Stable, metastable and unstable oil-in-water droplets

Abstract In this paper we bring together some recent results concerning the stability and properties of O/W microemulsion droplets in a ternary system composed of water, decane and the nonionic surfactant pentaethylene glycol dodecylether (C12E5). Stable microemulsion droplets can be prepared when the spontaneous curvature has a finite but not too low value. Near the limit of maximum oil solubilisation the droplets adopt a spherical shape with low polydispersity. Experimental results obtained from low shear viscosity, collective and long time self-diffusion and static light scattering show that the spherical droplets interact to a very good approximation as hard spheres over a large range of volume fractions. A supersaturated microemulsion can be prepared by a rapid temperature quench (drop) into the two-phase area where a smaller droplet size coexists with excess oil. In the two-phase area, we can distinguish a region near the microemulsion phase boundary where the droplets are metastable, from a region further away from the boundary where the droplets are unstable and the oil-phase nucleates instantaneously. Treating the initial phase separation as a homogeneous nucleation it is possible to calculate an activation energy within the curvature energy approach.

Key words Microemulsion – hard sphere – metastability – nucleation

Introduction

Microemulsions are thermodynamically stable liquid mixtures of water, oil and surfactant. While being macroscopically homogeneous, they are locally structured into polar and apolar domains separated by a surfactant-rich dividing surface. Due to the many ways of dividing space, microemulsions may show a large variation in microstructure. Under certain conditions, it is possible to stabilize spherical droplets of, say, oil in water with a low polydispersity and concentration invariant size. The conditions are a finite but not too low spontaneous curvature of the surfactant film and that the system is saturated with the dispersed oil [1, 2].

One such system, with the nonionic surfactant pentaethylene glycol dodecyl ether (C12E5), water and decane has recently been investigated in detail [3–5]. Spherical oil droplets were prepared with a surfactant-to-oil ratio \( \phi_s/\phi_o = 0.815 \), where \( \phi_s \) and \( \phi_o \) are the surfactant and oil volume fraction, respectively, over a large range of droplet volume fractions \( \phi = \phi_s + \phi_o \). The surfactant consists of
a dodecyl alkyl chain connected to an oligo ethylene oxide block of five ethylene oxide units. The microemulsion particles can be considered as spherical oil droplets of (hydrocarbon) radius \( r_{hc} \) covered by a dense brush of end-grafted penta ethylene oxide chains, as illustrated in Fig. 1, where the “grafting density” is approximately 45 \( \AA^2 \) per chain. This is a situation quite analogous to sterically stabilized “solid” colloid particles.

In this paper we bring together and review the results from different experimental techniques on this microemulsion. The results, which are compared with theory and with results from “solid” colloidal particles, demonstrate the existence of spherical droplets that, to a very good approximation, interact as hard spheres over a large range of volume fractions. At the end we will also briefly discuss the properties of the system when it is supersaturated with oil, i.e. when a sample is brought by a temperature change into the two-phase area corresponding at equilibrium to a saturated microemulsion coexisting with an excess oil phase.

**Solubilisation limit from curvature energy**

In theoretical analyses of the various self-assembly microstructures of nonionic surfactant–water–oil systems, the flexible surface model, using the curvature energy concept [6], has been found to be very useful [1, 2, 7–10]. Here, the relative stability of a given phase and microstructure results from an interplay of the curvature energy of the surfactant film and entropy, but where the mean-curvature energy appears to be particularly important [1]. The local-curvature energy density, \( g_c \), is often written to second order in the curvatures [6]:

\[
g_c = 2\kappa (H - H_0)^2 + \kappa K.
\]

Here \( H \) is the mean curvature, \( H_0 \) the spontaneous curvature, \( K \) the Gaussian curvature and \( \kappa \) and \( \kappa \) are the bending and saddle splay moduli, respectively.

Safran et al. [11] discussed the stability requirements for various shapes, comparing spheres, cylinders and planes. The sphere is the shape having the highest volume for a given interfacial area. Spherical oil-in-water droplets are therefore found at the phase boundary when the microemulsion is saturated with oil. Approximating the phase boundary as corresponding to the oil chemical potential \( \mu_0 = 0 \), the radius of the spheres is given by [2]

\[
r = \frac{1}{H_0} \left( \frac{1 + \frac{K}{2\kappa}}{ \kappa f(\phi) } \right),
\]

where the last term comes from the entropy of mixing, \( \phi \) being the volume fraction of micelles.

The interface separating oil and the alkyl chain of C\(_{12}\)E\(_5\) from the ethylene oxide chain and water is known to have an essentially invariant area, \( a_r \), per molecule, independent of the curvature. It is therefore useful to define the curvature at this particular interface, and the corresponding sphere radius, which we denote the hydrocarbon radius, \( r_{hc} \), becomes

\[
r_{hc} = \frac{3(\phi_o + 0.5\phi_s) l_s}{\phi_s}.
\]

Here \( l_s = v_s/a_r \) is the surfactant volume to area ratio where \( v_s \approx 700 \, \text{Å}^3 \). The factor 0.5\( \phi_s \) comes from the alkyl chain volume of C\(_{12}\)E\(_5\) having approximately half of the total molecular volume.

**Phase diagram**

The system under investigation is the C\(_{12}\)E\(_5\)/water/decane system. The partial phase diagram (data taken from ref. [3]) at constant surfactant to oil ratio, \( \phi_s/\phi_o = 0.815 \), is presented in Fig. 2, plotted as temperature vs. the volume fraction of surfactant plus oil. The phase diagram is made with heavy water (D\(_2\)O). In normal water the phase boundaries are shifted upwards by 1.5–2 °C, otherwise the phase diagrams are equivalent. We note that the phase diagram is very similar to that of the binary C\(_{12}\)E\(_5\)–water system [12]. At higher water contents we see the sequence of a liquid micellar phase (L\(_1\)), here oil swollen micelles, and lamellar phase (L\(_3\)) and a L\(_3\) (sponge) phase with