**Abstract:** The time-resolved fluorescence quenching method was applied to determine the micelle aggregation number of cationic single-chain surfactants dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB) and anionic surfactant sodium dodecyl sulfate (SDS). The concentration dependence of micelle aggregation number was found to be linear for all investigated surfactants in the concentration range 2‒15 × the value of critical micelle concentration of the respective surfactant. The values of micelle aggregation number were found in the range 30‒77. Different trends in the linear concentration dependence of micelle aggregation number were observed for cationic surfactants and for the anionic surfactant SDS. A small slope value was found for cationic surfactants, while the SDS micelle aggregation number concentration dependence showed significantly a larger slope value. The aggregation number increase with the increasing SDS concentration results in the micellar growth. Results from a simple analysis based on computer models of cationic and anionic surfactant molecules with dodecyl chains supports, the formation of intramicellar hydrogen bonding between surfactant molecules in SDS micelle shell.

**Keywords:** micelle aggregation number; fluorescence quenching; sodium dodecyl sulfate; hydrogen bonding

**1 Introduction**

Amphiphilic molecules are used in a variety of applications that take advantage of their ability to form self-assembled structures. Surfactants are amphiphilic molecules with relatively long (8–24 carbon atoms) hydrophobic tails and short hydrophilic heads. The self-assembling behaviour of amphiphilic molecules into colloidal aggregates has direct implications on a broad scale of processes, such as the performance of detergents, lubrication, molecular self-assembly, solubilisation of drugs and biologically efficient systems, non-viral gene transfecting agents etc. To provide a correct understanding of how these molecules behave, a description of surfactant aggregates at the molecular level is required. Simple molecular modeling software packages as well as more advanced Monte Carlo simulations [1,2] and molecular dynamics simulations [3-5] of surfactant micelles often provide valuable data, such as micelle diameter and aggregation number, which can be compared with those obtained by experimental methods. The aggregation number of surfactant micelles, which provides the number of surfactant molecules making up a micelle, represents one of the experimental characteristics describing micelles. Along with the hydrodynamic size and shape of micellar aggregate, it provides important information of the micellar structure. Therefore, an easy and reliable experimental determination of micellar aggregation number is of particular interest. A number of physical methods have been used for the determination of micelle aggregation number such as NMR spectroscopy [6,7], static light scattering (references in the text below), small-angle neutron scattering [8-10], small-angle X-ray scattering [11], fluorescence probing methods, and electron paramagnetic resonance [8,12-16]. Some of them are limited to the aggregation number determination at the surfactant concentration equal to CMC which only provides aggregation number values for isolated non-
interacting particles. Particularly, static light scattering represents an indirect method of the aggregation number determination through the calculation of molecular weight of surfactant aggregate at the surfactant CMC. The utilisation of this method for the aggregation number determination is rather complicated as it requires the independent determination of refractive index increment of the measured surfactant solution and the extrapolation of the data to the CMC which does not allow measurement of the concentration dependence of the aggregation number. Using this method, micelle aggregation numbers of some conventional single-chain ionic surfactants were determined at different solution ionic strength as published in the papers of Imae and Ikeda – dodecyltrimethylammonium bromide (DTAB) [17], dodecyldimethylammonium bromide [18] and chloride [19], dodecylpyridinium bromide [20], tetradecltrimethylammonium halides [21], sodium dodecyl sulfate (SDS) [22,23]. Small angle neutron scattering data permit the determination of the average charge of micelles, the average micelle aggregation number [24] as well as providing information on the micelle shape. Due to the complexity and high cost of the neutron scattering experimental facilities, this experimental method is not easily available for a routine determination of micelle aggregation number.

Fluorescence probing methods represent an important area of micelle aggregation number determination. There are steady-state [25-27] and time-resolved fluorescence methods which can be used for the determination of micelle aggregation number. The advantage of these methods is based on the fact that the aggregation number determination is affected neither by the micellar shape nor by the interactions between micelles. Time-resolved fluorescence quenching (TRFQ) represents a relatively easy and accurate method which is based on the calculation of the aggregation number from the fluorescence decay curves [28,29]. Unlike steady-state fluorescence measurements taking advantage of conventional spectrophotometers, this method requires the application of single-photon counting equipment LiveSpec II (Edinburgh Instruments) at the emission wavelength of 381 nm. The incident beam with the excitation wavelength of 340 nm was generated by a picosecond pulse diode laser. The fluorescence decay curves were recorded by the Edinburgh Instruments F900 software and fitted by the equation

\[ I(t) = I(0) \exp \left\{- \frac{t}{\tau_0} - \frac{t}{\tau_Q} \left[1 - \exp \left(- \frac{t}{\tau_Q} \right) \right]\right\} \]  

utilizing the Edinburgh Instruments FAST software module for non-linear fitting. \(I(t)\) and \(I(0)\) are fluorescence intensities at time \(t\) and zero, respectively. \(\tau_0, \tau_Q, R\) are three adjustable parameters representing the results of the non-linear fit. \(\tau_0\) is pyrene lifetime in the absence of quencher. \(\tau_Q\) is pyrene lifetime in the presence of quencher. In the presence of quencher, the fluorescence decay is described by the Eq. 1 with \(k_Q = 1/\tau_Q\) being the rate constant for intermicellar quenching. The fitting parameter \(R\) is equal to \(c_Q/c_{mic}\) which is the ratio of the quencher concentration \(c_Q\) to the concentration of surfactant micelles \(c_{mic}\). The relation can be rewritten as

\[ N = R \frac{(c - CMC)}{c_Q} \]  

In the literature, micelle aggregation numbers of single-chain ionic surfactants are mostly reported as single values at different concentrations and utilizing various experimental methods. The aim of this work is to provide concentration dependences of micelle aggregation number for the ionic surfactants DTAB, CTAB and SDS using the time-resolved fluorescence quenching method and to correlate the found concentration dependences of micelle aggregation number with intramicellar molecular structure.

2 Experimental procedure

2.1 Chemicals

The fluorescence quencher cetylpyridinium chloride was used as purchased from Sigma. Pyrene (Aldrich) was recrystallized prior to use and its ethanol stock solution was kept in dark. CTAB, DTAB and SDS (Sigma) were purified by multiple crystallisation from methanol and acetone-methanol mixtures.

2.2 Time-resolved fluorescence quenching

All fluorescence experiments were carried out with pyrene as a fluorescent probe. Cetylpyridinium chloride was used as the quencher. The fluorescence decay curves were recorded using a single-photon counting equipment LiveSpec II (Edinburgh Instruments) at the emission wavelength of 381 nm. The incident beam with the excitation wavelength of 340 nm was generated by a picosecond pulse diode laser. The fluorescence decay curves were recorded by the Edinburgh Instruments F900 software and fitted by the equation

\[ I(t) = I(0) \exp \left\{- \frac{t}{\tau_0} - \frac{t}{\tau_Q} \left[1 - \exp \left(- \frac{t}{\tau_Q} \right) \right]\right\} \]  

utilizing the Edinburgh Instruments FAST software module for non-linear fitting. \(I(t)\) and \(I(0)\) are fluorescence intensities at time \(t\) and zero, respectively. \(\tau_0, \tau_Q, R\) are three adjustable parameters representing the results of the non-linear fit. \(\tau_0\) is pyrene lifetime in the absence of quencher. \(\tau_Q\) is pyrene lifetime in the presence of quencher. In the presence of quencher, the fluorescence decay is described by the Eq. 1 with \(k_Q = 1/\tau_Q\) being the rate constant for intermicellar quenching. The fitting parameter \(R\) is equal to \(c_Q/c_{mic}\) which is the ratio of the quencher concentration \(c_Q\) to the concentration of surfactant micelles \(c_{mic}\). The relation can be rewritten as

\[ N = R \frac{(c - CMC)}{c_Q} \]
$N$ is micelle aggregation number, $c$ is surfactant concentration. The molar concentration ratio $c_Q/c_{\text{mic}}$ was set approximately to 1 which means one quencher molecule per surfactant micelle. The pyrene concentration was chosen to be less than 0.05 $\times$ quencher concentration which avoids the formation of pyrene excimers [36]. Individual solutions at a given surfactant concentration were prepared by dilution from the solution with the largest surfactant concentration. For each solution, the fluorescence decay curves were recorded and analyzed and the concentration plots of the aggregation number were constructed.

2.3 Molecular modeling

Molecular models of low-energy conformers of DTAB and SDS were created using the Alchemy III molecular modeling software for MS Windows (Tripos, Inc.) The Alchemy software allows molecules to be built using an expandable library of molecular fragments and a built-in energy minimizer. Within the Alchemy software, the potential energy $E$ of the molecule is being minimized as the sum of the following energy contributions:

$$E = E_{\text{str}} + E_{\text{ang}} + E_{\text{tor}} + E_{\text{vdw}} + E_{\text{oop}} + E_{\text{el}}$$

$E_{\text{str}}$ – bond stretch, $E_{\text{ang}}$ – deformation of bond angles, $E_{\text{tor}}$ – deformation of torsional angles, $E_{\text{vdw}}$ – van-der-Waals interactions, $E_{\text{oop}}$ – out-of-plane bending, $E_{\text{el}}$ – electrostatic interactions. The individual energy terms are expressed as follows:

$$E_{\text{str}} = \sum i \frac{1}{2} k_i d_i^2$$

$d_i$ – bond length in Å, $d_i^0$ – equilibrium bond length in Å, $k_i$ – force constant in kcal Å$^{-2}$ mol$^{-1}$

$$E_{\text{ang}} = \sum i \frac{1}{2} k_i \theta_i^0 (\theta_i - \theta_i^0)^2$$

$\theta_i$ – bond angle in degrees, $\theta_i^0$ – equilibrium bond angle in degrees, $k_i$ – force constant in kcal degree$^{-2}$ mol$^{-1}$

$$E_{\text{tor}} = \sum i \frac{1}{2} k_i (1 + \text{sign}(\text{peri}_i) \times \cos(\text{peri}_i \times w_i))$$

$w_i$ – torsional angle in degrees, $k_i$ – force constant in kcal mol$^{-1}$, peri – periodicity

The van der Waals interactions (Lennard-Jones potential) is defined as follows:

$$E_{\text{vdw}} = \sum \sum \frac{a_i}{r_{ij}^6} - \frac{2}{r_{ij}^{12}}$$

Summation is over 1-4 and more remote interactions. $E_{\text{oop}}$ – van-der-Waals constant in kcal mol$^{-1}$, $a_{ij} = r_{ij} / (R_i + R_j)$ – relative distance, $R_i$ – van-der-Waals radius of atom $i$ in Å

$$E_{\text{el}} = \sum \sum q_i q_j / 4 \pi \varepsilon r_{ij}$$

$q_i$ – partial charge of the atom $i$, $r_{ij}$ – interatomic distance between atoms $i$ and $j$, $\varepsilon$ – dielectric constant

3. Results and discussion

3.1 Pyrene spectra

The ratio I1/I3 of the intensities of the first (I) and third (III) vibronic peaks in pyrene is strongly dependent on the solvent polarity, that is 1.87 in water and 0.58 in cyclohexane [37,38]. Therefore, it is possible to use pyrene as an indicator of the change in the micropolarity of pyrene molecule environment which can be used e.g. for the determination of critical micelle concentration of surfactants. In Fig. 1, characteristic peaks in the pyrene spectrum are shown in the presence of CTAB micelles.
3.2 Concentration dependence of aggregation number

In Fig. 2, concentration dependence of aggregation number $N$ of CTAB micelles in the concentration range $0–15 \times \text{CMC}$ is plotted, as determined from the time-resolved fluorescence quenching measurements.

The concentration dependences of $N$ for CTAB micelles are plotted for three different emission wavelengths. As follows from the plot, a moderate increase of CTAB aggregation number with the increasing concentration is observed. Three wavelengths for the time-resolved fluorescence quenching experiment were chosen as the peak I. and III. wavelengths from the Fig. 1 and the wavelength 381 nm previously used in a similar TRFQ experiment [36]. As results from the plot, CTAB aggregation number is moderately increasing with the increasing surfactant concentration. The dependence on emission wavelength is very weak. The aggregation number values were found in the range 68–77. The previously published value at $10 \times \text{CMC}$ (denoted by the star symbol in Fig. 2) falls well into this range of aggregation number values.

The aggregation number of DTAB micelles does not depend on surfactant concentration within the inspected concentration range and lies within the range of values 49–57 (Fig. 3).

The aggregation number $N$ for micelles composed of the anionic surfactant SDS molecules increases approximately linearly with the increasing SDS concentration (Fig. 4). This trend of SDS aggregation number increase with the increasing concentration was also observed for the previously published data.

The plot of aggregation numbers vs. surfactant concentration dependence for all investigated surfactants CTAB, DTAB and SDS is shown in Fig. 5 and the data are plotted in Table 1.

3.3 Analysis of intramicellar interactions

As follows from Fig. 5, there is a significant difference in the slopes of aggregation number vs. concentration dependence between the anionic surfactant SDS (slope value 4.57) and the cationic surfactants DTAB (0.27) and CTAB (1.07). There is also a slight difference to be seen in the shape of the fluorescence decay curves for DTAB micelles (left column, Fig. 6 a–e) and those for SDS micelles (right column, Fig. 6 f–j) indicating a steeper decrease of SDS decay curves.
The slope value of micelle aggregation number vs. concentration dependence for both cationic surfactants is significantly smaller than that of SDS micelles. The small slope value indicates a weak dependence of aggregation number on surfactant concentration for DTAB and CTAB. On the contrary, aggregation number of SDS micelles significantly increases with the increasing SDS concentration which is an indication of micellar growth. Micellar growth is observed for micelles of anionic surfactant SDS while absent for DTAB and CTAB surfactants micelles. Aggregation number of ionic surfactant micelles does not change much with the increasing surfactant concentration in the concentration region close to the CMC and the micelles are spherical with a hydrophobic core of radius equal to the length of a fully stretched alkyl chain conformation [42]. In Fig. 7, molecules of DTAB (a) and SDS (b) in the straight conformation are shown.

The distance between the oppositely located oxygen atoms which are bonded to the central sulfur atom of SDS sulfate group, is 0.241 nm. The distance of the oppositely located methyl groups bonded to the central nitrogen atom of the polar ammonium head of DTAB molecule, is 0.243 nm (Fig. 7). As follows from the distance comparison, there is no significant difference in size of polar parts of SDS and DTAB. Therefore, the micellar growth of SDS micelles with the increasing SDS concentration cannot be related only to the geometry of molecule but may indicate a significant role of intermolecular interactions in the explanation of different aggregation behaviour of DTAB vs. SDS surfactant molecules. In molecular dynamics simulation studies of SDS micelles [43-50], interactions through hydrogen bonds and electrolyte ions were found as one of the main factors determining the micellar structure. As follows from the charge distribution in the polar parts of DTAB and SDS molecules which are shown in Fig. 8, the polar part of SDS molecule has a significant negative charge.

![Figure 4](image1.png)

**Figure 4:** SDS concentration dependence of aggregation number \( N \). The published aggregation number values taken from [26,33] are denoted by star symbols.

![Figure 5](image2.png)

**Figure 5:** Concentration dependence of aggregation number \( N \) for CTAB, DTAB and SDS micelles as determined from fluorescence decay measurements at the excitation wavelength 381 nm.

| Surfactant | \( c/\text{CMC} \) | \( R \) | \( N \) |
|------------|------------------|-------|-------|
| DTAB       | 2                | 0.440 | 51.3  |
| DTAB       | 3                | 0.326 | 50.8  |
| DTAB       | 4                | 0.291 | 50.9  |
| DTAB       | 5                | 0.279 | 52.1  |
| CTAB       | 5                | 4.911 | 66.8  |
| CTAB       | 10               | 4.906 | 75.1  |
| CTAB       | 12               | 4.877 | 76.0  |
| CTAB       | 15               | 4.870 | 77.3  |
| SDS        | 2                | 0.962 | 29.8  |
| SDS        | 4                | 0.735 | 45.5  |
| SDS        | 6                | 0.693 | 53.7  |
| SDS        | 8                | 0.712 | 61.8  |
| SDS        | 10               | 0.725 | 67.4  |

**Table 1:** Values of fitting parameter \( R \), micelle aggregation number \( N \) as a function of surfactant concentration \( c/\text{CMC} \) for DTAB, CTAB and SDS surfactants determined from fluorescence decay measurements at the excitation wavelength 381 nm.
This charge is represented by lone electron pairs on oxygen atoms of the sulfate group which may take part in the formation of hydrogen bonding. Hydrogen bonding between SDS head groups and water molecules aligns the water molecules in such manner that the hydrogen atoms are directed toward the head group [49]. The results from the molecular dynamics simulation of a 60 monomer sodium dodecyl sulfate micellar system containing 7579 water molecules [45] reveals that 60% of the water molecules in the closest vicinity to the micelle have one micelle-to-water hydrogen bond. Formation of hydrogen bonds is assumed between SDS heads as results indicate from the molecular dynamics simulation study of SDS adsorption at the graphite interface [48]. As a result of hydrogen bonding, the electrostatic repulsion reduction and hence, the micellar growth are also assumed in the present case which would correspond with the aggregation number data shown in Fig. 5. According to the molecular dynamics simulation study [49], the distance between hydrogen of water and the sulfate oxygen is approximately 0.19 nm whereas the sulfate oxygen-water oxygen distance is about 0.29 nm. This is close enough for the water surrounding the sulfate group to hydrogen bond to the head group with one hydrogen and still participate in hydrogen bonding with neighbouring water molecules [49]. According to the rough estimation, the area per sulfate group on the surface of a SDS micelle is equal to $4\pi R^2/N$ for a SDS micelle with $R = 2.2$ nm and $N = 60$ [44] which gives the area value of 1.01 nm$^2$. The longitudinal size of the area per SDS molecule may be related to the surface area per molecule as $(1.01)^{0.5} = 1.00$ nm. Given the hydrogen-to-hydrogen distance in water molecule is 0.163 nm, the maximum number of water molecules between the two neighbouring sulfate groups is approximately 6 water molecules.
Figure 7: Models of DTAB (bottom) and SDS (top) molecules in straight alkyl chain conformation.

Figure 8: Point charge distribution of DTAB (bottom) and SDS (top) molecules in straight alkyl chain conformation.
In all investigated cases, the linear dependence of the aggregation number on surfactant concentration was found. A difference in the slope values of micelle aggregation number vs. concentration dependence was observed between cationic surfactants and SDS. The small slope value indicates a weak dependence of aggregation number on surfactant concentration for DTAB and CTAB. Aggregation number of SDS micelles significantly increases with the increasing SDS concentration which indicates a micellar growth. As results from a simple analysis based on the computer models of cationic and anionic surfactant molecule with dodecyl chain, the formation of intramicellar hydrogen bonding between surfactant molecules in SDS micelle shell is assumed. The obtained results reveal the role of hydrogen bonding being an important factor controlling the values and concentration dependence of the aggregation number of single-chain ionic surfactant micelles.

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