Updated Determination of Properties of Mercury Complex with *o*-Sulfobenzeneazo Rhodanine by β-Correction Spectrophotometry

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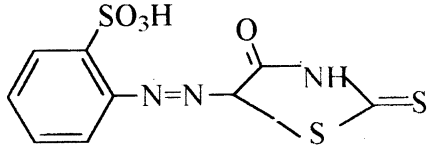
The reaction was studied between mercury(II) and new ligand *o*-sulfobenzeneazo rhodanine (SBAR) in acidic solution. The β-correction method was used to determine the properties of Hg(II) complex solution instead of the ordinary spectrophotometry. The composition ratio, the real absorptivity (ε) and cumulative stability constant (K) of Hg-SBAR complex were as follows: 2, 6.82×10^3 l mol^{-1} cm^{-1} at 535 nm and 3.40×10^{10}, respectively. The recommended method was more acceptable in theory and simpler in operation than the classical method.

INTRODUCTION

The synthesis of the ligand *o*-sulfobenezeneazo rhodanine (SBAR) was reported with the following structure and it was ever applied to the determination of palladium[1].



The traditional azo rhodanine compounds were often applied to the determination of trace amounts of noble metals. However, it was difficult for the ordinary spectrophotometric method to give out the accurate analysis of the complex because the investigation showed that the excess of new ligand SBAR had an obvious absorption at the work wavelength of the complex formed. The β-correction method[2] may eliminate the absorption interference of the excess of ligand form its metal complex to give the real absorbance of the formed complex and it was ever applied to the determination of many metal complex solutions[3–5]. Recently, the reaction between Hg(II) and SBAR was studied in detail in acidic solution. The composition ratio of Hg to SBAR was as follows: Hg : SBAR = 1 : 2. The stepwise real absorptivity (K) and stepwise stability constant (ε) of Hg complex were all determined. The recommended method was more acceptable in principle and simpler in operation than the classical methods such as molar ratio[6] continuous variation[7] and equilibrium movement[8], etc.

Principle

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 their 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 is 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.

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

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, . . . , γ) 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.

EXPERIMENTAL

Absorption spectra were recorded with UV-VIS 265 spectrophotometer in 10 mm glass cells. Standard Hg(II) solution, 10.0 mg/L was prepared with mercury chloride (G.P.) and diluted with non-ionic water (specific conductivity less than 0.3 μS/cm). SBAR solution, 1.00 mmol/L was dissolved in non-ionic water and stored in a dark bottle. The following acid solution was prepared: 5 mol/L sulfuric acid for the pH adjustment of Hg-SBAR solution.

50 microgram of standard mercury was taken in a 25 mL volumetric flask. Added 2.5 mL of sulphuric acid solution and 2.5 mL of 0.500 mml/L SBAR. Diluted to required volume and mixed. After 10 min, measured the absorbances at 460 and 535 nm respectively.

RESULTS AND DISCUSSION

Absorption Spectra: Figure 1 shows the absorption spectra of SBAR and its Hg complex solution. From curve 3, two wavelengths were selected such that the difference in absorbances reached maximum: 460nm (valley) and 535 nm (peak). From curves 1 and 2, $\beta = 0.134$ and $\alpha = 1.18$.

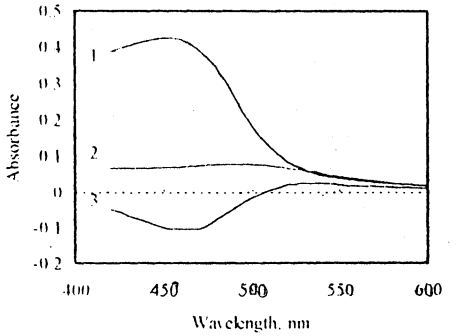


Fig. 1. Absorption spectra of SBAR and its Hg complex solution: 1. SBAR; 2. only Hg-SBAR complex solution; 3. Hg(50 μg)-SBAR solution: both 1 and 2 against water and 3 against reagent blank

Effect of Addition of SBAR Solution: By varying the addition of 0.500 mmol/L SBAR the absorbance of Hg complex solution was measured as shown in Figure 2. The effective percentage (η%) of ligand and the complexation ratio (γ') were calculated according to the above equations. Both η and γ' were shown in Figures 3 and 4, respectively. From Figure 4, the complex ratio of SBAR to Hg (50 μg) remained 2 when the addition of 0.500 mmol/L SBAR was more than 2.5 mL. Therefore, the formed complex was expressed as Hg $(SBAR)_2$. The effective amounts and the excess of SBAR in Hg complex solution were 38%

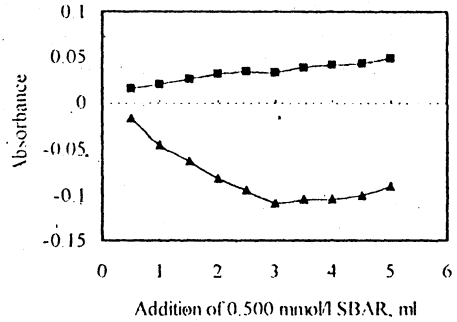


Fig. 2. Effect of the addition of 0.500 mmol/L SBAR: 1. ΔA and 2. $\Delta A'$.

and 62% respectively, when the complexation ratio approached to the final γ. Therefore, over 60% of the total addition of SBAR hadn't joined the complexation with Hg(II). It was indubitable that such high free SBAR affected certainly the absorption measurement of Hg-SBAR complexes.

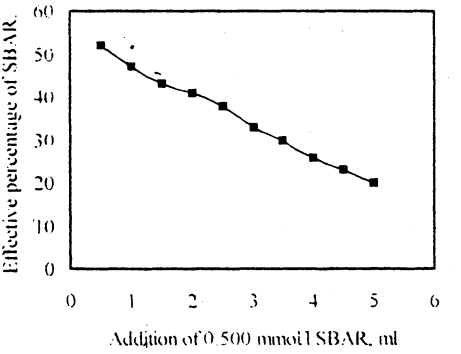


Fig. 3. Effect of the addition of 0.500 mmol/L SBAR on its effective percentage (η%) of SBAR

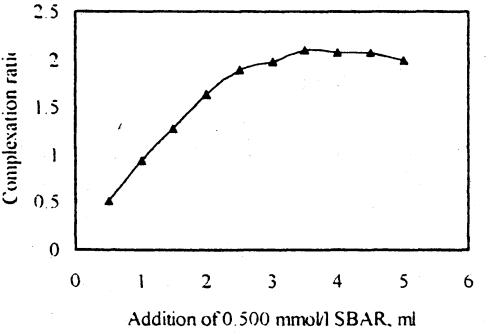


Fig. 4. Effect of the addition of 0.500 mmol/L SBAR on composition ratio (γ') of Hg-SBAR complex solution

Effect of pH and Reaction Time: This reaction cannot happen when pH more than 3. By varying hydrogen ion concentration, the results were showed in Figure 5. The effect of the reaction time was shown in Figure 6. The reaction between Hg(II) and SBAR was complete in 5 min.

Determination of Stability Constant and Real Molar Absorptivity: The following solutions were prepared for the determination of the stepwise stability constant and the stepwise real absorptivity of Hg-SBAR complex: 50.0 μg/25 mL Ag(I) with 0.500 and 1.80 μmol/25 mL SBAR. Four replicated determinations of each solution were carried out. The stepwise, cumulative stability constants (K) of $Hg(SBAR)_2$ were equal to 3.75×10^5, 9.07×10^4 and 3.40×10^{10} respectively. Its stepwise real molar absorptivities were equal to 4.67×10^3 and 6.82×10^3 l mol^{-1} cm^{-1} at 535 nm, respectively. This was determined in ionic strength 1.0 and at room temperature 10°C.

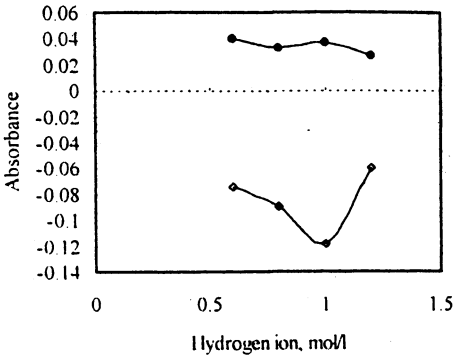


Fig. 5. Effect of H^+ concentration: 1. ΔA and 2. ΔA′.

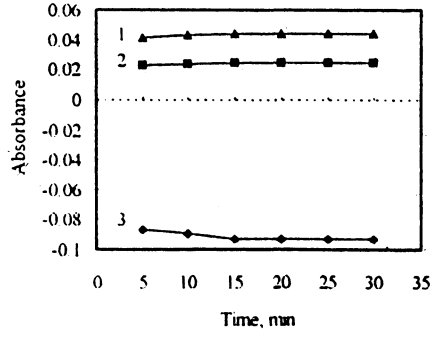


Fig. 6. Effect of time on absorbance of Hg-SBAR complex solution: 1. Ac at 535 nm; 2. ΔA at 535 nm; 3. ΔA′ at 460 nm.

ACKNOWLEDGEMENT

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