Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138 (2015) 807–810

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

An improved procedure for determination of the mean aggregation number of micelles

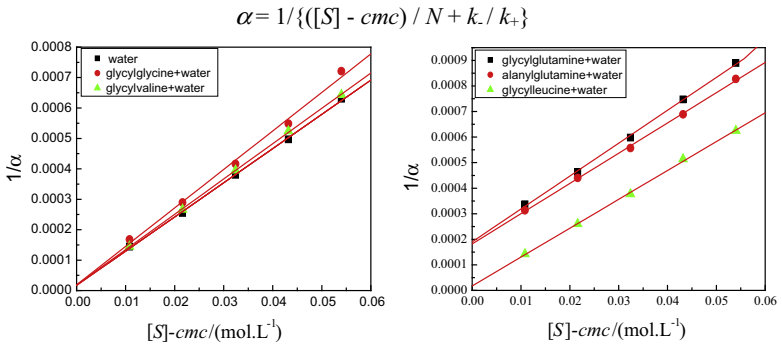
Shuangyan Wu [a], Masanori Tachiya [b], Zhenning Yan [a,*]

[a] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan 450052, PR China
[b] National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8565, Japan

HIGHLIGHTS

- An improved procedure for determination of the mean aggregation number of micelles is presented.
- This model assumes that a part of quencher molecules are in the aqueous phase.
- The aggregation numbers of sodium dodecyl sulfonate in aqueous dipeptide solution are determined.
- The association constant for quencher–micelle association can be calculated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 2 July 2014
Received in revised form 29 October 2014
Accepted 5 November 2014
Available online 13 November 2014

Keywords:
Fluorescence quenching method
Aggregation number
Sodium dodecyl sulfonate

ABSTRACT

In this paper, a theory of fluorescence quenching in micelles which enables a dynamic approach to the evaluation of the aggregation numbers of micelles is presented. This method is based on a detailed kinetic model of quenching of fluorescent probe developed by Tachiya (1975, 1982) and takes into account that a part of quenchers are associated with micelles but the remaining quenchers are in the aqueous phase. The approach presented is an improvement on a previous fluorescence quenching method (Turro and Yekta, 1978) and is applied to determine the aggregation number of sodium dodecyl sulfonate (SAS) in aqueous dipeptide solution using cetylpyridinium chloride as quencher. The values of aggregation number and association constant for quencher–micelle association are presented.

Introduction

The propensity of surfactants to self-aggregate into micelles in solvents is perhaps the most fascinating aspect of these molecules, and micelles remain one of the central topics of study within surface and colloid chemistry. Important characteristics of micelles are the critical micelle concentration (*cmc*) and their aggregation numbers (*N*) [1] (the average number of surfactant molecules per micelle) which is one of the fundamental parameter of micelles.

One of the most frequently applied methods to determine *N* is the fluorescence quenching technique [2]. It offers the possibility of a simple and fast method so necessary for studies of the theories of micelle formation [3–11], where *N* must be measured as a function of such parameters as temperature, pressure, and various concentrations. In contrast to other methods [12], fluorescence quenching also offers the advantage that the measurement of *N* is not restricted to surfactant concentrations near the *cmc* and is sensitive to the molecular environment of the probe.

In 1978 Turro and Yekta [13] proposed a method based on the quenching of fluorescence to determine the aggregation number of micelles. In the method the fluorescence intensity of a micelle

* Corresponding author. Tel.: +86 13643710678; fax: +86 371 67761744.
E-mail address: yanzzn@zzu.edu.cn (Z. Yan).

http://dx.doi.org/10.1016/j.saa.2014.11.008
1386-1425/

bound probe was measured as a function of quencher concentration. The mean aggregation number of micelles may be derived from the following equation.

$$\ln(I_0/I) = N[Q]/(S_T - cmc) \quad (1)$$

where I_0 and I are the fluorescence intensities of probe in the absence and presence of quencher, respectively, [Q] is quencher concentration, and S_T is the concentration of surfactant. The N value was calculated from the slope of the plot of $\ln(I_0/I)$ versus [Q]. The method is simple and fast but has significant limitations. As described, it assumes complete partitioning of the quencher into the micelle phase. However, generally speaking, this is not correct. A part of quencher molecules introduced in solution are in micelles and the remaining part is in the aqueous phase.

In this work, we take this effect into account and use the theory given by Tachiya in 1975 and 1982 [14,15] to develop a method for the determination of aggregation number on the basis of steady-state fluorescence quenching. The experimental system measures the quenching of the steady state fluorescence of pyrene in sodium dodecyl sulfonate micelles in aqueous dipeptides solution by cetylpyridinium chloride (CPC).

Material and methods

Materials

All of the reagents used in this study were provided by Sigma–Aldrich Shanghai Trading Co. Ltd. Three glycyl dipeptides 2-[(2-aminoacetyl)amino]acetic acid (commonly known as glycylglycine, CAS 556-50-3), 2-[(2-aminoacetyl)amino]-3-methylbutanoic acid (common name glycyl-L-valine, CAS 1963-21-9), and (2*S*)-2-[(2-aminoacetyl)amino]-4-methylpentanoic acid (commonly known as glycyl-L-leucine, CAS 869-19-2) (mass fraction purity of 0.990) were twice recrystallized from aqueous ethanol solution. Two glutamine dipeptides (2*S*)-2-[(2-aminoacetyl)amino]-4-acyl butyric acid (common name glycyl-L-glutamine, CAS 13115-71-4, mass fraction purity of 0.998) and (2*S*)-2-[(2-aminopropionyl)amino]-4-acyl butyric acid (common name L-alanyl-L-glutamine, CAS 39537-23-0, mass fraction purity of 0.992) were used as received. All of the dipeptides were dried for 24 h under vacuum at room temperature. Then they were stored over P_2O_5 in a desiccator before use. Anionic surfactant sodium dodecyl sulfonate (SAS, mass fraction purity over 0.99), pyrene (mass fraction purity 0.990) and cetylpyridinium chloride (CPC, mass fraction purity 0.98) were used without further purification. Water with a conductivity of $<1.0 \times 10^{-4}$ S m^{-1} was obtained by distilling deionized water.

Methods

Fluorescence spectra were recorded with a F7000 Hitachi fluorescence spectrometer at room temperature. Emission and excitation slit widths were fixed at 2.5 and 2.5 nm, respectively, with a scan rate selected at 240 nm min^{-1}. An excitation wavelength of 337 nm and emission wavelength recorded from 350 to 450 nm with a step of 1 nm were used to obtain the experimental results. The relative fluorescence intensities were easily found by measuring the relative heights of the peaks in the emission spectra for a quenched and unquenched solution, the latter being the same during one series of experiments. All systems were examined in a solution of 2.0×10^{-6} mol dm^{-3} pyrene used as a probe. The molality of dipeptides was kept to 0.02 mol dm^{-3}. The aggregation number was calculated by measuring the intensities of the first peak (373 nm) of different concentrations of the quencher (cetylpyridinium chloride) whose concentration was varied slightly to ensure the Poisson distribution for the quencher.

Theory—Decay kinetics of excited probe

In our study, the following kinetic model, which is hereafter referred to as the Tachiya model was used:

$$\begin{aligned} &P_n^* \xrightarrow{k_0} P_n, \quad n = 0, 1, \ldots, \\ &P_n^* + A \underset{(n+1)k_-}{\overset{k^+}{\rightleftharpoons}} P_{n+1}^*, \quad n = 0, 1, \ldots, \\ &P_n^* \xrightarrow{nk_q} P_n, \quad n = 1, 2, \ldots, \end{aligned} \quad (2)$$

Here P_n^* denotes a micelle containing an excited probe and n quencher molecules, while P_n denotes a micelle which contains n quencher molecules but no excited probe. A stands for a quencher molecule in the aqueous phase. k_0 is the total decay constant of the excited state in the absence of a quencher. k_+ is the rate constant for entry of a quencher molecule into a micelle, while k_- is the rate constant for exit of a quencher molecule from a micelle containing one quencher molecule. k_q is the rate constant for quenching of an excited probe in a micelle containing one quencher molecule. When a micelle contains n quencher molecules, the rate constant for exit of a quencher molecule from the micelle and the rate constant for quenching of an excited probe in the micelle should be nk_- and nk_q, respectively. In the above description, it is assumed that one micelle cannot contain more than one probe molecule.

On the basis of the above model, the distribution of quenchers among micelles obeys a Poisson distribution as shown below:

$$P_n^*(0) = (1/n!)(k_+[A]/k_-)^n P^*(0) \exp(-k_+[A]k_-), \quad n = 0, 1, \ldots. \quad (3)$$

where $P^*(0)$ is the initial total concentration of excited probes. [A] denotes the concentration of quencher molecules in the aqueous phase.

Further, the time-resolved kinetics of fluorescence quenching is generally described by the following equation:

$$P^*(t) = P^*(0) \exp\left[-\left(k_0 + \frac{k_q k_+[A]}{k_- + k_q}\right)t - \frac{k_q^2 k_+[A]}{k_-(k_- + k_q)^2}\{1 - \exp[-(k_- + k_q)t]\}\right] \quad (4)$$

where $P^*(t)$ is the total concentration of excited probes at time t.

In Tachiya model the following assumptions are involved: (1) There is no limit to the number of solubilized molecules in any one micelle, and there is no variation in the entry rate constant (k_+) with the number of solubilized molecules already present. (2) When a micelle contains n solubilized molecules, the rate constant for exit of a solubilized molecule from the micelle is n times as fast as when it contains one solubilized molecule. As Tachiya first showed in 1975 [14], these assumptions lead to the conclusion that the distribution of solubilized molecules obeys Poisson statistics. The assumption that there is no limit to the number of solubilized molecule in a micelle is not so bad when the average number of solubilized molecules in a micelle is relatively small.

The total fluorescence intensity I is given by

$$I = k_r \int_0^\infty P^*(t)dt \quad (5)$$

where k_r is the radiative decay rate constant. From Eqs. (4) and (5), it is straightforward to calculate the stationary fluorescence intensity from the time-resolved kinetics of fluorescence quenching. The following equation for the ratio of total fluorescence intensities in the presence and absence of a quencher is obtained:

$$\frac{I}{I_0} = k_0(k_- + k_q) \exp\left[-\frac{k_q^2 \bar{n}}{(k_- + k_q)^2}\right] \sum_{l=0}^{\infty} \frac{1}{l!} \left[\frac{k_q^2 \bar{n}}{(k_- + k_q)^2}\right]^l \times \frac{1}{k_0(k_- + k_q) + k_- k_q \bar{n} + l(k_- + k_q)^2} \quad (6)$$