Kinetic Study on the Reaction of Alkaline Fading of Crystal Violet in Microemulsions

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Keywords: Kinetic; Microemulsion; Crystal Violet

Abstract: In this experiment, the UV spectrophotometry was used to measure: (1) The reaction rate constants of alkaline fading of crystal violet in the NaOH aqueous solution at different concentrations; (2) The rate of alkaline fading of crystal violet in the microemulsions with different AOT concentration and different *R* values respectively. The reaction was found to be slower in the water cell of the microemulsion than in free water, and the reaction rate increased as the water to surfactant ratio *R* increased in the microemulsions system.

1. Introduction

Microemulsions are generally thermodynamic stable systems formed by the spontaneous formation of surfactants, co-surfactants, oils and water at appropriate ratios. In the W/O type microemulsion reaction, the water droplet is surrounded by a boundary film composed of a surfactant and a co-surfactant, which can be regarded as a microreactor. The size of the water droplet can be adjusted by changing the molar ratio of water and surfactant to control the reaction rate [1-4]. AOT is a commonly used surfactant in researches. The molecular head is extremely small, and the two alkyl tails are in medium length and branched. This structure determines that it is easy to form W/O microemulsion without adding co-surfactant [5, 6].

In this paper, the reaction rate of alkaline fading of crystal violet (CV) in microemulsion was determined by UV spectrophotometry. The effect of different sodium hydroxide concentrations on the first-order reaction rate and the effect of different *R* values as well as different AOT concentrations on the second-order reaction of the reaction rate were investigated.

2. Experiment

2.1. Materials

Crystal Violet: analytical reagent, Sinopharm Chemical Reagent Co., Ltd.; Sodium hydroxide: > 98% Laiyang Economic and Technological Development Zone Fine Chemical Plant; AOT: > 96% Alfa Aesar (Tianjin) Chemical Co., Ltd.; Phenolphthalein: analytical reagent, Sinopharm Chemical Reagent Co., Ltd.; n-decane: > 99% Tianjin Guangfu Fine Chemical Research Institute, The distilled water used in this experiment was double-distilled water.

2.2. Sample Preparation

A crystal violet solution with the concentration of 0.05 mol/L was prepared as a stock solution.

Weigh a certain amount of sodium hydroxide, transfer it to a 100 ml volumetric flask after dissolving it in double-distilled water, and prepare a sodium hydroxide solution with a concentration of about 0.09 mol/L. The concentration of sodium hydroxide was titrated with a standard solution of potassium hydrogen phthalate, and the exact concentration was 0.08720 mol/L. Dilute the above solution five times to obtain an aqueous solution of sodium hydroxide with the concentration of 0.01744 mol/L.

Take a certain amount of AOT in a 10 ml volumetric flask according to the experimental requirements, dissolved it in n-decane, and keep the constant volume. Then, made them up to AOT n-decane solution with the concentration of 0.05 mol/L, 0.10 mol/L, 0.15 mol/L, 0.20 mol/L for use.

2.3. Kinetic Measurement

1 μl of a CV aqueous solution was added into the cuvette, and the characteristic absorption peak of the CV was 590 nm, as shown in Figure 1. In this experiment, the measurement of the CV absorbance was carried out at a wavelength of 590 nm.

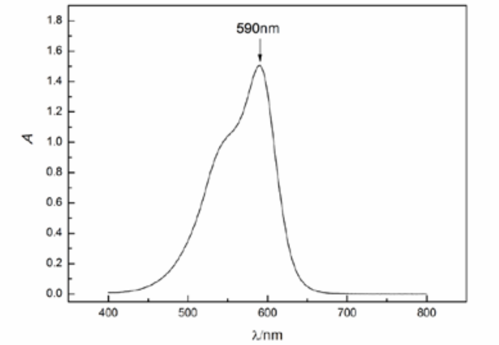

Figure 1 Variation of the absorption spectrum with wavelength of CV in water.

2.3.1. Measurement of Kinetics of Alkaline Fading of CV in NaOH Aqueous Solution.

Add 2.5 ml of distilled water and 0.01744 mol/L of NaOH aqueous solution to the cuvette of the reference cell and the sample cell, respectively, and add 1 μl of crystal violet aqueous solution to the sample cell again. Record the change in absorbance of crystal violet in NaOH aqueous solution at different time with the wavelength of 590 nm. As can be seen in Figure 2, the absorbance of crystal violet decreases with time.

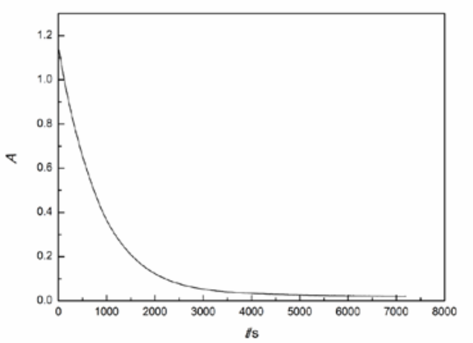

Figure 2 Plot of absorbance versus *t* for alkaline fading of CV in water/AOT/decane at λ = 590 nm at 298.15K.

2.3.2. Measurement of Kinetics of Alkaline Fading of CV in Microemulsion.

Add 2.5 ml of water/AOT/n-decane solution and NaOH/AOT/n-decane solution to the cuvette of the reference cell and the sample cell according to the *R* value required by the experiment, and add 1 μl of CV aqueous solution to the sample cell to measure the absorbance change of CV fading at different time.

2.4. Data Processing

The reaction of CV and sodium hydroxide is a second-order reaction [7]:

$$CV^{+} + OH^{-} \rightarrow CV\text{-}OH$$

The reaction rate is:

$$\gamma = -\frac{dc_{\mathrm{cv}}}{dt} = k_2 c_{\mathrm{cv}} c_{\mathrm{OH}} \tag{1}$$

k_2 is the second-order reaction rate constant. c_{cv} and c_{OH} are the concentrations of CV and sodium hydroxide ions, respectively. When the concentration of hydroxide ions is much larger than the concentration of CV, that is, $c_{\mathrm{OH}} >> c_{\mathrm{cv}}$, the reaction can be regarded as a pseudo first-order reaction.

Set

$$k_1 = k_2 c_{\mathrm{OH}} \tag{2}$$

Therefore

$$\frac{dc_{\mathrm{cv}}}{dt} = -k_1 c_{\mathrm{cv}} \tag{3}$$

The absorbance *A* of CV at different time *t* during the reaction was determined by ultraviolet spectrophotometry, using the Lambert-Beer's law and integrating eq 3 yields：

$$\ln A = \ln A_0 - k_1 t \tag{4}$$

It can be seen from Figure 3 that ln*A* and reaction time *t* are in a good linear correlation, and the slope is obtained by k_1.

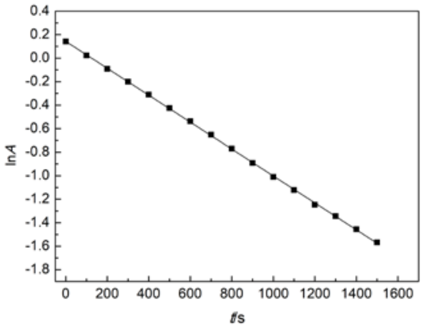

Figure 3. Plot of ln*A* versus *t* for alkaline fading of CV in water/AOT/decane at 298.15K.

3. Results and Discussion

Table 1 shows the first-order reaction rate constant of alkaline fading of CV in NaOH aqueous solution with different concentration. It can be seen from Table 1 that the first-order reaction rate constant of alkaline fading of CV with the increase of the concentration of NaOH gradually increase.

Table 1 Values of first order rate constant k_1 at various concentrations of NaOH for alkaline fading of CV in water/AOT/decane at 298.15K.

$c_{\mathrm{NaOH}}\times10^3$ (mol/L)	$k_1\times10^4$（s^{-1}）
0.698	1.43
1.744	4.22
2.790	7.82
3.488	10.56

It can be seen from Figure 4 that as the concentration of hydroxide ions increases, the rate of alkaline fading of CV increases accordingly. In an aqueous solution within a certain concentration range, the first-order reaction rate constant is proportional to the concentration of sodium hydroxide.

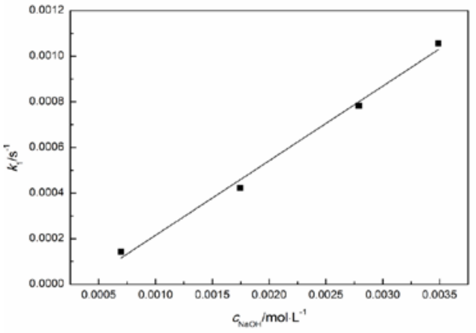

Figure 4 Plot of k_1 vs c_{NaOH} for alkaline fading of CV in water/AOT/decane at 298.15K.

Table 2 K_2 for alkaline fading of CV in water/AOT/decane microemulsions of different *R*.

R	$k_2 \times 10^3$ (mol^{-1}·L·s^{-1})
5	0.048
10	5.1
15	5.3
20	7.7
25	7.7
30	7.8

The concentration of AOT in the fixed microemulsion was 0.10 mol/L, and the value of *R* was changed to measure the second-order reaction rate constant for the alkaline fading of CV. The values are shown in Table 2.

As can be seen from Figure 5, when $R < 20$, the second-order reaction rate constant of the CV alkaline fading reaction gradually increases as it increases. This is because in the water/AOT/n-decane microemulsion system, when the *R* value is small, CV will associate with AOT, reducing the concentration of free CV ions, and the ion activity of CV in the water droplet was attenuated. The reaction of CV ions and hydroxide ions is carried out in the microemulsion water droplet, and the CV actually reacted with sodium hydroxide is less than the experimental preparation, so the reaction rate of CV in the microemulsion system increases with the increases of the water droplet. The larger the *R* value, the larger the water droplet of microemulsion, the weaker the association between CV and AOT, and the closer the activity of CV ions in the water droplet to the ion activity in pure water. So, with the increase of the water droplet, reaction rate constant is closer to the reaction rate constant in pure water [8].

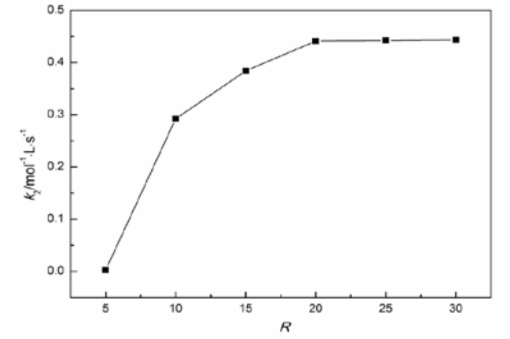

Figure 5 Plot of k_2 vs *R* for alkaline fading of CV in water/AOT/decane at 298.15K.

When the fixed *R* value is 10, the concentration of AOT is changed to measure the second-order reaction rate constant of the CV alkalic fading reaction at different AOT concentrations. As shown in Table 3.

It can be seen from Table 3 that when the *R* value is fixed, the rate constant of alkaline fading of CV does not change substantially in the microemulsion system of different AOT concentrations. That is, the concentration change of AOT has little effect on the second-order reaction rate constant. This is because changing the concentration of AOT while keeping the *R* value is essentially only changing the number of water droplets in the microemulsion without different size of the water droplets, so the structure and properties of the water in the water droplet are not changed [9, 10], that is, The different of the concentration of AOT only changed the concentration of the water droplet. On the other hand, both CV and hydroxide ions are present in the water droplet, and the concentration change of the water droplet does not cause concentration change of crystal violet and hydroxide ions in the water droplet. Therefore, the second-order reaction rate constant of the reaction does not substantially difference with changed AOT concentration and fixed *R* value.

Table 3 k_2 for the alkaline fading of CV in water/AOT/decane microemulsions of different AOT concentrations at 298 K.

c_{AOT} (mol/L)	$k_2 \times 10^3$(mol^{-1}·L·s^{-1})
0.05	5.62
0.10	5.57
0.15	5.79
0.20	5.64

4. Conclusion

In the W/O microemulsion system, when the AOT concentration is fixed, the second-order reaction rate alkaline fading of CV increases with the increase of *R* value; when the *R* value is fixed, the AOT of the microemulsion is increased, while the CV alkalic fading second-order reaction rate is almost unaffected, that is, k_2 is basically unchanged.

Acknowledgments

This work was financially supported by School-level Students Innovation and Entrepreneurship Training Program (No. cx2018051), Natural Science Foundation of Shandong Province, China (No. ZR2017BB015), the Higher Education Research Project of Shandong Province (No. J17KB065), and School Support Foundation of Jining Medical University (Nos. JY2017KJ015, JY2017KJ042). NSFC Cultivation Project of Jining Medical University (Nos. JYP2018KJ03, JYP2018KJ17, JYP2018KJ12).

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