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FLUORIMETRIC STUDIES OF MICELLAR PROPERTIES OF CETYLTRIMETHYLAMMONIUM BROMIDE IN ACETONITRILE-WATER MIXTURE

A. Janošević Ležaić¹, L. Pavun¹, D. Đikanović², J. Goronja¹, A. Malenović¹ and N. Pejić¹

¹*University of Belgrade-Faculty of Pharmacy, Vojvode Stepe 450, 11000 Belgrade, Serbia*

²*University of Belgrade - Institute for Multidisciplinary Researches, Kneza Višeslava 1, 11030 Belgrade, Serbia*

ABSTRACT

Aggregation of the cationic surfactant cetyltrimethylammonium bromide (CTAB) in water (W) and acetonitrile–water (ACN–W) mixtures of different composition (10–20% (v/v) of ACN) was studied through fluorescence measurements. The CTAB critical micellar concentration (CMC) and the micelle aggregation number (N_{agg}) were determined at $T = 22.0$ °C. It was found that for increasing volume ratios of ACN to W, the CMC value attains a minimum (1.22 mM) at 15% (v/v) ACN while N_{agg} is continuously decreasing as ACN content in the ACN–W mixture increases. The effect of this dipolar aprotic solvent on the CTAB micelle formation can be interpreted in terms of its considerably hydrogen bonding ability and influence on bulk-phase properties (solvophobic effect).

INTRODUCTION

When dissolved in a solvent (polar or nonpolar), CTAB, as other surfactants, under certain conditions (solvent, temperature, etc.) undergoes self-aggregation (micellization) forming at a specific surfactant concentration, the so-called critical micelle concentration (CMC), microheterogeneous supramolecular structures (micelles) that exist in equilibrium with the surfactant monomers from which it is formed. The average number of surfactant monomers in a micelle is referred to as micellar aggregation number (N_{agg}). These characteristic surfactant properties, CMC and N_{agg} , depend on the hydrocarbon tail length of the surfactant, the nature of counterion and on the ionic strength of the bulk.

aleksandra.janosevic@pharmacy.bg.ac.rs

As known, the very presence of even extremely small amounts of organic solvents in aqueous micellar solution, affects various micellar parameters (CMC, degree of counterion dissociation, N_{agg} , etc.). A particular organic solvent can be incorporated to some degree into the micelles, which causes changes in the surfactant aggregates characteristics either by solvent incorporation into the micellar aggregates or by modifying the bulk-phase properties (solvophobic effect). Changing solvent characteristics, allows us to examining the role of the aforementioned solvophobic effect and provides the increasing use of surfactants in applications which require water-free or water-poor media (as lubricants or cleaners).

In this work, the influence of ACN on micellar properties of CTAB, was studied using steady-state fluorescence. Recently, we have investigated the effects of this co-solvent on the micellization of CTAB, by conductometry [1]. In the present work our study is extended to ACN–W mixtures with different co-solvent composition (10–20 % (v/v)) at $T = 22.0$ °C. For those different ACN contents, the CMC and N_{agg} were determined in order to clarify the effect of ACN on CTAB micellization.

EXPERIMENTAL

Cetyltrimethylammonium bromide (Sigma-Aldrich), acetonitrile (J.T. Baker), pyrene (Sigma-Aldrich) and cetylpyridinium chloride (CPC, Krka) were used without any pretreatment.

Both the CMC and N_{agg} of CTAB in different media were determined by performing steady-state fluorescence measurements (using pyrene as the fluorescent probe) and static quenching method (using cetylpyridinium chloride, CPC as the quencher). The F13-221 P spectrofluorimeter (JobinYvon, Horiba, France), equipped with a 450W Xe lamp as an excitation source and a photomultiplier tube as detector, was used. The slits on the excitation and emission beams were both set at 1 nm. All measurements were performed at 22.0 ± 0.1 °C using a Peltier element. The excitation wavelength was 335 nm. The fluorescence emission spectra were recorded in the range of 350–500 nm.

For CMC determinations, fluorescence spectra of solutions with different CTAB concentrations (0.2–5.6 mM) and constant pyrene concentration (1 μ M) in both W and ACN–W mixtures were recorded. For the N_{agg} determinations, solutions with constant concentrations of both pyrene (2 μ M) and CTAB (20 mM) were prepared. Then, fluorescence quenching was done by the addition of CPC, the concentration of which varied in the range 0 – 100 μ M.

The CMC values of CTAB in different systems were determined with the pyrene emission vibrational fine structure method, the so-called pyrene 1:3 ratio method [2]. So, the pyrene (1 μM) fluorescence emission intensities of the first (I_1) and third (I_3) vibrational peaks ratio (I_1/I_3) with respect to the CTAB concentration in both, W and ACN–W mixtures at $T = 22.0\text{ }^\circ\text{C}$ were identified as typical Boltzmann type sigmoidal functions.

RESULTS AND DISCUSSION

The CMC values were obtained fitting the pyrene 1:3 ratio data versus the total surfactant concentration to the sigmoid of the Boltzmann type. Thus, the CTAB concentrations corresponding to the interception point of the horizontal and the steep parts of the 1:3 ratio plots, the CMC values, are listed in Table 1. To calculate the N_{agg} , steady-state fluorescence quenching measurements were used [3]. Briefly, the ratio of the logarithm of emission fluorescence intensity for surfactant solutions in the absence of quencher (I_0) and in the presence of the quencher (I_Q) was related to the total concentration of surfactant ($[C]$) as well as to the concentration of the quencher $[Q]$:

$$\ln \frac{I_0}{I_Q} = \frac{N_{\text{agg}} [Q]}{[C] - \text{CMC}}$$

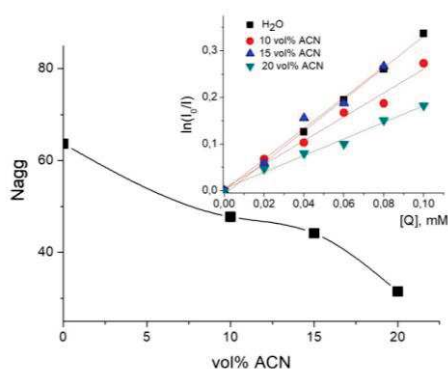


Figure 1. The N_{agg} versus the volume fraction of ACN in ACN–W mixtures. Insert: Plots of $\ln(I_0/I_Q)$ at 335 nm versus concentration of quencher $[Q]$; concentration of CTAB is 20 mM

The values of N_{agg} calculated from the slopes of the obtained linear plots $\ln(I_0/I_Q) = f([Q])$ (see the insert in Fig. 1.), are all summarized in Table 1.

In the mixed ACN–W solutions, N_{agg} decreases with ACN content increasing (Fig. 1). A similar type of decrease was obtained for CTAB by addition of some other polar organic solvents, such as ethanol [4]. The obtained "regular" behavior of ACN can be explained by the fact that ACN could break the ordered structure of water molecules around the micelles and replace those molecules in the micelle solvent shell [5].

Table 1. The CMC and N_{agg} of CTAB in W as well as in ACN–W mixtures

Vol% of ACN	CMC (mM)	N_{agg}
0	1.20	64
10	1.30	48
15	1.22	44
20	2.30	32

CONCLUSION

Micellar properties of CTAB in W and ACN–W mixtures were determined at constant temperature, $T = 22.0$ °C, using steady-state fluorescence measurements. In the examined range of ACN content in aqueous mixtures, the CMC values have a minimum at intermediate ACN concentration, while N_{agg} decreases for increasing ACN content in ACN–W mixtures. The effect of this co-solvent on the CTAB micelle formation can be interpreted in terms of ACN interaction with W and its possible influence on solvophobic interactions related to micellization.

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