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Spectrophotometric Titration of Iron Using Eriochrome Blue Black R and Cetyltrimethylammonium Bromide

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ABSTRACT

The ternary interaction of eriochrome blue black R (EBBR) with cetyltrimethylammonium bromide (CTAB) was investigated. Cetyltrimethylammonium bromide micelle provides complexation between Fe and EBBR with a catalytic field so as to sensitize the complexation. The aggregation of EBBR on CTAB is in accord with the Langmuir adsorption isotherm. The ternary interaction was characterized at pH 6.5 by the spectral correction technique and the Langmuir adsorption isotherm and the aggregate $Fe \cdot EBBR_6CTAB_{78}$ was formed. The reaction was applied to the sensitive determination of Fe traces in samples with satisfactory results.

Key Words: Cetyltrimethylammonium bromide; Eriochrome blue black R; Spectral correction technique; Langmuir adsorption isotherm, Determination of iron.

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INTRODUCTION

At present, for supersensitive analysis of a trace component, the addition of surfactant e.g., Triton X-100, or cetyltrimethylammonium bromide (CTAB) is often necessary.[1–3] The following models were previously proposed to explain the synergism (e.g., solubilization, stabilization, and sensitization) of surfactant: micelle extraction, synergism perturbation,[4] hydrogen bond formation,[5] asymmetric microenvironment,[6] etc. Currently, the study of surfactants is still very active.[7–10] Understanding its interaction with organic molecules is helpful to design a new-type of efficient surfactant and to select a suitable surfactant for ultra-trace analysis.

In a surfactant (S) solution, the aggregation of S molecules will form an electrostatic global micelle (Fig. 1, left) when S is at more than the critical micellar concentration (CMC). The electrostatic attraction between an oppositely charged dye (L) and the micelle results in the binding of L onto S by non-covalent bonding, i.e., by electrostatic attraction, hydrogen bonding, van der Waals forces, hydrophobic bonds, insertion, and molecular winding (Fig. 1, middle).[11] Thus, this explains the solubilization and stabilization actions of S. The addition of metal ions (M) causes a sensitive complexion with L adsorbed onto the micelle (Fig. 1, right) because L is enriched on S. Thus, the complexation becomes easy and rapid. Therefore, the micelle provides M–L complexation with a catalytic field. This reasonably explains the sensitization action of S. The interaction of L with S is only in a monolayer like as with biomacromolecules.[12] It obeys the Langmuir adsorption isotherm[13] as follows:

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L} \tag{1}$$

where K is the binding constant, C_L, the molar concentration of excess L and γ is the molar ratio of L adsorbed onto S. With an increase in L concentration, γ approaches a maximal binding number N. A plot of γ^{-1} vs. $C_L{}^{-1}$ is linear and both N and K can be calculated. Both C_L and γ are calculated by means of:[14]

$$\gamma = \eta \times \frac{C_{L0}}{C_S} \tag{2}$$

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

where

$$\eta = \frac{A_c - \Delta A}{A_0} \tag{4}$$

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]

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha\beta} \tag{5}$$

where $\Delta A'$ indicates the absorbance of the S–L solution measured, respectively, at the valley

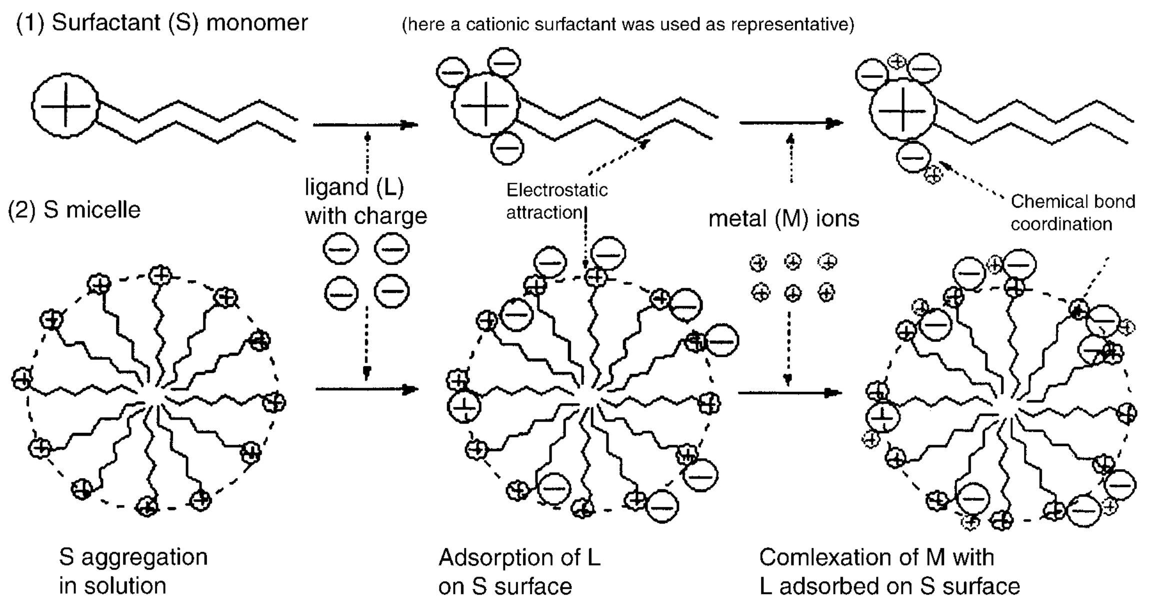

Figure 1. The adsorption of dye ligand (L) on surfactant (S) monomer (1) and micelle (2) and the sensitive complexation of metal (M) with L on S.

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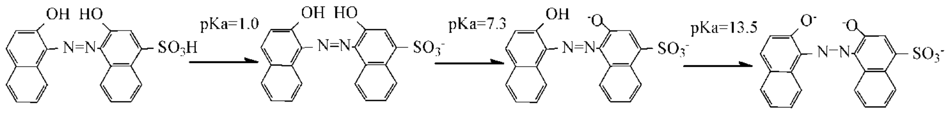
absorption wavelength λ_1. In general, α and β are the correction constants and they are calculated by directly measuring SL_N and L solutions.[11,12,14] In addition, the molar absorptivity (real $\varepsilon_r^{\lambda_2}$ not apparent $\varepsilon_a^{\lambda_2}$) of the adsorption product SL_N at λ_2 is directly calculated by the following relationship:[11]

$$\varepsilon_r^{\lambda_2} = \frac{mNA_c}{\delta\gamma C_M} \tag{6}$$

where m is the aggregation number of a micelle, δ is the cell thickness (cm), and the others have the same meanings as in the equations above.

The cooperation of both Langmuir adsorption and complexation will provide a very helpful experimental strategy for study of a ternary complex in the presence of a surfactant. It clearly gives the synergistic mechanism of a surfactant solution. In this work, the concrete interaction, CTAB with eriochrome blue black R (EBBR) at pH 6.5, was studied and the complexation between EBBR and Fe(II) was characterized. Eriochrome blue black R is an old dye ligand and, previously, it was used in the chelometric titration of Ca(II), Mg(II), and other metals.[15,16] Recently, EBBR was used for the determination of protein,[17] Mo,[18] and Cu.[19] Its pH-dependence at 25°C is given below:



It forms monovalent anion in neutral aqueous solution, so it may bind onto CTAB. The aggregation of EBBR on CTAB obeys the Langmuir monolayer adsorption. Results have shown that the maximal binding number of EBBR on CTAB is 3 at pH 6.5 and the binding constant of the EBBR–CTAB aggregate, $K_{\mathrm{CTAB-EBBR}} = 1.02 \times 10^5\,\mathrm{L\,mol^{-1}}$. The determination of iron has been accomplished by many methods, e.g., ICP-MS,[20] AES,[21] AAS,[22,23] spectrophotometry,[24,25] chromatography,[26,27] voltammetry and polarography,[28,29] etc. In this work, the combination of the Langmuir adsorption and complexation was applied to the spectrophotometric determination of Fe traces in samples; the recovery of iron is between 92.0% and 110% and the relative standard deviation (RSD) is less than 5.70%. The operation is simple and the apparatus is low cost and very universal. Besides, this method is characterized the interaction between Fe(II), EBBR, and CTAB.

EXPERIMENTAL

Materials

Absorption spectra were recorded on a TU1901 spectrophotometer (PGeneral, Beijing) with a 1-cm cell. The individual absorbance was measured on a Model 722 spectrophotometer (Shanghai 2nd Anal. Instruments) with 2-cm cells. The conductivity meter, Model DDS-11A (Tianjin 2nd Anal. Instruments), was used to measure conductivity together with a Model DJS-1 conductivity immersion electrode (electrode constant 0.98, Shanghai Tienkuang Devices) during production of deionized water below

$0.5\,\mu\Omega\,cm^{-1}$. The pH of the solution was measured with a pHS-2C acidity meter (Leici Instruments, Shanghai) and Model 630D pH Pen (Shanghai Ren's Electronics). The temperature was adjusted and remained constant in an electrically heated thermostated bath, Model 116R (Changjiang Test Instruments of Tongjiang, China). The content of Fe in samples was examined with a TAS-986 atomic absorption spectrophotometer (Beijing Purkinje General Instruments, China).

The stock standard of CTAB (10 mM) was prepared by dissolving CTAB (Shanghai Chemical Reagents) at 40°C in deionized water and then 1 mM CTAB was prepared daily. The EBBR solution (0.800 mM) was prepared by dissolving 0.208 g of EBBR (content 80%, purchased from Shanghai Xinzhong Chemicals) in 500 mL of deionized water. The CTAB–EBBR aggregate solution containing 0.400 mM EBBR was prepared by mixing 100 mL of 0.800 mM EBBR, 95.0 mL of 10 mM CTAB, and 5 mL of pH 6.5 buffer solution. It may be used after reaction for 20 min. The micellar aggregate $EBBR_6CTAB_{78}$ is formed in this solution. The acetate and ammonium buffer solutions from pH 4 to 10 were used to adjust the acidity of the solutions. NaCl solution (5.0 M) was used to adjust the ionic strength of the aqueous solution. The hydroxylamine hydrochloride solution (2%) was prepared to reduce Fe(III) to Fe(II). The masking reagent was prepared by mixing 100 mL of the thioglycolic acid solution [4% (v/v), initially neutralized to pH 6–7 with 10% NaOH], 50 mL of the trisodium citrate solution (4%) and 50 mL of the potassium–sodium tartrate solution (4%), which was used to complex the transition of alkaline earth and main group metals.

Methods

Adsorption of Eriochrome Blue Black R onto Cetyltrimethylammonium Bromide

Into a 25-ml calibrated flask, were added 1 μmol of CTAB, 2.5 mL of buffer solution and a known volume of the EBBR solution. The mixture was diluted to 25 mL with deionized water and mixed thoroughly. After 10 min, the absorbances were measured at 530 and 630 nm, with a 1-cm cell, against the reagent blank treated in the same way, but without CTAB; then, A_c of the aggregate was calculated.

Determination of Iron in Samples

A known volume of a sample solution, containing less than 10 μg of Fe (II), was taken into a 25 mL flask. Then, 2.5 mL of pH 6.5 buffer solution, 1 mL of the masking reagent, and 5.0 mL of the CTAB–EBBR aggregate solution were added. The solution was then diluted to 25 mL and mixed well. After 20 min, the absorbances were measured at 480 and 610 m with a 2-cm cell against a reagent blank without Fe; then, A_c of the ternary complex was calculated. For analysis of a solid sample, first its aqueous solution must be prepared as follows: pulverize 1 g of a sample, add it to a mixture of 5 mL of nitric acid and 5 mL of 5% hydroxylamine hydrochloride for 2 h, volatile the excessive nitric acid and hydroxylamine hydrochloride by boiling and, finally, neutralized to pH 6–7 with 5% NaOH and filter. Then, the filtrate was diluted to 100 mL with deionized water and colored and measured according to the same procedure as given above.

RESULTS AND DISCUSSION

Spectral Analysis

Interaction of Eriochrome Blue Black R with Cetyltrimethylammonium Bromide

The absorption spectra of the EBBR, CTAB–EBBR, and Fe–EBBR–CTAB solutions, recorded at pH 6.5, are shown in Fig. 2. From curve 1, the absorbance ratio of the CTAB–EBBR solution measured at 530 and 630 nm approaches a minimum when the molar ratio of CTAB to EBBR is over 5. In such solutions, all EBBR may be adsorbed by CTAB. Curve 3 gives the absorption spectrum of such a solution. From curves 2 and 3, the peak of the EBBR solution is located at 550 nm and that of the aggregate at 610 nm. The spectral red shift of the aggregate is 60 nm. However, from the relative spectrum 4, the peak and valley of the CTAB–EBBR solution against EBBR are located at 530 and 630 nm; such two wavelengths were used in the study of the adsorption interaction. From curves 2 and 3, the correction constants were calculated to be $\beta_1 = 0.376$ and $\alpha_1 = 0.842$. Therefore, the real absorbance of the CTAB–EBBR aggregate was calculated by $A_c = 1.46(\Delta A - 0.376\Delta A')$.

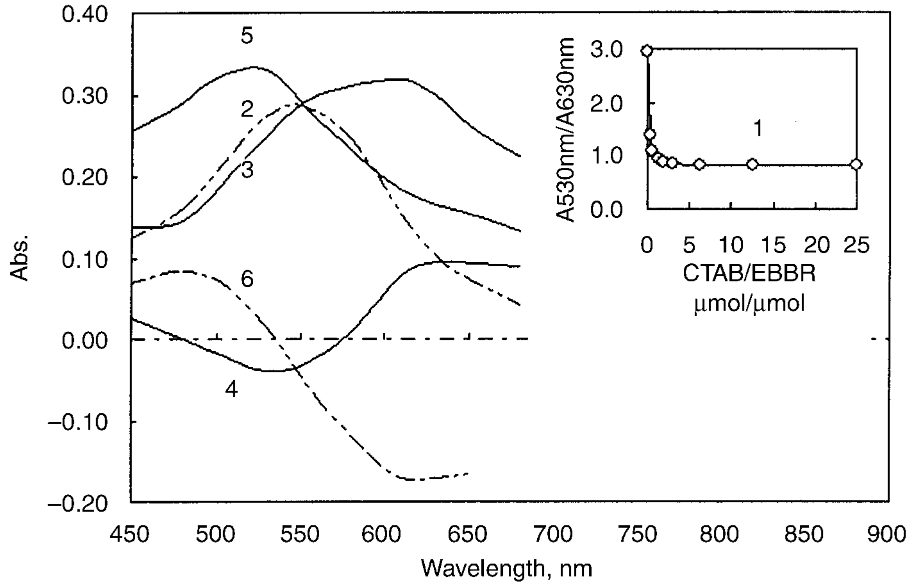


Figure 2. Absorption spectra of EBBR, EBBR–CTAB and Fe–EBBR–CTAB solutions at pH 6.5: 1, variation of A_{530nm} and A_{630nm} of the EBBR–CTAB solutions with increase in CTAB (between 0 and 40 μmol) which all contain 1.60 μmol of EBBR–CTAB (2 μmol); 2, EBBR (1.60 μmol) solution against water; 3, EBBR–CTAB adsorption aggregate (1.60 μmol) no containing free EBBR against water; 4, EBBR (1.60 μmol)–CTAB (0.50 μmol) solution against a reagent blank; 5, EBBR (0.80 μmol)–CTAB–Fe (6.0 μmol) complex solution containing no free EBBR–CTAB aggregate against water and 6, EBBR (2 μmol)–CTAB–Fe (5 μg) solution against a reagent blank. Curves 1–4 using 1-cm cell and the others using 2-cm cell.

Coordination Between Cetyltrimethylammonium Bromide–Eriochrome Blue Black R Product and Fe(II)

In the solution containing 0.400 mM EBBR and 4.50 mM CTAB at pH 6.5, the CTAB–EBBR aggregate was formed in solution and no free EBBR remained. Such a solution of 200 mL was prepared for complexing Fe(II), which is described in the Experimental section. From curve 5 in Fig. 2, the peak of the ternary complex is located at 510 nm. The spectral violet shift of the complex is 100 nm. From the relative spectrum 6, the peak and valley of the CTAB–EBBR–Fe(II) solution are located at 480 and 610 nm; such two wavelengths were used in the quantitative determination of Fe traces. From curves 2 and 5, the correction constants were calculated to be $\beta_2 = 0.452$ and $\alpha_2 = 0.628$. Therefore, the real absorbance of the ternary complex was calculated by $A_c = 1.40$ $(\Delta A - 0.452\Delta A')$.

Effect of pH

By varying pH of the solution, the absorbances of the CTAB–EBBR solutions were measured and the result is shown in Fig. 3. The increase of pH causes an increase of the absorbances. This is attributed to the fact that $EBBR^{2-}$ upto $EBBR^{3-}$ will be formed in basic medium, which is described in the Introduction section; the multivalent anion is easy to bind onto CTAB. However, many metal ions, e.g., Ca(II), Mg(II), Zn(II), Cd(II), Cu(II), and Mn(II) can complex EBBR sensitively in basic medium; so, the selectivity becomes poor. In this work, pH 6.5 buffer solution was added.

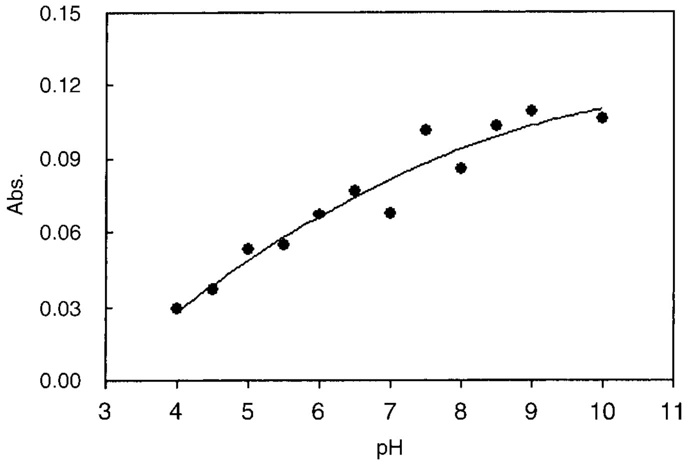


Figure 3. Effect of pH on the absorbance of the EBBR–CTAB solution all containing 1.60 μmol of EBBR and 0.500 μmol of CTAB, measured at 630 nm against the reagent blanks.

Effect of Ionic Strength and Temperature

In order to study the effect of ionic strength on the adsorption of EBBR on CTAB, 5 M NaCl was added. Its effect on the binding ratio of EBBR to CTAB is shown in Fig. 4. From curve 1, the binding ratio of EBBR to CTAB decreases with an increase in ionic strength of a solution between 0 and 2 M. This is attributed to the fact that much more Cl^- than EBBR was attracted onto CTAB to replace EBBR.

At various temperatures, the binding ratio of EBBR to CTAB is shown in Fig. 4. From curve 2, we can see that the ratio decreases with an increase in temperature, especially over 40°C. The ratio of EBBR to CTAB decreases by 10% per 10°C increase. This is attributed to the fact that a high temperature will result in the rapid desorption of EBBR from the EBBR–CTAB aggregate.

Effect of Time

At 15°C, the effect of time on the absorption of the CTAB–EBBR solution and that of the Fe–CTAB–EBBR complex solution are shown in Fig. 5. From curves 1 and 2, the absorbance of the adsorption product approaches a maximum and then remains almost constant after 10 min. Similarly, from curves 3 and 4, the absorbance of the ternary complex remains constant after 20 min. The absorption measurement of the adsorption solution was carried out after 10 min and that of the ternary complex solution after 20 min.

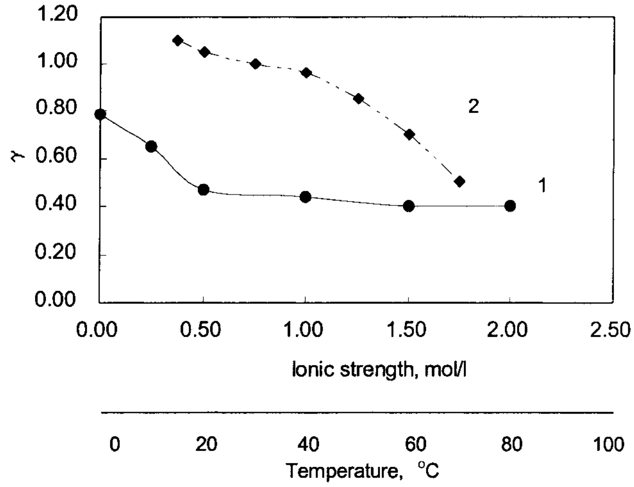


Figure 4. Effect of ionic strength (1) and temperature (2) on the binding ratio (γ) of EBBR to CTAB 1, solution containing 0.80 μmol of EBBR and 1 μmol of CTAB and 2, solution containing 1.60 μmol of EBBR and 0.500 μmol of CTAB.

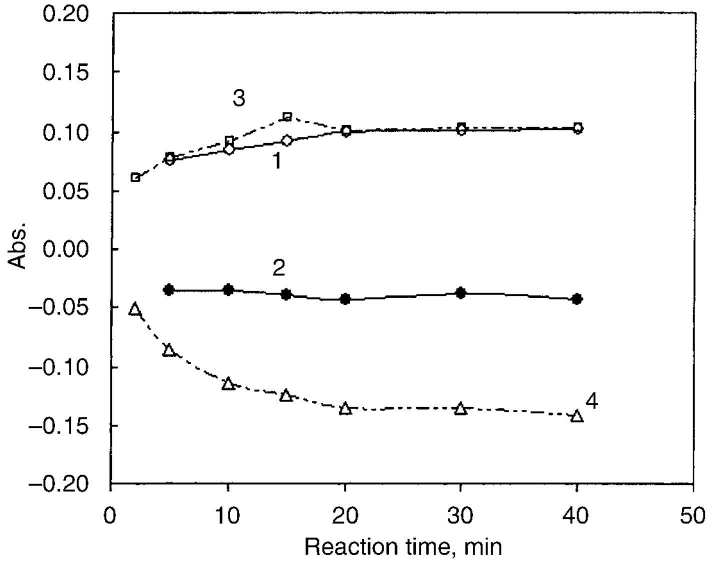


Figure 5. Effect of the reaction time on the absorbances of the EBBR–CTAB solution (1, at 630 nm and 2, at 530 nm) solution containing 0.80 μmol of EBBR and 1.00 μmol of CTAB and those of Fe–EBBR–CTAB solutions (3, at 480 nm and 4, at 610 nm; solution containing 2 μmol of EBBR in the EBBR–CTAB aggregate and 5 μg of Fe). Both against the reagent blank without CTAB. Both 1 and 2 using 1-cm cell and the others using 2-cm cell.

Effect of Eriochrome Blue Black R on Aggregation

Adsorption of Eriochrome Blue Black R on Cetyltrimethylammonium Bromide

The absorbances of the EBBR–CTAB solutions were measured by varying the EBBR concentration. Both C_L and γ of each were calculated and their relationship is shown in Fig. 6. Plots C_L^{-1} vs. γ^{-1} are linear. The binding of EBBR on CTAB obeys the Langmuir adsorption isotherm in only one monolayer. From the linear intercept, the maximal binding number of EBBR on CTAB was calculated to be $N = 3$ and the binding constant of the aggregate to be $K = 3.14 \times 10^4\,\mathrm{L\,mol^{-1}}$ from the slope of the line. The monomer aggregate is $EBBR_3CTAB$ and the maximal aggregate $(EBBR_3CTAB)_{78}$ only when CTAB is more than its CMC at 0.96 mM and EBBR is enough. In addition, the real (not apparent) molar absorptivity of $(EBBR_3CTAB)_{78}$ was calculated to be $\varepsilon_r^{630\mathrm{nm}} = 1.10 \times 10^6\,\mathrm{L\,mol^{-1}\,cm^{-1}}$.

Complexation Between Eriochrome Blue Black R–Cetyltrimethylammonium Bromide Aggregate and Fe(II)

By varying the addition of the EBBR–CTAB aggregate solution prepared in the Experimental section, which contained 0.400 mM EBBR, the complexation solutions were measured. The effective fraction of L, η of the EBBR–CTAB aggregate and the molar

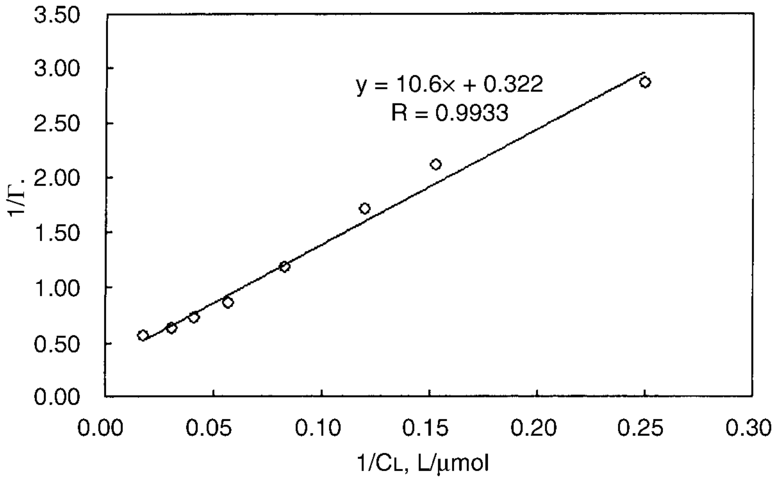


Figure 6. Plot γ^{-1} vs. C_L^{-1} (C_L, μmol/L).

ratio of L, γ of EBBR to Fe were calculated and their curves are shown in Fig. 7. From curve 2, γ approaches a maximum at 6 when the addition of the EBBR–CTAB aggregate solution is more than 3 mL. Therefore, the ternary complex Fe · $EBBR_6CTAB_{78}$ was formed. In the quantitative detection of iron in samples, 5 mL of the EBBR–CTAB aggregate solution was added. From curve 1, the effective EBBR–CTAB aggregate was only 27% of addition of the EBBR–CTAB aggregate. So, 73% of EBBR–CTAB aggregate is free in solution. Beyond all doubt, excessive aggregate certainly affected the absorbance measurement of the ternary complex.

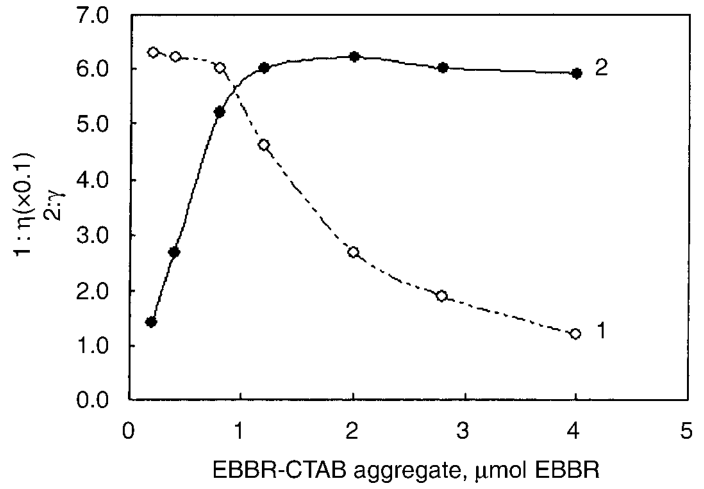


Figure 7. Effect of addition of the EBBR–CTAB aggregate on η (1) and γ (2) of EBBR to Fe (solution containing 5 μg of Fe at pH 6.5).

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In the determination of the formation constants, the spectral correction method is simple in operation and understandable in principle by comparison with the classical methods such as continuous variations,[30] etc.

Application to Determination of Fe Traces

According to the recommended procedures, the standard series of iron solutions were prepared and measured at pH 6.5 with the EBBR–CTAB aggregate as reactant and in the presence of the recommended masking reagent. The standard curves are shown in Fig. 8. Curve 1 is more linear, with a higher slope than curve 2. The regression equation of curve 1 is: $A_c = 0.0357x + 0.005$ (x-Fe, μg); it was used in the quantitative determination of Fe (II, III). From the slopes of the curves, the molar absorptivity of the complex was calculated to be $\varepsilon_{\text{real}}^{480\text{nm}} = 2.50 \times 10^4\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$ and $\varepsilon_{\text{apparent}}^{480\text{nm}} = 0.924 \times 10^4\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$. So, the correction method has much higher sensitivity than ordinary spectrophotometry. Six replicated determinations of 1 and 8 μg of standard Fe(II) gave a RSD 3.6% and 1.3% for the correction method, but RSD = 8.6 and 5.5% for ordinary spectrophotometry. So, the correction technique has a higher precision than ordinary spectrophotometry. The limit of detection (LOD) for $A_c = 0.010$ was calculated to be 0.30 μg of Fe in 25 mL of solution.

By adding the masking reagent into the blank, i.e., CTAB–EBBR solution without Fe, the experimental result indicated that the formation of the CTAB–EBBR aggregate was not affected. In the CTAB–EBBR–Fe solution, none of the following ions affected

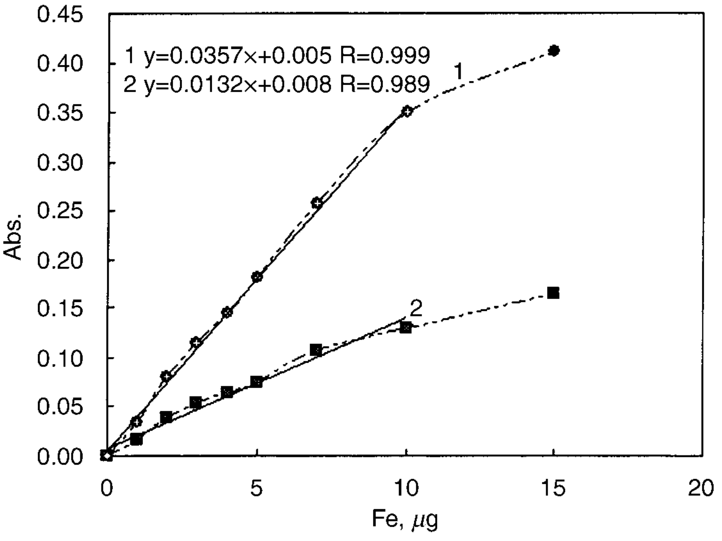

Figure 8. Standard curves for the determination of iron at 480 nm using 2-cm cell: 1, real absorbance (A_c) and 2, measured absorbance (ΔA).

the direct determination of 5 μg of Fe(II) (error less than 10%): 1 mg of alkaline metals, 0.5 mg of alkaline earths and common anions, e.g., Cl^-, SO_4^{2-}, F^-, NH_4^+, PO_4^{3-}, and NO_3^-; 0.1 mg of Zn(II), Pb(II), Al(III), Sn(II), Sb(III), As(III), and 0.05 mg of Ni(II), Cu(II), Mn(II), Co(II), Cd(II), Hg(II), Y(III), and Ce(III).

Four typical water samples were determined. Sample 1 was sampled from the Huaihe River, sample 2 from a local sewage pipe, sample 3 indicated 2% spinach, and sample 4 was 1% milk powder. Initially, drops of standard Fe(II) solution were added into samples 1 and 2. The determination results of samples are listed in Table 1. The recovery of Fe added is between 92.0% and 110% and the RSD is less than 5.70%. The determination of Fe in samples was carried and evaluated by AAS and its result is also listed in Table 1. The two methods give the same mean iron levels in samples.

Table 1. Determination of iron in samples.

Sample no.	Added	Found	Recovery (%)
1 (mg/l)	0.000	1.32, 1.38 1.44, 1.42 1.37, 1.42 Average 1.39 (1.31[a]) RSD 3.17%	
	1.00	2.31 (average for two determinations)	92.0
2 (mg/l)	0.000	4.71, 4.88 4.73, 4.91 4.82, 4.84 Average 4.81 (5.11[a]) RSD 1.67%	
	5.00	10.2 (average for two determinations)	108
3 (mg/g)	0.000	0.072, 0.084 0.075, 0.075 0.078, 0.081 Average 0.078 (0.069[a]) RSD 5.70%	
	0.050	0.133 (average for two determinations)	110
4 (mg/g)	0.000	0.104, 0.113 0.109, 0.114 0.101, 0.103 Average 0.107 (0.122[a]) RSD 4.64%	
	0.100	0.205 (average for two determinations)	98.0

[a] Average for 3 determinations by AAS.

CONCLUSION

This investigation of the EBBR–CTAB–Fe ternary reaction indicates that the CTAB micelle provides the complexation between Fe and EBBR with a catalytic field. EBBR is enriched on CTAB micelle by a non-covalent connection, e.g., electrostatic attraction, hydrogen bonding, hydrophobic bonding, and winding. This explains, reasonably, the solubilization of organic molecules in aqueous solution. Because the EBBR concentration in the micellar phase of CTAB is much more that in the absence of CTAB, the addition of Fe(II) will coordinate EBBR binding on micelle easily and rapidly. Its application to the spectrophotometric determination of iron is sensitive with an LOD at only 0.012 mg/L. The basic physics was described behind the combination of the Langmuir aggregation and spectral correction technique and surveyed some ongoing research on application to a dye ligand/surfactant/metal system.

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