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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.

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[α]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}\cdot$2Br are represented in Fig. 1.

All solutions were prepared with Milli-Q water.

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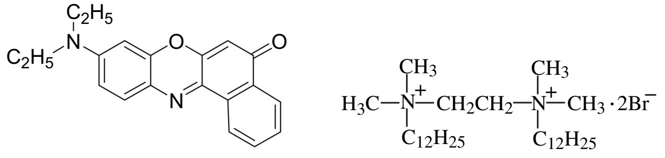

$$\mathrm{H_3C{-}\overset{CH_3}{\underset{C_{12}H_{25}}{\overset{+}{N}}}{-}CH_2CH_2{-}\overset{CH_3}{\underset{C_{12}H_{25}}{\overset{+}{N}}}{-}CH_3\cdot 2Br^-}$$

NR C_{12}-2-C_{12}·2Br

Fig. 1. Chemical structures of NR and C_{12}-2-C_{12}·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 2.0×10^{-6} mol·L^{-1}. The viscosities of aqueous surfactant solutions were measured with Ubbelohde viscometer. The dynamic viscosity (η) was calculated according to Eq. (1).

$$\eta = A\rho t - \frac{B\rho}{t} \tag{1}$$

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 ±0.1 °C.

3. Results and discussion

3.1. Sphere-to-rod-to-wormlike transition of C_{16}TABr micelle induced by KBr

As reported in ref [8], addition of KBr induced sphere-to-rod-to-wormlike transition of C_{16}TABr micelle. This case is used to investigate the fluorescence probe method. Fig. 2(I) shows the fluorescence spectra of NR in C_{16}TABr (10 mmol·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 C_{16}TABr(10 mmol·L^{-1})aqueous solution at 30 °C. As seen in Fig. 3(I), with the increase of C_{KBr}, I_a strongly increases and reaches a plateau at C_{KBr} = 0.1 mol·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 ^{1}H NMR gave out two characteristic KBr concentrations (0.1 and 0.2 mol·L^{-1}) corresponding to the transition of C_{16}TABr 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 C_{16}TABr 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 C_{16}TABr 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 mol·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 mol·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

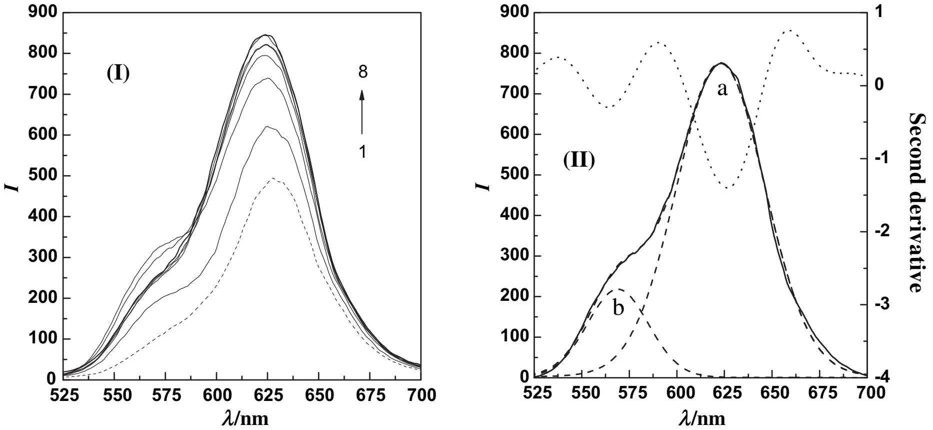

Fig. 2. (I) Fluorescence spectra of NR in C_{16}TABr (10 mmol·L^{-1}) aqueous solutions at 30 °C. From 1 to 8, KBr concentration is successively 0 (dashed line), 0.01, 0.06, 0.1, 0.14, 0.18, 0.24, 0.4 mol·L^{-1}. (II) Curve-fitting for the fluorescence spectrum of NR at 0.1 mol·L^{-1} KBr. The dotted line corresponds to the second derivative curve.

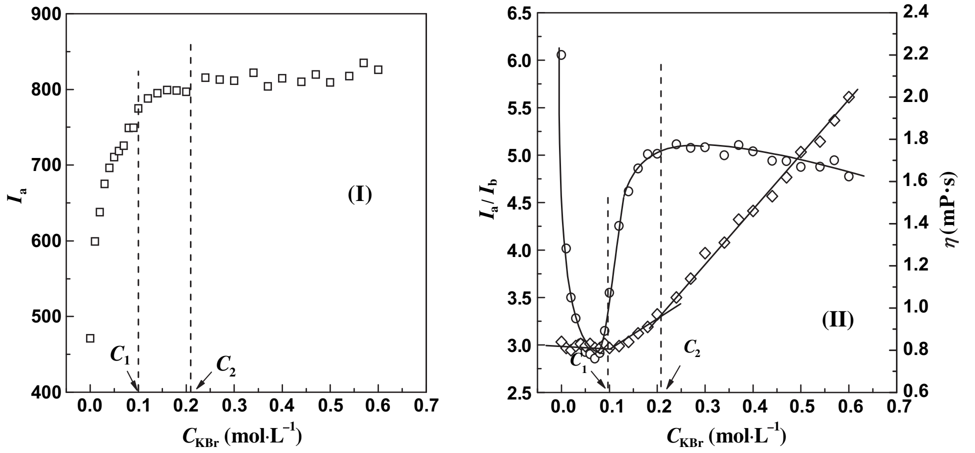

Fig. 3. (I) I_a as well as (II) I_a/I_b (○) and the zero-shear viscosity (η_0, ◇) as a function of KBr concentration in C_{16}TABr (10 mmol·L^{-1}) aqueous micellar solutions at 30 °C. The dashed lines correspond respectively to the two break points: C_1, sphere-to-rod transition and C_2, rod to worm-like transition.

microenvironment influencing on the spectroscopic behavior of solubilized probe. According to Baumanm equation [28], the effect of electric field on fluorescence intensity can be theoretically described as follows:

$$I^E = I^0\left(1 + KE^2\right) \tag{2}$$

where I^0 is the fluorescence intensity of probe in the absence of electric field effect, I^E is the intensity under the external electric field strength E, and K is the constant depending on the difference between the dipole moment of the emissive state and that of the ground state as well as the orientation of the emission transition moment relative to the electric field. As electrolyte, KBr screens the headgroup charge and reduces the electric field of the micellar surface. According to Eq.(2), the emission intensity of NR should decrease. The fact that I_a increasing instead of decreasing with the addition of KBr indicates another factor may play more pronounced role that is the hydrogen bonding of the carbonyl oxygen on the heterocycle with water molecule. In our previous work, the hydrogen bonding role has been stressed to have more important and sensitive effect on the spectroscopic behavior of NR than the electric field of the micellar surface [24]. KBr has 'salt-out' effect [29] and expels the solvated water of headgroups. As a result, the hydrogen bonding is weakened in the presence of KBr. It was known the formation of hydrogen bonding quenches the fluorescence due to the enhancement of intersystem crossing [29], stronger internal conversion [30] and vibrational deactivation [31]. Obviously, when the hydrogen bonding is weakened as in the present case, the emission intensity of NR will be enhanced. This should be the main reason leading to a rapid increase in I_a with the increase of C_{KBr}. When the rodlike micelles are formed, the surfactant molecules are closely packed in the aggregates. This increases the headgroup density on the surface and solvated water, and thus the hydrogen bonding is slightly strengthened, which quenches a part of fluorescence and leads to the plateau in plot of I_a versus C_{KBr}.

The particularity on the position of hydrogen bonding of NR with water molecules is worth stressing. For NR molecule, the carbonyl oxygen (electron acceptor) rather than the nitrogen of the diethylamino group (electron donor) prefers to interact with water by hydrogen bonding [32]. This hydrogen bonding at the electron acceptor facilitates the intramolecular charge transfer and greatly enhances the twist of molecule from planar state into two mutually perpendicular parts (TICT state) [33–35]. Therefore, though the hydrogen bonding quenches a part of fluorescence, it greatly enhances the TICT state formation and increases the relative population of TICT state to LE state (that is generally represented as the intensity ratio of the TICT band to LE band, I_a/I_b). Besides, the effect of the electric field of micellar surface on I_a is stronger than on I_b. According to Eq.(2), the constant K will increase with the increasing difference of dipole moment between the emission entities. The TICT state has much higher dipole moment than the LE state, leading to stronger effect of the electric field of micellar surface on the TICT state. Under the effect of KBr, both the hydrogen bonding and the surface electric field are weakened and therefore I_a/I_b rapidly drops with C_{KBr} (Fig. 3(II)). When the rod micelles are formed, the headgroup density on the surface and the solvated water increase. The increased hydrogen bonding makes I_a/I_b rising, resulting in a minimum in the plot of I_a/I_b versus C_{KBr}. On the other hand, the expression with the ratio I_a/I_b (normalized quantity) is also beneficial to enlarging these effects and making it more sensitive than I_a to probe for the transition of aggregates. This index has been successfully applied to probe for micelle-to-vesicle transition in AOT aqueous solution as reported in previous paper [24] and is also reflected in the detection of the wormlike micelle formation as seen in Fig. 3(II).

With the formation of wormlike micelles, an important change in the solubilizing position of probe takes place. Shobha et al. [36] studied the solubilization of various fluorescence or spin-labeled probes in different aggregates and concluded that the location of the probe depends on the ratio of the surface area to the volume (A/V) of the aggregate. In spherical micelles with enormous A/V, the probe generally locates at the micellar interface near the water. The A/V is reduced when the bilayer assemblies form, leading to the deeper burying of probe into the interior of bilayer. The rod micelle has only short length terminated by hemispherical endcaps of the same diameter as the rod, while wormlike micelles tend to be long and flexible chains, whose lengths can even reach several micrometers. This results in obviously small A/V ratio for wormlike micelle in comparison with that for rod micelle. Thus NR molecules are buried into the wormlike micelles with an orientation similar to their solubilization in AOT vesicles [24], i.e. with the diethylamino group (the electron donor) inside the non-polar hydrophobic region and the quinoid part (the electron acceptor) toward the palisade layer. As a result, the effect of the electric field coming from the ionized headgroup is greatly weakened and the electron acceptor also hardly interacts with water by hydrogen bonding. According to the above discussion, both the roles are disadvantageous to forming TICT state and therefore lead to decrease in I_a/I_b. This gives out a good response to the wormlike micelle formation.

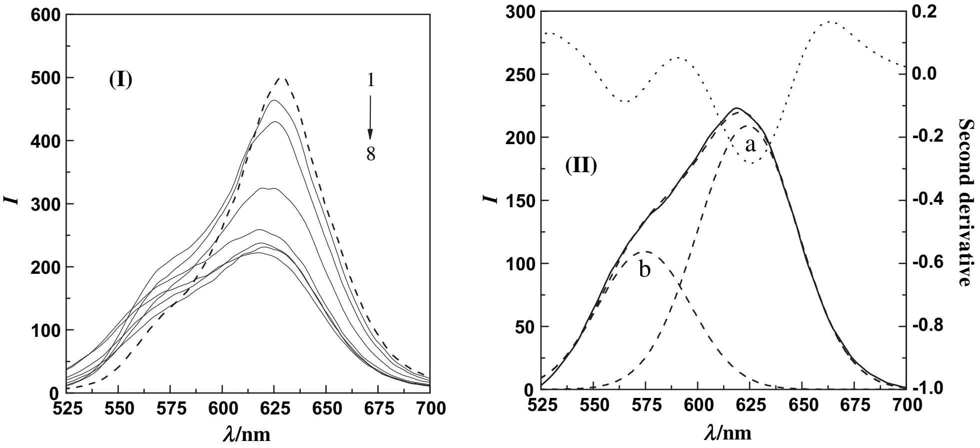

Fig. 4. (I) Fluorescence spectra of NR in $C_{16}TABr$ (25 mmol·L^{-1}) aqueous solutions at 35 °C. From 1 to 8, NaSal concentration is successively 0 (dashed line), 0.007, 0.01, 0.017, 0.024, 0.03, 0.05, 0.1 mol•L^{-1}. (II) Curve-fitting for the fluorescence spectrum of NR at 0.03 mol·L^{-1} NaSal. The dotted line corresponds to the second derivative curve.

3.3. Sphere-to-rod transition of $C_{16}TABr$ micelle induced by NaSal

Halide anions associate only moderately with surfactant cations and thus induced micellar gradual growth. Contrarily, organic anions such as salicylate can associate strongly with surfactant cations and promote the rapid growth of spherical micelle into rod or wormlike at low salt concentration. Aswal et al. [15] reported the critical concentration of NaSal inducing the sphere-to-rod transition of $C_{16}TABr$ micelle in 25 mmol·L^{-1} aqueous solution to be 24 mmol·L^{-1} measured by small angle neutron scattering (SANS) and viscosity. This case is now used to examine NR probing for the sphere-to-rod micelle transition.

Fig. 4(I) shows the fluorescence spectra of NR in $C_{16}TABr$ micellar solutions without and with NaSal. Similarly, the two emission subbands are revealed by deconvolution technique. The variation of I_a and I_a/I_b with NaSal concentration (C_{NaSal}) is shown in Fig. 5. Different from Fig. 3(I), the I_a in this case does not exhibit an initial increase but instead shows a rapid decrease with the increase of C_{NaSal}. Obviously, this phenomenon comes from NaSal effect since only the salt used is different in the two cases. Compared with KBr, salicylate anions associate strongly with surfactant cations [37]. This effectively screens the headgroup charge and greatly weakens the electric field of the micellar surface. On the other hand, NaSal is a ‘salt-in’ salt [38], increasing the solvated water around the headgroups and thus promoting the hydrogen bonding of NR with water. As discussed in Section 3.2, both the roles (decreased electric field and increased hydrogen bonding) remarkably reduce the intensity of fluorescence. The crossover between the rapid drop part and the almost horizontal part corresponds to 24.5 mmol·L^{-1} NaSal, agreeing well with the critical concentration (24 mmol·L^{-1}) reported by Aswal et al. on the sphere-to-rod transition of aggregates in the solution [15]. This is also reflected in a sharp increase in solution viscosity beyond this concentration (Fig. 5(II)). The result of Fig. 5 indicates that NR can probe for the transition of $C_{16}TABr$ micelle from spherical to rodlike induced by NaSal.

Interestingly, I_a/I_b exhibits a decrease rather than an increase though the hydrogen bonding is enhanced. This perhaps relates to the π-π interaction between the aromatic rings of NaSal and NR. The NaSal associating with the positive quaternary ammonium headgroups on the micellar surface certainly meets with the solubilized NR. The π–π interaction between the aromatic rings hinders the charge transfer on the large conjugated ring of NR and restricts the molecular twist from a planar configuration into two mutually perpendicular parts to a certain extent, resulting in the decrease in I_a/I_b as shown in Fig. 5(II). Through this case, one can realize the

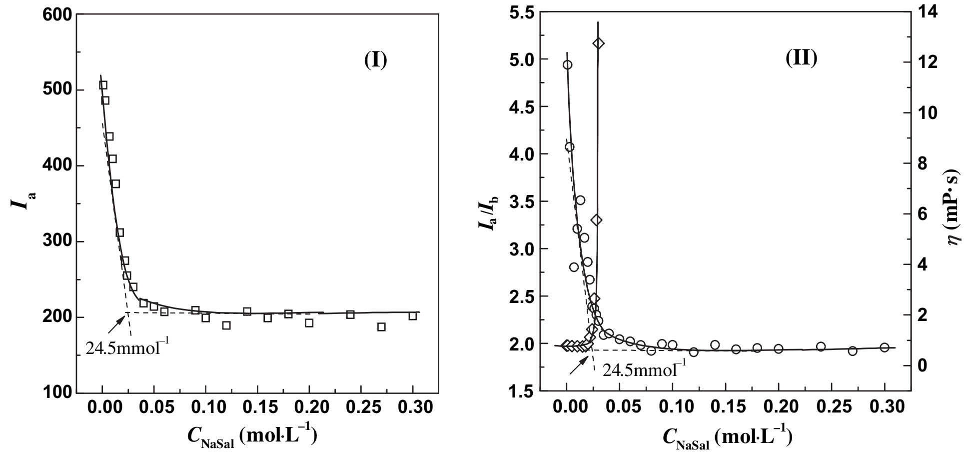

Fig. 5. I_a (I) and I_a/I_b (II) of NR as a function of NaSal concentration in $C_{16}TABr$ (25 mmol·L^{-1}) aqueous micellar solutions at 35 °C. The corresponding viscosity (η, ◇) variation is shown in (II).

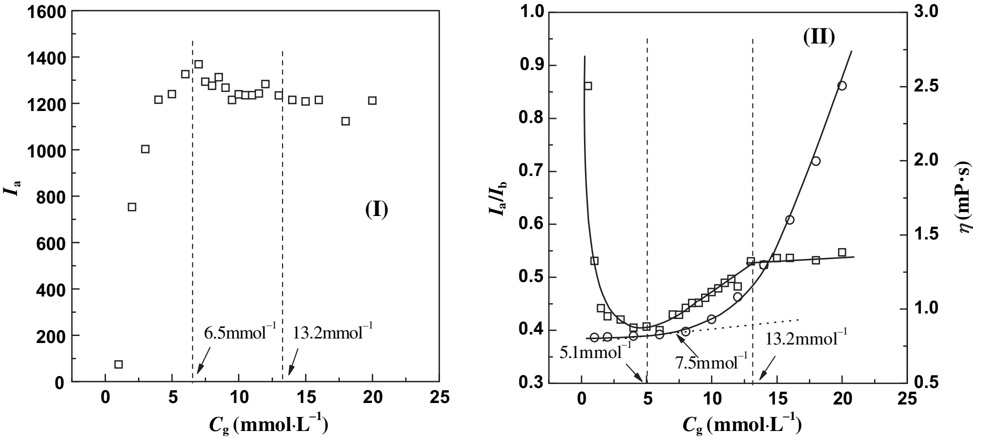

Fig. 6. Variation of I_a (I) and I_a/I_b (II) of NR with C_{12}-2-$C_{12}\cdot$2Br concentration (C_g) in aqueous solution at 25 °C. The corresponding viscosity (η, ◇) variation is shown in (II).

complexity of NR probing for the aggregate transition when some external factors are introduced. Though so, the turning point of curve (24.5 mmol·L^{-1}) still corresponds well to the critical NaSal concentration inducing the transition of C_{16}TABr micelle from spherical to rodlike.

However, NR fails to probe for the wormlike micelle formation in this case although NaSal strongly associates with positive quaternary ammonium of C_{16}TABr micelle and more strongly promotes wormlike micelle formation. Here the π–π interaction between the aromatic rings of NR and NaSal should be a disadvantageous factor as discussed above. Comparatively, for KBr only with weak associating ability, a whole picture for the transition from sphere-to-rod-wormlike micelles can be clearly seen by using NR as discussed in Section 3.1.

3.4. C_{12}-2-$C_{12}\cdot$2Br micelle growth depending on surfactant concentration

Gemini surfactant is made up of two amphiphilic moieties connected by a spacer group at the level of the headgroups. The introduction of spacer complicates the self-assemblies of Gemini surfactants since the length and the structure of spacer strongly affect the molecular geometry and the hydrophobic interactions between the alkyl tails [39]. Alkanediyl-α,ω-bis(dimethyl dodecyl ammonium bromide), referred to as C_{12}-s-$C_{12}\cdot$2Br, is a series of cationic Gemini surfactants investigated extensively. C_{12}-2-$C_{12}\cdot$2Br was found to form rodlike (even wormlike) micelles depending the concentration in the solution due to its cylinder-like molecular geometry [40,41]. Fig. 6 shows I_a and I_a/I_b of NR as a function of C_{12}-2-$C_{12}\cdot$2Br concentration (C_g), in which I_a rapidly increases with the increase of C_g and reaches a maximum, while I_a/I_b drops to a minimum. This is similar to the variation in Fig. 3 and therefore the maximum in I_a and the minimum in I_a/I_b can reflect the critical point of the rod micelle formation, the corresponding concentration is ca. 5–6.5 mmol·L^{-1} (0.31–0.40 wt%) depending on different indexes (I_a or I_a/I_b). This agrees well with the concentration region ($0.26 < C < 0.5$ wt%) coexisting of rodlike micelles with spheroidal ones as observed by cryo-TEM [37]. The dynamic viscosity (η) also starts to increase at slightly larger C_g (7.5 mmol·L^{-1}, Fig. 6(II)). Following the minimum, I_a/I_b reaches a plateau with the further increasing C_g and the turning point is 13.2 mmol·L^{-1} (0.81% wt%). This is also consistent with the observation of cryo-TEM in the concentration region of 0.5–1 wt% where the threadlike micelles become popular [42]. Thus NR again responds to the transition of C_{12}-2-$C_{12}\cdot$2Br micelle from sphere-to-rod-wormlike depending on the concentration.

4. Conclusions

NR can well probe for the transition of surfactant aggregate from sphere to rod, even to wormlike, in which the I_a/I_b is a more sensitive index to represent this transition than I_a. This is attributed to the special molecular structure of NR that has a large conjugated ring and the hydrogen bond ability with water molecules at the electron-acceptor group, leading to the sensitive response of the TICT state to the change of microenvironment when the aggregate transition from sphere-to-rod-to-wormlike takes place.

Acknowledgments

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