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Determination of Property Constants of Lead Complexes with Dibromo-*o*-carboxy-chlorophosphonazo and Dibromo-*p*-*p*′-dimethylsulfonazo

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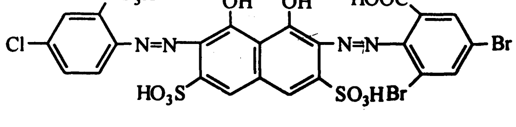
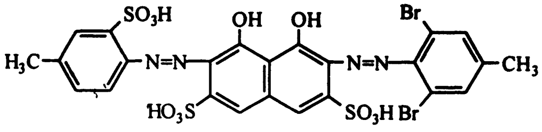
Two sensitive reactions between lead(II) and dibromo-*o*-carboxy-chlorophosphonazo (DBKCPA) at pH 8.5 between lead(II) and dibromo-*p*-*p*′-dimethylsulfonazo (DBMSA) at pH 9 were investigated. The β-correction spectrophotometry was applied to the determination of properties of Pb complex solutions instead of the ordinary method. The multi-coordination reaction was observed in Pb-DBKCPA reaction system. Results showed that the complex ratio of Pb(II) to DBKCPA and to DBMSA were equal to 1 : 7 and 1 : 2 respectively. Also, the cumulative stability constant (K) of $Pb((DBKCPA)_7$ was equal to 3.04×10^{34} and that of $Pb(DBMSA)_2$ 1.74×10^{10} and their end-step real absorptivities were as follows: $\varepsilon^{630}_{Pb(DBKCPA)_7} = 1.10 \times 10^4$ L mol^{-1} cm^{-1} and $\varepsilon^{650}_{Pb(DBMSA)_3}$ $= 3.37 \times 10^4$ L mol^{-1} cm^{-1} respectively.

INTRODUCTION

The synthesis of the two ligands, dibromo-*o*-carboxychlorophosphonazo (DBKCPA) and dibromo-*p*-*p*′-dimethylsulfonazo (DBMSA) were earlier reported[1, 2] and their structures are given below:



(1) dibromo-*o*-carboxychlorophosphonazo



(2) dibromo-*p*-*p*′-dimethylsulfonazo

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Both of these ligands are both azo dyes with the similar structure and were earlier applied in the determination of trace amounts of metals[3, 4] by the ordinary spectrophotometry, for example water hardness, etc. Because of the serious influence of excess of ligand on complex absorption, the spectral correction technique was used instead of the ordinary method because it may eliminate the above effect of excess ligand and work out the real absorption of the complex. It has been widely applied in the determination of properties of many complexes[5–7]. In the present report, the composition ratio, real absorptivity and stepwise stability constant of lead complexes with DBKCPA and DBMSA were determined easily and acceptably. It has notable advantages in operation and principle by comparing with the classical methods such as molar ratio[8], continuous variation[9], equilibrium movement[10], etc. The present investigation shows that the composition ratios of complexes were Pb : DBKCPA 1 : 7 and Pb : DBMSA 1 : 2. In addition, the cumulative stability constant (K) of $Pb((DBKCPA)_7$ was equal to 3.04×10^{34} and that of $Pb(DBMSA)_2$ 1.74×10^{10} and their end-step real absorptivities were as follows: $\varepsilon^{630}_{Pb(DBKCPA)_7} = 1.10 \times 10^4$ L mol^{-1} cm^{-1} and $\varepsilon^{650}_{Pb(DBMSA)_3} = 3.37 \times 10^4$ L mol^{-1} cm^{-1} respectively.

Principle

The following expression is developed for the determination of the real absorbances (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, then computed as follows:

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

The symbols $\varepsilon^{\lambda_1}_{ML_\gamma}$, $\varepsilon^{\lambda_2}_{ML_\gamma}$, $\varepsilon^{\lambda_1}_{L}$ and $\varepsilon^{\lambda_2}_{L}$ 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:

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

where

$$\eta = \frac{A_c - \Delta A}{A_0}$$

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 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.

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

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 $\varepsilon^{\lambda_2}_{ML_n}$ not apparent $\varepsilon^{\lambda_2}_{a}$, $n = 1, 2, \ldots, \gamma$) of complex ML_γ may be expressed as follows:

$$\varepsilon^{\lambda_2}_{ML_n} = \frac{A_c}{\delta C_M(\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n}\,\varepsilon^{\lambda_2}_{ML_{n-1}}$$

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

EXPERIMENTAL

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

Standard Pd(II) stock solution, 1000 mg/L, was prepared by dissolving 1 g high-purity lead (99.9%, Shanghai Reagents, China) in nitric acid (A.R. Shanghai Reagents). Standard Pd(II) use solution was prepared by diluting the 10 mg/L of Pd(II) solution. The ligand solution, 1 mmol/L DBKCPA, was prepared by dissolving DBKCPA (purified and provided by Changke Reagent Institute, Shanghai) in ethanol (A.R., Shanghai Reagents) and 1 mmol/L DBMSA (purified and provided by Changke Reagent Institute, Shanghai) was prepared with the same method as above. They must be stored in a dark bottle. The buffer solutions, pH 9 and 8.5, were prepared with ammonia water and ammonium chloride (both reagents are in analytical reagent grade and made in Beijing Chemical Factory).

Recommended Procedures: Forty micrograms of Pb(II) were taken in a 25 mL volumetric flask and add distilled water to about 10 mL. 2.5 mL of buffer solution and 2 mL of 1.00 mmol/L ligand solution were also added in volumetric flask. Diluted to desired volume and mixed well. After 20 min, measured the absorbances against reagent blank at wavelengths 560, 630 nm for Pb-DBKCPA reaction and at wavelengths 555, 650 nm for Pb-DBMSA reaction, respectively.

RESULTS AND DISCUSSIONA

Absorption Spectra: Fig. 1 shows the absorption spectra of ligands and their lead complex solutions. From curves 3 and 3′, two wavelengths of each system should be selected such that the difference in absorbances reaches maximum: 560 (valley absorption), 630 nm (peak absorption) for Pb-DBKCPA reaction and 555 (valley), 650 nm (peak) for Pb-DBMSA reaction. From curves 1, 1′, 2 and 2′, β and α were calculated to be 0.180, 0.209, 1.13 and 0.785, respectively. Both A_c expressions were as follows: $A_c = 1.26\ (\Delta A - 0.180\ \Delta A')$ for Pb-DBKCPA raction at 630 nm and $A_c = 1.20\ (\Delta A - 0.209\ \Delta A')$ for Pb-DBMSA reaction at 650 nm.

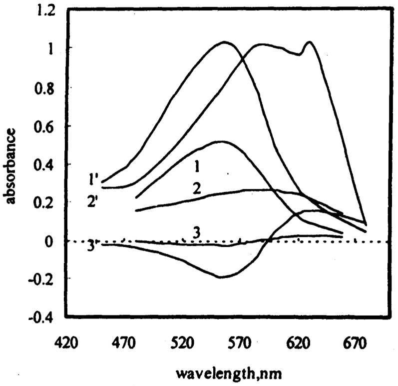

Fig. 1. Absorption spectra of DBKCPA, DBMSA and their lead complex solutions: 1-DBKCPA and 1′-DBMSA; 2. Pd-DBKCPA complex and 2′. Pb-DBMSA complex solution; 3. Pb-DBKCPA solution and 3′. Pb-DBMSA solution against reagent blank.

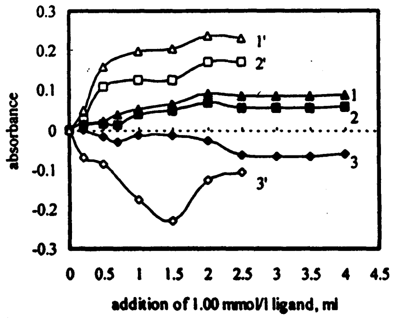

Fig. 2. Effect of the addition of 1 mmol/L ligands: 1. A_c of Pb-DBKCPA complex at 630 nm and 1′. that of DBMSA complex at 650 nm; 2. ΔA of Pb-DBKCPA solution at 630 nm and 2′. that of DBMSA solution at 650 nm; 3. $\Delta A'$ of Pb-DBKPCA solution at 560 nm and 3′. that of DBMSA solution at 555 nm.

Effect of Addition of Ligand Solution: By varying the addition of 1 mmol/L of ligands the absorbances of lead complex solutions were measured. The effective percentage (η%) of ligand and the complexation ratio (γ') were calculated according to the above equations. The values of η and γ' are shown in Fig. 3 and 4, respectively. It was found that from curves (in Fig. 3) the excess DBKCPA took up about 33% in the addition of 1 mmol/L DBKCPA 2 mL and the excess L DBMSA about 87% in the addition of 1 mmol/DBMSA 2 mL. It was indubitable that the excess ligand must affect the measurement of the complex absorption. From curves in Fig. 4, the complex ratio of Pb to DBKCPA remained the maximal value 7 when the addition of 1 mmol/L DBKCPA was more than 2 mL and the complex ratio of Pb to DBMSA approached maximum 2 when the addition of 1 mmol/L DBMSA was more than 1.50 mL. Therefore, the formed complex was expressed as $Pb(DBMSA)_2$.

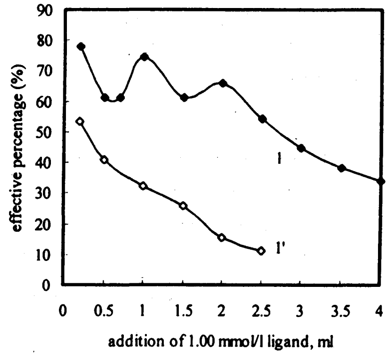

Fig. 3. Effect of the addition of 1 mmol/L ligands on the effective percentage (η%) of ligands: 1. Pb-DBKCPA reaction and 1'. Pb-DBMSA reaction.

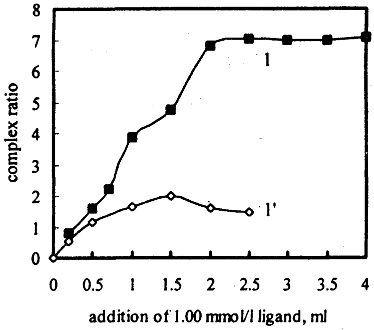

Fig. 4. Effect of the addition of 1 mmol/L ligands on composition ratio (γ') of lead complexes: 1. Pb-DBKCPA reaction and 1'. Pb-DBMSA reaction.

Effect of pH and Reaction Time: From curves in Fig. 5, it was found that the sensitivity of Pb-DBKCPA reaction came to maximum at pH 9 and that of pB-DBMSA reaction to maximum at pH 8.5. The effect of the reaction time is shown in Fig. 6. It indicates that the reactions between Pb(II) and DBKCPA and between Pb(II) and DBMSA were complete in 10 min.

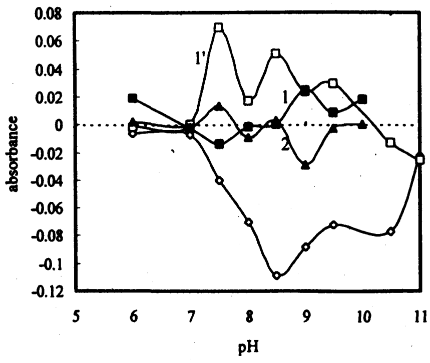

Fig. 5. Effect of pH on absorbance of lead complex solutions: 1. ΔA of Pb-DBKCPA solution at 630 nm and 1′. that of Pb-DBMSA solution at 650 nm; 2. ΔA′ of Pb-DBKCPA solution at 560 nm and 2′. that of Pb-DBMSA solution at 555 nm.

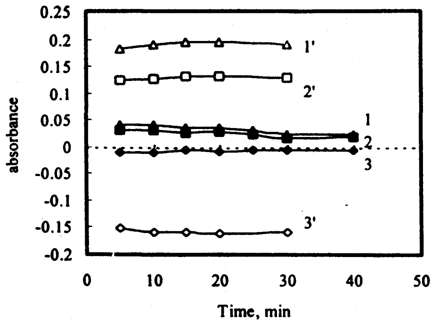

Fig. 6. Effect of time on absorbance of lead complex solutions: 1. ΔA of Pb-DBKCPA solution at 630 nm and 1′. that of Pb-DBMSA solution at 650 nm; 2. ΔA′ of Pb-DBKCPA solution at 560 nm and 2′. that of Pb-DBMSA solution at 555 nm. All are against reagent blank.

Determination of Stability Constant and Real Molar Absorptivity: The following solutions were prepared for the determination of stepwise stability constnat and stepwise real molar absorptivity of complexes: 40 μg/25 mL Pb(II) with 0.15, 0.50, 0.85, 0.90, 1.30, 1.70 and 1.80 μmol/25 mL DBKCPA and 40 μg/25 mL Pb(II) with 0.20, 0.80 μmol/25 mL DBMSA. Three replicated determinations of each solution were carried out. The results are shown in Table-1. The cumulative stability constant (K) of Pb(($DBKCPA)_7$ was equal to 3.04×10^{34} and that of $Pb(DBMSA)_2$ equal to 1.74×10^{10} both in ionic strength 0.025 at temperature 15°C. The stepwise real molar absorptivity, all $\varepsilon^{\lambda_2}_{ML_n}$ of Pb(($DBKCPA)_7$ and $Pb(DBMSA)_2$ were calculated according to the above equation and their values are listed in Table-1. The final values (not apparent) were as follow: $\varepsilon^{630}_{Pb(DBKCPA)_7} = 1.10 \times 10^4$ L mol^{-1} cm^{-1} and $\varepsilon^{650}_{Pb(DBMSA)_2} = 3.37 \times 10^4$ L mol^{-1} cm^{-1}.

TABLE-1

THE DETERMINATION OF STEPWISE STABILITY CONSTANT AND STEPWISE REAL ABSORPTIVITY (L mol^{-1} cm^{-1}) OF COMPLEX $Pb(DBKCPA)_7$ AT 630 nm AND $Pb(DBMSA)_2$ AT 650 nm IN IONIC STRENGTH 0.1 (ROOM TEMPERATURE 15°C)

n-th	$Pb(DBKCPA)_7$		$Pb(DBMSA)_2$	
	K_n	ε_r at 630 nm	K_n	ε_r at 650 nm
1st	2.55×10^5	0.15×10^4	3.88×10^5	1.59×10^4
2nd	1.88×10^5	0.39×10^4	4.49×10^4	3.37×10^4
3rd	1.38×10^5	0.39×10^4		
4th	2.94×10^4	0.50×10^4		
5th	1.19×10^5	0.77×10^4		
6th	2.94×10^4	0.77×10^4		
7th	4.47×10^4	1.10×10^4		
	Cumulative K = 3.04×10^{34}		Cumulative K = 1.74×10^{10}	

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