Journal of Colloid and Interface Science 364 (2011) 407–412

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

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Thermal-stability of mixed giant micelles of alkyltrimethylammonium surfactants and salicylate

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ARTICLE INFO

Article history:
Received 1 June 2011
Accepted 22 August 2011
Available online 28 August 2011

Keywords:
Giant mixed micelles
Thermal stability
Synergism
Flow properties

ABSTRACT

When diluted solutions of giant micelles are under turbulent flow, large attenuations of the turbulence can be observed due to the action of the micelles on the dissipative vortices formed within the flow. This particular property is rapidly lost when the solution is heated due breakup of the giant micelles. Based on this property, we present a thermal-flow study of a mixed giant micelle formed by the combination of two surfactants and sodium salicylate. One of the surfactants, cetyltrimethylammonium bromide (C_{16}TAB) was kept fixed, and the others were dodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB), octadecyltrimethylammonium bromide (C_{18}TAB), polyoxyethylene (10) oleyl ether (Brij 97) or sodium dodecyl sulfate (SDS). Thermal diagrams for the combinations of the surfactants reveal deviations of the ideality. For the cationic surfactants, a synergistic effect was only observed when C_{16}TAB was combined with the shorter surfactants.

1. Introduction

Changes in the surfactant concentration, ionic strength, or addition of binding co-solutes can induce the formation of long and flexible micelles, usually denominated worm-like or threadlike micelles [1,2]. This particular geometry can, in principle, be inferred, considering the idealized packing parameter, p, which is related to the head group area, the extended length and the volume of the hydrophobic part of the surfactant molecule [3]. For a spherical micelle $p < 1/3$ and for worm-like cylindrical micelles p is lower ($p = 1/3 - 1/2$), indicating these micelles require more equilibrated hydrophilic-to-hydrophobic ratios to achieve stability [4]. Aqueous solutions of giant micelles of cationic surfactants are easily formed in the presence of salicylate in quite low concentrations. This is mainly attributed to the favorable packing due to the insertion of the aromatic anions into the palisade of the micelle [5–7]. The effect is so subtle that, among the three isomers, the giant micelle is only substantially formed with the ortho-salicylate. For this isomer, the carboxylate group and the adjacent OH group stay always in the water phase. For the m- and p-isomers, the OH group is located less favorably near the interface and the hydrophobic core of the micelle [8]. The thermal stability of giant micelles is relevant to understanding the interactions between the components of this supramolecular structure. Although there are many papers describing the worm to rod-like micellar transition, few articles (see for instance Ref. [9]) describe their thermal stability, mainly when they are formed just above the cmc of the surfactant. Such dilute concentration regimes are interesting to avoid the entanglements of the chains of the micelles. Recently, we demonstrated that the breaking temperature of giant micelles can be clearly determined, using their special capability to facilitate the flow of the solution under turbulence [10]. This hydrodynamic drag reduction (HDR) phenomenon takes place in very diluted macromolecular solutions, being very useful to pump liquids for long distances expending less energy. The micelles themselves are continuously disintegrating and re-forming [11] and, for this reason, they are immune to undergoing mechanical degradation under turbulent flow. However, the structure of the giant micelles is preserved only up to a certain critical temperature. Beyond this temperature, the thermal energy overcomes the non-covalent interactions that maintain the long structure. The HDR property has proven to be ideal to investigate variations on the structure of giant micelles.

In this work we used the HDR effect to study the thermal stability of giant micelles of cetyltrimethylammonium bromide (C_{16}TAB) and salicylate, mixed with dodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB), octadecyltrimethylammonium bromide (C_{18}TAB). The results show synergistic effects only when C_{16}TAB is combined with the shorter alkyltrimethylammonium surfactants. However, considering the model of Rubingh and Holland [12], non-giant mixed micelles (systems without salicylate) behave ideally. The thermal synergism is also obtained by doping the giant micelle of C_{16}TAB and salicylate with sodium dodecyl sulfate. The deviation of the ideality can be clearly verified in diagrams in a range of compositions. These findings contribute to the understanding of the packing of the molecules

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doi:10.1016/j.jcis.2011.08.048

in the giant micelles, giving strategies to improve their thermal properties and eventually spreading their applications.

2. Materials and methods

2.1. Materials

Cetyltrimethylammonium bromide ($C_{16}TAB$), dodecyltrimethylammonium bromide ($C_{12}TAB$), tetradecyltrimethylammonium bromide ($C_{14}TAB$), octadecyltrimethylammonium bromide ($C_{18}TAB$), polyoxyethylene (10) oleyl ether (Brij 97) and sodium dodecyl sulfate (SDS) were obtained from Sigma and sodium salicylate (NaSal) was obtained from Merck. All reactants were used without any further treatment. The samples were prepared by dilution of previously prepared stock solutions. The stock solutions were prepared by weighting within (0.0001 g) adequate quantities of $C_{12}TAB$, $C_{14}TAB$, $C_{16}TAB$, $C_{18}TAB$, Brij 97, SDS or NaSal as required. Ultrapure water (18.2 MΩ cm) was used throughout. After preparation, the samples were heated to 75 °C for 1 h.

2.2. Methods

2.2.1. Hydrodynamic drag reduction – fundaments and measurements

The HDR experiments were carried out with a Haake RheoStress 1 rheometer equipped with a double-gap cell. A detailed description of this technique is present elsewhere [13,14]. The cup internal and external diameters were 17.75 and 21.70 mm, respectively, and the rotor internal and external diameters were 18.35 and 20.99 mm, respectively. The rotor length was 55.00 mm. The most attractive aspect involving the use of the rheometer to measure HDR is high reproducibility and accuracy, better than ±2.5% [15]. The sample fills the two gaps formed between the inner and outer cylindrical surfaces of the rotor, and the stationary cup. The centrifugal forces in the two compartments are different and at low angular velocities, Couette and Searle flows are experienced by the fluid at the inner and outer side of the rotor, respectively. On increasing the angular velocity, the first instability (named Taylor flow) is encountered in the liquid in the outer compartment, which consists of two counter-rotating pairs of vortices overlapped with the Couette flow [16,17]. On increasing the angular velocity, beyond the onset point, the Taylor vortices become wavy and smaller secondary vortices appear (named Gortler vortices). The flow field eventually becomes chaotic if the velocity is increased further [15]. Although the HDR phenomenon is still not clearly understood, according to de Gennes and Tabor [18] the HDR effect can be explained by the interaction of the polymer chain with the small vortices created within the turbulent flow. The process of stretching-contraction of the polymer chain affects the evolution of the vortice cascades (which dissipate the kinetic energy of the fluid) by storing some of the turbulence energy in the chain. The drag reduction effect caused by macromolecules in solution can be directly determined from the difference between the applied torque for the solution and for the pure solvent. To study the thermal stability of the giant micelles, the levels of HDR were determined by keeping the sample at a specific turbulent shearing rate (angular velocity = 612 rpm) and measuring the respective applied torque as a function of the temperature, in the range between 25 and 75 °C (±0.1 °C).

2.2.2. Tensiometer

The cmc of the mixed micelles were determined using surface tension measurements with a Sigma 701 tensiometer and using the du Nouy ring method. All measurements were made at 25 °C (±0.1 °C).

3. Results and discussion

3.1. Thermal stability of giant micelles

The main pre-requisite to observe the HDR effect is the presence of macromolecules with very high molar mass, and this condition is met in giant micellar systems. Although these supramolecular systems are immune to undergoing mechanical degradation, they are sensitive to temperature. Therefore, the combination of turbulent flow and heating allows the determination of temperatures at which the giant micelles are broken.

Fig. 1 shows typical flow curves (applied torque as a function of the temperature) for solutions of 2 mmol L^{-1} of alkyltrimethylammonium surfactants ($C_{12}TAB$, $C_{14}TAB$, $C_{16}TAB$, $C_{18}TAB$) and 1.2 mmol L^{-1} NaSal, in which the angular velocity (Ω) was fixed at 612 rpm and the temperature was raised from 25 to 75 °C (at ca. 0.8 °C/min). The flow curve for water was included in the figure as a guide to interpret the results.

The curve for each surfactant plus salicylate solution is complex, but in a range of temperature, the torques applied for the surfactant solutions are lower than those applied in water, and this is the signature of the HDR effect.

At least, two transitions T_1 and T_2, are observed for the surfactants plus NaSal solutions. The first transition, T_1, was defined at the onset temperature for the drag reduction. The transition is more evident for $C_{18}TAB$ in comparison with the ones for the other surfactants, but its interpretation is still unclear. At T_2, a sharp loss in the capability of the micelles to maintain levels of HDR is associated with the break of the long micelles. In contrast to this sharp transition, a smooth variation was observed when HDR was measured for supramolecular polymers of bis-urea in toluene and octane, indicating, in this case, a progressive fragmentation of the macromolecular aggregates [19]. Therefore we infer that, for the giant micelles, at T_2 a much more drastic break of the structures takes place. Beyond T_2, the sizes of fragments are not long enough to cause HDR, and the determination of their contour length is one attractive aspect to be investigated. We envisage this as a huge task, due to the experimental difficulties to obtain this molecular parameter under turbulent conditions.

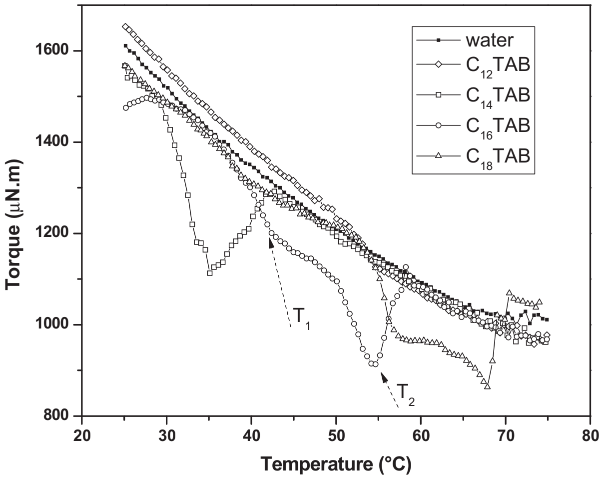

Fig. 1. Thermal-flow diagrams associated with the torque needed to be applied to the solution of the giant micelles to keep the angular velocity at Ω = 612 rpm. The concentrations of alkyltrimethylammonium surfactants ($C_{12}TAB$, $C_{14}TAB$, $C_{16}TAB$ and $C_{18}TAB$) and salicylate were, respectively, 2.0 mmol L^{-1} and 1.2 mmol L^{-1}. The lower torque in a range of temperature, relative to pure water, is the signature of the HDR effect. The effect is not observed for $C_{12}TAB$ in such conditions. The relevant temperatures T_1 and T_2 (in this case associated with the break of the giant micelles) are indicated for the $C_{16}TAB$ system.