

This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Determination of anionic surfactant in surface water by resonance light-scattering technology

Zhan-Guang Chen<sup>a</sup>; Yu-Rui Peng<sup>a</sup>; Fei Xie<sup>a</sup>; Wen-Yan Jiang<sup>a</sup>; Hang Zou<sup>a</sup>; Han-Di Qiu<sup>a</sup>; Jun-Hui Chen<sup>b</sup>

<sup>a</sup> Department of Chemistry, Shantou University, Shantou 515063, China <sup>b</sup> Medical College of Shantou University, Shantou 515031, China

Online publication date: 24 March 2010

**To cite this Article** Chen, Zhan-Guang , Peng, Yu-Rui , Xie, Fei , Jiang, Wen-Yan , Zou, Hang , Qiu, Han-Di and Chen, Jun-Hui(2010) 'Determination of anionic surfactant in surface water by resonance light-scattering technology', *International Journal of Environmental Analytical Chemistry*, 90: 7, 573 – 585

**To link to this Article:** DOI: 10.1080/03067310902822649

**URL:** <http://dx.doi.org/10.1080/03067310902822649>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Determination of anionic surfactant in surface water by resonance light-scattering technology

Zhan-Guang Chen<sup>a\*</sup>, Yu-Rui Peng<sup>a</sup>, Fei Xie<sup>a</sup>, Wen-Yan Jiang<sup>a</sup>,  
Hang Zou<sup>a</sup>, Han-Di Qiu<sup>a</sup> and Jun-Hui Chen<sup>b</sup>

<sup>a</sup>Department of Chemistry, Shantou University, Shantou 515063, China; <sup>b</sup>Medical College  
of Shantou University, Shantou 515031, China

(Received 17 November 2008; final version received 10 February 2009)

A sensitive and rapid method, without any extraction procedure, for the determination of the anionic surfactant expressed in the terms of sodium dodecyl benzene sulfonate (SDBS) by the resonance light scattering (RLS) technique is described in this paper. In the pH value 3.0 Britton-Robinson (BR) buffer, Victoria blue B (VBB) reacted with SDBS and produced large particles which resulted in the remarkable enhancement of the RLS intensity of VBB. The enhanced RLS intensity of the assay system was proportional to the concentration of SDBS in the range of 0.08–3.0 mg L<sup>-1</sup> and the correlation coefficient was  $r = 0.9996$ . The detection limit was 0.013 mg L<sup>-1</sup>. This method was applied to determine the anionic surfactant in the surface water samples and satisfactory results were obtained. The reaction mechanism was also studied and the interaction between VBB and SDBS was mainly governed by electrostatic effect and the  $\pi$ - $\pi$  stacking effect.

**Keywords:** anionic surfactant; sodium dodecyl benzene sulfonate (SDBS); resonance light scattering (RLS); Victoria blue B (VBB)

### 1. Introduction

Surfactants, as important ingredients of cosmetics, medicines and domestic detergents, enter waters and wastewaters mainly discharged by household and industrial laundering and other cleaning operations. The properties of surfactants such as foaming, emulsification and particle suspension have a number of benefits in industry and in people's daily lives, but a large number of surfactants discharged into the environment generate great public attention [1]. The concentrations of different surfactants in environmental water have been measured [2,3] and the removal or biodegradation has also been studied by researchers [4,5]. Anionic surfactants amount to more than 90% of the total ionic surfactants used. The authorities of the European Union established a maximum tolerated limit of 200 mg L<sup>-1</sup> for anionic surfactants in water supplies for human consumption [6]. The official method for anionic surfactants determination in water is Method 5540C. This method is based on the reaction of these compounds with methylene blue followed by an extraction with chloroform prior to the determination of the blue colour in the CHCl<sub>3</sub> by spectrophotometry at 652 nm [7]. In this analytical procedure,

---

\*Corresponding author. Email: kqlu@stu.edu.cn

solvent extraction, using plenty of  $\text{CHCl}_3$  which is toxic and a suspected carcinogen, took several hours to condense the concentration of anionic surfactants in the samples and removed most nonsurfactant aqueous-phase interferences; other reagents such as  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}_2$  used in the assay also jeopardised the healthy operators. This analytical method is notorious for the tedious procedure, the use of large volumes of toxic solvents, the amount of time it takes, and the complexity of the operation and there is a tendency to commit operation mistakes and error. Thus, many researchers paid great attention to improving the traditional method, and the alternative assays [8–10] and new methods [11,12] were developed. However, these reported methods have not yet completely avoided the extraction and alleviated the overlaborate procedures. Therefore, a sensitive, simple and rapid method for the determination of anionic surfactants in water is desirable.

Resonance light scattering, as an elastic scattering, occurred when the incident beam is close in energy to an absorption band. Based on the theory, Pasternack *et al.* established a resonance light scattering (RLS) technique to study the aggregations and assemble the micromolecules on the DNA on a common fluorescence spectrometer [13,14]. Huang *et al.* first used this technique for the determination of biological macromolecules [15,16]. Subsequently, this method, due to its convenience and sensitivity, attracts a lot of interest in qualitative analysis and quantitative analysis [17,18]. The use of the RLS technique to determine DNA [19,20], proteins [21–25], amino acid [26], medicines [27], and bacterial pathogens [28] has been reported in literature. The RLS technique was also used to analyse the surfactants in the environmental water [29]. A series of reagents, such as Rhodamine B [30], Acridine orange [31], Co (II)–5-Cl-PADAB [32], have been successfully exploited to determine ionic surfactant SDBS. Recently, determination of proteins and carbohydrates in the effluents from wastewater by RLS method has also been reported [33].

Victoria blue B (VBB), a triarylmethane dye (Figure 1), is a larger cationic molecule. Recently, as a promising dye, VBB has been explored to apply as an analytical reagent, which has been used as a sensitive RLS probe to analyse the Heparin [34] and so on. VBB was chosen as a common analytical reagent because of its chromophore in the molecule and larger cationic dye molecule. In addition, pure VBB is easily obtainable. However, VBB used as a RLS probe to determine the anionic surfactant has not been reported.

In the present study, we proposed a novel assay to determine anionic surfactants in water expressed in terms of linear sodium dodecyl benzene sulfonate (SDBS) concentration based

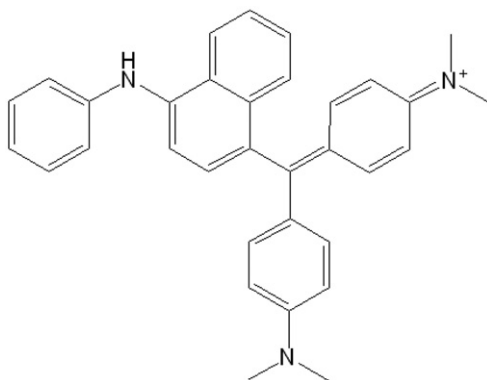


Figure 1. Structure of the VBB.

on the reaction between SDBS and VBB by the RLS technique. The RLS signal of VBB was very weak, but it can be drastically enhanced by adding SDBS. The enhancement of RLS intensity was proportional to the SDBS concentration and this method without any extraction was proved to be sensitive, simple, rapid, and inexpensive. This was an environmentally friendly procedure without using any toxic reagent. The water samples were analysed according to the procedure of the developed method and the results were obtained satisfactorily. The mechanism of the reaction between SDBS and VBB was also investigated by the RLS spectra, UV-vis absorption spectra, and fluorescence spectra.

## 2. Experimental

### 2.1 Apparatus and reagents

All the RLS spectra and fluorescence spectra were obtained on a Perkin-Elmer Model LS-55 spectrofluorometer equipped with a 1 cm  $\times$  1 cm quartz cuvette. Absorption spectra were measured with an Agilent 8453 ultraviolet spectrophotometer. An SA 720 instrument (Orion Research) was used to measure the pH of the solution. 9500 mL glass bottles cleaned by ethanol were used to collect the water samples.

Linear sodium dodecyl benzene sulfonate (SDBS) was employed as a representative anionic surfactant for calibration. Its structure is  $[\text{RC}_6\text{H}_4\text{SO}_3]^- \text{Na}^+$ , where R is a linear secondary alkyl group ranging from 10 to 13 carbon atoms in length, and the number of the average carbon atoms is 12 and the average molecular weight is 346.21. 0.0100 g SDBS (Sigma, USA) was precisely weighed and dissolved with doubly distilled water. The concentration of its stock solution was  $1.0 \times 10^{-3} \text{ mg L}^{-1}$  and  $1.0 \times 10^{-5} \text{ mg L}^{-1}$  of the working solution was obtained by diluting the SDBS stock solutions. All stock and working solutions were stored at 0–4°C. VBB purchased from Sigma was weighed precisely and dissolved with 10 mL ethanol. Its stock solution was obtained by diluting the dissolved VBB with doubly distilled water. The  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  of working solution was prepared by diluting the VBB stock solution.

The Britton-Robinson (BR) buffer solution was used to control the acidity of the solutions. The BR buffer solution was made up of  $0.04 \text{ mol L}^{-1}$  phosphoric acid,  $0.04 \text{ mol L}^{-1}$  acetic acid,  $0.04 \text{ mol L}^{-1}$  boric acid,  $0.2 \text{ mol L}^{-1}$  sodium hydroxide. The ionic strength of the solution was adjusted by  $0.1 \text{ mol L}^{-1}$  NaCl solution.

All reagents and solvents used were purchased at the highest commercial quality and used without further purification. The doubly distilled water was used throughout.

### 2.2 Measurement procedures

Into a 10 mL calibrated flask were added 2.0 mL BR buffer solution, 0.8 mL of the working solution of VBB, 0.4 mL NaCl solution, and appropriate volumes SDBS working solution or samples. The mixture was shaken softly and diluted to 10 mL with doubly distilled water, and then mixed thoroughly for the measurements of RLS spectra, absorption spectra, and fluorescence emission spectra.

All RLS spectra were obtained by scanning simultaneously the excitation and emission monochromators ( $\Delta\lambda = 0.0 \text{ nm}$ ) from 250.0 nm to 700.0 nm on a common spectrofluorometer. Both excitation and emission slit widths were kept at 5.0 nm and the RLS intensities were measured at 398.5 nm. The enhanced RLS intensity was presented as  $\Delta I_{\text{RLS}} = I_{\text{RLS}} - I_{\text{RLS}}^0$ . Where,  $I_{\text{RLS}}$  and  $I_{\text{RLS}}^0$  were the RLS intensities with and without SDBS, respectively.

### 3. Results and discussion

#### 3.1 Spectral characteristics

The RLS spectra of VBB in the absence and presence of SDBS were studied (Figure 2). It can be found that the RLS signal of VBB is very weak. With the addition of SDBS, the RLS signal of the system increased sharply over the wavelength range 250.0–500.0 nm. This phenomena indicated that the reaction between VBB and SDBS occurred and the large particles were produced which resulted in the altered RLS signal [14]. At pH value of 3.0, the cationic dye can be protonated to become the doubly-charged ion  $\text{HR}^{2+}$  based on the  $\text{pK}_a$  ( $\text{pK}_a = 4.5$ ) [34, 35], which can react with the ionic surfactant SDBS with negative charges by electrostatic effect. Considering the structure of the dye and SDBS, the  $\pi$ – $\pi$  interaction between aromatic rings contained both in the VBB and SDBS also contributed the combination of the two compounds. So the complex was formed and produced the enhanced RLS signal. The enhanced RLS intensity at 398.5 nm increased when the SDBS concentration increased, and therefore, it is a function of SDBS concentration.

#### 3.2 Effect of pH

The variation of the RLS intensity of the assay system was studied by changing pH values from 2.0 to 7.0 (Figure 3). When the pH value was in the range 2.0–7.0, the RLS intensity of the VBB assay system without SDBS was very weak and kept the relative stability. In pH value 2.0–4.5 solution, the enhanced RLS intensity was in small-amplitude changes and its maximum was obtained at pH 3.0. With the pH value increasing from 4.5 to 7.0, the enhanced RLS intensity decreased obviously. This is possibly related to the effect of pH on the structure of VBB. The  $\text{pK}_a$  value of  $\text{R}^+$  to  $\text{HR}^{2+}$  was 4.5 determined according to the literature [35]. When acidity was lower ( $\text{pH} \geq 4.5$ ), the dye could not be protonated enough and become molecules that lose their electrostatic attraction to the ionic surfactant SDBS. Under such conditions, the decreasing combination between SDBS and VBB weakened the enhanced RLS intensity of the assay system. However, the stronger acidity ( $\text{pH} \leq 2.5$ ) affected the negative charges of the ionic surfactant molecules and weakened the electrostatic interaction between SDBS and VBB which was not favourable for the enhanced RLS intensity. Therefore,  $\text{pH} = 3.0$  was chosen for the determination.

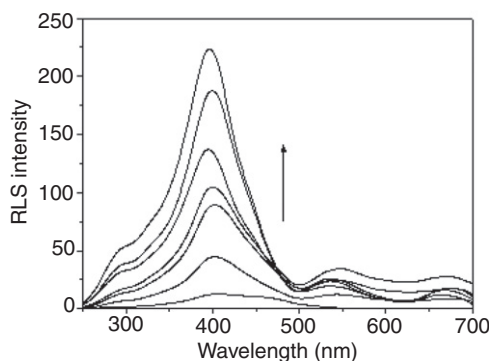


Figure 2. The RLS spectra of VBB in the absence and presence of SDBS. Note: VBB,  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ ; SDBS ( $\text{mg L}^{-1}$ ), 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 in the arrow;  $\text{pH} = 3.0$ ,  $31^\circ\text{C}$ .

### 3.3 Effect of VBB concentration

The effect of the VBB concentration on the RLS intensity was studied (Figure 4). The RLS intensity of the blanks system (VBB without SDBS) was very weak and increased slightly with the dye concentration increasing. However, the enhanced RLS intensity of the assay system in the presence of SDBS increased with the concentration of SDBS increasing and reached the maximum at  $0.8 \times 10^{-5} \text{ mol L}^{-1}$  of VBB. With the concentration of VBB further increasing, the RLS intensity decreased. The reaction between VBB and SDBS, to some extent, can be influenced by the concentration of VBB. When the concentration of the dye increased, the self-aggregation of VBB molecules could be occurred by the hydrophobic and  $\pi$ - $\pi$  interaction of the aromatic rings. The self-aggregation, not only produce the particles of VBB, but also weaken the combination of dye on the anionic surfactant SDBS. The increased RLS intensity of the blanks can be attributed to the particles of VBB and the enhanced RLS intensity of the VBB-SDBS system decreased due to the reduced combination between VBB and SDBS.

### 3.4 Effect of ionic strength

The influence of ionic strength on the RLS intensity of the assay system was investigated by altering the concentration of NaCl and the result was clearly presented (Figure 5).

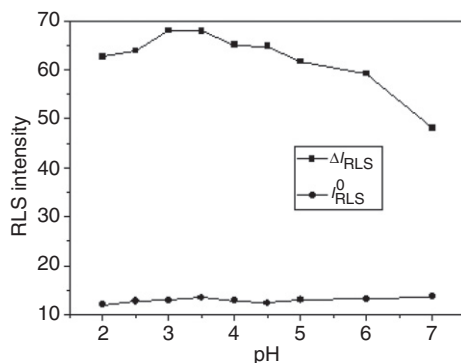


Figure 3. Effect of pH on the RLS intensity. Note: VBB  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ , SDBS  $1.0 \text{ mg L}^{-1}$ , NaCl  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ ,  $31^\circ\text{C}$ .

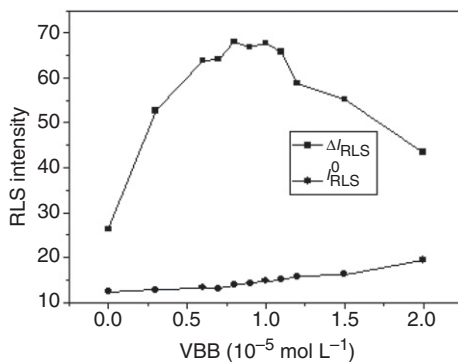


Figure 4. Effect of concentration of VBB on the RLS intensity. Note: SDBS  $1.0 \text{ mg L}^{-1}$ , NaCl  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ , pH = 3.0,  $31^\circ\text{C}$ .

It can be found that the RLS intensity of the blank system maintained relatively weak and stable with the increase of NaCl concentration. However, the enhanced RLS intensity of the VBB system in the presence of SDBS increased with the increase of NaCl concentration and reached a maximum at  $4.0 \times 10^{-3} \text{ mol L}^{-1}$  of NaCl. With the concentration of NaCl increasing further, the decreasing of RLS signal was present. These phenomena could be explained that, in the low concentration of NaCl, due to the thickness of the electrical double layer of SDBS decreasing with the small amount of  $\text{Na}^+$ , more dye molecules can bind on the ionic surfactant. However, when the concentration of NaCl is higher than  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ , the more  $\text{Na}^+$  can shield the negative charges of SDBS and the more  $\text{Cl}^-$  can shield the positive charges of VBB molecule. The effect of the electrostatic shielding of charges reduced the combination of VBB and SDBS and resulted in the decreased RLS intensity. It can also be seen that the decreasing of RLS intensity is not sharp, which indicated that the electrostatic interaction should be not only one driving force governing its combination.

### 3.5 Effect of temperature, incubation time, and addition orders

When the temperature of the circumstance of the assay system changed, the RLS intensity of the assay system was very unstable and the reproducibility was extremely poor. The effect of incubation temperature on the RLS signal has been investigated and the result is given (Figure 6). It is shown that temperature influenced the RLS intensity obviously. In the range  $29\text{--}32^\circ\text{C}$ , VBB facilely reacted with SDBS and maximum RLS intensity was produced. The temperature designed at  $31^\circ\text{C}$ , this method has high sensitivity and good reproducibility.

The effect of reaction time and stability of VBB-SDBS system was tested by measuring the RLS intensity every 2 min immediately after mixing. It was found that the reaction between VBB and SDBS occurred rapidly at  $31^\circ\text{C}$ , and the enhanced RLS intensity reached a maximum value in 10 min and maintained stable for at least 100 min.

The addition orders of reagents also influenced the RLS intensity of the assay system. The studies in this experiment showed that the order of BR buffer – VBB – NaCl – SDBS is better than others in terms of stability and intensity.

Therefore, the assay was operated after mixing the reagents (by the order BR buffer – VBB – NaCl – SDBS) 10 min at  $31^\circ\text{C}$  in the study.

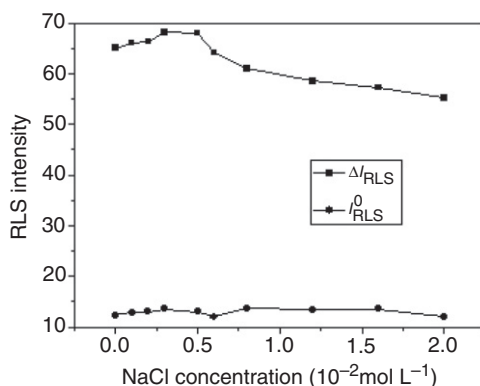


Figure 5. Effect of ionic strength on the RLS intensity.

Note: VBB  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ , SDBS  $1.0 \text{ mg L}^{-1}$ ,  $\text{pH} = 3.0$ ,  $31^\circ\text{C}$ .



### 3.6 Interference of foreign substances

Under the optimum conditions of the general procedure, the interference of the foreign substances on the determination of  $1.0 \text{ mg L}^{-1}$  SDBS was tested and the results were summarised (Table 1). It can be seen that most common substances in the water can be tolerant at a high concentration level. From Table 1, it can be seen that the effect of other surfactants on the assay system can be ignored when the concentrations were lower than  $10 \text{ mg L}^{-1}$ , which could be related to the structure and molecule size of the surfactant. However, the  $\text{Bi}^{3+}$  can be allowed only at  $1.0 \text{ mg L}^{-1}$ , but the concentration of  $\text{Bi}^{3+}$  in the water is at a relatively low concentration level generally. In addition, the sewage water samples diluted with doubly distilled water can minimise all these interferences. Furthermore, the effect of the small amount of active carbon, which was used to remove

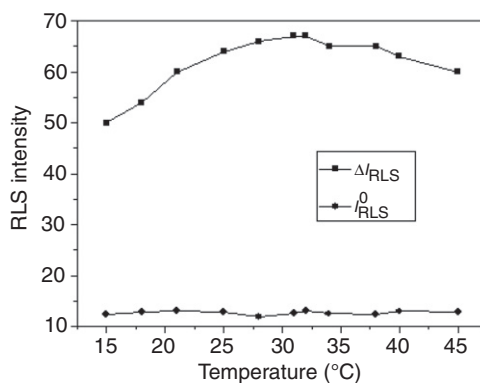


Figure 6. Effect of temperature on the RLS intensity.

Note: VBB,  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ ; SDBS  $1.0 \text{ mg L}^{-1}$ , NaCl  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ , pH = 3.0.

Table 1. Tolerance levels of foreign substances in the determination of  $1.0 \text{ mg L}^{-1}$  SDBS<sup>a</sup>.

Tolerance level ( $\text{mg L}^{-1}$ )	Foreign substances
$\geq 1000$	$\text{Na}^+$ , $\text{K}^+$ , $\text{Cl}^-$
$\geq 500$	$\text{Ca}^{2+}$ , $\text{Cu}^{2+}$ , $\text{NH}_4^+$ , $\text{Ba}^{2+}$ , $\text{SO}_4^{2-}$
$\geq 250$	EDTA, $\text{CO}_3^{2-}$
$\geq 200$	$\text{Mg}^{2+}$ , $\text{Ni}^{2+}$ , Urea, Citric acid
100	Benzene, Phenol, Benzidine, Aniline, Tween 80
$50^b/2^c$	Humic acid, fulvic acid
$\geq 20$	SLS <sup>d</sup> , SDS <sup>e</sup> , Tritonx-100
$\geq 10$	$\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $\text{Zn}^{2+}$ , $\text{Hg}^{2+}$ , CTMAB <sup>f</sup> , STAB <sup>g</sup>
1	$\text{Bi}^{3+}$

Notes: <sup>a</sup>Conditions: VBB  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ , NaCl  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ , pH = 3.0,  $31^\circ\text{C}$ .

<sup>b,c</sup>The tolerant concentrations of humic and fulvic acids with and without the disposal of active carbon, respectively.

<sup>d</sup>Sodium lauryl sulfate.

<sup>e</sup>Sodium dodecyl sulfate.

<sup>f</sup>Cetyltrimethyl ammonium bromide.

<sup>g</sup>Stearictrimethyl ammonium bromide.



the natural organics in the surface water sample, on enhanced RLS intensity was also studied. The result displayed that the influence of such small amount of active carbon can be ignored. Therefore, there was no interference from the substances potentially contained in the samples and this method can be useful and valuable in the practical application.

### 3.7 Calibration curves and sensitivities

Under the optimum conditions, the relationship between RLS intensity and SDBS concentration was investigated according to the above standard procedure, and the regression equation was constructed. The results showed that the linear relationship in the range 0.08–3.0 mg L<sup>-1</sup> was found between enhanced RLS intensity and SDBS concentrations and the regression equation was  $\Delta I_{\text{RLS}} = -1.8 + 70.32C$  (mg L<sup>-1</sup>). The relative coefficient is  $r = 0.9996$  and the linear range is 0.08–3.0 mg L<sup>-1</sup>. The detection limit was 0.013 mg L<sup>-1</sup>, which was calculated by  $3S_0/S$  here, 3 is the factor at the 99% confidence level,  $S_0$  is the standard deviation of the measurement on 14 blanks, and  $S$  is the slope of the calibration curve.

Comparison with other methods of determinations of SDBS was shown in this paper (Table 2). From the comparison, it can be seen that this proposed method was simple, sensitive and was more suitable for the application in the real samples.

For direct analysis of surface waters, sample volume on the basis of expected SDBS concentration was selected and the result was given (Table 3). If expected SDBS

Table 2. Comparisons with other methods to determine the SDBS in water samples.

Methods	Detection limit mg L <sup>-1</sup>	Linear range mg L <sup>-1</sup>	References
Alternative to the methylene blue method	10.0	35–300	[8]
Alternative to the methylene blue method	1.7	0.2–1.7	[9]
Fluorescence quenching method	0.029 ( $8.3 \times 10^{-8}$ mol L <sup>-1</sup> )	0–0.70 ( $0-2 \times 10^{-6}$ mol L <sup>-1</sup> )	[10]
LEDS <sup>a</sup> -based photometer	0.06	0.35–10.5 ( $1.0 \times 10^{-6}$ – $3.0 \times 10^{-5}$ mol L <sup>-1</sup> )	[11]
RLS	0.038	0–36.0	[12]
RLS	0.008	0.028–8.71	[13]
RLS	0.015	0.05–6.0	[14]
RLS	0.013	0.08–3.0	This work

Note: <sup>a</sup>Two light emitting diodes.

Table 3. Selecting sample volume on the basis of expected SDBS concentration.

Expected SDBS concentration mg L <sup>-1</sup>	Sample taken mL
0.16–0.8	5.0
0.8–1.0	2.0
1.0–3.0	1.0

concentration is above  $3.0 \text{ mg L}^{-1}$ , dilute samples with doubly distilled water in order to keep its concentration in the linear range.

### 3.8 Application to sample analysis

The lake water samples collected from reservoir in campus of Shantou University was stored at  $4^\circ\text{C}$  to minimise biodegradation or eliminate other chemical reactions. The river water samples collected from Meixi River in the city of Shantou were boiled for 1 hour and then were filtrated by qualitative filter paper. The filtrated samples were stored at  $4^\circ\text{C}$ . The sewage samples collected from the sewer in Shantou University were boiled for 1 hour and cooled for a moment, and then were filtrated. A small amount of active carbon was put into the filtrated water for the purpose of discolouring and eliminating the substances, and then removed the active carbon by filtrating. The filtrated samples were stored at  $4^\circ\text{C}$ .

According to the standard procedure, the proposed method was applied to determine the SDBS in the water samples. The accuracy and precision was validated by the recoveries of the standard addition method. All results of the analysis were displayed (Table 4). From the analytical results, it can be seen that the proposed method had high accuracy and fine precision with recoveries of 95.0–108.0%. The SDBS was also determined using the standard method for comparison (Table 4). The results showed that the present method with high sensitivity and fine accuracy was acceptable for the determination of SDBS in the real water samples.

### 3.9 Mechanism of the reaction

#### 3.9.1 The absorption spectra

A series of UV-vis absorption spectra of VBB in the absence and presence of SDBS were depicted (Figure 7). It displayed the marked changes that were induced in the absorption spectra of VBB upon addition of SDBS at pH value 3.0. The peak of VBB at  $617.0 \text{ nm}$  shifted to the short wavelength and its intensity decreased with addition of SDBS. When the concentration of SDBS was higher than  $1.6 \text{ mg L}^{-1}$ , the wider wave shape appeared and

Table 4. Analytical results of water samples<sup>a</sup>.

Sample	MB method	Present method			
	Found values $\pm$ S.D. ( $\text{mg L}^{-1}$ )	Found values $\pm$ S.D. ( $\text{mg L}^{-1}$ )	Added values ( $\text{mg L}^{-1}$ )	Total found values $\pm$ S.D. ( $\text{mg L}^{-1}$ )	Recovery (%)
River water A1	$0.20 \pm 0.06$	$0.24 \pm 0.02$	0.5	$0.76 \pm 0.02$	104.0
River water A2	$0.50 \pm 0.01$	$0.51 \pm 0.03$	0.5	$1.05 \pm 0.05$	108.0
River water A3	$1.10 \pm 0.02$	$1.09 \pm 0.07$	0.5	$1.58 \pm 0.05$	98.0
Domestic sewage B1	$0.55 \pm 0.06$	$0.55 \pm 0.04$	0.8	$1.33 \pm 0.04$	97.5
Domestic sewage B2	$0.81 \pm 0.04$	$0.79 \pm 0.05$	0.8	$1.62 \pm 0.03$	103.8
Domestic sewage B3	$1.02 \pm 0.05$	$1.03 \pm 0.07$	0.8	$1.79 \pm 0.04$	95.0
Lake water C1	$0.12 \pm 0.02$	$0.15 \pm 0.02$	0.8	$0.92 \pm 0.08$	96.3
Lake water C2	$0.26 \pm 0.01$	$0.27 \pm 0.02$	0.8	$1.06 \pm 0.01$	98.8
Lake water C3	$0.46 \pm 0.04$	$0.48 \pm 0.02$	0.8	$1.29 \pm 0.02$	101.3

Note: <sup>a</sup>Average of three determinations.

the peak shifted to 592.0 nm. The observed spectra changes were indicative of the formation of the complex between VBB and SDBS. When the concentration of SDBS was low, the electrostatic effect predominated the interactions between VBB and SDBS. The peak of VBB was slightly influenced by adding SDBS. However, when the concentration of SDBS increased ( $\geq 1.6 \text{ mg L}^{-1}$ ), the  $\pi$ - $\pi$  interaction between aromatic rings governed the combination of VBB and SDBS. So the large changes of the wave shape were observed.

### 3.9.2 The fluorescence emission

The binding of VBB and SDBS was also investigated by the changes in the fluorescence characteristics of the VBB bound to SDBS. It can be clearly seen (Figure 8) that the intensity of VBB fluorescence emission spectrum at 447 nm decreased with the addition of

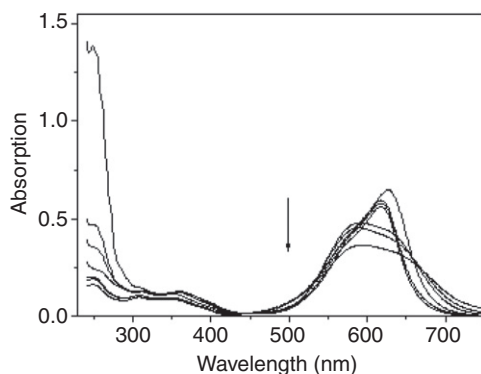


Figure 7. Absorption spectra of VBB in the presence of SDBS. Note: VBB,  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ ; SDBS ( $\text{mg L}^{-1}$ ), 0, 0.4, 1.0, 1.6, 2.0, 2.4, 3.0 in the arrow; NaCl  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ , pH = 3.0,  $31^\circ\text{C}$ .

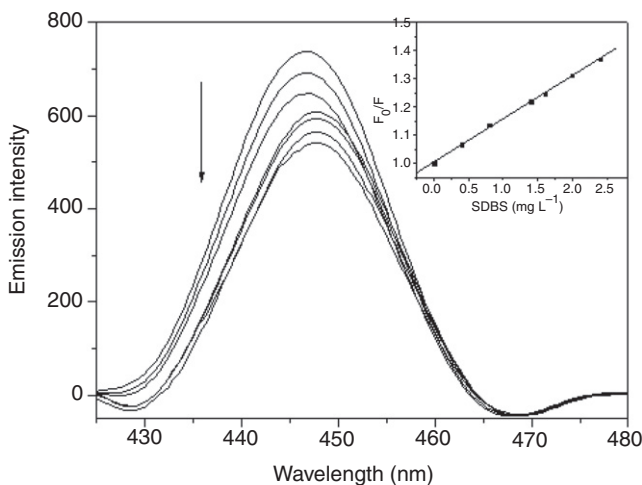


Figure 8. Fluorescence emission spectra of VBB in the absence and presence of SDBS. Excitation wavelength was 389 nm. Note: VBB,  $0.8 \times 10^{-5} \text{ mol L}^{-1}$ ; SDBS ( $\text{mg L}^{-1}$ ), 0, 0.4, 0.8, 1.4, 1.6, 2.0, 2.4 in the arrow; NaCl  $4.0 \times 10^{-3} \text{ mol L}^{-1}$ , pH = 3.0,  $31^\circ\text{C}$ . Insertion: Stern-Volmer plot for the SDBS-VBB. Note: the fluorescence intensity was measured with 477 nm emission. Slit widths were 5.0 nm/5.0 nm (excitation/emission).

SDBS, but the shape of the emission spectra changed little. With the concentration of SDBS increasing ( $\geq 1.6 \text{ mg L}^{-1}$ ), the peaks at 447 nm have a slight red shift. The deregulation of the fluorescence emission spectra is coincided to that of UV-vis absorption spectra above, which affirmed the conclusions obtained from previous experiments and came to a conclusion of the reaction of SDBS and VBB mainly governed by the electrostatic effect and  $\pi$ - $\pi$  stacking effect of aromatic rings again.

The fluorescence intensity of VBB, measured at 477 nm, was quenched by addition of SDBS. The fluorescence quenching data were analysed by The Stern-Volmer equation:

$$F_0/F = 1 + K_{SV}[Q]$$

where  $F_0$  and  $F$  were the fluorescence intensity in the absence and presence of SDBS, respectively,  $[Q]$  was the concentration of the SDBS, and  $K_{SV}$  is the Stern-Volmer quenching constant. The assay results (Figure 8) indicated that the Stern-Volmer plots were linear and  $K_{SV} = 1.5 \times 10^4$  (the linear relationship between  $F_0/F$  and  $[Q]$ ) was obtained. The results suggested that the possible quenching mechanism between SDBS and VBB was static quenching. From the  $K_{SV}$  value, it could be found that there was a strong interaction of SDBS and VBB.

#### 4. Conclusion

In the present work, the method for the determination of SDBS was developed by the RLS technique and the reaction between SDBS and RLS probe VBB was also studied. Under the optimum condition, the RLS intensity of VBB was largely enhanced by adding SDBS, and the enhancement of RLS intensity was proportional to the SDBS concentration. The effect of the ionic strength indicated that the reaction between SDBS and VBB occurred by electrostatic effect and  $\pi$ - $\pi$  stacking of the aromatic rings of the reactants. The above result was also confirmed by the changes of absorption spectra and fluorescence spectra. The built method was applied to determine the SDBS in the different water samples, and the recovery rates were 95.0–108.0%. The analytical parameters and the results from the determination of real samples demonstrated that this method has many advantages over the official method and other previously developed alternatives.

- (1) This method, completely avoiding the extraction procedure to eliminate the application of toxic reagents, is an environmentally friendly alternative to do the determinations of anionic surfactant in the surface water.
- (2) In the proposed assay, most taxing procedures (such as *peroxide treatment, ion pairing and extraction* in the official method) were removed, which simplified the determination of experiments.
- (3) On the other hand, in terms of the higher sensitivity and more selectivity, the detection limit of this method is  $0.013 \text{ mg L}^{-1}$  and there is no interference from most potential substances in the real water samples.
- (4) Furthermore, the developing approach is very fast and all the detection operations can be controlled by the computer. Under the optimum conditions, a sampling throughput is 60 per hour, which is almost ten times faster than the traditional method to determine the anionic surfactant.

Therefore, this assay characterised with sensitivity, simplicity, speediness, accuracy, and precision was practicable and useful to analyse SDBS in the water samples.

## Acknowledgements

All of the authors express their sincere thanks for the support from the National High Technology Research and Development Programme (863) Foundation of China (No. 2003AA2Z3162) and the support from the Science and Technology Items of the College of Science, Shantou University.

## References

- [1] H. De Henau, E. Mathijs, and W.D. Hopping, *Int. J. Environ. Anal. Chem.* **26**, 279 (1986).
- [2] Z.Z. Zhu, Z.J. Li, and Y. Liu, *Int. J. Environ. Anal. Chem.* **84**, 267 (2004).
- [3] A.F. Lavorante, C.K. Pires, Á. Morales-Rubio, M. Guardia, and B.F. Reis, *Int. J. Environ. Anal. Chem.* **86**, 723 (2006).
- [4] N. Schoutena, L.G.J. Van der Hamb, G.W. Euverinka, and A.B. De Haanc, *Wat. Res.* **41**, 4233 (2007).
- [5] D. Mantzavinos, D.M.P. Burrows, R. Willey, G. Biundo, S.F. Zhang, A.G. Livingston, and I.S. Metcalfe, *Wat. Res.* **35**, 3337 (2001).
- [6] Council Directive 80/778/EEC of 15 July 1980 Relating to the Quality of Water Intended for Human Consumption. *Official Journal*, 229, 11–29.
- [7] American Public Health Association, American Water Works Association and Water Pollution Control Federation, *Surfactants. Standard Methods for the Examination of Water and Wastewater*, 21st ed. (American Public Health Association, Washington, DC, 2005).
- [8] A. Pedraza, S.M. Dolores, S. Rubio, and D. Perez-Bendito, *Anal. Chim. Acta* **588**, 252 (2007).
- [9] E. Ródenas-Torralba, B.F. Reis, A. Morales-Rubio, and M. Guardia, *Talanta* **66**, 591 (2005).
- [10] C.Q. Zhu, H. Zheng, D.H. Li, S.H. Li, and J.G. Xu, *Spectrochim. Acta, A* **60**, 3173 (2004).
- [11] A.F. Lavorante, Á. Morales-Rubio, M. Guardia, and B.F. Reis, *Anal. Chim. Acta* **600**, 58 (2007).
- [12] T. Miliotis, M. Knutsson, J.Å. Jönsson, and L. Mathiasson, *Int. J. Environ. Anal. Chem.* **64**, 35 (1996).
- [13] R.F. Pasternack, C. Bustamante, P.J. Collings, L.A. Giannetto, and E.J. Gibbs, *J. Am. Chem. Soc.* **115**, 5393 (1993).
- [14] R.F. Pasternack and P.J. Collings, *Science* **269**, 935 (1995).
- [15] C.Z. Huang, K.A. Li, and S.Y. Tong, *Anal. Chem.* **68**, 2259 (1996).
- [16] C.Z. Huang, K.A. Li, and S.Y. Tong, *Anal. Chem.* **69**, 514 (1997).
- [17] W. Lu, B.S. Fernández Band, Y. Yu, Q.G. Li, J.C. Shang, C. Wang, Y. Fang, R. Tian, L.P. Zhou, L.L. Sun, Y. Tang, S.H. Jing, W. Huang, and J.P. Zhang, *Microchim. Acta* **158**, 29 (2007).
- [18] J. Ling, C.Z. Huang, Y.F. Li, Y.F. Long, and Q.G. Liao, *Appl. Spectrosc. Res.* **42**, 177 (2007).
- [19] Z.G. Chen, W.F. Ding, F.L. Ren, J.B. Liu, and Y.Z. Liang, *Anal. Chim. Acta* **550**, 204 (2005).
- [20] C.Q. Cai and X.M. Chen, *Spectrochim. Acta, A* **69**, 592 (2008).
- [21] Z.G. Chen, G.L. Liu, M.H. Chen, Y.R. Peng, and M.Y. Wu, *Anal. Biochem.* **384**, 337 (2009).
- [22] Z.G. Chen, J.B. Liu, and Y.L. Han, *Talanta* **71**, 1246 (2007).
- [23] Z.G. Chen, T.Y. Zhang, F.L. Ren, and W.F. Ding, *Microchim. Acta* **153**, 65 (2006).
- [24] Z.G. Chen, J.B. Liu, Y.Z. Liang, and F.L. Ren, *J. Biomol. Screen.* **11**, 400 (2006).
- [25] E. Vidal, M.E. Palomeque, A.G. Lista, and B.S. Fernández Band, *Anal. Bioanal. Chem.* **376**, 38 (2003).
- [26] Z.G. Chen, J.B. Liu, Y.L. Han, and L. Zhu, *Anal. Chim. Acta* **570**, 109 (2006).
- [27] Z.G. Chen, Y.R. Peng, J.H. Chen, and L. Zhu, *J. Pharm. Biomed. Anal.* **48**, 946 (2008).
- [28] P. Francois, M. Bento, P. Vaudaux, and J. Schrenzel, *J. Microbiol. Methods* **55**, 755 (2003).
- [29] C.X. Yang, Y.F. Li, and C.Z. Huang, *Anal. Bioanal. Chem.* **374**, 868 (2002).

- [30] J. Yuan, X.H. Wang, and J.L. Xie, P. T. C. A. (Part B: Chem. Anal.) (in Chinese) **42**, 24 (2006).
- [31] X.L. Xiao, Y.S. Wang, Z.M. Chen, Q.X. Li, Z.H. Liu, G.R. Li, C.Y. Lu, J.H. Xue, and Y.Z. Li, Spectrochim. Acta, A **71**, 398 (2008).
- [32] Q.L. Yang, Q.M. Lu, Z.F. Liu, S.P. Liu, G.C. Chen, H. Duan, D. Song, J. Wang, and J. Liu, Anal. Chim. Acta **632**, 115 (2009).
- [33] M.L. Zhang, G.P. Sheng, and H.Q. Yu, Wat. Res. **42**, 3464 (2008).
- [34] S.P. Liu, H.Q. Luo, N.B. Li, Z.F. Liu, and W.X. Zheng, Anal. Chem. **73**, 3907 (2001).
- [35] C.C. Zhang, F.S. Ye, and H.Q. Zhou, J. Southwest University N. Nat. Sci. (in Chinese) **31**, 177 (2005).