Spectrophotometric Investigation of Cadmium Complex Solution with *m*-Bromobenzenediazoaminoazobenzene

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Abastract: The synthesis of a new ligand, *m*-bromobenzenediazoaminoazobenzene (*m*-BBDA) was carried out. The reaction between *m*-BBDA and cadmium(II) was sensitive at pH over 12 and in the presence of emulsifier OP. Because of the high interference of excess of ligand β-correction theory was applied instead of the single wavelength method. This study gave the simple determination of the complex ratio, real molar absorptivity (ε) and step or cumulative stability constant (K).

Keywords: Beta-correction principle, cadmium complex, *m*-bromobenzenediazoaminoazobenzene

There are many spectrophotometric methods for the determination of cadmium such as with the following ligands or chromogenic agents: cadions [1], 5-Cl-β-PAN [2], di-2-pyridyl-methanone-2-(5-nitropyridyl) hydrazone [3] and so on. In our laboratory, the synthesis of a new chromogenic reagent, *m*-bromobenzenediazoaminoazobenzene (*m*-BBDA) was made and its structure is as follows
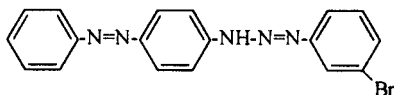
It was found to be sensitive for the complexation with Cd(II) at pH over 12. The maximal absorption of the complex product is at 480 nm but that of the ligand is at 560 nm in basic solution. The non-ionic surfactant, emulsifier OP is helpful to increase both the solubility of Cd-*m*-BBDA in aqueous solution and sensitivity of the reaction. Because of the difference between two wavelengths only 80 nm the excess of *m*-BBDA will interfere obviously the measurement of absorbance of the formed complex. As a result, single wavelength spectrophotometry is not feasible for the analysis of *m*-BBDA complexation solution with Cd(II). The recent dual-wavelength spectrophotometric method, named beta-correction method [4] has been applied for analysis of trace vanadium [5] and other metal ions because it may eliminate almost completely the effect of excess of chromogenic agent on absorbance of complex produced. In this paper, by means of this principle the characteristic factors of Cd-*m*-BBDA chelate can be calculated easily, for example complex ratio, real (not apparent) molar absorptivity and step or cumulative stability constant. The result was more acceptable and the operation simpler than the

conventional method such as molar ratio[6], continuous variation[7], equilibrium[8], *etc.*

From the following expression established in detail[9], the real absorbance (A_c) of a metal (**M**) complex (**ML$_\gamma$**) produced with a ligand (**L**) in solution is calculated.

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

where ΔA and $\Delta A'$ are the absorbances of the mixed solution of **ML$_\gamma$** and **L** measured at wavelengths λ_2 and λ_1 against the reagent blank (only **L** solution), respectively and both α and β are named correction factors which are calculated as follows.

$$\alpha = \varepsilon_{ML_\gamma}^{\lambda 1}/\varepsilon_{ML_\gamma}^{\lambda 2} \quad \text{and} \quad \beta = \varepsilon_L^{\lambda 2}/\varepsilon_L^{\lambda 1}$$

where $\varepsilon_{ML_\gamma}^{\lambda 1}$, $\varepsilon_{ML_\gamma}^{\lambda 2}$, $\varepsilon_{ML_\gamma}^{\lambda 1}$ and $\varepsilon_{ML_\gamma}^{\lambda 2}$ are the molar absorptivities of **ML$_\gamma$** and **L** at wavelengths λ_1 and λ_2 respectively, whose ratio may be computed after the direct determination of **L** and **ML$_\gamma$** solutions.

The real (not apparent) molar absorptivity $(\varepsilon_{ML_\gamma}^{\lambda 2})$ from A_c value and the amount (γ') of **L** to coordinate **M** in reaction may be expressed as follows.

$$\varepsilon_{ML_\gamma}^{\lambda 2} = A_c/(\delta C_M) \quad \text{and} \quad \gamma' = \eta \times C_L/C_M$$

where η is the reacted ratio of ligand, $\eta = (A_c - \Delta A)/Ao$, C_M is the molar concentration (mol/l) of **M** in beginning solution and δ is the thickness of the cell. C_L is the molar concentration (mol/l) of **L** in the beginning solution and Ao is the absorbance of the blank reagent (only **L**) measured at wavelength λ_2 against water reference. While γ' reaches maximum so that $\gamma = \gamma'$, where γ is a natural number to be named the complex number or stoichiometric ratio of the complex produced. In addition, the following expression was the first to be established for determination of the nth-step ($0 < n < \gamma$) stability constant (K_n) of complex **ML$_\gamma$** from the reaction equation: **ML$_{n-1}$** +**L**=== **ML$_n$**, which uses such a M-L solution to give the complexation ratio γ' between **n-1** and **n**.

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

From each K_n we can further calculate the cumulative constant (**K**) of complex **ML$_\gamma$** from the following expression: $K = K_1 \times K_2 \times ... \times K_n ... \times K_\gamma$

Experimental

Visible spectra were recorded with a Model 722 spectrophotometer (Shanghai, China) in 10 mm glass cells. Standard Cd(II) solution, 1000 mg/l: Prepared from 1.000 g high-purity cadmium. Standard Cd(II) working standard, 5.00 mg/l; chromogenic agent solution, 0.50 mmol/l *m*-BBDA: dissolving 191 mg of purified *m*-bromobenzenediazo-aminoazobenzene (*m*-BBDA) in 50 ml of acetone (A.R., Shanghai Reagent) and diluting to 1000 ml with acetone. It should be stored in a dark bottle. KOH solution, 5% (m/v) and emulsifier OP (Shanghai Organic) solution, 5% (v/v)

Ten micrograms of Cd was taken into a 25-ml volumetric flask. Add distilled water

to about 20 ml. Add 1 ml of 5% OP, 2 ml of 0.500 mmol/l _m_-BBDA and 0.5 ml of 5% KOH. Dilute to volume and mix well. After 10 min, measure absorbances at 480 and 560 nm against a reagent blank, respectively.

Results and Discussion

Figure 1 showed the absorption spectra of _m_-BBDA and Cd complex solution. From curve 3, two wavelengths should be selected such that the difference in absorbances was a maximum: 560 and 480 nm. β was equal to 0.768 from curve 1 and α 0.20 from curve 2. Hence, $A_c = 1.18(\Delta A - 0.768 \Delta A')$.

Figure 2 gave the effect of the addition of _m_-BBDA solution on absorbance of the complexation solution.

Figure 1 Absorption spectra of _m_-BBDA and its Cd complex solution: 1, 0.080 mmol/l _m_-BBDA against water; 2, Cd (more than 100 μg) complex solution with _m_-BBDA (0.040 mmol/l), against water; 3, Cd (10 μg) complexed solution with 0.040 mmol/l _m_-BBDA against reagent blank.

Figure 2 Effect of _m_-BBDA addition on complexation solution: 1, the reagent blank at 560 nm against water; 2, Cd (10 μg) chelate at 480 nm against the reagent blank; 3, same as 2 but at 560 nm; 4, Ac at 480 nm; 5, γ'

Absorbance   Absorbance

Wavelength nm   Addition of 0.50 mmol/l _m_-BBDA ml
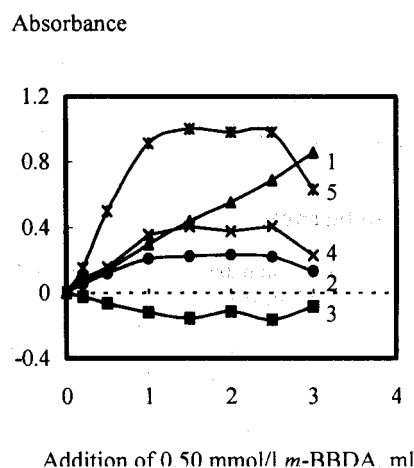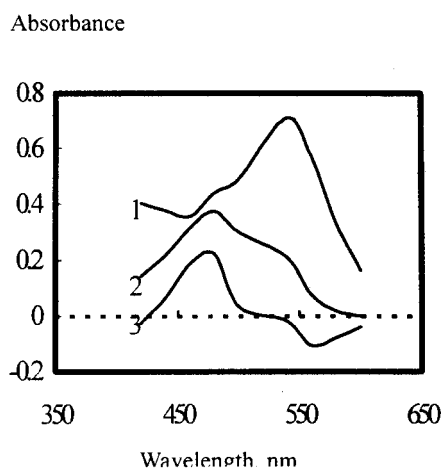
From curve 2, it is impossible for the complexation ratio of Cd to _m_-BBDA to be calculated accurately with the conventional molar ratio method by reason of unclearness of the inflexion point. Each A_c and γ' was obtained as shown in **Figure 2**. From curve 2, the maximum of γ' was equal to 4. Therefore, Cd $(m\text{-BBDA})_4$ was formed here. From curve 4 the real molar absorptivity $\varepsilon_{Cd(m\text{-BBDA})_4}^{480} = 1.14 \times 10^5$ l·mol^{-1}cm^{-1} but from curve 2 its apparent that $\varepsilon_{Cd(m\text{-BBDA})_4}^{480} = 6.47 \times 10^4$ l·mol^{-1}cm^{-1}.

Effect of Other Conditions

Varied pH of solution showed that the absorbances increased with the increase of pH. If pH was over 12 the absorbance come to maximal and remain almost constant. The real

absorbance (A_c) of Cd-*m*-BBDA complexation solution reached maximum while the addition of 5% OP was over 1.0 ml and 5% KOH over 0.5 ml. The effect of reaction time on A_c indicated that the reaction was complete in 10 min. The color remains almost constant for at least 4 hours.

Precision of Method

Eight replicate determinations of standard solution containing 5.00 µg Cd were carried out, the relative deviations (RDs) being between –9.3% and +8.3% and the relative standard deviation (RSD) being 5.5% for beta-correction method. However, the single wavelength method gave out the following results: RDs between –23% and +35% and RSD 18.5%. Both the precision and accuracy with beta-correction method were much higher than that with the single wavelength spectrophotometry. Therefore for analysis of such a complexation reaction the single wavelength method is unsuitable.

Determination of Stability Constant

The following solutions were prepared for the determination of stability constant of complex: 0.10 µmol/25ml Cd(II) with 0.10, 0.20, 0.30 and 0.50 µmol/25ml *m*-BBDA. The step and cumulative stability constant, K_n and K of Cd(*m*-BBDA)$_4$ were as follows: K_1= 8.58×10^5, K_2= 2.22×10^5, K_3= 1.08×10^5, K_4= 2.42×10^5 and K = 4.98×10^{21} (in ion strength 0.01 and at temperature 20 °C).

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