Structure of Microemulsions: Use of the Variable-Contrast Method Applied to Neutron Scattering*

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Microemulsions are colloidal systems which are made by a dispersion of minute droplets (a few hundred Å in diameter) of one component (water) in a continuous medium formed by another immiscible component (*e.g.* oil); the droplets are surrounded by a mixed film of surfactants. New information has been obtained about the distribution of the various components in the interior of the droplets. In contrast to other methods, this information is not dependent on inter-particle correlation. There is profound penetration of the continuous phase in the interfacial film and the droplets are poorly correlated.

Microemulsions are transparent 'pseudoternary' systems usually composed of emulsifier molecules and two other immiscible compounds such as water and oil. The most common idea about these systems is that they are made by the dispersion of droplets of one component in a continuous medium formed by another component. These droplets are very small, which explains the transparency of the system, and surrounded by a film of emulsifier molecules. Very little knowledge exists about the size and composition of the three 'phases': continuous phase, dispersed phase and interphase or interfacial film.

The results presented here were obtained with water–cyclohexane microemulsions. The interphase consists of a mixed film of sodium dodecyl sulfate and 1-pentanol. The volume fraction v of the dispersed phase, water, is in the range 0·01 to 0·04.

Small-angle neutron scattering (Jacrot, 1976; Marshall & Lovesey, 1971) has been used for two reasons:

- the microemulsion droplet dimensions are in the range of the inverse scattering vector (q^{-1}) for cold neutrons;
- the large difference of scattering length between the two isotopes H and D permits one, by the use of deuterated compounds (D_2O or C_6D_{12}), to obtain structural information about the various parts of a droplet.

Fig. 1(*a*), (*b*) and (*c*) represents the three different types of contrast which we used in these experiments. Diffusion length per unit volume is plotted as a function of the distance r to droplet centre. With contrasts (*a*) and (*b*) the droplet behaves like an homogeneous sphere. The radius of the sphere in case (*a*) corresponds to the 'water + polar head' of the droplet. In case (*b*) one could think at first glance that the radius is the 'total' radius of the droplet. In fact the radius is determined by the discontinuity of composition between the protonated droplet and the deuterated continuous phase.

With contrasts (*a*) and (*b*) measurements were performed at decreasing concentrations. Fig. 2 shows a typical Zimm's plot (Zimm, 1948) obtained with contrast (*a*). The extrapolation of the curve to zero concentration as a function of q gives the radius of gyration, and the curve of the intensity at zero q as a function of c gives the well known second virial coefficient of thermodynamic equations.
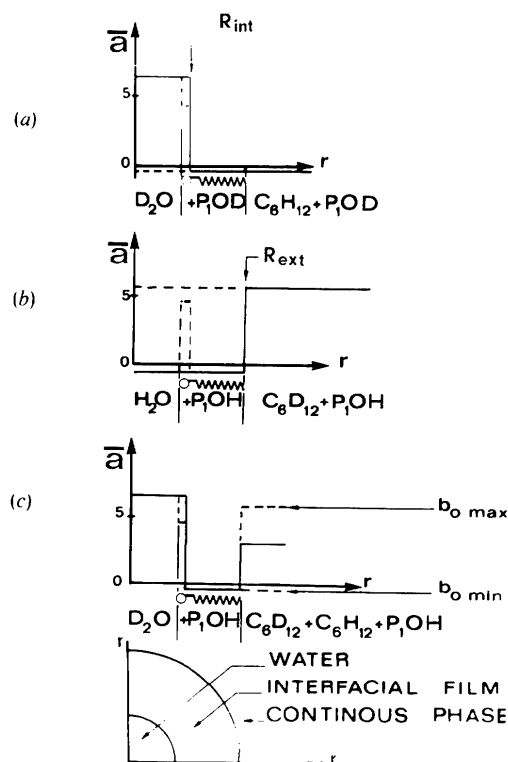
Fig. 1. Schematic representation of the various types of contrast used in the small-angle neutron scattering experiments. The lower part of the figure represents, on the same scale, the model for a droplet. The mean scattering lengths per volume unit $\bar{a}$ are in 10^{10} cm^{-2}.
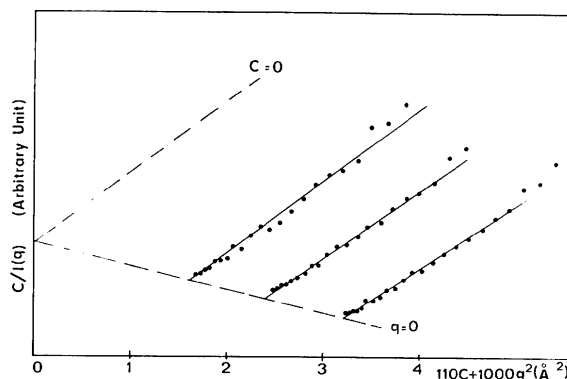

Fig. 2. Typical Zimm plot obtained from neutron scattering data of microemulsion (made of D_2O, C_6H_{12} and pentanol OD); the extrapolation to $C = 0$ gives the radius of gyration R_g and the extrapolation to $q = 0$ gives the second virial coefficient.

Fig. 1(c) represents the type of contrast obtained by the use of various mixtures of C_6H_{12}–C_6D_{12} coupled with D_2O
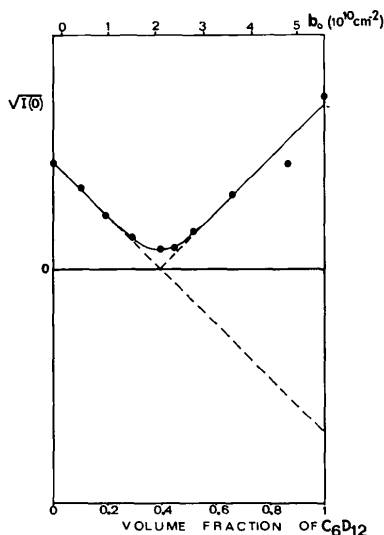

Fig. 3. The square root of the extrapolated zero-angle scattering intensity of microemulsion is plotted *versus* the volume fraction of C_6D_{12} of mixture C_6H_{12}/C_6D_{12}. b_0 is the mean coherent scattering length of the solvent.

(variable-contrast method). In that case we measured the coherent scattering cross section at zero momentum transfer as a function of the contrast between the droplets and the continuous phase (Stuhrmann, 1974). Fig. 3 shows the experimental results.

The conclusions of this study are the following: There is profound penetration of the continuous phase in the interfacial film and the droplets are poorly correlated; the negative virial coefficient observed in Fig. 2 indicates an attraction between the particles. The water radius is proportional to the volume of 'solubilized water' (at constant soap). This means that the polar head area of the surfactant is a determining factor of the structure.

The small-angle neutron scattering experiments were performed at the EL3 reactor in the Laboratoire Léon Brillouin (Saclay, France) and the data were collected on a multicounter. The mean wavelength was 7 Å, the wavelength spread 2 Å and the range of momentum transfer from 5×10^{-3} to 5×10^{-2} Å^{-1}.

A full paper on structural measurements of microemulsions has been submitted to the *Journal of Chemical Physics*.

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Phase Decomposition in Al_2O_3–SiO_2 Glasses*

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The kinetics of unmixing of SiO_2-rich compositions of ultra-rapidly quenched amorphous Al_2O_3–SiO_2 was investigated with both neutron (SANS) and X-ray (SAXS) small-angle scattering. Al_2O_3–SiO_2 glasses of 20, 25, 30, and 35% Al_2O_3 were prepared by extrusion at 1850° by water-cooled stainless-steel rollers. The samples were found by X-rays to be amorphous, and electron microprobe measurements showed the compositions to be ~ 21, 24, 28 and 33 ± 1–2% Al_2O_3, respectively. The samples were annealed in a vertical tube furnace in air. SANS experiments were carried out at the Jülich FRJ-2 reactor and SAXS at Oak Ridge National Laboratory.

Variation in thickness of the as-liquid-quenched glasses revealed that the samples were in various stages of decomposition. This was attributed to variations in quench rate,

causing thicker samples (*i.e.* poorly quenched) to be more decomposed and hence these exhibited larger decomposition spacings, as determined from SANS. Kinetic analyses were chosen for samples exhibiting the greatest quench rates and therefore the lowest states of decomposition.

There is considerable uncertainty in the literature on the location of a metastable miscibility gap in this system. A flattened liquidus on the SiO_2-rich side of the Al_2O_3–SiO_2 system implies that a region of liquid immiscibility does indeed exist, and the corresponding structures which are observed in light and electron microscopy are additional evidence for liquid–liquid immiscibility. Inherent problems with melting and crystallization of the intermediate compound, mullite, have precluded a firm determination of the equilibrium phase diagram and have seriously complicated studies of the kinetics of decomposition.

We attempted to delineate the decomposition process which occurs within the supposed miscibility gap (T_e of $\sim 1200\,°C$ at ~ 20 mol% Al_2O_3). Of particular interest to us