



Nile red probing for sphere-to-rod-to-wormlike micelle transition in aqueous surfactant solution

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ABSTRACT

Nile red (phenoxazone-9) was used as a fluorescence probe to detect the sphere-to-rod-to-wormlike micellar transition in the aqueous mixtures of cetyltrimethylammonium bromide and sodium salicylate or potassium bromide, and also in the aqueous solution of a Gemini surfactant, ethanediyl- α,ω -bis(dimethyl dodecyl ammonium bromide). The results showed the I_a/I_b of Nile red (the fluorescence intensity ratio of the twisted intramolecular charge transfer band to the planar locally excited band) was a more sensitive index than the I_a (the fluorescence intensity of the twisted intramolecular charge transfer band) to represent the micellar transition. This was attributed to the special molecular structure of Nile red that has a large conjugated ring and the can form hydrogen bond with water molecules at the electron acceptor group. This led to sensitive response of the twisted intramolecular charge transfer state of Nile red to the change of microenvironment.

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1. Introduction

Fluorescence probe technique with its remarkable sensitivity of the probe to the microenvironment change has been developed as an effective method to detect the micelle formation of surfactant in aqueous solution [1–6]. It was however rarely used to detect the transition of aggregates upon the addition of salt or the increase of surfactant concentration though such transition has been well known [7–18]. The twisted intramolecular charge transfer (TICT) probe is a particular fluorescence probe, whose molecule contains both electron donor and acceptor groups in chemical structure. The photo-induced full separation of intramolecular charge, which accompanies with the molecule twisting into two mutually perpendicular parts, produces the TICT type excited state that has much higher dipole moment than the ground state. This leads to the sensitive response of the probe to the change of microenvironment [19–21]. As a special TICT probe, Nile Red (NR) has a large conjugated ring in its molecule and the electron-accepting carbonyl oxygen that is able to form the hydrogen bond with water molecules [22,23] (see Experimental Section). In our previous work, such molecular structure of NR was found to have a very sensitive response to the microenvironment change in the surfactant aggregates and it can

well probe for the transition of AOT micelles to vesicles [24]. In the present work, NR is used to probe for the sphere-to-rod-to-wormlike micelle transition in various surfactant solutions induced by both adding inorganic/organic salts and increasing surfactant concentration. The results show that the I_a/I_b (the ratio of the intensities of TICT band to a planar locally excited (LE) band) of the fluorescence spectra of NR could well reflect the aggregate transition information.

2. Experimental

2.1. Materials

Nile Red (NR, phenoxazone-9, Acros) that is chemically known as 9-diethylamino-5H-benzo[*a*]phenoxazine-5-one ($C_{20}H_{18}N_2O_2$), cetyltrimethylammonium bromide ($C_{16}TABr$, Sigma) and sodium salicylate (NaSal, Shanghai Reagent Corporation of China, AR) were used as received. Potassium bromide (KBr, Shanghai Reagent Corporation of China, AR) was baked at 500 °C for 6 h. Ethanediyl- α,ω -bis(dimethyl dodecyl ammonium bromide) (referred to as C_{12} -2- C_{12} ·2Br) is a Gemini type surfactant. C_{12} -2- C_{12} ·2Br was synthesized by the reaction of *N,N,N',N'*-tetramethylethylenediamine with 1-Bromo-*n*-dodecane [25]. The molecular structures of NR and C_{12} -2- C_{12} ·2Br are represented in Fig. 1.

All solutions were prepared with Milli-Q water.

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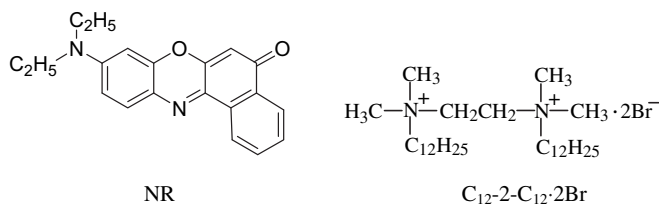


Fig. 1. Chemical structures of NR and C₁₂-2-C₁₂·2Br.

2.2. Methods

Fluorescence spectra were recorded on a Hitachi F4500 fluorescence spectrophotometer with xenon lamp and photomultiplier detector. Slit for excitation and emission monochromators was 5.0 nm. The excitation wavelength (λ_{ex}) was 480 nm. The concentration of NR used in all fluorescence measurements was $2.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. The viscosities of aqueous surfactant solutions were measured with Ubbelohde viscometer. The dynamic viscosity (η) was calculated according to Eq. (1).

$$\eta = A\rho t - \frac{B\rho}{t} \quad (1)$$

where t is the efflux time, ρ is the density of sample. A and B are the calibration constants of the viscometer. The experimental temperature was controlled by a DC-0506 hypothermal thermostatic bath (shanghai Hengping instrument factory) with the accuracy of $\pm 0.1 \text{ }^\circ\text{C}$.

3. Results and discussion

3.1. Sphere-to-rod-to-wormlike transition of C₁₆TABr micelle induced by KBr

As reported in ref [8], addition of KBr induced sphere-to-rod-to-wormlike transition of C₁₆TABr micelle. This case is used to investigate the fluorescence probe method. Fig. 2(I) shows the fluorescence spectra of NR in C₁₆TABr ($10 \text{ mmol} \cdot \text{L}^{-1}$) micellar solutions. Deconvolution technique has been used to resolve the subbands hidden in the spectrum by Gaussian program (Peakfit Version 4.12, Seasolve). The number and location of the subbands were determined by the second derivation of the spectrum. The sum of the optimum subbands was required to perfectly satisfy the original contour of the spectrum. An example of the curve-fitting is shown in Fig. 2 (II). In the

absence of KBr (the spectrum is represented as dashed line), the two subbands centered at 572 nm and 629 nm are successively attributed to the emission of the planar locally excited (LE) state and the twisted intramolecular charge transfer (TICT) state since the TICT state has much higher dipole moment than the LE state and therefore it locates on the long wavelength [20]. With addition of KBr, both the subbands show strengthened.

The emission intensity (I_a) of TICT band is shown in Fig. 3(I) as a function of KBr concentration (C_{KBr}) in C₁₆TABr ($10 \text{ mmol} \cdot \text{L}^{-1}$) aqueous solution at $30 \text{ }^\circ\text{C}$. As seen in Fig. 3(I), with the increase of C_{KBr} , I_a strongly increases and reaches a plateau at $C_{\text{KBr}} = 0.1 \text{ mol} \cdot \text{L}^{-1}$ (shown as C_1 in Fig. 3). A slightly higher plateau seems to be observed at a higher concentration of KBr (shown as C_2 in Fig. 3), however, it is not clear. The results of dynamic light scattering (DLS) and ^1H NMR gave out two characteristic KBr concentrations (0.1 and $0.2 \text{ mol} \cdot \text{L}^{-1}$) corresponding to the transition of C₁₆TABr micelles from sphere-to-rod and from rod-to-wormlike, respectively [8]. The C_1 revealed in the plot of I_a versus C_{KBr} as the critical concentration for the curve reaching the plateau is very good consistent with the first characteristic concentration reported in ref [8]. This indicates that the I_a can well respond to the formation of C₁₆TABr rod micelles. However, this index does not show a clear change at C_2 . This means that it fails to represent the further transition of C₁₆TABr micelles from rod-to-wormlike.

Fig. 3(II) shows the variation of I_a/I_b (the intensity ratio of TICT band to LE band) with C_{KBr} and a minimum appears at ca. $0.07 \text{ mol} \cdot \text{L}^{-1}$ KBr, reflecting the micelle transition from spherical to rodlike as mentioned above. Besides, a clear and irrefutable inflection at the concentration C_2 also appears in the plot of I_a/I_b versus C_{KBr} . This inflection ($0.21 \text{ mol} \cdot \text{L}^{-1}$) agrees well with the second characteristic concentration reported by Zhang et al. [8] showing the micellar transition from rod-to-wormlike. This indicates that the I_a/I_b of NR can even respond to the formation of wormlike micelles. In our previous work, the I_a/I_b of NR also sensitively responded to the AOT aggregate transition from micelles to vesicles as a maximum in the plot of I_a/I_b versus C_{AOT} . Obviously, the I_a/I_b of NR is a more sensitive index than I_a for the detection of aggregate transition.

3.2. Interpretation for the spectroscopic behavior of NR

It is known that NR is solubilized into the palisade layer of micelle [26,27]. The palisade layer of micelle consists of the charged headgroups, the solvated water round the headgroups and the α , β even γ methylene groups of alkyl tail, which constitutes the

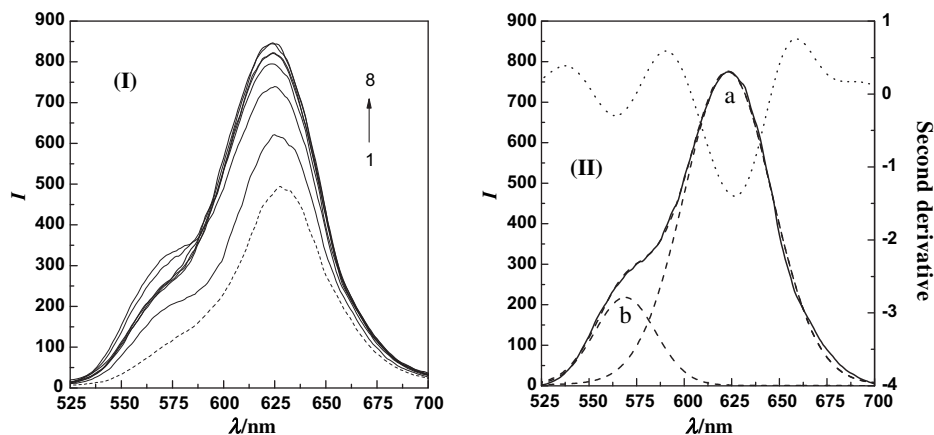


Fig. 2. (I) Fluorescence spectra of NR in C₁₆TABr ($10 \text{ mmol} \cdot \text{L}^{-1}$) aqueous solutions at $30 \text{ }^\circ\text{C}$. From 1 to 8, KBr concentration is successively 0 (dashed line), 0.01, 0.06, 0.1, 0.14, 0.18, 0.24, 0.4 $\text{mol} \cdot \text{L}^{-1}$. (II) Curve-fitting for the fluorescence spectrum of NR at $0.1 \text{ mol} \cdot \text{L}^{-1}$ KBr. The dotted line corresponds to the second derivative curve.

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