ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ
V. 71, N 2 JOURNAL OF APPLIED SPECTROSCOPY March — April 2004

COMPLEXATION ON MICELLES AND ITS APPLICATION: PONTACHROME VIOLET SW/CETYLTRIMETHYLAMMONIUM BROMIDE/Cu(II) TERNARY COMPLEXATION

S.-Q. Xia [a], L.-Y. Jiang [b], and H.-W. Gao [a*]

[a] State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, Shanghai, 200092, P. R. China; e-mail: hwgao@mail.tongji.edu.cn
[b] Department of Textile Engineering, Nantong Institute of Technology, P. R. China

The ternary interaction of pontachrome violet SW (PCV) with cetyltrimethylammonium bromide (CTAB) and Cu(II) at pH 10.5 has been investigated by a microsurface adsorption—spectral correction (MSASC) technique. The aggregation of PCV on CTAB obeyed the Langmuir isothermal adsorption. Results showed that the binding constant of the CTAB-PCV aggregate was $K = 2.68 \cdot 10^5$ *liter·mol*$^{-1}$*. The ternary monomer complex* $Cu \cdot PCV \cdot CTAB_2$ *was formed. The complexation between Cu and PCV is sensitive in the presence of CTAB and selective in the presence of thioglycolic acid, trisodium citrate, and p-phenanthroline, and it was applied to the determination of Cu trace with satisfactory result.*

Keywords: *microsurface adsorption—spectral correction technique, cetyltrimethylammonium bromide, pontachrome violet SW, langmuir aggregation, determination of copper.*

КОМПЛЕКСООБРАЗОВАНИЕ НА МИЦЕЛЛЕ И ЕГО ПРИМЕНЕНИЕ: ОБРАЗОВАНИЕ ТРОЙНОГО КОМПЛЕКСА ПОНТАХРОМОВОГО ФИОЛЕТОВОГО SW С БРОМИДОМ ЦЕТИЛТРИМЕТИЛАММОНИЯ и Cu(II)

С.-К. Хиа [а], Л.-Я. Джианг [б], Х.-В. Гао [а*]

УДК 535.34

[а] Государственная главная лаборатория по контролю за загрязнением и повторного использования ресурсов, Школа по изучению окружающей среды, университет Тончжи, Китайская Народная Республика, 200092, Шанхай; e-mail: hwgao@mail.tongji.edu.cn
[б] Факультет текстильной техники, Наньтунский технологический институт, Китайская Народная Республика

(Поступила 30 июня 2003)

Методом микроповерхностной абсорбции—спектральной коррекции изучено тройное взаимодействие понтахромового фиолетового SW (ПХФ) с бромидом цетилтриметиламмония (ЦТАБ) и Cu(II) при pH 10.5. Агрегация ПХФ на ЦТАБ соответствует ленгмюровской изотермической адсорбции. Для образующегося агрегата ЦТАБ-ПХФ рассчитана постоянная связывания $K = 2.68 \cdot 10^5$ *л·моль*$^{-1}$*. Обнаружен тройной мономерный комплекс Cu—ПХФ—ЦТАБ*$_2$*. Образование комплекса Cu с ПХФ чувствительно к присутствию ЦТАБ и селективно в присутствии тиогликолевой кислоты, тринатрийцитрата и п-пенантролина, что можно использовать для определения малых количеств Cu с удовлетворительной точностью.*

Ключевые слова: *метод микроповерхностной адсорбции—спектральной коррекции, бромид цетилтриметиламмония, понтахромовый фиолетовый SW, ленгмюровская агрегация, определение меди.*

Introduction. A surfactant is often used in the detection of a trace component because of its sensitization effect [1, 2]. A number of synergism mechanisms were proposed as follows: synergism perturbation [3], hydrogen bond formation [4], micelle catalysis [5], and asymmetric microenvironment [6]. Study of the surfactant is in progress [7—10]. Understanding its interaction with other organic compounds or ions is significant to select a suitable synergism agent in trace analysis and to synthesize a new type of efficient detergents.

In a surfactant (S) solution, the aggregation of S molecules will form an electrostatic global micelle when S is present above the critical micellar concentration (CMC). So, an oppositely charged dye ligand (L) will bind on S by the electrostatic attraction and the other, by noncovalent action [11, 12]. In an S-L solution, the addition of a metal ion (M) will cause a sensitive complexation of M with L adsorbed on S because the concentration of L on S or its micelle is much higher than that in the aqueous phase. Therefore, the S micelle provides the M-L complexation with a catalytic field. Thus, S accelerates the M-L complexation. The aggregation of L on S occurs via Langmuir isothermal adsorption [13] only in a monolayer. Thus, it accords with

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_{\mathrm{L}}}, \tag{1}$$

where K is the equilibrium constant, C_{L} the concentration of the excess L, and γ the molar ratio of L adsorbed to S. Within increase in L concentration, γ will approach a maximum, called the binding ratio N. The plot of γ^{-1} vs. C_{L}^{-1} is linear and from this N and K are calculated. Both C_{L} and γ are calculated by means of [14]:

$$\gamma = \eta \frac{C_{\mathrm{L}_0}}{C_{\mathrm{S}}}, \tag{2}$$

$$C_{\mathrm{L}} = (1-\eta)C_{\mathrm{L}_0}, \tag{3}$$

where

$$\eta = \frac{A_{\mathrm{c}} - \Delta A}{A_0}. \tag{4}$$

Both C_{S} and C_{L_0} are the concentrations of S and L added initially and η indicates the effective fraction of L, A_{c}, A_0, and ΔA are the real absorbance of the S-L product, the measurement absorbance of the reagent blank against water, and that of the S-L solution against reagent blank directly measured at the peak wavelength λ_2, respectively, A_{c} is calculated by [15]:

$$A_{\mathrm{c}} = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta}, \tag{5}$$

where $\Delta A'$ indicates the absorbance of the S-L solution measured at the valley absorption wavelength λ_1, α and β are correction constants. In addition, the molar absorptivity (real $\varepsilon_{\mathrm{r}}^{\lambda_2}$, not apparent $\varepsilon_{\mathrm{a}}^{\lambda_2}$) of the adsorption product SL_N at λ_2 is also directly calculated by the following equation:

$$\varepsilon_{\mathrm{r}}^{\lambda_2} = \frac{NA_{\mathrm{c}}}{\delta\gamma C_{\mathrm{S}}}, \tag{6}$$

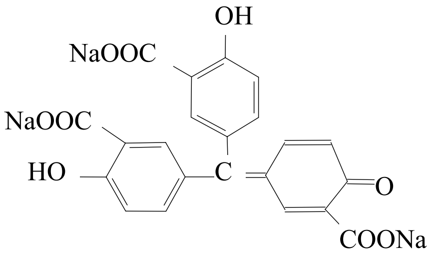
where δ is the cell thickness (cm).

The following equation was established for determining the stability constant (K) of a complex ML_N:

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_{\mathrm{L}}^{N}}. \tag{7}$$

From plots γ^{-1} vs. C_{L}^{-N}, we can calculate the formation constant (complexation ratio N and binding constant K) of the complex ML_N in the presence of the S micelle.

In this work, the ternary interaction of cetyltrimethylammonium bromide (CTAB) with pontachrome violet SW (PCV) and Cu (II) at pH 10.5 has been studied. The structure of PCV is given below:



Pontachrome Violet SW

It forms a trivalent anion in neutral medium, so it is adsorbed on CTAB. The effect of ionic strength and temperature on the aggregation of PCV on CTAB was studied, and the ternary reaction among PCV, CTAB, and Cu (II) was characterized. Also, we attempted to apply the method to the quantitative detection of trace amounts of Cu in water samples. The limit of detection of Cu is only 0.025 mg/liter and both the accuracy and precision of this method were satisfactory.

EXPERIMENTAL

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 a DJS-1 conductivity immersion electrode (electrode constant 0.98) (Shanghai Tienkuang Devices) to produce deionized water of $<0.5\ \mu\Omega^{-1} \cdot \mathrm{cm}^{-1}$. The pH of the solution was measured with a pHS-2C acidity meter (Leici Instruments, Shanghai, China) and a Model 630D pH Pen (Shanghai Ren's Electronics). The temperature was adjusted and maintained constant in a Model 116R electrically heated thermostatic bath (Changjiang Test Instruments of Tongjiang, China).

The stock standard solution of CTAB (10 mmol/liter) was prepared by dissolving CTAB (Shanghai Chemical Reagents) in deionized water, and the CTAB working solution (1 mmol/liter) was prepared daily by diluting the stock solution. The PCV solution, 0.7 mmol/liter, was prepared by dissolving 0.2478 g of PCV in 50 ml of DMF and diluted it to 500 ml with deionized water. The CTAB-PCV adsorption aggregate solution was prepared by mixing 50 ml of PCV (0.7 mmol/liter), 50 ml of the CTAB solution (10 mmol/liter) and 16.7 ml of pH 10.5 buffer solution. In this solution, the micellar aggregate $PCV_{5\sim6}CTAB_{78}$ was formed. Standard stock Cu(II) solution, 100 μg/ml (1.56 μmol Cu/ml), was prepared by dissolving 0.1 g of pure copper (content >99.95 %) in 10 ml of HNO_3 solution (1+1) and then diluting to 1000 ml with deionized water. Standard Cu(II) working solution (5 μg/ml) was prepared by diluting the above solutions. Ammonia buffer solutions between pH 7 and 11 were used to adjust the acidity of the CTAB-PCV-Cu solution. A masking reagent was prepared by dissolving 1 g of thioglycolic acid, 1 g of trisodium citrate, and 2 g of p-phenanthroline in 100 ml of deionized solution, and it was used to mask Ni(II), Cd(II), Pb(II), Fe(II), and Co(II) in the detection of Cu trace. Two mol/liter NaCl was used to adjust the ionic strength of solutions.

General Procedures. *Interaction of CTAB with PCV:* Into a 10 ml calibrated flask were added 1 ml of 1 mmol/liter CTAB, 1 ml of the buffer solution, and an appropriate volume of the PCV solution (0.7 mmol/liter). The mixture was diluted with deionized water to 10 ml and mixed thoroughly. After 5 min, the absorbances were measured at 540 and 635 nm respectively in a 1-cm cell against the reagent blank treated in the same way without CTAB, and then we calculated A_c of the binary adsorption aggregate. *Determination of Copper:* 5 ml of a water sample was added initially and 1 ml of the masking reagent was added before the addition of PCV solution. The other operations are the same as above. After 10 min, absorbances were measured at 510 and 600 nm respectively in a 2-cm cell against the reagent blank treated in the same way without Cu, and then A_c of the ternary complex is calculated.

RESULTS AND DISCUSSION

Analysis of Absorption Spectra. The absorption spectra of the PCV, CTAB-PCV, and CTAB-PCV-Cu solutions at pH 10.5 are shown in Fig. 1. From curve 1, the peak absorption of the PCV solution is located at 540 nm. From graph 2, we observe that the absorbance ratio of the solutions at 540 and 635 nm approaches a minimum when the concentration of CTAB is more than 7 times that of PCV. Such solutions contain no free PCV. Curve 3 gives the absorption spectrum of the CTAB-PCV aggregate showing the peak at 590 nm. So the spectral red shift of the CTAB-PCV aggregate is 50 nm. From the relative spectrum 4, the peak and valley of the CTAB-PCV solution against PCV are located at 635 and 540 nm. Therefore, the two wavelengths were used to study the adsorption interaction. From curves 1 and 3, the correction coefficients were calculated to be $\beta = 0.125$ and $\alpha = 1.13$. Therefore, the real absorbance of the CTAB-PCV aggregate is calculated by $A_c = 1.165(\Delta A - 0.125\Delta A')$. In curve 5, the peak of the CTAB-PCV-Cu product in solutions not containing free PCV and free CTAB-PCV aggregate is located at 510 nm. So the spectral blue shift of the CTAB-PCV-Cu product is 85 nm. However, from the relative spectrum 6, the peak and valley of the CTAB-PCV-Cu solution against the CTAB-PCV aggregate are located at 510 and 600 nm. Therefore, the two wavelengths were used to study the complexation. From curves 3 and 5, the correction coefficients were calculated to be $\beta = 0.471$ and $\alpha = 0.112$. Therefore, the real absorbance of the CTAB-PCV-Cu product is calculated by $A_c = 1.056(\Delta A - 0.471\Delta A')$.

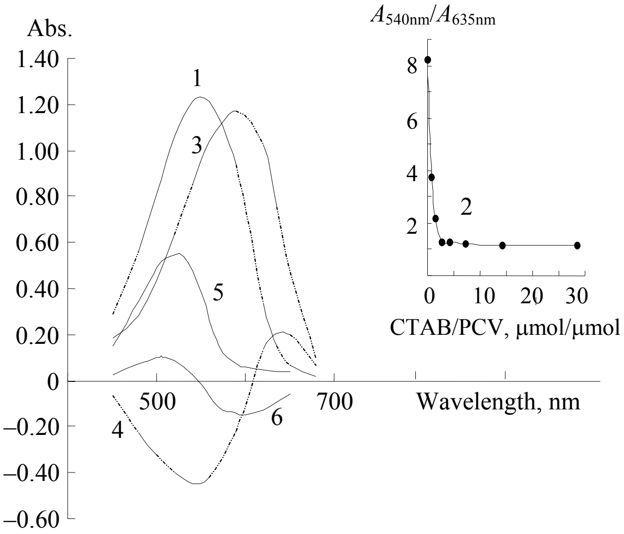
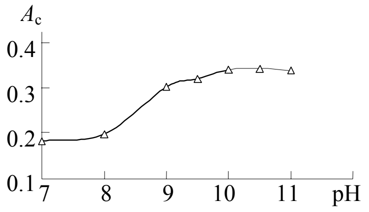
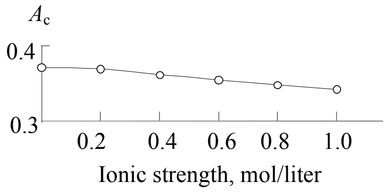


Fig. 1. Absorption spectra of PCV, PCV-CTAB, and Cu-PCV-CTAB solutions at pH 10.5: 1) PCV (0.7 μmol) solution; 2) variation of the absorbance ratio of solution measured at 540 and 635 nm with the initial molar ratio of CTAB to PCV; 3) PCV (0.7 μmol)-CTAB (20 μmol) solution without free PCV; 4) PCV (0.7 μmol)-CTAB (1 μmol) solution; 5) PCV (0.3 μmol)-CTAB (4.27 μmol)-Cu (200 μg) solution without free PCV and free CTAB-PCV aggregate; 6) PCV (0.3 μmol)-CTAB (4.27 μmol)-Cu (5 μg) solution. Curves 4 and 6 are against the blank and the others are against water

Effect of pH, Ionic Strength, and Temperature on Aggregation. By varying the pH of the solutions, the absorption of the CTAB-PCV solutions was measured and the absorbances are shown in Fig 2. From curve 1, A_c approaches a maximum when the pH is above 9. This is attributed to PCV$^-$ anion formation in basic solution, which may be attracted easily and closely to CTAB. A pH 10.5 buffer solution was used.

In order to investigate the effect of ionic strength on the aggregation of PCV on CTAB a NaCl solution was added and its effect is shown in Fig. 3. From curve 1, up to an ionic strength of 1 M, A_c of the PCV-CTAB aggregate decreases slightly with increase in ionic strength. This is attributed to the fact that the positively charged CTAB is attracting much more Cl$^-$.





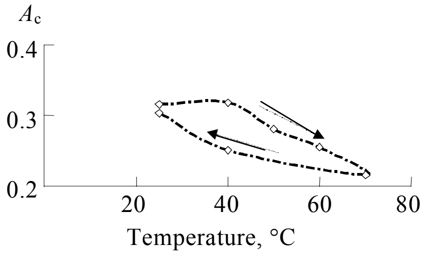


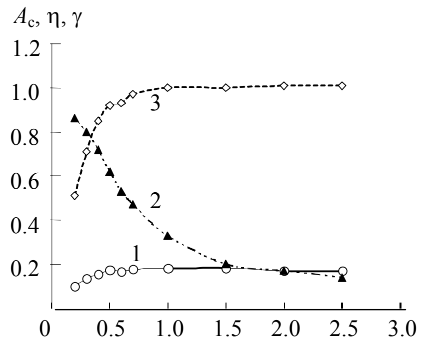
Fig. 2. Effect of pH on A_c of the aggregate in the solution initially containing 0.7 μmol of PCV and 1.0 μmol of CTAB

Fig. 3. Effect of ionic strength on A_c of the aggregate in the solution initially containing 0.7 μmol of PCV and 1.0 μmol of CTAB

Fig. 4. Effect of temperature on A_c of the aggregate in the solution initially containing 0.7 μmol of PCV and 1.0 μmol of CTAB

The effect of temperature on A_c of the PCV-CTAB aggregate is shown in Fig 4. From curve 1, A_c of the PCV-CTAB aggregate decreases with increase in temperature, especially above 40 °C. However, A_c of the PCV-CTAB aggregate may return to the initial point when the temperature decreases. So the adsorption of PCV on CTAB is reversible.

Characterizaiton of the aggregation. Into a solution containing 0.1 mmol/liter CTAB, the PCV solution was added to examine the adsorption of PCV on CTAB. C_L and γ of each solution was calculated, and plots γ^{-1} vs. C_L^{-1} are shown in Fig 5. The points around curve 1 are linear. So the adsorption of PCV on CTAB obeys Langmuir isothermal adsorption. The linear equation is regressed as $\gamma^{-1} = 2.09 + 7.46C_L^{-1}$ (C_L — μM). From the line intercept, the binding ratio of PCV to CTAB is calculated to be 0.5. Therefore, the monomer aggregate is expressed as PCV · CTAB$_2$ and the maximal micellar aggregate as (PCV · CTAB$_2$)$_{40}$ only when both CTAB is above its CMC (0.96 mM) and the concentration of PCV is enough. From the slope, the binding constant K of the aggregate was calculated to be $2.68 \cdot 10^5$ liter · mol^{-1} (at 25 °C). In addition, $\varepsilon_r^{\lambda_2}$ of the aggregate (PCV · CTAB$_2$)$_{40}$ was obtained to be $3.65 \cdot 10^5$ liter · mol^{-1} · cm^{-1} at 635 nm. Similarly, the plot γ^{-1} vs. C_L^{-1} of the Cu-PCV-CTAB solutions is shown in Fig 5. Curve 2 is linear. The linear equation is regressed as $\gamma^{-1} = 0.937 + 0.885C_L^{-1}$ (C_L — μM).



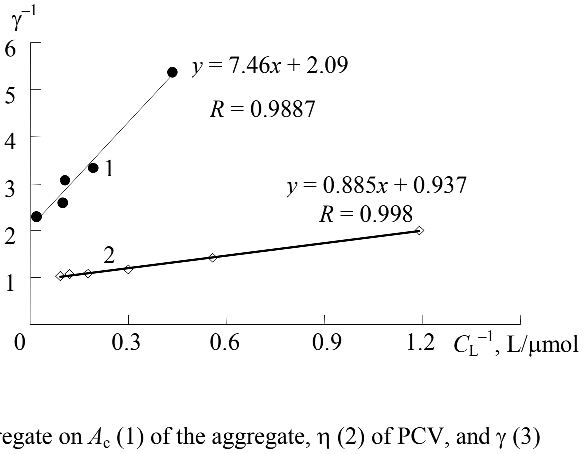


Fig. 5. Effect of addition of the CTAB-PCV- aggregate on A_c (1) of the aggregate, η (2) of PCV, and γ (3) of PCV to Cu in the solution initially containing 5 μg of Cu(II) at pH 10.5

Fig. 6. Plots γ^{-1} vs. C_L^{-1}: 1) CTAB-PCV interaction and 2) Cu-PCV complexation

From the intercept, the complexation ratio of PCV to CTAB is 1 and it gives the same result as above. From the slope, the stability constant of the complex was calculated to be $K = 1.13 \cdot 10^6$ (at 25 °C). In addition, we calculated the real molar absorptivity of the complex to be $\varepsilon_r = 2.25 \cdot 10^4$ liter · mol^{-1} · cm^{-1} at 510 nm (ε_a is only $1.15 \cdot 10^4$ liter · mol^{-1} · cm^{-1}). By varying the addition of the micellar aggregate $PCV_{5\sim6}CTAB_{78}$ solution, the Cu-PCV-CTAB solutions were measured. The A_c of the PCV-CTAB-Cu complex and η of PCV and γ of PCV to Cu were calculated. The plots are shown in Fig 6. From curves 1 and 3, A_c remains constant and γ approaches a maximum at 1 when the addition of the PCV-CTAB aggregate is over 0.5 ml. Therefore, the ternary complex $Cu \cdot PCV \cdot CTAB_2$ is formed and the micellar aggregate $(Cu \cdot PCV)_{5\sim6}CTAB_{80}$ may be formed only when the concentration of CTAB is more than CMC. So 1 ml of the PCV-CTAB aggregate solution was added for the determination of copper. From curve 2, only 29 % of the PCV-CTAB aggregate was complexed upon the addition of the PCV-CTAB aggregate solution, and 71 % is still free in solution. Obviously, such an excess of CTAB-PCV aggregate will affect the absorbance measurement of the ternary complex. Therefore the spectral correction technique was applied instead of classical spectrophotometry.

Calibration Graph and Precision for Determination of Cu Traces. The addition of the recommended masking reagent is useful to mask Co(II) and Pb(II) but will also decrease the sensitivity. According to the recommended procedures, standard series of Cu solutions were prepared and measured at pH 10.5 with the PCV-CTAB aggregate as reactant and in the presence of the masking reagent. The standard curves are shown in Fig 7. Curves 3 and 2 are more linear with greater slope than curve 1. So the correction technique has higher sensitivity than ordinary spectrophotometry. Six replicated determinations of 5 µg of Cu(II) gave the relative standard deviation RSD 2.3 % but RSD 6.9 % for ordinary spectrophotometry. So the correction technique has higher precision than ordinary spectrophotometry. The detection limit of Cu for $A_c = 0.010$ was calculated to be only 0.25 µg in 10 ml of solution.

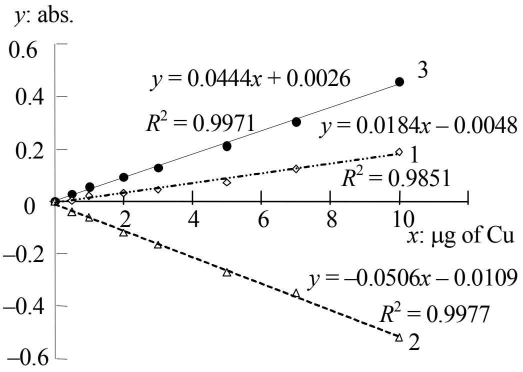


Fig. 7. Standard curves for the determination of Cu at pH 10.5: 1) absorbance measured at 510 nm against the blank; 2) same as 1 but at 600 nm and 3) A_c

Effect of Foreign Ions. By adding the recommended masking reagent, none of the following ions affected the direct determination of 5 µg of Cu(II) (error less than 10 %): 0.5 mg of alkaline metal ions, 0.2 mg of alkaline earths and anions, e.g., F^-, PO_4^{3-}; 0.1 mg of Mn(II), Zn(II), Cd(II), Al(III) and 0.05 mg of Pb(II), Ni(II), Fe(II) and 2.0 µg of Co(II), Hg(II).

Determination of Cu in Water Samples. Three samples were tested. Sample 1 was sampled from the Huaihe River, sample 2 from a local sewage pipe, and sample 3 from wastewater. The results are given in Table 1. We see that the recovery of Cu added is between 95 and 105 % and the RSD is less than 4.5 %. The determination of Cu in water samples was carried out and evaluated by AAS and its result is given in Table 1, too. We observe that the two methods give the same results.

Table 1. Determination of Copper in Samples with PCV at pH 10.5 in the Presence of a Masking Reagent

Sample No.	Added Cu, µg	Found, µg
1	0	0.088 ± 0.004 (0.082*) RSD 4.5 %
	0.1	0.189 ± 0.006 Rec. 101 %
2	0	0.232 ± 0.008 (0.221*) RSD 3.4 %
	0.2	0.422 ± 0.012 Rec. 95.0 %
3	0	0.716 ± 0.018 (0.709*) RSD 2.5 %
	0.5	1.241 ± 0.021 Rec. 105 %

* One determination by AAS.

Conclusions. The combination of Langmuir isothermal adsorption and spectral correction techniques provides a very helpful experimental strategy to study a ternary complex in the presence of a surfactants. It describes clearly the synergism mechanism of surfactants. The enrichment of charged ligand on micelle accelerated its dissolution in aqueous medium and its coordination with metal ion.

Acknowledgement. Financial support is gratefully acknowledged from the National High Technology Research and Development Program of China (863 Program, No 2002AA601320).

[1] **S.A.Kulichenko and S.O.Fessenko.** Anal. Chim. Acta, **481** (2003) 149—153
[2] **A.Fernández-González, R.Badía, and M.E.Díaz-García.** J. Pharm. Biomed. Anal., **29** (2002) 669—679
[3] **Y.X.Ci and M.M.Yang.** Chin. Sci. Bull., **16** (1983) 980—983
[4] **Y.X.Zheng, L.D.Li, and S.Q.Sun.** Chin. J. Chem. Reagents, **6** (1984) 273—276
[5] **S.B.Savvin, P.K.Chernova, and L.M.Kudravtseva.** Zh. Anal. Khim., **33** (1978) 2127—2133
[6] **W.B.Qi and L.Z.Zhu.** Chem. J. Chin. Univ., **7** (1986) 407—409
[7] **R.Zana and Y. Talmon.** Nature, **362** (1993) 229—233
[8] **A.Knaebel, R.Oda, and E.Mendes.** Langmuir, **16** (2000) 2489—2492
[9] **L.T.Okano, F.H.Quina, and O.A.El-Seoud.** Langmuir, **16** (2000) 3119—3123
[10] **R.Oda, I.Huc, and S.J.Candau.** Chem. Commun. (**1997**) 2105—2106
[11] **H.W.Gao and W.Q.Xu.** Anal. Chim. Acta, **458** (2002) 417—423
[12] **H.W.Gao, M.L.Ye, J.Z.Ge, and T.J.Wang.** J. Appl. Spectr., **69** (2002) 667—674
[13] **I.Langmuir.** J. Am. Chem. Soc., **40** (1918) 1361—1402
[14] **H.W.Gao and J.F.Zhao.** J. Appl. Spectr., **70** (2003) 297—302
[15] **H.W.Gao and J.X.Yang.** Colloids Surf. A, **205** (2002) 283—292