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Characterization of Fluorescent Surfactant Aggregates by Fluorimetric and Viscosimetric Techniques

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Summary. A combination of fluorimetric and viscosimetric methods was used to characterize N,N-dimethyl-N-2-(4-(*t*-butylphenoxy)ethoxy)ethyl-N-hexadecylammonium chloride (*BDHC*), a double-tailed surfactant with dissimilar tail groups. *BDHC* was observed to fluoresce at 315 nm when excited at 274 nm, a feature which could be utilized to determine its critical micelle concentration (*CMC*). A value of 3.98×10^{-5} *M* was obtained and was observed to be slightly temperature dependent with a $T_{\min}$ of 25.35°C. Fluorescence quenching experiments using 4-nitroaniline as a quencher were performed in order to determine the aggregation number which was found to be 42.0. The hydrodynamic radius of 21.91 Å was obtained using data from viscosimetric experiments. These data, together with the *Tanford* and *Einstein-Stokes* relationships, were used to determine the micellar structure (spherical) and the diffusion coefficient ($D = 0.97 \times 10^{-6}\,\mathrm{cm^2/s}$), respectively. The ΔG of micellization for *BDHC* was determined to be −34.9 kJ/mol.

Keywords. Fluorescence; Hydrodynamic; Micelle; Surfactant; Viscosity.

Charakterisierung fluoreszierender oberflächenaktiver Aggregate mittels Fluorimetrie und Viskosimetrie

Zusammenfassung. Die Verbindung N,N-Dimethyl-N-2-(4-(*t*-butylphenoxy)ethoxy)ethyl-N-hexadecylammoniumchlorid (*BDHC*), eine oberflächenaktive Substanz mit zwei unterschiedlichen Seitenketten, wurde mittels einer Kombination von fluorimetrischen und viskosimetrischen Methoden charakterisiert. Anregung bei 274 nm ruft eine Fluoreszenz bei 315 nm hervor; diese Eigenschaft wurde zur Bestimmung der kritischen Micellenkonzentration (*CMC*) herangezogen. Es wurde ein geringfügig temperaturabhängiger Wert von 3.98×10^{-5} *M* gefunden ($T_{\min} = 25.35$°C). Quenchexperimente mit 4-Nitroanilin ergaben eine Aggregationszahl von 42.0, viskosimetrische Untersuchungen einen hydrodynamischen Radius von 21.91 Å. Die erhaltenen Daten erlauben zusammen mit den Beziehungen nach *Tanford* und *Einstein-Stokes* die Bestimmung der Micellenstruktur (sphärisch) und des Diffusionskoeffizienten ($0.97 \times 10^{-6}\,\mathrm{cm^2/s}$). Das ΔG der Micellenbildung für *BDHC* beträgt −34.9 kJ/mol.

Introduction

Fluorescence spectrophotometry is one of the major techniques that is commonly used for the characterization of micellar properties, such as aggregation number

[1–5], micellar interior microviscosity [2, 6, 7], and diffusion coefficient [7–10]. For these determinations it is not required that the micelle under study be fluorescent, but rather that it has the capacity to solubilize a fluorescent probe. In itself, fluorimetry is not used as a direct method for critical micelle concentration determination. This is due, in part, to the fact that most surfactants that form micelles are not fluorescent. For the characterization of such surfactants, other techniques that respond to some physical property of their micelles or their monomers are used. Typical techniques are surface tensiometry and conductometry [11–22]. However, for surfactants that contain a fluorophore (e.g. benzyl, phenyl, or phenoxy), it should be feasible to carry out a direct fluorometric characterization of their micellar properties. The model surfactant selected for this investigation is N,N-dimethyl-N-2-(4-(*t*-butylphenoxy)ethoxy)ethyl-N-hexadecylammonium chloride (*BDHC*) whose structure is shown in Fig. 1.

Results and Discussion

As can be seen from Fig. 1, *BDHC* is a double-tailed surfactant with dissimilar tail groups. Its fluorescent properties are probably due to the phenoxy moiety. Advantage was taken of this phenomenon for the determination of the critical micelle concentration and other relevant parameters of *BDHC* using fluorometry (Table 1).

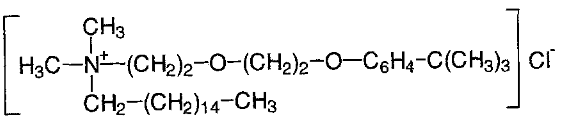
Critical micelle concentration

Fig. 2 shows a plot of the relative fluorescence intensity as the concentration is varied. Obviously, there is a change in the slope in the intensity-concentration curve. The two linear segments intersect at a concentration of 3.98×10^{-5} *M*; this value was taken to be the critical micelle concentration (*CMC*) for this surfactant. The critical micelle concentration of double-tailed surfactants of chain length greater than 14 has not, to the authors' knowledge, been studied. However, studies of double-tailed surfactants of shorter chain lengths have been made [1, 2, 12]. The relative *CMC* of those surfactants showed a decrease with increase chain length. This is consistent with what is observed for single chain surfactants. The *CMC* for *BDHC* observed in this work is in agreement with what should be expected of double-tailed surfactants of this size.

Determination of the aggregation number

In order to determine the aggregation number *N* of the *BDHC* micelle, the usual technique of fluorescence quenching was used [26]. The data therefrom were plotted as shown in Fig. 3 in accordance with Eq. (1).

$$\ln(I_0/I) = ([Q]N)/[S] - CMC \tag{1}$$



$$\left[H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2-(CH_2)_{14}-CH_3}{N^{+}}}-(CH_2)_2-O-(CH_2)_2-O-C_6H_4-C(CH_3)_3 \right] Cl^-$$

Fig. 1. Structure of *BDHC*

Table 1. Characteristic parameters of *BDHC*

CMC	$3.98 \times 10^{-5} M$
Aggregation number (N)	42.0
Hydrodynamic radius (R_H)	21.91 Å
Diffusion coefficient (D)	0.97×10^{-6}
ΔG of micellization	−34.91 kJ/m
Structure factor (v/al_c)	0.26
Structure	Spherical

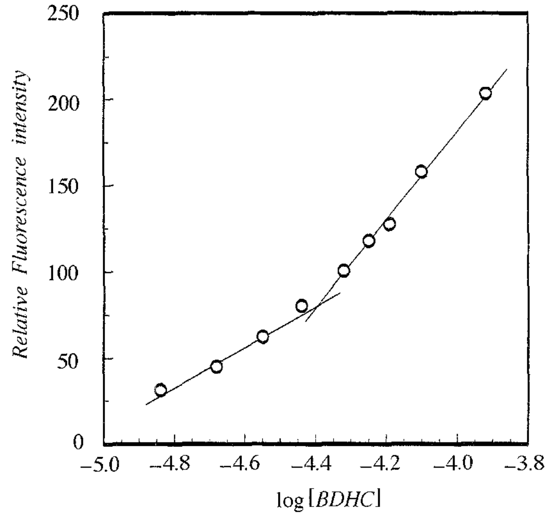


Fig. 2. Observed fluorescence intensity *vs.* log of *BDHC* concentration

I_0 and I are the fluorescence intensity of *BDHC* in the presence and absence of quencher Q, respectively, and $[S]$ is the total surfactant concentration. The slope of this plot was used to determine the aggregation number for this surfactant, and a value of 42 was obtained. This value appears reasonable considering the size of the surfactant and the concentration range at which studies were carried out. Hexadecyltrimethylammonium bromide (*CTAB*) is a surfactant that has been extensively studied. Its N value at 25°C is taken to be 61 [11]. One of the tail groups of *BDHC* is the hydrophobic part of *CTAB*. However, the other tail group, although containing two oxygen atoms, is not sufficiently hydrophilic to increase the solubility of *BDHC* in water and hence to increase its aggregation number. In fact, the solubility of *BDHC* in water was observed to be about an order of magnitude lower than that of *CTAB*. With a decrease in solubility, the aggregation number also tends to decrease. The lower N value observed here relative to *CTAB* is consistent with this fact.

Determination of the hydrodynamic radius

In order to better characterize the size of the *BDHC* micelle, its hydrodynamic radius was determined using the hydrodynamic sphere model [27]. This model assumes that the intrinsic viscosity ($[\eta]$) of a spherical macromolecular system is related to its hydrodynamic radius R_H by Eq. (2).

$$[\eta] = (10\pi N_A R_H^3)/3M \quad (2)$$

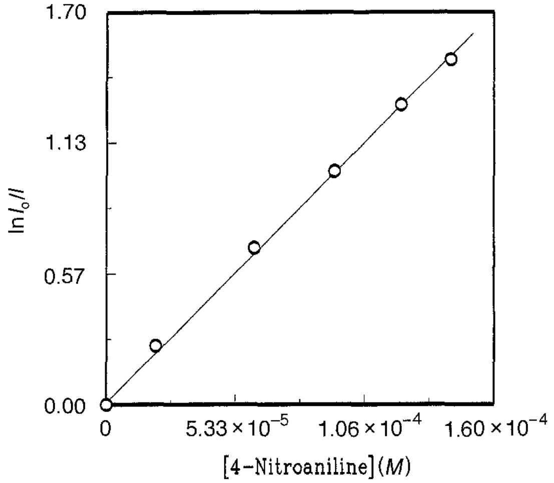


Fig. 3. Ratio of ln of fluorescence intensity in the presence and absence of quencher *vs.* quencher concentration

In this equation, N_A is *Avogadro*'s number, and M is the molar mass of the solute. In order to obtain the intrinsic viscosity for *BDHC*, its inherent viscosity η' $(1/S\ln\eta/\eta_0)$ was plotted *vs.* $1/S$ (S: surfactant concentration). As can be seen from Fig. 4, a good linear relationship was obtained. The intrinsic viscosity $[\eta]$ at $\eta_c = 0$ was found to be 125 ml/g. This value was used to obtain a hydrodynamic radius of 21.91. Å from Eq. (2) which is in good agreement with the theoretically calculated value of 22.26 Å using Eq. (3) developed by *Zana* [28].

$$R = 1.6 + 1.265(m + 1) + 0421m'' \tag{3}$$

R is the micellar hydrodynamic radius in angstroms, m is the number of carbons of the longest hydrocarbon chain of the surfactant minus one, and m'', is the number of carbons in the substituting alkyl chain.

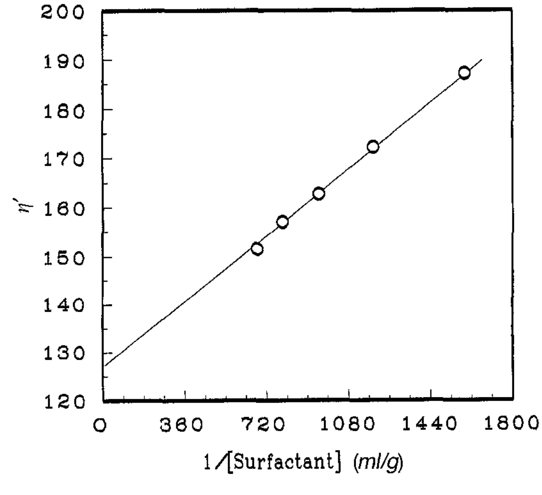


Fig. 4. Inherent viscosity *vs.* reciprocal of *BDHC* concentration

The obtained hydrodynamic radius together with the observed solution viscosity (1.02 cP) at the *CMC* were used to calculate a diffusion coefficient of 9.77×10^{-7} cm^2/s *via* the well known *Stokes-Einstein* relation $D = kT/6\pi\eta R_\mathrm{H}$.

Determination of the micellar structure

The structure of the micelles was evaluated by first determining the micellar volume using the *Tanford* relation $(v' = 55 + 26.9\ (m + m'))$ for a double-chain surfactant of chain length l_c [28]. For the purposes of this determination, l_c is the length of the longer one of the two hydrophobic chains of *BDHC*; it is related to the number of carbon atoms in the chain by the following relation [29]:

$$l_\mathrm{c} = 1.5 + 1.265m \tag{4}$$

The value of l_c calculated from Eq. (4) was 20.475 Å and afforded a micellar volume of 754.4 Å^3. The area of the micelle was determined by the method of *Evans et al.* [30].

$$a = 4\pi R_\mathrm{H}^2/N \tag{5}$$

N and R_H are the aggregation number and hydrodynamic radius, respectively. The headgroup area calculated using the above relation was 143.56 Å^2. With these figures, the structural parameterr v/al_c, was determined to be 0.26. This suggests a spherical micelle for *BDHC* within the concentration range studied.

Determination of the temperature dependence of CMC

The *CMC* of *BDHC* exhibits a marginal sensitivity towards temperature changes. In the range of temperatures studied in the present investigation (10 to 55°C), a variation over only 0.30 units was observed. In order to avoid clustering, only two representative *CMC*-temperature profiles are shown in Fig. 5.

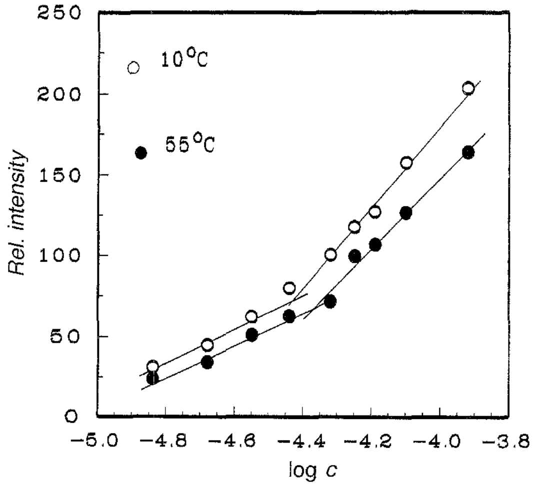


Fig. 5. Observed fluorescence intensity *vs.* log of *BDHC* concentration at 10 and 55°C

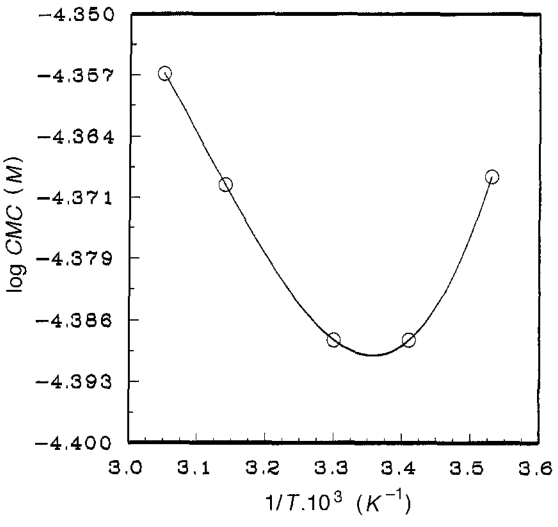


Fig. 6. Log of observed *CMC vs.* reciprocal temperature

The overall pattern of change is in agreement with what is expected for cationic surfactants, that is, a decrease in *CMC* to a minimum and a change in slope thereafter. A minimum temperature of 25.35°C was observed (Fig. 6). This value is consistent with $T_{\min}$ values expected for cationic surfactants [12]. The small influence of temperature on *CMC* for *BDHC* may be interpreted from the point of view of micelle structure. It appears that *BDHC* forms a very tight micelle. A compact micelle has been observed to show little tendency for growth [31]. As a consequence, an increase in temperature will only have a minimal effect on the overall *CMC* of the specific surfactant at moderate temperatures. This is in accordance with our observations.

Conclusions

It has been shown in this work that a total surfactant characterization by direct fluorimetry is feasible. A double-tailed surfactant with dissimilar tailgroups, *BDHC*, has been used as model to demonstrate this fact. Relevant micelle parameters such as critical micelle concentration and the aggregation number, determined directly by this technique gave values that are in good agreement with those obtained using conventional techniques. The hydrodynamic radius obtained using viscosimetry in combination with fluorometry was also in good agreement with theoretical values. The effect of temperature on *CMC* which is low in the case of *BDHC*, can also be easily determined by fluorometry.

Experimental

Materials

4-nitroaniline (99+ pure), 4-*t*-butylphenol (99%), and 2,2′-dichlorodiethyl ether (99%) were obtained from Aldrich Chemicals Co. Inc.

Syntheses

Hexadecyldimethylamine

This compound was prepared by the method of *Pine* and *Sanchez* [23]. Hexadecylamine (26.8 g, 90% purity, 0.100 mol) was placed into a 250 ml round-bottomed flask. Ethanol (30 ml, 95%) was added. The mixture was stirred at 25°C, and 26 ml of 90% formic acid were added. During this operation the flask was cooled with an ice bath in order to keep the temperature at 28–32°C. The ice bath was removed, and 21 ml of 37% formaldehyde solution were added at such a rate that the temperature remained below 40°C. The mixture was stirred magnetically and heated to reflux for 2.6 h (77–79°C). Upon cooling to room temperature, 3 *M* NaOH was added until the mixture was strongly basic. The upper layer was separated, washed with 100 ml of water, and dried over 5 g of potassium carbonate. The product was decanted and distilled at 203–209°C (5 mm). The yield was 14.7 g (55%).

BDHC

The synthesis of *BDHC* was carried out by the procedure of *Brunson* [24] and *Buckingham et al.* [25]. 4-*t*-butylphenol was converted to its sodium salt by treatment with aqueous sodium hydroxide. 2,2′-Dichlorodiethyl ether was added, and the mixture was stirred and heated at reflux for 6.5 h at 110°C. The resulting mixture was filtered by gravity and subjected to vacuum distillation. After removal of unreacted ether, the product distilled at 176–180°C (8 mm) as a colorless liquid. This product was refluxed with N,N-dimethylhexadecylamine for 24 h (110°C) and allowed to cool to room temperature. The solvent was then removed on a rotary evaporator, and the residue was stirred with ether to give a colorless solid which was recovered by vacuum filtration. The product is hygroscopic and was therefore stored under nitrogen in a dessicator until needed. The purity, which was greater than 98%, was determined by argentometric and potentiometric titrations.

Methods

Fluorescence measurements

All luminescence measurements were performed using a Perkin Elmer luminescence spectrophotometer model LS50 B. The excitation and emission wavelengths were 225 and 301 nm, respectively. For the *CMC* determination, solution concentration varied from 0.7×10^{-5} to 1.2×10^{-4} *M*. The fluorescence quenching studies were carried out using 4-nitroaniline as a quencher with concentrations varying from 0 to $1.42 \times 10^{-4} M$ at a fixed surfactant concentration of $4.0 \times 10^{-3} M$. All measurements were made at room temperature (26.0 ± 0.2°C).

Temperature studies

The influence of temperature on the critical micelle concentration of *BDHC* was determined by fluorimetry in the range from 10 to 55°C±0.2°C. Temperature was controlled using a refrigerated bath and a circulator, model KT-2 supplied by Haake, Germany.

Viscosity measurements

The viscosity experiments were carried out using a Brookfield Viscometer model RDVD II +. Unless otherwise specified, all measurements were performed at a constant temperature 26± 0.2°C with the viscometer spindle speed set at 50 rpm.

Acknowledgments

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