

## Pressure-induced structural transition of nonionic micelles

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**Abstract.** We report dynamic light scattering and small angle neutron scattering studies of the pressure-induced structural transition of nonionic micelles of surfactant polyoxyethylene 10 lauryl ether (C12E10) in the pressure range 0 to 2000 bar. Measurements have been performed on 1 wt% C12E10 in aqueous solution with and without the addition of KF. Micelles undergo sphere to lamellar structural transitions as the pressure is increased. On addition of KF, rod-like micelles exist at ambient pressure, which results in rod-like to lamellar structural transition at a much lower pressure in the presence of KF. Micellar structural transitions have been observed to be reversible.

**Keywords.** Micelles; dynamic light scattering, small angle neutron scattering.

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### 1. Introduction

Micelles are formed by a delicate balance of two opposing forces: while hydrophobic attraction brings the surfactant molecules together, the micelle size is limited by the electrostatic or hydrophilic repulsion between headgroups [1]. These two forces are modified when an external pressure is applied to the micellar solution. It is believed that both the hydrophobic and hydrophilic interactions are weakened on applying pressure [2]. This makes pressure one of the important parameters to tune the structure of micelles. Herein, we report dynamic light scattering (DLS) and small angle neutron scattering (SANS) studies of the pressure-induced structural transition of nonionic micelles of surfactant polyoxyethylene 10 lauryl ether (C12E10). DLS measures the time-dependent fluctuations in the intensity of scattered light [3]. The rate of the fluctuations is determined through the autocorrelation analysis technique. The calculated autocorrelation function enables the determination of the diffusion coefficient, which then can be used to predict the structural transitions. On the other hand, SANS with the possibility to vary the contrast is an ideal technique for studying hydrogenous systems such as micellar solutions. It provides information about the geometry and conformation of the scattering particles [4].

## 2. Experimental

Nonionic surfactant C12E10 was purchased from SIGMA. Samples were prepared by dissolving known amounts of surfactant and salts in D<sub>2</sub>O. The use of D<sub>2</sub>O as solvent instead of H<sub>2</sub>O provides better contrast for hydrogenous components in neutron experiments. All the measurements were performed on 1 wt% C12E10 in aqueous solution with and without the addition of KF. Pressure dependence measurements were performed using a 5000 bar high-pressure cell having two parallel thick sapphire windows [5]. An in-house built DLS set-up was used that can mount this pressure cell. Small angle neutron scattering experiments were performed on the SANS-I instrument at the Swiss Spallation Neutron Source, SINQ, Paul Scherrer Institut, Switzerland [6].

## 3. Analysis of data

The signal generated by the light scattering from diffusing particles can be analysed by its intensity autocorrelation function  $g^I(\tau)$  [3]

$$g^I(\tau) = 1 + C \exp(-2DQ^2\tau), \quad (1)$$

where  $C$  is an experimental parameter which mainly depends on the detection optics and alignment.  $D$  is the diffusion coefficient of the particle and  $Q$  is the magnitude of wave vector transfer. The hydrodynamic size related to  $D$  is calculated using Stoke–Einstein relationship.

In SANS experiment one measures the coherent differential scattering cross-section ( $d\Sigma/d\Omega$ ) as a function of wave vector transfer  $Q$ . For a system of monodisperse particles, it is given by [4]

$$\frac{d\Sigma}{d\Omega}(Q) = n(\rho_p - \rho_s)^2 V^2 P(Q) S(Q), \quad (2)$$

where  $n$  is the number density of the particles,  $\rho_p$  and  $\rho_s$  are, respectively, the scattering length densities of the particle and the solvent, and  $V$  is the volume of the particle.  $P(Q)$  is the intraparticle structure factor and is decided by the shape and size of the particle.  $S(Q)$  is the interparticle structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to interparticle interactions. In the case of dilute solutions, interparticle interference effects are negligible, and  $S(Q) \sim 1$ .

## 4. Results and discussion

DLS data on C12E10 micelles with varying pressure are shown in figure 1. The measurements are performed on two samples in the absence and presence of salt KF. Figure 1a shows the data on the pure 1 wt% C12E10 micellar solution. At pressures up to 1700 bar, DLS data show a single decay which correspond to about 80 Å hydrodynamic size (diameter) of the micelles. As the pressure is increased beyond 1700 bar, a very slow second decay is developed, whose contribution increases

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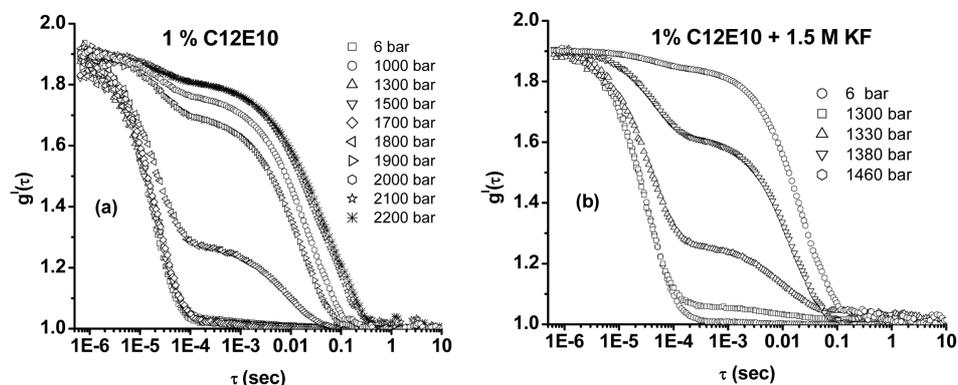


Figure 1. DLS data of pressure effect on (a) 1 wt% C12E10 and (b) 1 wt% C12E10 in the presence of 1.5 M KF.

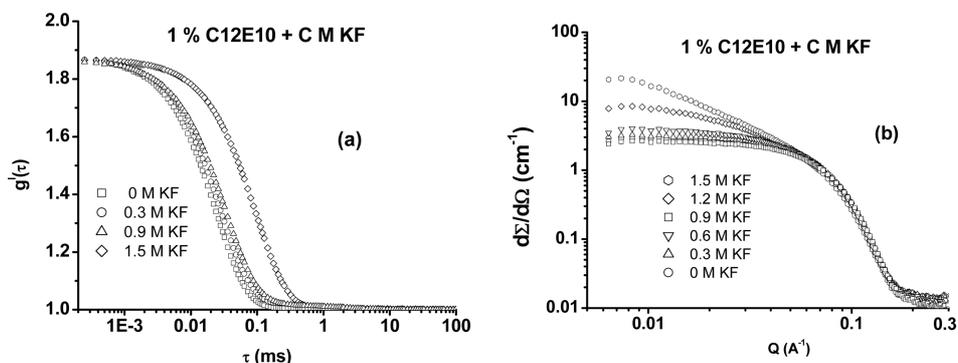


Figure 2. (a) SANS and (b) DLS data on 1 wt% C12E10 in the presence of varying KF concentrations.

with increasing pressure. This is clearly an indication of some type of structural transition of C12E10 micelles with pressure. On addition of KF (figure 1b), the pressure required to induce structural transition of C12E10 micelles is brought down to approximately 1300 bar from 1800 bar.

The effect of the addition of KF on C12E10 micelle is explained in figure 2. DLS and SANS data on C12E10 micelles at varying concentrations of KF are shown in figure 2. It is observed in DLS data that the decay of autocorrelation function becomes slower with increase in concentration KF. This is an indication of increase in the size of the micelle on addition of KF. SANS data show a build-up of scattering intensity in the low- $Q$  region approaching  $1/Q$  dependence with the addition of KF. This suggests that the micelles grow and spherical micelles in the absence of salt transform to rod-like at higher KF concentrations [7].

Figure 3 shows the reversibility of the pressure-induced structural transition when the pressure is decreased. The data are measured at different times when the pressure is lowered from 1400 bar to 900 bar. These results show that it takes more than half an hour for the pressure-induced structure to get back to its original state.

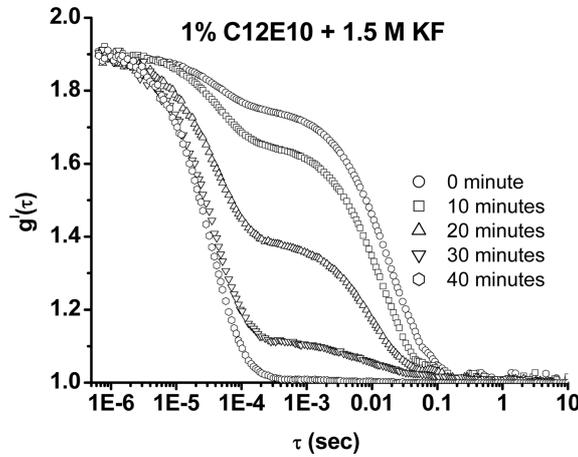


Figure 3. DLS data of time evolution of reversibility of micellar structural transition when the pressure is decreased to 900 bar from 1400 bar.

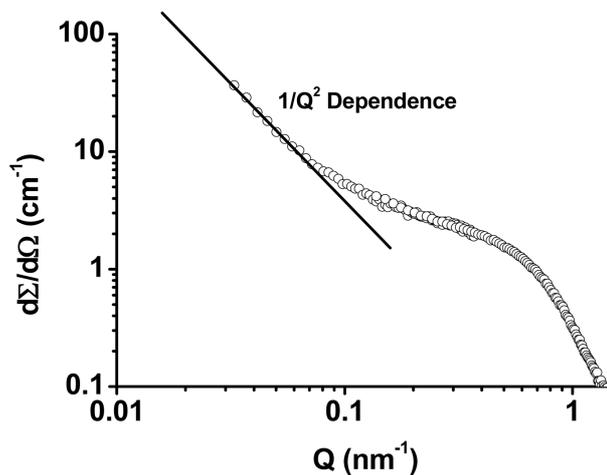


Figure 4. SANS data on 1 wt% C12E10 micellar solution at a pressure of 2000 bar.

Figure 4 shows the SANS data on 1 wt% C12E10 micellar solution at a pressure of 2000 bar. At higher  $Q$  region, the data show a similar  $Q$  dependence to that at ambient pressure (figure 2b). However, in the low- $Q$  region the data show a linear region on log-log scale with a slope of  $-2$ . This SANS result in combination with the DLS results of very slow decay of micellar structures at higher pressure suggests the formation of lamellar structure [8]. This transition perhaps occurs as a result of a strong pressure-induced weakening of the hydrophilic over hydrophobic interactions. It is also clear from figures 1 and 4 that both the micelles and lamellar structure coexist at high pressures in these systems.

In summary, DLS and SANS studies show nonionic C12E10 micelles undergoing sphere to lamellar structural transition as the pressure is increased. On addition of

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KF, rod-like micelles exist at ambient pressure, which results in rod-like to lamellar structural transition at a much lower pressure in the presence of KF. These micellar structural transitions have been observed to be reversible.

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