

Aggregation of a Dye on a Surfactant: Interaction of Coomassie Brilliant Blue G250 with Cetyltrimethylammonium Bromide and Determination of the Cationic Surfactant in Water

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ABSTRACT

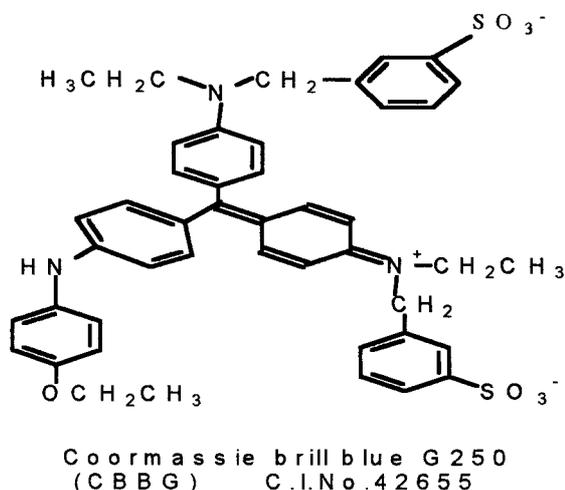
The interaction of Coomassie brilliant blue G250 (CBBG) with cetyltrimethylammonium bromide (CTAB) has been investigated at pH 9.50 by the microsurface binding-spectral correction (MSASC) technique. The experiments confirmed that the aggregation of CBBG on CTAB obeys the Langmuir isothermal adsorption. The aggregate was characterized. Results showed that the monomer aggregate, CBBG₂CTAB was formed at 30°C with a binding constant of 6.46×10^3 . The aggregation was applied to the quantitative determination of the cationic surfactant in water samples with satisfactory results.

Key Words: Langmuir aggregation; Coomassie brilliant blue G250; Cetyltrimethylammonium bromide; Determination of cationic surfactant.

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INTRODUCTION

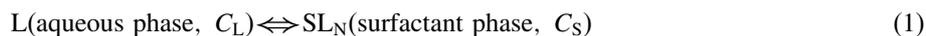
In trace analysis, a surfactant is often used to increase the reaction sensitivity because of its synergism function. Some earlier mechanisms^[1-3] have been applied to explain the synergism between others, micelle extraction, synergism perturbation, electrostatic field aggregate, hydrogen bond formation, micelle catalysis, asymmetric microenvironment. In the present work, a novel method named a microsurface binding-spectral correction (MSASC) technique^[4-6] was applied, instead of those above to investigate the interaction between a surfactant and small molecules or ions. The aggregation of Coomassie brilliant blue G250 (CBBG) on cetyltrimethylammonium bromide (CTAB) was selected as an example. The structure of the dye is given below:



It forms a bivalent anion in aqueous solution that can be adsorbed on CTAB. The dye is often used in the quantitative detection of protein^[7,8] with high sensitivity. Results showed that the aggregation obeys the Langmuir monolayer adsorption. The binding ratio of CTAB to CBBG is 1 : 2 at 30°C. The analysis of the samples showed that the mean recovery of standard CTAB is between 100% and 105% and the relative standard deviation (RSD) is less than 9.3%.

PRINCIPLE AND CALCULATION

In a surfactant (S) solution, the aggregation of dye molecules (L) on S occurs to reach the equilibrium:



The following Langmuir isothermal adsorption equation is used:^[9]

$$\frac{1}{\gamma} = \frac{1}{N} + \frac{1}{KNC_L} \tag{2}$$



where K is the binding constant, C_L the molarity of the excess L and γ the molar ratio of L adsorbed onto S. With the increase in L concentration, γ approaches the maximal aggregation number, N . Plot γ^{-1} vs. C_L^{-1} should be linear and both N and K may be calculated. In the equation above, C_L and γ are calculated by the relations:^[10–12]

$$\gamma = \eta \times \frac{C_{L0}}{C_S} \quad (3)$$

$$C_L = (1 - \eta)C_{L0} \quad (4)$$

where

$$\eta = \frac{A_c - \Delta A}{A_0} \quad (5)$$

where C_S and C_{L0} 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 aggregate, the absorbance of L solution 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 means of:^[13]

$$A_c = \frac{\Delta A - \beta \Delta A'}{1 - \alpha \beta} \quad (6)$$

where $\Delta A'$ indicates the absorbance of the S–L solution measured at the valley absorption wavelength λ_1 . Both α and β are correction constants.^[12,13]

EXPERIMENTAL

Apparatus and Materials

Absorption spectra were recorded on a TU 1901 Spectrophotometer (PGeneral, Beijing). The pH of solutions was measured on a PHS-2C acidity meter (Leici Instruments, Shanghai). The temperature was adjusted and remained constant in an electrically heated thermostatic bath, Model 116R (Changjiang Test Instruments of Tongjiang, China).

Preparation of Solutions

Standard CTAB solution, 1.00 mM was prepared by dissolving CTAB (A. R., Beijing Chemical Reagents, Beijing, China) in deionized water and further diluted. The CBBG solution, 1.00 mM was prepared by dissolving 0.2134 g of CBBG (content 90%, Shanghai Chemical Reagents Supply Center of Chinese Medicines, Shanghai, China) in 250 mL of DMF. The acetate and ammonium buffer solutions between pH 4.10 and 9.96 were prepared to adjust the acidity of the interaction solution. NaCl (2.0 mol/L) was used to adjust the ionic strength of solution. Na₂EDTA solution (5%) was prepared to mask the foreign metal ions possibly co-existing in the samples. All reagents were used without further purification.



Measurements

- i. *Interaction of CBBG with CTAB.* Into a 25-mL calibrated flask, were added an appropriate working solution of CTAB, 2.5 mL of pH 9.50 buffer solution, and a known volume of CBBG solution. The mixture was diluted to 25 mL with de-ionized water and mixed thoroughly. Measurements were made at 582 and 482 nm, respectively, against the blank treated in the same way without CTAB.
- ii. *Preparation of samples and quantitative determination of CTAB.* Two samples were determined. Sample 1 (1#) was sampled from drinking water and sample 2 (2#) from a lake. In both of them, drops of the CTAB solution were added. A sample of 10.00 mL was taken in a 25-mL volumetric flask, 1.0 mL of 1.00 mmol/L CBBG and 1 mL of Na₂-EDTA solution (5%) was added. The next procedures were according to the same operation as (i) above.

RESULTS AND DISCUSSION

Spectral Analysis

The binding interaction between CBBG and CTAB was carried out. The absorption spectra of the CTAB-CBBG solutions at various pHs are shown in Fig. 1. By comparing

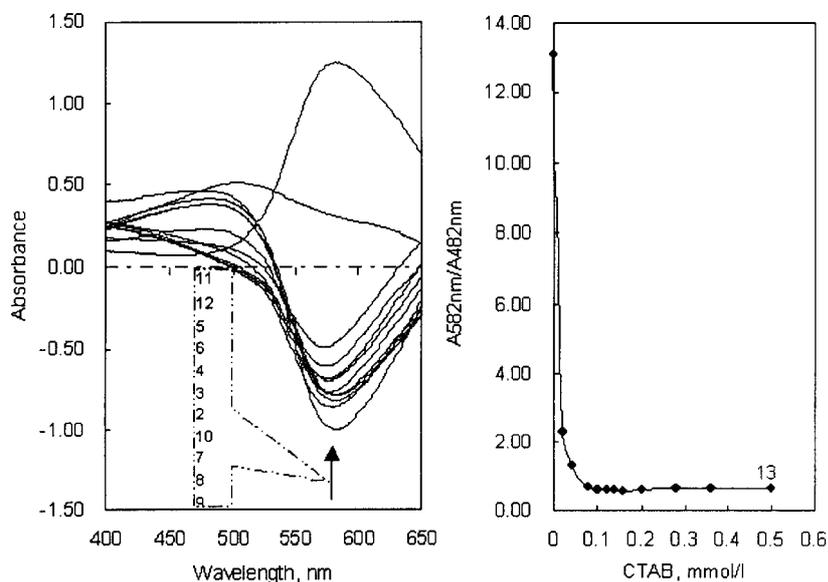


Figure 1. Absorption spectra of CBBG and its CTAB solutions: from 1 to 10: solutions containing 0.060 mmol/L CBBG and 0.080 mmol/L CTAB, respectively, at pH 4.10, 5.50, 6.71, 7.50, 7.84, 8.34, 9.28, 9.50, 9.84, and 9.96, against reagent blank; 11—0.040 mmol/L CBBG at pH 9.50, against water; 12—0.060 mmol/L CBBG plus 0.400 mmol/L CTAB, against water; 13—variation of A₅₈₂ nm/A₄₈₂ nm of the solutions containing 0.040 mmol/L CBBG with CTAB molarity at pH 9.50, measured at 582 and 482 nm against water.



their peaks and valleys, it was visible that curve 8 gives the maximal difference between peak and valley. pH 9.50 buffer solution was added. From curve 11, we observe that the absorption peak of the CBBG solution is located at 584 nm. From curve 13, the absorbance ratio, $A_{582\text{ nm}}/A_{482\text{ nm}}$ reaches a minimum and remains constant for CTAB higher 0.08 mmol/L. It shows that the CBBG was adsorbed completely in such solutions. Curve 12 gives the absorption spectrum of the CBBG-CTAB aggregate, and its peak is located at 504 nm. The spectral blue shift of the aggregate of 80 nm is identified by comparing curves 11 and 12. From curve 8, its peak and valley are located at wavelengths 482 and 582 nm, respectively. Therefore, these two wavelengths were used in this work. From curves 11 and 12 or 13, the correction coefficients were calculated to be $\beta = 0.076$ and $\alpha = 0.577$. So, $A_c = 1.05 (\Delta A - 0.076\Delta A')$.

Effect of Ionic Strength

In order to investigate the effect of ionic strength of the solution on the aggregation of CBBG on CTAB, 2.0 M NaCl was added, its effect is given in Fig. 2. γ remains almost constant. This is attributed to the fact that the aggregation of Cl^- on CTAB is much weaker than that of CBBG.

Effect of Temperature and Reaction Time

The variation of γ between 30°C and 70°C is shown in Fig. 3. The binding number of CBBG decreases slightly with increase in temperature. This is attributed to desorption of CBBG from its CTAB aggregate. This observation agrees with the common nature of surface adsorption.

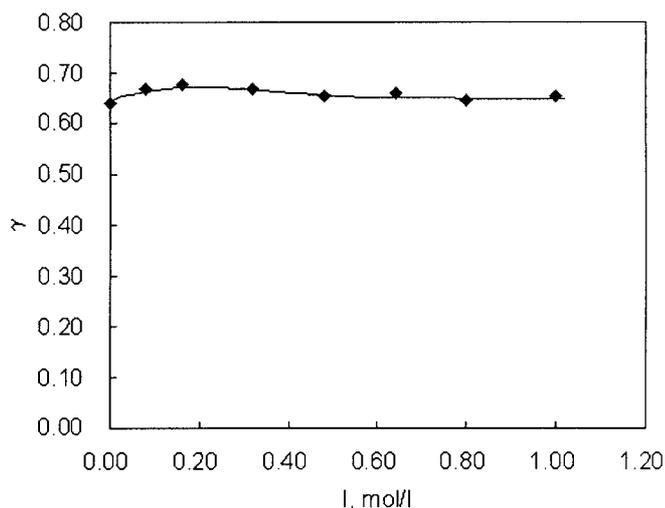


Figure 2. Effect of ionic strength on γ in solutions containing 0.040 mmol/L CBBG and 0.06 mmol/L CTAB at pH 9.50.



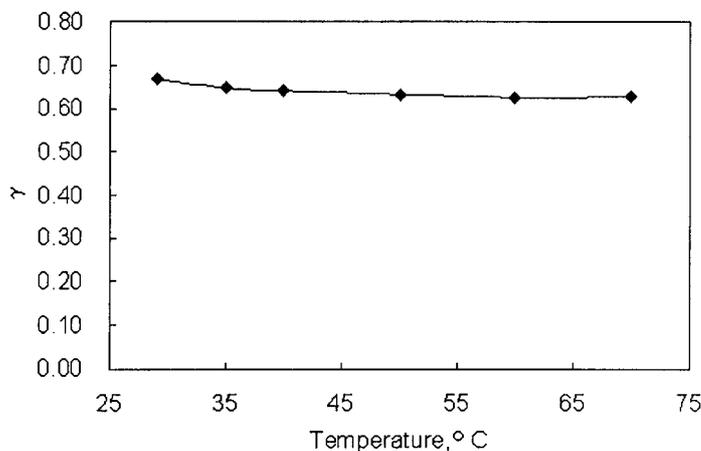


Figure 3. Effect of temperature on γ in solutions containing 0.040 mmol/L CBBG and 0.06 mmol/L CTAB at pH 9.50.

At 30°C, the effect of time showed that γ approached a constant after 20 min of reaction. So we measured the absorbance of the solutions after 20 min.

Characterization of the Aggregation

By varying the addition of the CBBG solution, the absorption of various CTAB solutions was measured at 30°C and the γ and C_L values of each solution were calculated. Their relationship is also shown in Fig. 4. The γ^{-1} vs. C_L^{-1} plots were linear and the straight line indicates that the aggregation of CBBG on CTAB obeys the Langmuir

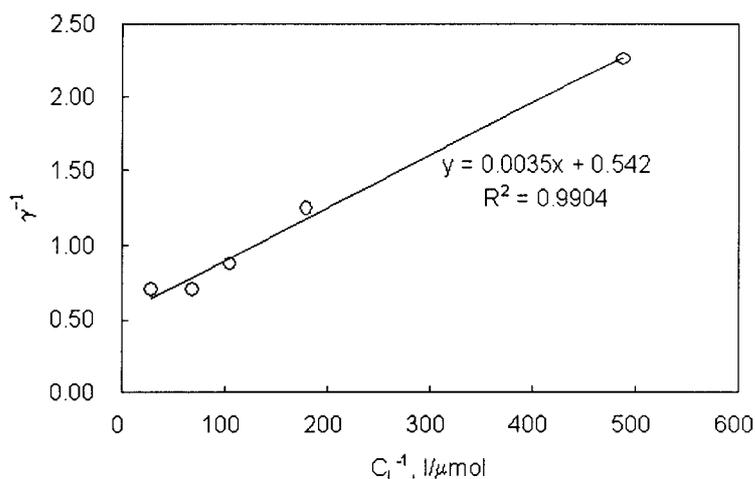


Figure 4. Plot γ^{-1} vs. C_L^{-1} (C_L , $\mu\text{mol/L}$), solution containing 0.040 mmol/L CTAB at 30°C.



isothermal adsorption. From the intercept of this line, the binding number was calculated to be $N = 2$ at 30°C . Therefore, the monomer aggregate is expressed as $\text{CBBG}_2 \cdot \text{CTAB}$ at 30°C . The big micellar aggregate $(\text{CBBG}_2 \cdot \text{CTAB})_{78}$ at 30°C will be formed only when CTAB is over the CMC 0.96 mmol/L and CBBG concentration is sufficient. The binding constant of the monomer aggregate calculated from the slope of the line was $K = 6.46 \times 10^3$ at 30°C . In the determination of the binding number and binding constant, the spectral correction method has definite advantages in operation and principle compared to such classical methods as the Scatchard model^[14] or molar ratios, etc.

Application to the Determination of the Cationic Surfactant

Calibration Graph and Precision

The standard series of CTAB solutions were prepared and measured at pH 9.50 and in the presence of EDTA, where 1.00 mL of the CBBG solution was added. The result is shown in Fig. 5. Curve 1 is linear between 0 and $400 \mu\text{g}$ of CTAB, but curve 2 gives a maximal sensitivity. Therefore, plots $\log(-\Delta A')$ vs. x (x -CTAB amount/ μg) could be used in the analysis of samples. The detection limit was calculated to be only $10 \mu\text{g}$ of cationic surfactant in 25 mL of solution. Six replicated determinations of $80 \mu\text{g}$ of CTAB

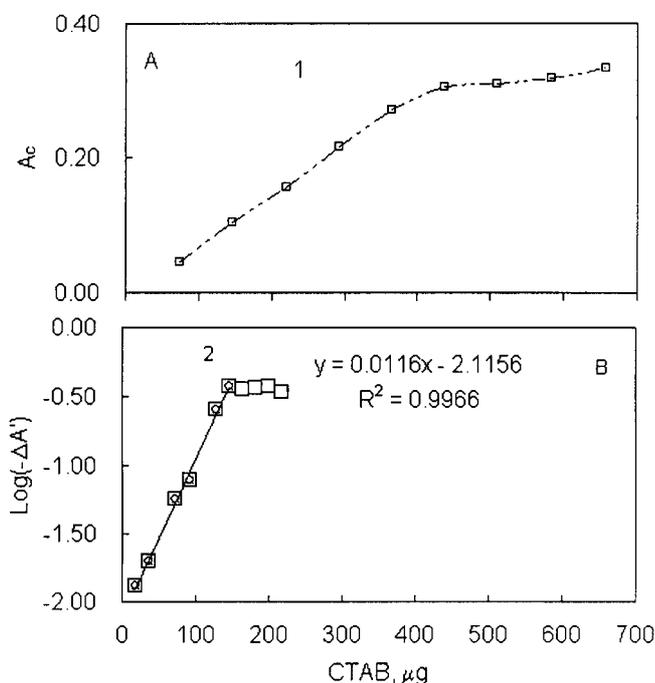


Figure 5. Standard curves for determination of the cationic surfactant with CBBG at pH 9.50: 1— A_c of the CBBG-CTAB aggregate; 2— $\log(-\Delta A')$ vs. x (x -CTAB amount/ μg).



Table 1. Determination of the cationic surfactant in samples with CBBG as reactant at pH 9.50 in the presence of EDTA.

Sample	Added	Found (mg/L)	
1	Only 1.00 mL of sample	2.82 ± 0.09	RSD: 3.2%
	1.00 mL of sample + 2.92 mg/L CTAB (standard)	5.88 ± 0.15	Recovery: 105%
2	Only 1.00 mL of sample	1.50 ± 0.14	RSD: 9.3%
	1.00 mL of sample + 3.65 mg/L CTAB (standard)	5.16 ± 0.30	Recovery: 100%

were carried out. The mean result is $82 \pm 7 \mu\text{g}$, the mean recovery 102.5% with a RSD 8.7%.

Effect of Foreign Ions

By adding 1 mL of 5% EDTA–Na₂ solution into 25 mL solution in the general procedures, none of the following ions affected the direct determination of 50 μg of CTAB (less than 10% error): 0.5 mg of anionic detergent; 0.2 mg of Mg(III), Ba(II); 0.1 mg of Fe(II), Al(III) and 10 μg of Zn(II), Fe(II), Cu(II), Pb(II), Ni(II), and Cr(III).

Analysis of Samples

The analysis of the samples and the recovery of standard CTAB are given in Table 1. Four replicated analyses of the samples have shown that the mean recovery of CTAB lies between 100% and 105% and the RSD is below 9.3%.

CONCLUSIONS

Spectrophotometry is a classical, but still very useful, method for the determination of trace components, especially in the morphological analysis of a compound^[15,16] and in the investigation of a chemical interaction mechanism.^[17] The results of our investigation on the interaction of CBBG with CTAB support the Langmuir monolayer adsorption mechanism of the dye on the surfactant molecule. Though the MSASC technique’s sensitivity is somewhat limited, it does improve both the precision and accuracy of trace analysis and offers the additional benefits of simplicity and versatility.

ABBREVIATIONS

CBBG	Coomassie brilliant blue G250
CTAB	Cetyltrimethylammonium bromide
CMC	Critical micellar concentration
MSASC	Microsurface binding-spectral correction technique
RSD	Relative standard deviations
EDTA	Ethylene diamine tetraacetic acid



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