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# Determination of Properties of Cadmium, Cobalt, Manganese and Copper Complexes with 1-(6-Bromo-2-Benzothiazolylazo)-2-Naphthol

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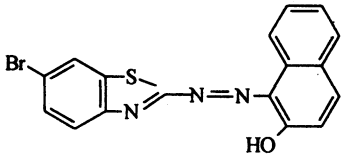
The updated determination method of properties of several metal complexes was reported recently. The reactions were studied between four metals: Cd(II), Co(II), Mn(II) and Cu(II) and 1-(6-bromo-2-benzothiazolylazo)-2-naphthol (BBTAN) at pH 11. The β-correction method was used instead of the ordinary spectroatphotometry, because of the influence on each other of free ligand and its complex. The composition ratios, the stepwise real molar absorptivity (ε) and stepwise or cumulative stability constant (K) of M-BBTAN (M = Cd, Co, Mn or Cu) complexes were all worked out. The recommended method was more acceptable in principle and simpler in operation than the classical method.

## INTRODUCTION

Recently, the synthesis of the new ligand, 1-(6-bromo-2-benzothiazolylazo)-2-naphthol (BBTAN) was carried out with the following structure.




The ligand was sensitive to form complexes with cadmium, cobalt, manganese and copper at pH 11. The complex solutions showed blue and the ligand showed red. It was difficult for the ordinary spectrophotometric method to give out the accurate analysis because the excess of BBTAN influenced the real absorption of the complexes formed. The new dual-wavelength principle, β-correction method[1] may eliminate the absorption interference of the excess of ligand to give the real absorbance of the complex and it was ever applied to the determination of many metal complex solutions[2–4]. Recently, this method was applied to determine the properties of metal complex solution. In this report, the reactions between various metal ions (Cd, Co, Mn and Cu) and BBTAN were studied in detail at pH 11 and in the presence of emulsifier OP. The composition ratio of metal to BBTAN, the stepwise real absorptivity (K) and stepwise stability constant (ε) of metal complexes were all determined. The recommended method was more acceptable in principle and simpler in operation than the classical methods such as molar ratio[5], continuous variation[6], equilibrium movement[7], etc.

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## EXPERIMENTAL

Absorption spectra were recorded with a TU1201 spectrophotometer (PGeneral, Beijing) in 10 mm glass cells.

Standard Cd(II), Co(II), Mn(II) and Cu(II) solutions, all 10 mg/L, were prepared by dissolving their salts (G.P.) and diluting with non-ionic water (specific conductivity less than 0.3 μS/cm). BBTAN solution, 1 mmol/L, was prepared by dissolving 1-(6-bromo-2-benzothiazolylazo)-2-naphthol in acetone and stored in a dark bottle. pH 11 buffer was prepared with borate for adjusting the acidity of the reacted solution. 1% emulsifier OP was prepared to increase the analytical sensitivity.

**Reaction Procedures:** 30 μg of standard metal salt [Cd(II), Co(II), Mn(II) and Cu(II)] was taken in 25 mL volumetric flasks and added 2.5 mL of pH 11 buffer, 1 mL of OP solution and 1 mL of BBTAN solution respectively and diluted to volume and mixed well. After 20 min, measured the absorbances at 505 and 625 nm against reagent blank, respectively. Calculated the real absorbance ($A_c$) of complex by the following expression:

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta} \quad \text{where } \alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda_1}}{\varepsilon_{ML_\gamma}^{\lambda_2}} \quad \text{and} \quad \beta = \frac{\varepsilon_L^{\lambda_2}}{\varepsilon_L^{\lambda_1}}$$

The terms $\Delta A$ and $\Delta A'$ were the absorbances of the reacted solution at 625 and 505 nm against the reagent blank, respectively. The coefficients $\alpha$ and $\beta$ were named correction factors. The terms $\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_L^{\lambda_1}$ and $\varepsilon_L^{\lambda_2}$ were the molar absorptivities of complex and ligand at 505 and 625 nm, respectively.

## RESULTS AND DISCUSSION

**Absorption Spectra:** Fig. 1 showed the absorption spectra of BBTAN and its Cd(II) complex solutions (Cd(II) was used to represent other three metals because their complexes were found to have the same absorption spectra). From

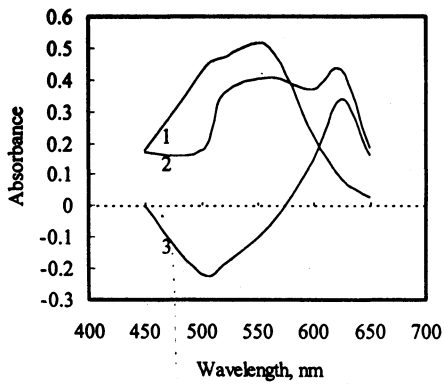


Fig. 1. Absorption spectra of BBTAN and its Cd complex solution at pH 11 and in the presence of OP: 1. BBTAN (1 μmol/25 mL); 2. only Cd (1 mg/25 mL)-BBTAN (1 μmol/25 mL) complex solution; 3. Cd (30 μg/25 mL)-BBTAN (1 μmol/25 mL) reacted solution both 1 and 2 against water and 3 against reagent blank.

curve 3, two wavelengths were selected such that the difference in abosrbances reached maximum: 505 (valley) and 625 (peak) nm. From curves 1 and 2, both $\beta$ and $\alpha$ were calculated as follows $\beta = 0.188$ and $\alpha = 0.450$.

**Effect of pH and Reaction Time:** The reaction between Cd(II) and BBTAN may happen at pH between 8 and 13 as shown in Fig. 2. The sensitivity remained constant between pH 8 and 11. In this study pH 11 was selected. The effect of the reaction time was shown in Fig. 3. This reaction was complete in 10 min. The measurement of absorbances should be carried out in 10 min after the addition of BBTAN solution.

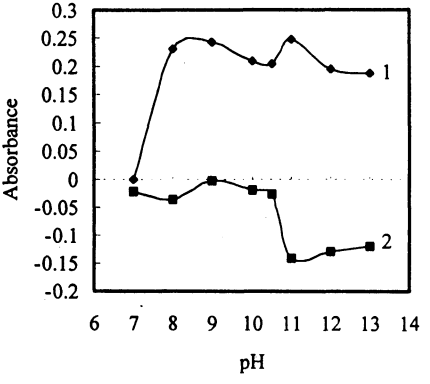


Fig. 2. Effect of pH on absorbance of Cd (20 μg/25 mL)-BBTAN (1 μmol/25 mL) solution at pH 11 and in the presence of OP: 1. ΔA at 625 nm and 2. ΔA′ at 505 nm, against reagent blank.

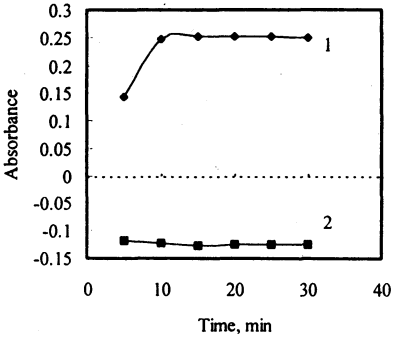


Fig. 3. Effect of the reacted time on absorption of Cd (20 μg/25 mL)-BBTAN (1 μmol/25 mL) complexation solution at pH 11 and in the presence of OP: 1. ΔA at 625 nm and 2. ΔA′ at 505 nm, against reagent blank.

**Determination of Properties of Complexes Solutions:** By varying the addition of 1 mmol/L BBTAN, the absorption of each complex solution was measured and results were shown in Fig. 4. The effective percentage ($\eta$) of BBTAN and the complexation ratio ($\gamma$) were calculated according to the following equations.

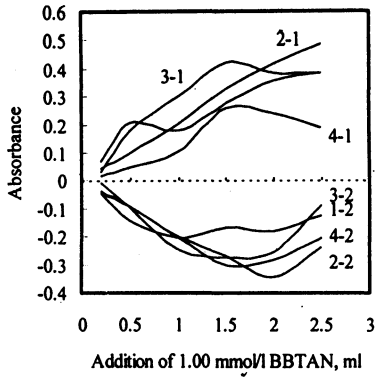


Fig. 4. Effect of the addition of 1 mmol/L BBTAN: 1. xCd (30 μg/25 mL)-BBTAN solution, 2. xCo (30 μg/25 mL)-BBTAN solution, 3. xMn (30 μg/25 mL)-BBTAN solution and 4. xCu (20 μg/25 mL)-BBTAN solution, x – 1 – ΔA and x – 2 – ΔA′, all against reagent blank.

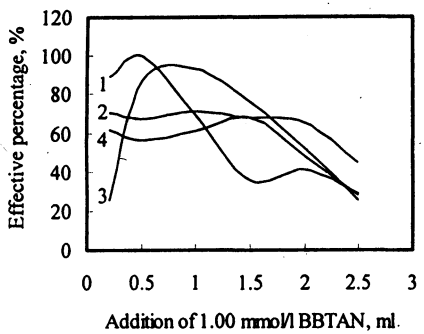


Fig. 5. Effect of the addition of 1 mmol/L BBTAN on its effective percentage (η%): 1. Cd (30 μg/25 mL), 2. Co (30 μg/25 mL), 3. Mn (30 μg/25 mL), 4. Cu (30 μg/25 mL).

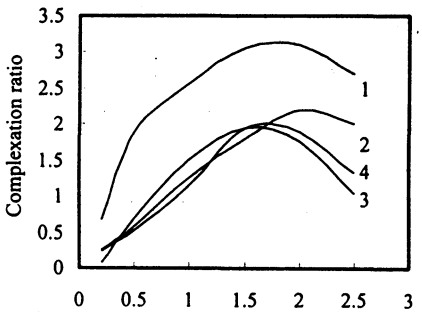


Fig. 6. Effect of the addition of 1 mmol/L BBTAN on the composition ratio (γ′) of M-BBTAN complex solution: 1. Cd (30 μg/25 mL), 2. Co (30 μg/25 mL), 3. Mn (30 μg/25 mL), 4. Cu (30 μg/25 mL).

$$\gamma' = \eta \times \frac{C_L}{C_M} \quad \text{where } \eta = \frac{\alpha\Delta A - \Delta A'}{(1-\alpha\beta)A_0'}$$

The terms $C_M$ and $C_L$ are the concentrations (mol/L) of metal and BBTAN in the beginning. $A_0'$ is the absorbance of the blank regent at 505 nm. If $\gamma'$ approached to a natural number $\gamma$ and remained constant, such a number was named the stoichiometric ratio of the complex produced. Both $\eta$ and $\gamma'$ curves are shown in Fig. 3 and 4, respectively. From curves in Fig. 4, the complex ratio of BBTAN to Cd approached to 3 and that of Co(II), Mn(II) and Cu(II) approached to 2 when the addition of 1 mmol/L BBTAN was equal to 1.5 mL. Therefore, the formed metal complexes were expressed as $Cd(BBTAN)_3$, $Co(BBTAN)_2$, $Mn(BBTAN)_2$ and $Cu(BBTAN)_2$, respectively. From curves in Fig. 3 when the addition 1.5 mL of BBTAN solution was used, the effective percentage of BBTAN were equal to only 35% in Cd (30 μg/25 mL)-BBTAN solution, 68% in Co (30 μg/25 mL)-BBTAN solution, 76% in Mn (30 μg/25 mL)-BBTAN solution and 68% in Cu (30 μg/25 mL)-BBTAN solution, respectively. The excess of BBTAN in the reaction solutions took up 65%, 32% 24% and 32% respectively. It was indubitable that the free BBTAN will interfere with the real absorption of complexes.

The following solutions were prepared for the determination of the stepwise stability constant and the stepwise real absorptivity of metal-BBTAN complexes: 30 μg/25 mL Cd(II) with 0.180, 0.360 and 0.900 μmol/25 mL BBTAN, 30 μg/25 mL Co(II) with 0.450 and 1.08 μmol/25 mL BBTAN, 30 μg/25 mL Mn(II) with 0.360 and 0.900 μmol/25 mL BBTAN, 30 μg/25 mL Cu(II) with 0.450 and 1.08 μmol/25 mL BBTAN. Three replicated determinations of each solution were carried out. We have calculated each of the stepwise stability constants of complexes and their stepwise absorptivities by the following expressions, respectively. Results were shown in Table-1.

TABLE-1
DETERMINATION OF THE STEPWISE STABILITY CONSTANTS AND THE STEPWISE REAL ABSORPTIVITIES (1 $mol^{-1}$ $cm^{-1}$) OF COMPLEXES $M(BBTAN)_\gamma$ IN IONIC STRENGTH 0.025 AND ROOM TEMPERATURE 10°C

| M-L reaction | Stability constant, K | | | Real absorptivity ε at 625 nm | | |
|---|---|---|---|---|---|---|
| | $K_1$ | $K_2$ | $K_3$ | $\varepsilon_{ML}$ | $\varepsilon_{ML_2}$ | $\varepsilon_{ML_3}$ |
| Cd-BBTAN | $4.66 \times 10^5$ | $4.02 \times 10^5$ | $2.28 \times 10^5$ | $1.50 \times 10^4$ | $2.23 \times 10^4$ | $4.45 \times 10^4$ |
| Co-BBTAN | $2.48 \times 10^5$ | $1.92 \times 10^5$ | | $1.01 \times 10^4$ | $1.57 \times 10^4$ | |
| Mn-BBTAN | $3.08 \times 10^5$ | $2.35 \times 10^5$ | | $1.21 \times 10^4$ | $2.21 \times 10^4$ | |
| Cu-BBTAN | $1.28 \times 10^5$ | $2.21 \times 10^5$ | | $0.66 \times 10^4$ | $2.59 \times 10^4$ | |

$$K_n = \frac{\gamma' + 1 - n}{(n-\gamma')(C_L - \gamma' C_M)} \text{ and the cumulative constant (K), } K = \prod_{n=1}^{\gamma} K_n$$

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

The term n indicated the *n*-th complex and this complexation ratio $\gamma'$ must be between **n** – **1** and **n** by preparing the reaction solution. The term $\delta$ indicates the thickness of cell, often 1 cm. The cumulative stability constants (K) of the different metal complexes were as follows $Cd(BBTAN)_3$ $4.27 \times 10^{16}$, $Co(BBTAN)_2$ $4.76 \times 10^{10}$, $Mn(BBTAN)_2$ $7.24 \times 10^{10}$ and $Cu(BBTAN)_2$ $2.83 \times 10^{10}$ respectively. All the stability constants were determined in ionic strength 0.025 and at room temperature 10°C. From Table-1, the high-step absorptivity of $M(BBTAN)_\gamma$ was always more than the low-step one.

## ACKNOWLEDGEMENTS

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