Structure of Microemulsion-based Organo-gels

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Water-in-oil microemulsions can form thermo-reversible gels on addition of the water-soluble (bio)polymer gelatin; a small-angle neutron-scattering (SANS) study, supported by electrical conductivity measurements, provides evidence that the aqueous content of the gel consists of a rigid network of gelatin–water rods coexisting with microemulsion droplets.

Water and oil can form thermodynamically stable, optically transparent dispersions of aqueous microdroplets in an oil-continuous medium. These water-in-oil *microemulsions* are formed in the presence of suitable surfactants.[1] It has been found recently that such oil-rich fluids can form thermo-reversible gels on addition of the water-soluble (bio)polymer gelatin.[2—4] The microemulsion-based 'organo-gels' thus formed have useful properties, such as higher electrical conductivity. Potential applications for the organo-gels include their use as vehicles for phase transfer catalysis, reverse enzyme synthesis, and oil-soluble trans-dermal drug release.

To optimise the function of these new materials, it is clearly important to obtain information on the structure of the gels and the effect of concentration and temperature on that structure. One of the most powerful techniques for structure determination of microemulsions is small-angle neutron-scattering (SANS), which has been applied to both dilute[5,6] and concentrated systems.[7,8] Previously, we reported tracer-diffusion and conductivity measurements[4] on the organo-gels, as well as a preliminary analysis of neutron diffraction data for highly-concentrated organo-gels.[9] These results, together with NMR data,[10] suggested the existence of extensive gelatin-containing, ion-conducting aqueous channels and a mobile oil phase. A different structure, consisting of gelatin-containing droplets linked through the oil phase by gelatin bridges, has also been proposed.[3] The work reported here on these novel and interesting systems provides direct evidence for a dramatic change of microstructure on addition of gelatin, which is amenable to quantitative analysis.

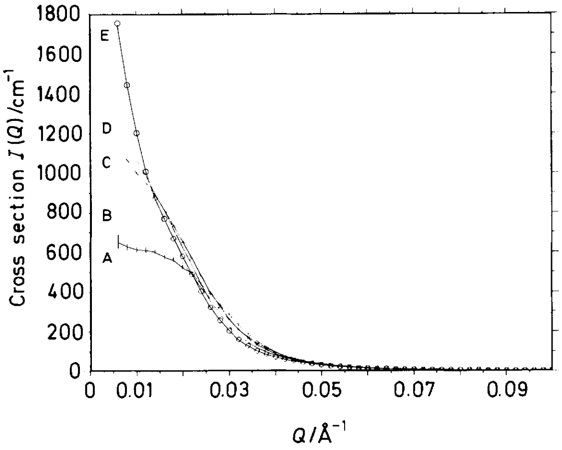

Figure 1. Small-angle neutron scattering, $I(Q)$ *vs.* Q for 10% (v/v) D_2O, 0.1 M AOT surfactant, in n-heptane, with increasing amounts of gelatin. A: (solid line, with error bars) microemulsion with no gelatin, B: (solid line) 0.5% (w/v) added gelatin, C: (x) 1.0% (w/v) gelatin, D: (solid line) 2.0% (w/v) gelatin, E: (○) 3.5% (w/v) gelatin.

The procedure used for making the gels is as follows: gelatin powder (Sigma, acid-processed pigskin gelatin, bloom 300) is heated with the required amount of water (for neutron scattering, deuterium oxide, Aldrich, 99.8% D is used) at 50—55 °C until a homogeneous, transparent liquid is formed. Then a solution of AOT (Aerosol-OT, sodium bis-2-ethylhexylsulphosuccinate, Sigma 99%) in n-heptane (Fisons, 99.5%) at the same temperature is added to the aqueous liquid, and the mixture shaken vigorously until a viscous, homogeneous dispersion is obtained. On cooling to 25 °C, a transparent gel is formed. If carried out carefully, several different approaches result in the same equilibrium gel structure as determined by electrical conductivity measurements.

SANS spectra were obtained on the LOQ instrument associated with the ISIS pulsed spallation neutron source at the Rutherford-Appleton Laboratory. Scattering of neutrons of wavelengths 2.2—10 Å was measured as a function of time and angle. Instrumental and background effects were accounted for using standard procedures. The scattered intensity was converted to absolute cross-sections in units of cm^{-1} per steradian by comparison with standard polymer samples.[11] The cross-section is a function of scattering vector $Q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the angle of scatter and λ is the neutron wavelength. Large structural entities are associated with scattering in the low-Q region; the higher-Q region permits the exploration of smaller size domains.

We report a concentration study in which a well-defined microemulsion droplet dispersion of 10% (v/v) D_2O (5.5 M) stabilised by 0.1 M AOT in n-heptane (H) was perturbed by the addition of increasing amounts of gelatin up to a concentration of 3.5% (w/v). The scattering length–density profile across the (gelatin + water + surfactant head group)/(surfactant tail + heptane) scattering boundary was assumed to be a single, sharp step. Thus the scattering profiles reflect the aqueous structural domains. The results are shown in Figure 1. Samples A—C are low-viscosity fluids; samples D and E are gels of increasing rigidity with gelatin concentration. In the absence of gelatin, the microemulsion consists of polydisperse droplets which are well described by a Schultz distribution,[12] with number-mean radius 56 Å and standard deviation 17 Å. As gelatin is added, extra scattering appears in the low-Q region whilst that at high-Q decreases slightly but keeps the same form. This is characteristic of larger structures resulting from the formation of aggregates or a network. The change is consistent with data from electrical conductivity studies at 1 kHz (Figure 2), which provide evidence in support of the formation of percolating network (water-continuous) structures at about 2.5% (w/v) gelatin. If a non-percolating aggregate structure were formed, then no dramatic increase of conductivity would be expected.

Further information concerning the structure can be gained from a plot of log $[I(Q)]$ against $\log(Q)$ for gels and microemulsions (Figure 3). The strong scattering from the

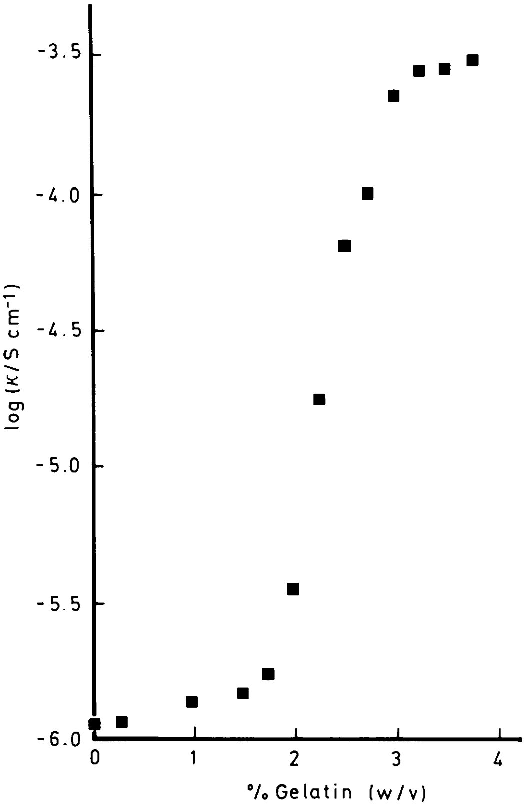

Figure 2. Log(electrical conductivity) *vs.* gelatin concentration including samples A—E, measured at 1 kHz and 25 °C.

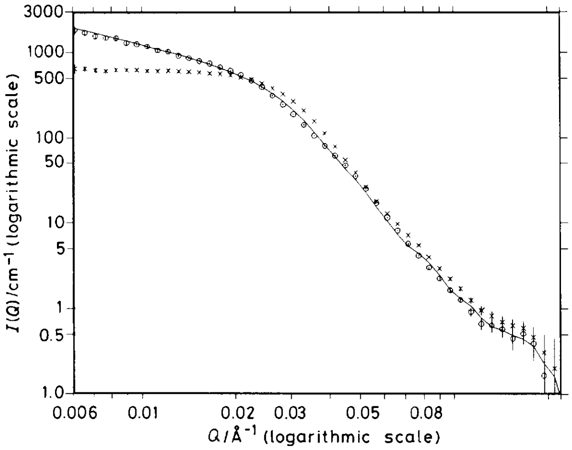

Figure 3. $I(Q)$ (logarithmic scale) *vs.* Q (logarithmic scale), samples with 10% (v/v) D_2O and 0.1 M AOT surfactant in n-heptane. (○) Gel with 3.5% (w/v) gelatin (sample E in Figure 1); solid line, least-squares fit with long rods, radius 102 (±6) Å, length ≥700 Å plus 72 (±6)% of microemulsion (sample A) marked (x). All experimental data points have statistical errors bars of ± one standard deviation. Gel mesh size is estimated as *ca.* 1300—1800 Å. The fits included small, flat backgrounds to compensate for discrepancies in previously subtracted incoherent scattering.

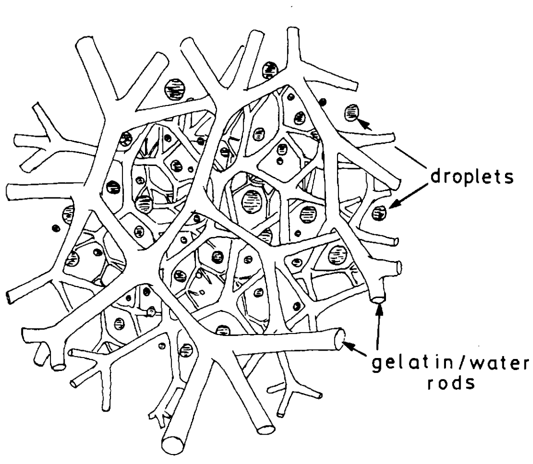

Figure 4. Diagram of structure of a microemulsion-based organo-gel: aqueous microemulsion droplets in equilibrium with a network of rods of gelatin and water, surrounded by the surfactant AOT.

3.5% (w/v) gelatin organo-gel has a slope in the low-Q region (0.006—0.02 Å^{-1}) of around -1, which then tends to a slope of -4 at high Q, whence it follows the behaviour of the parent microemulsion.

The high-Q exponent is consistent with scattering from a smooth interface. The surface area may be calculated using the Porod method[13] to be ~3 × 10^5 cm^2/ml, which corresponds to an area of 50 Å^2 per AOT molecule if all the surfactant is at the oil–water interface. The high-Q scattering intensity decreases with increasing gelatin concentration. This may be accounted for by the decrease in contrast between the oil and aqueous (now gelatin-containing) domains. In this case, the interfacial area is essentially unchanged on addition of gelatin, suggesting that AOT remains at the interface in both the microemulsion and the gel.

Following the analysis of Freltoft *et al.*,[14] it would be tempting to ascribe the additional scattering at low Q to a fractal aggregate. However, for a percolation cluster close to a critical point the predicted slope is -2.0, as calculated from the Ornstein–Zernike approach[15] and observed for (polymer-free) AOT-stabilised microemulsions.[5,6] Such structures are highly temperature dependent, in contrast to the behaviour observed for the organo-gel E which did not change in the temperature range 5—25 °C. If spherical droplets were aggregating according to an isotropic cluster–cluster aggregation model, one of the most open structures possible in such systems, the predicted slope is -1.75.[16] The observation of a slope of -1 here suggests that we have an anisotropic aggregation mechanism[17] which leads to the formation of a self-similar network of fractal dimension unity: *i.e.* rod-like on all length scales between the particle size (rod width) and the mesh size. A simpler explanation, more suited to this Q range and consistent with the high conductivities and diffusivities of aqueous species in the organo-gels,[4] is that the additional scattering at low Q is due to the formation of rods. The scattering from a long cylinder goes approximately as Q^{-1} over much of its Q range. The data are, indeed, well fitted by a monodisperse rod,[18] of radius ~100 Å. Approximately 70% of the original experimental scattering from the parent microemulsion is also present. Thus, we propose that the AOT-coated aqueous domains of the organo-gel comprise a network of rigid rods, co-existing with droplets having the same size distribution as the gelatin-free microemulsion, (Figure 3). Other results at similar concentrations also suggest that only 20—30% of the aqueous phase was involved with gelatin, the rest remaining as droplets.

A 25% (w/v) aqueous (D_2O) gelatin gel gave Q^{-1}-dependent, very weak scattering over the entire Q range, consistent with long rods of radius less than 15 Å, very different from its behaviour in the organo-gel. Gelatin is hydrolysed collagen and the latter exists in the natural state as long, thin rods of triple helix of about 7 Å outer radius and length about 3000 Å.[19,20]

Even for the fluid microemulsions which contain low concentrations of gelatin, extra scattering is observed at low Q (Figure 1). Fits to data using the method described above suggest the presence of discrete gelatin-containing rods, consisting of up to 90% water, with radius 100 Å and length around 250 Å in equilibrium with the parent microemulsion.

Analysis of the data for the gelled systems indicates that, in the 100 Å radius rods, the gelatin is associated with a roughly equal volume of water. Thus, there must be many gelatin molecules arranged together in the rod. This may be analogous to the arrangement of collagen in its natural state into larger fibres. The overall rod diameter may be determined by the preferred radius of curvature of the AOT surfactant layer in thermodynamic equilibrium with the remaining water/surfactant droplets.

Electron micrographs of aqueous gelatin indicate that the gel network is tetrahedral,[19] as expected for a triple helix. If one assumes a bond-diluted cubic lattice of rods of co-ordination 4, for an organo-gel of composition 0.1 M AOT, 10% (v/v) water, and 3.5% (w/v) gelatin, a mesh size of 1300—1800 Å is suggested. This distance is on a scale not probed by the Q range in our experiment, but is consistent with the conclusions of Luisi and co-workers from NMR studies of a mesh size of up to 2000 Å.[10]

Very recently, Eicke *et al.*[21] have published a light and X-ray scattering study of similar gel systems. They focus on a fractal analysis of data at lower Q, assuming the model proposed in ref. 3. Their observations would broadly support the neutron-scattering analysis reported in this paper. Less complex oil-rich systems (steroidal gels[22] and L_2 microemulsions[23]) formed in the absence of polymer have been shown to comprise a network of rods.

In conclusion, the results indicate that a clear change in microstructure is observed on gelation of the microemulsion which is consistent with the formation of an extensive network of rigid rods of water and gelatin surrounded by a shell of surfactant, this being in equilibrium with microemulsion water droplets.

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