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Ultrasonic Relaxation Studies of Sodium Octyl Sulphate Complexes with Synthetic Polymers and a Protein in Aqueous Solution

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The ultrasonic relaxation spectra of sodium octyl sulphate solutions in the presence of poly(vinylpyrrolidone), poly(vinyl alcohol), poly(4-vinylpyridine) and bovine serum albumin have been investigated. When these results are compared with those found for pure micellar sodium octyl sulphate solution it is found that in all cases the relaxation times τ for the monomer $\rightleftharpoons$ aggregate exchange process are such that graphs of $1/\tau$ against surfactant concentration exhibit minima at concentrations close to the critical micelle concentration (c.m.c.) of the pure surfactant. In the sodium octyl sulphate/macromolecule complexes the minima observed in the $1/\tau$ plots are more pronounced than in the pure soap. At concentrations well above the c.m.c. the relaxation behaviour in the presence of polymer is very similar to that of pure surfactant. The minima in $1/\tau$ are discussed in terms of the Aniansson and Wall equation for monomer–micelle exchange.

The interactions between surfactants and macromolecules have been extensively studied.[1–6] A considerable understanding of the equilibrium properties of these systems has been obtained mainly through measurements of macroscopic quantities, spectroscopic changes induced in the macromolecule and by observing changes in the surfactant molecules.[3] Unfortunately, these equilibrium studies shed very little light on the mechanism of these interactions; for example, note the recent models put forward to describe the nature of protein/surfactant complexes.[4–6] In this connection a combined kinetic and equilibrium approach is desirable, but in the above systems there is a paucity of kinetic data because the reactions involved are extremely rapid and apparently complex. In "pure" surfactant solutions we have shown that the ultrasonic relaxation technique can be used as a probe to study the dynamic interchange of monomeric surface active agent ions with micelles of some C_6–C_{11} anionic and cationic detergents.[7–9] These studies were followed by further relaxation measurements on solutions containing surfactant micelles in the presence of small molecules.[10] As an extension to these studies we are currently investigating the ultrasonic relaxation spectra of surfactant/macromolecule solutions and we report here our measurements on sodium octyl sulphate/poly(vinylpyrrolidone),/poly(vinyl alcohol),/poly(4-vinylpyridine) and/bovine serum albumin solutions.

EXPERIMENTAL

The ultrasonic absorption measurements were made using the Eggers resonance method[11] and a conventional pulse technique.[12] The measurements were carried out over the frequency

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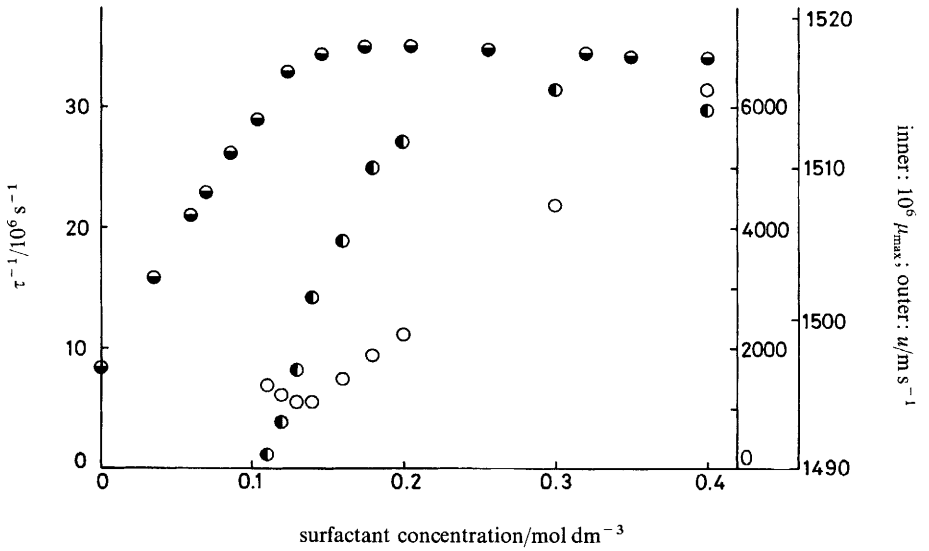

FIG. 1.—Plots of $1/\tau$ (○), μ_{max} (◐) and ultrasonic velocity (◒) against surfactant concentration for sodium octyl sulphate.

range 1–105 MHz at a temperature of 298 K. The relaxation data were analysed using a computer minimisation program and in all cases the data were consistent with a single time constant and accuracies in the relaxation time, amplitude and velocity data are, respectively, ±2, ±5 and ±0.03%. The sodium octyl sulphate (SOS) was obtained from Cambrian Chemicals, the poly(vinyl-pyrrolidone) (PVP) (molecular weight ≈44000) and poly(vinyl alcohol) (PVA) were B.D.H. samples, the poly(4-vinylpyridine) was obtained from Polysciences and the bovine serum albumin (BSA) was supplied by Sigma London Chemicals.

PRELIMINARY CONSIDERATIONS

In the use of the ultrasonic method to study the chemical relaxation of very fast reactions, it is necessary to interpret macroscopic measurements in terms of the microscopic behaviour of the system. The assignment of the molecular origin of relaxations which occur in surfactant/macromolecule complexes requires careful consideration since it is well known that solutions of both surfactants and also macromolecules exhibit ultrasonic relaxations.[13–15] In order to ascertain the best experimental conditions for the present relaxation measurements a preliminary consideration of the above effects is necessary.

PURE SURFACTANT SOLUTIONS

In general, anionic and cationic surfactant solutions do not show any excess ultrasonic absorption below their critical micelle concentrations (c.m.c.). However, at the c.m.c. a single relaxation process is observed and at concentrations exceeding this value the amplitude of this relaxation is relatively large. Extensive measurements have shown that the origin of this single relaxation is associated with the dynamic interchange of the monomeric surface active agent ions with the micellar unit.[7–10,13] The typical concentration dependence of the reciprocal of the relaxation time and the relaxation amplitude for this exchange process are shown in fig. 1 for sodium octyl sulphate.

The relaxation time associated with this exchange process becomes progressively shorter as the length of the hydrocarbon tail decreases.[8] We have also shown that in our present frequency range of 1–105 MHz this relaxation cannot be detected in solutions of surfactants whose hydrocarbon chain length is greater than C_{12} as the relaxation time is too slow. This relaxation process is associated with monomer–micelle exchange and has been described by Wyn-Jones and coworkers[7,8,16] in terms of a very simple two state model which assumes monomer–micelle association to be a collision between a small particle, the monomer, and a large particle, the micelle. Following this work, Aniansson and Wall[17–19] developed a very detailed model to describe the relaxation data associated with the formation of micelles from monomers in terms of a stepwise aggregation phenomenon involving the normal micelle distribution function. For a monomer–micelle exchange process[20–22] both models lead to relaxation equations which are consistent with the experimental measurements. The relaxation equation of the Aniansson model is now generally accepted because of the inherent details concerning the micellisation process.

AQUEOUS SOLUTIONS OF POLY(VINYLPYRROLIDONE), POLY(VINYLALCOHOL) AND BOVINE SERUM ALBUMIN

In aqueous solution, PVP, PVA and BSA exhibit broad ultrasonic relaxation spectra which are characterised by a distribution of relaxation times.[23–25] In addition, over the pH range 4.4–8.0 the ultrasonic relaxation spectrum of BSA is unchanged, as is shown in fig. 2. For these macromolecules the "average" relaxation times are apparently independent of concentration whereas the amplitude parameters appear to be directly proportional to the concentration. The most significant difference in the ultrasonic relaxations of BSA and the synthetic polymers is that for similar concentrations the amplitude of the relaxation of BSA is much greater than that of, for example, PVP, as is shown in fig. 2. These data are consistent with the origin of this relaxation being intramolecular and one must assume that a significant part of this absorption must be associated with conformational changes in the macromolecules.

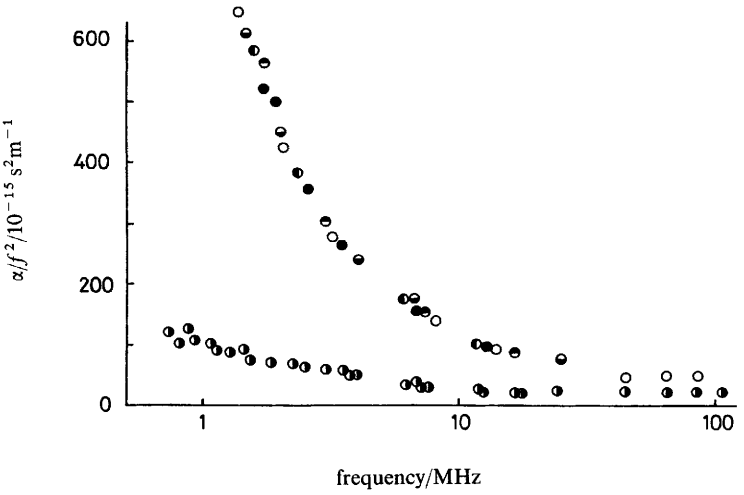

FIG. 2.—Plots of the quantity α/f^2 against frequency for bovine serum albumin at pH 4.4 (○), 5.0 (◓), 6.6 (◑), 7.6 (●) and 8.0 (◒) and for poly(vinylpyrrolidone) (◐) at a concentration of 5% w/v.

Equilibrium studies on the binding of surfactants to both PVP[26–28] and BSA[1,29,30] have shown that once binding commences, the surfactant induces a conformational change in the macromolecule. On this basis one could speculate that several interactions, for example, surfactant binding to the polymer, monomer–micelle exchange and conformational changes in the macromolecules as well as those induced by the binding surfactant, could contribute to the ultrasonic relaxation observed for these systems. In view of our experimental frequency range which limits the resolution of relaxation spectra characterised by distributions of relaxation times, it is desirable to carry out measurements under conditions where the different contributions of these various interactions can be qualitatively estimated. The main purpose of the present study is to investigate the kinetics associated with the binding of surfactants to macromolecules and in this connection intramolecular contributions due to the relaxation of the macromolecules can be eliminated by simply choosing concentrations of the macromolecules at which the amplitude of this process is almost negligible. For this investigation these conditions are met with solutions containing either 0.1% BSA, 2% PVP or 2% PVA. The surfactant chosen for the binding experiments was sodium octyl sulphate, since it has previously been shown[8] that the ultrasonic method can be used to monitor the exchange process involving the monomeric surface agent ions and the micelles in aqueous solutions above its c.m.c. It is also known from equilibrium studies that SOS binds to both PVP[28] and BSA.[30]

RESULTS AND DISCUSSION

The concentration dependence of the reciprocal relaxation times ($1/\tau$), sound velocities (u) and maximum absorptions per wavelength (μ_{max}) for "pure" SOS as well as SOS in the presence of BSA and PVP are shown in fig. 1, 3 and 4. The data for PVA are very similar to those for PVP. Superficially, all of these results appear to be very similar. However, a detailed inspection of the data reveals many interesting and noteworthy features.

The c.m.c. of "pure" surfactant can be determined by the break in the sound velocity/concentration plot.[8] If we examine the velocity data in detail it is clear that for the "pure" surfactant a narrow range of concentration exists around the c.m.c.

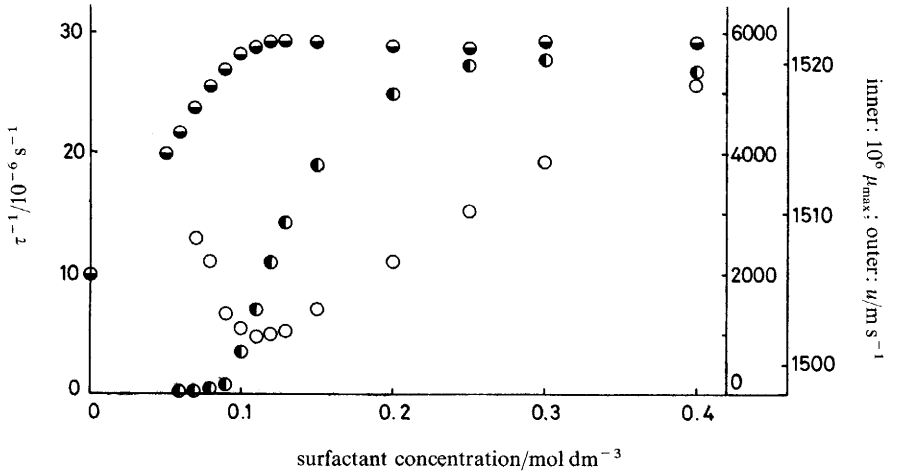

FIG. 3.—Plots of $1/\tau$ (○), μ_{max} (◐) and ultrasonic velocity (◒) against surfactant concentration for 0.1% bovine serum albumin/sodium octyl sulphate.

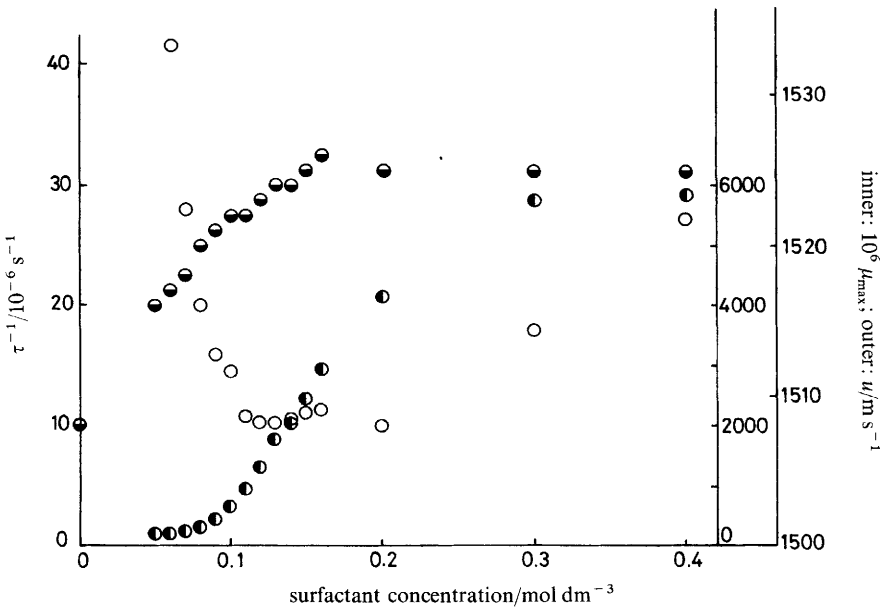

FIG. 4.—Plots of $1/\tau$ (○), μ_{max} (◐) and ultrasonic velocity (◒) against surfactant concentration for 2% w/v poly(vinylpyrrolidone)/sodium octyl sulphate.

where the velocity data are not well defined. There is also a break in the velocity/concentration data for SOS in the presence of the macromolecules showing that critical concentrations exist for these solutions. In the surfactant/macromolecule complexes the break points observed in the velocity data occur over a wider concentration region than those found for the pure surfactant solution.

If we examine the reciprocal relaxation time against concentration plot for the "pure" surfactant there is a minimum in the $1/\tau$ values at a concentration which is slightly greater than the c.m.c. There is no evidence, however, of a relaxation below the critical micelle concentration. For SOS in the presence of the macromolecules the minima in the $1/\tau$ against concentration plots are more pronounced and occur over a wider concentration range. Furthermore, this concentration range is the same as that in which the velocity data are not well defined. Although critical concentrations cannot be measured precisely in the surfactant/macromolecule solutions, there is no doubt that a relaxation in these solutions is observed at concentrations below those at which micelles "proper" are formed.

In order to interpret the experimental data in this concentration region it is necessary to examine the results of the equilibrium studies where it has been established that SOS binds to both PVP[28] and BSA.[30] In the case of the protein a binding isotherm is available[30] and in the region where $1/\tau$ decreases with increasing concentration of SOS, the evidence from the equilibrium binding experiment indicates that the surfactant forms pre-micellar aggregates (sometimes called submicelles or pre-micelles) along the protein chain. The existence of pre-micellar aggregates has also been invoked[31] to account for the equilibrium behaviour of many solutions of "pure" short chain length surfactants at concentrations around their c.m.c.s. For many of these surfactants there is evidence of minima in $1/\tau$ against concentration plots[32–34]. The introduction of a macromolecule into a surfactant solution induces binding and as this process proceeds with increasing sur-

factant concentration the macromolecule provides a base for the bound surfactant monomers to form nuclei, which in turn make it much easier for pre-micellar aggregates to be formed. As a result of this behaviour the velocity data are less well defined around the c.m.c. and in addition there is a more pronounced curvature in the relaxation time against concentration plots. The relaxation data in this concentration region exhibit weak amplitudes and a definite decrease in the $1/\tau$ values with increasing surfactant concentration.

The relaxation data observed at the lowest surfactant concentrations in these macromolecule/surfactant solutions are associated with the perturbation of the equilibrium between monomers and pre-micellar aggregates.

At first sight the occurrence of minima in $1/\tau$ against concentration plots for a relaxation involving aggregates is surprising and it is interesting to speculate as to their origin. To do this we consider the relaxation equation for the fast relaxation time τ_1 obtained by Aniansson and co-workers:[17–19]

$$\frac{1}{\tau_1} = \frac{k^+}{n} C + \frac{k^+[A_1]}{n}\left(\frac{n}{\sigma^2} - 1\right) \tag{1}$$

where C is the total surfactant concentration, $[A_1]$ is the concentration of surfactant monomer, σ^2 is the variance of the micelle distribution curve, n is the mean aggregation number and k^+ is an average rate constant for the association of monomers to the micelles.

For the purpose of this discussion we consider this equation in the form

$$\frac{1}{\tau_1} = \frac{k^-}{\sigma^2} + \frac{k^-(C - [A_1])}{n[A_1]} \tag{2}$$

where k^- is the dissociation rate constant.

We note that n can be expected to increase with increasing C and that the relative changes can be expected to be greatest when $(C - [A_1])$ is small. Since σ^2 is typically of order of n this could well result in a parallel increase in σ^2 with increasing C, in which case if k^- is constant the first term on the r.h.s. of eqn (2) will decrease with increasing C. At the concentration where the effect is observed one expects the second term to be very small, since $(C - [A_1])/[A_1] \ll 1$, to increase with increasing C and to dominate the first term when $(C - [A_1])/[A_1] \gg 1$. Hence it can be argued that the observed minima in $1/\tau_1$ result from these opposing trends. An alternative explanation is that the second term on the r.h.s. of eqn (2) exhibits a minimum with increasing C. When k^- and $[A_1]$ are both constant this can occur only if the concentration of micellar aggregates decreases with increasing C. This implies that during the growth of pre-micellar aggregates the aggregation number increases in such a way that the actual molar concentration of the aggregate decreases.

A third possibility is that $k^-/[A_1]$ decreases with increasing C. To show this we note that[35]

$$k^- = \sum_r k_r^- C_r \Big/ \sum_r C_r \tag{3}$$

where

$$\sum_r C_r = (C - [A_1 1])/n$$

TABLE 1.—VALUES OF k^+/n FOR SOLUTIONS STUDIED

solution	$(k^+/n)/10^{-6}$ $s^{-1}mol^{-1}\,dm^3$
sodium octyl sulphate	108
sodium octyl sulphate + poly(vinylpyrrolidone)	99
sodium octyl sulphate + poly(vinyl alcohol)	90
sodium octyl sulphate + poly(4-vinylpyridine)	77
sodium octyl sulphate + bovine serum albumin	73

and k_r^- is the appropriate rate constant for the release of monomer by the rth micellar species. The term of interest may now be written as

$$\sum_r k_r^- C_r/[A_1].$$

Provided that the k_r^- do not depend on C this term can decrease with increasing C only if some $C_r/[A_1]$ decrease with increasing C. This is also not possible for non-ionic surfactants but can arise for ionic surfactants if the micelles formed when $(C - [A_1])$ is small bind fewer counterions per micellar surfactant ion than the micelles formed at higher concentrations. The reason for this is that the increase in the counterion concentration with increasing C favours the formation of aggregates which bind counterions most effectively. If this does occur and

$$\sum_r C_r$$

increases with increasing C then for

$$\sum_r k_r^- C_r/[A_1]$$

to decrease with increasing C it is also necessary that the k_r^- for those species whose C_r decrease be greater than for the species whose C_r increase. In other words, the residence time of surfactant ions in the aggregates formed when $(C - [A_1])$ is small must be less than for those formed when $(C - [A_1])$ is large.

For solutions well above the c.m.c. in which micelles proper form it is apparent from fig. 1, 3 and 4 that the differences in $1/\tau_1$ for a given surfactant concentration are relatively small. The data at these concentrations can be described by the Aniansson and Wall equation [eqn (1)] in the normal way and analysis of the plots gives the values of k^+/n shown in table 1. These results suggest that macromolecules have but little effect on the state of aggregated surfactant under these conditions. It would appear that polymer addition slightly increases the residence time of aggregated surfactant ions. This in turn supports the view that a significant fraction of aggregated surfactant is associated with the macromolecules, because otherwise the residence time in aggregated form would presumably be unaffected. A convincing experiment to confirm that the micelles are in fact incorporated along the polymer chain is obtained with the water insoluble polymer poly(4-vinylpyridine). A 1% solution of this polymer was solubilised by micellar SOS solution and the relating relaxation data are very close to those obtained for the other macromolecules.

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