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Spectrophotometric determination of sodium dodecylbenzene sulphonate using congo red

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A new spectrophotometric method is developed to determine sodium dodecylbenezene sulphonate (SDBS) in natural water without the use of organic hydrophobic solvents and two-phase extraction. In BR buffer solution (*p*H 2.03), SDBS replaces sodium diphenyl diazo-bis-α-naphthylamine-4-sulphonate (Congo red, CR) in CR-cetylpyridinium chloride (CPC) system. Application of absorbance ratio difference (ARD) to this replacement reaction gives a new spectrophotometric method for the determination of SDBS. The absorbance measurements are made at 590 nm and 469 nm. Results have shown that absorbance ratio difference (ΔA_r) gives linear curve in the range of 3.3 -139.4 mg/L for SDBS. The limit of determination of SDBS (3δ/k) is 1.1 mg/L. The method has been employed to determine SDBS in natural water with satisfactory results. Relative standard deviation was less than 5%, and the recovery was about 103.7%. The method is comparable to new methylene blue (NMB) method.

Keywords: Linear alkylbenezene sulphobates, Sodium dodecylbenezene sulphonate, Cetylpyridinium chloride, Congo red, Absorbance ratio difference

Linear alkylbenezene sulphobates (LASs) are anionic surfactants, which are widely used in modern industry. Due to their extensive use LASs have became one of the most familiar organic pollutants due to their environmental effects[1]. LASs impact cell's osmotic permeability[2,3], interact with some membrane proteins[4], cause chronic toxicity[5-7], and even influence the dissolved oxygen in water[4]. Hence, it is very important to determine LASs in natural water.

There are many methods for the determination and estimation of LASs in water, such as chromatography[8,9], electrochemical[10] and spectrophotometric methods[11,12]. The most widely used spectrophotometric method in anionic surfactant analysis is the so-called two-phase extraction method. In this method, the negatively charged anionic surfactant is extracted in a hydrophobic organic solvent like chloroform and a lipophilic ion-pair is formed with a positively charged ionic dye[13]. This procedure is currently used as a standard method; however, it suffers from several drawbacks, such as the toxicity of chloroform, turbidity of the solution, interferences by other components, time-consumed and so on[12]. So some alternative spectrophotometric methods without two-phase extraction have been developed to detect LASs[14-16].

In the present work, sodium diphenyl diazo-bis-α-naphthylamine-4-sulphonate (Congo red, CR) has been used to determine the sodium dodecylbenezene sulphonate (SDBS) in water. In the method, CR is reacted with cetylpyridinium chloride (CPC) at *p*H 2.03, which changes the colour of CR solution. When SBDS is added into this solution, SDBS reacts with CPC, too. As a result, the SDBS-CPC ion-pair compound is formed by replacing CR in CR-CPC system. The solution regains its original colour of CR. Combining this replacement reaction with absorbance ratio difference (ARD) method, a new spectrophotometric method has been developed for determination of trace levels of SDBS in natural water. This method is more convenient since it does not require a time-consuming extraction process and no use of organic solvents. It is a more environmentally friendly method for the determination of anionic surfactant in natural water.

Experimental Procedure

Apparatus and instruments

The absorption spectra of CR were recorded with a Model Lambda-25 spectrometer (Perkin-Elmer, USA). The spectrometer was managed by UV WinLab software (Version 2.85.04). The *p*H of

solutions was measured with a Model pHS-25 acidity meter (Shanghai Precise Sci. Instrum., China). A Model BCD-196 refrigerator freezer (Meiling Production of Anhui Province, China) was used to store the solutions.

Reagents and solutions

Sodium dodecylbenezene sulphonate (SDBS) and cetylpyridinium chloride (CPC) were purchased from Shanghai Reagent Company. A SDBS solution (1.0 mmol/L) was prepared by dissolving 0.1742 g SDBS in 500 mL deionized water. Similarly, CPC solution (1.0 mmol/L) was prepared. Congo red (CR) was purchased from Shanghai Yuanhang Reagent Company. CR solution (0.6667 mmol/L) was prepared by dissolving 0.2322 g CR in 500 mL deionized water. The Britton-Robinson (BR) buffer solution (*p*H 2.03) was prepared using phosphoric acid, acetic acid, boric acid and sodium hydroxide. The buffer[17] is used to adjust the acidity of solution to find a proper and highly sensitive condition for this new spectrophotometric system. All other reagents used in this work were of analytical reagent grade.

Method

(i) Interaction between SBDS and CPC-CR

Into the flasks, 1.0 mL of BR buffer solution (*p*H 2.03), 0.6 mL of 0.6667 mmol/L CR solution and appropriate volumes of CPC solution (1.0 mmol/L) were added. The solution mixture was diluted to 5.0 mL with deionized water and mixed well. Then, 0.6 mL of SBDS solution was added in each flask. The contents in each flask were diluted to 10.0 mL with deionized water and mixed well. After 5 min, the absorbances of the SDBS-CPC-CR solutions against the reagent blank (CPC-CR) were measured. The absorbances (λ_1 and λ_2) were measured at 469 nm and 590 nm, respectively.

For understanding the mechanism of SDBS interaction with CPC-CR, solutions were added into four 10.0 mL flask as follows: (i) 0.60 mL of 0.6667 mol/L CR and 1.0 mL of BR buffer solution; (ii) 0.60 mL of 0.6667 mmol/L CR, 0.2 mL of 1.0 mmol/L CPC and 1.0 mL of BR buffer solution; (iii) 0.60 mL of 0.6667 mmol/L CR, 0.2 mL of 1.0 mmol/L CPC, 0.60 mL of 1.0 mmol/L SDBS and 1.0 mL of BR buffer solution; (iv) 0.60 mL of 0.6667 mmol/L CR, 0.60 mL of 1.0 mmol/L SDBS and 1.0 mL of BR buffer solution. Finally, the contents in each flask were diluted to 10.0 mL with deionized water and mixed well. After reacting for 5 min, the absorption spectra of these solutions were measured against water.

(ii) Determination of SDBS

For SDBS interaction with CPC-CR system, the absorbance ratio difference method (ARD)[18] can be used to determine the SDBS content in the system, as per Eq. (1),

$$\Delta A_r = pC_{M0} + q \qquad \ldots(1)$$

where ΔA_r is the difference of absorbance ratio of the solutions; C_{M0} is the concentration of SDBS, and p and q are constants when λ_1, λ_2 and the reaction condition are selected. Here, 1.0 mL of BR buffer solution (*p*H 2.03), 0.6 mL of 0.6667 mmol/L CR and 0.2 mL of 1.0 mmol/L CPC solution were added; the resultant solution was diluted to 5.0 mL with deionized water and mixed well. Then pretreated water samples were added to the flasks. The solutions were diluted to 10.0 mL with deionized water and mixed well. After 5 min, the absorbance of the reaction solution was measured at 590 nm and 469 nm against water. $A_r = A_{590nm}/A_{469nm}$. Thus,

$$A_r = A_r - A_r^0 = \frac{A_{590nm}}{A_{469nm}} - \frac{A_{590nm}^0}{A_{469nm}^0} \qquad \ldots(2)$$

where A^0_{590nm} and A^0_{469nm} are the absorbance of reagent blank (CPC-CR) against water. Finally, the SDBS concentration in the sample was calculated from plot of ΔA_r versus C_{M0}.

Determination of effect of foreign substances

The effects of foreign substances on the determination of 0.02 mmol/L SDBS with 0.04 mmol/L CR and 0.02 mmol/L CPC was investigated using the developed method. These foreign substances were added into the flasks containing BR buffer solution, CR, CPC and SDBS. Then the absorbance of the reaction solution was measured at 590 nm and 469 nm against water.

Results and Discussion

In *p*H 2.03 BR buffer solution, negatively charged CR reacts with positively charged CPC and forms an ion-pair through electrostatic interaction[17], as evident from the difference between curves 1 and 2 in Fig. 1. Because SDBS also forms anionic species at *p*H 2.03, negatively charged CR don't react with SDBS due to the electrostatic exclusion between SDBS and CR.

Hence, there is no obvious difference between the curves 1 and 4 (Fig. 1). Another phenomenon which takes place is that SDBS reacts with CPC-CR and alters the colour of the solution, as indicated by the difference between curves 2 and 3. Curves 1, 3 and 4 have the same shape, and same λ_{max}, which was about 555 nm; while for curve 2, its shape is different from that of curves 1, 3 and 4, and its λ_{max}, (475 nm) is also different from that of curves 1, 3 and 4. In other flask, when in BR buffer solution, CR and SDBS were added first followed by CPC, at first, there was no obvious change in the solution's colour with the addition of CPC. But the colour of solution gradually changed when excessive CPC was added (The data is not shown). With the initial addition of CPC, the entire CPC reacts with SDBS available in solution; the colour of solution did not change due to the absence of free CPC. When excessive CPC is added, some residual CPC remains in the solution after reacting completely with SDBS. This residual CPC reacts with CR in solution and changes the colour of solution. So the interaction of SDBS and CPC was more preferred than of CPC and CR. All these experimental results indicated that negatively charged SDBS replaces CR in CPC-CR system, form SDBS-CPC ion-pair (Fig. 2).

In this reaction, the amount of CPC used and the ratio between CPC and CR is important. If there is not enough CPC for formation of ion-pair CPC-CR. SDBS may not react with CPC-CR completely. But if too much CPC is added, some of these CPC may directly react with SDBS without the formation of CPC-CR. This may not change the colour of the solution and thus is not favourable for the determination of SDBS. On the contrary, it may influence the determination of SDBS. So there is an optimal CPC concentration for obtaining complete reaction. Here, when 0.2 mL of 1.0 mmol/L CPC was added, the difference between wave crest and wave hollow was biggest, as evident from curve 3 in Fig. 3. This difference could indicate the interaction between SDBS and CR-CPC[19]. This bigger difference was also favourable for the determination of SDBS in ARD method[19]. Here, 0.2 mL of 1.0 mmol/L CPC was the most appropriate condition for the current experiment, the corresponding ratio of CPC to CR was 1:2. This ratio was used in all the experiments, and the working wavelengths were selected as 469 nm and 590 nm, respectively.

Determination of SDSB

SDSB reacts with CPC in the absence of CR with no obvious change in the colour of system. SDBS,

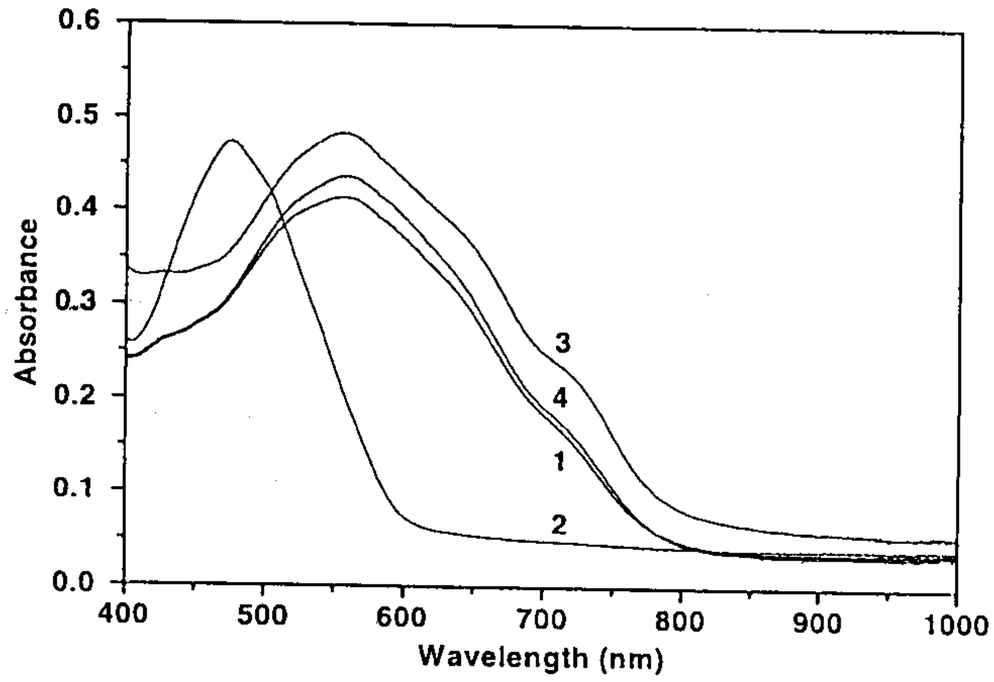

Fig. 1 — Variation of absorption spectra of different solutions. 1: 0.04 mmol/L CR in *p*H 2.03 BR buffer solution; 2: 0.04 mmol/L CR and 0.002 mmol/L CPC in *p*H 2.03 BR buffer solution; 3: 0.04 mmol/L CR, 0.002 mmol/L CPC and 0.002 mmol/L SDBS in *p*H 2.03 BR buffer solution; 4: 0.04 mmol/L CR and 0.002 mmol/L SDBS in *p*H 2.03 BR buffer solution. All absorption spectra are measured against water.

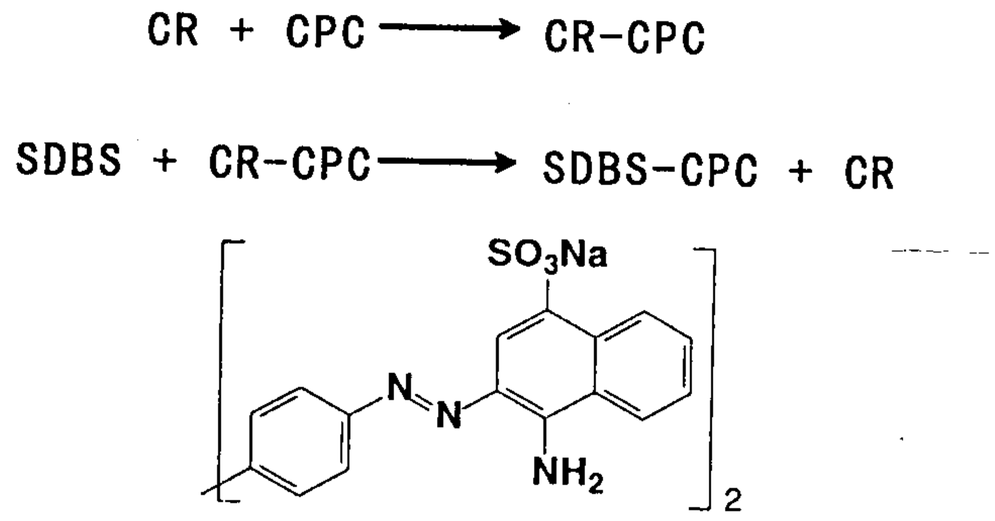

Fig. 2 — Structure of CR and the reaction scheme of SDBS with CR and CPC.

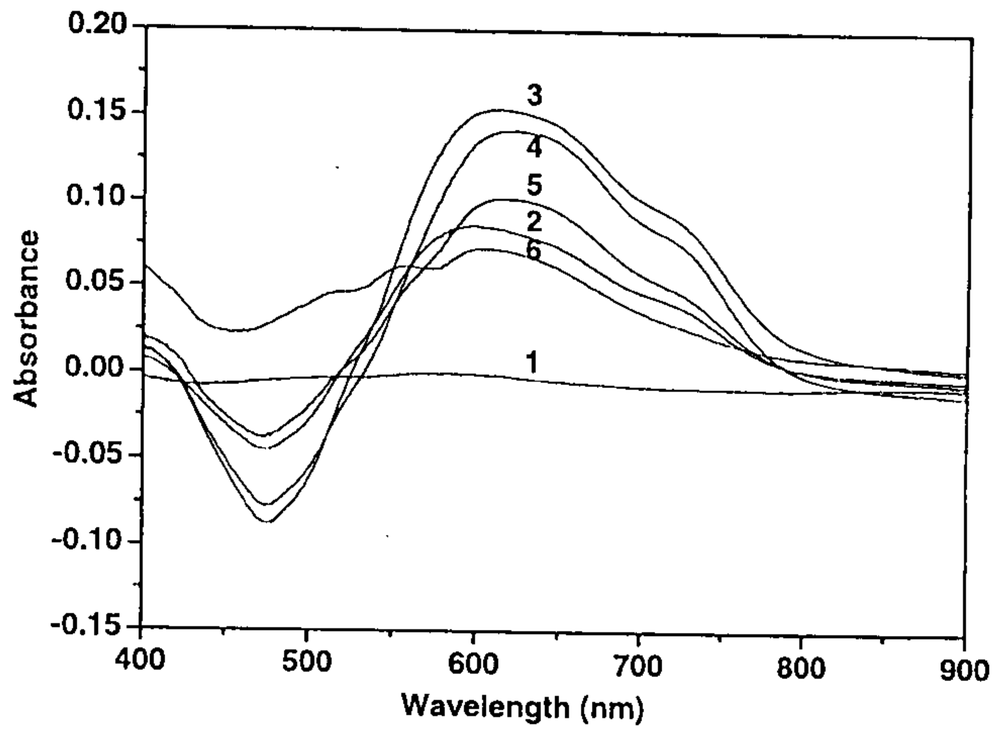

Fig. 3 — Variation of absorption spectra of solutions with different concentration of CPC with 0.04 mmol/L CR and 0.006 mmol/L in *p*H 2.03 BR buffer solution. From 1 to 6, the concentrations of CPC are 0, 0.001, 0.002, 0.003, 0.004 and 0.005 mmol/L respectively. The absorption spectra are measured against reagent blank (without the addition of SDBS).

being negatively charged can not react with CR due to electrostatic repulsion. But SDBS can react with CPC in the presence of CR. During this process, the colour of the system changes. In the present system CPC-CR may be regarded as a composite spectrometric probe. As evident from Eq. (1), in the lower concentration range, ΔA_r versus C_{M0} was linear. In this method, factor of sensitivity p was found to be inversely proportional to the spectrometric probe's concentration; the lesser the amount of CPC-CR are added, the higher sensitivity is observed[18]. However, too low value of CPC and CR could cause an obvious error of measurement because of increase of fraction of instrument background noise[19]. Thus an optimal concentration of the spectrometric probe for obtaining a higher analytical sensitivity needs to be assigned. In the present study, series of standard curves of SDBS with different concentration of probe were prepared (Fig. 4 and Table 1). The results indicated that when CR is changed from 0.02 to 0.06 mmol/L, correspondingly CPC needs to be changed from 0.01 to 0.03 mmol/L, and correspondingly the slope coefficients p of standard curves also changes from 22624 to 10414 L/mol. These results indicate that higher p could be obtained at lower concentration of CR-CPC, which is in accordance with ARD theory. However, increase in the fraction of instrument background noise at lower concentration of CR-CPC may influence the analytical sensitivity of system. In view of these two aspects, a suitable concentration of CR and CPC should be selected for the highest analytical sensitivity in the determination of SDBS. In the present work, 0.04 mmol/L CR and 0.02 mmol/L CPC were selected as the most appropriate concentrations.

Effects of foreign substances

The experimental results indicated that none of the following species affect the direct determination of even 0.00002 mol/L SDBS (error less than 5%): Na^+, 460; Cl^-, 710; Al^{3+}, 10.0; NH_4^+, 5.0; Ba^{2+}, 4.0; Cu^{2+}, 0.5; Ca^{2+}, 5; Mg^{2+}, 10.0; Zn^{2+}, 4.0; NO_3^-, 15.0; PO_4^{3-}, 2.0; SO_4^{2-}, 20.0; Fe^{2+} , 2.0; Fe^{3+} 0.2 and urea, 300 mg/L. The organic compounds, such as glucose, 1.0; BSA, 0.6 and DNA, 1.0 mg/L also didn't influence the determination of SDBS.

Analysis of samples

Natural water sample was pretreated with 0.45 μm filter membrane. Then the water sample was added into

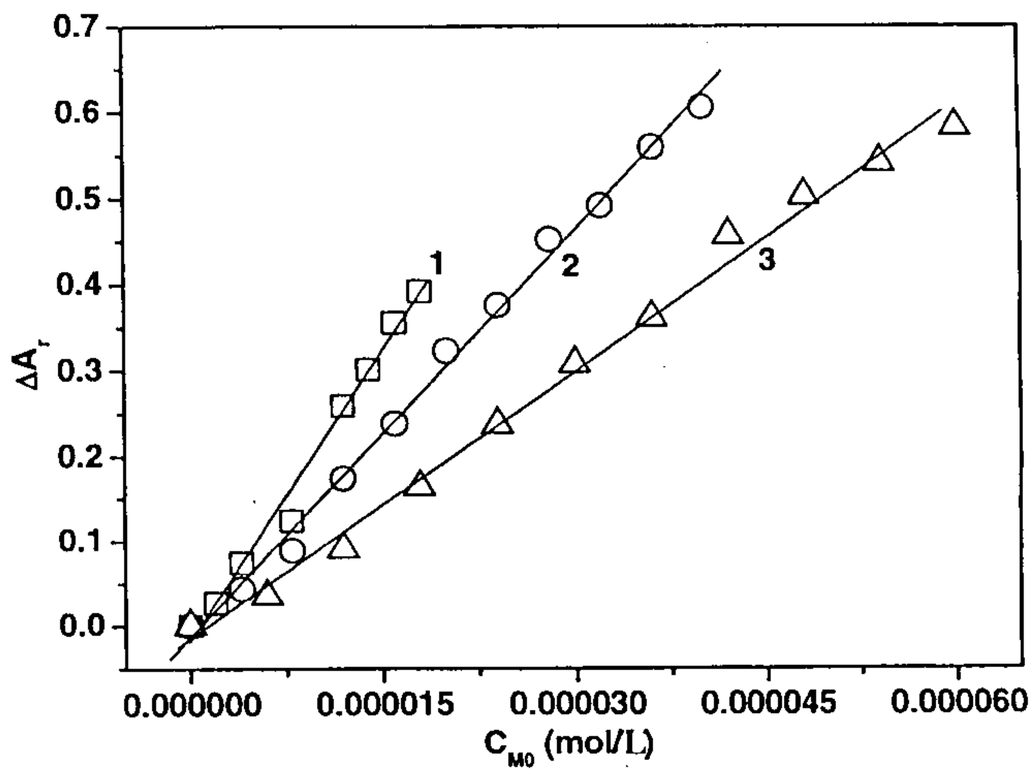

Fig. 4 — Variation of SDBS's standard curve of different concentration of CPC and CR in *p*H 2.03 BR buffer solution. From 1 to 3, the concentrations of CR are 0.02 mmol/L, 0.04 mmol/L and 0.06 mmol/L; corresponding concentrations of CPC are 0.001 mmol/L, 0.002 mmol/L and 0.003 mmol/L. With the addition of more CR and CPC, the slopes of curves decrease.

Table 1 — The linear regression equations and LOD of SDBS at *p*H 2.03

SDBS (mol/L)	CR (mmol/L)	CPC (mmol/L)	Regression Equation	R*	LOD** (mg/L)
0-0.00002	0.2	0.01	ΔA_r=22624 C_{M0} – 0.0178	0.9938	1.43
0-0.00004	0.4	0.02	ΔA_r=15882 C_{M0} – 0.0133	0.9978	1.10
0-0.00006	0.6	0.03	ΔA_r=10414 C_{M0} – 0.0148	0.9962	1.48

*Linear correlation coefficient; **LOD of SDBS in 10 mL of flask was calculated by LOD=3δ/k

Table 2 — Determination of SDBS with this method at pH 2.03 and with NMB method

Sample	Standard SDBS (mg)*	Found by this method (mg/L)**	Found by NMB method (mg/L)***	RSD (%)
1	0.000	8.230	7.482	4.3
2	0.156	24.414	22.145	3.7

*Added into 10 mL flask; **, *** Average of three duplicate experiment results

the flask with *p*H 2.03 buffer solution, CR and CPC. The absorbance of the solution was measured according to the described procedure. The results given in Table 2 showed that SDBS in natural water can be determined by this method (8.230 mg/L). The results were comparable to that determined by NMB method (7.482 mg/L). In addition, with the addition of SDBS into the sample, the recovery was calculated to be about 103.7%. So it is a useful method for the determination of SDBS in natural water with satisfactory experimental results.

Conclusions

A new spectrometric method has been developed for determination of SDBS in natural water. Negatively charged CR reacts with positively charged CPC in *p*H 2.03 BR buffer solution through electrostatic interaction. SDBS replaces CR in CR-CPC system. Combining this reaction with absorbance ratio difference method, a new method is established to determine SDBS in natural water. This method doesn't require organic hydrophobic solvents and time consuming two-phase extraction operation.

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