Micellar crowding and branching in a versatile catanionic system

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HIGHLIGHTS

- How obstruction and hydration hinder water diffusion.
- The Tokuyama model successfully describes micellar crowding.
- [14]N NMR relaxation reveals fast surface diffusion of DDAB in branched micelles.
- Rheology: oscillatory response related to material elasticity and wall slippage.

GRAPHICAL ABSTRACT
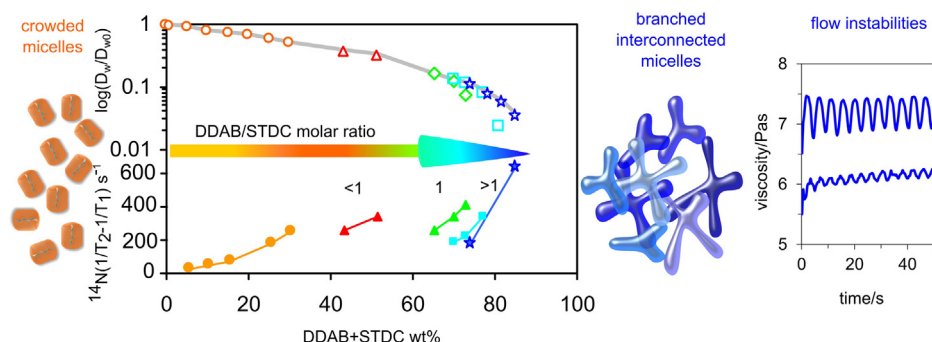
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ABSTRACT

The catanionic system didodecyldimethylammonium bromide (DDAB)-sodium taurodeoxycholate (STDC)-D_2O is characterized by an exceptionally extended L_1 region. The comparison of self-diffusion coefficient of the solvent and the DDAB embedded in the micelles provided information about hydration of the aggregates. Moreover, correlating self-diffusion and ^{14}N NMR relaxation measurements new insight could be obtained regarding the translational and rotational micellar motions in the crowded solutions of systems with 0.2 DDAB-STDC molar ratio. ^{1}H 2D NMR spectra gave some hints about the mutual arrangement of DDAB and STDC within the aggregates. For samples with 1.8 and 2.6 DDAB/STD molar ratios the ^{14}N data were in agreement with the presence of somewhat branched, interconnected micelles. [23]Na and [81]Br dynamic parameters resulted particularly sensitive to the surrounding environment.

The peculiar rheological behaviour of the, highly concentrated, branched micelles samples, namely the steady oscillations in the step tests, was found to be an example of instability originated by the combined effect of material elasticity and slippage at the fixed wall.

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1. Introduction

The association of the two surfactants didodecyldimethylammoniun bromide (DDAB) and sodium taurodeoxycholate (STDC),

which differ under various respects beside charge, gives rise to a variety of intriguing self-assembly motifs, as revealed by Marques et al. [1–4]. STDC is a bile salt (Fig. 1) and the association of bile salts with double-chained surfactants has extensively been investigated in order to understand the assembly of bile salts with phospholipids.

The sodium cholate-lecithin-water system displays a large isotropic phase, L_1, region [5]. It becomes by far more extended in the case of DDAB-STDC-D_2O [1]. Noteworthily, detailed rheological and NMR diffusivity measurements enlightened a dramatic microstructural change occurring at the equimolar line, from dis-

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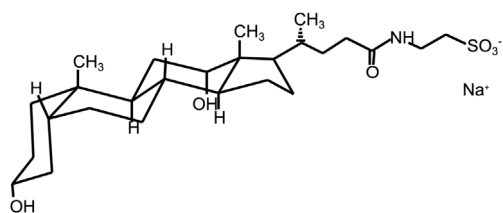
Fig. 1. Molecular structure of sodium taurodeoxycholate.

Table 1
Composition of the samples, volume fractions of dry surfactant and "hydrated micelles" and hydration numbers.

wt%	Φ_{surf}	Φ_{mic}	N_{hydr}
$W_s = 0.2$			
1	0.01	0.03	42
5	0.04	0.12	37
10	0.09	0.21	31
15	0.13	0.30	28
25	0.23	0.48	25
30	0.27	0.56	23
$W_s = 0.4$			
43.3	0.41		
51.5	0.49		
$W_s = 1$			
65	0.63	0.93	11
70	0.68	0.95	9
72.9	0.71	0.97	8
$W_s = 1.8$			
70	0.69	0.97	10
72.9	0.72	0.98	8
77.4	0.76	0.99	7
$W_s = 2.6$			
74.5	0.74	0.99	8
78.5	0.78	0.99	6
82.2	0.81	0.99	5
85.3	0.84	1	4

crete to branched, interconnected micelles [4]. The main subject of the present work are both systems, at high concentrations, at which studies on isotropic systems are not very common. The former kind of aggregates, present at prevailing STDC, are a kind DDAB doped bile salt micelles. They allow the study of crowding in a micellar system. At present, translational and rotational diffusion in concentrated systems of colloidal particles has been arising great interest due to its relevance to technological applications and to biology. The high cytoplasm concentration, 30%, which incidentally matches the maximum considered concentration for the micellar system of DDAB-STDC (at 1:5 molar ratio), is postulated to play a paramount role in the in vivo functioning of proteins.

Conversely, the systems at high DDAB content, which correspond to branched, somewhat interconnected micelles, are a rather rare self-assembly motif and, on the macro scale they are characterized by surprisingly small elastic contributes and viscosities [4]. They will be investigated in order to get deeper insight into their peculiar rheological behaviour, in particular into the oscillatory step rate response [6].

We make an extensive use of multinuclear NMR spectroscopy because it is an unsurpassed technique to study concentrated, isotropic systems, aiming at gaining information on the systems mainly at the microscopic-molecular level, not much considered in the previous studies. Being dynamics and structure intimately related in complex fluids, the relaxation parameters of the quadrupolar nuclei naturally present in the CTAB systems, namely, ^{14}N of DDAB ammonium head-group and ^{23}Na and ^{81}Br of the monoatomic counterions, will be employed, as well as ^{1}H NMR spectra aimed at revealing the mutual arrangement of the two surfactants.

The experimental data are discussed extensively exploiting the analytical tools that are provided by up to date theoretical work. This smart procedure is very convenient to the experimentalist because it allows to gain easily and quickly the significance of the outcomes of the experiments.

2. Material and methods

2.1. Sample preparation

Sodium taurodeoxycholate (95% purity) and didodecyldimethylammonium bromide (98% purity) were used without any further purifications, deuterium oxide (^{2}H$_2$O) is 99% D. All chemicals were purchased from Sigma-Aldrich.

The composition of the samples, expressed by means of the total surfactant concentration, C_s, i.e. (DDAB + STDC) wt%, and of the DDAB/STDC molar ratio (W_s) is reported in Table 1 and Fig. S1. The samples were chosen along five dilution lines, i.e. five different W_s were considered.

The mixtures were carefully heated in water bath at 40 °C, and then stirred using a small magnetic stirrer (for the concentrated ones). They were let to stand at room temperature to attain equilibrium for about one month before any measurement. The phase behaviour of the mixtures was checked under cross polarizers and no birefringence was detected. For the NMR measurements, the samples were transferred into 5 mm Pyrex NMR tubes, which were flame-sealed and left for two weeks at 25 °C to equilibrate.

2.2. Multinuclear NMR measurements

The ^{1}H, ^{14}N and ^{23}Na NMR measurements were carried out at 30 °C on a JEOL Eclipse 400 (9.4 T) NMR spectrometer operating at 399.78 MHz for proton, 107.97 MHz for ^{81}Br, 105.75 MHz for ^{23}Na and 28.89 MHz for ^{14}N. To record the ^{14}N data with a 10 mm probe, the 5 mm tube of the sample was inserted into a 10 mm NMR tube containing water. Temperature was controlled within ±0.5 °C by means of a Jeol NM-EVTS3 variable-temperature unit.

Typically spectral widths of 2.8 kHz over 16 K complex points for ^{1}H, 21.6 kHz over 4 K for ^{81}Br, 1 kHz over 1 K for ^{23}Na, and 1 kHz over 256 complex points for ^{14}N were used, accumulating 16 scans for ^{1}H, 16,000 for ^{81}Br and 8 for ^{23}Na, respectively. For ^{14}N a variable number of scans, between 500 and 4000, was required to obtain satisfactory spectra depending on the DDAB concentration. For the $C_s = 1\%$ sample, due to the low S/N ratio, 8000 scans were accumulated and the number of data points was halved. Prior to Fourier transformation all the data were zero-filled four times, except the ^{14}N ones, which were zero-filled eight times.

The T_1 for ^{14}N and for ^{23}Na were determined by a nonlinear least-squares fit of the inversion-recovery curves obtained using 20 different τ values and the T_2 for ^{23}Na were measured by means of the Hahn echo experiment employing 20 different τ value.

The line-width at half-height, $\Delta\nu_{1/2}$, were provided by the best fit of the line-shape to a Lorenztian function through the Jeol software Delta [7] and the ^{14}N T_2 values by means of the relation $\Delta\nu_{1/2} = \pi^{-1} T_2^{-1}$.

2.3. Rheological measurements

Step rate tests were carried out at 25 ± 0.1 °C on a strain-controlled rheometer RFS III (Rheometrics, USA), equipped with a Couette cell (inner radius 17 mm, gap 1.06 mm) and a Peltier system for temperature control. The samples, which had been homogenized and then kept in a thermostated bath at 25 °C for 24 h, were equilibrated for at least 20 min after filling the geometry and prior to conducting any measurement.