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MICROSTRUCTURES IN AN OIL-in-WATER MICROEMULSION : A NMR SELF-DIFFUSION STUDY

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Abstract -We present accurate measurements of oil and surfactant self-diffusion coefficients made in the microemulsion phases of the pentaethylene glycol dodecyl ether ($C_{12}E_5$)-water-decane system, using the "Pulsed Gradient Simulated-Echo" NMR technique
Microstructures of three microemulsion phases obtained with different surfactant-to-oil weight ratios have been analysed. Particular attention was focused on the phase boundaries where the microemulsions consist of normal oil swollen micelles in equilibrium with excess oil. Increasing the temperature, a micellar growth was supported by self-diffusion results and finally a bicontinuos phase was found.

INTRODUCTION

Surfactant- water-oil mixtures can form a very large variety of microstructured liquids and liquid crystals. During the last few years we have seen an increase in the experimental determination of microstructures of ternary solutions which are generally referred to as microemeulsions[1].

Microemulsions are isotropic and thermodynamically stable mixtures which present an interesting colloidal heterogeneity. Comparable amounts of oil and water usually form a bicontinous structure in a certain temperature range, whereas in the oil or water corner of the Gibbs triangle, nanometer sized droplets of water in oil (W/O) or oil in water (O/W) are formed.

In this study we focus on a particular surfactant-water-system containing the non ionic surfactant pentaethylene glycoldodecyl ether ($C_{12}E_5$), heavy water and decane. Water rich microemulsion phases have been prepared with three different surfactant-to-oil weight ratios (R). The $C_{12}E_5$/decane weight ratios were kept constant at values at $R_1 \approx 50/50$, $R_2 \approx 40/60$ and $R_3 \approx 30/70$, thus we have studied three different areas in the temperature-composition phase prism as illustrated in Fig.1. Surfactant and oil self-diffusion coefficients as a function of temperature were measured with accurate and precise FT NMR self-diffusion experiments. Here particular attention was focused on the phase boundary where the microemulsions, consisting of normal oil-swollen micelles, are in equilibrium with excess oil.

We have also observed the structural changes with increasing temperature from this boundary up to the lamellar liquid crystal phase.

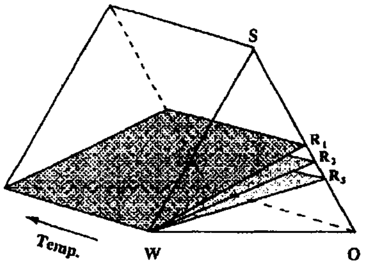


Figure 1- Concentration-temperature phase prism and the areas analysed.

EXPERIMENTAL SECTION

The surfactant, $CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_5OH$ ($C_{12}E_5$), was obtained from Nikko Chemicals and was used without further purification. The decane (99.9%) and heavy water were purchased from Sigma. Studies of phase equilibria were performed using a thermostated water bath with the samples contained in sealed ampoules equipped with magnetic bars. Phase boundary temperatures were checked by visual inspection, polarising microscopy and by analysis of ^2H-NMR spectra of deuterated water. Macroscopic phase separation was found to be very slow in heterogeneous regions. Mixtures in these regions were therefore centrifuged for many hours until macroscopic phase separation was achieved.

Self-diffusion coefficients of oil and surfactant molecules were performed using the Stimulated Spin-Echo experiment (Tanner) which consists of three RF pulses and a pair of short magnetic gradient pulses. The echo signal amplitude, A, for a given chemical species is given by :

$$A(t) = A_o e^{-kD}$$

where A_o is the amplitude in the absence of an applied gradient and the time function $k=(\gamma\delta g)^2(\Delta-\delta/3)$ depends on the experimental variables. Self-diffusion coefficients were calculated by a least-squares fit of the observed echo amplitude for different values of δ (the gradient pulse delay). Stimulated spin echo experiments as a function of temperature were performed on a Bruker WM 300. The reproducibility and precision of the self-diffusion coefficients was estimated to be about +/- 2%.

GENERAL PHASE BEHAVIOUR

In this section we report some of the basic self-assembly properties of the ternary $C_{12}E_5$/decane/water system at three constant surfactant-to-oil ratios, namely R_1=50/50, R_2=40/60 and R_3=30/70.

A partial schematic phase diagram (omitting three-phase regions) of the water rich part (≥70 wt.% water) of the R_1 system is shown in Fig.2a. The phase diagram is plotted as temperature versus the total weight percent of surfactant and oil (wt% S+O). The data are in agreement with the paper of Olsson et al.[2].

A microemulsion phase (L_1) is stable within the approximate temperature range 24-31 °C. At lower temperatures, the microemulsion coexists with an essentially pure oil phase (L_1+O). Above the L_1 phase a lamellar liquid cristalline phase (L_α) is formed. At higher water contents (>90 wt.% water) however, the upper phase boundary of the microemulsion phase corresponds to a lower consolute boundary, with a critical point. Here, the microemulsion splits into a dilute (with respect to surfactant and oil) and a concentrated phase that are in equilibrium.

The phase diagram of the ternary system at the surfactant-to-oil ratio of R_2=40/60 is shown in Fig.2b. This phase behaviour is qualitatively similar to that of the R_1 system. An important and noteworthy difference is that with increasing temperature the microemulsion phase shows a decreased stability range and the equilibrium line with excess oil is shifted to a temperature of 27°C. Also the upper phase boundary is slightly displaced in temperature, while the lamellar phase presents a similar range of existence when compared to the R_1 system.

In Fig.2c we show the phase diagram of the system at the surfactant-to-oil ratio R_3=30/70. The equilibrium between the microemulsion and excess oil is now at a higher temperature and the range of stability of the microemulsion phase is drastically reduced. Another important point which we should observe is the disappearance of the lamellar phase and a two phase region (L_1+W) is observed up to a surfactant plus oil weight fraction of wt%(S+O)=50.

The structural evolution of this ternary system with temperature may be related, within the flexible surface model, to the strong temperature dependence of the spontaneous curvature (H_o) of the surfactant monolayer. Water changes from a good to a bad solvent for the oligoethylene oxide chains with increasing temperature resulting in a change in H_o from being preferable towards oil (here defined as H_o>0) to preferable towards water (H_o<0).

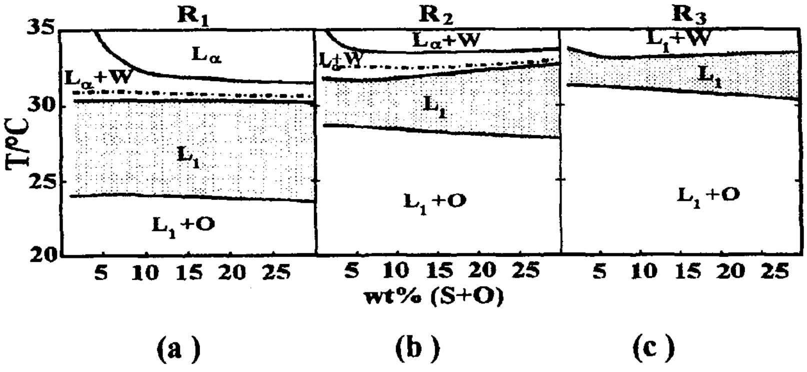


Figure 2- Partial phase diagrams of $C_{12}E_5/D_2O$/decane system at three S/O weight fraction.

In the microemulsion (L_1) phase the curvature is towards oil ($H_0>0$), while in the lamellar phase at higher temperatures, the curvature of the planar surfactant films are on average zero. The curvature free energy density also predicts that the phase separation of the microemulsion phase with excess oil (L_1+O) would occur at a certain value of H_0. On this boundary, which has been termed the *'emulsification failure'* boundary, the model predicts spherical droplets, corresponding to a maximum curvature for a given interfacial area to enclosed volume ratio.

SELF-DIFFUSION AND MICROSTRUCTURES

Measurements of self-diffusion coefficients by means of the PGSE technique have evolved to become one of the most important tools in the characterisation of surfactant systems[3]. This is particularly true for microemulsion liquid solutions where there is a direct connection between the self-diffusion coefficients of mixture components and the phase microstructure. Here it is convenient to summarise the following limiting cases:

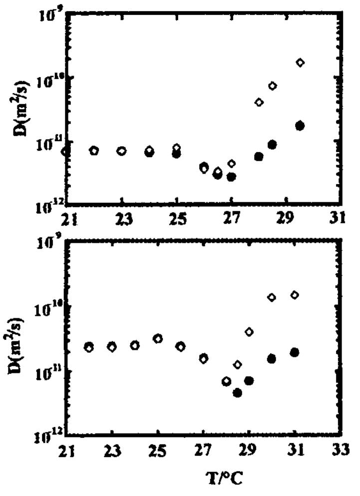
a) ***Oil-in-water droplet structure***: $D_{water}>>D_{oil}$ and $D_{surf} \approx D_{oil} \approx D_{droplet}$. D_{water} will be of the same order of magnitude as neat water.

b) ***Water-in-oil droplet structure***: $D_{water}<<D_{oil}$ and $D_{surf} \approx D_{water} \approx D_{droplet}$. D_{oil} will be of the same order of magnitude as neat oil.

c) ***Bicontinuos structure***: D_{water} and D_{oil} both high while D_{surf} is low. D_{oil} and D_{water} will be of the same magnitude as neat liquids.

In this section we report the temperature dependence of the surfactant and oil self diffusion coefficients for the three microemulsion phases at different $C_{12}E_5$/decane ratios.

In Fig.3 we show the self-diffusion data for the microemulsion phase R_1, for two mixtures with wt%(S+O)=10 and wt%(S+O)=20. The self-diffusion behaviour is almost the same in both mixtures. Within the temperature range 20-28°C $D_{oil}=D_{surf}$, suggesting that the two components are present in the same aggregate (oil droplet structure). Above and below the "emulsification failure" boundary the droplets diffuse at the same rate indicating that the aggregate size remains constant. Increasing the temperature, oil and surfactant self-diffusion still remains constant but takes a minimum value which is due to an increase of the droplet sizes. Olsson et al.[4] have pointed out that this behaviour is consistent with a limited growth from spherical to prolate micelles with an axial ratio ≤ 3.5. At temperatures around 27-28 °C, surfactant and oil show different self-diffusion coefficients suggesting the presence of a bicontinous microemulsion structure.



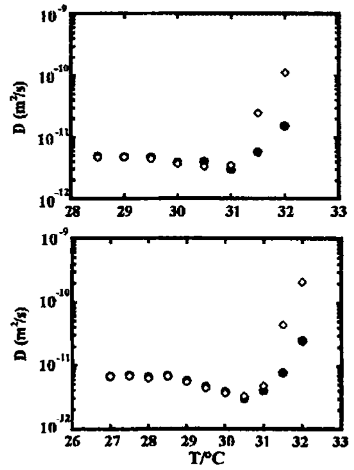


Figure 3 (Left) Temperature dependence of oil (◊) and surfactant (●) self-diffusion coefficients across the microemulsion phase of the R_1 system. Lower: wt% (S+O)=10, Upper: wt% (S+O)=20.

Figure 4(Right): Temperature dependence of oil (◊) and surfactant (●) self-diffusion coefficients across the microemulsion phase of the systems R_2 (lower) and R_3 (upper). wt% (S+O)=20 for both..

Fig.4 shows the temperature dependence of oil and surfactant self-diffusion for the R_2 and R_3 systems. Close to the lower phase boundary the surfactant and oil diffuse at the same rate, indicating translation in the same aggregate, namely oil droplets.

For the R_2 system a small minimum in the self-diffusion data was observed as the temperature increased. This effect was interpreted, as for the system R_1, as a change from spherical to prolate micelles. Calculations similar to those made by Olsson[4] gave in this case an axial ratio of ca. 2.3. No minimum, however, was observed in the self-diffusion coefficients for the R_3 system. Increasing the temperature from the low phase boundary, the oil droples continue to have a constant self-diffusion coefficient.

The self-diffusion coefficients for the R_1 and R_2 systems increase dramatically at the same temperature, 31 °C. The surfactant and oil diffusion are no longer equal, with the oil diffusing faster than the surfactant (bicontinous structure).

CONCLUSION

Temperature dependence experiments of oil and surfactant self-diffusion coefficients have been performed on three microemulsions phases where the surfactant-to-oil weight ratio was R_1=50/50, R_2=40/60 and R_3=30/70. Interesting results have been obtained concerning the structural transitions induced by temperature. We may summarise the findings as follows:

1) In agreement with previous studies, all three systems show a globular structure close to the "emulsification failure" boundary.
2) With increasing the temperature the R_1 and R_2 systems present a minimum in the self-diffusion date due to structural transition from spherical to prolate micelles. In the R_3 system this effect is absent.
3) The oil and surfactant self-diffusion coefficients increase dramatically with the temperature and diverge, indicating the onset of a bicontinous structure.

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