Determination of Characteristic Constant of Strontium Complexes with Dibromo-*o*-Carboxy-Chlorophosphonazo and Dibromo-*p*-Methyl-Methlsulfonazo

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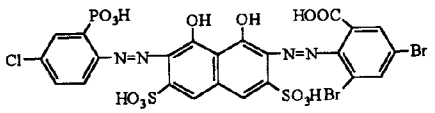
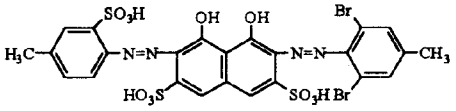
Summary: The two reactions were both sensitive between strontium(II) and dibromo-*o*-carboxy-chlorophosphonazo (DBKCPA) at pH 10.5 as well as between strontium and dibromo-*p*-methyl-methlsulfonazo (DBMMSA) at pH 8.5. The β-correction dual-wavelength spectrophotometric method was applied to the determination of properties of Sr 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 Sr(II) to DBKCPA and to DBMMSA were equal to 1:7 and 1:2 respectively. In addition, this investigation still brought out the easy determination of the stepwise real molar absorptivity (ε) and stepwise or cumulative stability constant (K) of Sr-DBKCPA and Sr-DBMMSA complexes.

Introduction

The synthesis of the ligands, DBKCPA and DBMMSA were reported in 1996 [1, 2]. Their structures were followed:



(1) dibromo-o-carboxy-chlorophosphonazo



(2) dibromo-p-methyl-methlsulfonazo

It was found that the two ligands both are diazo compounds with the similar structure. They were applied to the determination of trace amounts of metals [3, 4] by the ordinary spectrophotometry for example water hardness, etc. Because of the serious effect of excess ligand on the complex absorption the beta-correction spectrophotometry was studied to eliminate the effect of excess ligand. This new method has been applied to the determination of many metal complex solutions [5-7]. The composition ratio, stepwise real molar absorptivity and stepwise stability constant of strontium complex with DBKCPA was determined in detail in this report. The beta-correction method was more acceptable in principle and simpler in operation than the conventional method such as molar ratio [8], continuous variation [9], equilibrium movement [10], *etc.* The updated investigation showed that the complex between Sr(II) and DBKCPA was Sr:DBKCPA = 1:2 at pH 10.5 and the complex between Sr and DBMMSA was Sr:DBMMSA=1:3 at pH 8.5.

Principle

From 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 ΔA′ 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 then computed as follows.

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$$\alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda 1}}{\varepsilon_{ML_\gamma}^{\lambda 2}}$$

and

$$\beta = \frac{\varepsilon_L^{\lambda 2}}{\varepsilon_L^{\lambda 1}}$$

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 molar ratio (γ') of the effective L to M may be expressed as follows.

$$\gamma' = \eta \times \frac{C_L}{C_M}$$

where

$$\eta = \frac{A_C - \Delta A}{A_O}$$

Here, the symbol η indicates the reacted percentage of L and both C_M and C_L are the concentrations (mol/l) of M and L in the beginning. A_o 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 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: $ML_{n-1} + L \equiv\equiv ML_n$. 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.

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

From each K_n the cumulative constant (K) of complex ML_γ is able to 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 a M-L reaction the stepwise absorptivity (real $\varepsilon_{ML_n}^{\lambda 2}$ not apparent $\varepsilon_n^{\lambda 2}$, n=1, 2, γ) of complex ML_γ may be expressed as follows:

$$\varepsilon_{ML_n}^{\lambda 2} = \frac{A_C}{\delta C_M (\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n} \varepsilon_{ML_{n-1}}^{\lambda 2} \quad \text{In}$$

this equation, the symbol δ is cell thickness (cm) used and the others have the same meanings as the above.

Results and Discussion

Absorption Spectra

Figure 1 showed the absorption spectra of ligands and their strontium complex solutions. From curves 3 and 3', two wavelengths of each should be selected at their valley and peak absorption so as to obtain the maximal analytical sensitivity: 520, 600 nm for Sr-DBKCPA reaction and 555, 630 nm for Sr-DBMMSA reaction. From curves 1, 1', 2 and 2', β and α were equal to 0.439, 0.209, 0.82 and 0.785, respectively. The following expressions were established: Ac=1.56(ΔA-0.439ΔA') for Sr-DBKCPA reaction at 600 nm and Ac=1.20(ΔA-0.209ΔA) for Sr-DBMMSA reaction at 630 nm.

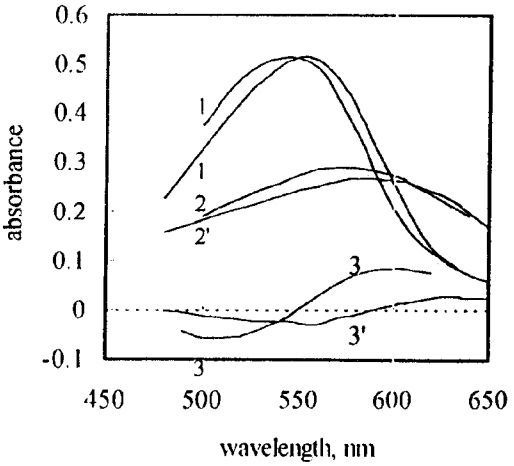

Fig. 1 Absorption spectra of DBKCPA, DBMMSA and their strontium complex solutions: 1- DBKCPA and 1'- DBMMSA; 2- Sr-DBKCPA complex and 2'- Sr-DBMMSA complex; 3- Sr-DBKCPA and 3' - Sr-DBMMSA against reagent blank.

Effect of Ligand Concentration

By varying the addition of 1.00 mmol/l ligands the absorbances of strontium complex solutions were measured. The effective percentage (η%) of ligands and the complexation ratio (γ') to Sr(II) were worked out. All ηs and γ's were shown in Figure 3 and 4, respectively. From curves in Figure 4,

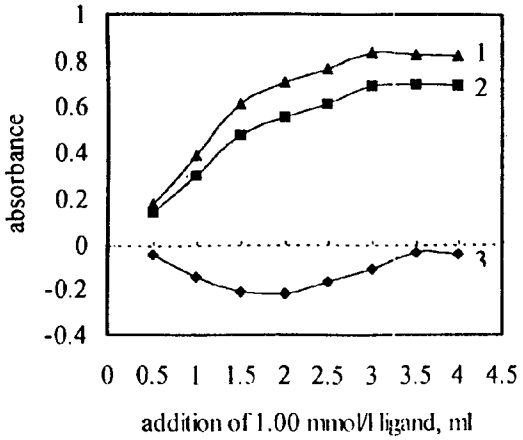

Fig. 2 Effect of the addition of 1.00 mmol/l ligand: 1-ΔA of Sr-DBKCPA complex at 600 nm; 2- A_c of Sr-DBKCPA solution at 600 nm; 3- ΔA′ of Sr-DBKCPA solution at 520 nm

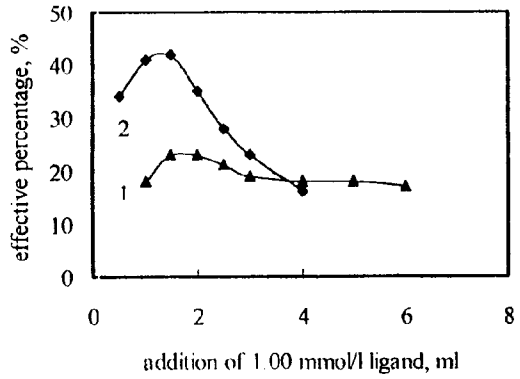

Fig. 3 Effect of the addition of 1.00 mmol/l ligands on the effective percentage (η%) of ligands: 1-Sr-DBKCPA reaction and 2- Sr-DBMMSA reaction

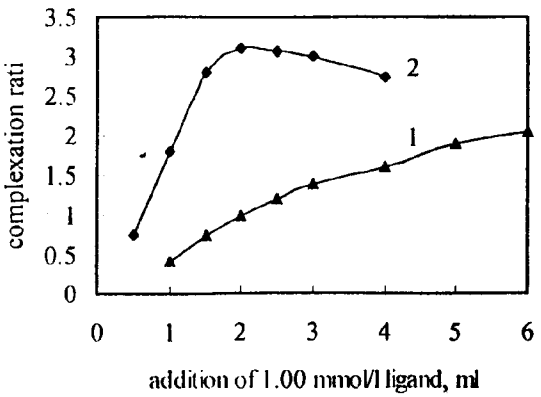

Fig. 4 Effect of the addition of 1.00 mmol/l ligands on composition ratio (γ′) of strontium complexes: 1-Sr-DBKCPA reaction and 2- Sr-DBMMSA reaction

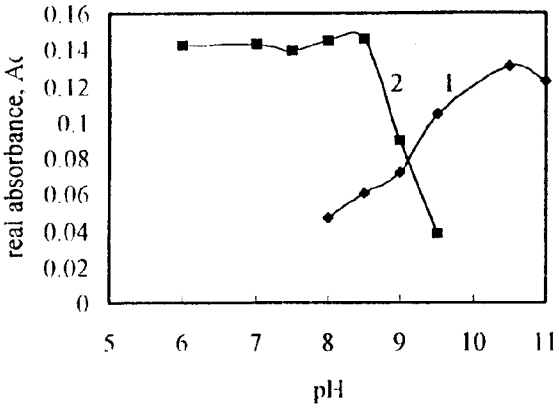

Fig. 5 Effect of pH on absorbance of strontium complex solutions: 1- A_c of Sr-DBKCPA solution at 600 nm and 2- that of Sr-DBMMSA solution at 630 nm

the complex ratio of Sr to DBKCPA reached maximum 2 when the addition of 1.00 mmol/l DBKCPA was more than 5.0 ml and the complex ratio of Sr to DBMMSA approached to maximum 3 when the addition of 1.00 mmol/l DBMMSA was more than 1.50 ml. From curves Figure 3 the excess DBKCPA took up about 82% in the minimum addition (γ′ approached to 2) 5.00 ml of 1.00 mmol/l DBKCPA and the excess DBMMSA about 58% in the minimum addition (γ′ approached to 3) 1.50 ml of 1.00 mmol/l DBMMSA. It was indubitable that so much excess, over half of ligand certainly affected the measurement of the complex absorption.

Effect of pH and Reaction Time

From curves in Figure 5, it was found that the sensitivity of Sr-DBKCPA reaction came to maximum at pH between 10 and 11 and that of Sr-DBMMSA reaction to maximum at pH between 6 and 8.5. The effect of the reaction time was shown in Figure 6. The reactions between Sr(II) and DBKCPA

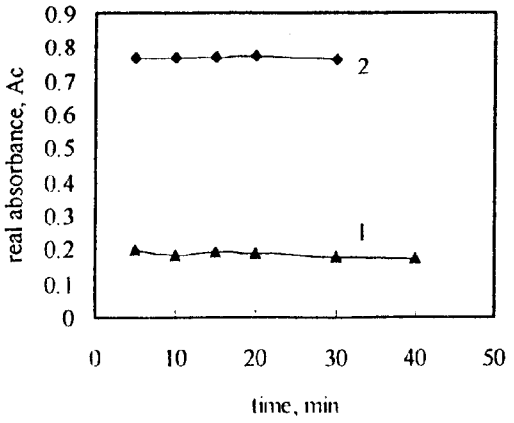

Fig. 6 Effect of time on absorbance of strontium complex solutions: 1- A_c of Sr-DBKCPA solution at 600 nm and 2- that of Sr-DBMMSA solution at 630 nm

and between Sr(II) and DBMMSA were both complete in 10 min because the real absorbances remained maximum.

Determination of Stability Constant and Real Molar Absorptivity

The following solutions were prepared for the determination of stepwise stability constant and stepwise real molar absorptivity of complexes: 40.0 μg/25ml Sr(II) with 1.00 and 2.50 μmol/25ml DBKCPA and 20.0 μg/25ml Sr(II) with 0.40, 0.80 and 1.40 μmol/25ml DBMMSA. Six replicated determinations of each solution were carried out. Results were shown in Table 1. The cumulative stability constant (K) of $Sr((DBKCPA)_2$ was equal to 2.32×10^8 and that of $Sr(DBMMSA)_3$ equal to 1.13×10^{14} both in 0.025 mol/l ionic strength solution and temperature 15 °C. The stepwise real molar absorptivity, all $\varepsilon_{MLn}^{\lambda 2}$ of $Sr((DBKCPA)_2$ and $Sr(DBMMSA)_3$ were calculated as shown in Table 1, too. The final real values (not apparent) were followed: $\varepsilon_{Sr(DBKCPA)2}^{600nm}=1.55\times10^4$ and $\varepsilon_{Sr(DBMMSA)3}^{630nm}=7.92\times10^4\,l\cdot mol^{-1}cm^{-1}$.

Experimental

Apparatus and Reagents

Absorption spectra were recorded with a UV-VIS 265 spectrophotometer (Shimadzu, Japan) in 10 mm glass cells.

Table-1: The determination of stepwise stability constant and stepwise real absorptivity ($l.mol^{-1}.cm^{-1}$) of complex $Sr(DBKCPA)_2$ at 600 nm and $Sr(DBMMSA)_3$ at 630 nm in 0.025 mol/l ionic strength solution (room temperature 15 °C)

n-th	$Sr(DBKCPA)_2$		$Sr(DBMMSA)_3$	
	K_n	ε_r at 600 nm	K_n	ε_r at 630 nm
1st	3.10×10^4	1.14×10^4	9.49×10^4	2.03×10^4
2nd	7.49×10^3	1.55×10^4	7.17×10^4	4.88×10^4
3rd			1.66×10^4	7.92×10^4
Cumulative	$K=2.32\times10^8$		Cumulative	$K=1.13\times10^{14}$

Standard Sr(II) solution, 1000 mg/1: Prepared from 1.000 g high-purity strontium. Standard Sr(II) working standard, 10.00 mg/l; ligand solutions, 1.00 mmol/l DBKCPA dissolved in water and 1.00 mmol/l DBMMSA in water. They should be stored in dark bottles. Buffer solutions of pH 10.5 and 8.5.

Recommended Procedure

Standard solution containing twenty micrograms of Sr(II) was taken into a 25-ml volumetric flask. Added distilled water to about 10 ml. Added 2.5 ml of buffer solution and 2 ml of 1.00 mmol/l ligand. Diluted to volume and mixed well. After 10 min, measured the absorbances against reagent blank at wavelengths 520, 600 nm for Sr-DBKCPA reaction and at wavelengths 555, 630 nm for Sr-DBMMSA reaction, respectively.

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