Investigation of Properties of Trace Zinc Complex Solution with 1-(6-Bromo-2-Benzothiazolylazo)-2 Naphthol

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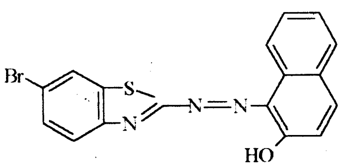
The two reactions were both sensitive between zinc(II) and 1-(6-bromo-2-benzothiazolylazo)-2-naphthol (BBTAN) at pH 8 and 10. The β-correction method was applied to the determination of properties of Zn complex solutions. The complex ratio of Zn(II) to BBTAN was equal to 1 : 4 at pH 8 and 1 : 3 at pH 10. This investigation still brought out the easy determination of the stepwise real absorptivity (ε) and the stability constant (K) of Zn-BBTAN complex.

INTRODUCTION

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



The two reactions were found between zinc(II) and BBTAN at pH 8 and 10. The former formed the red complex from the yellow ligand solution and the latter formed the blue complex from the red ligand solution. Becuase of the serious effect of excess BBTAN on the complex absorption the β-correction spectrophotometry[1, 2] was used in this paper instead of the ordinary spectrophotometry, because it may eliminate the effect of excess ligand. The composition ratio, the stepwise real absorptivity and the stepwise stability constant of zinc complexes with BBTAN were worked out in detail. The recommended method was more acceptable in principle and simpler in operation than the classical method, for example the molar ratio[3], the continuous variation[4], the equilibrium movement[5], etc. The updated investigation showed that the complexes between Zn(II) and BBTAN were Zn : BBTAN = 1 : 4 at pH 8 and 1 : 3 at pH 10.

The following expression was 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 factors and they are able to be measured from only ML_γ solution and L solution and then computed as follows:

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

The symbols $\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_L^{\lambda_1}$ and $\varepsilon_L^{\lambda_2}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2, respectively.

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

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

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_1. if γ' reaches maximum and remains constant, it was thought that $\gamma = \gamma'$ where γ is a natural number and it is named the stoichiometric 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 $ML_{n-1} + L = ML_n$. 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.

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

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

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

where all symbols have the same meanings as the above. In fact, this method is one of dual-wavelength spectrophotometric methods but it is different from the others[6–8] in principle and operation.

EXPERIMENTAL

Visible spectra were recorded with a UV-VIS 265 spectrophotometer in 10 nm glass cells.

Standard Zn(II) solution, 1000 mg/L was prepared by dissolving 1 g high-purity zinc with hydrochloric acid and standard Zn(II) work solution, 10 mg/L was prepared daily by diluting the above solution. The ligand solution, 1 mmol/L BBTAN was prepared by dissolving in dimethylformamide (DMF) and stored in a dark bottle. The buffer solutions, pH 8 and 10, were prepared with borate for controlling the acidity of the reacted solutions. The non-ionic surfactant, elmulsifier OP, 1% was prepared to increase the analytical sensitivity.

Recommended Procedures: 20 micrograms of Zn(II) were taken in a 25 mL volumetric flask. Added distilled water to about 10 mL. Added 2.0 mL of buffer solution, 1 mL of OP solution and 1.0 mL of 1.00 mmol/L BBTAN. Diluted to required volume and mixed well. After 10 min, measured the absorbance at wavelengths 445 and 575 nm (pH 8 solution), 500 and 620 nm (pH 10 solution) against reagent blank, respectively.

RESULTS AND DISCUSSION

Absorption Spectra: Figure 1 shows the absorption spectra of ligand and its zinc complex solutions. From curve 3-x, two wavelengths of each solution should be selected at its valley and peak absorption so as to reach the maximal sensitivity: 445 and 575 nm for Zn-BBTAN reaction at pH 8, and 500 and 620 nm for that at pH 10. From curves 1-x, $\beta = 0.230$ (pH 8) and 0.219 (pH 10). From curve 2-x, $\alpha = 0.348$ (pH 8) and 0.415 (pH 10).

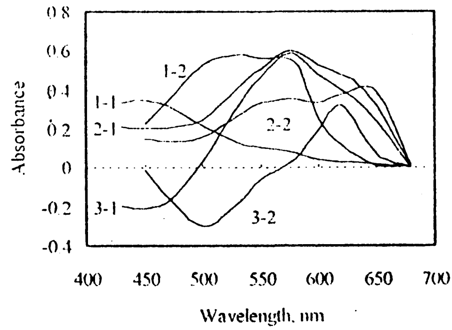


Fig. 1. Absorption spectra of BBTAN and its zinc complex solution: 1-x. BBTAN; 2-x. only Zn-BBTAN complex solution; 3-x. Zn(20 μg)-BBTAN reacted solution against reagent blank: x-1. at pH 8 and x-2. at pH 10

Effect of BBTAN Concentration: By varying the addition of 1 mmol/L BBTAN the absorbances of zinc complex solutions were measured. Results are shown in Figure 2. The effective percentage (η%) of BBTAN and the complexation ratio (γ') to Zn(II) were worked out from equations described in principle. All η and γ are shown in Figures 3 and 4, respectively. From curves in Figure 4,

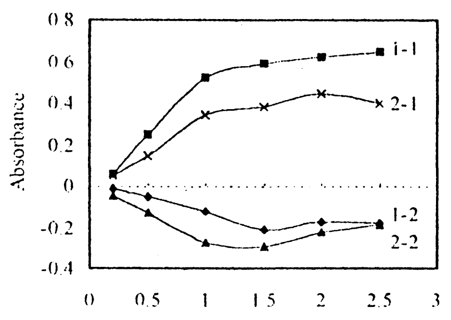


Fig. 2. Effect of the addition of 1.00 mmol/L BBTAN: 1-x. ΔA of Zn-BBTAN complex solution; 2-x. ΔA′ of Zn-BBTAN solution: x-1. at pH 8 and x-2. at pH 10

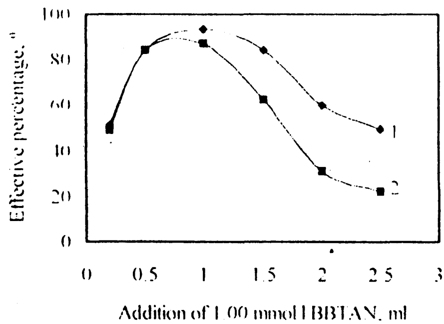


Fig. 3. Effect of the addition of 1.00 mmol/L BBTAN on its effective percentage (η%): 1. at pH 8 and 2. at pH 10

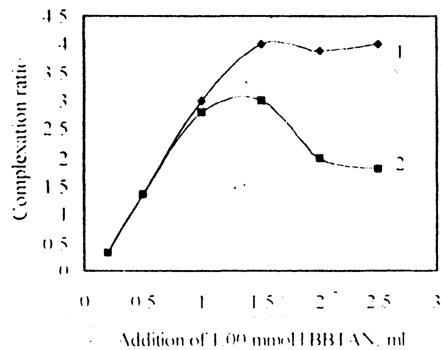


Fig. 4. Effect of the addition of 1.00 mmol/L BBTAN on composition ratio (γ′) of Zn-BBTAN complex: 1. at pH 8 and 2. pH 10

the complex ratio of Zn to BBTAN reached maximum 4 at pH 8 and 3 at pH 10 when the addition of 1.00 mmol/L BBTAN was more than 1.0 mL.

Effect of pH and Reaction Time: The effect of pH on absorbances is shown in Figure 5; the absorption of Zn-BBTAN solution came to maximum at pH 8 at

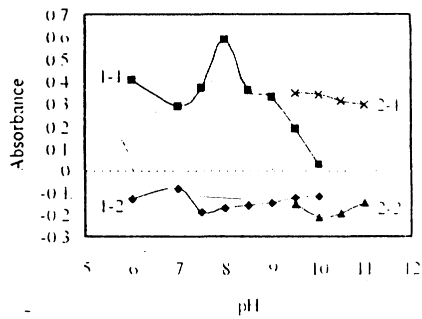


Fig. 5. Effect of pH on the absorption of Zn-BBTAN complex solution: 1-x ΔA, 2-x. ΔA′. x-1. at pH 8 and x-2. at pH 10

445 and 575 nm. However, the absorption of Zn-BBTAN solution came to maximum at pH 10 at 500 and 620 nm because the movement of spectra happened. Therefore, in this work the two reactions were both studied. The effect of the reaction time showed that both reactions were complete in 5 min.

Determination of Stability Constant and Real Molar Absorptivity: The following solutions were prepared for the determination of stepwise stability constant and stepwise real absorptivity of complexes: 20.0 μg/25 mL Zn(II) with 0.30, 0.60, 1.00, 1.20 μmol/25 mL BBTAN at pH 8 and 0.25, 0.60, 0.90 μmol/25 mL BBTAN at pH 10. Six replicated determinations of each solution were carried out. Results are shown in Table-1. The cumulative stabilty constant (K) of $Zn(BBTAN)_4$ at pH 8 was equal to 3.96×10^{20} and that of $Zn(BBTAN)_3$ at pH 10 equal to 8.96×10^{15} in ionic strength 0.025 and temperature 10°C. The stepwise real absorptvity, both $\varepsilon_{ML_n}^{\lambda_2}$ of $Zn(BBTAN)_n$ was calculated as shown in Table 1.

TABLE-1
DETERMINATION OF STEPWISE STABILITY CONSTANT AND STEPWISE REAL ABSORPTIVITY ($l\ mol^{-1}\ cm^{-1}$) OF COMPLEX $Zn(BBTAN)_n$ IN IONIC STRENGTH 0.025 AT 10°C

n-th	$Zn(BBTAN)_4$ at pH 8		$Zn(BBTAN)_3$ at pH 10	
	K_n	ε_r at 575 nm	K_n	ε_r at 620 nm
1st	2.87×10^5	1.74×10^4	3.41×10^5	1.32×10^4
2nd	1.33×10^5	3.06×10^4	3.56×10^5	2.38×10^4
3rd	8.10×10^4	4.94×10^4	7.28×10^4	4.18×10^4
4th	1.28×10^5	4.97×10^4		

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