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ORIGINAL CONTRIBUTION

Detecting the micellization of anionic surfactants by a colorimetric and fluorescent probe based on electrostatic attraction

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Abstract A novel fluorescent probe labeled with cation, N-n-alkyl-4-(1-methylpiperazine)-1,8-naphthalimide iodide ([C_8ndi]I), has been applied as a colorimetric and fluorometric probe for detecting the micellization of anionic surfactants. The critical micellization concentration (cmc) of anionic surfactants can be conveniently determined by the change on absorption and fluorescence spectra of [C_8ndi]I. The probe displays highly sensitive and selective spectroscopic responses accompanied with distinctive color change (from colorless to light green). These methods are proved to be reliable as the results are in accordance with those of the standard methods. Besides the advantage of visual detection, the multiple spectroscopic methods (absorption and fluorescence) by using [C_8ndi]I as probe are also simple and convenient. One can choose any spectroscopic parameter, such as position or intensity of the absorption and emission peaks, to monitor the micelle formation process of anionic surfactants.

Keywords Critical micellization concentration · Anionic surfactant · Probe · Naphthalimide · Absorption spectrum · Fluorescence spectrum

Introduction

Surfactants are water-soluble surface-active agents which are widely employed in traditional industry, biomedical systems, synthesis of nanomaterials, and so on [1–3]. Applications of surfactants are basically owing to their self-assemble behaviors in water. It is well-known that above a particular concentration, called critical micelle concentration (cmc), surfactants form thermodynamically stable micelles and show significant property changes accordingly. There are many well-known techniques for determining the cmc of a surfactant, including surface tension method, electrical conductivity method, light scattering technique, nuclear magnetic resonance method and fluorescence spectrum method, etc. But they still show some limitations, such as relatively time-consuming and tedious procedures, no in situ response, and relatively low sensitivity. Therefore, it is always attractive to find a simple and sensitive method for in situ cmc determination.

Spectrophotometric and spectrofluorometric methods, with their many inherent merits, including high sensitivity, high specificity, and real-time in situ response, have been extensively used in scientific research, quality control for industrial production, and environment or physiological detection [4–12]. Kriwanek and coworkers used a zwitterionic indicator, pyridinium N-phenoxide betaine, to determine the micellar aggregation behavior of homologous N-alkyl betaines [13]. Novaki and coworkers reported on the use of solvatochromic probes to determine the microscopic polarity of water at their solubilization sites in cationic micelles [14, 15]. Gao and coworkers designed and synthesized a probe, sodium 12-(N-dansyls)amino-dodecanate, for detecting the shape transitions between micelles and vesicles and micellar growth [16, 17]. Qian and coworkers used "on-off-on" fluorescent sensors to detect anionic surfactant SDS with high sensitivity and selectivity [18]. Inspired by these reports, we designed a relatively sensitive and universal probe for detecting the micellization of anionic surfactants with spectroscopic methods.

Naphthalimide (NDI), a prototype intramolecular charge transfer (ICT) fluorophore, has been extensively used as strongly absorbing and colorful dye because of its desirable photophysical properties, such as high photostability, large

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Stokes' shift, high fluorescence quantum yields, strong absorption and emission in the visible region, and insensitivity to pH [19–24]. The ICT electronic structure endows the absorption and fluorescence spectra of NDIs with a high sensitivity towards solvent polarity [25, 26]. It is well-known that the self-assemble process of surfactant is always accompanied by the changes of the microenvironments. This can be sensitively detected by the fluorescence probe, since the fluorescence emission is very sensitive to the local environment [27, 28].

In the present work, a cationic surfactant dye, N-n-alkyl-4-(1-methylpiperazine)-1,8-naphthalimide iodide ([C_8ndi]I), was specifically designed to detect the micellization of anionic surfactants. It presents dramatic color change as well as significant spectroscopic change upon the micelle formation of anionic surfactants in aqueous solution. By comparing with the traditional methods, the absorption and fluorescence methods based on [C_8ndi]I were demonstrated to be reliable and accurate. [C_8ndi]I is a promising new fluorescence probe for measuring the cmc of anionic surfactants.

Experimental section

General methods

Electronic absorption spectra were recorded on a UV-2450 spectrophotometer (SHIMADZU, Japan). The steady-state fluorescence measurements were carried out on a FLS920 fluorescence spectrometer (Edinburgh Instruments). The excitation wavelength is 350 nm. Electrical conductivity measurements were employed on a low-frequency conductivity analyzer (Model DDSJ-308A, Shanghai Precision & Science Instrument Co., Ltd. of China). Each conductivity was recorded when its stability was better than 1 % within 3 min. The temperature was controlled by thermostatic bath (Karlsruhe, Germany, accuracy±0.1 °C). Surface tension measurements were carried out on a model JYW-200B tensiometer (Chengde Dahua Instrument CO., Ltd., accuracy±0.1 mN/m) using the ring method. All measurements were repeated until the values were reproducible. ESI-MS were measured on Q-TOF LC/MS 6510 (Agilent). ^{1}H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer with the solvent peak as internal standard (in $CDCl_3$).

Materials

N-n-octyl-4-(1-methylpiperazine)-1,8-naphthalimide iodide ([C_8ndi]I) was prepared following the procedures reported in our previous work [29]. The compound was characterized by ^{1}H NMR and ESI-MS mass spectra (see "Electronic supplementary material"). Sodium dodecylsulfate (SDS, 99 %) was obtained from Alfa Aesar, while sodium dodecylbenzenesulfonate (SDBS, 95 %) and sodium dodecanoate (SD, 98 %) were purchased from Aladdin. Sodium dodecylsulfonate (SDSO, 99 %) was bought from J&K. Triply distilled water was used as solvent throughout the experiments. Methanol and ethyl acetate were of analytical grade and were purified by the standard methods before use. All other chemicals were purchased from commercial source and used as received without further purification.

Results and discussion

Absorption and fluorescence spectra of [C_8ndi]I in different polar solvents

The molecular structure of [C_8ndi]I is shown in Chart 1. As an ICT compound, the spectroscopic properties of NDI are very sensitive to the polarity of its surroundings. Based on this consideration, the absorption and fluorescence spectra of [C_8ndi]I in various solvents with different polarities were measured. The results are summarized in Table 1, and the spectra of [C_8ndi]I in three different solvents are shown in Fig. S1 in the supplementary materials. As expected, the maximal absorption and emission bands of [C_8ndi]I redshifted obviously along with the increase of solvent polarity. For example, the maximal absorption and emission bands redshifted for 13 and 37 nm, respectively, when the solvent changed from $CH_3COOC_2H_5$ to H_2O. This is because the first excited state of naphthalimide is an ICT state; a polar environment provides a larger stabilization to the ICT state than the nonpolar environment does. Therefore, the energy gap between the first excited state and ground state in polar environment is smaller than that in nonpolar solvent.

The molar extinction coefficient (ε) and the fluorescence quantum yield of [C_8ndi]I are also solvent dependent (Table 1). The molar extinction coefficients and fluorescence quantum yields decrease following the order of CH_3OH> H_2O>$CH_3COOC_2H_5$. This is because the absorption and fluorescence spectra are affected not only by the polarity of the solvents but also by the aggregation of [C_8ndi]I. The well-known Lambert-Beer law works only for a diluted solution [30–32] where the self-aggregation of solute can be avoided completely. The self-aggregation of [C_8ndi]I causes a significant local concentration increase, which will lead to a decrease on molar extinction coefficient. The solubility of [C_8ndi]I in methanol is better than that in water and ethyl acetate; therefore, the molar extinction coefficient of [C_8ndi]I

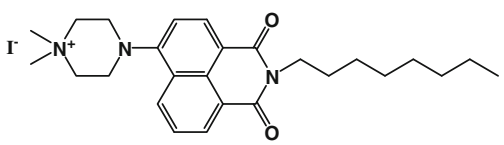

Chart 1 Molecular structure of [C_8ndi]I

Table 1 Photophysical properties of [C_8ndi]I in solvents with different polarities

Solvent	λ_{max}^{abs} (nm)	λ_{max}^{flu} (nm)[a]	ε (mol^{-1} L cm^{-1})	Φ_f (%)[b]	Dielectric constant (F m^{-1})
$CH_3COOC_2H_5$	374	486	2.20×10^4	15.48	6.0
CH_3OH	375	506	3.20×10^4	41.43	33.0
H_2O	387	523	2.91×10^4	23.81	78.5

[a] The excitation wavelength was 350 nm

[b] With rhodamine 6G in ethanol (Φ_f=95 %) as standard

in methanol is larger than that in water and ethyl acetate. Fluorescence quantum yield is much more sensitive to the aggregation than the molar extinction coefficient does. Aggregation leads to significant decrease on the fluorescence quantum yields [33]. As methanol is a good solvent for [C_8ndi]I, no aggregation happens in methanol. Thus, the fluorescence quantum yield of [C_8ndi]I in methanol is larger than that in water and ethyl acetate.

Effect of [C_8ndi]I on self-assembly of anionic surfactants

Our objective is to use [C_8ndi]I as a fluorogenic sensor to detect the cmc of anionic surfactants. In the present work, four common anionic surfactants, sodium dodecylsulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), sodium dodecylsulfonate (SDSO), and sodium dodecanoate (SD), were selected as model compounds. Since [C_8ndi]I may take part in the formation of micelle of anionic surfactants, the effects of [C_8ndi]I on the cmc values of anionic surfactants in water should be clarified first. Base on these considerations, surface tension and electrical conductivity of anionic surfactants in water with the presence of [C_8ndi]I were examined. Figure 1a compares the plots of surface tension (γ) versus concentration of SDS at 25 °C with or without [C_8ndi]I. The surface tension of SDS aqueous solution decreases progressively along with the increase of SDS concentration to a certain value, indicating the formation of micelles. The cmc value of SDS determined by this method is ~5.0 mM which is a little bit lower than the reported value ~8 mM [34]. It is clear that the micellization process of SDS is not affected by the presence of [C_8ndi]I (lower than 0.05 mM). Figure 1b shows the plots of electrical conductivity (κ) as a function of concentration of SDS with or without [C_8ndi]I. The result is consistent with that of surface tension experiments. The detected cmc, ~5.7 mM, is also lower than the reported value. This error is acceptable in this study. Electrical conductivity experiments for SDBS, SDSO, and SD are shown in Fig. S2 in the supplementary materials. The results demonstrate successfully that the presence of [C_8ndi]I (lower than 0.05 mM) does not affect the cmc values of anionic surfactants, and [C_8ndi]I

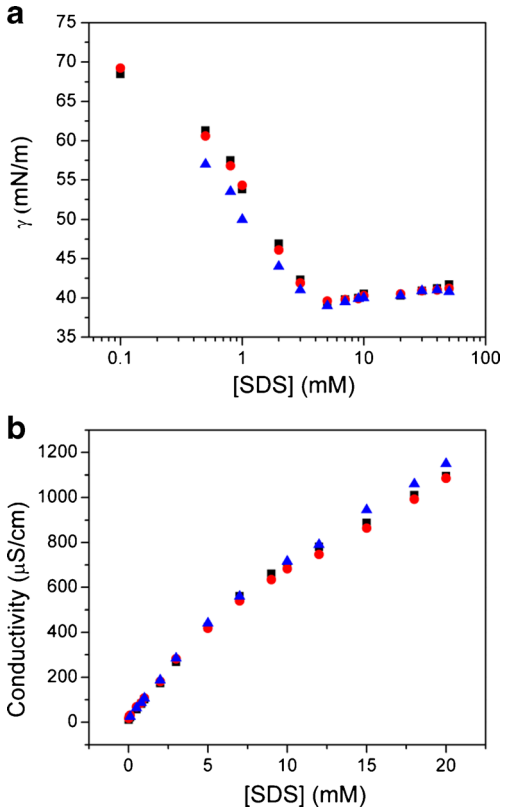

Fig. 1 Effects of [C_8ndi]I on the aggregation behavior of SDS in aqueous solution at 25 °C determined by surface tension (**a**) and electrical conductivity (**b**). *Square* without [C_8ndi]I, *circle* 0.01 mM [C_8ndi]I, *triangle* 0.05 mM [C_8ndi]I

may be used as a fluorogenic sensor to detect the cmc of anionic surfactants.

Probing the cmc values of anionic surfactants

The absorption spectra of [C_8ndi]I (0.01 mM) upon the addition of different amounts of SDS (as an example of anionic surfactants) is illustrated in Fig. 2. It can be clearly seen that along with the increase of the concentration of SDS, the maximal absorption bands redshift from 370 to 377 nm accompanied with obvious intensity change. Simultaneously, a dramatic color change, from colorless to light-green, was clearly recognized by naked eyes for the solution (Fig. 2 inset).

As shown in Fig. 2, when the concentration of SDS is smaller than cmc, ion pairs between positive charge $[C_8ndi]^+$ and negative charge SD^- are expected to form due to the electrostatic interactions. Therefore, the absorption at this stage is mainly from the contribution of [C_8ndi]I-SDS complexes, whose maximal absorption band is at 370 nm. When SDS concentrations were larger than cmc, [C_8ndi]I-SDS complexes dissociated and SDS molecules rearranged to form micelles with all the [C_8ndi]I molecules incorporated into the SDS micelles. The reported dielectric constant at the SDS micelle interface is about 36.6 F m^{-1} [35], slightly larger

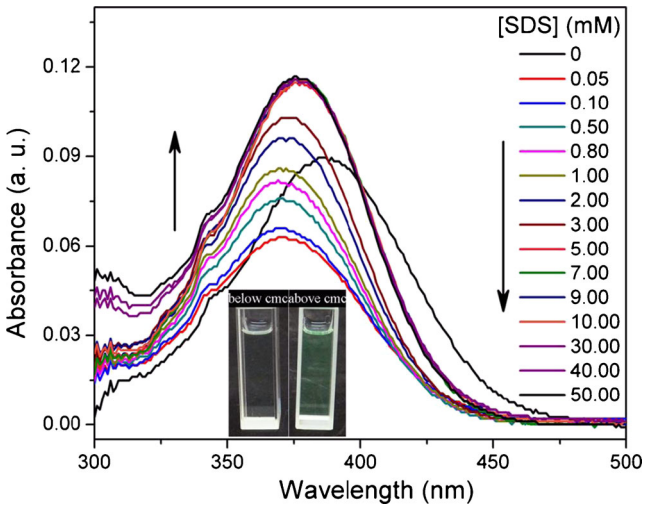

Fig. 2 Variation on the absorption spectra of 0.01 mM [C8ndi]I in water with increasing concentration of SDS. The *arrow* indicates the spectral change direction with increasing concentration of SDS. *Inset* color changes of [C8ndi]I (0.02 mM) upon addition of SDS below cmc (*left*) and above cmc (*right*)

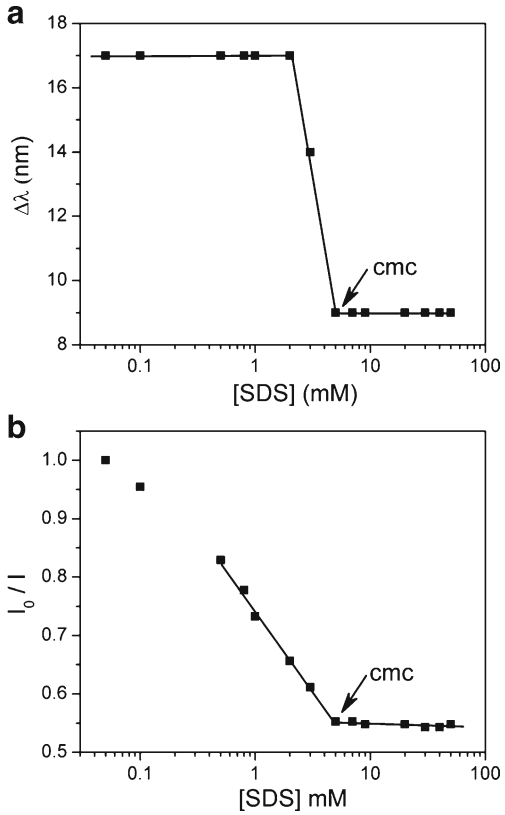

Fig. 3 **a** Variation of maximal absorption band with increasing concentration of SDS. The wavelength of maximal absorption band of [C8ndi]I in pure water is set as standard. **b** The plots of I_0/I against the concentration for SDS

than the dielectric constant of CH_3OH, 33.0 F m^{-1} [35]. Therefore, the maximal absorption band in SDS micelles (377 nm) has slightly redshifted comparing with that in CH_3OH (375 nm). In our previous work [29], the maximum absorption band of [C_8ndi]I micelle is measured to be at 376 nm, which is similar to the maximal absorption band in SDS micelles (377 nm); therefore, it is expected that the [C_8ndi]I molecules are included into SDS micelles. Based on the redshift of the maximal absorption bands of [C_8ndi]I probe, the cmc values of anion surfactants can be detected.

The shift on the maximal absorption band ($\Delta\lambda=\lambda_0-\lambda$, where λ_0 refers to the wavelength of the absorption band of [C_8ndi]I in pure water (387 nm) and λ refers to the wavelength of the absorption maximum of [C_8ndi]I in SDS solutions) along with the concentration increase of SDS is shown in Fig. 3a. The values of $\Delta\lambda$ decrease sharply to a certain value, indicating a sudden change on the microenvironment of [C_8ndi]I, which is owing to the formation of micelle. The cmc value of SDS determined by $\Delta\lambda$ is 5 mM, which is consistent with those measured by surface tension and conductivity methods.

As shown in Fig. 2, along with the increase of the concentration of SDS, the apparent absorbance increases gradually to a constant value. The change on the absorption intensity is closely related to the aggregation of [C_8ndi]I in water. Along with the increase on the concentration of SDS, the aggregates of [C_8ndi]I are gradually changed into monomeric [C_8ndi]I-SDS complexes, which consequently leads to the increase on the absorption intensity. When the concentration of SDS is larger than the cmc, the SDS molecules rearrange to form micelles with all the [C_8ndi]I molecules incorporated into micelle in monomeric form [18], and the absorbance of [C_8ndi]I reaches a constant value. Therefore, the cmc values of anion surfactants can also be detected by the changes on the absorbance of probe [C_8ndi]I.

The absorbance of [C_8ndi]I in the most diluted SDS aqueous solution is set as standard (I_0), by comparing I_0 with the absorbance at more concentrated SDS solutions (I), the quantitive effects of SDS concentration on the absorbance of [C_8ndi]I were obtained. Figure 3b shows the plots of I_0/I against the concentrations for SDS. Along with the increase on the concentration of SDS, the magnitudes of I_0/I decrease gradually to a certain value, indicating the formation of micelle. The breakpoint of the plot corresponds to the cmc (5 mM), which is also consistent with the results deduced from other methods.

Figure 4 shows the emission spectra of 0.01 mM [C_8ndi]I in water with different concentrations of SDS. It was expected that the maximal emission band should shift similarly to the red as that observed for the maximal absorption band. However, large redshift on maximum emission band has not been found. On the contrary, small blueshift is found when the SDS concentration is lower than cmc. When 0.05 mM SDS was added into the [C_8ndi]I aqueous solution, the maximal emission band of [C_8ndi]I blueshifted sharply by 20 nm (from 523 to 503 nm). The emission band at 523 nm is

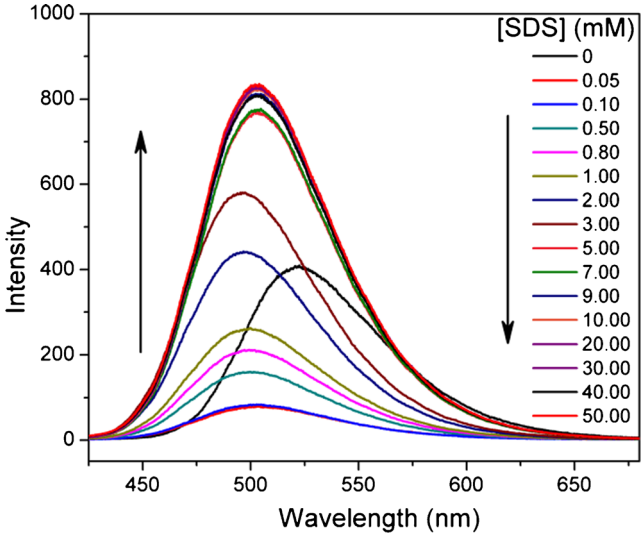

Fig. 4 Variation on the emission spectra of 0.01 mM [C_8ndi]I in water with increasing concentration of SDS. The *arrow* indicates the spectral change direction with increasing concentration of SDS

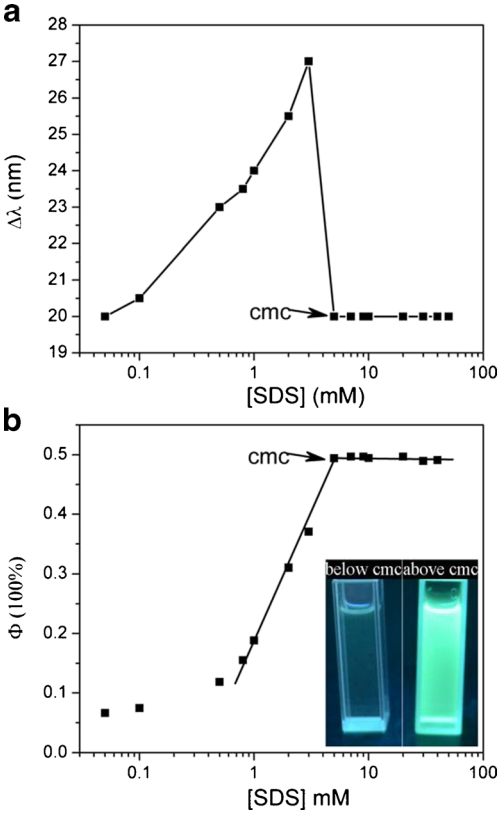

Fig. 5 **a** Shift of maximal emission band with increasing concentration of SDS. **b** Variation in the fluorescence quantum yield with increasing concentration of SDS. *Inset* images of [C_8ndi]I (0.02 mM) upon addition of SDS below cmc (*left*) and above cmc (*right*) under UV light. The excitation wavelength was 365 nm

assigned to [C_8ndi]I in water, while the emission band at 503 nm is attributed to [C_8ndi]I-SDS complex. Because the hydrophobic alkyl chains of SDS nearby [C_8ndi] in [C_8ndi]I-SDS complex provide a relative nonpolar environment for the probe molecule [C_8ndi], the fluorescence of [C_8ndi] blue-shifts significantly. With further increase on the concentration of SDS from ~0.05 to 3.00 mM (below cmc), the nonpolar environment of [C_8ndi] provided by hydrophobic alkyl chains of SDS is gradually enforced further; therefore, the maximal emission band gradually blueshifts from 503 to 496 nm. But when SDS concentration increases from 3.00 to 5.00 mM, the maximal emission band redshifts back to about 503 nm, which is owing to the formation of SDS micelles. The emission band at 503 nm is ascribed to [C_8ndi]I in micelles. So, the redshift of maximal emission band is attributed to the change of fluorescence species from [C_8ndi]I-SDS complex to [C_8ndi]I. When SDS concentrations are higher than cmc, all [C_8ndi]I molecules insert into SDS micelles as monomers, and the microenvironment for [C_8ndi]I keeps unchanged; therefore, the maximal emission bands are fixed at about 503 nm.

The shift of the maximal emission band of [C_8ndi]I in SDS solution with respect to [C_8ndi]I in pure water ($\Delta\lambda=\lambda_0-\lambda$, where λ_0 refers to the wavelength of the emission band of [C_8ndi]I in pure water and λ refers to the wavelength of the emission maximum of [C_8ndi]I in SDS solutions) along with the concentration increase of SDS is shown in Fig. 5a. The $\Delta\lambda$ increases progressively to a maximum 27 nm and then decreases sharply to a certain value. The sharp turning point of $\Delta\lambda$ along with the SDS concentration increase is an indication of the formation of SDS micelle. The cmc value evaluated by this method is 5.00 mM, which is also consistent with the results of other methods as mentioned above.

Besides the shift on the wavelength of the maximal emission band, the emission intensity of [C_8ndi]I is also sensitive to the presence of SDS. Addition of 0.05 mM SDS to [C_8ndi]I aqueous solution results in a significant decrease on the emission intensity, which can be attributed to the formation of [C_8ndi]I-SDS complexes. The photoinduced electron transfer from the negatively charged head group of SDS to the fluorophore might occur within this complex and thus quench the emission of [C_8ndi]I [18]. When all the [C_8ndi]I molecules change into [C_8ndi]-SDS complexes, the fluorescence intensity reaches a minimum value. In order to confirm the existence of SDS-[C_8ndi]I complex, the temperature-dependent absorption and fluorescence spectra of 0.01 mM [C_8ndi]I in 0.05 mM SDS aqueous solution are recorded. Intermolecular aggregation is sensitive to the temperature; thus, the SDS-[C8ndi]I complex can be broken by an increase in temperature. The results shown in Fig. S3 reveal clearly that along with the increase of temperature, the maximal absorption and emission bands were redshifted gradually and the intensity decreased first and then recovered, signifying the SDS-[C_8ndi]I complexes were being dissociated gradually. When the concentration of SDS increases further, the polarity of the microenvironment of [C_8ndi] in solution decreases

gradually due to the increasing number of hydrophobic alkyl chains nearby and consequently causes the increase on the fluorescence intensity of [C_8ndi]. When the SDS concentration is greater than 5.00 mM, all [C_8ndi]I molecules incorporate into SDS micelles in the form of monomer. The emission intensity reaches a constant value. By monitoring the changes on the emission intensity along with the increase on the concentration of SDS, the cmc of SDS can be accurately determined.

Because the fluorescence intensity is a relative value, which is affected by the experimental conditions, such as the slit width, the intensity of the excitation light, etc., we use fluorescence quantum yield instead of the fluorescence intensity during the cmc determination. The change of fluorescence quantum yield (Φ) of [C_8ndi]I along with the increase of SDS concentration is shown in Fig. 5b. The fluorescence quantum yield is measured with rhodamine 6G in ethanol (95 %) as reference. Along with the increase of SDS concentration, the Φ increases progressively to a maximum, indicating the formation of SDS micelle. The cmc of SDS determined by this method is 5 mM, which is consistent with the results of surface tension, electrical conductivity, and absorption methods, indicating that the fluorescence method is reliable. Figure 5b inset shows the fluorescence images of [C_8ndi]I upon addition of different amounts of SDS. A dramatic solution color change from colorless to bright green was clearly recognized by naked eyes, which provide a simple and fast method to determine the presence of anionic surfactant micelles. This dramatic color change may be attributed to the enhancement of the fluorescence quantum yield.

When the concentration of [C_8ndi]I probe is increased to 0.05 mM, the testing performance is shown in Figs. S4 and S5. At this condition, the cmc of SDS determined by the absorption and emission spectra is about 0.06 M, which is a little bit larger than the values obtained by the tradition methods. The result obtained at 0.05 mM [C_8ndi]I is acceptable, but low concentration sensor may be better.

We have also studied the response of [C_8ndi]I to other anionic surfactants with different hydrophilic headgroups, such as sulfonate group (SDBS, SDSO) and carboxylate group (SD). The absorption and fluorescence spectra of [C_8ndi]I in the aqueous solutions of these anionic surfactant were measured (results are shown in "Electronic supplementary material"). The cmc values of these anionic surfactants determined by the absorption and fluorescence methods using [C_8ndi]I as probe are summarized in Table 2. All the results are consistent with those obtained by electrical conductivity method. For anionic surfactants (SDBS and SDSO) with sulfonate group, the maximal emission bands shift only about 4 nm during micellization. The small shifts may bring large error during result calculation; therefore, the shift of maximal emission band ($\Delta\lambda_{max}^{em}$) is not suitable for determining the cmc of anionic surfactants with sulfonate group. But we can still measure the cmc values of these anionic surfactants by absorbance (I_0/I) and fluorescence quantum yield (Φ) (Figs. S6 and S7 in the supplementary materials). The variations of absorption and fluorescence spectra of [C_8ndi]I in the solution of anionic surfactants with carboxylate group (SD) are similar to those in SDS aqueous solution (Fig. S8 in the supplementary materials). The cmc value of SD can be determined by all of the four methods mentioned above.

Table 2 Cmc of different anionic surfactants determined by electronic conductivity, shift of maximal absorption band ($\Delta\lambda_{max}^{abs}$), absorption intensity (I_0 / I), shift of maximal emission band ($\Delta\lambda_{max}^{em}$) and fluorescence quantum yield (Φ)

Anionic surfactant	cmc (mM)					
	Electronic conductivity	$\Delta\lambda_{max}^{abs}$	I_0/I	$\Delta\lambda_{max}^{em}$	Φ	Literature
SDBS	1.4	–	1.3	–	1.7	1.5[a]
SDSO	10.9	11	10.5	–	11.8	9.7[b]
SD	24.8	27.6	27.4	27	27.3	26.0[c]

[a] Reported in ref [34]

[b] Reported in ref [36]

[c] Reported in ref [37]

Conclusions

A new naphthalimide-based cationic fluorescent surfactant, [C_8ndi]I, was developed as a fluorescent probe for the determination of anionic surfactant cmc. The absorption and fluorescence spectra of this probe are sensitive to the microenvironment polarity and composition of fluorescent molecules. [C_8ndi]I can form a complex with the anionic surfactants driven by the electrostatic attraction between the cationic and anionic headgroups [18]. Therefore, it is applicable to probe the micellization process of anionic surfactants. The cmcs of various anionic surfactants evaluated by the absorption and fluorescence spectra of this probe are proved to be reliable by comparing with that measured by traditional methods [37–39].

Compared with the most commonly used pyrene probe [40–42], [C_8ndi]I is relatively water soluble, and hence, the procedures of sample preparation is relatively simple. Moreover, the reported probes, such as pyrene and $E_T(30)$ [13], can be used to determine cmc by only one spectroscopic method, either fluorescence or absorption spectrum. But with [C_8ndi]I as probe, the cmcs of anionic surfactants can be determined by the shifts of maximal absorption and emission band ($\Delta\lambda_{max}^{abs}$, $\Delta\lambda_{max}^{em}$), the changes on absorption intensity (I_0 / I), and changes on fluorescence quantum yield (Φ); this has actually reduced the requirement for apparatus. In extreme cases, the micelle process can be monitored easily by

naked eyes, and no instrument is needed at all. We believe that the significance of the present work is not just limited to the development of a fast, simple, and convenient approach for determining cmc for anionic surfactants. It provides also important information for the design of fluorescence sensor for other colloid and micelle systems.

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References

1. Nikhil R, Jana LG, Catherine JM (2001) Wet chemical synthesis of high aspect ratio cylindrical gold nanorods. J Phys Chem B 105: 4065–4067
2. Wang X, Zhuang J, Peng Q, Li YD (2005) A general strategy for nanocrystal synthesis. Nature 437:121–124
3. Bhat PA, Rather GM, Dar AA (2009) Effect of surfactant mixing on partitioning of model hydrophobic drug, naproxen, between aqueous and micellar phases. J Phys Chem B 113:997–1006
4. Germain ME, Knapp MJ (2008) Discrimination of nitroaromatics and explosives mimics by a fluorescent Zn(salicylaldimine) sensor array. J Am Chem Soc 130:5422–5423
5. Srikun D, Miller EW, Domaille DW, Chang CJ (2008) An ICT-based approach to ratiometric fluorescence imaging of hydrogen peroxide produced in living cells. J Am Chem Soc 130:4596–4597
6. Neelakandan PP, Hariharan M, Ramaiah D (2006) A supramolecular ON-OFF-ON fluorescence assay for selective recognition of GTP. J Am Chem Soc 128:11334–11335
7. Zhang X, Woggon WD (2005) From the first fluorescent sensor of pyrovanadate to the functional model of vanadium haloperoxidase. J Am Chem Soc 127:14138–14139
8. Yoshihara T, Druzhinin SI, Zachariasse KA (2004) Fast intramolecular charge transfer with a planar rigidized electron donor/acceptor molecule. J Am Chem Soc 126:8535–8539
9. Seo J, Kim S, Park SY (2004) Strong solvatochromic fluorescence from the intramolecular charge-transfer state created by excited-state intramolecular proton transfer. J Am Chem Soc 126:11154–11155
10. Vázquez M, Fabbrizzi L, Taglietti A, Pedrido RM, González-Noya AM, Bermejo MR (2004) A colorimetric approach to anion sensing: a selective chemosensor of fluoride ions, in which color is generated by anion-enhanced π delocalization. Angew Chem 116: 1996–1999
11. Kobiro K, Inoue Y (2003) A new chiral probe for sulfate anion: UV, CD, fluorescence, and NMR spectral studies of 1:1 and 2:1 complex formation and structure of chiral guanidinium-p-dimethylaminobenzoate conjugate with sulfate anion. J Am Chem Soc 125:421–427
12. Silva AP, McClenaghan ND (2000) Proof-of-principle of molecular-scale arithmetic. J Am Chem Soc 122:3965–3966
13. Kriwanek J, Miller R (1995) UV/vis spectroscopic investigations of micellisation of homologous N-alkyl betaines using the dye indicator ET(30). Colloids Surf A Physicochem Eng Asp 105:233–242
14. Novaki LP, Seoud OAE (2000) Microscopic polarities of interfacial regions of aqueous cationic micelles: effects of structures of the solvatochromic probe and the surfactant. Langmuir 16:35–41
15. Tada EB, Novaki LP, Seoud OAE (2001) Solvatochromism in cationic micellar solutions: effects of the molecular structures of the solvatochromic probe and the surfactant headgroup. Langmuir 17: 652–658
16. Gao LN, Song Q, Huang X, Huang JB (2008) A new surfactant-fluorescence probe for detecting shape transitions in self-assembled systems. J Colloid Interface Sci 323:420–425
17. Gao LN, Zhao L, Huang X, Xu BC, Yan Y, Huang JB (2011) A surfactant type fluorescence probe for detecting micellar growth. J Colloid Interface Sci 354:256–260
18. Qian JH, Qian XH, Xu YF (2009) Selective and sensitive chromo- and fluorogenic dual detection of anionic surfactants in water based on a pair of "on-off-on" fluorescent sensors. Chem Eur J 15:319–323
19. Xu ZC, Baek KH, Kim HN, Cui JN, Qian XH, Spring DR, Yoon ISJ (2010) Zn^{2+}-triggered amide tautomerization produces a highly Zn^{2+}-selective, cell-permeable, and ratiometric fluorescent sensor. J Am Chem Soc 132:601–610
20. Lee MH, Han JH, Kwon PS, Bhuniya S, Kim JY, Sessler JL, Kang C, Kim JS (2012) Hepatocyte-targeting single galactose-appended naphthalimide: a tool for intracellular thiol imaging in vivo. J Am Chem Soc 134:1316–1322
21. Veale EB, Frimannsson DO, Lawler M, Gunnlaugsson T (2009) 4-Amino-1,8-naphthalimide-based Tröger's bases as high affinity DNA targeting fluorescent supramolecular scaffolds. Org Lett 11: 4040–4043
22. Xu ZC, Qian XH, Cui JN (2005) Colorimetric and ratiometric fluorescent chemosensor with a large red-shift in emission: Cu(II)-only sensing by deprotonation of secondary amines as receptor conjugated to naphthalimide fluorophore. Org Lett 7:3029–3032
23. Veale EB, Gunnlaugsson T (2008) Bidirectional photoinduced electron-transfer quenching is observed in 4-amino-1,8-naphthalimide-based fluorescent anion sensors. J Org Chem 73: 8073–8076
24. Qian X, Xiao Y, Xu Y, Guo X, Qian J, Zhu W (2010) "Alive" dyes as fluorescent sensors: fluorophore, mechanism, receptor and images in living cells. Chem Commun 46:6418–6436
25. Gomez DE, Fabbrizzi L, Licchelli M (2005) Why, on interaction of urea-based receptors with fluoride, beautiful colors develop. J Org Chem 70:5717–5720
26. Pais VF, Remon P, Collado D (2011) OFF-ON-OFF fluorescence switch with T-latch function. Org Lett 13:5572–5575
27. Ahmadi MF, Rusling JF (1995) Fluorescence studies of solute microenvironment in composite clay-surfactant films. Langmuir 11:94–100
28. Karukstis KK, McDonough JR (2005) Characterization of the aggregates of N-alkyl-N-methylpyrrolidinium bromide surfactants in aqueous solution. Langmuir 21:5716–5721
29. Zhao YY, Li XY (2013) Aggregation behavior of naphthalimide fluorescent surfactants in aqueous solution. Colloid Polym. Sci. doi: 10.1007/s00396-013-3100-0
30. Harris DC (2003) Quangtitative chemical analysis, W. H. Freeman 6ed.
31. Siddiqui MSU, Stanley RJ (2005) A cryogenic optical waveguide spectrometer for the measurement of low-temperature absorption spectra of dilute biological samples. Anal Biochem 337:121–129
32. Guldi DM, Hungerbühler H, Asmus KD (1999) Inhibition of cluster phenomena in truly water soluble fullerene derivatives: biomolecular electron and energy transfer processes. J Phys Chem B 103: 1444–1453
33. Wang YF, Chen YL, Li RJ, Wang Q, Su W, Ma P, Wasielewski MR, Li XY, Jiang JZ (2007) Amphiphilic perylenetretracarboxyl diimide dimer and its application in field effect transistor. Langmuir 23: 5836–5842
34. Hansen JS, Vararattanavech A, Plasencia I, Greisen PJ, Bomholt J, Torres J, Emnéus J, Hélix-Nielsen C (2011) Interaction between sodium dodecyl sulfate and membrane reconstituted aquaporins: a comparative study of spinach SoPIP2;1 and E. coli AqpZ. Biochim Biophys Acta 1808:2600–2607

35. Tamoto Y, Segawa H, Shirota H (2005) Solvation dynamics in aqueous anionic and cationic micelle solutions: sodium alkyl sulfate and alkyltrimethylammonium bromide. Langmuir 21:3757–3764
36. Reichardt C (2003) Solvents and solvent effects in organic chemistry, 3rd edn. Wiley-VCH, Verlag GmbH & Co. kGaA, Weinheim, p 330
37. Kumar S, Singh P, Mahajan A, Kumar S (2013) Aggregation induced emission enhancement in ionic self-assembled aggregates of benzimidazolium based cyclophane and sodium dodecylbenzenesulfonate. Org Lett 15:3400–3403
38. Klevens HB (1953) Structure and aggregation in dilute solution of surface active agent. J Am Oil Chem Soc 30:74–80
39. Bujake JE, Goddard ED (1965) Surface composition of sodium lauryl sulphonate and sulphate solutions by foaming and surface tension. Trans Faraday Soc 61:190–195
40. Turro NJ, Kuo PL (1987) Novel excimer forination of pyrene in micelles of a crown ether surfactant. J Phys Chem 91: 3321–3325
41. Honda C, Itagaki M, Takeda R, Endo K (2002) Solubilization of pyrene in C_nE_7 micelles. Langmuir 18:1999–2003
42. Yan H, Cui P, Liu CB, Yuan SL (2012) Molecular dynamics simulation of pyrene solubilized in a sodium dodecyl sulfate micelle. Langmuir 28:4931–4938