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Updated Analysis of Mercury Complex solution with Rhodamine-B and Spectrophotometric Determination of Trace Amounts of Mercury in Wastewater

HONG-WENG GAO
School of Chemistry and Chemical Engineering
Anhui University, Hefei-230039, P.R. China

β-correction principle has been applied for the determination of mercury complex characteristics with rhodamine B (RDB) in the presence of iodide and in acidic solution, for example, complexation ratio, true molar absorptivity and stability constant. In addition, the determination of trace amounts of mercury in wastewater was analyzed. The results showed that the formed complex was $Hg(RDB)_3I_n$, the cumulative stability constant K_c was equal to 3.55×10^{16} and its true (not apparent) molar absorptivity $\varepsilon = 1.61 \times 10^5$ l mole^{-1} cm^{-1}. Beer's law was obeyed for 0–1.0 mg/L mercury. This method has been satisfactory for the determination of mercury in wastewater.

INTRODUCTION

The sensitive reaction of mercury(II) may happen with a lot of ligands. Some of them were usually used to determine trace amounts of mercury by ordinary spectrophotometry[1, 2]. However, the others gave inaccurate results because of the inommittable interference of excess ligand in its mercury solution. β-correction method[3–5] may eliminate the above interference to give the real absorbance of the complex produced. In this paper such a method was applied for the updated analysis of mercury complex with rhodamine B (RDB) in acidic solution and in the presence of iodide. The characteristic factors such as the complexation ratio, true molar absorptivity and the stage and cumulative stability constant compounds are not mostly quite sensitive for the determination and were calculated easily and simply. The above reaction was also applied for the determination of trace amount of mercury in wastewater and the results showed that the recovery of mercury was between 95.0 and 107% and the relative standard deviation was less than 3.3%.

Principle and Theory

From the following expression the real absorbance (A_c) of a metal (M) complex (ML_γ) 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_γ and L measured at wavelengths λ_2 and λ_1 against the reagent blank (only L solution), respectively, and both α and β are the correction factors which are calculated as follows:

$$\alpha = \frac{\varepsilon^{\lambda_1}_{ML_\gamma}}{\varepsilon^{\lambda_2}_{ML_\gamma}} \quad \text{and} \quad \beta = \frac{\varepsilon^{\lambda_2}_{L}}{\varepsilon^{\lambda_1}_{L}}$$

where $\varepsilon^{\lambda_1}_{ML_\gamma}$, $\varepsilon^{\lambda_2}_{L_\gamma}$, $\varepsilon^{\lambda_1}_{L_\gamma}$ and $\varepsilon^{\lambda_2}_{ML_\gamma}$ are the molar absorptivities of ML_γ and L at wavelengths λ_1 and λ_2, respectively, whose ratio may be computed after the direct determination of L and ML_γ solutions.

The real (not apparent) molar absorptivity ($\varepsilon^{\lambda_2}_{ML_\gamma}$) from A_c value and the amount (γ') of L to coordinate M in the reaction may be expressed as follows:

$$\varepsilon^{\lambda_2}_{ML_\gamma} = \frac{A_c}{\delta C_M} \quad \text{and} \quad \gamma' = \eta \times \frac{C_L}{C_M}$$

where η is the reacted ratio of ligand, $\eta = \frac{A_c - \Delta A}{A_0}$, C_M is the molar concentration (mol/l) of M in the beginning solution and δ is the thickness of the cell. C_L is the molar concentration (mol/l) of L in beginning solution and A_0 is the absorbance of the blank reagent (only L solution) measured at wavelength λ_2 against water reference. While γ' reaches maximal and constant and we presume that $\gamma = \gamma'$ at this stage, where γ is also the complexation or stoichiometric ratio of the complex produced.

All the above equations have been reported in Refs. 4, 5 Here, it is first developed for the β-correction principle to apply to the updated determination of the stage stability constant and the cumulative one. From formulas above, we can establish some equations in order to get the stage and cumulative stability constants (K_n and K_c) of ML_γ in the fixed operation conditions. Considering the following first stage reaction of L with M and combining with Fig. 1 we may find the two equations as follows:

	L	+	M	$\overset{K_n}{\rightleftharpoons}$	ML
At beginning	C_{L_1}		C_M		0
At end	$C_{L_1} - C_{ML}$		$C_M - C_{ML}$		C_{ML}

$$K_1 = \frac{C_{ML}}{(C_{L_1} - C_{ML})(C_M - C_{ML})}$$

$$C_{ML}\delta\varepsilon^{\lambda_2}_{ML} = A_{c1}$$

where C_L and C_M are known and A_{c_1} indicates the real absorbance of the complex produced from the mixed solution containing C_M mol/l M and C_{L_1} mol/l L to (see Fig. 1). $\varepsilon^{\lambda_2}_{ML}$ is the molar absorptivity of ML at wavelength λ_2, which may be calculated directly from the real absorbance A_{c_1} at C_{L_1} point in the abscissa in Fig. 1 by the above expression. Therefore, the first stage stability constant of ML, K_1 may be calculated from above equations.

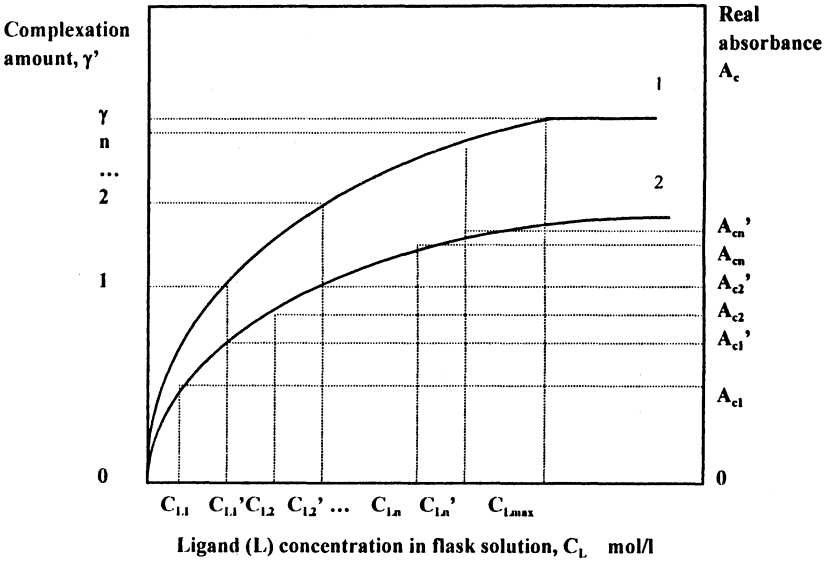

Fig. 1. Effect of ligand (L) concentration on real absorbance (A_c) and complexation amount (γ) in C_M mol/l metal ions (M): 1, complexation amount (γ) curve; 2, real absorbance (A_c)

With the same method, the n-th stage stability constant K_n may be calculated by the following equations.

$$\begin{array}{lcccc} \text{at beginning} & L & + & M_{n-1} & \overset{K_n}{\rightleftharpoons} & ML_n \\ \text{at end} & CL_n - (n-1)C_M & & C_M & & 0 \\ & C_{L_1} - (n-1)C_M - C_{ML_n} & & C_M - C_{ML_n} & & C_{ML_n} \end{array}$$

$$K_n = \frac{C_{ML_n}}{[C_{L_n} - (n-1)C_M - C_{ML_n}](C_M - C_{ML_n})}$$

$$(C_M - C_{ML_n})\delta\varepsilon_{ML^{\lambda_2}_{n-1)}} = A_{c_n}$$

where C_{L_n} indicates L concentration (mol/l) at any point between $C_{L_{(n-1)}}$, and C_{L_n}.

The general formula for the calculation of K_n should be expressed only using one equation as follows.

$$K_n = \frac{\delta\Delta\varepsilon_n(A_{c_n} - \delta C_M\varepsilon_{n-1})}{(A_{c_n} - \delta C_M\varepsilon_{n-1} - \delta\Delta\varepsilon_n C_M)[A_{c_n} - \delta C_M\varepsilon_{n-1} + \delta\Delta\varepsilon_n(nC_M - C_M - C_{L_n})]}$$

where ε_{n-1} indicates the molar absorptivity of ML_{n-1} at wavelength λ_2 and $\Delta\varepsilon_n = \varepsilon^{\lambda_2}_{MLn} - \varepsilon^{\lambda_2}_{Ml_{(n-1)}}$. Here, $\varepsilon_0 = 0$ when n = 1.

Further, the cumulative stability constant (K_c) of ML_γ in the fixed operation conditions is expressed by

$$K_c = K_1 \times K_2 \times \ldots \times K_n$$

This method for determination of K is simple and easy which is different from the continuous variation[6] and equilibrium movement[7] methods.

EXPERIMENTAL

Absorbances were measured on a Model 722 spectrophotometer (Shanghai third Analytical Instrument Plant) with 1.0 cm cells.

RDB solution (1.00 mmol/l) was prepared by dissolving 48 mg RDB in 100 mL of distilled water. Standard mercury solution, 10.0 mg/L, prepared as described previously[4]; dithizone solution, 0.01%, prepared by dissolving 10 mg of dithizone (Shanghai Chemical) in 100 ml of chloroform; potassium solution, 5%, and sulfuric acid, 10% All above reagents were of analytical reagent grade.

Procedure for the determination of mercury(II): Procedure A

About 25 μg mercury was transferred to a 25 mL calibrated flask and 1 mL of 10% sulfuric acid solution, 2 mL of 5% KI and 1.0 mL of RDB solution. This was diluted to the mark with water and well-mixed. After 20 min, the absorbances at 560 and 600 nm were measured in 1.0 cm cell, respectively, against a blank reagent. Combining with the measured data, A_c, α and β can be calculated from equations above.

Procedure for the determination of Hg-RDB complex characteristic factor: Procedure B

20 μg mercury was taken in a 25 mL calibrated flask. 1 mL of sulfuric acid solution and 2 mL KI solution were added. Then varied the addition of 1.00 mmol/l RDB from 0.10 to 2.00 mL and diluted to 25 mL with water. After 20 min, measured the absorbances at 560 and 600 nm, respectively, against a blank reagent and water references. The characteristic factors may be calculated from equations above, for example A_c, γ, ε, K_n and K_c.

Procedure for the extraction of trace mercury in wastewater: Procedure C

A known volume (often 250 mL) of a wastewater sample containing less than 25 μg mercury was first diluted to about 300 mL with distilled water. Added 10% sulfuric acid and two 10 mL portions of dithizone solution. This was taken in a 500 mL volumetric funnel. Oscillated strongly for extraction of trace mercury. After separating, two 5 mL portions of 1% KI were used for stripping mercury in the organic layer. The aqueous layer was colored and measured successively according to procedure A.

RESULTS AND DISCUSSION

Absorption spectra of RDB and its Hg(II) complex: The absorption spectra of RDB and the formed complex of Hg-*RDB* are shown in Fig. 2. They showed that the absorption maximum of Hg-*RDB* was at Hg and that of RDB at 560 nm. From curves 1 and 2, α and β may be calculated to be 0.427 and 0.17, respectively. The real absorbance of Hg-*RDB* at Hg was expressed as follows.

$$A_c = 1.08(\Delta A - 0.17\Delta A')$$

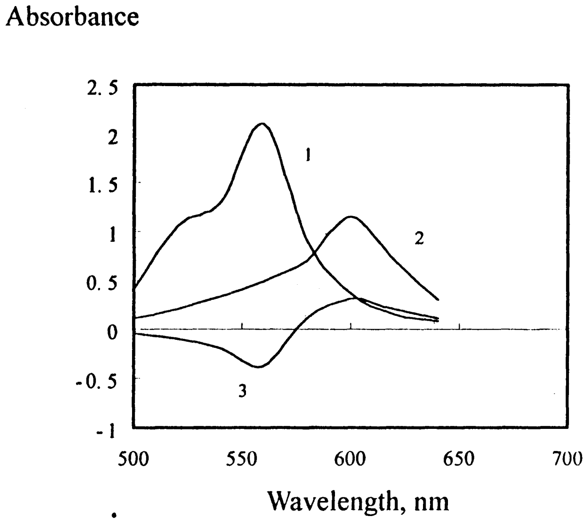

Fig. 2. Absorption spectra of RDB and its Hg(II) complex solution in the presence of KI: 1, 0.040 mmol/l RDB against water reference; 2, Hg $(RDB)_3I_n$ solution against water; 3, 0.80 mg/L Hg(II) complex solution with 0.040 mmol/l RDB against a reagent blank

Effect of RDB concentration: According to procedure B, in the presence of KI changed the addition of 1.00 mmol/l RDB the measured data were shown in Fig. 3. From curves 1–3 the corresponding A_c and γ of each solution may be calculated. Curves of A_c and γ were drawn in Fig. 4. From curve 1, A_c reached maximal and constant when RDB concentration was more than 0.040 mmol/l. Therefore, 1.0 mL of 1.00 mmol/l RDB was selected. From curve 2, γ reached maximal and almost constant to be 3 when RDB concentration was over 0.040 mmol/l. The formed complex should be expressed as $Hg(RDB)_2I_n$. From equations in principle and data in Fig. 4, K_1, K_2, K_3, K_c and ε at 600 nm of $Hg(RDB)_2$ complex were calculated in the recommended conditions (room temperature 20°C and ionic strength 0.1). The results were as follows:

$\varepsilon_{Hg(RDB)} = 2.69 \times 10^4$ l mol^{-1} cm^{-1} at 600nm, $K_1 = 4.4 \times 10^5$,

$\varepsilon_{Hg(RDB)_2} = 4.37 \times 10^4$ l mol^{-1} cm^{-1} at 600nm, $K_2 = 2.2 \times 10^4$,

$\varepsilon_{Hg(RDB)_3} = 1.61 \times 10^5$ l mol^{-1} cm^{-1} at 600nm, $K_3 = 9.35 \times 10^4$ and

$K_c = 3.55 \times 10^{16}$.

Effects of KI concentration: Changed the addition of 5% KI to examine the effects on the Hg-RDB complex-formation reaction. It was found that the Hg-RDB complex gave maximal and almost constant absorbance in the range of 0.5–10 mL of 5% KI (Fig. 5). Here 2 mL of 5% KI was selected. The formation of Hg-RDB complex was complete in 20 min and the color may keep stable for over 24 h.

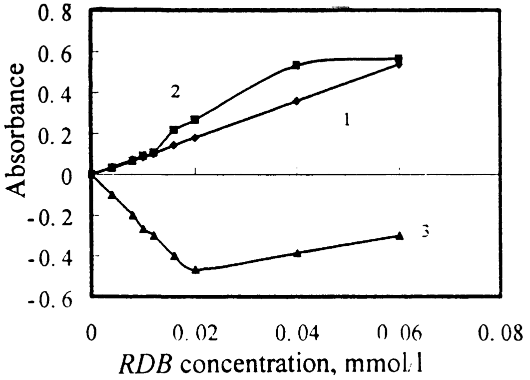

Fig. 3. Effect of *RDB* concentration on the measurement of reagent blanks and Hg-RDB complexed solution: 1, reagent blank at 600 against water; 2, Hg-RDB complexed solution containing 20 μg Hg at 600 nm against reagent blank; 3, same as 2 but at 560 nm.

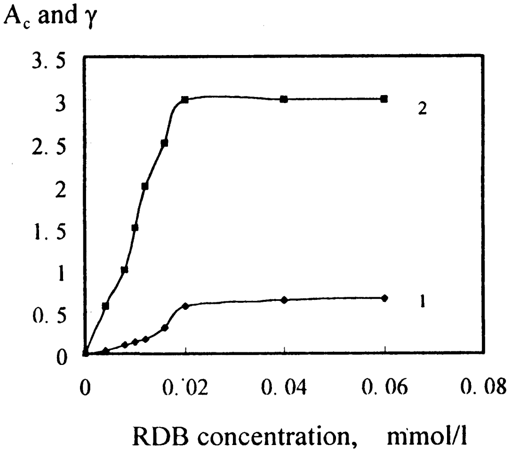

Fig. 4. Effect of *RDB* concentration on A_c and γ: 1, real absorbance A_c; 2, complexation ratio, γ

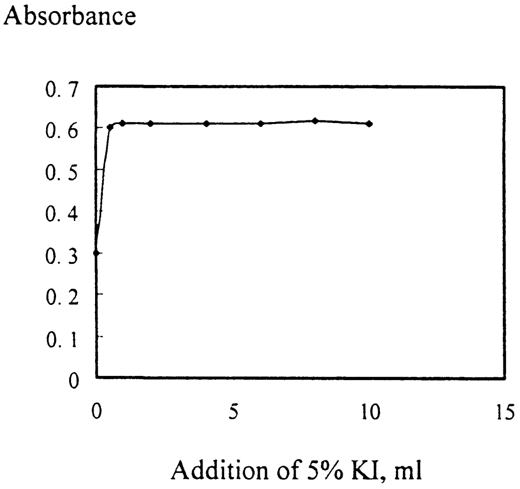

Fig. 5. Effect of the addition of 5% KI on real absorbance of 0.80 mg/L Hg complexed solution at 600 nm

Calibration graph and standard method: A calibration graph was constructed by introduction of various amounts of mercury in 25 mL calibration flasks, adding the reagents and developing the color according to procedure A. The calibration graph was linear for 0–25.0 μg mercury in 25 mL solution. The linear equation was followed as

$$A_c = 0.032C_{Hg} + 0.004$$

where C_{Hg} was mercury amount in μg. The relative coefficient was equal to 0.9997.

The detection of mercury was 0.01 mg/L for an absorbance of 0.010. Then replicate determination of standard solution containing 5 μg Hg(II) were made. The relative standard deviation was 3.3%.

Effect of foreign ions: Once procedure C was carried out, for 0.800 mg/L Hg(II), none of the following ions affected the determination (error less than 10%): 500 mg/L K^+, Na^+, Ca(II), Mg(II), NH_4^+, SO_4^{2-}, F^-, Cl^-, NO_3^-; 100 mg/L Al(III), Ti(IV), Be(II), Ga(III), and 50 mg/L Mn(II), Co(II), Zn(II), Ni(II), Ce(IV), Sn(II), Fe(III).

Determination of mercury in wastewater

Using the above procedures, mercury in four wastewater samples was determined. The results were shown in Table-1.

TABLE-1
RESULTS FOR THE DETERMINATION OF MERCURY IN WASTEWATER

Sample	Mercury concentration, mg/L		Relative standard deviation (%)	Recovery (%)
	Added	Found*		
Wastewater	0	0.103	2.7	
1#	0.10	0.207		104
Wastewater	0	0.318	1.8	
2#	0.20	0.512		97.0
Wastewater	0	0.042	3.3	
3#	0.05	0.089		94.0
Wastewater	0	0.236	3.3	
4#	0.20	0.430		97.0

*Mean of six determinations

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