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Short communication

Effect of sodium dodecyl benzene sulfonate on the absorption spectrum and determination of crystal violet in aqueous solution

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ABSTRACT

The effect of sodium dodecyl benzene sulfonate (SDBS) on the absorption spectrum of crystal violet (CV) in an aqueous solution was studied by spectrophotometry. The results showed that when the SDBS concentration was lower than the critical micelle concentration (CMC), the absorption spectrum of CV was altered significantly. However, the effect was eliminated when the SDBS concentration was higher than the CMC, and the absorption maximum of the solution gradually reached that of a SDBS-free CV solution. A new method was thus proposed for the determination of the CV concentration in an aqueous solution containing an anionic surfactant. Under the optimal conditions, i.e., a detection wavelength of 584 nm, a SDBS concentration of 4.8 mmol L^{-1} and a reaction time of 1 h, the linear range of the method was 0.16×10^{-2} mmol L^{-1}–1.6 mmol L^{-1}.

1. Introduction

Surfactants play an important role in the dyeing and finishing industries due to the fact that they can greatly improve the solubility of dyes and enhance the leveling, the dyeing rate and the color fastness of dyes [1,2]. Furthermore, surfactants themselves are present in most of the industrial wastewater streams generated in the dye production or utilization processes. Therefore, it is important to determine the dye concentration in an aqueous solution containing a surfactant.

The interaction between dyes and surfactants has been studied using spectrophotometry [3–5]. The resulting data showed that the surfactant had a great effect on the absorption spectrum of the dye when the surfactant concentration was lower than its critical micelle concentration (CMC) [6]. It was therefore difficult to determine the dye concentration in aqueous solution containing a surfactant by directly using the normal spectrophotometry method [7]. Several papers reported the methods for the determination of the dyes for example crystal violet (CV) using performance liquid chromatography, liquid chromatograph-mass spectrometer and resonance rayleigh scattering [8–10]. These methods had low limits of detection, but they were costly.

CV is a typical basic dye and sodium dodecyl benzene sulfonate (SDBS) is often used as the surfactant in dyeing and finishing. In this paper, the effect of the SDBS concentration on the absorption spectrum of CV was studied in order to establish a method to determine the CV concentration in an aqueous solution containing SDBS. It was observed that when the SDBS concentration in the aqueous solution was above the CMC, the absorption maximum of the CV solution containing SDBS gradually approached that of the CV solution without SDBS, and the absorbance of the aqueous solution changed regularly with the CV concentration. This made it possible to determine the CV concentration containing SDBS by using spectrophotometry.

2. Experimental

2.1. Materials and instruments

CV, SDBS, NaCl and Na_2SO_4 (Tianjin Taihe Pharmacy Co. Ltd., China) are all of analytical grades and used without further purification. Distilled water was used in all experiments. U-3010 UV–visible double-beam spectrophotometer (Japan HITACH) and 752N UV–Vis spectrophotometer (Shanghai Precision Scientific Instrument Co. Ltd., China) were used to measure the absorbance of the aqueous solution.

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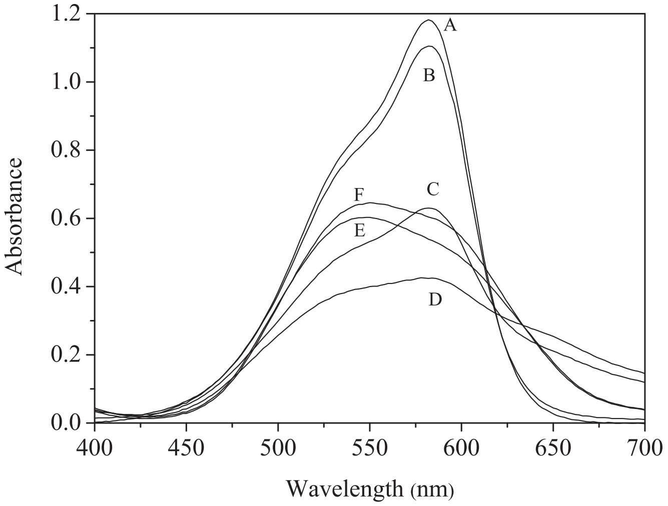

Fig. 1. Absorption spectrum of the solution (lower than the CMC of SDBS) $c_{CV} = 1.8 \times 10^{-2}$ mmol L^{-1}; $c_{SDBS}(\times 10^{-2}$ mmol $L^{-1})$: 0(A), 2(B), 10(C), 20(D), 60(E), 120(F).

2.2. Experimental methods

A certain amount of the sample solution containing CV was mixed with some SDBS in a 50 mL volumetric flask. Distilled water at room temperature (about 20 °C) was then added to the volumetric flask drop by drop until the liquid level reached exactly 50 mL. The solution was allowed to settle for 60 min. Then, its absorbance or visible absorption spectrum was measured by 752N UV–Vis spectrophotometer or UV–visible double-beam spectrophotometer, respectively.

3. Results and discussion

3.1. Absorption spectrum

The aqueous solution containing CV and SDBS was scanned by the UV–visible double-beam spectrophotometer to obtain their absorption spectra in the visible region. The results are shown in Fig. 1. In the visible region, SDBS did not absorb, but CV had an absorption maximum [11]. If the effect of SDBS on the absorption spectrum was considered negligible, the determination of the CV concentration in an aqueous solution containing SDBS would be the same as that in an aqueous solution without SDBS.

However, CV carries the positive charge and SDBS carries the negative charge in the aqueous solution. Therefore, when the SDBS concentration in the aqueous solution is lower than its CMC (2.1 mmol L^{-1}, 20 °C) [12], SDBS and CV interact with each other and form the dye-surfactant complex by electrostatic interaction. The reaction equation of CV and SDBS is shown in Fig. 2. Consequently, the formation of the dye-surfactant complex impacts greatly on the CV absorption spectrum. Fig. 1 shows that with the increase in the SDBS concentration (lower than its CMC), the height of absorption peak changed significantly and the blue shift occurred.

U-3010 UV–visible spectrophotometer was used to scan the absorption spectrum of the aqueous solution which contained CV (1.8×10^{-2} mmol L^{-1}) and SDBS (2.0 mmol L^{-1}–8.0 mmol L^{-1}, which were higher than the CMC of SDBS). The results are shown in Fig. 3.

It can be seen from Fig. 3 that when the SDBS concentration increased to above the CMC, the absorption maximum of the solution returned to that of the surfactant-free CV solution. At the same time, the absorbance had a significant increase and tended to be stable at a constant value. When the SDBS concentration in the aqueous solution was close to the CMC, the surfactant aggregation occurred and the micelles began to form. The dye-surfactant complex became unstable and was dissociated gradually. Therefore, the height and position of the absorption peak reached a constant value. As a result, when the SDBS concentration in the CV solution was lower than the CMC, SDBS should be added into the solution to maintain the SDBS concentration above the CMC, so that the effect of SDBS on the CV concentration measurement would be eliminated. 584 nm was chosen as the optimal measurement wavelength in this method.

3.2. Optimization of reaction conditions

3.2.1. SDBS concentration

The absorbance of the same aqueous solution used in Fig. 3 was measured at 584 nm. The effect of the SDBS concentration on the absorbance is shown in Fig. 4. As the SDBS concentration increased,

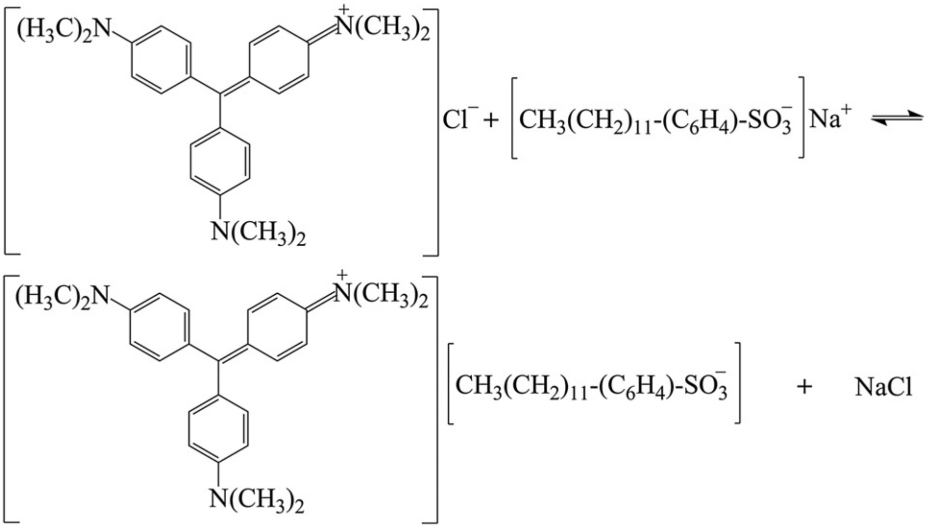

Fig. 2. Reaction equation of CV and SDBS.

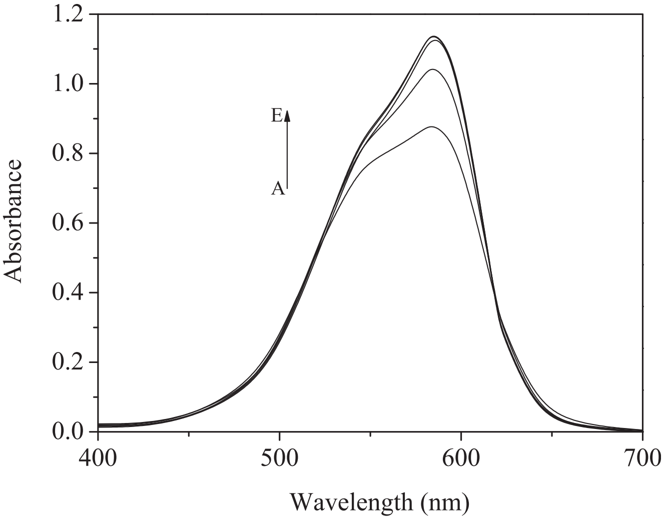

Fig. 3. Absorption spectrum of the solution (higher than the CMC of SDBS) $c_{CV} = 1.8 \times 10^{-2}$ mmol L^{-1}; c_{SDBS}(mmol L^{-1}): 2.0(A), 2.8(B), 4.8(C), 6.0(D), 8.0(E).

the micelles in the aqueous solution became more stable and more dye-surfactant complexes were dissociated. So the absorbance of the aqueous solution rose gradually. When the SDBS concentration was higher than 4.8 mmol L^{-1}, stable SDBS micelles would be formed in the aqueous solution and the dye-surfactant complex dissociated completely. As a result, the absorbance leveled out. In conclusion, when the SDBS concentration was higher than 4.8 mmol L^{-1}, the effect of the SDBS concentration on the absorbance became insignificant.

3.2.2. *Acidity*

Because the color of the CV solution changes with pH value [13], the solution pH value was controlled in the experiments. SDBS is a strong-alkali weak-acid salt and it has a weak buffer action. As shown in Fig. 5, when the SDBS concentration reached 1.0 mmol L^{-1}, the pH value of the solution stabilized around 10.30. When the SDBS concentration in the experiment was higher than 4.8 mmol L^{-1}, it was not necessary to adjust pH value by adding a buffer solution.

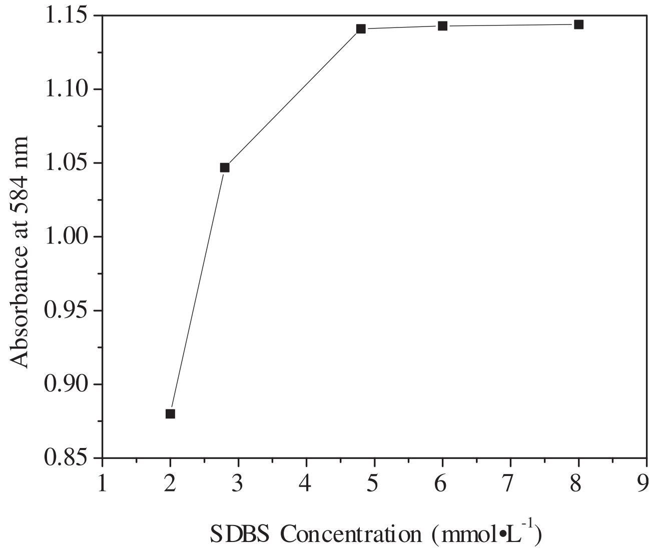

Fig. 4. Effect of the SDBS concentration on the absorbance (at 584 nm) $c_{CV} = 1.8 \times 10^{-2}$ mmol L^{-1}.

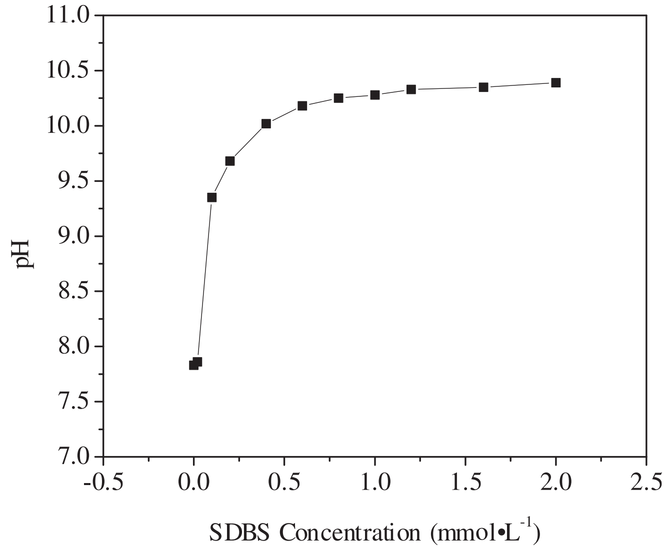

Fig. 5. Effect of the SDBS concentration on the pH value of the solution.

3.2.3. *Reaction time*

A fading process of CV and changes in the absorbance with the time have been reported [14]. Hence the effect of the reaction time on the measurement has to be considered. The concentrations of CV and SDBS in the aqueous solution were 1.8×10^{-2} mmol L^{-1} and 4.8 mmol L^{-1}, respectively. The absorbance of the aqueous solution was then measured hourly by the UV–visible double-beam spectrophotometer at 584 nm. The effect of the reaction time on the absorbance of the aqueous solution at 584 nm is shown in Fig. 6. Since the SDBS concentration was higher than the CMC, stable micelles were formed in the aqueous solution. Under the protection of the micelles, the fading process of CV in alkaline solution was limited. The absorbance of the solution was relatively stable, changing only 2.7% in 5 h. To reduce further error caused by the fading phenomenon, the reaction time was chosen to be 1 h.

3.2.4. *Ionic strength*

The effect of the ionic strength on the measurement was studied by adding different amounts of NaCl to the solution. The

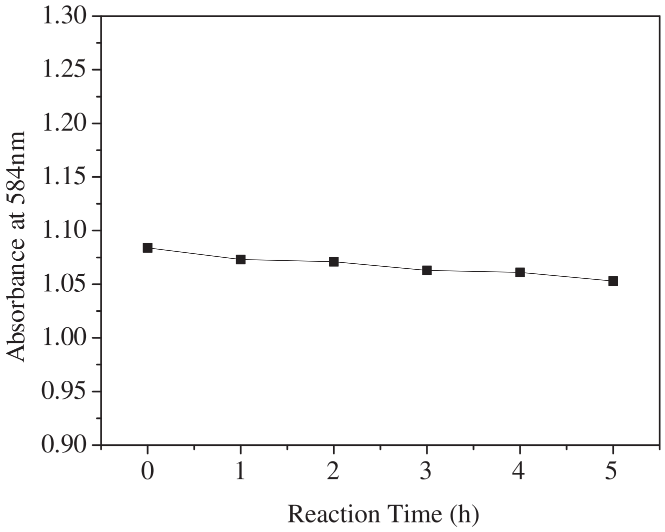

Fig. 6. Effect of the reaction time on the absorbance (at 584 nm).

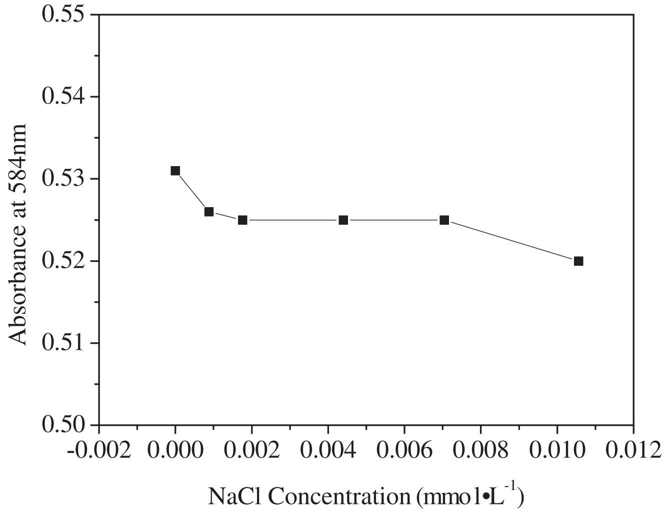

Fig. 7. Effect of the ionic strength on the absorbance (at 584 nm).

concentrations of CV and SDBS in aqueous solution were 0.88×10^{-2} mmol L^{-1} and 4.8 mmol L^{-1}, respectively. Fig. 7 shows that even the NaCl concentration was up to 10 mmol L^{-1}, which was 1200 times higher than the CV concentration, the maximal relative error was only 2.3%. The absorbance had minor differences because of the effect of the micelles. Therefore the effect of the ion strength could be neglected in the process of the CV concentration determination in the CV and SDBS mixed aqueous solution.

3.3. Linear range and detection limit

To investigate the linear range and detection limit of the proposed method, 8 samples of different CV concentrations (0.16×10^{-2} mmol L^{-1}–1.80×10^{-2} mmol L^{-1}) were prepared. The concentration of SDBS in all the samples were the same (4.8 mmol L^{-1}).

These solutions were all put at room temperature (20 °C) for 1 h. Then the absorbance was measured by the 752N UV–Vis spectrophotometer at 584 nm. The correlation between the absorbance and the CV concentration is shown in Fig. 8. When the absorbance was from 0.10 to 1.20, the absorbance and the CV concentration had a good linear relationship. The regression equation of the standard working curve was presented as $A = 0.605c_{CV}$, where A was the absorbance of the aqueous solution at 584 nm and c_{CV} was the CV concentration (10^{-2} mmol L^{-1}). The linear correlation coefficient was $R = 0.9996$ and the detection limit was 0.020×10^{-2} mmol L^{-1}.

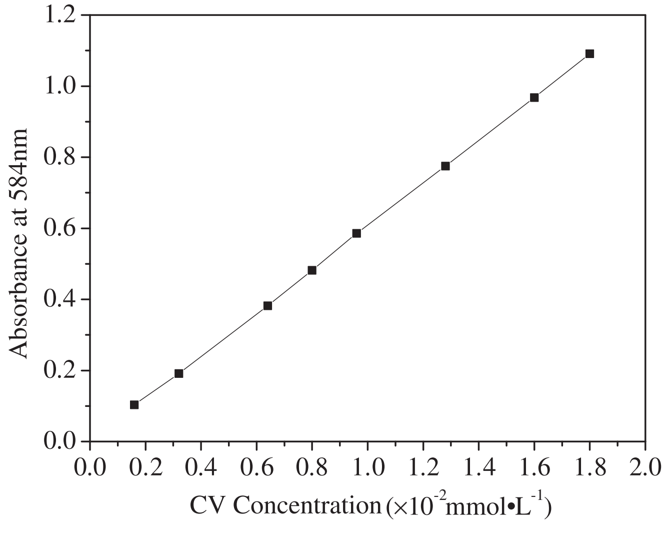

Fig. 8. Standard working curve.

Table 1
Assay result of CV.

No.	CV in the initial wastewater (mmol L^{-1})	CV added (mmol L^{-1})	CV in the mixture (mmol L^{-1})	Recovery of the CV added (%)
1	0.035	–	–	–
2	–	0.024	0.0592	100.8
3	–	0.040	0.0751	100.3
4	–	0.120	0.1548	99.8

3.4. Effect of the interfering substances

The effect of the interfering substances on the CV concentration determination was studied using an aqueous solution containing CV at 1.2×10^{-2} mmol L^{-1}. The interfering substances included the cationic ions K^+ and Na^+, the anionic ions NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$ and HPO_4^{2-}. The maximal relative error was less than 3.3% when the concentrations of Na^+, NO_3^-, Cl^-, CO_3^{2-} and SO_4^{2-} were less than 1200 times of CV, and the concentrations of K^+, $H_2PO_4^-$ and HPO_4^{2-} were less than 500 times of CV. This rendered the effect of the interfering substances insignificant.

3.5. An application of the proposed method

The method developed in the present study was used for determining the CV concentration in a printing and dyeing wastewater from a factory in Hebei, China containing CV and SDBS. Rather than only measuring the absorbance of the initial sample, the wastewater was mixed with different volumes (3.0 mL, 5.0 mL and 15.0 mL) of a standard solution containing 0.4 mmol L^{-1} CV. SDBS was then added into these mixed solutions to make the SDBS concentration higher than 4.8 mmol L^{-1}. The mixed solutions were placed at room temperature (20 °C) for 1 h and then the absorbance of the mixed solutions was measured at 584 nm by 752N UV–Vis spectrophotometer. The CV concentrations in both the initial wastewater and in these mixed solutions were measured. The results are shown in Table 1. All concentrations were based on the volume of the final mixed solution.

Measurement No. 1 was for the initial wastewater sample without the addition of the standard solution. The CV concentration was found to be 0.035 mmol L^{-1}. Measurements No. 2 to No. 4 were for the mixtures of the initial wastewater and different volumes of the 0.4 mmol L^{-1} CV solution. Materials balance was checked by the recovery rate of the CV that was added to the wastewater sample by mixing it with the standard solution, which was calculated by (CV in the mixture − CV in the initial wastewater)/CV added.

The materials balance shows that the method is of satisfactory precision and accuracy.

4. Conclusions

The absorption spectrum of CV varied with the changes in the SDBS concentration in an aqueous solution. When the SDBS concentration was higher than the CMC, the absorption maximum of the aqueous solution containing CV and SDBS gradually reached that of the CV solution without SDBS. Accordingly, a new method was developed to determine the CV concentration in aqueous solution containing the anionic surfactant SDBS. Under the optimal conditions, i.e., a detection wavelength of 584 nm, an SDBS concentration of 4.8 mmol L^{-1} and a reaction time of 1 h, the linear range of the method was 0.16×10^{-2} mmol L^{-1}–1.6 mmol L^{-1}.

Acknowledgments

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