

Langmuir Aggregation of Stain on Ionic Surfactant and its Application: Interaction of Bromo-Pyrogallol Red with Cetyl Trimethylammonium Bromide (CTAB) and Determination of Molybdenum Traces

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The microphase adsorption-spectral correction (MPASC) technique was described and applied to study the interaction of bromo-pyrogallol red (BPR) with cetyl trimethylammonium bromide (CTAB). The synergism mechanism of micelles was analyzed and discussed. The large electrostatic micelle adsorbs the chromophore in only the monolayer, and the adsorption obeys the Langmuir adsorption. The formation of the (BPR)₇₈•(CTAB)₇₈ aggregate accelerates the Mo-BPR complex reaction. Experimental results showed the adsorption constant of the adsorption aggregate 6.20×10^5 and its molar absorptivity $\epsilon_r^{610\text{nm}} = 1.40 \times 10^6 \text{ l mol}^{-1} \text{ cm}^{-1}$. For analysis of samples, the recovery of Mo was between 97.4 and 107% and the RSD was less than 4.39%.

INTRODUCTION

A surfactant is of ten quite useful in sensitive determination of trace amounts of a component due to its solubilization, stabilization, sensitivity enhancement and so on. Some earlier models were proposed to explain the synergism mechanism, e.g. synergism perturbation,¹ hydrogen bond formation,² micelle catalysis,³ asymmetric microenvironment⁴ and others. The study on surfactant solution is active⁵⁻⁸ because its special function. A surfactant molecule usually has a long chain and various aggregation forms in aqueous solution, e.g. spherical, worm-like, tubules and lamellae.⁹ Its surface (cetyl trimethylammonium bromide (CTAB) as representative) will adsorb small ions with an opposite charge, e.g. aggregation of Cl⁻ or stain anions in only a monolayer.¹⁰ The interaction of a surfactant with a stain often occurs just like a precipitation-stain adsorption. In a surfactant (S) solution, the aggregation of S molecules will form an electrostatic global micelle (Fig. 1-left) when S is more than the critical micellar concentration (CMC). So, the electrostatic attraction of a ligand (L) with opposite charge occurs in the micelle until the kinetic equilibrium (Fig. 1-middle). Because of the electrostatic attraction, the solubilization of L occurs in the S solution. The addition of metal ions (M) will cause the sensitive complex ion of M with L adsorbed in micelle phase (Fig. 1-right). Because the concentration of L in micelle phase is much higher than that in aqueous phase, the reaction is very easy and quite rapid. Like a catalyst carrier, the presence of

the micelle accelerates the M-L complex reaction. All L molecules are concentrated on S micelle so the complexation between a metal (M) and L in the micelle phase becomes rapid and sensitive. This causes the enhancement of the sensitivity. Similarly, the same electrostatic adsorption of L on S monomer surface can occur when S is less than CMC (Fig. 1-(1)). The aggregation of L on S surface is in only a monolayer. It obeys the Langmuir adsorption¹¹ and the following equilibrium occurs: L (aqueous phase, C_L) ⇌ SL_N (surfactant phase, C_S) in L-S solution. The Langmuir equation is used:

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

where K is the equilibrium constant and C_L the concentration of the excess L and γ is the molar ratio of L adsorbed to S. With an increase in L concentration, γ will approach a maximum, called the adsorption ratio N . The γ^{-1} vs. C_L^{-1} is linear and from this we may calculate N and K . Both C_L and γ are calculated by means of:¹²⁻¹³

$$\gamma = \eta \times \frac{C_{L0}}{C_S} \quad (2)$$

$$C_L = (1 - \eta)C_{L0} \quad (3)$$

where:

$$\eta = \frac{A_c - \Delta A}{A_o} \quad (4)$$

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where both C_S and C_{L0} are the concentration of the 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. The A_c is calculated by means of:¹²

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta} \quad (5)$$

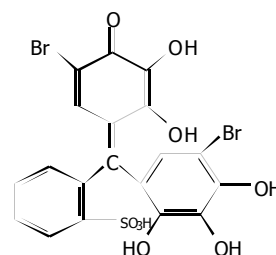
where $\Delta A'$ indicates the absorbance of the S-L solution measured respectively at the valley absorption wavelength λ_1 . In general, α and β are the correction constants and they are calculated by measuring directly S_{LN} and L solutions.¹³ In addition, the molar absorptivity (real $\epsilon_r^{\lambda_2}$ not apparent $\epsilon_a^{\lambda_2}$) of the adsorption product S_{LN} at λ_2 is also directly calculated by the following equation:

$$\epsilon_r^{\lambda_2} = \frac{mNA_c}{\delta \gamma C_M} \quad (6)$$

where δ is the cell thickness (cm) and the others have the same meanings as in the equations above.

The cooperation of both the Langmuir adsorption and the spectral correction technique will provide a very helpful experimental strategy for study of chromophore or its metallic complex's adsorption in surfactant solution. This method is named Micro Phase Adsorption-Spectral Correction (MPASC) provides a very helpful experimental strategy for the study of the aggregation of chromophores on surfactant micelles. It

has been applied to the investigation of the biomolecular solution.¹⁴ In the present article, we have studied the aggregation of bromo-pyrogallol red (BPR) on CTAB and its application to the sensitive determination of trace amounts of molybdenum. The structure of the stain is given below:



Bromo-pyrogallol red (BPR)

It forms negative ions in a neutral medium and can be adsorbed by cationic surfactant CTAB. The relationship between the adsorption ratio of BPR to CTAB and free BPR molarity is in accordance with the Langmuir adsorption. Results showed that the maximal adsorption ratio of CTAB to BPR is 1:2 at pH 6.0 and the adsorption constant $K_{CTAB-BPR} = 6.20 \times 10^5$. In addition, the coordination of Mo with the BPR in the CTAB-BPR aggregate has been made and discussed. The CTAB micellar surface has concentrated a lot of BPR and provided an active place like catalyst for the complex reaction between Mo and BPR. The aggregation of BPR on CTAB and the coordination of Mo with BPR have been applied to the quantitative determination of Mo trace in samples. The recovery of molybdenum is between 97.4 and 107% and the

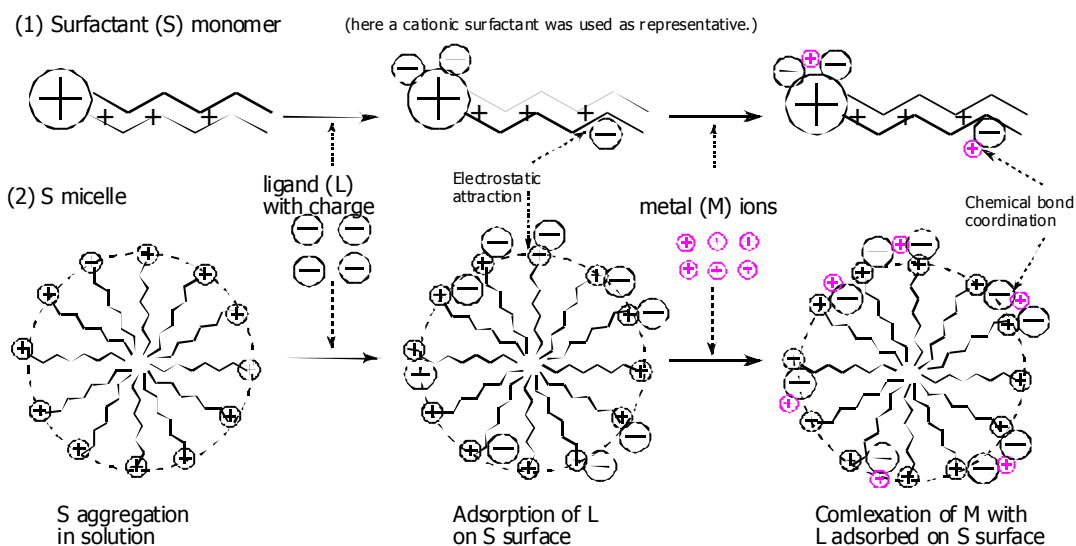


Fig. 1. The adsorption of ligand (L) molecules on surfactant (S) monomer (1) and micelle (2) surface and the sensitive complexation of a metal (M) with L adsorbed on S surface.

RSD less than 4.39%.

EXPERIMENTAL SECTION

Apparatus and Materials

Absorption spectra were recorded on a UV/VIS 265 Spectrophotometer (Shimadzu, Japan) with 1-cm and the individual absorbance was measured on a Model 722 spectrophotometer (Shanghai Analytical Instruments) with 2-cm cells. The conductivity meter, Model DDS-11A (Tianjin Sec. Anal. Instrument.) was used to measure conductivity together with Model DJS-1 conductivity immersion electrode (electrode constant 0.98, Shanghai Tienkuang Device Works) in production of deionized water below $0.5 (\mu\Omega\text{cm})^{-1}$. The pH of solutions was measured on a pH S-2C acidity meter (Leici Instrument, Shanghai) and Model 630D pH Pen (Shanghai Ren's Electric). The temperature was adjusted and remained constant in an electrically heated thermostat bath, Model 116R (Changjiang Test Instruments of Tongjiang, China).

The standard stock CTAB (10.00 mM) was prepared by dissolving cetyl trimethylammonium bromide (CTAB) (Shanghai Chemical Reagents Centre) at 40°C in deionized water and then 1.00 mM CTAB was prepared daily. BPR solution (0.500 mM) was prepared by dissolving 0.1590 g of bromo-pyrogallol red (BPR, content 88%, produced by Shanghai 3rd Reagents) in 500 mL of deionized water. $1.92 \mu\text{mol/l}$ ($\text{BPR}_2 \cdot \text{CTAB}$)₇₈ aggregate (containing 0.300 mM BPR) was prepared by mixing 100 mL of 0.500 mM BPR, 34 mL of 5.0 mM CTAB, 10 mL of pH 6.0 buffer solution and 23 mL of deionized water. It can be used after 20 min. The standard Mo solution, 10.0 $\mu\text{g Mo/mL}$ was prepared by dissolving ammonium molybdate in deionized water. The acetate and ammonium buffer solutions between pH 4.5 and 10 were used to adjust the acidity of solutions. The masking reagent, 5% EDTA-2Na was prepared in the determination of molybdenum traces, which was used to complex other transition, alkaline earth and main group metals.

Methods

Adsorption of BPR on CTAB micelles

Into a 25 mL calibrated flask were added 0.200 μmol of CTAB, 2.5 mL of buffer solution and a known amount of BPR solution. The mixture was diluted to 25 mL with deionized water and mixed thoroughly. After 5 min, absorbances were measured at 545 and 610 nm, respectively, against the reagent blank treated in the same way without CTAB, and then A_c of the adsorption product was calculated.

Determination of molybdenum in samples

A known volume of a sample solution containing less than 10 μg of Mo was placed in a 25 mL flask. To which was added 2.5 mL of pH 6.0 buffer, 1 mL of the masking reagent and 3.0 mL of $1.92 \mu\text{mol/l}$ ($\text{BPR}_2 \cdot \text{CTAB}$)₇₈ aggregate. It was diluted to 25 mL and mixed well, then put in a 40°C constant temperature bath for reacting 20 min; absorbances were measured at 575 and 615 nm, respectively, against a reagent blank without Mo and A_c of the ternary complex was calculated.

RESULTS AND DISCUSSION

Spectral Analysis

The interaction of BPR with CTAB

The absorption spectra of the CTAB-BPR solution at pH 6.0 are shown in Fig. 2, where 0.200 μmol of CTAB and 0.250 μmol of BPR were added. From curve 1, the ratio of absorbance of the CTAB-BPR solution at 545 nm to that at 610 nm approaches minimum and remains constant when the molar number ratio of CTAB to BPR is over 2. So CTAB may adsorb the complete BPR when mixed with 2.0 μmol of CTAB and 0.60 μmol of BPR at pH 6.0. This indicates no free BPR in such a solution and curve 4 gives the solution's spectrum. We find that the spectral peak of BPR solution is located at 555 nm and that of the adsorption aggregate at 560 nm. The spectral red shift is only 5 nm. However, the relative spectral peak and valley are located at 545 and 610 nm from curve 3. So the two wavelengths were used in the study of the adsorption. From curves 2 and 4, the correction coefficients were calculated to be $\beta_1 = 0.110$ and $\alpha_1 = 1.30$. Therefore, $A_c = 1.17 (\Delta A - 0.110 \Delta A')$ for calculating real adsorption of the CTAB-BPR aggregate.

The coordination between BPR in the aggregate and Mo

The absorption spectra of the CTAB-BPR-Mo solutions and that of their ternary complex are shown in Fig. 2. By comparing curves 5 and 2, we observe the peak of the ternary complex is located at 615 nm. The spectral peak of the ternary complex is 55 nm longer than that of the CTAB-BPR product. From curve 6, the peak and valley of the CTAB-BPR-Mo mixture are located at 615 and 575 nm, respectively. So the two wavelengths were used in this work. From curves 2 and 5, $\beta_2 = 0.248$ and $\alpha_2 = 0.638$. Therefore, $A_c = 1.19 (\Delta A - 0.248 \Delta A')$ for calculating the real absorbance of the ternary complex.

Effect of pH on Aggregation of BPR on CTAB

By varying the pH of a solution, the adsorption of the

CTAB-BPR solution was measured and the effect of pH on the adsorption ratio of BPR to CTAB is shown in Fig. 3. From curve 1, we observe that the increase of acidity of a solution causes a decrease in absorbance. This is attributed to the fact that BPR contains more negative charges until BPR^{6-} is formed in a strong basic solution. A stain with more charges is easier to be attracted by the opposite point charge. However, by comparing the difference between curves 1 and 2 and considering their action selectivity between Mo and BPR, we selected pH 6.0 here.

Effect of Temperature on Aggregation of BPR

At various temperatures, the adsorption ratio of BPR to

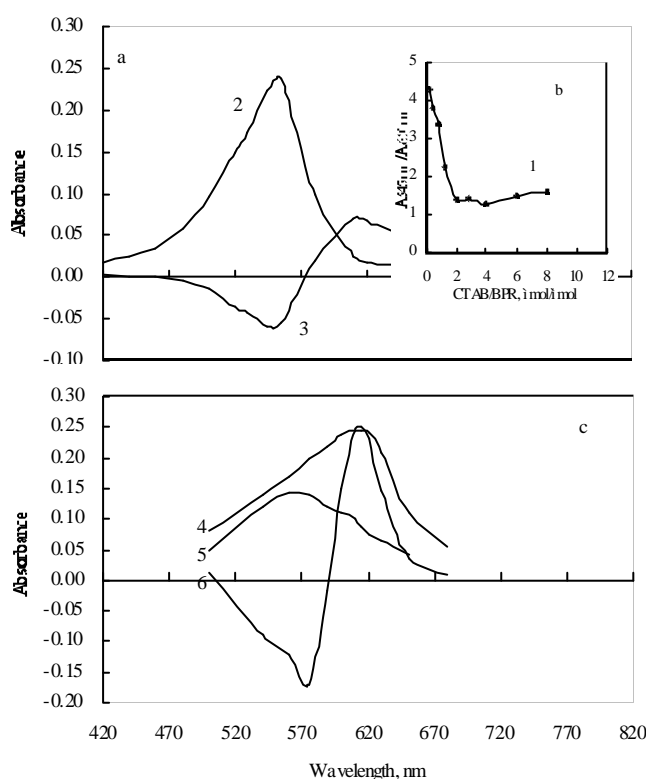


Fig. 2. Absorption spectra of BPR, BPR-CTAB and Mo-BPR-CTAB solutions at pH 6.0: 1- variation of $\text{Absorbance}_{545\text{nm}}$ and $\text{Absorbance}_{610\text{nm}}$ of the BPR-CTAB solutions with an increase in CTAB (between 0 and 5 μmol) which all contain 0.25 μmol of BPR; 2- BPR (0.25 μmol) solution against water; 3- BPR-CTAB aggregate solution not containing free BPR against water; 4- BPR (0.60 μmol)-CTAB (1.80 μmol) solution against a reagent blank; 5- BPR (0.60 μmol)-CTAB-Mo (5.0 μmol) complex solution not containing free BPR-CTAB product against water and 6- BPR (0.60 μmol)-CTAB-Mo (20.0 μg) solution against a reagent blank.

CTAB is shown in Fig. 4. The adsorption ratio decreases with an increase in temperature, especially over 70 °C. This is attributed to the fact that the higher temperature will cause the rapid desorption of BPR from the CTAB surface. Such a phenomenon is in accordance with the common law of surface adsorption.

Effect of Time on Aggregation of BPR on CTAB

At a temperature of 10 °C, the effect of time on the adsorption in reaction between CTAB and BPR is shown in Fig. 5. Curves 1 and 2 indicate that the CTAB-BPR adsorption reaction at pH 6 approaches a maximum in 5 min. Curves 3-6 give the effect of time on the complex reaction between BPR in the CTAB-BPR aggregate and Mo in the presence of EDTA at temperatures of 10 and 40 °C. From curves 3 and 4, the re-

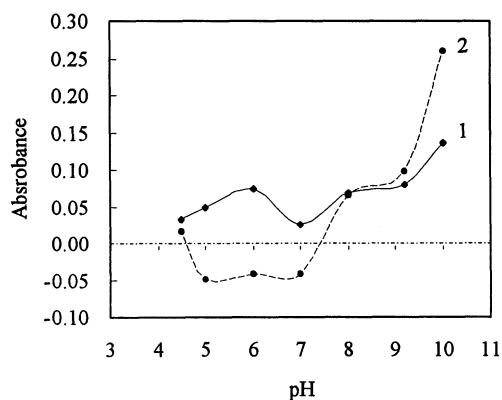


Fig. 3. Effect of pH on the absorbance of the BPR-CTAB solutions all containing 0.250 μmol of BPR and 0.200 μmol of CTAB: 1- at 610 nm and 2- at 545 nm, both against water.

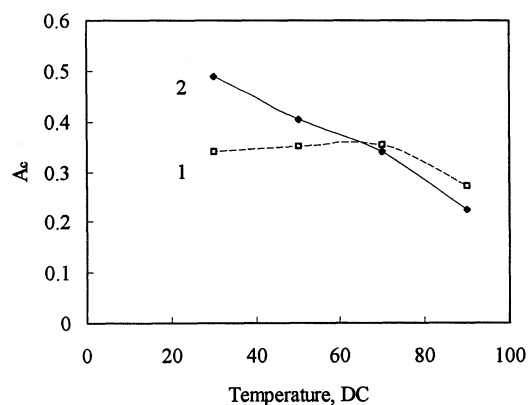


Fig. 4. Effect of temperature on the real absorbance of the BPR-CTAB aggregate in the solutions containing: 1- 2.00 μmol of BPR and 5.0 μmol of CTAB and 2- 2.00 μmol of BPR and 2.50 μmol of CTAB.

action is slow at 10 °C. It becomes very fast at temperatures of 40 °C. So the absorbance measurement of the CTAB-BPR adsorption solution was carried out after 5 min at room temperature and that of the ternary complex was made after 20 min at temperatures of 40 °C.

Effect of BPR Concentration

The adsorption of BPR on CTAB

By varying the BPR concentration, the adsorption of the adsorption solutions was measured. Calculations of their C_L and γ and their relationship is shown in Fig. 6. We observe that curve C_L^{-1} vs. γ^{-1} is linear (correction coefficient $R = 0.993$). So, the adsorption of BPR on CTAB obeys the Langmuir monolayer adsorption. The regression equation is

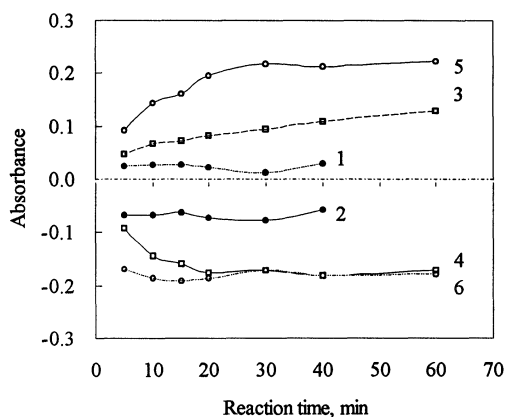


Fig. 5. Effect of the time on absorbances of the BPR-CTAB solution (1- at 610 nm and 2- at 545 nm) containing 0.250 μmol of BPR and 0.200 μmol of CTAB and those of Mo-BPR-CTAB solutions (3- and 5- at 615 nm and 4- and 6- at 575 nm) (solution containing 0.60 μmol of BPR-CTAB product and 20.0 μg of Mo), all against reagent blank. 1-, 2-, 3- and 4- at 10 °C and both 5- and 6- at 40 °C.

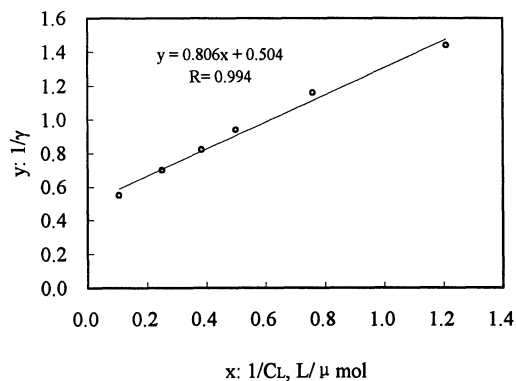


Fig. 6. γ^{-1} vs. C_L^{-1} , (C_L unit: $\mu\text{mol/l}$).

$\gamma^{-1} = 0.504 + 0.806 C_L^{-1}$ (C_L - μM). So the adsorption constant was calculated to be $K = 6.20 \times 10^5$ and the adsorption ratio of CTAB to BPR to be $N = 2.0$. When CTAB is more than CMC 0.96 mM, the large aggregate $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ will be formed. The real (not apparent) molar absorptivity of the aggregate micelle was calculated to be $\epsilon_r^{610\text{nm}} = 1.40 \times 10^6 \text{ l mol}^{-1} \text{ cm}^{-1}$.

The complex reaction between BPR in the aggregate and Mo

In fact, 1.92 $\mu\text{mol/l}$ $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ aggregate was formed in the solution initially containing 0.300 mM BPR and 1.0 mM CTAB because CTAB concentration is more than CMC. Such a solution was prepared in "Materials" for sensitively complexing Mo. By varying the addition of the $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ solution, the ternary complex solution was measured and η of the $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ product and γ of complex were both calculated. Their curves are shown in Fig. 7. From curve 2, we see that the composition ratio γ of BPR to Mo reaches maximum at 2 when the addition of the $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ solution is more than 2.0 mL. Therefore, the final ternary complex is expressed as $\text{Mo} \cdot \text{BPR}_2 \cdot \text{CTAB}$. In the quantitative determination of molybdenum in samples, 3.0 mL of the $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ aggregate solution was added. From curve 1, we find that the effective $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ aggregate takes up only 50%, so half of the $(\text{BPR}_2 \cdot \text{CTAB})_{78}$ aggregate is free in the solution. Beyond all doubt, such excess of the aggregate will affect the absorbance measurement of the ternary complex.

In the determination of the adsorption or complex ratio and equilibrium constant, the spectral correction method is advanced in operation and principle by comparing with classical methods such as the Scatchard model,¹⁵ molar ratios,¹⁶ continuous variations¹⁷ and equilibrium movement.¹⁸

Calibration Graph and Precision for Determination of Mo

According to the recommended procedures, the stan-

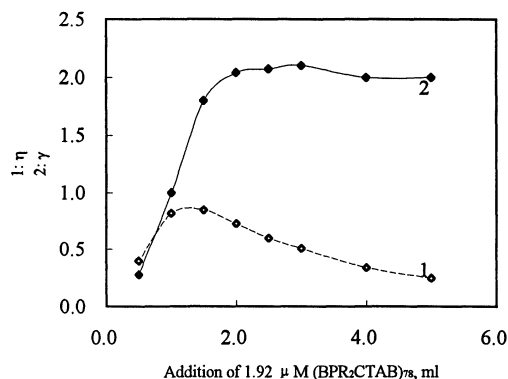


Fig. 7. Effect of addition of the BPR-CTAB aggregate on η (1) and γ (2) of BPR to Mo (solution containing 20.0 μg of Mo).

standard series of molybdenum solutions were prepared and measured at pH 6.0 using the BPR-CTAB aggregate as reagent in the presence of EDTA. The regression equation is: $A_c = 0.0309x - 0.042$ (x -Mo, μg). From the slopes of curves, the molar absorptivity of complex was calculated to be $\epsilon_{\text{real}}^{615\text{nm}} = 7.43 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $\epsilon_{\text{apparent}}^{615\text{nm}} = 5.74 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. So the correction method has higher sensitivity than ordinary spectrophotometry. Six replicated determinations of 5.00 and 25.0 μg of standard Mo(VI) gave the relative standard deviation RSD = 2.8 and 1.1% for the correction method but RSD = 9.6 and 5.2% for ordinary spectrophotometry. So the correction method has higher precision than ordinary spectrophotometry. The detection limit of Mo for $A_c = 0.010$ was calculated to be 0.30 μg in 25 mL of solution.

Effect of Foreign Ions

By adding the EDTA solution, none of the following ions affected the direct determination of 20.0 μg of molybdenum (VI) (error less than 10%): 0.5 mg of alkaline earths and common anions, e.g. Cl^- , Ca^{2+} , Mg^{2+} , F^- and PO_4^{3-} , 0.2 mg of Al(III), Zn(II), Pb(II), As(III) and 0.1 mg of Ni(II), Fe(II, III), Cu(II), Mn(VI), Co(II), Cd(II) and Hg(II).

Determination of Mo in Sample

Two samples were determined. Sample 1 was sampled from Huaihe River sample 2 from a local sewage pipe. In the samples, drops of standard Mo solution were added. The determination results are given in Table 1. We see that the recovery of standard Mo is between 97.4 and 107% and the RSD less than 4.37%.

CONCLUSION

The investigation of the interaction of BPR with CTAB micelle supports the monolayer adsorption of BPR molecules on micelles. Though the MPASC technique has not given a higher sensitivity than other methods such as RLS.¹⁹ However, it may meet precision and accuracy criteria and offers

the additional benefits of simplicity and versatility. We still understand the classical spectrophotometric method can play an important role in the synergism of surfactant micelle, e.g. solubilization and enhanced sensitivity and their application to the quantitative determination of metal traces.

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Key Words

MPASC technique; Cetyl trimethylammonium bromide (CTAB); Bromo-pyrogallol red (BPR); Microelectrostatic field; Langmuir aggregation; Determination of molybdenum.

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Table 1. Determination of Mo in Samples

Sample Number	Added, μg	Found, $\mu\text{g}/10 \text{ mL}$	Recovery, %
1#	0.000	3.31 ± 0.15 RSD 4.39%	97.4
	5.00	8.18 ± 0.22	
2#	0.000	5.95 ± 0.14 RSD 2.37%	107
	5.00	11.3 ± 0.31	