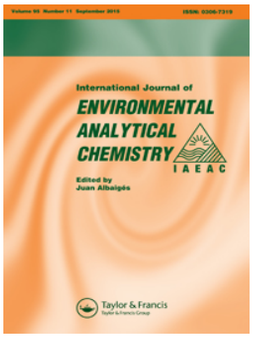

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Flow-injection chemiluminescence method for determination of critical micelle concentration of surfactants

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In this study, chemiluminescence (CL) behaviour of Luminol-H_2O_2 in the presence of the different concentrations of four surfactants, cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB), sodium dodecyl sulphate (SDS) and polyoxyethylene dodecyl ether (Brij-35), was investigated. A novel method for the direct determination of critical micelle concentration (CMC) of the surfactants using flow-injection CL is described. Under the optimum conditions, the luminescence intensity of the Luminol-H_2O_2 system increased gradually with increasing concentration of the surfactants before the CMC, but rapidly reached to the emission maximum at the CMC, followed by a decrease after the CMC. The concentrations of the surfactants corresponding to the luminescence maximum are in agreement with the literature CMC values. The main factors affecting the determination of CMC are discussed. The mechanistic studies show that the luminescence peaks observed in the experiment were mainly because of the protective effect of the micelle against the transition of the excited species and the retarding effect of the micelle structures on the CL reaction rate.

Keywords: flow-injection; chemiluminescence; critical micelle concentration; surfactant

1. Introduction

Many types of surfactants have been used widely not only in industry and agriculture, but also in scientific research such as nanoparticle synthesis [1–3], drug delivery systems [4–6], magnetic imaging [7], adsorption and surface modification studies [8] and water purification [9]. The concentration of a surfactant in an aqueous solution is known to increase, and the micelle formation occurs at a concentration known as the critical micelle concentration (CMC). Solutions containing surfactants exhibit drastic changes in their physicochemical properties such as surface tension, electrical conductivity and detergent activity at the CMC. Therefore, finding the CMC is very important. The traditionally used methods for the detection the CMC are electrical conductivity [10–13], surface tension [14,15] and dye solubilisation [16]. In addition, other methods such as speed of sound [17], spectrophotometry [18–20], capillary electrophoresis [21–23], nuclear magnetic resonance [24] and micellar electrokinetic chromatography [25] have been used for the determination of CMC. Previously, various methods used to detect the CMC often led to different numerical estimates, not because of measurement errors or inaccuracies, but because the CMC is a range rather than an exact value. These methods are very powerful; however, most of the methods reported for the determination of CMC have some shortcoming in the determination of CMC such as the necessity of high purity of dye with the method of dye solubilisation, low sensitivity in low purity of surfactants

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with the method of surface tension and limit in non-surfactants with the method of dye solubilisation. Thus, the exploration of new methods for the determination of the CMC is very necessary.

In recent years, extremely sensitive analytical techniques based on chemiluminescence (CL) and bioluminescence systems have received considerable attention. In particular, these techniques combined with flow injection (FI), simplicity of detection, low detection limit, wide calibration range and short analysis times are some of the characteristics that make the methods attractive. Meantime, the CL intensity was found to enhance when surfactants were introduced into the CL system. So far, there has been an increasing number of reports [26–28] on the micelle-enhanced CL.

Herein, we report a simple, rapid and sensitive FI-CL method for the determination of CMC of four representative surfactants, namely cetyltrimethylene bromide (CTAB), cetyltrimethylammonium bromide (CPB), sodium dodecyl sulphate (SDS) and polyoxyethylene dodecyl ether (Brij-35).

2. Experimental

2.1. *Reagents*

Stock solution of luminol (1.0×10^{-3} M) was prepared by dissolving 0.0177 g of luminol (Fluka, Switzerland) in 25 mL of 0.1 M of NaOH and further diluted to 100 mL with water. The solution was stored in refrigerator and was stable for at least two weeks. The standard solution was prepared by diluting the stock solution with water.

A H_2O_2 (1.0×10^{-2} M) solution was prepared by diluting 30% (w/w) H_2O_2 (Shanghai Taopu Chemical and Industrial Factory, Shanghai, China).

A buffer solution of pH 9.60 was prepared by mixing 11.10 mL of 0.1 M NaOH and 50 mL of 0.025 M $Na_2B_4O_7$ and further diluted to 100 mL with water.

A buffer solution of pH 11.40 was prepared by mixing 9.10 mL of 0.1 M NaOH and 50 mL 0.5 M Na_2HPO_4 and further diluted to 100 mL with water.

A buffer solution of pH 11.85 was prepared by mixing 20.00 mL 0.1 M NaOH and 50 mL 0.5 M Na_2HPO_4 and diluted to 100 mL with water.

A solution of pH 12.50 was prepared by dissolving 0.128 g NaOH and further diluted to 100 mL with water.

Surfactants, CTAB, CPB, SDS and Brij-35, were purchased from Shanghai Chemical Reagent Co. (Shanghai, China). A series of different types and concentrations of the surfactant solutions were prepared according to the requirement of the experiment.

All other chemicals were of analytical reagent grade and used as purchased from Sinopharm Chemical Reagent Co., Ltd, China. Water was distilled using an Aquarius GSR-500 automatic water distillation apparatus (Advance Mfs, Inc., Tokyo, Japan). All the experiments were performed at room temperature.

2.2. *Apparatus*

The flow system for the CL detection of the four types of surfactants is shown in Figure 1. Two peristaltic pumps (Xi'an Remax Company, Xi'an, China) with four channels are used to deliver the reactants to the flow cell. CL measurement was recorded using an injection flow fluorescent luminescence-E mode FI-CL analysis system (Xi'an Remax Company, Xi'an, China). Light measurement data (I_{CL}) were obtained using an automatically controlled computer. Data acquisition and treatment were performed by the REMAX software running under Windows 2000. CL emission spectra were recorded using a Hitachi F-4500 spectrofluorimeter (Tokyo, Japan) equipped with a FI system.

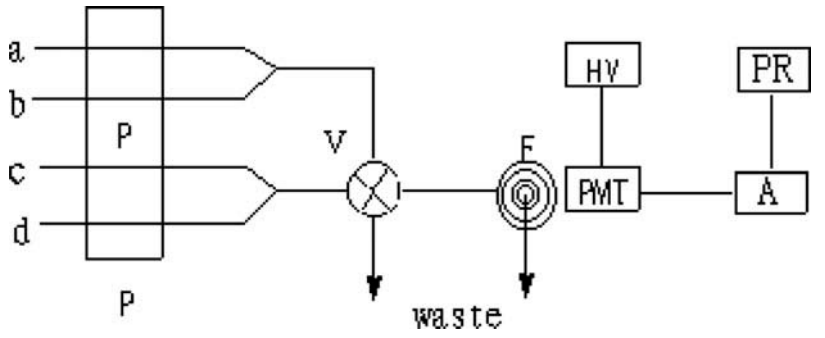

Figure 1. Schematic diagram of the FI system: (a) sample solution; (b) carrier solution (water); (c) luminol solution; (d) H_2O_2 solution. P, peristaltic pump; V, six-way injection valve; F, flow-cell; PMT, photomultiplier tube; A, amplifier; PR, printer; HV, negative voltage.

Kinetic curves of CL were measured using a 632-type Biochemical luminescence meter (Beijing Atomic Nuclear Instrumental Factory, Beijing, China) using a static injection manifold.

2.3. *Procedure*

The surfactants in variable concentration ranges were placed in 10 mL volumetric flasks, diluted with water to the mark and mixed thoroughly. A schematic diagram of the FI-CL system is shown in Figure 1. One peristaltic pump was used to carry surfactants and carrier solution (water), and another pump was used to carry H_2O_2 and luminol solutions. The pumps were used at the global flow rate of 2.5 mL/min for CPB and SDS and 3.0 mL/min for CTAB and Brij-35 until a stable baseline was observed. The different surfactant solutions were injected using a six-way injection valve fitted with a 150-μL sample loop. Then, 150-μL surfactant solution was merged into the stream of luminol and H_2O_2 solutions, reaching to the flow cell to produce the CL intensity signal, and the concentration of surfactants was quantified by the maximum CL intensity.

3. Results and discussion

3.1. *Optimisation of conditions for the determination of CMCs*

To obtain an ideal CL peak signal, all the experimental conditions including the order of mixture of the reagents, the concentration of luminol (the range 2×10^{-5} M–1.0×10^{-4} M) and H_2O_2 (from 0.2 to 0.5×10^{-2} M), reactant media, pH (from 9.0 to 13.00) and the global flow rate (in the range 0.50–3.80 mL/min) were optimised in detail, and the results are listed in Table 1. The optimised conditions were used for the subsequent experiments. In fact, these above conditions did not affect the time and position of the appearance of the maximum CL peak. Modifying experimental conditions such as the concentration of luminol and H_2O_2, reactant media, pH and flow rate, only increase or decrease the intensity value of CL according to our observations. Therefore, the proposed method is easy to handle.

The global flow rate is a critical parameter in FI analysis set-ups with CL detection. The effect of the flow rate in the range 0.50–3.80 mL/min on the CL intensity of the system was investigated. A general improvement in the emission intensity was obtained by increasing the flow rate in the range 0.50–3.80 mL/min. Lower flow rates resulted in lower CL emission, whereas higher flow rates led not only greater consumption of the reagents but also poor

Table 1. Selection of optimum conditions.

Surfactants	Luminol ($\times 10^{-5}$ M)	H_2O_2 ($\times 10^{-2}$ M)	Reaction media	pH	Flow rate (mL/min)
CTAB	6.0	1.0	NaOH-Na_2HPO_4	11.85	3.00
CPB	8.0	1.0	NaOH	12.50	2.50
SDS	6.0	1.0	NaOH-$Na_2B_4O_7$	9.60	2.50
Brij-35	6.0	1.0	NaOH-Na_2HPO_4	11.40	3.00

reproducibility. Therefore, in this study, the flow rates in the range 2.5–3.0 mL/min were selected for different surfactants. It should be emphasised that too low flow rates affected the CMC measurement, leading to a positive error (0.8% for Brij-35, 1.1% for CTAB, 1.2% for CPB and 1.5% for SDS) in the CMC measurement.

3.2. *Dependence of CL intensity on the concentration of surfactants*

Figure 2 shows the representative CL profile of the emission intensity vs. time with varying concentrations of Brij-35 in the range 0.1×10^{-4} M to 5.0×10^{-4} M, indicating that the CL intensity increased gradually with increasing concentration of Brij-35 before the CMC, but rapidly reached to the maximum once the concentration of Brij-35 approaches the CMC and then decreased with further increase in the concentration.

A clear CL maximum peak was observed in the plot of CL intensity vs. concentration of the surfactants CTAB (the range 8.0×10^{-4} M to 11.0×10^{-4} M, Figure 3a), CPB (the range 8.0×10^{-4} M to 10.0×10^{-4} M, Figure 3b), SDS (the range 7.0×10^{-4} M to 10.0×10^{-4} M, Figure 3c) and Brij-35 (the range 0.1×10^{-4} M to 3.0×10^{-4} M, Figure 3d).

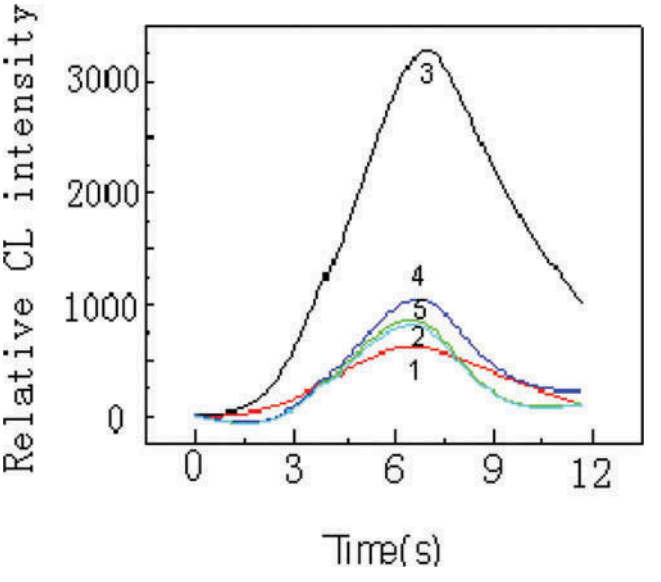

Figure 2. CL emission intensity vs. time profile with varying concentrations of Brij-35. Concentrations of Brij-35 (from 1 to 5): 0.1×10^{-4}, 0.5×10^{-4}, 1.2×10^{-4}, 2.0×10^{-4}, 5.0×10^{-4} M. For other conditions see Table 1.

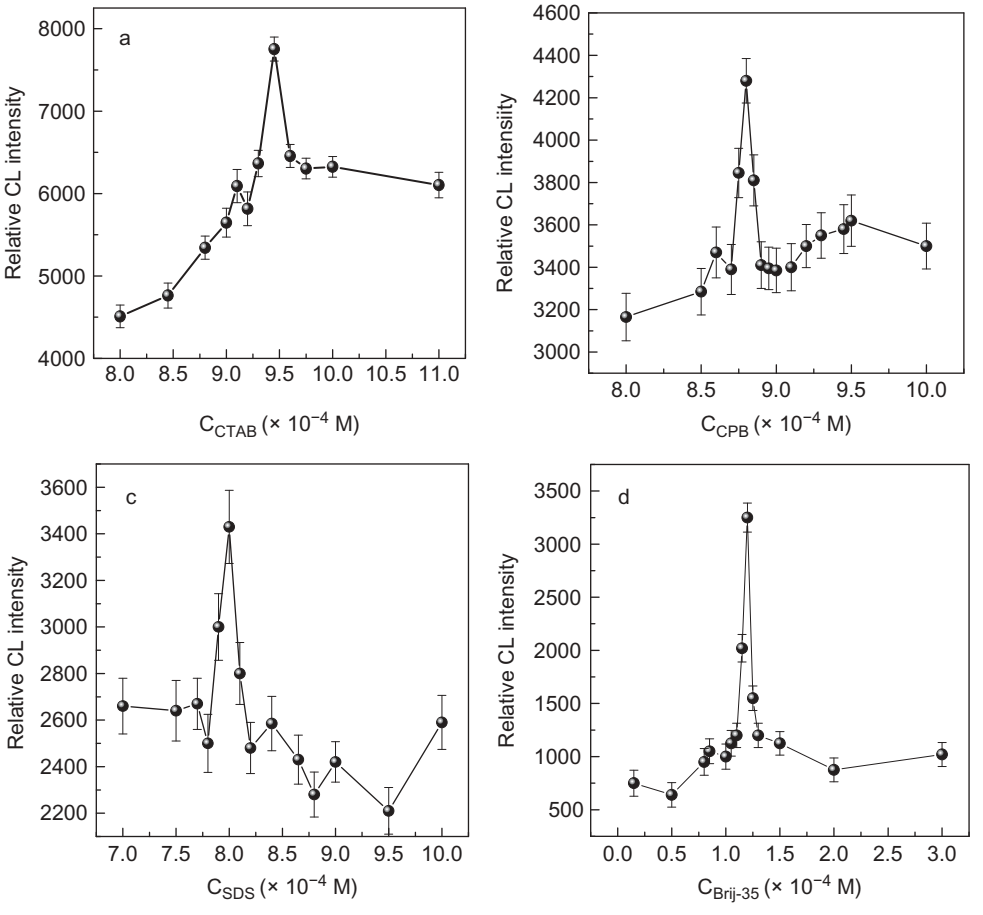

Figure 3. Chemiluminescence intensity of luminol-H_2O_2-surfactant system as a function of surfactant concentration: (a) CTAB; (b) CPB; (c) SDS; (d) Brij-35. For experimental conditions see Table 1.

3.3. *Evaluation of the results for CMC data*

The CL peak signal corresponding to the concentration value of 1.2×10^{-4} M (Figure 3d) is in good agreement with the CMC values of Brij-35 [15,20,29–34]. Similar CL maximum peak was observed in the plot of CL intensity vs. concentration of the surfactant for other surfactants such as CTAB (9.4×10^{-4} M), CPB (8.8×10^{-4} M) and SDS (84×10^{-4} M) systems (Figure 3a–c); therefore, the CMC determination was very satisfying (Table 2). It is desirable to find a suitable CL system that can be used for the determination of CMC for all types of surfactants. Fortunately, luminol-H_2O_2 system used in this method was proven to be suitable for non-ionic (e.g., Brij-35) and ionic surfactants (e.g., cationic surfactants, CTAB and CPB; anionic surfactant, SDS), indicating that the proposed method is very feasible.

Other surfactants such as sodium dodecyl benzene sulphate (SDBS), polyethylene glycol octylphenyl ether (PEGOPE) and polyoxy-ethylene *p*-octylbenzyl ether (Triton X-100) were also investigated; however, the clear CL maximum at the CMC was hardly observed and may probably be improved by finding a proper CL system to replace the luminol-H_2O_2 system by carefully controlling the experimental conditions.

Table 2. CMC values of the surfactants using the proposed method.

Surfactants	CMC ($\times 10^{-4}$ M) by this method	CMC ($\times 10^{-4}$ M) from literature data	Other techniques	References
CTAB	9.4	9.2–9.8	Surface tension, dye solubilisation, speed of sound	[15–17]
CPB	8.8	9.0	Resonance Rayleigh scattering	[18]
SDS	84	81–85	Surface tension, speed of sound, fluorescence	[15,17,19]
Brij-35	1.2	0.48–1.7	Surface tension, spectrophotometry	[15,20,30–35]

3.4. *Effect of salts on CMC values*

The addition of inorganic salts is well known to change the CMC [35]. Using this method, Brij-35 and CTAB were selected as the representative surfactants for the investigation of the salt effect on the CMC (Table 3), and the results show that the CMC values of the surfactants decreased gradually with increasing NaCl concentration, indicating that the FI-CL method can provide a good indication to the CMC change resulting by the salt effect.

3.5. *Mechanism of the CL peak at CMC*

The CL emission spectra of luminol-H_2O_2 reaction in the presence of the surfactants were recorded, showing a maximum at 425 nm. This result is consistent with the previous report for the oxidation of luminol [36], indicating that the luminescent substance in this system is still 3-aminophthalate ion produced in the excited state by the redox reaction, generating CL while returning to the ground state. As a matter of fact, sensitive CL in the presence of surfactant in the micelle media could arise by altering the microenvironment of the CL reaction. The cage structure of micelle is helpful for stabilising the excited state and preventing it from quenching [28,37]. Through the protective microenvironment, the excited species, 3-aminophthalate ion, could be concentrated in the core of micelles, which is more hydrophobic than the Stern region and has lower nonirradiative transition. This result shows that the CL intensity of the surfactant in the micelle media increased. Therefore, the increase in the CL intensity with increasing concentration of the surfactants to the CMC can be attributed to the protective effect of the micelle.

The protective effect of the micelle undoubtedly existed in the CL system in which the concentration of surfactant exceeds the CMC indicating that the CL intensity would further increase after the CMC. The CL kinetics curves that have been obtained with Brij-35 as a representative surfactant recorded by using a static injection manifold (Figure 4) provide a proof. As shown in Figure 4, the CL intensity of the system of luminol-H_2O_2 continuously increases when the concentration of surfactant exceeds the CMC. However, the time required to

Table 3. Effect of the concentration of NaCl on the CMCs of CTAB and Brij-35.

C_{NaCl} (M)	0.01	0.05	0.10	0.20	0.40
Brij-35 (0.1 mM)	–	1.20	1.15	1.10	1.00
CTAB (0.1 mM)	9.40	9.00	8.60	4.00	–

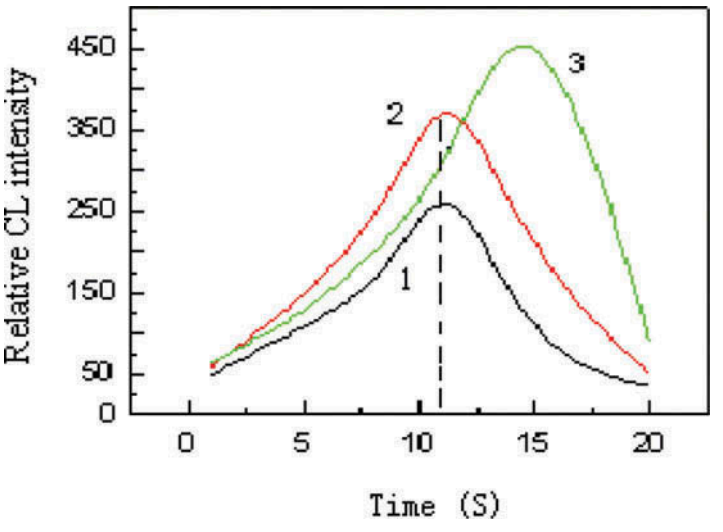

Figure 4. CL kinetic profile of Luminol-H_2O_2 system close to the CMC of Brij-35 measured through static injection manifold. Concentrations of Brij-35 (from 1 to 3): 0.8×10^{-4} M, 1.2×10^{-4} M, 1.8×10^{-4} M.

reach the maximum CL intensity corresponding to the concentration of the surfactants greater than the CMC increases to 15 s (Figure 4; Curve 3) from 11 s (Figure 4; Curves 1 and 2) as compared to that of the system when the concentration of the surfactant is less than the CMC. Furthermore, from Figure 4, the CL intensity of the system when the concentration of the surfactants is higher than the CMC at 11 s is not the maximum emission intensity and would be lower than that at the concentration value equal to the CMC. This accounts for the decrease in the CL intensity after the CMC, because the CL data in this study are obtained using a FI manifold, performed by controlling the flow rate or time. The experimental result shows that too low flow rates would lead to error in the CMC measurement, further supporting the suggestion.

The formation of the micelle is a complicated procedure because surfactants exist as monomers in an aqueous media of very lower concentration. With increasing concentration of surfactants, bulky or loosely packed hydrophilic and/or thin hydrophobic groups, the formation of spherical micelles is easy. At the CMC, micelles are considered to be spherical. However, at concentration slightly above the CMC, the spherical micelles begin to form rod or cylindrical micelles. In concentrated solutions (much higher than the CMC), lamellar micelles form [15] and these compact structures possibly hinder superoxide radical anion, which can react with luminol to delay the time of approaching the maximum CL intensity after the CMC. Based on the experiments, the two main factors proposed for the CL peak forming at the CMC of the surfactants are the protective effect of the micelle against the nonirradiative transition of the excited species and the retarding effect of the micelle structures on the CL reaction rate.

4. Conclusions

A new FI-CL method was developed for the determination of the CMC of surfactant. Luminol-H_2O_2 system used in this method is proven to be suitable for non-ionic (e.g., Brij-35) and ionic surfactants (e.g., cationic surfactants, CTAB and CPB; anionic surfactant, SDS), indicating that the proposed method is rather feasible except for SDBS, PEGOPE and Triton X-100 surfactants.

The FI-CL method was found to be simpler and more rapid than the traditional methods such as electrical conductivity, surface tension and dye solubilisation. The preliminary mechanism based on the experiment indicates that the luminescence peaks observed were mainly because of the protective effect of the micelle against the nonirradiative transition of the excited species and the retarding effect of the micelle structures on the CL reaction rate.

Disclosure statement

No potential conflict of interest was reported by the authors.

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