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Structural organization of cetyltrimethylammonium sulfate in aqueous solution: The effect of Na_2SO_4

Eloi Feitosa [a,*], Marcelo Rodrigo Savério Brazolin [a], Rose Mary Zumstein Georgetto Naal [b], Maria Perpétua Freire de Morais Del Lama [b], Josias R. Lopes [c], Watson Loh [c], Marilena Vasilescu [d]

[a] *Departamento de Física, IBILCE/UNESP, 15054-000, São José do Rio Preto, São Paulo, Brazil*
[b] *Faculdade de Ciências Farmacêuticas de Ribeirão Preto, USP, Ribeirão Preto, São Paulo, Brazil*
[c] *Instituto de Química, Universidade Estadual de Campinas, Campinas, São Paulo, Brazil*
[d] *Institute of Physical Chemistry, Bucharest, Romania*

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Abstract

We used dynamic light scattering (DLS), steady-state fluorescence, time resolved fluorescence quenching (TRFQ), tensiometry, conductimetry, and isothermal titration calorimetry (ITC) to investigate the self-assembly of the cationic surfactant cetyltrimethylammonium sulfate (CTAS) in aqueous solution, which has SO_4^{2-} as divalent counterion. We obtained the critical micelle concentration (cmc), aggregation number (N_{agg}), area per monomer (a_0), hydrodynamic radius (R_H), and degree of counterion dissociation (α) of CTAS micelles in the absence and presence of up to 1 M Na_2SO_4 and at temperatures of 25 and 40 °C. Between 0.01 and 0.3 M salt the hydrodynamic radius of CTAS micelle $R_H \approx 16$ Å is roughly independent on Na_2SO_4 concentration; below and above this concentration range R_H increases steeply with the salt concentration, indicating micelle structure transition, from spherical to rod-like structures. R_H increases only slightly as temperature increases from 25 to 40 °C, and the cmc decreases initially very steeply with Na_2SO_4 concentration up to about 10 mM, and thereafter it is constant. The area per surfactant at the water/air interface, a_0, initially increases steeply with Na_2SO_4 concentration, and then decreases above ca. 10 mM. Conductimetry gives $\alpha = 0.18$ for the degree of counterion dissociation, and N_{agg} obtained by fluorescence methods increases with surfactant concentration but it is roughly independent of up to 80 mM salt. The ITC data yield cmc of 0.22 mM in water, and the calculated enthalpy change of micelle formation, $\Delta H_{mic} = 3.8\ \mathrm{kJ\,mol^{-1}}$, Gibbs free energy of micellization of surfactant molecules, $\Delta G_{mic} = -38.0\ \mathrm{kJ\,mol^{-1}}$ and entropy $T\Delta S_{mic} = 41.7\ \mathrm{kJ\,mol^{-1}}$ indicate that the formation of CTAS micelles is entropy-driven.

Keywords: Cationic surfactant; Micelle; Aggregation number; Surface tension; Dynamic light scattering; Steady-state fluorescence; Time resolved fluorescence; Conductimetry; Tensiometry; Isothermal titration calorimetry

1. Introduction

Surfactant micelles have widely been investigated to clarify their structure–function correlation, as well as their application in many colloidal domains [1–11]. Micelle application in many fields requires the knowledge of properties including cmc, Krafft point, degree of dissociation, size, geometry, cloud point (for nonionic surfactants), and phase behavior. Most of these properties depend on the surfactant chemical structure and composition as well as the solvent characteristics.

There is increasing interest in homologous surfactants (e.g., quaternarium nitrogen-based surfactants) since they allow a systematic investigation of the lyophilic/hydrophilic contribution to the properties of surfactant containing systems. For example, in investigating the affinity of homologous surfactants for proteins in solution to elucidate the nature of the driving force in protein denaturation [3] or to condense DNA in surfactant microemulsion droplets or vesicles [1] for gene therapy.

The properties of cetyltrimethylammonium chloride and bromide (CTAC and CTAB) micelles are well known [4–6,8].

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[*] Corresponding author. Fax: +55 17 3221 2247.
E-mail address: eloi@ibilce.unesp.br (E. Feitosa).

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Deviation in structural properties of these micelles has been attributed to the stronger affinity of Br^- for the micelle surface relative to Cl^-. CTAS micelles, that have the divalent counterion SO_4^{2-}, on the other hand, are not so well characterized, [7–9] probably because this surfactant is not readily available commercially. The strong binding of SO_4^{2-} to the micellar surface yields CTAS micelle properties, which differ considerably from those of their homologues that have monovalent counterions [8]. Consequently, the phase behavior of CTAS greatly differs from that of the homologue CTAB in water [9,10] and, furthermore, divalent counterions, like SO_4^{2-}, affect the micelle size [6], reactivity, yield fusion of surfactant aggregates [12] and modify the phase diagram of the surfactant [9,10]. Thus, the stronger affinity of divalent ions to surfactant aggregates strongly complicates the understanding of the physical phenomena related to the ion specificity [7].

In this communication we report some physicochemical properties of CTAS micelles, including the critical micelle concentration (cmc), aggregation number (N_{agg}), hydrodynamic radius (R_{H}), area per monomer (a_0) at the air/water interface, degree of counterion dissociation (α), and the enthalpy, entropy, and Gibbs energy of CTAS micellization as a function of Na_2SO_4 concentration at temperatures of 25 and 40 °C. Overall, the cmc, size and α of CTAX micelles (X being the surfactant counterion) decrease with the counterion binding strength in the sequence $Cl^- > Br^- > SO_4^{2-}$.

2. Materials and methods

The fluorescence quenchers 3,4-dimethylbenzophenone (DMBP) and cetylpyridinium chloride (CpyC) were used as purchased from Sigma, and pyrene (Py) (Sigma) was recrystallized by ordinary procedures [13]. Recrystallized cetyltrimethylammonium sulfate (CTAS) was obtained from cetyltrimethylammonium bromide (CTAB) (Sigma) by counterion exchange using the following procedures: a mixture of $CTAB/Ag_2SO_4$ was sonicated for 5.5 h in a bath-type (Microsonic SX-10). The AgBr precipitate was removed by gravity followed by solution filtration, and the ethanol removed by evaporation. CTAS crystals were recrystallized using acetone:methanol (9:1). Recrystallized Na_2SO_4 (Merck) and high quality ultra pure Milli-Q water were used in sample preparations.

2.1. Dynamic light scattering (DLS)

DLS measurements were made using an apparatus equipped with an ALV wide-band, multi-tau, digital autocorrelator for assembling the data. An Ar ion laser operating at $\lambda = 488$ nm was used as light source. From the measured normalized intensity time correlation function, $g_2(t)$, we obtained through the inverse Laplace transform analysis the relaxation time distribution, and from the moments of this distribution the diffusion coefficients of the particles [14,15]. The treatment of the data was done using a nonlinear algorithm (REPES) which minimizes the sum of the squared differences between the experimental and calculated $g_2(t)$ values [15]. The hydrodynamic radius, as well as information about interparticle interactions, is estimated from the concentration dependence of the diffusion coefficient. For polydisperse solutions, $g_2(t)$ is related to the relaxation time (τ) through the Laplace transform [16]:

$$g^1(t) = \int_{-\infty}^{+\infty} \tau A(\tau) e^{-t/\tau} \, d\ln\tau, \tag{1}$$

where $g_2(t) = \beta |g^1(t)|^2$, β is a constant characteristic of the equipment and $A(\tau)$ is the relaxation distribution to be determined. The mean diffusion coefficients (D) are obtained from the moments of the distributions through the relation $D = \Gamma/q^2$ in the limit of zero angle, where $\Gamma = \tau^{-1}$ is the relaxation rate, $q = (4\pi n_0/\lambda)\sin\theta$ is the magnitude of the scattering vector, θ is the scattering angle and n_0 is refractive index of pure solvent. $\tau A(\tau)$ was plotted against $\log\tau$ to provide an equal area representation [15]. The hydrodynamic radius (R_{H}) is obtained using the Stokes–Einstein equation,

$$R_{\mathrm{H}} = \frac{kT}{6\pi\eta_0 D_0}, \tag{2}$$

where D_0 is the diffusion coefficient at infinite dilution obtained from the diffusion coefficient vs surfactant concentration plots, k is the Boltzmann constant, T is the absolute temperature, and η_0 is the solvent viscosity.

2.2. Steady-state fluorescence

The fluorescence emission spectra of pyrene solubilized in the CTAS solutions were obtained using a F4500 Hitachi spectrofluorometer operating in the wavelength range 350–550 nm with the fluorescence probe excited at $\lambda_{\mathrm{ex}} = 310$ nm. The ratio of the first to the third vibronic peaks of the pyrene emission spectra reflects the micropolarity of the moiety in which pyrene is solubilized, and can be used to obtain the cmc of surfactants in aqueous solution [4,17].

To obtain the micelle aggregation number (N_{agg}) we used the Turro–Yekta method, given by the equation [18]

$$\ln\frac{I_0}{I} = \frac{[\mathrm{Q_m}]}{[\mathrm{M}]}, \tag{3}$$

where I and I_0 are the fluorescence intensities of Py in the absence and presence of the quencher CpyC, $[\mathrm{Q_m}]$ and $[\mathrm{M}]$ are the molar concentration of quencher and micelles, and

$$[\mathrm{M}] = \frac{[\mathrm{S_m}]}{N_{\mathrm{agg}}}, \tag{4}$$

where $[\mathrm{S_m}]$ is the concentration of micellized surfactant. Equation (3) was derived under the assumption that the probe and quencher are within the micelle core and obey the Poisson distribution, and that the probe fluoresces only in the absence of the quencher.

2.3. Time-resolved fluorescence

Time-resolved fluorescence decay data were collected with the single photon counting technique. The setup uses a mode-locked Nd-YAG laser to synchronously pump a cavity-dumped