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THE KINETICS OF FORMATION AND BREAKDOWN OF PRE-HEXAGONAL PHASE AGGREGATES IN FLUID-ISOTROPIC AMPHIPHILIC SOLUTIONS

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Résumé. — Quand on change la composition d'une solution liquide isotrope pour passer à une phase cristal liquide, on observe souvent une nette augmentation de la viscosité. Un comportement viscoélastique peut aussi apparaître, ce qui suggère l'existence d'un ordre à longue distance ou réseau dans le système. À partir de l'élargissement observé dans les spectres NMR haute résolution [a, 6], on a démontré récemment que ces changements sont dus aux molécules amphiphiles. Les molécules amphiphiles forment des micelles en forme de longues cylindres et, quand ceux-ci s'organisent en réseau hexagonal, la phase cristal liquide hexagonal est formée. Les micelles cylindriques peuvent être considérées comme des agrégats prétransitionnels de la phase hexagonale.

Dans ce travail, nous essayons de décrire le mécanisme et la cinétique de la formation et disparition de ces agrégats dans des solutions contenant du sodium dodécyl sulfate et de l'hexadécyl diméthyl ammonio propane sulphonate. Des solutions viscoélastiques apparaissent pour des solutions au voisinage de la forme hexagonale [6]. En diluant une des solutions d'un amphiphile pur ou de l'eau, les micelles cylindriques se déforment pour former des micelles sphériques dans un temps variant de quelques minutes à plusieurs jours. La cinétique de cette transformation peut être mesurée par l'élargissement des raies RMN ou par diffusion de la lumière. Une comparaison des résultats obtenus par ces deux techniques montre que les micelles se disssocient en une seule étape et non par une perte progressive de monomères.

La formation des micelles cylindriques peut aussi être observée par RMN ou diffusion de la lumière. Quand les solutions viscoélastiques sont préparées en ajoutant des solutions d'amphiphile pure, on observe un accroissement lent de la concentration des micelles cylindriques qui se produit aussi en un temps allant de quelques minutes à une semaine. Les cinétiques sont complexes et dépendent de la composition en amphiphile.

Dans les solutions à l'équilibre, il y a deux types de procédés dynamiques qui permettent l'échange de monomères amphiphiles entre les deux types de micelles. L'un est l'échange rapide de monomères entre les micelles sphériques et les agrégats prétransitionnels de la phase hexagonale. Le second est la continuelle formation et déformation de ces agrégats prétransitionnels.

Abstract. — When the composition of a fluid isotropic solution is altered so that it approaches a liquid crystal phase boundary a marked increase is often observed in the solution viscosity. Viscoelastic properties can occur also, and this suggests that some long range order or network is present in the system. From the line broadening observed in high-resolution NMR spectra [a, b], we have recently demonstrated that these changes are associated with the amphiphile molecules. The amphiphile molecules form long cylindrical micelles, and when these are packed in a hexagonal array the hexagonal liquid crystal phase is formed. The cylindrical micelles can be regarded as pre-hexagonal phase aggregates.

In this paper we describe an investigation into the formation and breakdown kinetics and mechanism for these aggregates in solutions containing sodium dodecyl sulphate and hexadecyl dimethyl ammonio propane sulphonate. Viscoelastic solutions occur in solutions adjacent to the hexagonal phase boundary [6]. On dilution with pure amphiphile solutions or water the cylindrical micelles break up to form spherical micelles in a time varying from minutes to several days. The kinetics of the process can be measured by NMR line broadening, or light scattering; a comparison of the results from the two techniques indicates that the cylindrical micelles dissociate in one step, and not by a gradual loss of monomers.

The formation of the cylindrical micelles can also be followed using NMR or light scattering. When viscoelastic solutions are prepared by mixing pure amphiphile solutions a slow build-up in the concentration of the cylindrical micelles is observed, again the changes occur over a period varying from minutes to weeks. The kinetics are complex and are dependent on amphiphile composition.

In solutions at equilibrium two dynamic processes that exchange amphiphile monomers between the two types of micelle are present. One is the rapid exchange of monomers between the spherical micelles and the prehexagonal phase aggregates. The second is the continual build-up and breakdown of the pre-hexagonal phase aggregates themselves.

In liquid crystalline (l. c.) phases the molecules are arranged in an ordered structure which exists over very large distances compared to the molecular dimensions. However, the molecules themselves undergo rapid translational and rotational motions. In most normal isotropic liquids the molecules also undergo rapid motions, and no long range order exists. Medium or long range order does occur in a few isotropic liquids and these are normally liquids that can be changed into an l. c. phase by small temperature or composition alterations. The existence of this order can be inferred from the fact that some of their properties are similar to those of the adjacent l. c. phase. For example, Hayward and Packer [1] have inferred the existence of weak long range order in liquid N-(p-methoxy-benzylidine)-p'-butyl-aniline (MBBA) from the time dependence of NMR measurements of translational diffusion. This is presumably due to the presence of pre-l. c. aggregates.

In most lyotropic l. c. systems, and particularly those containing soaps or detergents, the isotropic solutions formed by adding solvent (water) to the l. c. phases contain surfactant molecules aggregated in micelles. These micelles have a spherical shape at low concentrations, but many authors have now reported that a micelle conformational change occurs at concentrations well above the critical micelle concentration (c. m. c.), (for examples see ref. [2-6]). This conformational change is thought to involve an increase in the micellar aggregation number resulting in the formation of cylindrical or other shaped micelles and these can be regarded as pre-l. c. aggregates.

In previous studies of mixed surfactant systems we have reported that isotropic solutions adjacent to phase boundaries can exhibit properties indicative of medium or long range order [7, 8]. In these solutions small changes in surfactant composition can cause large changes in viscosity, and viscoelastic properties can be observed. The viscosity changes were also correlated with changes in surfactant molecular motions by n. m. r. measurements. The change in solution properties was attributed to the presence of large cylindrical micelles. In addition, the n. m. r. measurements could only be explained by the presence of a large number of small (spherical) micelles, and it was proposed that a dynamic equilibrium occurred between the two types of micelle [7, 8]. The large cylindrical micelles can be regarded as the components of the hexagonal phase, and a study of their properties should contribute to a greater understanding of the properties of this phase.

In the mixed surfactant system hexadecyl dimethyl ammonio propane sulphonate (HDPS-I)/Sodium dodecyl sulphate (SDS) the properties of the solutions were dependent on the method of preparation, and were time dependent [8, 9].

\[
\text{CH}_3
\begin{array}{c}
\text{CH}_3 (\text{CH}_2)_{15} \text{N}^+ \text{(CH}_3)_2 \text{SO}_3^-
\end{array}
\]

Preparation of dilute surfactant solutions by the addition of distilled water to concentrated viscoelastic solutions (see Fig. 1) gave samples with initial viscoelasticity which decayed over a period varying from hours to weeks. The same composition prepared by mixing dilute surfactant solutions was not viscoelastic.

The time dependent properties were attributed to the slow breakdown of the cylindrical micelles responsible for the viscoelastic behaviour. The presence of cylindrical micelles gave rise to a broadening of the surfactant n. m. r. resonances, and the change in this broadening was used to measure the kinetics of the process [9]. Similar changes were also measured using the time dependent intensity of the scattered incident light, and combination of the light scattering and n. m. r. data enable the mechanism of cylindrical micelle breakdown to be deduced (see below).

For some samples with higher surfactant concentrations it was also observed that the viscosity and viscoelasticity increased with time after initial mixing. This is attributed to the slow formation of the cylindrical micelles [9, 10]. The build-up process is more complex than the reverse process and possibly involves two distinct stages [10].

Since a dynamic equilibrium exists between the small micelles and the large cylindrical micelles, information on the build-up process can be inferred from a knowledge of the breakdown rates and the equilibrium properties. In this paper we report measurements of the breakdown process at different temperatures. The rates were measured using the n. m. r. and light scattering techniques reported previously [9], and the results are used to develop further the model for the breakdown process. In addition, we report some initial measurements of the rate of formation of the large micelles.

1. Experimental. — 1.1 MATERIALS. — HDPS was prepared by the method of Clunie et al. [11]; after recrystallization from acetone and isopropanol the material was > 99 % pure by elemental analysis and exhibited no minimum in the surface tension vs log concentration plot (\(\text{cmc} = 4.5 \times 10^{-5} \text{ mol dm}^{-3}\) at 308 K). SDS was BDH specially pure grade with \(\text{cmc} = 8.3 \times 10^{-3} \text{ mol dm}^{-3}\) at 298 K, and was used without further purification. D_2O was \(\beta\) Scientific Chemicals 99.7 % pure grade. H_2O was deionised and distilled.
1.2 Measurements. — 1.2.1 N. M. R. — Solutions of HDPS in D₂O and SDS in D₂O were prepared separately and mixed in appropriate volumes to give a range of samples within the viscoelastic region (see Fig. 1) from HDPS/SDS = 3.2 : 1.8 to HDPS : SDS = 4.1 : 0.9 (weight ratio). In each case the SDS solution was added to the HDPS solution to eliminate any order of mixing disparities (later work verified that no such effects exist in this system). The initial solution concentration was 5.0 % (wt) total surfactant. Equilibrated samples were diluted to 1.0 % by addition of D₂O.

Light scattering was a convenient technique for half-lives in the range 3 min-2 hr. The time taken for air bubbles to rise to the surface (2-3 min) prevented the measurement of shorter half-lives by this technique.

2. Results. — 2.1 N. M. R. Measurements of breakdown process. — The changes in n. m. r. line width (Δνₘᵣ) that occur on dilution of a sample within the viscoelastic region to a point outside are illustrated in figure 2. Immediately after dilution there is no change in Δνₘᵣ but then an exponential decrease in Δνₘᵣ occurs. We have proposed [7, 8] that Δνₘᵣ is a weighted average of the individual line widths due to surfactant molecules in small micelles (Δνₛ) and large cylindrical micelles (Δνₖ). If the fraction of surfactant in small and cylindrical micelles is denoted by Pₛ and Pₖ respectively, then Δνₘᵣ is given by eq. (1).

It has been shown [9] that Pₛ ≈ Pₖ and Δνₛ ≈ Δνₖ:

\[ \Delta νₘᵣ = Pₛ Δ νₛ + Pₖ Δ νₖ. \]  

(1)

The value of Δνₛ can be obtained from the final line width for samples outside the viscoelastic region. Since Pₛ ≈ 1, changes in Δνₘᵣ are due to changes in the second term, Δνₖ. The logarithmic relationship between the change in Δνₘᵣ and time show that the decrease in the concentration of the cylindrical micelles
is first order, and the rate constant can be determined using eq. (2):

\[ \Delta V_{\text{obs}}(t) = (\Delta V_1 - \Delta V_f) e^{-k_b t} + \Delta V_f \]  

(2)

\( \Delta V_{\text{obs}}(t) \) = line width observed at time \( t \); \( \Delta V_1 \) = initial line width; \( \Delta V_f \) = final line width (= \( \Delta V_f \)); \( k_b \) = breakdown rate constant.

The values of \( k_b \) vary over several orders of magnitude, corresponding to reaction half lives of minutes to days, depending on the surfactant molar ratio [10]. Values of \( k_b \) for particular molar ratios at different temperatures are shown in figure 3.

As shown in figure 2 the values of \( k_b \) measured by n. m. r. and light scattering for the same solution are equal within experimental error. Since the n. m. r. results are a function of the number and size of the large micelles while \( I \) depends on the number and the square of the size of the large micelles, the identical values of \( k_b \) show that only the number of large micelles changes with time. This indicates that the size of the large micelles is constant, and thus breakdown by a process involving gradual loss of surfactant monomers is not a significant mechanism in the present case. Breakdown must occur by a sudden disruption (explosion) of the whole micelle.

The dependence of light scattering measurements of \( k_b \) is shown in figure 3. The results cover only a small range of temperatures because of instrumental limitation. However, the similarity of the slopes for different molar ratios is sufficient to suggest that the large differences in breakdown rates are not due to changes in the activation energy, but to a dependence of the activation entropy on surfactant molar ratio.

2.3 N. M. R. STUDIES OF BUILD-UP PROCESS. — It is possible to observe increases in the n. m. r. line width as a function of time by mixing pure surfactant solutions to give a final composition within the viscoelastic region. Initial measurements of \( \Delta V_{\text{obs}} \) have been made for solutions containing 5.0 \% total surfactant concentration. The changes take place over periods varying from minutes for samples at the HDPS side of the viscoelastic region to weeks for samples at the SDS side. The kinetics appear to follow the relationship shown in eq. (3) for samples containing HDPS : SDS 4.0 : 1.0 (Fig. 4a):

\[ \Delta V_{\text{obs}} = (\Delta V_f - \Delta V_i) (1 - e^{-k_b t}) \]  

(3)

The situation becomes more complex as the SDS content is increased and the line width changes do not follow this relationship (Fig. 4b).
3. Discussion. — 3.1 Mechanism of breakdown of cylindrical micelles. — The similarity of rate constants \( (k_0) \) measured by n. m. r. and light scattering shows that breakdown occurs via complete dissociation of the cylindrical micelle over a short time interval [9]. The sharp increase in \( k_0 \) for samples close to the edge of the viscoelastic region shows that the cylindrical micelles become more unstable as the composition approaches these boundaries. One further important result to note is that these boundaries of the viscoelastic region (Fig. 1) lie along lines of constant HDPS : SDS molar ratios. Dilution of viscoelastic samples to regions outside these molar ratios results in breakdown times equal to the time of mixing the solutions [9]. To account for these results we propose that breakdown of cylindrical micelles occurs via a mechanism that involves the micellar composition reaching a point represented by the boundary of the viscoelastic region. These compositions correspond to the critical composition indicated below.

\[
\text{Cylindrical Micelle}
\]

\[
\text{average composition}
\]

\[
\text{corresponding to molar ratio HDPS : SDS of a : b}
\]

(i) Loss of HDPS monomers ;
Gain of SDS monomers

(ii) Loss of SDS monomers ;
Gain of HDPS monomers

\[
\text{Cylindrical micelle with critical composition HDPS : SDS mol-ratio}
\]

\[
\text{of X_2 : Y_2}
\]

\[
\text{rapid breakdown}
\]

\[
\text{small micelles, rapidly attain average composition (a : b)}
\]

In any micellar solution there will be a distribution of micellar compositions. The distribution will correspond approximately to that given by a binomial distribution function. Exchange between the different compositions occurs by gain and loss of surfactant monomers. In the present case the large cylindrical micelles are estimated to contain \( \sim 10^8 \) monomers. For any overall average composition there will be a finite concentration of micelles having the critical composition for breakdown. Calculations based on this approach can reproduce [9, 10] the overall pattern of breakdown rates observed. Clearly any cylindrical micelle can breakdown via two routes, but again calculations show that one route is normally favoured. The rate is a function of the difference in molar ratios between the overall solution composition and the critical composition, the rate decreasing as this difference increases.

The time taken for this process can be calculated if it is assumed that the rate of gain or loss of both surfactant monomers is approximately the same. Then, following Muller [11], the process can be approximated by a random walk method. If the time taken for each monomer exchange is \( t \), and \( n \) steps are required to go from composition \( a : b \) to \( X_1 : Y_1 \) (or \( X_2 : Y_2 \)) the total time required is given by:

\[
\text{time} \approx n^2 t \quad \text{i. e. rate} \; x^1/n^2 \approx \frac{k \text{ exch}}{n^2}
\]

\( k \text{ exch-rate of monomer/micelle exchange} \).

The activation parameters derived from the data in figure 3 (given in Table I) provide a test for this model. Using standard equations we can write

\[
\Delta H (\text{\#}) - T \Delta S (\text{\#}) \approx - RT \ln \left( \frac{k \text{ exch}}{n^2} \right).
\]

The difference between rates for different molar ratios at various temperatures should be reflected in change of \( T \Delta S (\text{\#}) \). The value of \( \Delta H (\text{\#}) \) would be expected to be constant over all molar ratios since the same basic process (monomermicelle exchange) applies.

This is clearly confirmed from Table I and figure 3. The measured values of \( \Delta H (\text{\#}) \) are similar while the differences in \( \Delta S (\text{\#}) \) are much larger. Using these latter differences it is possible to estimate the difference

\( \text{(*) Denotes activation parameters.} \)
The figures in brackets are the average temperatures for which the values are calculated.

in the number of monomer-micelle exchange steps required for breakdown between micelles in the centre of the viscoelastic region and those at the edge (using eq. (5)).

\[
\Delta \Delta S(\star) = (\Delta S(\star))_a - (\Delta S(\star))_{a'} \simeq R \ln \left( \frac{(n_a)^2}{(n_a')^2} \right)
\]

where \(a\) and \(a'\) refer to different compositions.

Using the values corresponding to molar ratios of HDPS : SDS 3.5 : 1.5 and 4.1 : 0.9 the difference in the number of steps is a factor \(\sim 12\).

This represents a very simple model because it does not allow for different sizes of cylindrical micelles, and different rates of monomer-micelle exchange for different surfactants. However, the model does seem qualitatively correct.

3.2 MECHANISM OF BUILD-UP. — If the build-up mechanism is via monomer addition to small micelles, resulting in the formation of cylindrical micelles, then the relationship expressed in eq. (3) would be expected for the change in the n. m. r. linewidths. The relationship holds for samples close to the HDPS boundary but with increasing SDS content the experimental results increasingly deviate from the form of eq. (3). This may be connected with the larger micellar size nearer the SDS boundary where monomer addition is a less favourable process and is in competition with, for example aggregation of micelles via micellar collision.

The build-up and breakdown mechanisms proposed have been shown to be qualitatively correct but need more refinement in detail. It is intended to pursue this in future work when particular attention will be paid to micellar size and composition distribution and to build-up mechanisms other than monomer addition.

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