1. RANDOM Bicontinuous Microemulsions

A) Introduction

Since the early model of ordered bicontinuous structures generated by minimal surfaces proposed by Scriven[1], two models of random bicontinuous structures[2-4] have been published in which the local curvature of the surfactant film strongly fluctuates.

These random bicontinuous structures and the statistical configurations of the oil, water and surfactant are described by simple mean-field models[2,4,5] in which the volume of the microemulsion is divided into elementary cells of mean size $\xi$, randomly filled by oil and water, the surfactant being distributed at the oil water interface.

The models differ mainly by the way the random geometry is generated. In the original Talmon-Prager model[2], the cells are generated by a random Voronoi tessellation and their size distribution is large. In contrast to Talmon and Prager, de Gennes-Jouffroy-Levinson[4] and also Widom[5] assume that the film stiffness forbids the curvature fluctuations at spatial scales smaller than $\xi_K$, the persistence length of the surfactant layer. This length is the basic size of the cells, which are taken to be identical and cubic.

In both models, by contrast to the well-known equation giving the radius $R$ of water in oil spheres:

$$R = 3\phi_w/C^O_S,$$

the mean size $\xi$ of the oil and water elementary volumes, which is the length scale ($\sim 100$ Å) of the random structure, is related to the microemulsion composition by the geometrical constraint:

$$\xi = 6\phi_o \phi_w/C^O_S,$$

in which $\phi_o$ and $\phi_w$ are the oil and water volume fractions ($\phi_o + \phi_w = 1$), and $C^O_S$...
the surfactant concentration (number of molecules per unit volume), and Σ the area per surfactant molecule in the film ($\Sigma \sim 60 \text{ Å}^2$).

Equation (2) interpolates continuously between the case of water in oil droplets ($\Phi_W < 1$) and the case of oil in water droplets ($\Phi_O < 1$). In the models of random microemulsions, the average mean curvature of the film $<\kappa>$ (by convention positive for W/O droplets) increases continuously with $\Phi$, at constant interfacial area ($C_0$ constant); $<\kappa>$ is negative for $\Phi_O < 0.5$ and positive for $\Phi_O > 0.5$, and it vanishes by symmetry when the microemulsions contain as much oil than water (inversion point, $\Phi_O = \Phi_W$).

A particularly interesting case of a microemulsion system is "the Winsor III Microemulsion" which appears when an oil, surfactant and brine system separates in three phases. The "middle phase" microemulsion is associated with extremely low interfacial tensions ($\sim 10^{-3}$ dynes/cm) and has many industrial applications in enhanced oil recovery and phase transfer. Its structural organization is not well understood. Several features are particularly interesting:

a) such microemulsions are associated with extremely low interfacial tensions;

b) they appear in a range of salinity of the brine where the spontaneous curvature of the amphiphilic film (which is strongly dependent on electrostatic repulsions) could be very low;

c) if they also correspond to highly flexible films they could be good candidates for testing the random bicontinuous models which were proposed recently[2,4].

To test this prediction, different techniques have been used: conductivity measurements[6], self-diffusion coefficient measurements [7,8], electron microscopy[9] and scattering techniques[10-16]. However, as the measurement of transport coefficients only yields very indirect information on the microemulsion structure and as it has not yet been possible to obtain artefact-free electronmicroscopy pictures of the middle-phases[17], the main information on these systems comes presently from small angle X-rays and neutron scattering experiments.

By using these techniques and the method of contrast variation with deuterated molecules[18] and studying a very representative and well-known system[19], we have obtained four main experimental results[12,13,15]:

i) A well-defined surfactant film, evidenced by an asymptotic behavior of the scattered intensities, exists even in "critical" Winsor microemulsions.

ii) The characteristic microemulsion size $\xi$, defined as a mean radius of curvature and drawn from the spectra in the intermediate range of scattering vector, $q$, follows experimentally from the prediction (2).

iii) When $\Phi_O = \Phi_W$, the macroscopic concentration fluctuations of water and surfactant (measured from the scattering at zero angle for different contrasts) are not correlated.

iv) The intensity scattered only by the oil and the water exhibits a pronounced peak at a given scattering vector $q^*$ proportional to the surfactant concentration $C_0$.

Let us recall that in any scattering experiment the important parameter is the scattering vector $q$, related to the scattering angle $2\theta$ and wavelength $\lambda$ by