Substitution Coordination Approach for Selective Determination of Complex: Pontachrome Violet SW/Fe(III)/Cu(II) System

Hong-Wen Gao[a,b]* (郜洪文) and Nai-Liang Hu[b] (胡乃梁)

[a]*College of Chemical Engineering, Zhejiang University of Technology, Hangzhou-310014, P. R. China*
[b]*Department of Chemistry, Anhui University, Hefei-230039, P. R. China*

The Substitution Coordination for Selective Determination (SCSD) was proposed by studying the complexations of pontachrome violet SW (PCV) with Fe(III) and Cu(II) at pH 5.5. The updated approach to the determination of binding constants of a complex was established by the spectral correction technique (SCT). The substitution complexation Cu(II) + Fe(PCV) → Cu(PCV) + Fe(III) has been applied to the direct selective determination of copper traces by the SCT with a high sensitivity.

INTRODUCTION

The spectral correction technique (SCT) has been applied extensively in study of analytical, complex, and supramolecular chemistry. [1-3] However, it can increase the accuracy and precision but not improve the selectivity in trace analysis. For this purpose, the substitute coordination approach was proposed, and it indicates a metal to substitute for another metal from its complex. The former metal ions must have a much stronger complexation with the selected ligand than most other metals. This method may give a high selectivity in trace analysis. Here, the reaction of copper(II) to substitute Fe(III) from its pontachrome violet SW (PCV) complex at pH 5.5 has been investigated in detail and used in the quantitative determination of Cu in samples with satisfactory results by the SCT. Additionally, an approach to the determination of binding constants of a complex was given, too.

PRINCIPLE AND CALCULATION

At the coordination equilibrium: N L (Ligand) + M (Metal) $\Leftrightarrow$ ML_N (complex), the molar ratio (γ) of the effective L to M, the molar concentration (C_L) of free L are calculated by relations (1) and (2). The complexation of L with M may be regarded as a particular Langmuir monolayer adsorption[4] of L on M but the binding force is chemical bond not electrostatic attraction. So the maximal formation ratio of L to M and the binding constant (K, different from equilibrium constant) of complex ML_N are obtained by regressing γ^{-1} vs. C_L^{-1} by relation (3):

$$\gamma = \frac{\alpha \Delta A - \Delta A'}{\delta \varepsilon_L (1 - \alpha \beta) C_M} \quad (1)$$

$$C_L = C_{L0} - \frac{\alpha \Delta A - \Delta A'}{\delta \varepsilon_L (1 - \alpha \beta)} \quad (2)$$

and

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L} \quad (3)$$

Here the symbols ΔA and $\Delta A'$ are the absorbances of the solution, respectively measured at peak and valley wavelengths λ_2 and λ_1. The correction constants α and β may be calculated.

EXPERIMENTAL SECTION

Apparatus and Reagents

Absorption spectra were recorded on a TU1901 Spectrophotometer (PGeneral, Beijing) and independent absorbance was measured on a Model 722 spectrophotometer. A DDS-11A conductivity meter, (Tianjin Second Analytical Instruments) was used to measure conductivity together with DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices) in product of deionized water of less than 0.5 μScm. The pH of the solution was measured with a Delta 320-S pH meter (Mettler Toledo).

Stock standard solutions of Cu (100.0 mg/L) and Fe (100.0 mg/L) were prepared by dissolving their high purity metals in concentrated nitric acid and diluting with deionized

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* Corresponding author. Fax: +86-551-5106110; e-mail: gaohongw@mail.hf.ah.cn

wa ter. The PCV so lu tion (0.700 mmol/L) was pre pared by dis solv ing 0.2478 g of pontachrome vi o let SW (PCV) in 50 mL of DMF and then di lut ing to 500 mL with deionized wa ter. Stan dard Cu(II) and Fe(III) so lu tions (10.00 μg/mL) were pre pared by di lut ing the above so lu tions. The ace tic buffer so lu tion (pH 5.5) was used to ad just the acid ity of the so lu tion. The Fe(PCV) so lu tion (0.200 mmol/L) by mix ing 14.3 mL of 0.700 mmol/L PCV, 28.6 mL of the stock stan dard Fe(III) so lu tion and 5 mL of pH 5.5 buffer so lu tion and di lut ing to 50.0 mL. In this solution, only Fe(PCV) but not $Fe(PCV)_2$ is formed be cause it con tains highly ex ces sive and free Fe(III).

General Procedures

De ter mi na tion of prop erty con stants of Fe and Cu with PCV: Into a 10 mL cal i brated flask were added 10.00 μg of Fe(III) or Cu(II), 1.0 mL of the buffer so lu tion and an ap pro pri ate vol ume of 0.700 mmol/L PCV. The mix ture was di luted with deionized wa ter to 10 mL and mixed thor oughly. Af ter 5 min, absorbances of the so lu tions were mea sured at 520 and 445 nm, re spec tively, against the re agent blank and treated in the same way with out Fe(III) or Cu(II), and then A_c of the com plex was cal cu lated.

Quantitative De ter mi na tion of Cu: A known vol ume of a sam ple so lu tion con tain ing less than 20μg of Cu was added into a 10-mL vol u met ric tube along with 1.0 mL of the pH buffer so lu tion and cer tain a vol ume of Fe(PCV) so lu tion. Af ter 10 min, mea sured absorbances at 520 and 445 nm with 2-cm cell, re spec tively against the re agent blank treated in the same way with out Cu and then A_c of the sub sti tu tion com plex was cal cu lated.

RE SULTS AND DIS CUS SION

Spectral analysis

The re ac tions be tween PCV and Fe(III) and Cu(II) at pH 5.5 were car ried out and the ab sorp tion spec tra are shown in Fig. 1. From curves 1, 2 and 3, the spec tral peak of PCV, Fe-PCV and Cu-PCV com plexes are lo cated at 490, 520 and 460 nm, re spec tively. From curves 4 and 5, the two wave-lengths: both 520 and 445 nm should be se lected in this work. From curves 1, 2 and 3, the cor rec tion con stants were cal cu lated to be $\beta_{PCV} = 0.521$ and $\alpha_{Fe(PCV)} = 0.471$, $\beta'_{PCV} = 1.94$ and $\alpha_{Cu(PCV)} = 0.254$. So the real absorbance (A_c) of com plex ML_N is cal cu lated[3] by $A_C = 1.33(\Delta A - 0.521\Delta A')$ in the Fe-PCV so lu tion and $A_C = 1.95(\Delta A - 1.94\Delta A')$ in the Cu-PCV so lu tion.

Determination of Fe-PCV and Cu-PCV Complexes

By vary ing the ad di tion of PCV in Fe (10.0 μg) and Cu (10.0 μg) so lu tions, γ vs. C_{L0} and γ^1 vs. C_L^{-1} are shown in Fig.
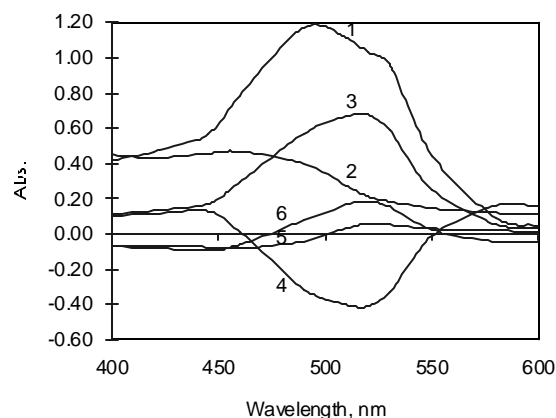

Fig. 1.   The ab sorp tion spec tra of PCV, PCV-Cu(II), PCV-Fe(III) and PCV-Fe-Cu so lu tions at pH 5.5: 1- PCV; 2- Fe-PCV and 3- Cu-PCV com plex; 4- Fe-PCV and 5- Cu-PCV solutions against the PCV so lu tion; 6- Fe(PCV)-Cu so lu tion against the Fe(PCV) so lu tion.
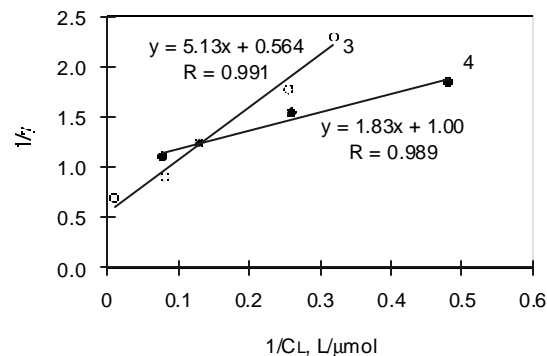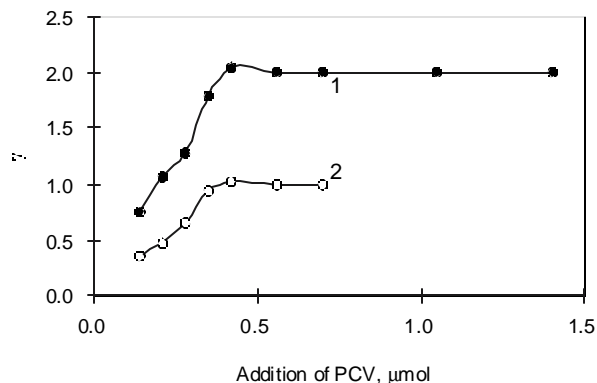

Fig. 2. γ vari a tion in Fe-PCV (1) and Cu-PCV (2) so lu tions and γ^{-1} vs. C_L^{-1} [3- $Fe(PCV)_2$ and 4- Cu(PCV)].

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2. From curves 1 and 2, we also observe that both γ approach the maximums at $N = 2$ and 1, respectively. So the final complexes: $Fe(PCV)_2$ and $Cu(PCV)$ are formed. From the slope rate of lines 3 and 4, the anastomotic results were observed. The binding constant of $Fe(PCV)_2$ was calculated to be $K = 1.95 \times 10^4$ and that of $Cu(PCV)$ is $K = 5.46 \times 10^5$. In addition, from the slope of lines 3 and 4, we confirm the same binding ratio of the complexes as those above. Therefore, we believe that the recommended calculation of the binding constants of a complex is simpler and more reliable than the conventional methods.[5-6]

Substitution of Fe by Cu

From the two K values above, Cu(II) may substitute Fe(III) from its PCV complex because K of the Cu-PCV complex is near to 30 times that of the Fe-PCV complex. This substitution phenomenon has been observed in the experiment. The substitution reaction is suggested as followed: $Cu(II) + Fe(PCV) \rightarrow Cu(PCV) + Fe(III)$. A large excess of Fe(III) was added into the PCV solution to make the coordination complete, forming Fe(PCV). Such a solution contains only both Fe(III) and Fe(PCV). The experimental result has indicated no free PCV in the solution containing Fe(III) more than 5 times molarity of PCV. In such a solution, the addition of other metals has been found not to alter its absorption spectrum except for Cu(II). Therefore, the substitution complexation may be used for the selective determination of Cu traces.

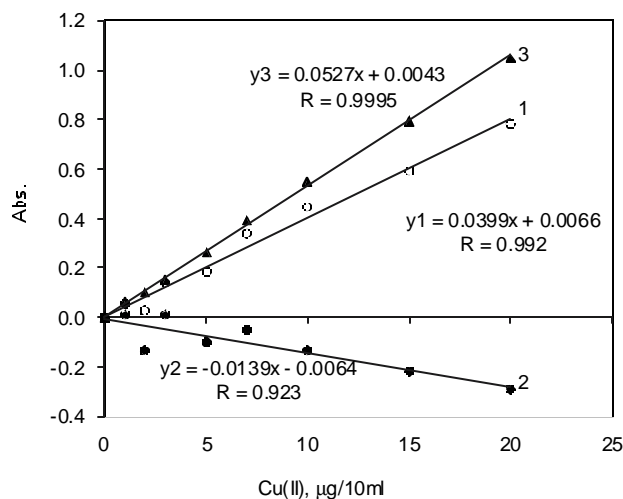

Fig. 3. Calibration graphs for the determination of Cu(II): 1-ΔA measured at 520 nm, 2-$\Delta A'$ measured at 445 nm and 3- A_c calculated.

QuantitativeDetermination of Cu

The solution mixed 1.00 mmol/L Fe(III) with 0.200 mmol/L PCV forms 0.200 mmol/Fe(PCV) complex at equilibrium. It was used as a new stain for the determination of Cu traces. Many metal ions, such as Pb(II), Zn(II), Ni(II), Cd(II), Al(III), Hg(II), rare earth, alkali earth metals and normal anions, have not been found to interfere with the direct determination of Cu. The calibration graphs are shown in Fig. 3. We observe that lines 1 and 2 have much poorer linearity and less slope rate than line 3. Therefore, the SCT is more suitable to a substitution complexation than ordinary spectrophotometry. The approach has been applied to analysis of wastewater samples and it gave identical results with the AAS.

TREND AND FOREGROUND

The SCT and SCSD provide a very helpful experimental strategy for the determination of binding constants of a metal complex and trace analysis even though the sensitivity is lower than the other methods *e.g.* RLS.[7] We believe that the cooperation of the SCT and other methods, *e.g.* flow injection analysis (FIA) and fluorimetry, will improve sensitivity and understanding that the classical spectrophotometry may still play an important role in study of the coordination of a ligand with metal or a probe with macromolecule.

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