Ultrasonic Relaxation Associated with a Water Exchange Process in Concentrated Surfactant Solutions and Lyotropic Liquid Crystals

By GORDON J. T. TIDDY
(*Unilever Research, Port Sunlight Laboratories, Port Sunlight, Wirral, Merseyside* L62 4XN)
and MICHAEL F. WALSH and EVAN WYN-JONES
(*Department of Chemistry and Applied Chemistry, University of Salford, Salford* M5 4WT)

Summary Ultrasonic relaxation measurements on a variety of surfactant solutions in the micellar and liquid crystalline phases show a relaxation process whose width is slightly broader than that expected for a single relaxation time, the origin of which is attributed to a pertubation of an equilibrium involving 'bound' and 'free' water molecules; in the vicinity of the boundaries which separate different phases of the surfactant solutions, an additional relaxation process has been observed.

WHEN surfactants are dissolved in water, micelles are formed at the critical micellar concentration (CMC). Once micelles are formed the monomer surfactant concentration remains fairly constant, and any further surfactant added is present in the solution in the form of micelles. As the concentration of surfactant is increased further, the micelles can sometimes change shape and in many surfactant solutions there is a phase change from an isotropic micellar solution to a lyotropic liquid crystalline phase. Several different lyotropic liquid crystalline phases have been identified, these being the lamellar, hexagonal, reversed hexagonal, and cubic phases.[1-3]

Anionic, cationic, and non-ionic surfactants can form these liquid crystalline phases[1-3] and the phase diagrams of many individual surfactants are well characterised. The transition between isotropic micellar solution and liquid crystalline phase, or between different liquid crystalline phases, is usually first order. However, the two phase regions are often narrow for two component systems (surfactant + water) but can be much larger for mixtures with more components. The transition to different phase structures can arise as a result of concentration and/or temperature changes.

In dilute isotropic solutions of surfactants containing micelles, chemical relaxation studies have proved useful in understanding the kinetics associated with the formation of micelles. Two relaxation times have been identified,[4] one in the sub-microsecond range associated with monomer micelle exchange, and one in the millisecond range which is concerned with the dissolution of the micelle. For many surfactants in dilute solution, the fast relaxation time has been extensively studied using the ultrasonic method. There is, however, very little information about the chemical relaxation behaviour of concentrated surfactant solutions or lyotropic liquid crystals.

We report here the results of our preliminary investigations of concentrated micellar solutions and lyotropic liquid crystals prepared from a range of surfactants. The relaxation process observed appears to arise from the exchange between surfactant bound and free water.

The ultrasonic measurements were carried out using an Eggers' resonance method and also a conventional pulse technique covering the frequency range 0·5—100 MHz. The following surfactants are commercial products which were carefully purified before use: Aerosol OT (Fischer Scientific Co., U.S.A.), pentaethylene glycol dodecyl ether ($C_{12}EO_5$) and tetraethylene glycol dodecyl ether ($C_{12}EO_4$) (both Nikkol Ltd., Japan), monocaprylin (Unilever Ltd.), mono-olein (Eastman Ltd.), sodium octyl sulphate (Cambrian), sodium dodecyl sulphate (Henkel), cetyltrimethylammonium bromide CTAB (B.D.H.), and caesium oleate.

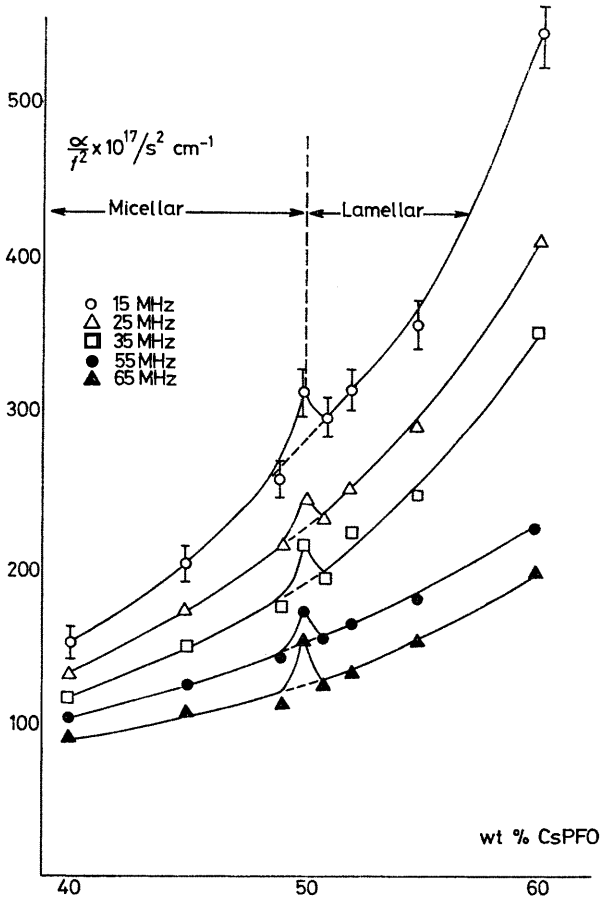

FIGURE 1. CsPFO–H_2O system at 41 °C.

Caesium perfluoro-octanoate (CsPFO) and caesium oleate were prepared by neutralising caesium carbonate (Cambrian) with pentadecafluoro-octanoic acid (Fluorochem) and oleic acid (B.D.H.), respectively. When solutions of these surfactants were investigated in the liquid crystal forms, the phase structures were checked using optical polarisation microscopy.

An investigation of the concentration dependence of the fast relaxation process in sodium octyl sulphate shows that in isotropic micellar solutions at high surfactant concentration (*ca.* 1 M) the amplitude of the monomer–micelle exchange process becomes very weak and eventually cannot be detected. At the same time a new relaxation process with a much lower relaxation frequency (<1 MHz) is observed, whose amplitude increases with increasing surfactant concentration. A relaxation process showing similar concentration dependence has been observed in concentrated micellar solutions of CsPFO, sodium dodecyl sulphate, $C_{12}EO_5$, and caesium oleate, but, surprisingly, not in micellar solutions of CTAB up to 0·9 M. Ultrasonic absorption measurements have also been carried out in liquid crystals formed from CsPFO, Aerosol OT, $C_{12}EO_4$, mono-olein, and monocaprylin. As a result of their high viscosity it is only possible to carry out pulse measurements over the frequency range 15—105 MHz in many of the phases. A relaxation is observed in all cases and the typical behaviour of α/f^2 across different phase boundaries is shown in Figures 1 and 2. These data show that there is a sharp

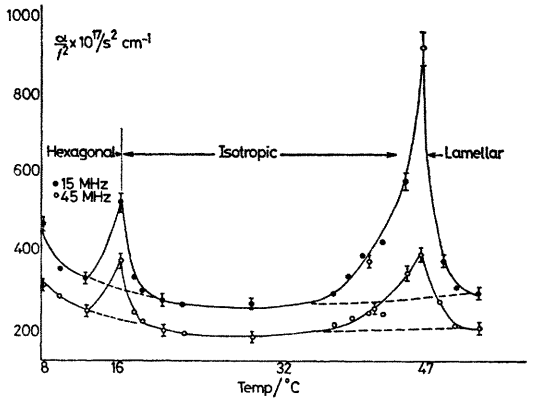

FIGURE 2. 42·5 wt % $C_{12}EO_5$–H_2O system.

increase in α/f^2 at temperatures and concentrations close to phase boundaries. A relaxation process is also observed at temperatures and concentrations well separated from the phase boundaries. To a first approximation we can assume that the contribution to α/f^2 from this relaxation process and the prominent effect close to the phase boundaries are additive. This means that the two effects can be resolved as shown in Figures 1 and 2. It is clear that the relaxation which is observed at concentrations well separated from the phase boundaries is a process that continues through all the phases with an amplitude which increases with increasing surfactant concentration and decreases with increasing temperature. Clearly the molecular origin of the process being perturbed by the sound wave to cause this relaxation is independent of phase structure. In the majority of cases this relaxation spectrum is slightly broader than that predicted by a single time constant.

Ultrasonic absorption measurements of chemical relaxation processes can be interpreted in terms of the microscopic behaviour of the system. The present measurements on these surfactants both in lyotropic liquid crystal phases and concentrated micellar solutions show that the 'average' frequency and amplitude of the relaxation process are very similar in all cases. Thus, the origin of the relaxation does not depend on the counter-ion, the chain length, the structure of the hydrophobic chain, the hydrophilic head group, or the structure of the surfactant aggregate. The relaxation, however, only occurs in concentrated surfactant solutions.

The only molecular mechanism that is common to all these surfactants in all the different phases is exchange between free water molecules and those hydrogen bonded to the surfactant head group.

The absence of relaxation in CTAB is consistent with this explanation, since there are no sites available at which water can bind to the head group. Other possible mechanisms which could give rise to ultrasonic absorption involving counter-ions or alkyl chains can be eliminated, because the process is similar both with non-ionic and ionic surfactants and with fluorocarbon and hydrocarbon surfactants. We offer further evidence for this water exchange mechanism in Figure 3, which shows that the relaxation process is slower for the same concentrations of CsPFO in deuterium oxide, as expected.

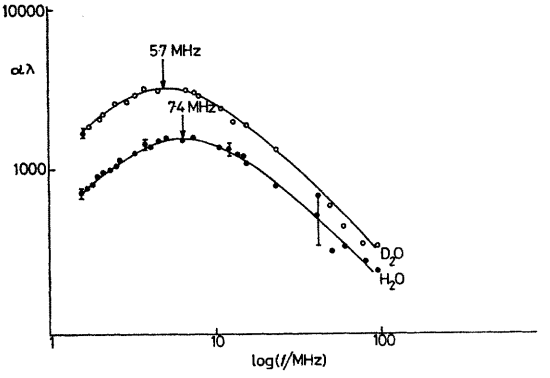

FIGURE 3. 30 wt % CsPFO at 25 °C.

There is no doubt that the additional effects observed at temperatures and concentrations close to the phase boundary are similar to those found near the critical point in several liquid mixtures and also near phase boundaries of thermotropic liquid crystals. During the phase change there is a reorganisation of water molecules and chain conformation which may contribute to this overall relaxation process.

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