Surface and associated studies between Coomassie brilliant blue G250 and CTAB in Aqueous Solution

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Abstract. The interaction of surfactant cetyltrimethylammonium bromide (CTAB) with anionic dye Coomassie brilliant blue G250 (CBBG250) in aqueous solution and its effect on the formation of CTAB micelles were studied by UV-Vis spectrophotometry and electrical conductivity methods. By establishing the micellar model and measuring the electrical conductivity of CTAB in CBBG250 aqueous solution, we get the values of the critical micelle concentration at different temperatures from 298.15K to 338.15K, which are essentially the same as the range of concentrations of regular change in absorbance. It suggests that the critical micelle concentration of CTAB in CBBG250 aqueous solution is larger than in aqueous solution because some surfactant molecules in micelles are associated with CBBG250 molecules.

1. Introduction
In recent years, the interaction between dyes and surfactants has been widely used in dyeing technology, ion recognition [1], photographic industry [2], medicine and so on [3]. Therefore, more and more people have paid attention to it in recent years [4-9]. Coomassie brilliant blue G250 (CBBG250) is an anionic dye and is commonly used for the determination of protein content [10-12]. Cationic surfactant cetyltrimethylammonium bromide (CTAB) is widely used as an adjuvant in textile finishing processes which can improve the dyeing process [13, 14]. Therefore, the explorations of the interaction between dyes and surfactants are very valuable. When the concentration of the surfactant in aqueous solution reaches a certain value, the surfactant molecules spontaneously become an ordered assembly, such as micelles, vesicles, and the like. These ordered assemblies have their own unique properties because of their structural differences. Due to this particular phenomenon, Muntaha et al. [15] have been interested in changes in the electrical conductivity and spectral behavior before and after micelle formation in dye-surfactant systems. The study found that the association mechanism of dyes with different concentrations of surfactants are different. In addition, many factors, such as pH [16], alcohol [17], solvent [18], salts [19], etc [20-24], may have a significant impact on the reaction process between dye and surfactant, which make the reaction mechanism 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 hydrogen bonding,ionic bonding, van der Waals force or hydrophobic interaction. Study the interactions of dyes with surfactants in aqueous solutions can provide useful information about the mechanism according to dye-surfactant interactions thermodynamics and kinetics of dyeing process.
2. Experimental

2.1 Apparatus
LabTech UV-2100 UV-Vis spectrophotometer was used to measure the absorption spectra and absorbance. In order to measure electrical conductivity, an electrical conductivity meter, model DDS-307 was used. For maintaining five different temperatures from 298.15K to 338.15K, a thermostat was used.

2.2 Materials
The dye CBBG250 was obtained from Sinopharm Chemical reagent co., LTD. CTAB was obtained from Shanghai Zhongqin Chemical Reagent Co., Ltd, China, LTD.

2.3 Methods

![Absorbance graph](image)

Figure 1. The absorption spectra of (1) CBBG250 in aqueous solution, (2) CBBG250 in CTAB aqueous solution ($C_{\text{CBBG250}}^0 = 2.0 \times 10^{-5} \text{ mol/L}$, $C_{\text{CTAB}}^0 = 1.2 \times 10^{-5} \text{ mol/L}$) and (3) CTAB in aqueous solution.

As shown in Fig. 1, the spectrum of CBBG250 in aqueous solution (curve 1) has a strong absorption peak at 584 nm, the adding of CTAB (curve 2) makes the characteristic absorption peaks of CBBG250 change both in the strength and position (bathochromic shift). The phenomenon indicates the existence of association between CBBG250 and CTAB. The test is conducted at the wavelength of 584 nm and 298.15K, which makes the different values of absorbance maximum. Moreover, in order to reduce the system error, all the values of absorbance are measured generally in the range of 0.1~1. In the study, we determinate the association equilibrium constant $K$ between CBBG250 and CTAB in aqueous solution by varying the CBBG250 concentration from $1.0 \times 10^{-5}$ to $2.2 \times 10^{-5} \text{ mol/L}$ and the CTAB concentration from $2.2 \times 10^{-5}$ to $1.0 \times 10^{-5} \text{ mol/L}$. The total concentrations of CBBG250 and CTAB are set up to be constant value ($C_{\text{CTAB}}^0 + C_{\text{CBBG250}}^0 = 3.2 \times 10^{-5} \text{ mol/L}$).

3. Results and discussion

3.1 The micellization thermodynamic parameters of CTAB in aqueous solution and Coomassie brilliant blue G250 aqueous solution

In order to consider the formation of micelles in CTAB in aqueous solution and CBBG250 aqueous
solution, a reasonable physical model was established.
Assuming that there is a micelle $M$ formed by a CTAB molecule, where there are $N$ surfactants ions $S^+$, $P$ antiprotons $C^-$, then their micellization process can be expressed as [34-36]:
\[ NS^+ + PC^- \rightarrow M^{N-P} \] (1)

The equilibrium constant can be expressed as:
\[ K' = \frac{[M^{N-P}]}{[S^+]^N[C^-]^P} \] (2)

The Gibbs function is given in the form of a molar concentration:
\[ \Delta G_m^0 = \frac{-RT \ln K'}{N} \] (3)

Since the micelles are formed at this time, the micelle concentration is negligible. We can get:
\[ \Delta G_m^0 \approx \frac{RT}{N} \left( N \ln[S^+] + P \ln[C^-] \right) \] (4)

When it is easy to form micelles, the overall system is electrically neutral, so it can be concluded that:
\[ [S^+] = [C^-] \] (5)

The inverse ion dissociation degree $\beta$ of the system (the ratio of the electrical conductivity before and after the critical micelle concentration) [37] can be expressed as:
\[ \beta = \frac{P}{N} \] (6)

Taking into account the concentration of surfactant at this time can almost replace the cmc value is:
\[ [S^+] \approx \text{cmc} \] (7)

Based on the above formula, the Gibbs function in micelles can be expressed as:
\[ \Delta G_m^0 = RT(1 + \beta) \ln \text{cmc} \] (8)

Then according to the definition:
\[ \Delta G_m^0 = \Delta H_m^0 - T \Delta S_m^0 \] (9)

Finally, the enthalpy change $\Delta H_m^0$ and entropy change $\Delta S_m^0$ of the reaction are calculated by using linear fitting.

According to the micellar thermodynamics model, the electrical conductivity of CTAB in aqueous solution and CBBG250 aqueous solution before and after cmc were measured under different temperature conditions. As can be seen in Fig. 2, when CTAB reaches a certain concentration range, the value of the electrical conductivity appears to be a step point, which is the critical micelle concentration of CTAB at that temperature and solution.
Figure 2. The electrical conductivity of CTAB in aqueous solution at various temperatures.

(a): without CBBG250 (b): with CBBG250

Through the above electrical conductivity data, combined with micellar thermodynamics model, the final micellar thermodynamic parameters of CTAB are listed in Tables 1 and 2. By analyzing the data in Table 1, it can be seen that the value of \( \text{cmc} \) increases as the temperature increases. Because the increase in temperature will increase the frequency of thermal motion of the particles, making the micelles less likely to form. At the same time, higher the temperature requires more counterions around the micelle to form micelles. So the temperature rise is always accompanied by an increase in the counterion dissociation degree \( \beta \).

Table 1. The \( \text{cmc} \) values of CTAB in aqueous solution at different temperatures

| \( T(\text{K}) \) | \( \text{cmc} \)(mol/L) | \( \beta \) | \( \Delta G_m^0 \) (kJ/mol) | \( \Delta H_m^0 \) (kJ/mol) | \( \Delta S_m^0 \) (J/mol/K) |
|-----------------|-----------------|--------|-----------------|-----------------|--------------------|
| 298.15          | 8.25\times10^{-4} | 0.41   | -24.83          |                 |                   |
| 308.15          | 8.66\times10^{-4} | 0.45   | -26.16          |                 |                   |
| 318.15          | 8.87\times10^{-4} | 0.52   | -28.28          |                 |                   |
| 328.15          | 9.14\times10^{-4} | 0.53   | -29.25          |                 |                   |
| 338.15          | 9.64\times10^{-4} | 0.60   | -31.24          |                 |                   |

Table 2. The \( \text{cmc} \) values of CTAB in the presence of CBBG250 at different temperatures

| \( T(\text{K}) \) | \( \text{cmc} \)(mol/L) | \( \beta \) | \( \Delta G_m^0 \) (kJ/mol) | \( \Delta H_m^0 \) (kJ/mol) | \( \Delta S_m^0 \) (J/mol/K) |
|-----------------|-----------------|--------|-----------------|-----------------|--------------------|
| 298.15          | 8.47\times10^{-4} | 0.51   | -26.48          |                 |                   |
| 308.15          | 8.82\times10^{-4} | 0.54   | -27.69          |                 |                   |
| 318.15          | 8.93\times10^{-4} | 0.60   | -29.70          |                 |                   |
| 328.15          | 9.19\times10^{-4} | 0.65   | -31.55          |                 |                   |
| 338.15          | 10.44\times10^{-4} | 0.70   | -32.86          |                 |                   |
The increase of temperature and counter ion dissociation lead to the decrease of $\Delta G_m^0$. From Tables 1 and 2 we can see $\Delta G_m^0 < 0$, which means that this is a spontaneous process; $\Delta H_m^0 > 0$ shows that the formation of the CTAB micelle is an endothermic process; $\Delta S_m^0 > 0$ indicates that the process is entropy driven.

The $cmc$ values of CTAB in aqueous solution and CBBG250 aqueous solution are respectively 8.25×10$^{-4}$ mol/L and 8.47×10$^{-4}$ mol/L at 298.15K. This data is also consistent with the concentration range obtained in the spectral scan (8.0×10$^{-4} \sim$1.0×10$^{-3}$ mol/L). Two experiments supported each other, ensured the accuracy of the experiment result.

By comparing the data in Tables 1 and 2, it was found that the critical micelle concentration of CTAB in CBBG250 aqueous solution was significantly increased than that in aqueous solution. This phenomenon suggests that CBBG250 molecules are associated with surfactant molecules in micelles, so the formation of micelles is more difficult, the micelles need more surfactant molecules to form agglomerates, resulting in an increase in critical micelle concentration. Similarly, the association between CBBG250 and CTAB occupies part of the original counter ion position, so that the number of residual counter ions increases and the dissociation degree of counter ions increases.

4. Conclusion
The interaction between CBBG250 and CTAB in aqueous solution can be illustrated by the redshift of the spectrum at 584 nm. According to micellarization model, It was found that the Gibbs free energy $\Delta G_m^0$ is reduced in micelles formation, which means that this is a spontaneous process; $\Delta H_m^0 > 0$ 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.

The $cmc$ of CTAB obtained by the spectra is 8.0×10$^{-4} \sim$1.0×10$^{-3}$ mol/L and obtained through electrical conductivity is 8.47×10$^{-4}$ mol/L. The results of the two methods were consistent. It was also found that critical micelle concentration and the inverse ion dissociation degree of the two systems increased with increasing temperatures, and the $cmc$ of CTAB in CBBG250 aqueous solution is larger than in aqueous solution because some surfactant molecules in micelles are associated with CBBG250 molecules. This study is of significance for a better understanding of the association mechanism of dyes with surfactants.

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References
[1] O. Prakash, S. Kumar, and S. P. Mushran, 1979. *Talanta*. 26, 1167.
[2] I. S. Boris, Russ. 1994. *Chem. Rev.* 63, 231.
[3] H. Akbaş, and C. Kartal, 2007. *Dyes Pigm.* 72, 383.
[4] H. Akbaş, and C. Kartal, 2006. *Spectrochim. Acta, Part A.* 65, 95.
[5] T. Shen, R. Xiao, Q. Wang, L. Yang, and N. Wang, 2014. *J. Dispersion Sci. Technol.* 35, 435.
[6] R. K. Dutta, and S. N. Bhat, Bull. 1993. *Chem. Soc. Jpn.* 66, 2457.
[7] P. Forte-Tavčer, 2004. *Dyes Pigm.* 63, 181.
[8] S. M. Ghoreishi, M. Behpour and A. G. Farsani, 2007. *Dyes Pigm.* 74, 585.
[9] N. Wang, and M. Zhao, 2016. *J. Dispersion Sci. Technol.* 37, 190.
[10] X. X. Han, Y. Xie, B. Zhao, and Y. Ozaki, 2010. *Anal. Chem.* 82, 4325.
[11] L. T. Jin, and J. K. Choi, 2004. *ELECTROPHORESIS* 25, 2429.
[12] B. M. Löffler, and H. Kunze, 1989. *Anal. Biochem.* 177, 100.
[13] R. T. Buwalda, and J.B. F. N. Engberts, 2001. *Langmuir*. 17, 1054.
[14] N. Wang, S. J. Xiao, and C. W. Su, 2016. *Colloid Polym. Sci*. 294, 1305.
[15] S. T. Munfaha, and M. N. Khan, 2014. *J. Mol. Liq*. 197, 191.
[16] L. D. L. Miranda, C. R. Bellato, M. P. F. Fontes, M. F. de Almeida, J. L. Milagres, and L. A. Minim, 2014. *Chem. Eng. J*. 254, 88.
[17] C. Samsonoff, J. Daily, R. Almog, and D. S. Berns, 1986. *J. Colloid Interface Sci*. 109, 325.
[18] B. Samiey, and S. Ahmadi, 2013. *J. Solution Chem*. 42, 151.
[19] P. K. Behera, S. N. Panda, and S. Sahu, 2013. *J. Mol. Liq*. 177, 110.
[20] R. K. Dutta, and S. N. Bhat, Bull. 1992. *Chem. Soc. Jpn*. 65, 1089.
[21] J. Yang, 2004. *J. Colloid Interface Sci*. 274, 237.
[22] S. S. Shah, R. Ahmad, S. W. H. Shah, K. M. Asif, and K. Naem, 1998. *Colloids Surf., A*. 137, 301.
[23] Y. Miyashita, and S. Hayano, Bull. 1981. *Chem. Soc. Jpn*. 54, 3249.
[24] H. Lin, H. Zhu, J. Guo, and N. Wang, 2017. *J. Dispersion Sci. Technol*. 38, 1410.
[25] S. Chandravanshi, and S. K. Upadhyay, 2012. *Color. Technol*. 128, 300.
[26] W. Liu, and R. Guo, 2006. *Colloids Surf., A*. 274, 192.
[27] N. Wang, H. Lin, and H. Zhu, 2016. *J. Solution Chem*. 45, 1689.
[28] Z. H. Ren, Ind. Eng. 2014. *Chem. Res*. 35, 10035.
[29] S. Bračko, and J. Špan, 2001. *Dyes Pigm*. 50, 77.
[30] B. Simončič, and M. Kert, 2002. *Dyes Pigm*. 54, 221.
[31] W. Liu, and R. Guo, 2005. *J. Colloid Interface Sci*. 290, 564.
[32] B. Gohain, S. Sarma, and R. K. Dutta, 2008. *J. Mol. Liq*. 142, 130.
[33] H. Margenau, 1939. *Rev. Mod. Phys*. 11, 1.
[34] R. Zana, 1996. *Langmuir*. 12, 1208.
[35] J. N. Phillips, 1955. *Transactions of the Faraday Society*. 51, 561.
[36] A. Ali, S. Uzair, N. A. Malik, and M. Ali, 2014. *J. Mol. Liq*. 196, 395.
[37] S. Chandravanshi, and S. K. Upadhyay, 2013. *J. Dispersion Sci. Technol*. 34, 1308.