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# Study on Association of Coomassie Brilliant Blue G250 and CTAB at Different Temperatures

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**Abstract**

**In this paper, the association of anionic dyes Coomassie brilliant blue G250 (CBBG250) with cationic surfactant CTAB was studied by spectroscopy. It can be seen from the spectra that the characteristic absorption peak of CBBG250 is changed obviously by the addition of CTAB. We establish a reasonable association reactions physical model to obtain a series of thermodynamic parameters such as the equilibrium constant, Gibbs free energy and entropy of the association reaction at different temperatures. The experimental results show that the elevated temperature is favorable for the association reaction. The higher the temperature, the greater will be the degree of molecule association.**

***Keywords: CBBG250; CTAB; Equilibrium constant; Gibbs free energy; Entropy***

## Introduction

As the surfactant with sterilization, wetting, solubilization, emulsification, dispersion and a series of functions, it can be widely used in the leather industry [1], dyeing auxiliaries [2,3] and so on. Dyes are materials that color fibers and other materials. In recent years, dyes are not limited to the dyeing and printing of textiles, and are used in many sectors such as paint, plastics, leather, and food. The interaction of dyes with surfactants plays a very important role in textile dyeing, micellar catalysis, micellization, photography, printing inks, and some chemical studies such as biochemistry, analytical chemistry, and light perception [4]. Therefore, more and more people pay attention to the interaction between dyes and surfactants [5-12]. Coomassie brilliant blue G250 (CBBG250) is an anionic dye and is commonly used for the determination of protein content [13-15]. Cationic surfactant cetyltrimethylammonium bromide (CTAB) is widely used as an adjuvant in textile finishing processes which can improve the dying process [16,17]. Therefore, the exploration of the interaction between the dye and the surfactant is very valuable. In addition, many factors, such as pH [18], alcohol [19], salts [20], etc [4,21-24], may have a significant impact on the reaction process between dye and surfactant, which make the reaction mechansim extremely complicated. Usually, most of the researchers [25,26] take advantage of conductometry [19,27], UV-Vis spectroscopy [28], surface tension method [29], cyclic voltammetry, potentiometry [30], fluorescence method [31] to investigate the reaction mechanism. Many scientific literatures [32,33] point out that dye-surfactant is more likely linked by

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hydrogen bonding, ionic bonding, van der Waals force or hydrophobic interaction. But the study of these mechanisms is still imperfect, so it is important to delve deeper into it.

## Experimental

### Apparatus and materials

LabTech UV-2100 UV-Vis spectrophotometer was used to measure the absorption spectra and absorbance. In order to weigh chemicals, analytical balances, model FA12048 was used. For maintaining different temperatures, a thermostat was used. The dye CBBG250 was obtained from Sinopharm Chemical reagent co., LTD. CTAB was obtained from Shanghai Zhongqin Chemical Reagent Co., Ltd, China, LTD.

### Methods

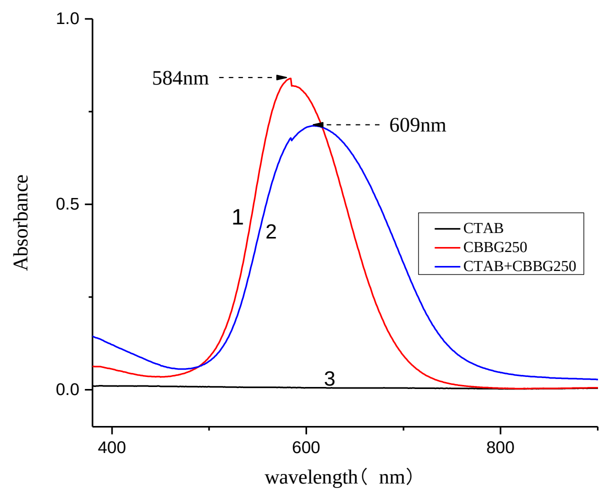


FIG. 1. **CBBG250 spectra: (1) CBBG250 in aqueous solution, (2) CBBG250 in CTAB aqueous solution ($C_{CBBG250}$ = $2\times10^{-5}$ mol/L, $C_{CTAB}$ = $1.2\times10^{-5}$ mol/L), (3) CTAB in aqueous solution.**

## Results and Discussion

### The association equilibrium constant and spectrogram between CBBG250 and CTAB in aqueous solution

Assumptions the association equilibrium constants K can be expressed as

$$K = \frac{C_x}{(C^0_{\text{CTAB}} - C_x)(C^0_{\text{CBBG250}} - C_x)} \qquad (1)$$

Where $C_x$ is the concentration of reaction product. $C^0_{\text{CTAB}}$, $C^0_{\text{CBBG250}}$ are respectively initial concentrations of CTAB and CBBG250.

Based on the Beer-Lambert Law, the absorbance of unit thickness absorbing layer can be expressed as

$$A = \varepsilon_{\text{CBBG250}} C^0_{\text{CBBG250}} \qquad (2)$$

Where $A$ is the absorbance of CBBG250, $\varepsilon_{\text{CBBG250}}$ is molar absorptivity of CBBG250.

When the reaction reaches equilibrium, the measured absorbance should be expressed as

$$A' = \varepsilon_{\text{CTAB}}(C^0_{\text{CTAB}} - C_x) + \varepsilon_{\text{CBBG250}}(C^0_{\text{CBBG250}} - C_x) + \varepsilon_x C_x \qquad (3)$$

Where $\varepsilon_{\text{CTAB}}$, $\varepsilon_x$ is respectively molar absorptivity of CTAB and reaction product. As shown in **FIG. 1**, the molar absorption coefficient of CTAB can be ignored at the wavelength of 584 nm that is $\varepsilon_{\text{CTAB}} \approx 0$.

Then the Equation (3) can be translated into the following expression

$$A' = \varepsilon_{\text{CBBG250}}(C^0_{\text{CBBG250}} - C_x) + \varepsilon_x C_x \qquad (4)$$

From the above, the following equation can be obtained:

$$\frac{C^0_{\text{CTAB}} \cdot C^0_{\text{CBBG250}}}{A - A'} = \frac{1}{\varepsilon_{\text{CBBG250}} - \varepsilon_x} \cdot \left[\frac{1}{K} + (\varepsilon_{\text{CTAB}} + \varepsilon_{\text{CBBG250}})\right] - \frac{A - A'}{(\varepsilon_{\text{CBBG250}} - \varepsilon_x)^2} \qquad (5)$$

At a certain temperature, $(\varepsilon_{\text{CTAB}} + \varepsilon_{\text{CBBG250}})$ is set up to be constant value.

According to chemical reaction so thermal equation, the Gibbs free energy $\Delta_{\text{r}} G_{\text{m}}$ may be expressed as

$$\Delta_{\text{r}} G_{\text{m}} = -RT \ln K \qquad (6)$$

According to Gibbs - Helmholtz equation:

$$\Delta_r G_m = \Delta_r H_m - T\Delta_r S_m \qquad (7)$$

$\Delta_{\text{r}} H_{\text{m}}$ and $\Delta_{\text{r}} S_{\text{m}}$ are obtained from the intercept and slope of the plot of $\Delta_{\text{r}} G_{\text{m}}$ versus $T$.

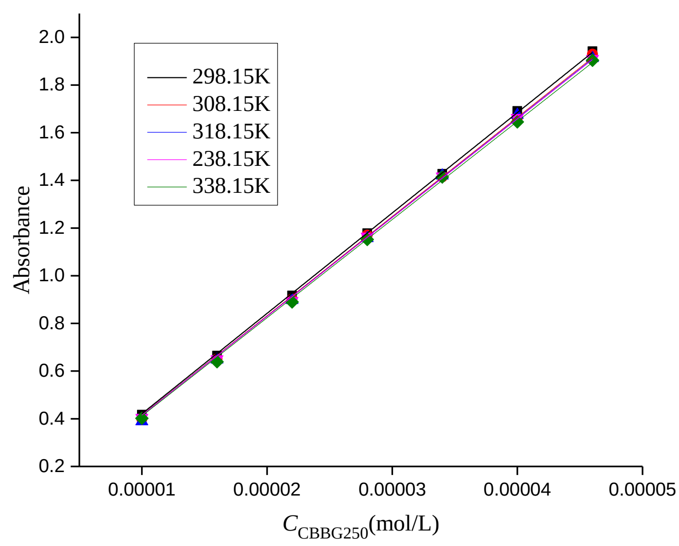


FIG. 2. **The absorbance of CBBG250 in aqueous solutions of different concentrations at 584 nm at different temperatures.**

**[CBBG250]: $1.0\times10^{-5}$ mol/L, $1.6\times10^{-5}$ mol/L, $2.2\times10^{-5}$ mol/L, $2.8\times10^{-5}$ mol/L, $3.4\times10^{-5}$ mol/L, $4.0\times10^{-5}$ mol/L, $4.6\times10^{-5}$ mol/L**

**FIG. 2** shows the absorbance of different concentrations of CBBG250 in 584 nm at different temperatures. By linear fitting we get $\varepsilon_{\mathrm{CBBG250}}$ in 584 nm at different temperatures, as shown in **TABLE 1**. It can be seen that the $\varepsilon_{\mathrm{CBBG250}}$ decreases with increasing temperature.

| *T* | **298.15K** | **308.15K** | **318.15K** | **328.15K** | **338.15K** |
|---|---|---|---|---|---|
| $\varepsilon_{\mathrm{CBBG250}}$ | 42109.7 ± 84.1 | 41618.3 ± 160.0 | 41512.2 ± 196.7 | 41447.8 ± 130.6 | 41186.0 ± 163.9 |

**TABLE 1: The $\varepsilon_{\mathrm{CBBG250}}$ in 584 nm at different temperatures**

According to the model requirements, the sum of the initial concentrations of CBBG250 and CTAB is set up to be constant value ($3.2\times10^{-5}$ mol/L) at different temperatures (308.15 K, 318.15 K, 328.15 K, 338.15K) measure the absorbance of the system. At different temperature, a plot between $\frac{C^0_{\mathrm{CTAB}}\cdot C^0_{\mathrm{CBBG250}}}{A-A'}$ and $A-A'$ get different straight line as shown in **FIG. 3-6.**

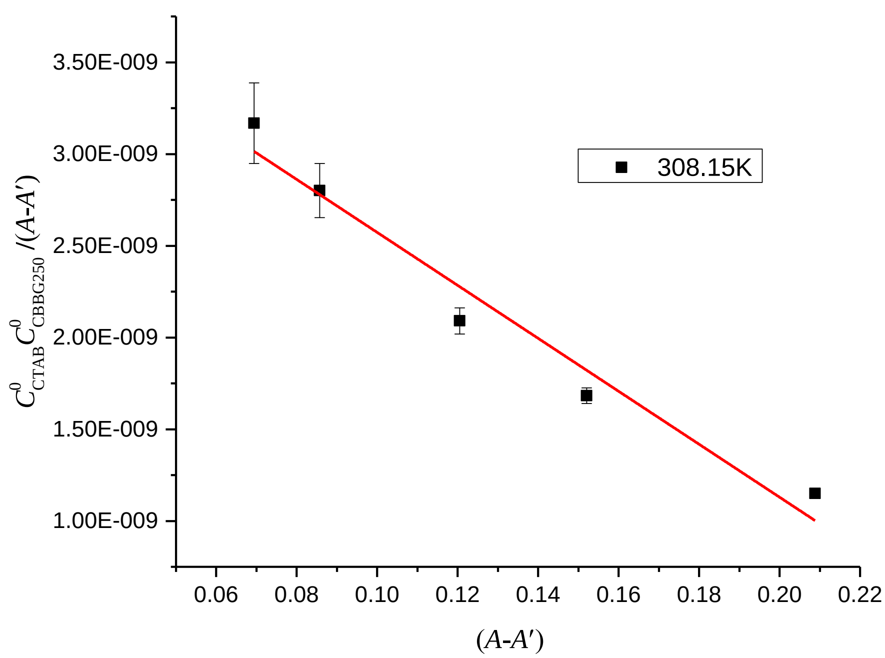


FIG. 3. **Plot of $\frac{C^0_{\mathrm{CTAB}}\cdot C^0_{\mathrm{CBBG250}}}{A-A'}$ *vs.* $(A-A')$ at 308.15K.**

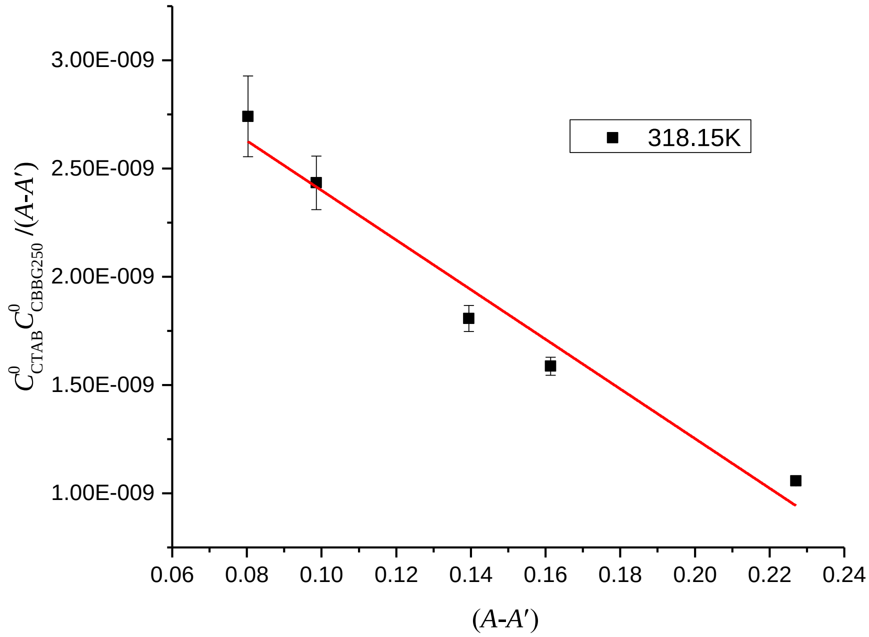


FIG. 4. **Plot of** $\frac{C^0_{CTAB}\cdot C^0_{CBBG250}}{A-A'}$ ***vs.*** $(A-A')$ **at 318.15K.**

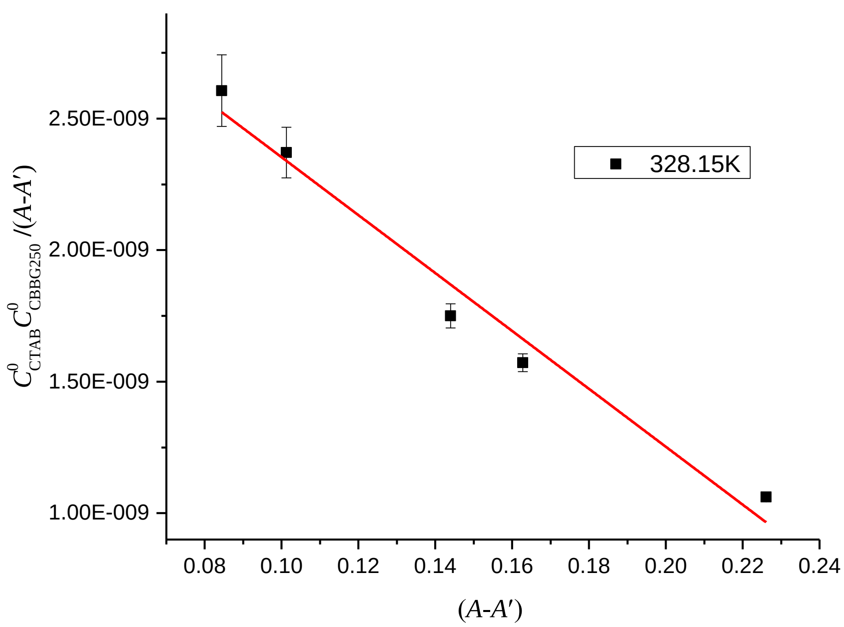


FIG. 5. **Plot of** $\frac{C^0_{CTAB}\cdot C^0_{CBBG250}}{A-A'}$ ***vs.*** $(A-A')$ **at 328.15K.**

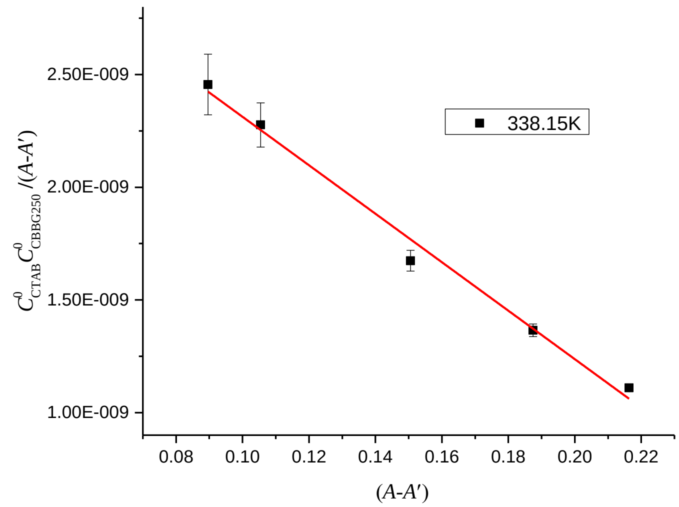


FIG. 6. **Plot of** $\frac{C^0_{\mathrm{CTAB}} \cdot C^0_{\mathrm{CBBG250}}}{A-A'}$ ***vs.*** $(A-A')$ **at 338.15K**

Then $K$ and $\varepsilon_x$ are obtained at different temperatures from the slope and intercept based on **FIG. 3-6**. By the Equation (6) the obtained $K$ can be used to calculate $\Delta_r G_m$ , the results are shown in **TABLE 2**.

| ***T*(K)** | $\varepsilon_x$ **×10$^4$** | ***K*×10$^5$ (L/mol)** | $\Delta_r G_m$ **(kJ/mol)** |
|---|---|---|---|
| 308.15 | 3.328 ± 0.073 | 6.82 ± 0.031 | -34.41 ± 0.089 |
| 318.15 | 3.215 ± 0.068 | 8.30 ± 0.067 | -36.05 ± 0.213 |
| 328.15 | 3.191 ± 0.060 | 10.81 ± 0.042 | -37.90 ± 0.157 |
| 338.15 | 3.154 ± 0.077 | 14.89 ± 0.180 | -39.96 ± 0.205 |

**TABLE. 2. The thermodynamic constants of CBBG250 associated with CTAB at different temperatures.**

By analyzing the data in **TABLE. 2**, it can be seen that the association equilibrium constant $K$ increases with increasing temperature, indicating that the temperature rise is conducive to the positive direction of the reaction. At the same time, the reaction of Gibbs free energy $\Delta_r G_m < 0$, indicating that the reaction is spontaneous, and the higher the temperature, the greater the absolute value of Gibbs free energy, it indicates that the elevated temperature plays an important role in the reaction, the higher the temperature, the greater the degree of association.

According to the Equation 7 and using the Origin software for linear fitting to get **FIG. 7**. Finally, we obtained the $\Delta H_m^0$ =22.703 ± 2.147 kJ/mol and $\Delta S_m^0$ = 0.185 ± 0.007 kJ/mol/K from the intercept and slope of the line, respectively. $\Delta H_m^0 > 0$ shows that this reaction is an endothermic process. In general, the enthalpy change of the chemical bond is greater than 60 kJ/mol. Therefore, the association between CBBG250 and CTAB is not only the chemical bond; it is more likely linked by hydrogen bonding, ionic bonding, van der Waals force or hydrophobic interaction, and so on. $\Delta S_m^0$ > 0 indicates that the process is entropy driven.

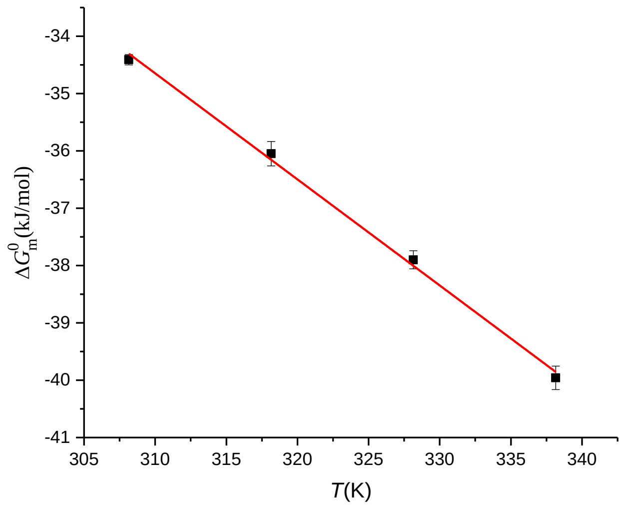


FIG. 7. **Plot of $\Delta_r G_m$ *vs.* $T$.**

## Conclusion

The interaction between CBBG250 and CTAB in aqueous solution can be illustrated by the redshift of the spectrum at 584 nm. According to association reactions physical model, the relevant thermodynamic parameters of CBBG250 and CTAB association at different temperatures were obtained. It can be seen that the association equilibrium constant *K* increases with increasing temperature, indicating that the temperature rise is conducive to the positive direction of the reaction. At the same time, the reaction of Gibbs free energy $\Delta_r G_m$ < 0, indicating that the reaction is spontaneous; $\Delta H_m^0$ > 0 shows that the formation of the CTAB micelle is an endothermic process and $\Delta S_m^0$ > 0 indicates that the process is entropy driven. With the value of $\Delta H_m^0$, we derive the force between CBBG250 and CTAB is not only the chemical bond, it is more likely linked by hydrogen bonding, ionic bonding, van der Waals force or hydrophobic interaction, and so on.

## Acknowledgements

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