Asian Journal of Chemistry Vol. 12, No. 2 (2000), 548–552

Analysis of Properties of Trace Aluminium Complex Solution with Dibromo-*o*-Carboxy-Chlorophosphophonazo

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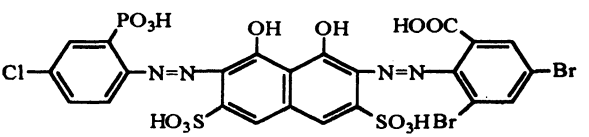
The two reactions were both sensitive between aluminium(III) and dibromo-*o*-carboxy-chlorophosphonazo (DBKCPA) at pH 7. The β-correction dual-wavelength spectrophotometric method was applied to the determination of properties of aluminium complex solutions because it was able to eliminate the interference of excess ligand in the reaction system. The multi-coordination reaction was found in such a complex system because the complex ratio of Al(III) to DBKCPA was equal to 1 : 2. In addition, the investigation still brought out the easy determination of the stepwise real molar absorptivity (ε) and the stepwise or cumulative stability constant (K) of Al-DBKCPA complex.

INTRODUCTION

The synthesis of the ligand dibromo-o-carboxy chlorophosphonazo (DBKCPA) (**1**) was reported in 1996[1]. Its structure was as follows:



(1) dibromo-o-carboxy-chlorophosphonazo

It was even applied to the determination of trace amount of metal, *e.g.*, water hardness[2] by ordinary spectrophotometry. Because of the serious effect of excess ligand on the complex absorption, β-correction spectrophotometry[3, 4] was studied to eliminate the effect of excess ligand. The composition ratio, the stepwise real molar absorptivity and the stepwise stability constant of aluminium complex with DBKCPA were determined in detail in this report. The β-correction method was more acceptable in principle and simpler in operation than the conventional methods such as molar ratio[5], continuous variation[6], equilibrium movement[7], etc. The updated investigation showed that the complex between Al(III) and DBKCPA was Al : DBKCPA = 1 : 2 at pH 7.

The following expression is 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 the correction factors and they can be measured from only ML_γ solution and L solution and then computed as follows.

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.

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

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

$$\gamma' = \eta \times \frac{C_L}{C_M} \qquad \text{where} \qquad \eta = \frac{A_c - \Delta A}{A_0}$$

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_2. If γ' reaches maximum and remains constant, it was thought that $\gamma = \gamma'$ where γ is a natural number and it is called 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 as to form the complex ratio γ' between $n-1$ and n and studied successively.

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

From each K_n the cumulative constant (K) of complex ML_γ can be calculated from the following expression: $K = K_1 \times K_2 \times \ldots \times K_n \ldots \times K_\gamma$. In addition, from such an 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:

$$\varepsilon_{ML_n}^{\gamma_2} = \frac{A_c}{\delta C_M(\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \varepsilon_{ML_{n-1}}^{\gamma_2}$$

In this equation all symbols have the same meanings as the above.

EXPERIMENTAL

Visible spectra were recorded with a UV-vis 265 spectrophotometer (PE Co. Ltd.) in 10 mm glass cells.

Standard Al(III) solution, 100 mg/L was prepared by dissolving 1.000 g high-purity aluminium with chlorhydric acid and standard Al(III) working standard, 10.00 mg/L, was prepared daily by diluting the above solution. The ligand solution, 1.00 mmol/L DBKCPA, was prepared by dissolving in water and stored in a dark bottle. The buffer solution, pH 7 was prepared to adjust the acidity of the reaction solutions with ammonium acetate.

Recommended Procedure: Ten micrograms of Al(III) was taken in a 25 mL volumetric flask. Added distilled water to about 10 mL. Added 2.0 mL of buffer solution and 1.00 mL of 1.00 mmol/L DBKCPA. Diluted to volume and mixed well. After 10 min, measured the absorbances at wavelengths 540 and 630 nm against reagent blank respectively.

RESULTS AND DISCUSSION

Absorption Spectra: Figure 1 shows the absorption spectra of ligand and its aluminium complex solution. From curve 3, two wavelengths should be selected at its valley and peak absorption so as to obtain the maximal analytical sensitivity: 540 and 630 nm for Al-DBKCPA reaction. From curves 1 and 2, β and α were equal to 0.185 and 0.781 respectively. The following expression was established: $A_c = 1.17(\Delta A - 0.185\Delta A')$ at 630 nm.

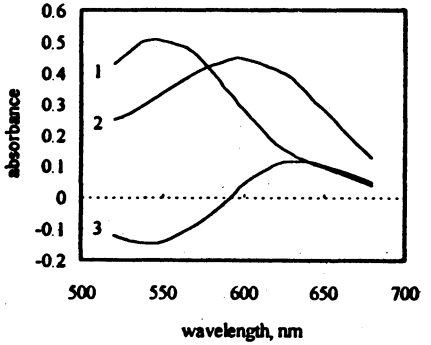


Fig. 1. Absorption spectra of DBKCPA and its aluminium complex solution: 1. DBKCPA; 2. only Al-DBKCPA complex solution; 3. Al-DBKCPA solution against reagent blank.

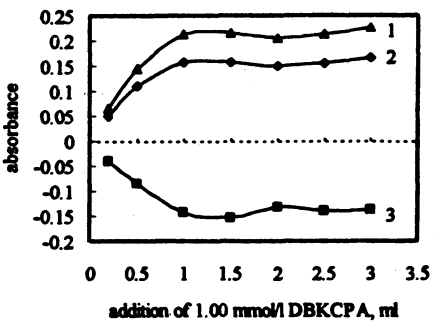


Fig. 2. Effect of the addition of 1.00 mmol/L DBKCPA: 1. ΔA of Al-DBKCPA complex at 630 nm; 2. Ac of Al-DBKCPA solution at 630 nm; 3. $\Delta A'$ of Al-DBKCPA solution at 540 nm

Effect of Ligand Concentration: By varying the addition of 1.00 mmol/L DBKCA the absorbance of aluminium complex solution was measured. The effective percentage (η%) of DBKCA and the complexation ratio (γ') to Al(III) were worked out. All η's and γ's were shown in Figures 3 and 4, respectively. From the curve in Figure 4, the complex ratio of Al to DBKCPA reached maximum 2 when the addition of 1.00 mmol/L DBKCPA was more than 1.0. From curve in Figure 3 the excess DBKCPA took up about 25% in the minimum addition (γ' approached to 2) 1.00 ml of 1.00 mmol/I DBKCPA. It was indubitable that such an excess will certainly affect the amount of absorption.

Effect of pH and Reaction Time: From the curve in Figure 5, it was found that the sensitivity of Al-DBKCPA reaction came to maximum at pH between 5 and 7.5. The effect of the reaction time is shown in Figure 6. The reaction between Al(III) and DBKCPA was complete in 5 min.

Determination of Stability Constant and Real Molar Absorptivity

The following solutions were prepared for the determination of stepwise

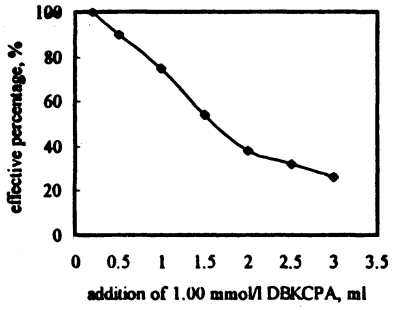


Fig. 3. Effect of the addition of 1.00 mmol/L DBKCPA on its effective percentage (η%)

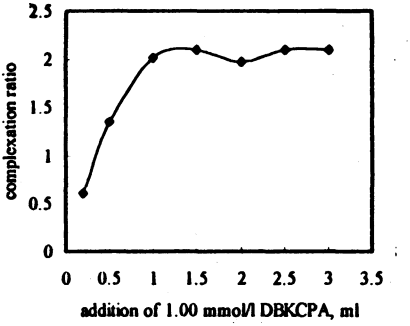


Fig. 4. Effect of the addition of 1.00 mmol/L DBKCPA on composition ratio (γ') of Al-DBKCPA complex

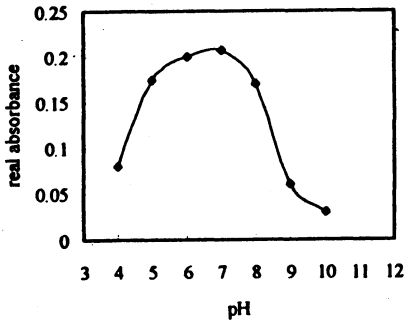


Fig. 5. Effect of pH on real absorbance of Al-DBKCPA complex solution at 630 nm

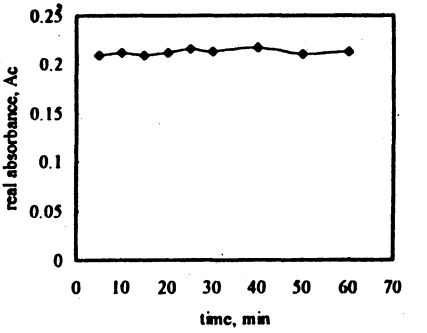


Fig. 6. Effect of time on real absorbance of Al-DBKCPA complex solutions at 630 nm

stability constant and stepwise real molar absorptivity of complex: 6.00 μg/25 mL Al(III) was mixed with 0.200 and 0.500 μmol/25 mL DBKCPA respectively. Six replicated determinations of each solution were carried out. Results are shown in Table-1. The cumulative stability constant (K) of

TABLE-1
THE DETERMINATION OF STEPWISE STABILITY CONSTANT AND STEPWISE REAL ABSORPTIVITY (L mol^{-1} cm^{-1}) OF COMPLEX Al-$(DBKCPA)_2$ AT 630 nm AND IN IONIC STRENGTH 0.025 AT 15°C)

nth	Al-$(DBKCPA)_2$	
	K_n	ε_r at 630 nm
1st	5.33×10^6	7.62×10^3
2nd	1.00×10^6	1.40×10^4

Cumulative $K = 5.33 \times 10^{12}$.

Al-(DBKCPA)$_2$ was equal to 5.33×10^{12} at ionic strength 0.025 and temperature 15°C. The stepwise real molar absorptivity, $\varepsilon^{\lambda 2}_{ML_n}$ of Al-(DBKCPA)$_2$, was calculated as shown in Table 1, too. The final real values (not apparent) were obtained as follow: $\varepsilon_{Al(DBKCPA)_2} = 1.40 \times 10^4$ L mol^{-1}cm^{-1} at 630 nm.

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(*Received*: 19 November 1999; *Accepted:* 14 December 1999) AJC-1945