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Dual-wavelength Spectrophotometric Determination of Properties of Titanium Complex Solution with *o*-Chlorophenylfluorone

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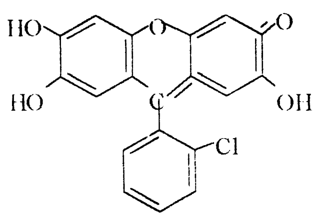
The ligand, *o*-chlorophenylfluorone (*o*-CPF) was sensitive to complex titanium (Ti) at pH 6.0 and in the presence of triton x-100. The spectral correction principle was applied to the determination of the characteristic factors of the complex instead of ordinary spectrophotometry because of the interference of excess of *o*-CPF. Results showed that the formed complex was expressed as $Ti(o\text{-}CPF)_3$ and its cumulative stability constant was equal to 8.50×10^{16}.

INTRODUCTION

Titanium (Ti) exists in nature. The ligands such as pyrocatechol violet[1] and TMPF[2] are often used to complex trace amounts of titanium. The synthesis of a phenylfluorone derivant, *o*-chlorophenylfluorone (*o*-CPF) was reported[3] with the following structure.



It was ever applied to the determination of trace amounts of vanadium[4]. The reaction between Ti(IV) and *o*-CPF was sensitive at pH 6.0 and in the presence of non-ionic surfactant, triton x-100. The colour of the reaction solution changed into blue from orange because of the maximal absorption of the complex product being at 575 nm and that of *o*-CPF at 475 nm. The ordinary spectrophotometry was not suitable for the investigation of Ti-*o*-CPF complex because the excess of *o*-CPF interfere the direct measurement of the real absorption of the complex. The method, β-correction spectrophotometry[5], has been applied[6–8] for the investigation of many complexes and the determination of trace amounts of metals

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because it may eliminate the effect of excess of *o*-CPF to give out the real absorption of complex. It was different from other dual-wavelength analyses[9, 10]. By means of this principle some property factors of Ti-*o*-CPF complex were worked out easily, *e.g.*, the complex ratio, real (not apparent) absorptivity and stepwise stability constant. The recommended method was different from the following classical methods: the molar ratio[11], continuous variation[12] and equilibrium movement[13], etc.

EXPERIMENTAL

Absorption spectra were recorded with a UV/VIS 265 spectrophotometer (Shimadzu, Japan) with 1.0 cm cells and pH was measured with a Model PHS-2C acidimeter (Xiaoshan, China).

Standard Ti(IV) solution, 100.0 mg/L was prepared according to the following method. The liquid form (0.1688 g) of titanium dioxide (Shanghai Reagents) together with 3 g of potassium disulfate (Shanghai Reagents) at 700°C in a muffle roaster. After cooling, the melt was dissolved with 5% sulfuric acid and the solution was diluted to 1000 mL with deionized water.

Standard Ti(IV) use solution, 10.0 mg/L, was prepared daily with the above standard Ti solution.

The ligand solution, 10.0 mmol/L *o*-CPF was prepared by dissolving 0.3190 g of *o*-chlorophenylfluorone (*o*-CPF, Changke Reagents) in 1000 mL of absolute alcohol (AR, Shanghai Reagent). It should be stored in a dark bottle at 5°C.

The buffer, pH 6.0 solution, was prepared with acetate and acetic acid so as to adjust the acidity of the complex solution.

The non-ionic surfactant solution, 1% triton x-100, was used to increase both the solubility of the complex and the sensitivity of the reaction.

Recommended Procedures

10 μg of Ti was taken in a 25 mL volumetric flask. Added deionized water to about 10 mL. Added 1 mL of triton x-100 solution and a known volume of *o*-CPF solution. Diluted to required volume and mixed well. After 5 min, measured absorbances at 575 and 475 nm against a reagent blank, respectively and calculate the real absorbance (Ac) of the complex according to the following expression:

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta} \quad \text{where} \quad \alpha = \frac{\varepsilon_{ML_\gamma}^{\lambda_1}}{\varepsilon_{ML_\gamma}^{\lambda_2}} \quad \text{and} \quad \beta = \frac{\varepsilon_L^{\lambda_2}}{\varepsilon_L^{\lambda_1}}$$

The terms ΔA and $\Delta A'$ were the absorbances of the reaction solution at 575 and 475 nm against the reagent blank, respectively. The coefficients α and β were named correction factors. The terms $\varepsilon_{ML_\gamma}^{\lambda_1}$, $\varepsilon_{ML_\gamma}^{\lambda_2}$, $\varepsilon_L^{\lambda_1}$ and $\varepsilon_L^{\lambda_2}$ were the molar absorptivities of complex and ligand at 475 and 575 nm, respectively.

RESULTS AND DISCUSSION

Absorption Spectra: Figure 1 shows the absorption spectra of *o*-CPF and Ti complex solution at pH 6.0; two wavelengths should be selected such that the difference in absorbance was a maximum: 475 (valley absorption) and 575 nm (peak absorption) from curve 3. The term β of *o*-CPF solution was equal to 0.069 from curve 1. By the same method, α of Ti-*o*-CPF complex was equal to 0.328 from curve 2.

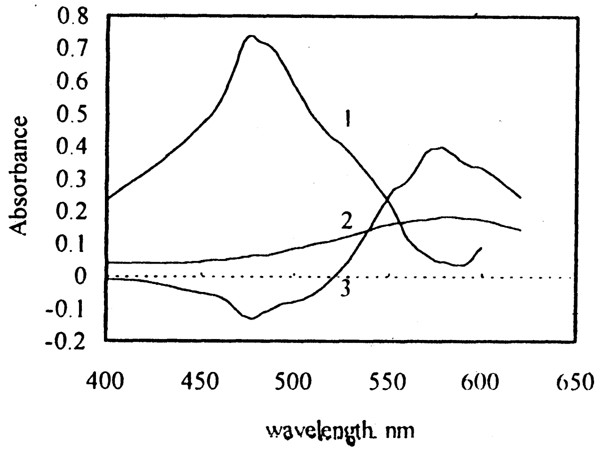

Fig. 1 Absorption spectra of *o*-CPF and Ti-*o*-CPF complex solutions at pH 6.0: (1) 1.50 μmol *o*-CPF against water; (2) Ti (0.10 mg)-*o*-CPF (0.10 μmol) complex solution against water; (3) Ti (10 μg)-*o*-CPF (1.50 μmol) reacted solution against a reagent blank.

Effect of *o*-CPF Concentration: Figure 2 shows the effect of the addition of *o*-CPF solution. From curve 1, it is difficult for the complex ratio of Ti to *o*-CPF to be calculated accurately with the molar ratio method because of the

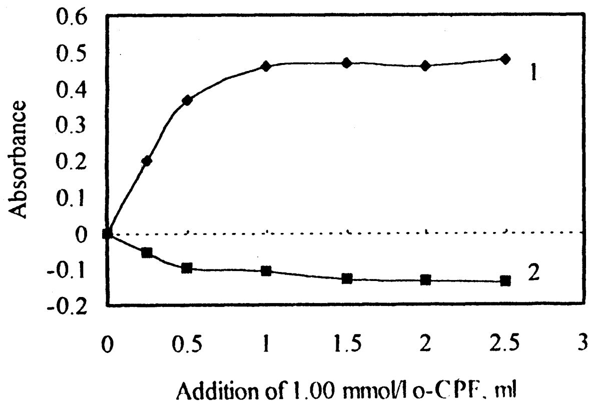

Fig. 2 Effect of *o*-CPF concentration on absorbance of Ti (10 μg) complex solution: (1) 575 nm, and (2) 475 nm, both against reagent blank

unclearness of the inflexion point. The absorbance (A_c), effective percentage (η) of the complex and the complex ratio (γ') of each solution were calculated according to the following expressions:

$$\gamma' = \eta \times \frac{C_L}{C_M} \quad \text{where} \quad \eta = \frac{\alpha\Delta A - \Delta A'}{(1-\alpha\beta)A_0'}$$

The terms C_M and C_L indicate the concentrations (mol/L) of Ti and *o*-CPF in the beginning, respectively. A_0' Was the absorbance of the blank reagent at 475 nm against water. Their curves are shown in Figure 3. From curve 3, γ' approachs to 3 when the addition of *o*-CPF solution is only about 40% at the addition of 1.5 mL. The excess of *o*-CPF reached 60% and it was inevitable for the free *o*-CPF to affect the accurate measurement of the complex absorption.

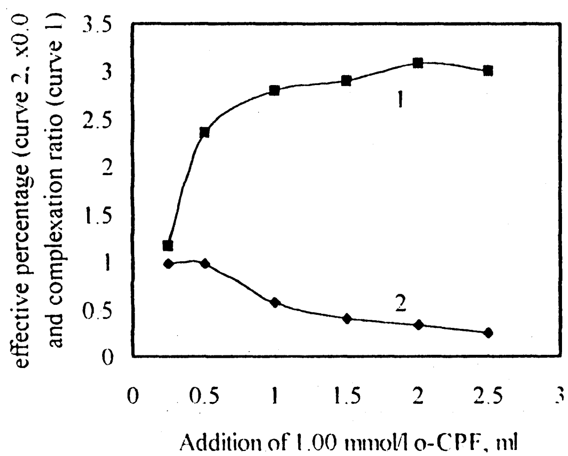

Fig. 3 Effect of *o*-CPF concentration on η and γ' of Ti (10 μg) complex solution: (1) η, and (2) γ'

Effect of pH and Time: By varying pH of solution, the effect curve is shown in Figure 4. The absorbance reached maximum and remained constant when pH was between 5 and 7. In this study, pH 6.0 buffer was used. The effect of the reaction time is shown in Figure 5. From curves the reaction was complete in 5 min. The solution's absorption was found to remain almost constant for at least 2 h.

Determination of Stability Constant and Stepwise Absorption of Complex

The stepwise stability constant (K_n), cumulative stability constant (K) and stepwise absorptivity (ε) of the complex can be calculated from the following equations:

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

and the cumulative constant (K)

$$K = \prod_{n=1}^{\gamma} K_n$$

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

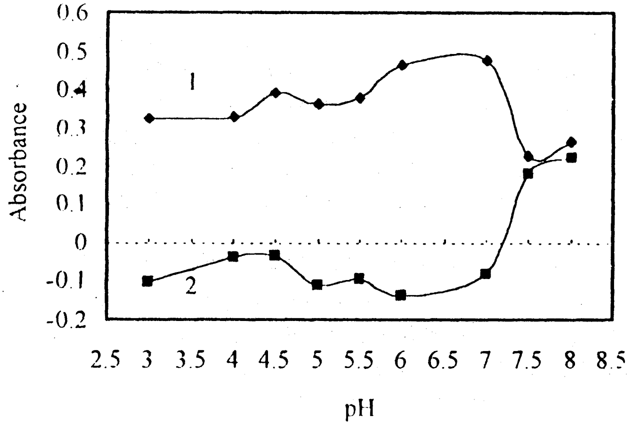

Fig. 4 Effect of pH on absorbance of Ti (10 μg)-*o*-CPF complex solution: (1) ΔA at 575 nm and (2) ΔA′ at 475 nm.

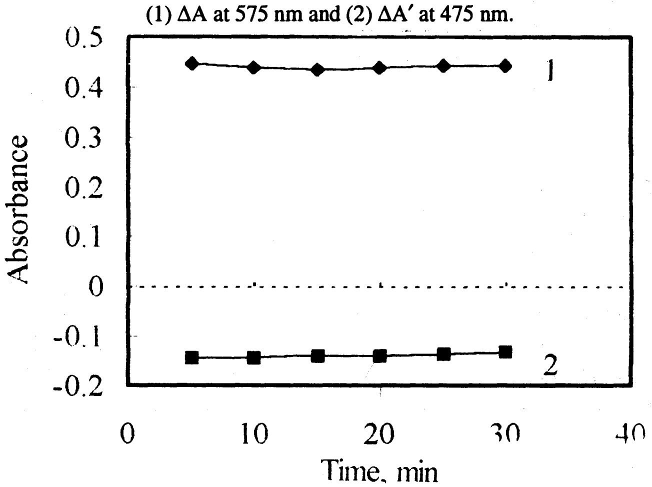

Fig. 5 Effect of the reaction time on absorbance of Ti (10 μg)-*o*-CPF complex solution: (1) ΔA at 575 nm, and (2) ΔA′ at 475 nm.

The term *n* indicates the *n*-th complex and δ the thickness of cell. The complex ratio γ′ must be between (n − 1) and n by preparing the mixed solution. The following solutions were prepared for the determination of the above stability constant and absorptivity of the complex: 5.00 μg Ti(IV) with 0.100 μmol *o*-CPF, 2.00 μg Ti(IV) with 0.100 μmol *o*-CPF and 10.0 μg Ti(IV) with 0.900 μmol *o*-CPF. All were at temperature 10°C and in ionic strength 0.025. Results were listed in Table-1. The cumulative stability constant of $Ti(o\text{-}CPF)_3$ was calculated to be 8.50×10^{16} and the real absorptivity of the end-step complex to be 6.44×10^{4} L mol^{-1} cm^{-1} at 575 nm.

TABLE-1
THE DETERMINATION OF STEPWISE STABILITY CONSTANT AND STEPWISE REAL ABSORPTIVITY OF TI-*o*-CPF COMPLEX AT pH 6.0 AND IN PRESENCE OF TRITON x-100

n-th	$Ti(o\text{-}CPF)_3$	
	K_n, ionic strength 0.025 at 10°C	ε_r, L mol^{-1} cm^{-1} at 575 nm
1st	7.82×10^{5}	2.18×10^{4}
2nd	6.97×10^{5}	4.42×10^{4}
3rd	1.56×10^{5}	6.44×10^{4}
	Cumulative $K = 8.50 \times 10^{16}$	

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REFERENCES

1. D.L. Zhang and X.L. Zeng, *Chin. J. Anal.Chem.*, **17**, 520 (1989).
2. W.M. Lin and M. Chen, *Henliang Fenxi*, **2**, 37 (1986).
3. Q.R. Luo, *Henliang Fenxi*, **2**, 1 (1986).
4. M. Hou and Q. Luo, *Lihua Jianyan, Huaxue Fence*, **35**, 508 (1999).
5. H.W. Gao, *Asian J. Chem.*, **11**, 319 (1999).
6. H.W. Gao and H.L. Shi, *Zhur. Anal. Khim.*, **52**, 1152 (1997).
7. H.W. Gao, *Chem Anal.*, **39**, 699 (1994).
8. ————, *Indian J. Chem.*, **37A**, 367 (1998).
9. H. Watanabe and H. Ohmori, *Talanta*, **26**, 959 (1979).
10. M.C. Valencia, S. Boudra and M. Bosque-Sendra, *Analyst*, **118**, 1333 (1993).
11. V.N. Tikhonov, *Zh. Anal. Khim.*, **30**, 1501 (1975).
12. W. Likussar, *Anal. Chem.*, **45**, 1926 (1973).
13. A.I. Laearev, *Zavod. Lab.*, **41**, 534 (1975).

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