

THE EFFECT OF PRESSURE ON THE KINETICS OF SODIUM  
LAURYL SULFATE MICELLE FORMATION

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INTRODUCTION

In the past decade rapid advances have been made toward the elucidation of the kinetics of micelle formation [1,2]. The micellar processes which occur are relatively fast (half-lives less than one second) and must therefore be studied using special techniques, such as temperature-jump, pressure-jump or ultrasonic absorption methods. In the time range extending from  $1/10^9$  seconds to 1 second, two or three relaxations have been observed. Several processes have been postulated to account for the relaxations. For an anionic detergent these include: (1) Association/dissociation of a single detergent molecule to/from a micelle:



(2) Counterion association/dissociation to/from the micelle:



(3) Micellization/dissolution:



(4) Micelle aggregation:



(5) Change of micelle shape:



For pure surfactants the three relaxations can only be detected at concentrations above the critical micelle concentration (cmc). One of the three relaxations has been observed only at high surfactant concentrations. Graber et al. [3] attributed this relaxation ( $\tau_0$ ) to changes of micelle shape (Eq. (5)).

In the microsecond time range a relaxation ( $\tau_1$ ) has been detected by ultrasonic absorption [3,4] and shock tube methods [5]. Yasunaga et al. [4] suggested that this relaxation was due to counterion binding (Eq. (2)). However, Graber et al. [3] postulated that a monomer exchange process was responsible for  $\tau_1$  (Eq. (1)).

In the millisecond time range a relaxation ( $\tau_2$ ) has been detected by temperature-jump, pressure-jump and stopped-flow methods [5,6]. This relaxation has been attributed to micelle aggregation (Eq. (4)) by Colen [8] and to a stepwise micellization/dissolution process (Eq. (3)) by Hoffman et al. [1].

The effects of concentration, temperature, ionic strength, type of surfactant head group and counterion, and hydrocarbon chain length on the relaxation times have been investigated [1-7]. However, the effects of pressure have been neglected. We have, therefore, investigated the effects of pressure on the kinetics of sodium lauryl sulfate (also called sodium dodecyl sulfate, SDS or NaLS) micelle formation.

#### MATERIALS AND METHODS

A temperature-jump apparatus has been constructed which is capable of operating at pressures up to 1200 atmospheres (Fig. 1). The apparatus is equipped to detect light scattered  $90^\circ$  from the incident beam. A Hanovia 901B-11 mercury-xenon lamp was used as a light source. To keep the light intensity as high as possible, no monochromator or filters were used. Scattered light was detected by an EMI 9558Q photomultiplier tube. The current from the photomultiplier was fed through a nulling-filtering circuit to a Biomation 610 transient recorder. The final output could be displayed on a chart recorder, on an oscilloscope, or in digital form on paper tape.

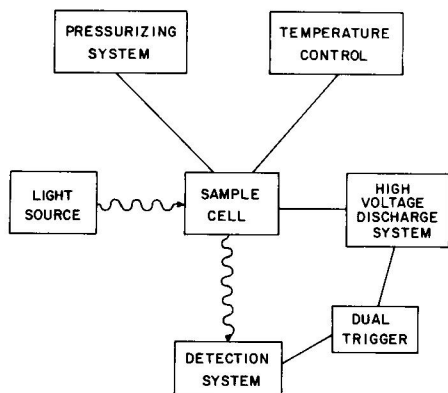


Fig. 1. The temperature jump apparatus.

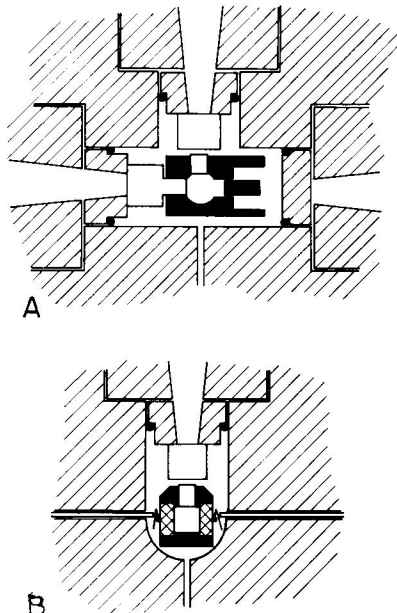


Fig. 2. The sample cell in place within the pressure vessel: a) side view cross-section, b) end view cross-section.

The pressure vessel was constructed from No. 17-4 PH stainless steel and was cylindrical in shape (16.5 cm length, 15.25 cm diameter). A 2.86 cm hole was drilled through the center along the cylindrical axis. A second 2.86 cm hole was drilled perpendicular to the first for observation of light scattered at  $90^\circ$ . Details of the pressurizing system, high-voltage discharge system, and high-pressure electrical leads have been described elsewhere [9].

Sapphire windows were anchored with epoxy to stainless steel seats (Fig. 2). These seats were held in place by plugs which screwed into the pressure vessel. Viton O-rings prevented the pressurizing fluid from flowing past the seats. The sample cell was constructed from black delrin. Stainless steel electrodes (1.27 cm diameter) were situated parallel to the light path. The volume contained by the sample cell was one milliliter. A movable delrin plug compensated for volume changes of the sample solution. The sample cell was surrounded by silicone oil. This liquid acted both as a pressurizing fluid and as an insulator which prevented the high voltage from shorting to the pressure vessel. The electrodes, windows, and movable plug were wrapped with teflon tape and snugly fitted into the delrin sample cell. To prevent shear stresses from breaking the sapphire windows, the exit window was separated into two pieces. A thin layer of transparent silicone oil transmitted light between the two window parts.

Sodium lauryl sulfate (BDH--Gallard-Schlesinger) was purified by successive extractions with diethyl ether and recrystallizations from water. Evidence of purity was provided by surface tension measurements which showed a monotonic

decrease with increasing surfactant concentrations for aqueous solutions. All solutions were prepared from deionized, double-distilled water. All solutions contained 0.2 molal NaCl to raise the conductance. All cell parts which were to be exposed to the sample solutions were thoroughly cleaned and rinsed with filtered water in order to minimize dust. Immediately prior to introduction into the sample cell, the solution was filtered through a 0.22  $\mu\text{m}$  Millipore filter.

Temperature jumps were made from  $21 \pm .1^\circ\text{C}$  to  $25 \pm .3^\circ\text{C}$ . The size of the temperature jump was calibrated using a phenol red solution.

### RESULTS

The critical micelle concentration for sodium lauryl sulfate in 0.2 molal NaCl is approximately  $10^{-3}$  molal [10]. For surfactant concentrations below  $10^{-3}$  molal, no relaxations could be detected by our apparatus. This is in agreement with the findings of other researchers [1,5].

For concentrations between the cmc and three times the cmc, only one relaxation characterizable by a single exponential was observed. The amplitudes of the relaxation indicated that the intensity of scattered light was decreasing with increasing temperature. This relaxation appears to be the same " $\tau_2$ " observed by other investigators [6,11,12]. Figure 3 and Table I demonstrate that pressures up to 680 atm. have no discernable effect on this relaxation time.

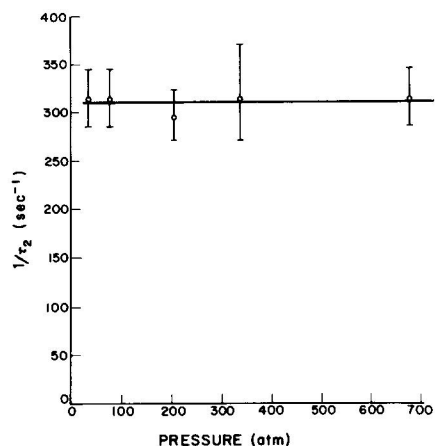


Fig. 3. Plot of reciprocal relaxation time,  $\tau_2^{-1}$  vs. pressure for 0.003 molal SDS, 0.2 molal NaCl at  $25^\circ\text{C}$ .

Hoffmann et al. [1] have developed an expression relating  $\tau_2$  to the parameters of a stepwise micellization/dissolution mechanism:

$$\tau_2 = \left[ \sum \left( \frac{1}{k_s^- \bar{A}_s} \right) \right] \left( \bar{A}_1 (1 - (\sigma^2/n)) \right) + \left( \sigma^2 A_T \right) / (n) / (n^2) \quad (6)$$

The results reported here indicate either that pressure causes each parameter to vary in such a way that the effects cancel, or more probably that pressure has only a small effect on each parameter.

Table I. Relaxation Time  $\tau_2$  and  $\tau_3$  for SDS at Different Pressures and Concentrations (25°C and 0.2 molal NaCl)\*

Concentration \ Pressure (atm)	0.001 molal		0.002 molal	
	$\tau_2$ (ms)	$\tau_3$ (ms)	$\tau_2$ (ms)	$\tau_3$ (ms)
34	2.5	N.D.	2.5	N.D.
68	2.6	N.D.	2.4	N.D.
204	2.5	N.D.	2.6	N.D.
340	2.6	N.D.	2.4	N.D.
476	N.D.	N.D.	2.5	N.D.
680	N.D.	N.D.	2.3	N.D.
Concentration \ Pressure (atm)	0.003 molal		0.01 molal	
	$\tau_2$ (ms)	$\tau_3$ (ms)	$\tau_2$ (ms)	$\tau_3$ (ms)
34	3.2	N.D.	2.2	38.8
68	3.2	N.D.	2.1	43.6
204	3.4	N.D.	2.0	50.8
340	3.3	N.D.	2.0	68.4
680	3.2	N.D.	1.9	87.3
Concentration \ Pressure (atm)	0.03 molal		0.05 molal	
	$\tau_2$ (ms)	$\tau_3$ (ms)	$\tau_2$ (ms)	$\tau_3$ (ms)
34	2.1	19.7	1.6	9.2
204	2.0	30.2	1.6	10.9
340	2.0	39.3	1.5	22.3
680	1.9	60.9	1.6	43.7

\* The standard deviations of the relaxations were typically between 10 and 15 percent of the mean value.

N.D. means not detectable.

No relaxation was detected that could have been associated with  $\tau_1$ . This suggests that the process responsible for  $\tau_1$  does not cause significant changes in the intensity of scattered light.

At relatively high surfactant concentrations (0.01 molal and above) a second, slower relaxation was observed. As with  $\tau_2$ , the amplitudes of the relaxation indicated that the intensity of scattered light decreased with increasing temperature. This can not be the relaxation designated  $\tau_0$  since Graber et al. [3] reported that  $\tau_0$  was in the nanosecond time range. Thus, we have labeled the new relaxation " $\tau_3$ ". Table I and Fig. 4 show that  $\tau_3$  increases significantly with increasing pressure. At low pressures  $\tau_2$  and  $\tau_3$  may be so close that it is possible to mistakenly perceive the two relaxations as one. However, the application of pressure effectively resolves the two relaxations. Table I also shows that  $\tau_3$  decreases significantly with increasing concentration. At low surfactant concentrations it is possible that  $\tau_3$  may occur in a time range too slow to be detected by our apparatus (one second or more).

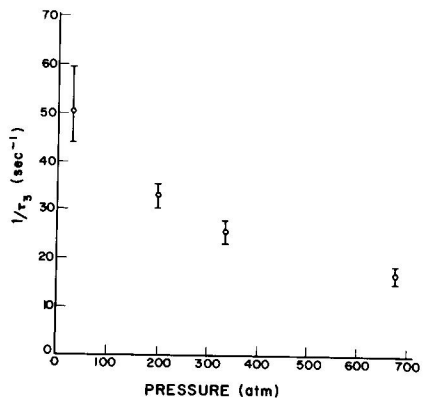
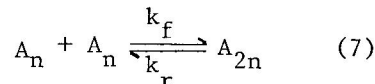


Fig. 4. Plot of reciprocal relaxation time,  $\tau_3^{-1}$  vs. pressure for 0.03 molal SDS, 0.2 molal NaCl at 25°C.

Sodium lauryl sulfate is known to form spherical micelles at concentrations near the cmc and rod-shaped micelles at high surfactant concentrations [13]. Thus, changes in micelle shape may be responsible for  $\tau_3$ . Shape changes could occur by a micellar aggregation/dissociation process (Eq. 4). Large, rod-shaped micelles could break up into (or be formed from) two or more small, spherical micelles. This mechanism could account for the concentration dependence of  $\tau_3$ . Higher surfactant concentrations result in more micelles (of all shapes and sizes), which in turn allow the aggregation process to proceed at higher rates. Assuming that micellar aggregations can be simply described by the process



an expression can be developed which relates  $\tau_3$  to the rate constants:

$$1/\tau_3 = k_r + 4k_f \bar{A}_n \quad (8)$$

Assuming  $\bar{A}_n$  increases linearly with total surfactant concentration, then

$$1/\tau_3 = k_r + K k_f A_T \quad (9)$$

Equation (9) is consistent with the observed variation of  $1/\tau_3$  with concentration. Using Eq. (9) and the data from Table I, an activation volume of about 70 ml/mol has been calculated for the forward step.

Hoffmann et al. [1] have argued that micellar aggregation is improbable because of the electrostatic repulsion between the micelles. However, under conditions of high ionic strength and high concentrations of micelles, aggregations are more likely to occur. The fact that  $\tau_3$  appears to be the slowest of the micellar relaxations may be due to the size and charge of the aggregating species.

Shape changes could also result from a stepwise association (or dissociation) of monomers into (or from) micelles. The concentration and pressure dependence of  $\tau_3$  could be rationalized using this mechanism. However, it would be difficult to explain why  $\tau_3$  is slower than  $\tau_2$ . In Hoffmann's model,  $\tau_2$  is caused by a stepwise micellization/dissolution process [1]. The concentrations of micelles having aggregation numbers greater than one but less than the mean aggregation number are very low [13]. The rate limiting step in the  $\tau_2$  process is believed to be the aggregation of singly dispersed surfactant molecules with these micelles [1]. If a stepwise mechanism is also responsible for shape changes, then the concentrations of all reacting species would be high, and  $\tau_3$  would be expected to be faster than  $\tau_2$ . Thus, the stepwise mechanism for changes of micelle shape does not adequately explain the results.

In summary, a new relaxation is reported for sodium lauryl sulfate micelle formation. Application of pressure effectively resolves the new relaxation from a previously reported relaxation. The new relaxation is tentatively attributed to micellar aggregation.

#### ACKNOWLEDGMENT

The authors would like to thank Professor P. Mukerjee for advice and aid in the purification of SDS.