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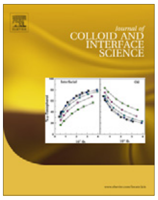

Micellization of dodecyltrimethylammonium bromide in water–dimethylsulfoxide mixtures: A multi-length scale approach in a model system

Véronique Peyre [a,b,c,*], Sabah Bouguerra [d], Fabienne Testard [e]

[a] UPMC Univ Paris 06, UMR7195, PECSA, Paris F-75005, France
[b] CNRS, UMR7195, PECSA, Paris F-75005, France
[c] ENSCP, UMR7195, PECSA, Paris F-75005, France
[d] Institut Préparatoire aux Etudes d'Ingénieur de Tunis, Laboratoire de Physico-Chimie des microstructures et microsystèmes, I.P.E.S.T., La Marsa, University of Carthage, Tunisia
[e] CEA, DSM/IRAMIS/SIS2M/Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et, Supramoléculaire, UMR 3299, Saclay, Gif-sur-Yvette F-91191, France

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ABSTRACT

The micellization in mixed solvent was studied using conductimetry, density measurements (molar volumes), and small angle neutron scattering (SANS) to explore dodecyltrimethylammonium bromide (DTABr) micelle formation throughout the entire composition range of water–dimethylsulfoxide (DMSO) mixtures. As the concentration of DMSO was increased in the mixture, the critical micelle concentration (CMC) increased, the aggregation number decreased and the ionization degree increased, until no aggregates could be detected any more for DMSO molar fraction higher than 0.51. The results were consistent with the presence of globular micelles interacting via a coulombic potential. The experimental CMC values and aggregation numbers were successfully reconciled with a molecular thermodynamic model describing the micellization process in solvent mixtures (R. Nagarajan and C.-C. Wang, Langmuir 16 (2000) 5242). The structural and thermodynamic characterization of the micelles agreed with the prediction of a dissymmetric solvation of the surfactant entity: the hydrocarbon chain was surrounded only by DMSO while the polar head was surrounded only by water. The decrease in the ionization degree was due to the condensation of the counterions and was definitely linked to the geometrical characteristics of the aggregates and by no means to the CMC or salinity. This multi-technique study provides new insight into the role of solvation in micellization and the reason for the decrease in ionization degree, emphasizing the dissymmetric solvation of the chain by DMSO and the head by water. This is the first time that, for a given surfactant in solvent mixtures, micellization is described using combined analysis from molecular to macroscopic scale.

1. Introduction

The existence of micelles in organic or hydro-organic solvents has drawn considerable attention over the past decades [1–26] for their fundamental and industrial applications, and there is still much interest in the nature of the micellization mechanism in polar organic solvent and their aqueous mixtures. In the delicate balance of forces that rules micellization, a solvent's capability to enable micellization is said to relies on its cohesive energy density, which encompasses all of the solvent's intermolecular forces (comprising H-bonds) [25]. It is remarkable that this parameter be sufficient and does not request any information on the surfactants specificity. For instance, in the case of ionic surfactants, the electrostatic interactions between surfactants heads indeed plays a particularly important role in the formation of the aggregates. We address the question of the solvent key parameter for micellization by studying a cationic surfactant in water–DMSO mixtures. Continuously changing the solvent's quality by mixing two solvents with different properties provides an opportunity to finely explore the dependence of the micellization mechanism upon the surrounding medium. Moreover, many properties of water–DMSO mixtures present an extremum at the molar fraction $x_{DMSO} = 0.33$, but the existence of an extremum of micellization for the same solvent composition is not obvious.

Among the aprotic solvents able to promote micellization, DMSO is indeed controversial. DMSO is a polar solvent completely miscible with water, and water–DMSO mixtures have been studied extensively, from experimental point of view (e.g., dielectric constants, viscosity, surface tension, partial molar volumes, densities, heat capacities, etc.) and theoretically [27–34]. The molar fraction of DMSO, $x_{DMSO} = 0.33$, was found to be a threshold for many properties such as viscosity, excess enthalpy of mixing,

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* Corresponding author. Address:: Université Pierre et Marie Curie–Paris 6, UMR7195, Case courrier 51, 4, place Jussieu, 75252 Paris Cedex 05, France.
E-mail address: veronique.peyre@upmc.fr (V. Peyre).

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and the chemical shift of protons [31], due to the formation of the complex containing 1DMSO:$2H_2O$ [30]. By varying the composition of water–DMSO mixtures, the solutions range between a highly structured solvent with many H-bonds (water), to a solvent with no H-bonds (DMSO). Micellization has been studied in such mixtures and the composition $x_{DMSO} = 0.33$ was also found to be a limit after which no micelles form, but these results are somewhat contradictory depending on the techniques and surfactants explored [13–22]. The main reason for this situation is that monotechnique approaches, which are the most common, cannot report of the various aspects of micellization and can only render a partial view of the phenomenon. The question is thus still open whether micellization also presents an extremum or a threshold at this DMSO composition. For this purpose, we established a set of data about the micellization of dodecyltrimethylammonium bromide (DTABr), using several complementary techniques to provide a description of the micelles from several points of views.

Although DTABr has been well characterized in water by various techniques including surface tension, X-rays, conductivity [35,36], small angle neutron scattering (SANS) [37–39], light scattering [40] or combinations of several techniques [35,41], little is known about its behavior in a mixed solvent, since homologues of DTABr with longer chains are studied more frequently. The scope of this study was first to link the main parameters of the micelles (i.e., critical micelle concentration [CMC], aggregation number, and ionization degree) to the relevant solvent characteristics (i.e., cohesive energy density, surface tension, and dielectric constant) and secondly, to determine some of the details of the micellization process at the molecular level and describe the solvation phenomenon in water–DMSO mixtures having compositions below and above $x_{DMSO} = 0.33$. The onset of micelle formation was determined by conductimetry and volumetry, whereas the size and effective charge of the micelles were obtained from SANS. Molecular thermodynamics according to the model proposed by Nagarajan and Wang [23] was used to calculate the CMC and clarify the forces driving micellization. This model is widely cited but seldom tested and, to our knowledge, it has not been validated on solvents other than alcohols mixed with water (e.g., ethyleneglycol [23] and ethanol [24]). In parallel, the changes of the DTABr environment were explored through density measurements, which allowed us to determine partial molar volume values and provided insight to the molecular organization of the DTABr environment. This multi-view approach at different length scales rendered valuable information that ultimately improved our understanding of the solvent effects on the self-assembly of amphiphilic compounds.

2. Materials and methods

2.1. Products

DTABr obtained from Acros Organics was recrystallized twice from acetone-ether before use. DMSO obtained from SDS-Carlo Erba was distilled under vacuum and used rapidly afterward. Tetraethylammonium bromide was obtained from Janssen Chimica and used as received. Water was of ultrapure quality (18 MΩ-cm).

Solvents (i.e., mixtures of water and DMSO) were prepared by first adding the desired amount of DMSO to a volumetric flask. Almost all the necessary amount of water was added immediately and the flask was left at room temperature for 24 h before adjusting the final volume with water. Since the mixture of DMSO and water is exothermic, this procedure allowed spontaneous degassing, cooling down, and changes in the volume of the solution to take place before the final solution was obtained. The solvents named *y* v% DMSO thus contained a volume *y* of pure DMSO mixed with water in a total volume of 100. The notation x_{DMSO} stands for the final DMSO molar fraction. All DTABr solutions in the solvents were formulated by weight and, if needed, the concentrations were calculated by their densities.

2.2. Conductimetry

Conductimetry measurements were made at 298.0 ± 0.1 K, with a Philips PM6303 conductimeter operating at 1000 Hz and calibrated with KCl. Aliquots of DTABr stock solutions (between 0.4 and 0.6 mol kg^{-1}) in the solvent were added to a sample volume of the same solvent, and the conductance was recorded after the signal stabilized (2–5 min). In the solvent of composition $x_{DMSO} = 0.50$, the stock solution was 0.21 mol kg^{-1} to avoid crystallization of DTABr at higher concentrations. The curves were drawn in two runs: one in which the stock solution samples were diluted by adding solvent and the other in which the stock solution samples were added to samples of solvent.

2.3. Densities and molecular volume determination

Densities were measured at 298.15 K on an Anton Paar DMA 5000 electronic densitometer. Temperature accuracy was ±0.01 K. All solutions were prepared by weighing. The precision of the density values was $\pm(5 \times 10^{-6})$ kg dm^{-3}. For calibration, the density of pure water at 298.15 K was taken as 0.997043 kg dm^{-3}.

The apparent molar volumes V^{app} for DTABr in different solvents were calculated from the experimental density values of solutions using the following equation [42]:

$$V^{app} = \frac{1}{m}\left(\frac{1}{\rho} - \frac{1}{\rho^{\circ}}\right) + \frac{M}{\rho} \quad (1)$$

where *m* is the molality of a solution of DTABr in the solvent, *M* the molecular weight of DTABr, and ρ and ρ° are the densities of the solution and the solvent, respectively.

2.4. Phase diagram

The transitions between a clear solution and a precipitate were determined by visual inspection of the DTABr solutions in water–DMSO mixtures. To avoid supersaturation effects, all samples were first placed at 277 K until crystals formed. They were then left at ambient temperature (∼295 K) for one week before being analyzed. The whole procedure was repeated twice on the same samples.

2.5. Small angle neutron scattering (SANS)

We used D_2O and deuterated DMSO to enhance the scattering contrast of the micelles/solvent and to minimize the incoherent hydrogen background. Experiments were performed at the Laboratoire Léon Brillouin (LLB), Saclay (France) using the PAXE spectrometer of the Orphée reactor. Quartz optical cells with a 1 mm path length were mounted on a thermostated brass block at a temperature of 298 ± 0.5 K. The overall angular range ($0.011 < q$ ($Å^{-1}$) $\leqslant 0.46$) was accessed with three configurations: $\lambda = 4.5$ Å, $D = 105$ cm; $\lambda = 6$ Å, $D = 254.7$ cm; and $\lambda = 10$ Å, $D = 505$ cm. The acquisition time was between 30 and 60 min for each sample, depending on the configuration used. Neutron detection and counting was achieved with a built-in two-dimensional sensitive detector composed of 64 × 64 cells. Standard LLB data treatments were used for radial averaging and correction for the empty cells and electronic background.

The samples were prepared by weight and the concentrations are listed in Table 1. For the solvents containing the higher DMSO