Langmuir Aggregation of Bordeaux R on a Cationic Surfactant and Its Application to Sensitive Quantitative Determination of Copper

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The microphase adsorption-spectral correction (MPASC) technique has been applied to the study of the interaction between cetyl trimethylammonium bromide (CTMAB) and the dye Bordeaux R (BR) at pH 9.6. The aggregation of BR on the CTMAB surface obeys the Langmuir adsorption isotherm. The aggregation of BR on CTMAB accelerates the complexation between Cu(II) and BR. Results at 25°C show that the adsorption constant of the CTMAB–BR 1:1 aggregate is 6.80×10^4. In the presence of CMTAB, the Cu–Br complex with a mole ratio of 2:1 has a cumulative stability constant of 1.08×10^{11}. The cooperative adsorption and complexation have been applied successfully in a sensitive determination of trace amounts of copper.

1. INTRODUCTION

Currently there is increasing interest in research on supramolecular chemistry: for example, biomacromolecules, surfactant micelles, and polymers. In supersensitive analysis for trace components, especially by spectrometry,[1–3] the use of a surfactant is often necessary. Models have been proposed to explain synergistic effects of surfactants (solubilization, stabilization, enchanced sensitivity, etc.) in processes such as micelle extraction,[4] synergistic perturbation,[5] electric-field aggregation,[6] hydrogen bond formation,[7] micellar catalysis,[8] and formation of asymmetric microenvironments.[9]

The interaction of an ionic surfactant with a dye often occurs much like precipitation stain adsorption. A surfactant molecule typically has a long alkyl chain and

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(1) Surfactant (S) monomer (cationic surfactant as an example)
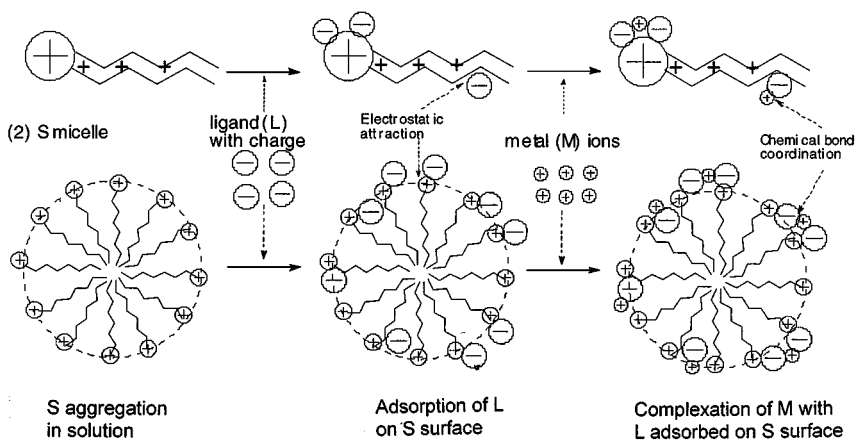
Fig. 1. (1) Adsorption of ligand (L) molecules on surfactant (S) monomer; (2) adsorption of L on the micelle surface and sensitive complexation of metal (M) with L adsorbed on S.

exhibits various aggregation forms in aqueous solution: *e.g.*, spherical, wormlike, tubular, and lamellar.[10] In a surfactant (S) solution, the aggregation of S molecules will form a globular micelle (Fig. 1, left) when the concentration of S is above the critical micelle concentration (CMC). The electrostatic attraction of a ligand (L) with opposite charge causes the ligand to aggregate in the micelle until kinetic equilibrium (Fig. 1, middle) is attained. Thus L is solubilized in the S solution. The addition of metal ions (M) will cause a sensitive complexation of M with L adsorbed in the micelle phase (Fig. 1, right). Because the concentration of L in the micelle phase is much higher than in the aqueous phase, the complexation reaction is quite rapid. Like a catalyst carrier, the presence of the micelle facilitates the M-L complexation. This causes enhancement of the sensitivity. Similarly, electrostatic adsorption of L at the surface of the S monomer can occur when the concentration of S is less than the CMC [Fig. 1 (1)].

The aggregation of L on the S surface is in the form of a monolayer.[11] The adsorption obeys the Langmuir isotherm[12] so that an equilibrium is established between free L in the L–S solution and L in the aggregate SL_N. The Langmuir equation is

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

where K is the equilibrium constant, C_L is the concentration of unadsorbed L, and γ is the moles of L adsorbed per mole of S. With increasing concentration of L, γ approaches a maximum, called the adsorption ratio N. The dependence of C_L^{-1} *vs.* γ^{-1} is linear and, from this, we may calculate N and K. C_L and γ are calculated

by means of the following equations[13,14]

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

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

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

where C_S and C_{L0} are, respectively, the concentrations of S and of L added initially, and η denotes the effective fraction of L adsorbed. A_C, A_0, and ΔA are, respectively, the true optical absorbances of the S–L aggregate, the measured absorbance of the reagent blank against water, and that of the S–L solution against the reagent blank measured directly at the peak wavelength λ_2. A_c is calculated by means of[14]

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

where $\Delta A'$ indicates the absorbance of the S–L solution measured at the valley absorption wavelength λ_1. In general, α and β are correction constants, which are calculated by directly measuring solutions of SL_N and of L.[15] In addition, the true absorptivity $\varepsilon_r^{\lambda_2}$ (not the apparent quantity $\varepsilon_a^{\lambda_2}$) of the adsorption aggregate SL_N at λ_2 is also directly calculated using the equation

$$\varepsilon_r^{\lambda_2} = \frac{mNA_C}{\delta\gamma C_S} \tag{6}$$

where m is the micelle number and δ is the cell thickness (cm).

The following equation[15] has been established for the calculation of the nth step stability constant K_n of the metal complex ML_N

$$K_n = \frac{\gamma + 1 - n}{(n - \gamma)(C_L - \gamma C_M)} \tag{7}$$

where n indicates the step number of the complex and the other symbols have the meanings given above. The cumulative constant K of the complex ML_N is calculated as: $K = K_1 \times K_2 \times \ldots \times K_n \ldots \times K_\gamma$. The nth step true (not apparent) absorptivity $\varepsilon_{ML_n}^{\lambda_2}$ of the metal complex or surfactant-dye product ML_N is formulated as follows

$$\varepsilon_{ML_n}^{\lambda_2} = \frac{A_C}{\delta C_M(\gamma' + 1 - n)} - \frac{n - \gamma'}{\gamma' + 1 - n}\varepsilon_{ML_{n-1}} \tag{8}$$

where $\varepsilon_{ML_{n-1}}^{\lambda_2}$ indicates the $(n - 1)$th step absorptivity of complex ML_N.

The cooperative character of Langmuir adsorption and complexation provides a very helpful experimental strategy for study of a ternary complex in the presence of a surfactant. It clearly provides a the synergistic mechanism for complexation in a surfactant solution. In this work, we have specifically studied the interaction of
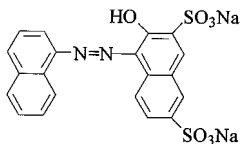
Fig. 2. Structure of Bordeaux R.

the cationic surfactant CTMAB with the dye Bordeaux R (BR) at pH 9.6 and then the complexation between the CTMAB–BR aggregate and Cu(II). The structure of BR is given in Fig. 2. It forms anions and is adsorbed on the CTMAB surface. Quantitative results derived from spectrophotometric measurements are discussed below.

2. EXPERIMENTAL

2.1. Apparatus and Reagents

Absorption spectra were recorded on UV/VIS 265 Spectrophotometer (Shimadzu, Japan) Absorbances were also measured independently on a Model 722 spectrophotometer. The pH of solutions was measured with a pHS-2C acidity meter (Leici Instrument, Shanghai) and a Model 630D pH Pen (Shanghai Ren's Electric Co. Ltd.). The temperature was maintained constant by an electrically heated thermostat bath, Model 116R (Changjiang Test Instruments, Tongjiang, China).

CTMAB (1.00 mmol-L^{-1}) and Cu(II) (10.0 mg-L^{-1}) solutions were prepared as stock solutions. The dye solution, 1.00 mmol-L^{-1} BR was prepared by dissolving 0.3590 g of dye, BR content 70% (purchased form Shanghai Chemical Reagents Supply) in 500 ml of deionized water. The borax–boric acid buffer solutions (between pH 6 and 11.4) and 1.00 mol-L^{-1} NaOH solution were used to control the acidity of the solution. All reagents were of analytical grade and were used without further purification.

2.2. General Procedures

Into a 25-ml calibrated flask were added 1.0 μmol of standard CTMAB or 20 μg of copper [as Cu(II) salt], 2.5 ml of buffer solution, and 1.00 mL of 1.00 mmol-L^{-1} BR solution. The mixture was then diluted with deionized water to 25 ml and mixed thoroughly. After 10 min, absorbances were measured at 520 and 630 nm (CTMAB solution) or 520 and 450 nm (Cu solution), respectively, against a blank treated in the same way without CTMAB or copper. Then the absorbance A_c of the product was calculated according to Eq. (1).

3. RESULTS AND DISCUSSION

3.1. Absorption Spectra

Absorption spectra of CTMAB–BR solutions at several pH values are shown in Fig. 3. The peak and valley are located at 630 and 520 nm from curves 1–4, curve 2 giving the highest absorbance. Curve 5 is the spectrum of the Cu–BR solution at pH 9.6. From spectra 6, 7, and 8 of BR, CTMAB–BR product, and Cu–BR complex, we observe that the respective peak absorbances are at 520, 510, and 500 nm. Relative to BR, the spectral violet shifts for CTMAB–BR aggregate and for Cu–BR complex are thus only 10 and 20 nm. From curves 2 and 5, the two wavelengths 520 and 630 nm were used in the analysis of CTMAB–BR solution, and both 520 and 450 nm used in the analysis of Cu–BR solutions. The inset b in Fig. 3 shows the variation of the absorbance ratio of the CTMAB–BR solutions measured at 520 and 630 nm at pH 9.6 with the CTMAB:BR mole ratio. We
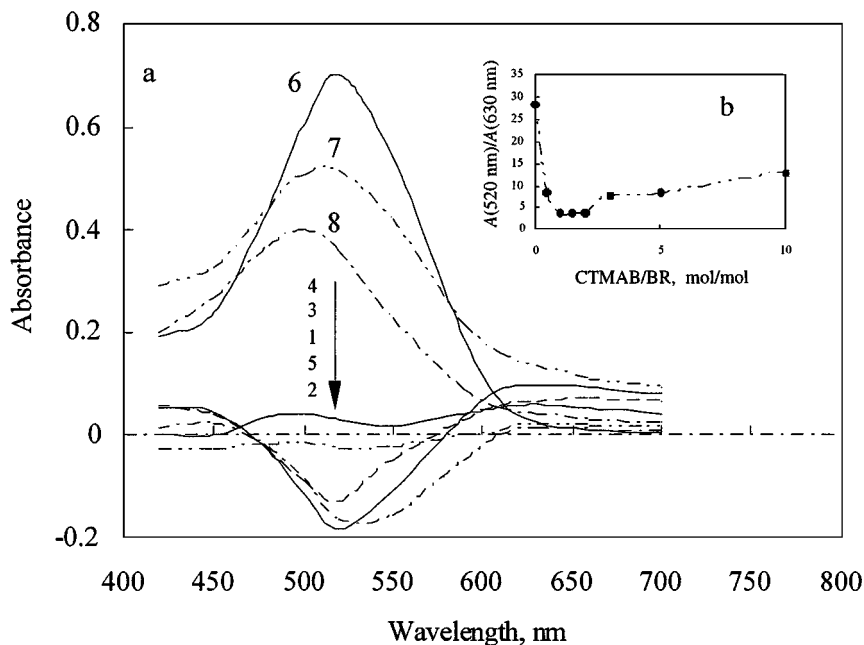

Fig. 3. (a) Absorption spectra of BR, BR–CTMAB, and Cu–BR solutions at pH 9.6. Spectrum 1: 1.00 μmol BR + 1.00 μmol CTMAB at pH 7.2; spectra 2, 3, and 4: same as 1 but at pH 9.6, 11.4, and 13, respectively; spectrum 5: 1.00 μmol BR + 20 μg Cu at pH 9.6; spectrum 6: 1.00 μmol BR; spectrum 7: 1.00 μmol BR + 2.00 μmol CTMAB; spectrum 8: 1.00 μmol BR + 500 μg Cu; spectra 6, 7, and 8 against water; the others against the reagent blank. All amounts refer to 25 mL of solution. Inset (b): effect of mole ratio of CTMAB to BR on the ratio of absorbances of solution measured at 520 and 630 nm.

see that the ratio reaches a minimum when CTMAB molarity is between 1 and 2 times that of BR. Therefore, a solution containing 1.5 μmol of CTMAB and 1.00 μmol of BR no longer contains free BR. Curve 7 gives the spectrum of the CTMAB–BR aggregate. From curves 6, 7, and 8, the correction coefficients were calculated as $\beta_1 = 0.034$ and $\alpha_1 = 3.83$ in CTMAB–BR solution, and $\beta_2 = 0.341$ and $\alpha_2 = 1.34$ in Cu–BR solution. Therefore, the true absorbance of the CTMAB–BR adsorption product was calculated as $A_c = 1.15(\Delta A - 0.031\Delta A')$ and the true absorbance of the Cu–BR complex in the presence of CTMAB by $A_c = 1.84(\Delta A - 0.341\Delta A')$.

3.2. Effects of pH, Temperature, and Reaction Time

The absorption of CTMAB–BR and Cu–BR solutions was measured as the pH was varied. The effect of pH on the adsorption ratio of BR to CTMAB is shown in Fig 4. We observe that little adsorption occurs in both acidic and strongly basic solution. Between pH 8.8 and 10.4, the adsorption ratio approaches
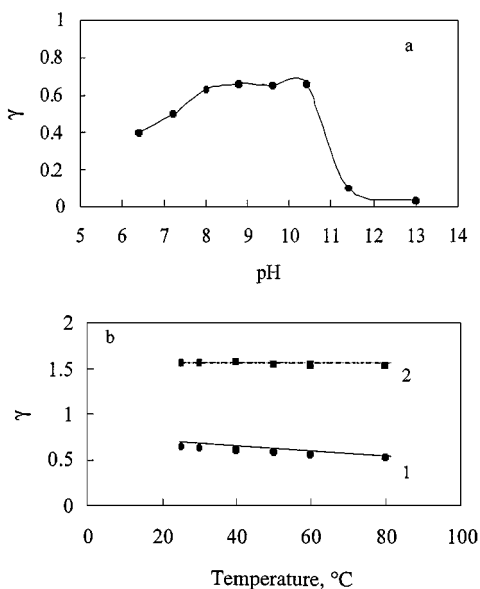
Fig. 4. (a) Effect of pH on γ of solution containing 1.00 μmol BR + 1.00 μmol CTMAB. (b) Effect of temperature on γ for CTMAB–BR interaction in solution containing 1.00 μmol BR + 1.00 μmol CTMAB (plot 1), and for Cu–BR complexation in solution with 1.00 μmol BR + 20 μg Cu (plot 2). All amounts refer to 25 mL of solution.

a maximum. This is attributed to the formation of the ion BR^{2-}, which is strongly attracted by the microelectrostatic fields of CTMAB monomer or the micelle.

The adsorption of BR on CTMAB and the coordination reaction between the BR–CTMAB aggregate and Cu(II) were investigated at pH 9.6. The BR:CTMAB adsorption ratio and the Cu:Br ratio in the Cu–Br complex are shown as functions of temperature in Fig. 4b. From curve 1, the BR:CTMAB ratio is seen to decrease about 10% per 10°C increase between 25 and 80°C. This is in accord with the common nature of a surface adsorption. The Cu:Br ratio is almost invariant with temperature.

AT 25°C, both the adsorption and the coordination at pH 9.6 are complete in 10 min. The absorbance measurement was carried out after coloring for 10 min.

3.3. Effect of BR Concentration

3.3.1. Adsorption Interaction between BR and CTMAB

The optical absorbances of CTMAB solutions were measured for various amounts of added 1.00 mmol-L^{-1} BR solution. The resulting values of C_L and γ are plotted as $1/\gamma$ vs. $1/C_L$ in Fig. 5. The linear plot shows that the adsorption of BR on CTMAB obeys the Langmuir monolayer adsorption isotherm. The regression equation is: $\gamma^{-1} = 1.01 + 14.7 \, C_L^{-1}$, with C_L in μmol-L^{-1}; the linear correlation coefficient is $R = 0.975$. From the intercept, the limiting adsorption ratio of BR to CTMAB is calculated to be 1.0. Therefore, if the aggregate is written as: $(BR \cdot CTMAB)_m$, m is 1 when the CTMAB concentration is less than the CMC of 0.96 mmol-L^{-1} and m is 78 when the CTMAB concentration is greater then the CMC. From the slope, the adsorption constant K of the monomer aggregate is
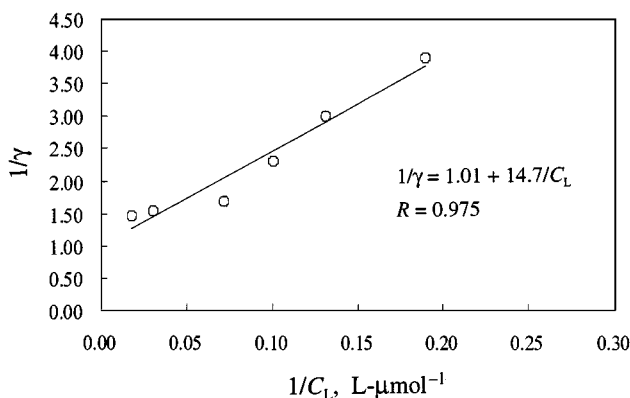

Fig. 5. Relation between the binding ratio γ of adsorption product and molarity of free BR (C_L, μmol-L^{-1}) in BR–CTMAB solution at pH 9.6.

6.80×10^4 at 25°C. In addition, the true (not apparent) molar absorptivity $\varepsilon_r^{\lambda_2}$ of the micellar aggregate (BR ● CTMAB)$_{78}$ is determined to be 2.92×10^5 L-mol^{-1}cm^{-1} at 630 nm.

3.3.2. Coordination Reaction between BR and Cu(II) in the Presence of CTMAB

Different amounts of 1.00 mmol-L^{-1} BR solution were added to CTMAB solutions containing 20 μg Cu(II). Using the spectrophotometric data, η and γ for these solutions were calculated and the resulting curves are shown in Fig. 6. The composition ratio γ for Cu:Br approaches a maximum of 2 when more than 1.5 mL of the BR solution is added. Therefore, the final aggregate is Cu BR$_2$ · CTMAB$_2$ when the CTMAB concentration is below the CMC and (Cu BR$_2$ · CTMAB$_2$)$_{39}$ when the CTMAB concentration is above the CMC.

For quantitative determination of copper, 1.0 ml of 1.00 mmol-L^{-1} BR solution was added. From Fig. 6a, we see that only 49% of the BR is complexed with this amount of BR, so that further addition of BR will affect the measured absorbance of the final complex. Two solutions were prepared for the determination of the stability constant K and the true absorptivity ε of the Cu–BR complex: (1) 20.0 μg of Cu(II) with 0.250 μmol BR and (2) 20.0 μg of Cu(II) with 0.750 μmol of BR.
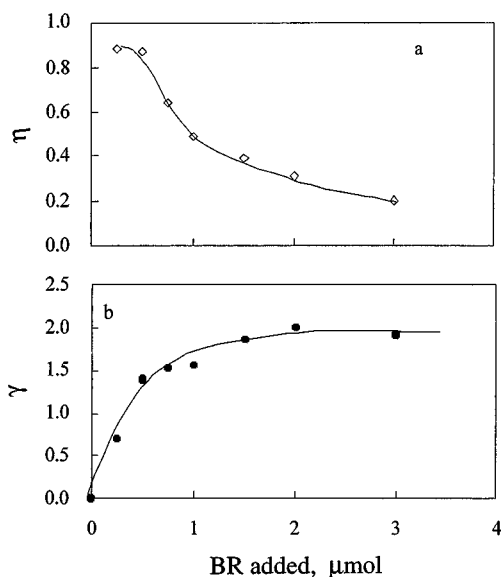
Fig. 6. Effect of addition of BR on (a) η of BR and (b) γ of the Cu–BR complex in BR–CTMAB solution at pH 9.6 containing 20 μg Cu per 25 mL.

Four replicate determinations for each case showed that $A_c(1) = 0.068 \pm 0.003$, $\gamma(1) = 0.668 \pm 0.024$, and $A_c(2) = 0.140 \pm 0.005$, $\gamma(2) = 1.50 \pm 0.028$. The calculated stepwise stability constants of the Cu–BR complex were $K_1 = 1.22 \times 10^6$ and $K_2 = 8.89 \times 10^4$ at 25°C, so that $K = K_1 K_2 = 1.08 \times 10^{11}$. The absorptivities are $\varepsilon_1 = 8.13 \times 10^3$ and $\varepsilon_2 = 1.43 \times 10^4$ L-mol^{-1}-cm^{-1} at 450 nm. In the determination of these parameters, the spectral correction method is an advance in principle and in practice over the classical methods using the Scatchard model,[16] mole ratios,[17] continuous variation,[18] or equilibrium shifting.[19]

3.4. Quantitative Determination of Cationic Surfactant and Copper

3.4.1. Calibration Graph

Standard series of CTMAB and Cu(II) solutions were prepared and measured at pH 9.6. Their regression equations are: $A_c = 0.138x - 0.01$ (x-μmol CTMAB) with a linear correlation coefficient $R = 0.9972$), and $A_c = 0.00673x - 0.003$ (x-μg Cu) with $R = 0.9994$. This shows that the spectral correction method gives better accuracy and higher sensitivity than ordinary spectrophotometry. The detection limit is 0.1 μmol of cationic surfactant and 1.5 μg of Cu in 25 ml of solution.

3.4.2. Effects of Foreign Ions

In the absence of a masking reagent, foreign substances such as positive and negative ions and organic compounds hardly affected the direct determination of CTMAB and Cu. There was less than 10% error for the following amounts in 25 mL of solution: 2 mg of Cl$^-$, F$^-$, Ac$^-$, C$_2$O$_4^{2-}$, Triton X-100, SDBS, amino acid, Ca(II), Mg(II); 0.5 mg of NH$_4^+$, I$^-$, Al(III), Mn(II), Ti(IV), Ni(II); 0.2 mg of acetone, Cu(II), Co(II), Cd(II), Zn(II), Pb(II), Fe(III).

3.4.3. Samples Analyzed

Three samples were analyzed: sample 1, water from the Huaihe River; sample 2 from sewage; and sample 3 prepared in the laboratory. The results showed that the recovery of CTMAB and copper is between 93.6 and 102% and between 96.8 and 110%, respectively, with relative standard deviations (RSD) 4.6 and 3.1%.

4. CONCLUSION

The interaction of BR with CTMAB is found to conform to the Langmuir adsorption of BR on the surfactant molecular surface, due presumably to electrostatic attraction. The concentration of the dye on micelle accelerates its dissolution and coordination with a metal. We have described the basic physics behind

the cooperative effects of the Langmuir aggregation and complexation and discussed some ongoing research on application to a stain/surfactant/metal system. We believe that classical spectrophotometry can still play an important role in studies to explain the synergism of a surfactant in the quantitative determination of trace components in solution.

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