

# SURFACTANTS IN SOLUTION

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## PRESSURE-JUMP STUDIES ON MICELLAR RELAXATION TIME AND ITS EFFECT ON VARIOUS TECHNOLOGICAL PROCESSES

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The stability of micelles can be characterized by several methods. Jump techniques have proven most useful, where the relaxation of a physical parameter is observed as the system goes from one thermodynamic state to another. Fast ( $\tau_1 < 100 \mu\text{s}$ ) and slow ( $\tau_2 > 1 \text{ ms}$ ) relaxation processes have been observed in surfactant solutions. The pressure-jump technique has been used to characterize slow relaxation for many ionic surfactant solutions and mixtures.

Micellar stability influences many processes of interest (e.g. foaming, wetting, solubilization, etc.). It can be shown that a maximum in micellar relaxation time (which is related to the micellar stability) correlates to reduced foamability, a minimum in fabric wetting rate, a maximum in gas bubble size and emulsion droplet size, and a maximum in oil and hydrophobic solids (dye) solubilization rates in micellar solutions.

### INTRODUCTION

The association of many classes of surface active molecules into micellar aggregates in solution is a well known phenomenon. The presence of micelles

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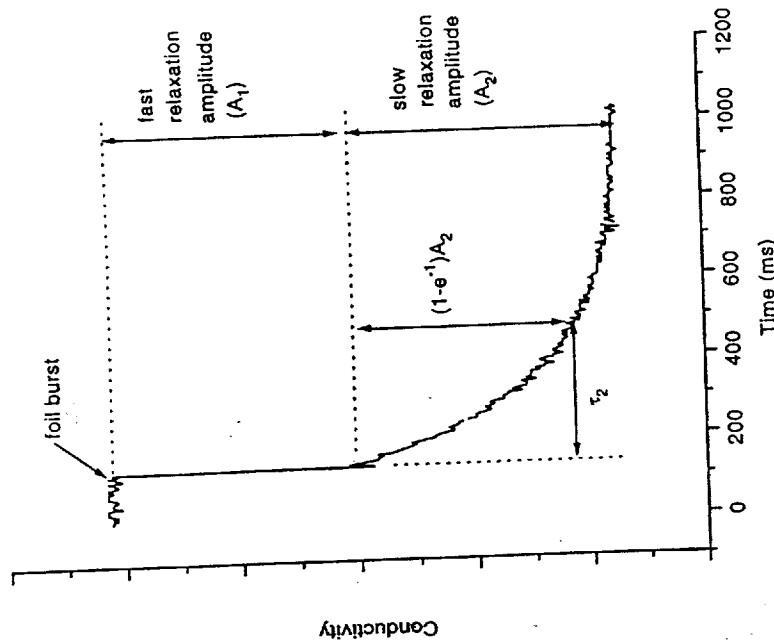


Figure 1. Typical pressure-jump conductivity signal.

#### Measurements Using Pressure-Jump

A good review of the literature on the kinetics of micellization was written by Muller<sup>1</sup>. This review covers relaxation measurements for both fast and slow relaxation times. There are 24 articles mentioned in this review paper concerning pressure-jump measurements, covering the period 1972 to 1978. The author notes that the slow relaxation kinetics have been investigated for anionic detergents with varying carbon number and different counterions, as well as a number of the cationic surfactants, but little has been published on the zwitterionic and nonionic surfactants. An additional review was published shortly thereafter<sup>2</sup>, and a later review of chemical relaxation methods was published by Lang and Zana<sup>3</sup> in 1987. There are relatively few references in the period after Muller's review. Table 1 briefly summarizes these additional pressure-jump data and the excursions performed in each investigation<sup>4-15</sup>.

30 seconds, allowing equilibrium to be reached, and then the pressure is suddenly released (in approximately 1 microsecond by the foil rupture) to ambient pressure. Both the fast and slow relaxation phenomena are clearly visible in this graph. The fast relaxation time,  $\tau_1$ , accounts for half of the initial drop. The remaining drop is the exponential decay due to the slow relaxation time. The time coefficient  $\tau_2$ , measured from this curve is 0.2 seconds.

One can visualize the effect of the pressure drop on the surfactant population. At high pressure, there are fewer micelles, and a higher monomer concentration. When the pressure is reduced, the equilibrium cmc is lower and thus the system wants to form more micelles and reduce the monomer concentration. The fast relaxation process involves individual surfactant molecules entering neighboring micelles. The monomer concentration is reduced very quickly, in just microseconds, and the resulting drop in conductivity can be seen in figure 1. Under this situation, however, no more micelles have been formed, and the micelles that do exist have each absorbed a few additional monomers resulting in an increase in aggregation number. The slow relaxation process serves to correct this, as micelles will be created from the remaining excess pool of monomers which are still above the cmc. The undesirably large micelles will also change, either disintegrating entirely, shedding a few monomers by the fast relaxation process, or disintegrating and re-forming from monomers in solution, to reach the desired aggregation number. We assume the same relaxation time for micelles with a slightly larger aggregation number than the equilibrium value. This whole process is the much slower "slow relaxation process" as measured by  $\tau_2$ , and seen in Figure 1, and can take anywhere from milliseconds to seconds. The gradual decrease in solution conductivity is observed while all this activity is going on.

An example of the apparatus used for pressure-jump measurements is that of Dia-Log GmbH, Düsseldorf, Germany. In this apparatus a surfactant solution sample and a salt (KCl) solution of equivalent conductance form two opposing resistances in a bridge circuit. The two samples are pressurized equally in an autoclave up to a pressure of 120 bar. Sufficient time is given, usually at least five times the expected relaxation time, for the system to equilibrate. The pressure is then increased slightly above 120 bar, where a foil tape on one end of the pressurized chamber will burst, releasing the pressure back to ambient in less than 100  $\mu$ s. By comparing the conductivity of the two cells using the bridge circuit, the relaxation of the conductivity from the high pressure value to the ambient pressure value will be observed. Both the fast and slow relaxation times are observable (Fig. 1), but only the time constant of the slow process can be determined. The relative amplitudes of both the fast and slow processes can be determined.

repulsion in the micelles is minimized. At 200 mM for SDS at 25°C, micellar stability ( $\tau_2$ ) is maximum. The maximum  $\tau_2$  shifts to lower SDS concentrations upon addition of salt to the solutions<sup>12</sup>. A supporting evidence for a structural transition in the vicinity of 200 mM was found recently using fluorescence and spin label probes<sup>25</sup>. In the range of 100 to 200 mM SDS, the fluorescent probes indicate a change in the micelle interior microenvironment polarity and viscosity, and the spin label evidence shows a change in the motional freedom of the surfactant molecules and their segments. Both of these results can be explained by an increase in the molecular packing in micelles up to 200 mM SDS, and a shape change from spherical to cylindrical micelles beyond 200 mM SDS concentration.

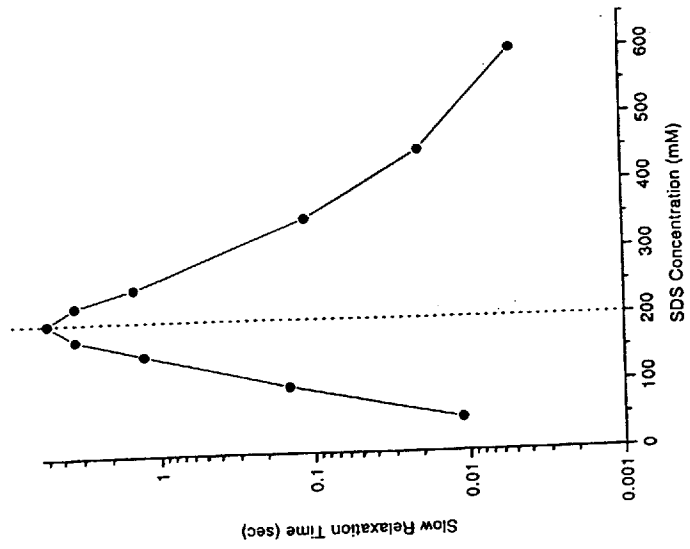


Figure 2. Slow relaxation time vs. SDS concentration.

### SOME EXPERIMENTAL RESULTS ON MICELLAR RELAXATION TIME

Figure 2 shows the slow relaxation time ( $\tau_2$ ) of SDS solutions at 25°C as a function of concentration. The cmc at this temperature is 8.2 mM. At this

concentration,  $\tau_2$  is less than a millisecond. As the concentration increases up to 200 mM,  $\tau_2$  increases up to a maximum of 5.0 seconds, but  $\tau_2$  decreases from this maximum as the concentration increases further. The molecular mechanism for change in relaxation time as a function of concentration was proposed by Oh, et al.<sup>23,26</sup>

### Addition of Alcohols

The micellar stability of SDS can be greatly influenced by the presence of other species. The addition of alcohols of various carbon numbers<sup>14</sup> (Fig. 3) shows that micellar stability of 100 mM SDS solutions is decreased by the addition of methanol, ethanol, propanol and butanol. These short chain alcohols are thought to labilize the micelles, lowering the activation energy of formation of the micelle nucleus size, or decreasing the activation energy of formation of the micelle nuclei. For pentanol, a region exists, up to 50 mM, where stability is enhanced.

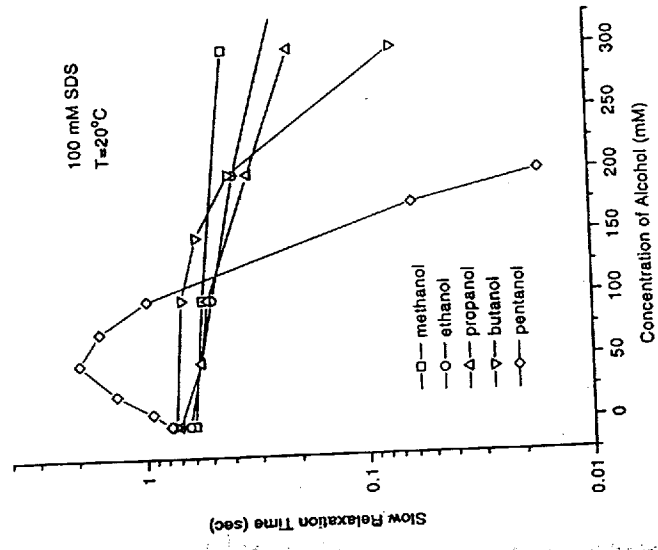


Figure 3. Variation of the slow relaxation time ( $\tau_2$ ) of 100 mM SDS as a function of alcohol concentration.

a maximum occurred upon adding 50 mM of hexanol.

### Oil Solubilization and Detergency

The rate of solubilization of oil is also influenced by micellar stability. This process can be simulated by measuring the rate of solubilization of an oil into a micellar aqueous solution across an oil/water interface<sup>26</sup>. It is shown in Figure 5 that the maximum rate of solubilization of a given amount of benzene into an SDS solution occurs at a concentration of 200 mM, where  $\tau_2$  is the highest. The proposed explanation for this behavior is that the most stable micelles provide a more hydrophobic environment in their cores than less stable micelles. This hydrophobic environment allows a more rapid solubilization of nonpolar molecules into the aqueous solution.

Greater detergency action is also provided by stable micelles. Figure 5 shows the solubilization of an oil soluble dye, Orange OT, into SDS solutions of varying concentrations. In this experiment, fabric was treated with a benzene solution of the dye, and the benzene was allowed to evaporate. The fabric was then placed into an agitated solution of SDS. Solubilization of the dye represents the ability to clean a fabric of adsorbed hydrophobic materials. The maximum rate of solubilization of dye occurred at 200 mM<sup>26</sup>.

### Bubble formation

Any process involving the formation of bubbles in a surfactant solution will be influenced by the dynamic surface tension at the forming air/water interface. A reduction in the surface tension will lower the energy required to form a new interface. For spherical bubbles, the area per volume is  $3/r$ , where  $r$  is the radius of the bubble. If the surface tension is high, the required area for a given volume of gas is minimized by increasing the bubble radius. A reduction of surface tension is achieved by populating the interface with surface active molecules. The availability of surfactant is influenced by micellar stability, and a higher surface tension and larger bubble radius will result from a high micelle stability.

Above 50 mM SDS concentration, the increasing lifetime of the micelles has a noticeable effect in slowing down the surface tension reduction of the forming bubbles by limiting the supply of monomers, resulting in bubbles of larger radii (Fig. 5). The bubble radius increases up to 200 mM, also the maximum in  $\tau_2$  for SDS, and then falls, along with the decrease in micellar stability above 200 mM.

of the cmc, and any surfactant beyond that will be in the micellar form.

In a process where the interface is being created at a sufficiently rapid rate, the bulk phase monomer concentration in the vicinity of this new interface will become depleted. For the monomer population to be re-supplied from micelles, it is required that the micelles disintegrate. Of course, some monomers can leave the micelles in a very short time, as governed by the fast relaxation process. However, this is limited because the micelles have a desired aggregation number, so only a few monomers could depart by the fast process and leave micelles with aggregation numbers near their desired value. The bulk of the re-supply of the monomer population must occur through a disintegration of the micelles, a process quantified by the slow relaxation time,  $\tau_2$ . In cases where the micelles are most stable, and  $\tau_2$  is large, the micelles will not replenish the monomer population fast enough to satisfy the demands of the growing interface, and thus surface or interfacial tension will be higher than the equilibrium value.

One may wish to operate a process in a regime where a higher surface tension is desired, and thus create interface fast enough or have conditions consistent with the most stable micelles. Alternately, it may be desirable to have the lowest surface tension possible, and the creation of new interface will either have to be slow enough or solution conditions will need to be chosen so that the micelles are not very stable.

The following sections cover a range of phenomena that occur in industrial processes, such as foaming, solubilization, emulsification, bubble creation, and fabric wetting. The influence of micellar stability on these phenomena is described.

### Foamability

The production of foam is enhanced by the presence of surface active molecules. Without surfactant, the surface tension of the air/water interface is too high (approximately 72 dyne/cm at 20°C) and the foam immediately breaks. Foamability and foam stability over time are influenced by the surface tension of the air/water interface, the surface viscosity, the viscosity of the liquid in the foam film, foam bubble size, and diffusion of gas through the liquid film<sup>27</sup>.

During foam formation, the stability of micelles influences the ability of surfactant to populate newly created foam surfaces. A reduced foamability (Fig. 5) for SDS solutions at the point of maximum  $\tau_2$  (200 mM) has been demonstrated<sup>15</sup>. A minimum in foamability at the maximum in  $\tau_2$  is also found to be true for the mixtures of SDS and hexanol. In the case of 50 mM SDS solutions, a maximum in  $\tau_2$  occurred upon addition of 70 mM of hexanol, whereas for 100 mM SDS solutions,

4. At the second critical concentration of surfactant, foamability is minimum, the emulsion droplet size is maximum, the rate of wetting is slowest, the rate of solubilization is fastest, and the detergency is maximum.
5. The kinetics of micelles or relaxation processes in micelles are very important in influencing the efficiency of various technological processes such as foaming, emulsification, wetting, and detergency.

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