containing  $0.50 \mu\text{mol TMK}$  at  $620 \text{ nm}$  against reagent blank; 1-2, same as 1-1 but at  $440 \text{ nm}$ ; 2-1, Cu-BPR system containing  $1.00 \mu\text{mol BPR}$  at  $620 \text{ nm}$  against reagent blank; 2-2, same as 2-1 but at  $560 \text{ nm}$

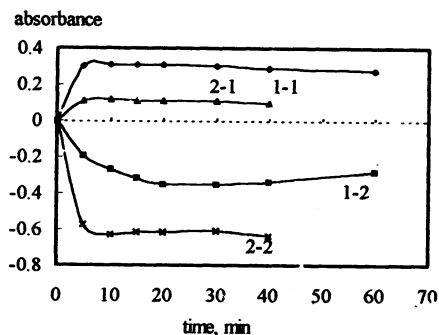


Fig. 5. Effect of colour-developed time on measurement of copper complex solution containing  $20 \mu\text{g Cu(II)}$ : 1-1, Cu-TMK-SDBS system containing  $0.50 \mu\text{mol TMK}$  at  $620 \text{ nm}$  against reagent blank; 1-2, same as 1-1 but at  $440 \text{ nm}$ ; 2-1, Cu-BPR system containing  $1.00 \mu\text{mol BPR}$  at  $620 \text{ nm}$  against reagent blank; 2-2, same as 2-1 but at  $560 \text{ nm}$ ;

TABLE-1  
DETERMINATION OF STEPWISE ABSORPTIVITY AND STABILITY CONSTANT OF COPPER COMPLEX AT pH 7, ION STRENGTH 0.01 AND TEMPERATURE  $25^\circ\text{C}$

M-L solution	Average $A_c$ of three determinations at $620 \text{ nm}$	Average $\gamma$	Average $K_2 \times 10^6$	Average $\epsilon_r^{620}$	$\text{L mol}^{-1} \text{ cm}^{-1}$
Cu ( $0.004 \text{ mmol/L}$ )- TMK ( $0.008 \text{ mmol/L}$ )	0.043	0.910	$K_1$ 2.330	1st step ML	$1.18 \times 10^4$
Cu ( $0.004 \text{ mmol/L}$ )- TMK ( $0.012 \text{ mmol/L}$ )	0.063	1.550	$K_2$ 0.218	2nd step $\text{ML}_2$	$1.89 \times 10^4$
Cu ( $0.004 \text{ mmol/L}$ )- BPR ( $0.008 \text{ mmol/L}$ )	0.057	0.902	$K_1$ 2.180	1st step ML	$1.58 \times 10^4$
Cu ( $0.004 \text{ mmol/L}$ )- TBPR ( $0.012 \text{ mmol/L}$ )	0.076	1.550	$K_2$ 0.230	2nd step $\text{ML}_2$	$2.16 \times 10^4$

### ACKNOWLEDGEMENTS

This work was supported by both the Natural Science Foundation of Anhui Province (No. 99045332) and that of the Education Council of Anhui Province (No. 99JL0003).

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(Received: 29 August 2001; Accepted: 24 October 2001)

AJC-2502