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Kinetic Spectrophotometric Determination of Trace Sodium Lauryl Sulfate Based on Catalytic Oxidation of Butyl Rhodamine B

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In 1.0 M of sulfuric acid medium, sodium lauryl sulfate has a catalytic effect on the oxidation reaction of butyl rhodamine B (BRhB) by potassium periodate at 80 ºC. Based on this principle, a novel catalytic kinetic method for the determination of sodium lauryl sulfate is developed. A linear range was presented over the range of 0.10-1.10 μg/mL for sodium lauryl sulfate at 552 nm. The detection limit of the method was 0.035 μg/mL for sodium lauryl sulfate. The method has been satisfactorily applied to the determination of sodium lauryl sulfate in water sample and detergent with satisfactory results.

Key Words: Sodium lauryl sulfate, Butyl rhodamine B, Potassium periodate, Catalytic oxidation, Kinetic spectrophotometry, Water, Detergent.

INTRODUCTION

Sodium lauryl sulfate (SLS)[1] is an anionic surfactant. As surfactants are widely applied to the fields of oil industry, plastic, rubber, leather industry, paper-making, printing industry, weaving printing and dyeing industry, pick sand industry, metal machining, agricultural medicine, fertilizer, *etc*., in recent years[2], the amount of the SLS that was let into waste waters was largely increased and this has caused the decrease in self-cleaning ability of water body and the decrease in contents of dissolved oxygen in water body[3]. This resulted in the pollution to environment and it harmed aquicolous biology. To actualize the monitoring of surfactants has become one important task in the work of environmental monitoring. The studies and establishment of highly sensitive methods for the determination of sodium lauryl sulfate have an important environmental significance. As spectrophotometry has the advantages of low instrumentation cost, high sensitivity, operation simplicity and low analytical cost, it was found application in the determination of anionic surfactants[3,4]. Methylene blue spectrophotometry is a commonly used method for the determination of sodium lauryl sulfate[3-6]. However, this kind of methods needs to use toxic organic extractive reagent such as chloroform, toluene, *etc*., for extraction and has emulsification, which is not convenient for operation. As kinetic spectrophotometry[7-9] has the advantages of high sensitivity, low detection limit, it has aroused scientists' enormous

interests in trace analysis. However, report on the determination study of SLS is very few by kinetic spectrophotometry. Pourreza *et al.*[10], reported use of the inhibitive effect of SLS on aniline blue-thiosulfate reaction to establish a kinetic spectrophotometric method for the determination of SLS. In this article, it is observed that in 1.0 M of sulfuric acid medium SLS catalyzes the oxidation discolouring reaction of butyl rhodamine B by KIO_4 at 80 ºC. Based on this fact, a novel kinetic spectrophotometric method for the determination of sodium lauryl sulfate has been established. The proposed method has been applied to the determination of sodium lauryl sulfate in water sample and detergent with satisfactory results. It does not need any extraction using toxic organic solvent and has the advantages that the analytical cost is low, the sensitivity is high and the operation is simple.

EXPERIMENTAL

In this study, all the reagents used were of analytical grade and all solutions were prepared with deionized distilled water.

A stock solution of SLS containing 1000 μg/mL SLS was prepared by dissolving 0.0500 g of SLS in 50 mL of water. 10.0 μg/mL of working solution were obtained by suitable dilution of the stock standard solution with water. A 4.0×10^{-4} M of butyl rhodamine B (BRhB) solution was prepared by dissolving 0.0107 g of BRhB in 50 mL of water. A 2.5×10^{-3} M of potassium periodate solution was obtained by dissolving 0.0288 g of KIO_4 in 50 mL of water. 1.0 M of sulfuric acid

solution was prepared by appropriate dilution of its concentrated solution.

Absorbance was measured with a 722S spectrophotometer (Shanghai Lingguang Technique Co. Ltd., China), using 1 cm cells. The reaction temperature was controlled by A HH-2 digital display constant temperature water-bath thermostat (Jiangsu Jintan Ronghua Apparetus Manufacture Co. Ltd., China). A stopwatch was employed to record the reaction time.

Recommended procedure: In this procedure the following order was adopted, 1.0 mL of 4.0×10^{-4} M BRhB solution, 1.0 mL of 1.0 M H_2SO_4 solution and 1.0 mL of 2.5×10^{-3} M KIO_4 solution were subsequently placed into two 50 mL comparison tubes, respectively. In the one comparison tube, an appropriate amount of SLS solution (for conditional optimization experiments: 35.0 µg) was put in the mixed solution (catalytic reaction), while the other one without SLS acted as the non-catalytic reaction. The mixtures were diluted up to the mark with water, shaken and then heated with a water bath of 80 ℃ for 12 min. Then, the mixtures were taken out and cooled down for 5 min by running water to terminate the reaction. The absorbance A_0 of the non-catalytic reaction solution and the absorbance A of the catalytic reaction solution were determined at 552 nm in 1-cm cells against water, then $\Delta A = A_0 - A$ was calculated for SLS determination.

Procedure for the determination of SLS in water sample: 10 mL of tap water sample was taken and determined for SLS according to the general procedure. The methylene blue spectrophotometry[3] was employed as a contrast method for comparison.

Procedure for SLS in detergent: One mL of detergent was taken and diluted to the constant volume of 100 mL with water. A 1.0 mL of the solution was taken and determined according to the general procedure for the determination of sodium lauryl sulfate. The methylene blue spectrophotometry[3] was employed as a contrast method for comparison.

RESULTS AND DISCUSSION

The absorption curves of different system were drawn according to the general procedure and the results of absorption spectra are shown in Fig. 1. Curve-a shows an absorption of BRhB. It can be seen that after KIO_4 was added to BRhB solution (curve-b), the absorbance decreased. This indicates that KIO_4 oxidized BRhB to discolour. The red colour of BRhB became shallow. After SLS was added to the system, KIO_4 + BRhB (curve-c), absorbance of the system obviously decreased, showing that SLS accelerated the discolouring oxidation reaction rate of BRhB by KIO_4 and the SLS has a catalytic effect on the reaction (curve-d). The maximum absorption wavelengths of the catalytic and non-catalytic reactions were both located at 552 nm. In the present work, 552 nm was selected as the determination wavelength.

Effect of acidity: According to the general procedure, 0.1, 0.3, 0.5, 0.9, 1.0, 1.1, 1.2, 1.5 mL of 1.0 M sulfuric acid were, respectively added to study the effect of acidity. The results indicated that the absorbance difference (ΔA) of the net catalytic reaction increased as the amount of sulfuric acid increased over 0.1-1.0 mL. At 1.0 mL, it attained a maximum absorbance difference (ΔA). Then, ΔA decreased as the amount
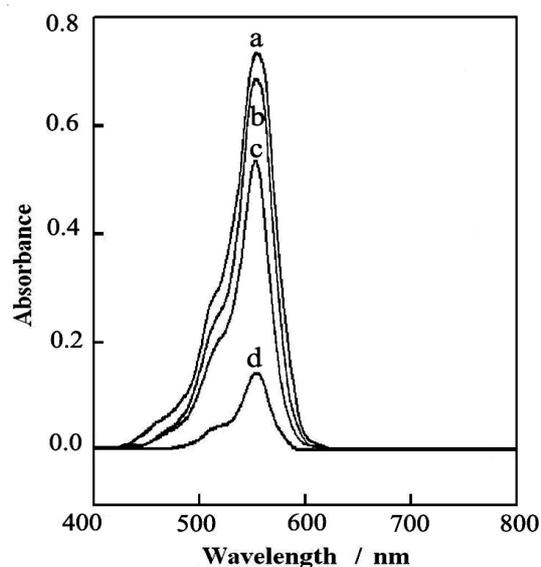

Fig. 1. Absorption spectra: (a) BRhB (against water); (b) BRhB + KIO_4 (against water) - non-catalytic reaction A_0; (c) RhB + KIO_4 + SLS (against water) - catalytic reaction A; (d)- net catalytic reaction, $\Delta A = A_0 - A$; [SLS] = 0.70 µg/mL; [H_2SO_4] = 2.0×10^{-2} M; [KIO_4] = 5.0×10^{-5} M; [BRhB] = 8.0×10^{-6} M

of sulfuric acid increased. Hence, 1.0 mL of 0.10 M sulfuric acid solution was chosen for further studies.

Effect of the amount of BRhB: 0, 0.2, 0.5, 0.8, 1.0, 1.2, 1.4 mL of 4.0×10^{-4} M BRhB solution were, respectively added to make experiments of the effect of BRhB. The results showed that when the amount of BRhB was over the range of 0-1.0 mL, ΔA continuously increased. At 1.0 mL, ΔA reached a maximum. Then, ΔA gradually decreased as the amount of BRhB increased. In this work, 1.0 mL of 4.0×10^{-4} M BRhB solution was selected as the optimum amount.

Effect of the amount of KIO_4: 0, 0.2, 0.5, 0.8, 0.9, 1.0, 1.1, 1.2, 1.4 mL of 2.5×10^{-3} M KIO_4 solution were, respectively added to study the effect of KIO_4. The results showed that ΔA of the net catalytic reaction continuously increased when the amount of KIO_4 was over 0-1.0 mL. At 1.0 mL, ΔA attained a maximum. Then, ΔA decreased with increasing the amount of KIO_4. Thus, 1.0 mL of 2.5×10^{-3} M KIO_4 solution was chosen as the optimum amount.

Effect of temperature: The experimental results showed that below 60 ℃ both the catalytic and non-catalytic reactions were very slow. When the temperature of water bath was over 60-80 ℃, ΔA increased as the temperature increased. At this time, the kinetic reactive rate increased as the temperature increased. When the temperature reached 80 ℃, ΔA attained a maximum. At this time, the kinetic reactive rate was a maximum and the sensitivity was the highest. As the temperature increased over the range of 80-100 ℃, ΔA gradually decreased. At this time, the kinetic reactive rate and sensitivity decreased as the temperature increased. Therefore, 80 ℃ was adopted as the optimum working temperature in the present work. A regression calculation for the data over 60-80 ℃ was made and the regression equation obtained was as follows: $\log \Delta A = -2.492 \times 10^3 \times 1/T + 6.250$, with a correlative coefficient of r = 0.9958. According to the equation, the apparent activation energy of the catalytic reaction obtained was E_a = 47.71 kJ/mol.

TABLE-1
DETERMINED RESULTS OF SAMPLES

Sample	Found (n = 13)	Average	Relative standard deviation (RSD, %)	Added	Recovered	Recovery (%)	Methylene blue spectrophotometric contrast method[3] (g/ mL)
Tap water (µg/mL)	0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0	0	0	0600	0.595	99.2	0
Detergent (g/mL)	0.114, 0.115, 0.105, 0.117, 0.115, 0.102, 0.109, 0.119, 0.108, 0.109, 0.118, 0.112, 0.114	0.112	4.58	0.400	0.404	101	0.112

Effect of heating time: The experimental results indicated that when heating time was 1-12 min, ΔA increased with the increase in heating time. At this time, the kinetic reactive rate and reactive sensitivity increased as the heating time increased. ΔA reached a maximum at 12 min. At this time, the kinetic reactive rate and reactive sensitivity were the highest. As heating time further increased over the range of 12-18 min, ΔA decreased. At this time, the kinetic reactive rate and reactive sensitivity decreased as the heating time increased. In the present work, the optimum heating time was adopted to be 12 min. At this time, the reactive sensitivity was the highest. When ΔA was in the range of 1-12 min, ΔA and the time (t) presented a linear relationship. By plotting ΔA to t, the linear regression equation between the absorbance difference and heating time was obtained as follows: $\Delta A = 7.02 \times 10^{-3} t$ (min) + 0.0129, with a correlative coefficient of 0.9958, where t is heating time. From this equation the rate constant of the catalytic reaction was calculated to be $k = 1.170 \times 10^{-4} s^{-1}$ and the half life was 6.08 min.

Stability of system: Under the optimum experimental conditions the determination of the system stability were made. When 0.70 µg/mL of SLS was determined, the variation of ΔA was less than 5 % within 2.5 h and the system remained stable.

Analytical figures of merit: The experimental results showed that under the optimum experimental conditions the linear range of determination of SLS by the present procedure was 0.10-1.10 µg/mL and its linear regression equation was $\Delta A = 0.1697C$ (C: µg/mL) - 0.0052, with a correlative coefficient of r = 0.9925. According to the general procedure, eleven replicate determinations of reagent blank were made and the detection limit of the method was calculated to be 0.035 µg/mL by 3S/K method, where S is the standard deviation of 11 replicate reagent blank determinations and K is the slope of the standard working curve, respectively. The average value of thirteen replicate determinations of 0.70 µg/mL SLS was 0.70 µg/mL and its relative standard deviation was 1.3 %. The results indicated that the present procedure has very good reproducibility and precision. The precision of the procedure for real sample was checked by repetitive analyses (n = 13) of the sample and the results are listed in Table-1. The results in Table-1 indicate satisfactory precision for the proposed method.

Interference study: Under the optimum experimental conditions, the effect of coexisting substances was studied. When 0.70 µg/mL SLS was determined and a relative error was controlled within ± 5 %, the allowable amounts of co-existing substances are as follows (mass multiple, m/m): PO_4^{3-} (360); emulsifier OP (195); Ti^{4+} (140); ethylenediamine-tetraacetic acid (130); I^- (85); F^- (75); Bi^{3+} (65); cetyltrimethyl-amonium bromide (60); Tween-80 (55); tartaric acid (30); Mo(VI) (15); NO_3^- (12); Ce^{4+} (10); Fe^{2+} (9); Th^{4+} (5); Eu^{3+}, acetic acid (7); oxalic acid (6); Li^+ (4) ; Si^{4+} (3); Ca^{2+}, Zn^{2+} (2); Al^{3+} (1.5); Mg^{2+}, sodium dodecyl sulphonate (0.8); Fe^{3+}, Ba^{2+} (0.6); Cd^{2+} (0.3); Cu^{2+}, MnO_4^- (0.2).

Application: The proposed method was successfully applied to the determination of SLS in water sample and detergent and the results obtained are shown in Table-1. It can be seen that the analytical results of the proposed method agreed well with those of the methylene blue spectrophoto-metric method[3]. The analytical results of practical sample determined by the proposed method were excellent.

Conclusion

In this article, a novel method was developed for the kinetic spectrophotometric determination of trace SLS using SLS - BRhB-KIO_4 system. The apparent activation energy of the catalytic reaction was 47.71 kJ/mol. A good linear relationship was presented over the range of 0.10-1.10 µg/mL for SLS with a detection limit of 0.035 µg/mL. The proposed method has been satisfactorily used in the determination of water sample and detergent with good results.

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