TIME DOMAIN SPECTROSCOPIC DIELECTRIC PERMITTIVITY MEASUREMENTS ON AOT/WATER/ISO-OCTANE

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A large dielectric relaxation in the megahertz range is observed in AOT/water/iso-octane systems in the reversed micellar phase, containing variable amounts of water. Its properties are investigated and it is concluded that a particle-size-dependent process is responsible.

1. Introduction

Water and oil can be mixed in arbitrary ratios in the presence of sufficient surfactant molecules. It is generally accepted that, at low volume fractions of the dispersed phase (either water or oil), the solution consists of small spheres of water (or oil) surrounded by a layer of surfactant molecules in a continuous oil (or water) phase [1]. However, the structure of surfactant/water/oil mixtures (microemulsions) containing similar amounts of water and oil is as yet unresolved and is currently the subject of intensive research. The existence of a separate, bicontinuous phase has been proposed [2,3].

These systems are usually studied by NMR or light, neutron and X-ray scattering techniques [1–3], but so far only a few studies utilizing dielectric spectroscopy have been reported.

Hanai et al. [4] have shown that water, solubilized in oil with a minimal use (<5%) of special surfactants, behaves as a normal binary water-in-oil system. Its dielectric behaviour can be explained in terms of the properties of mixed systems and theories of interfacial polarization [4,5]. In contrast, systems containing higher surfactant concentrations exhibit anomalous dielectric behaviour [6].

Here we present dielectric permittivity measurements on the ternary system AOT/water/iso-octane. Sodium di-2-ethylhexyl sulfosuccinate (Aerosol OT, AOT) is an anionic surfactant with two hydrocarbon tails and can be employed to stabilize micro-emulsions without the use of co-surfactants. The use of time domain spectroscopy [7–9] enabled us to cover a larger range of frequencies (≈1–1000 MHz) than that in refs. [4,6]. In this way we were able to measure the complete relaxation of the system.

The results show that the magnitude and relaxation time of the observed relaxation depend on the size of the individual water spherules giving rise to the anomalous dielectric behaviour, reported previously [6]. By working with a fixed particle size we find that the dielectric behaviour can be explained quantitatively for low (<20%) volume fractions of water.

2. Experimental

Measurements of dielectric permittivity were carried out with a conventional Tektronix time domain reflectometry system (7S12), coupled to a PDP 11/23 computer for data acquisition and analysis. The lower frequency range (≈1–200 MHz) was covered by multiple reflection and the higher frequencies (≈100–1000 MHz) by single reflection techniques [6–8]. The experiments were carried out at room temperature. The solutions were made of commercial Aerosol OT (Fluka, purum), iso-octane (Baker) and de-ionized, quadruple destilled water. Although the solutions were

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easily cleared by shaking, they were sonicated for about 1 min after preparation. No phase separation was observed over a period of several weeks.

3. Results and discussion

The ternary system AOT/water/iso-octane is characterized by two parameters:

$$W_0 = \frac{[H_2O]}{[AOT]}, \quad S_0 = \frac{[\text{iso-octane}]}{[AOT]}.$$

In all our samples W_0 and S_0 were chosen so as to produce the reversed micellar phase (L_2 in ref. [10]). The permittivity spectra were measured as a function of W_0 and S_0 and a typical spectrum is shown in fig. 1. It can be seen that the system exhibits a relaxation process characterized by a broad distribution of relaxation times in the 10–100 MHz frequency range. The spectra can be described in terms of the low-frequency limit ϵ_0, the high-frequency limit ϵ_∞ and a mean relaxation time τ. Here τ is defined as the reciprocal frequency ν halfway through the dispersion curve $\epsilon'(\nu)$:

$$\epsilon'(\nu = \tau^{-1}) = \epsilon_\infty + \tfrac{1}{2}(\epsilon_0 - \epsilon_\infty), \qquad (1)$$

where ϵ' is the real part of the permittivity ϵ.

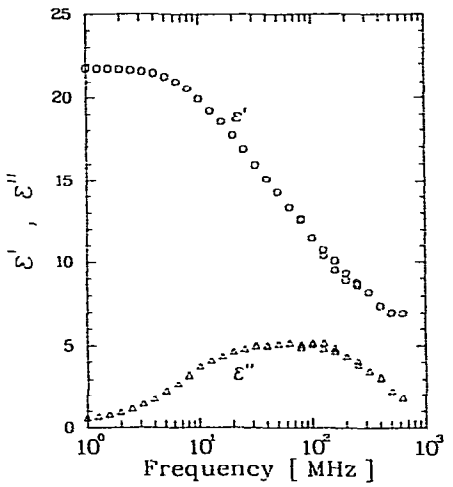

Fig. 1. Real part ϵ' and imaginary part ϵ'' of the complex permittivity $\epsilon = \epsilon' - i\epsilon''$ as a function of frequency of a solution with $W_0 = 15$ and $S_0 = 5.5$. Results of multiple reflection (1–200 MHz) and single reflection (100–700 MHz) are shown.

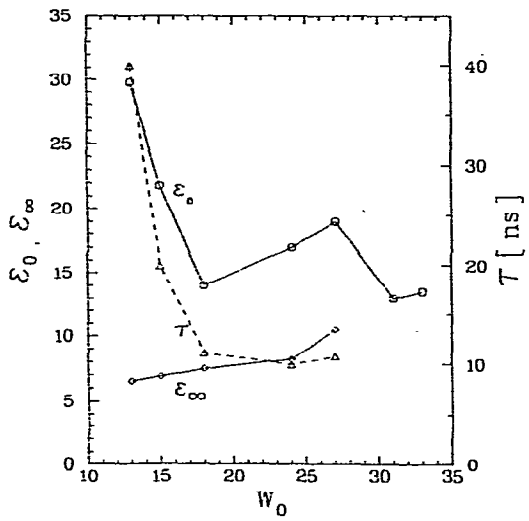

Fig. 2. Low-frequency limit ϵ_0, high-frequency limit ϵ_∞ and mean relaxation time τ as a function of W_0. The lines serve as a guide to the eye.

Fig. 2 shows the values of these parameters obtained for a system with $S_0 = 5.5$ as a function of W_0. It is seen that ϵ_0 reaches high values at low water contents and decreases on increasing W_0 in the range $13 < W_0 < 20$. The scatter in the values may be due to thermal variations as the temperature of the sample cell was not regulated. Nevertheless, the same general trend has also been observed in preliminary experiments using a HP 4917 impedance analyser and a temperature-controlled cell. The same behaviour can be seen in the results, reported in ref. [6], where we estimate that $S_0 = 14$. The values of the mean relaxation time show a similar dependence on W_0. On the other hand, the high-frequency permittivity ϵ_∞ increases monotonically with W_0. As different values of W_0 correspond to different micelle sizes [11], we can conclude that the observed relaxation is caused by a size-dependent process.

The validity of the description of the system in terms of "water particles" can be investigated by carrying out the experiments as a function of S_0 at constant W_0. This amounts to fixing the particle size [11] and measuring the permittivity of the system as a function of the particle concentration, i.e. volume fraction, of water.

Fig. 3 shows the behaviour of ϵ_0 in such an experiment with $W_0 = 33$ (radius of water sphere $\approx$6.0 nm

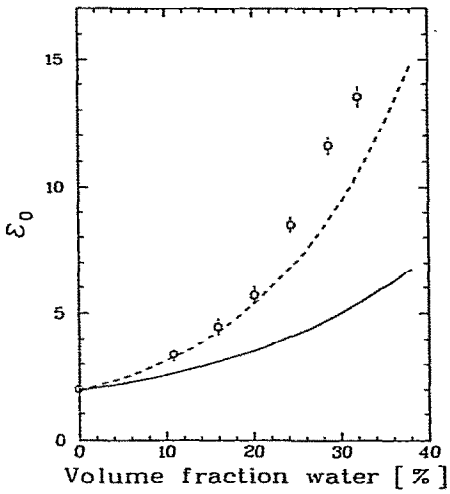

Fig. 3. Low-frequency limit ϵ_0 of solutions with constant water/surfactant ratio $W_0 = 33$ as a function of volume fraction water. In calculating volume fractions a volume of 660 A^3 of the AOT molecule [11] is assumed. The solid line represents Bruggeman's mixture equation for a binary water-in-oil solution. In calculating the dashed curve, interfacial polarization and polarizability of the surfactant layer have been taken into account.

[11]). Here ϵ_0 increases monotonically as a function of water content, although the results cannot be explained in terms of a simple water-in-oil model and Bruggeman's mixture formula [5], even at very low concentrations. This description may not in fact be very realistic for our system for the following reasons. Firstly, AOT is an ionic surfactant, its associated Na^+ ions may be expected to influence the dielectric properties of the water droplets. Secondly, the permittivity does not drop sharply from 80 (water) to 2 (oil) at the water/surfactant interface. Rather we expect it to decrease continuously across the AOT layer as a result of water penetration and the polarizability of the AOT molecules. Thirdly, the validity of the Bruggeman approach may be questioned at the high particle concentrations used in our study, where effects due to the close packing of the particles may become important. Finally we note the current discussions on bicontinuous phases [2,3], negating a description with separate water spherules at high concentrations.

We took account of the first two considerations by assuming a Maxwell–Wagner "short circuit" [5] of the water sphere at low frequencies and introducing a smooth decrease of ϵ over the AOT layer, following ref. [12]. In this way we calculated the dashed curve in fig. 3. A much better agreement with the experimental results is obtained up to 20% water (micelle fraction 35%). It is as yet unclear whether the discrepancy at higher concentrations is due to failure of Bruggeman's expression or the occurrence of a bicontinuous phase. Further work is in progress to clarify this point.

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