



## Determination of Micellar Aggregation Numbers of Gemini Surfactant in Aqueous Solution by Steady-State Fluorescence Quenching Method

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(Received: 12 September 2011;

Accepted: 6 June 2012)

AJC-11549

A new kind of Gemini surfactant synthesized from the intermediate 1-bromo-2-(2-bromoethoxy)ethane and dodecyl dimethyl amine by using isopropanol as solvent. The critical micellar concentration (CMC) value of Gemini 12-Y-12 determined by Steady-state fluorescence quenching (SSFQ) method is basically in agreement with the value by surface tension method. The micellar aggregation numbers ( $N_{agg}$ ) of this surfactant are essentially constant when the concentrations of the quencher were selected in  $2.0 \times 10^{-4}$ - $5.0 \times 10^{-4}$  mol L<sup>-1</sup>. The  $N_{agg}$  of the Gemini surfactant increases linearly with the increase of surfactant concentration in the range of 4-9 times of critical micellar concentration and critical micellar aggregation numbers obtained by extrapolation method is 13.2.

**Key Words:** Gemini surfactant, Fluorescence probe, Micellar aggregation numbers.

### INTRODUCTION

Gemini surfactants are made of two hydrophobic chains and two polar headgroups covalently attached through a spacer group<sup>1,2</sup>. Because of this unique structure, Gemini surfactants exhibit superior properties to those of conventional surfactants, such as lower CMC, better wetting properties, lower limiting surface tensions, unusual aggregation morphologies and so forth<sup>3-5</sup>. Attempts to correlate the aggregate properties with that of the molecular features of surfactant are important for developing new surfactant systems for specific applications.  $N_{agg}$  is a structurally relevant parameter that contains indirect information on the micellar size and shape<sup>6</sup>. Many methods can be used to determine the  $N_{agg}$ , for instance, static light scattering (SLS), small angle neutron scattering (SANS), or fluorescence probing techniques. Light scattering requires extrapolation to low concentrations and small angle neutron scattering is very costly and the facilities are not generally available. Steady-state fluorescence quenching (SSFQ) involves measurements of the fluorescence emission intensity at increasing quencher concentration, using a spectrofluorometer<sup>7,8</sup>. Since this apparatus is easily found in most laboratories, this method has been quite popular for determining  $N_{agg}$  values in all types of surfactant-containing systems. In this work, a new kind of Gemini surfactant was synthesized<sup>9,10</sup>. The  $N_{agg}$  values were determined by using SSFQ method and their influencing factors were also discussed.

### EXPERIMENTAL

**Synthesis of the intermediate 1-bromo-2-(2-bromoethoxy)ethane:** The dibromo precursor was synthesized by the addition of phosphorus tribromide to diethylene glycol in a dropwise manner over a period of 1 h at 0 °C<sup>11</sup>. Then the mixtures were stirred with concomitant heating at 50-60 °C for 12 h. The reaction mixture was then cooled to ambient temperature and dissolved in chloroform (25 mL). Water was added slowly and the mixture was transferred into a separatory funnel. The organic layer was separated out after washing with water, sodium bicarbonate and again with water and finally passed through a bed of anhydrous sodium sulfate. The resulting chloroform solution was concentrated and loaded on a silica gel column (60-120 mesh) and was eluted with hexane to give a colorless liquid.

**Synthesis of the Gemini surfactant:** The surfactant was obtained by refluxing the dibromo precursor with N,N-dimethyl dodecyl tertiary amine in dry ethanol at 80 °C for 72-96 h<sup>12</sup>. At the end of this period, solvent was removed under vacuum from the reaction mixture and the solid thus obtained was recrystallized several times from 10 mL of ethyl acetate containing 5 mL of ethanol to obtain solid surfactants as pure product as determined from <sup>1</sup>H NMR spectra analysis. For convenience, the surfactants is abbreviated as Gemini12-Y-12.

### Structure characterization of the Gemini surfactant:

The proton chemical shifts  $\delta$  of the various groups are: long-chain alkyl  $\text{CH}_3$ - $\delta$  0.86 (6H),  $-\text{CH}_2$ -  $\delta$  1.29 (36H),  $-\text{N}-\text{C}-\text{CH}_2$ -  $\delta$  1.71 (4H),  $-\text{N}-\text{CH}_2$ -  $\delta$  3.63 (4H);  $-\text{N}-\text{CH}_3$  3.45 (12H); connected group  $-\text{N}-\text{C}-\text{CH}_2$ -  $\delta$  4.04 (4H),  $-\text{N}-\text{CH}_2$ -  $\delta$  4.35 (4H); the peak of impurity  $\delta$  2.61 (See supplementary material from author on request).

**Determination of  $N_{\text{agg}}$  values of the Gemini12-Y-12 surfactant:** Fluorescence was used to study the micropolarity of the gemini surfactant from measurement of the pyrene polarity index ( $I_1/I_3$ ) at a concentration above the CMC.  $I_1/I_3$  is the ratio of the intensities of the first and the third vibronic peaks in the fluorescence emission spectrum of pyrene.

Firstly, ternary solution system (probe/surfactant/ quencher) were prepared as follows: put a certain concentration hexadecylpyridinium chloride methanol solution into 10 mL volumetric flask, blow dry the methanol by high purity nitrogen and add a certain concentration surfactant solution to scale. Then carry out ultrasonic dispersion at constant temperature for 12 h. Secondly, Binary solution (probe/surfactant) were prepared the same as the above steps except adding quencher. The third, the fluorescence intensities were measured using a Hitachi F-4500 spectrofluorometer. Pyrene was excited at 335 nm and the emission spectra were scanned from 350-500 nm, excitation and emitting optical grating both set at 2.5 nm, scanning speed at 500 nm/min, experimental temperature at 25 °C. The  $N_{\text{agg}}$  were calculated by the following equation<sup>13</sup>:

$$\ln\left(\frac{I_0}{I_1}\right) = C_Q \frac{N_{\text{agg}}}{(S_T - S_{\text{cmc}})}$$

$I_0$ : fluorescence intensity of pyrene without adding quencher,  $I_1$ : fluorescence intensity of pyrene as adding quencher,  $C_Q$ : concentration of quencher,  $N_{\text{agg}}$ : micellar aggregation numbers,  $S_T$ : total concentration of the surfactant,  $S_{\text{cmc}}$ : critical micellar concentration of the surfactant.

## RESULTS AND DISCUSSION

**Determination of the CMC for Gemini12-Y-12 by steady-state fluorescence quenching method:** Fig. 1 shows the fluorescence emission spectrum of pyrene in the Gemini 12-Y-12 solution at the concentration of  $4.4 \times 10^{-3} \text{ mol L}^{-1}$ . The CMC for Gemini12-Y-12 was reduced when plotted the pyrene polarity index ( $I_1/I_3$ ) versus the surfactant concentration (Fig. 2). When the surfactant concentration is less than CMC, the ratio of  $I_1$  and  $I_3$  changes slightly, the reason is that the surfactant molecular mostly presented as monomer in aqueous solution. The increasing of surfactant concentration has little effect on the change of the present environment where pyrene stayed in. After the surfactant concentration exceeds CMC, the surfactant molecular began to form micellar. Hydrophobic pyrene was transferred from aqueous solution and solubilized in hydrophobic region of micellar fence. With the increasing of surfactant concentration, further surfactant moleculars squeezed into the micellar already formed so that they were arranged much closer and compelled the water which have originally penetrated into the micellar fence layer to enter into the bulk water. As a result, the intensity ratio of the third vibronic band to the first vibronic band becomes smaller as

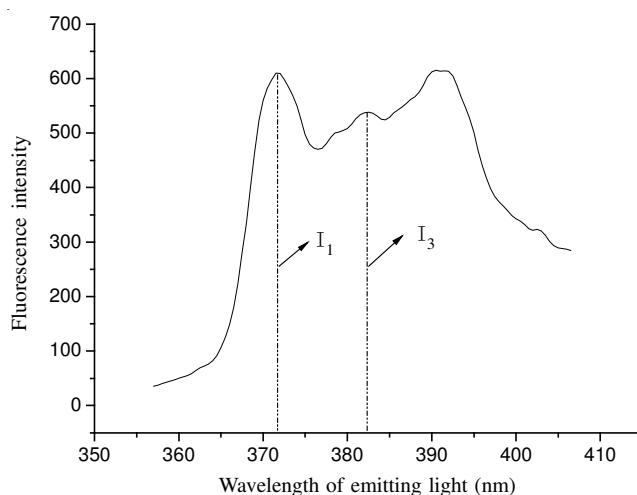


Fig. 1. Fluorescence emission spectrum of pyrene in the Gemini12-Y-12 solution

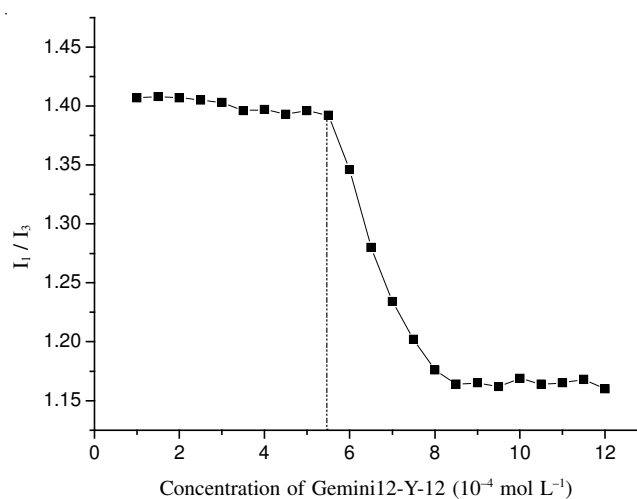


Fig. 2. CMC curve of the Gemini12-Y-12 determined by SSFQ method

the decrease of polarity of pyrene environment until the second abrupt change point corresponds to the CMC value. The value ( $5.5 \times 10^{-4} \text{ mol L}^{-1}$ ) determined by steady-state fluorescence probe method is basically in agreement with the value ( $5.6 \times 10^{-4} \text{ mol L}^{-1}$ ) by surface tension method<sup>14</sup>.

**Selection of proper instrument parameters for fluorophotometer:** Slit width of fluorophotometer excitation and emitting optical grating are very important measuring parameters. If slit width of excitation optical grating ( $E_x$ ) is over-size, this goes against that the exciting light is monochromatic light (335 nm), usually smaller  $E_x$  is better. At the same time slit width of emitting optical grating ( $E_m$ ) could not be expanded without limit. It could easily cause the overlapping of peak shape in emission spectrum of pyrene if  $E_m$  is too large in the experiment. During the experiment, two proper parameter conditions ( $E_x = 2.5 \text{ nm}$ ,  $E_m = 2.5 \text{ nm}$  and  $E_x = 2.5 \text{ nm}$ ,  $E_m = 5.0 \text{ nm}$ ) were fixed. The  $N_{\text{agg}}$  has little difference at the two situations (Table-1). Thus,  $E_x$  and  $E_m$  were both set at 2.5 nm.

**Confirmation of the range of quencher concentration:** Fig. 3 shows the fluorescence emission spectrum of pyrene as adding different concentrations of quencher in the Gemini 12-Y-12 solution at the concentration of  $4.4 \times 10^{-3} \text{ mol L}^{-1}$ .

TABLE-1  
INFLUENCE OF  $E_x$  AND  $E_m$  ON  
THE  $N_{agg}$  OF THE GEMINI12-Y-12

Surfactant concentrations ( $\text{mol L}^{-1}$ )	$N_{agg}$ ( $E_x = 2.5 \text{ nm}$ , $E_m = 2.5 \text{ nm}$ )	$N_{agg}$ ( $E_x = 2.5 \text{ nm}$ , $E_m = 5.0 \text{ nm}$ )
$1.65 \times 10^{-3}$	9.72	9.02
$2.75 \times 10^{-3}$	17.51	18.45
$3.75 \times 10^{-3}$	19.63	20.77
$5.50 \times 10^{-3}$	28.31	29.34
$6.60 \times 10^{-3}$	34.32	33.72

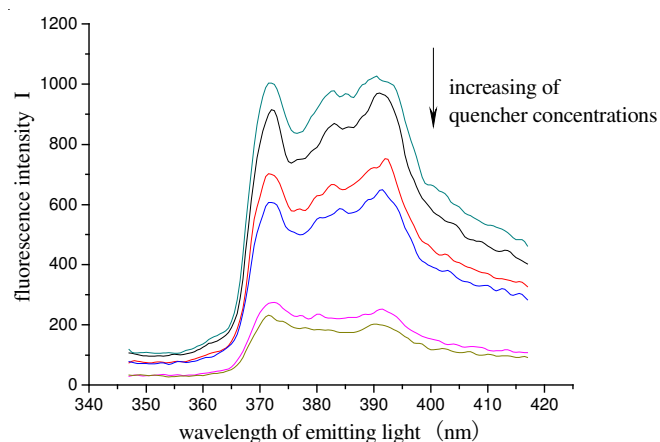


Fig. 3. Influence of different concentrations of quencher in Gemini12-Y-12 solution to the fluorescence emission spectrum of pyrene

Fluorescence emission intensity of pyrene decreases gradually with the increasing of quencher concentrations. The  $N_{agg}$  at different concentrations of quencher in a certain Gemini 12-Y-12 solution could be calculated according to the equation mentioned in experimental section.

Fig. 4 shows the effect of quencher concentration on the  $N_{agg}$ . The probable reason for the changing of the  $N_{agg}$  is that both probe and quencher can be solubilized in the micellar, causing variation of its shape and size when determining the  $N_{agg}$  by SSFQ method. Thus, so far as what we have done in our experiments the optimum results indicated that the quencher concentration should be as lower as possible on condition that the ratio of quencher concentration and micellar concentration is far less than 1. Therefore, the proper concentrations of the quencher were selected in  $2.0 \times 10^{-4}$ - $5.0 \times 10^{-4} \text{ mol L}^{-1}$ .

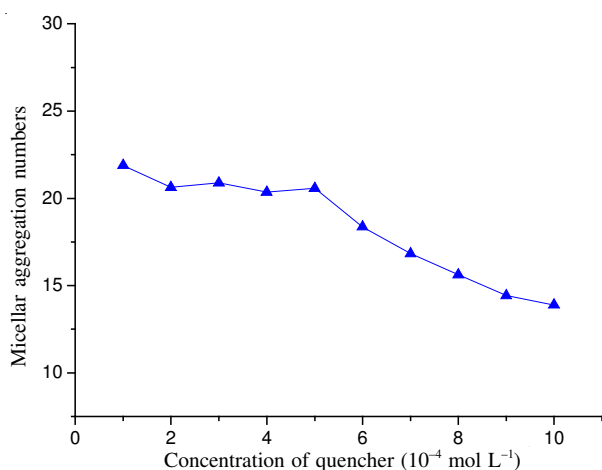


Fig. 4. Relationship between the  $N_{agg}$  and the concentration of quencher

**Effect of Gemini12-Y-12 concentration on micellar aggregation number:** Gemini12-Y-12 surfactant solution concentrations ranging from 2-12 times of CMC were prepared by using pyrene saturated solution and choosing quencher concentration at  $2.0 \times 10^{-4} \text{ mol L}^{-1}$ . The  $N_{agg}$  were determined by using SSFQ method.

It has been shown from Fig. 5 that the  $N_{agg}$  are relatively low at the period of 2-3 times of CMC. That could be the porosity between the surfactant molecules in the micellar leads to the weak hydrophobic interaction between the alkane chain which forms the driving force of the orderly molecular aggregates formed by the surfactant spontaneously and also the micellar could not solubilize sufficient probe and quencher that affect their Poisson distribution in micellar systems. When the concentration of the surfactant is greater than 10 times of CMC, the test result is slightly higher. The main reason is quite likely that surfactant monomer could not be merged into original microsphere micellars with regular structure along with the increasing of surfactant concentration. Therefore, more surfactant molecular gathered around original microsphere micellars by means of winding and twisting and formed rod-like, vesicle-like and layered irregular structures. At the the interval of 4-9 times of CMC, The  $N_{agg}$  increase about linearly with the increasing of surfactant concentration. The simple linear regression equation of the  $N_{agg}$  and surfactant concentration can be obtained, it is  $N_m = 1.9527 \times 10^3 C(\text{mol L}^{-1}) + 12.09$   $R^2 = 0.9985$ . It could be concluded that the critical aggregation number (13.2) calculated from the linear regression equation is nearly consistent with the one by extrapolation method.

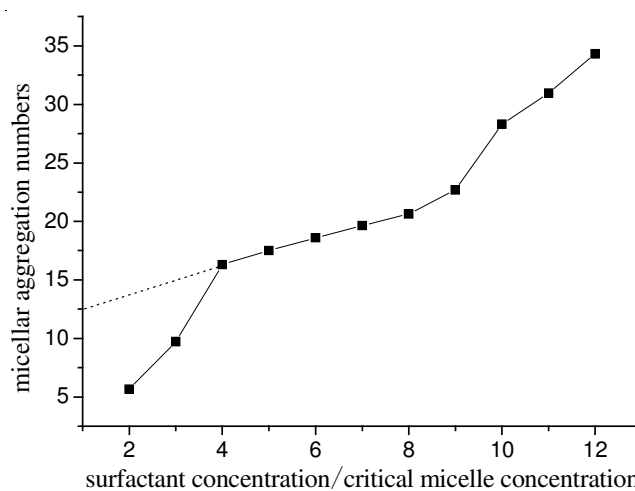


Fig. 5. Relationship between the  $N_{agg}$  and the concentrations of the surfactant

## Conclusion

The critical micelle concentration value of Gemini 12-Y-12 determined by steady-state fluorescence quenching method in which pyrene was used as a fluorescence probe and cetylpyridinium chloride as a quencher is basically in agreement with the value by surface tension method. The  $N_{agg}$  of this surfactant are essentially constant when the concentrations of the quencher were selected in  $2.0 \times 10^{-4}$ - $5.0 \times 10^{-4} \text{ mol L}^{-1}$ . The  $N_{agg}$  of the Gemini 12-Y-12 increases linearly with the increase

of surfactant concentration in the range of 4 to 9 times of critical micelle concentration and critical micellar aggregation numbers obtained by extrapolation method is 13.2.

#### ACKNOWLEDGEMENTS

The authors thank the China Pharmaceutical University for the use of nuclear magnetic resonance apparatus and Jiangsu University Natural Science Fund (10KJD430007) and Nantong University Natural Science Fund (09Z011 and 10Z014) for financial support.

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