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# Structural characterization of glass-forming oil/water microemulsions by neutron scattering

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Small angle neutron scattering (SANS) has been used to establish the dispersed droplet character of a class of pseudo-three-component oil/water (o/w) microemulsions which can be cooled continuously into the glassy state without either crystallization or microemulsion destabilization. SANS of toluene microemulsions at low volume fractions ( $\sim 0.5\%$ ) of toluene indicate a droplet radius of  $270 \pm 10$  Å. At normal concentrations ( $\sim 33$  vol % oil), the droplet size cannot be determined precisely but the presence of a droplet state of small polydispersity is established for toluene, *p*-xylene, benzene, CS<sub>2</sub>, and CCl<sub>4</sub> by the presence of a sharp peak in the scattered neutron intensity vs  $Q$  plots. Average interdroplet separations range from 200 to 300 Å, implying average radii of  $\sim 125$  Å. Such radii are consistent with freeze-fracture electron microscope studies of the same or similar systems. Variable temperature studies on toluene microemulsions during both cooling and warming cycles in the temperature range ambient to 100 K, show only minor ( $\sim 10\%$ ) changes in the interdroplet separation down to 220 K at which temperature diffusion through the viscous matrix phase becomes too slow to permit further emulsion structure changes on the time scale of the cooling experiment. The origin, and some possible exploitations, of this unusual stability against temperature change are discussed.

## INTRODUCTION

The spontaneous formation of microscopically dispersed states (microemulsions) of normally immiscible liquids is a phenomenon which has received much attention in recent years<sup>1-3</sup> for both practical (e.g., oil recovery) and academic reasons. Of particular interest to us have been oil-in-water-type microemulsions in which the aqueous matrix phase has been modified by additives such that no ice or other crystallization occurs during cooling. Under these circumstances it appears that the microemulsion state can be preserved indefinitely by cooling to temperatures below the glass transition temperature of the aqueous phase. This possibility has useful applications, both for the investigation of the microemulsion structures themselves and for the study of certain aspects of the liquids which may be chosen to be the microdispersed phase.

In previous papers<sup>4,5</sup> we have reported the phenomenon of simple molecular liquids (such as benzene and carbon tetrachloride) failing to crystallize during cooling when in microemulsion form. We and others<sup>6,7</sup> have also reported electron microscope studies of microemulsions in both dilute and concentrated in the oil phase which have suggested the possibility of detailed characterization not only of the average size and the distribution of sizes but also of the *shapes* of the dispersed phase particles. The latter, particularly their dynamic variations, of which a "stopped-action" picture is

presumably preserved in the vitrified microemulsion, have been the subject of elegant and interesting theoretical treatments<sup>8,9</sup> and it is reasonable to hope that systematic electron microscope study of microemulsions vitrified at different temperatures by use of matrix phases of different glass transition temperature may provide useful tests of such theories.

A necessary preliminary to any such study, and also to any study of crystallization rates of the dispersed liquids, is an adequate knowledge of the behavior of the microemulsion in response to temperature change. To date we have only the qualitative observation that xylene in aqueous phase microemulsions seems to be indefinitely stable at  $-100^\circ\text{C}$ <sup>4</sup> and the unsettling observation of very different droplet sizes in separate freeze fracture electron microscope studies of nominally the same microemulsion.<sup>6</sup>

Neutron scattering at small angles (SANS) provides a powerful method of obtaining information on the microstructural details of particle dispersions<sup>10</sup> and has been widely used in earlier studies of microemulsion structures.<sup>11</sup> In most cases the neutron scattering powers of dispersed and matrix phase differ sufficiently that there is no trouble in obtaining intensity vs scattering angle (or wave vector) plots of good information quality. In particular, by deuterating nonexchanging hydrogen positions in the dispersed phase, the contrast profile can be caused to occur at the boundary of the oil droplet rather than at the more diffuse, and size-variable surfactant-aqueous phase boundary, hence in principle allows good definition of the *actual* droplet size, and also size distribution, to be obtained. Finally, with good sample

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temperature control, full information on the variation of the time-averaged structure with temperature can be obtained, and the reversibility or otherwise of any changes observed can be investigated

We have therefore carried out a SANS study of the structures of several of the more interesting examples of the microemulsion phenomenon described in our earlier work and have examined in detail the temperature dependence of one of them. The study fully confirms the droplet microemulsion character of these systems, and the relative insensitivity of the structure to temperature.

## EXPERIMENTAL SECTION

The noncrystallizing aqueous phase of composition 75 mol %  $\text{H}_2\text{O}$ , 25 mol % 1,2 propandiol (PG)<sup>4,5</sup> was prepared from triply distilled water and analytical grade PG. As surfactant, we used the commercial Tween 80 supplied by Merck. The high HLB (hydrophilic-lyophilic balance) value of this surfactant helps ensure a dispersed oil phase (HLB = 15). Microemulsions of the same volume ratio O:W:S of (33.3/38.6/28) used in the original studies<sup>5</sup> (see Fig. 1) were prepared by mixing of the appropriate volumes of analytical grade perdeuterated benzene, toluene, *p*-xylene, and  $\text{CS}_2$ . For the  $\text{CCl}_4$  case it was necessary, as before<sup>5</sup> to add extra "oil" in order to obtain a clear phase.

The microemulsion samples were studied at two wavelengths, 7 and 15 Å using the Sans spectrometer PACE at the Saclay neutron scattering facility. Most studies were conducted at ambient temperature at an initial oil concentration of 33.3 vol % and at various dilutions with water; the dilutions ranged from 1:1 to 100:1 (see Fig. 1). In the case of the toluene microemulsion, the sample of original concentration (i.e., 0:1 dilution) was studied at temperatures varying between ambient and 100 K in a cycle, accumulating a total of 30 separate spectra. Some spectra were taken *during* cooling from room temperature to 100 K at  $\sim 10 \text{ K min}^{-1}$  while others were taken at fixed temperatures. When the glass transition of the matrix is approached ( $T_g = 164 \text{ K}$ ), the small variation of microemulsion structure with tempera-

ture seen at high temperatures ceases, as described in more detail below.

## RESULTS AND DISCUSSION

Figure 2 shows an example of the raw data of this study—a plot of the scattered neutron intensity vs the wave vector  $Q$  obtained with 7 Å incident neutron wavelength for the benzene sample. The sharp peak at  $Q_{\text{max}} = 0.0216 \text{ Å}^{-1}$  is related to the distances between droplets in the microemulsion state of the sample.<sup>10,11</sup> This interaction peak results from the product of the form factor  $P(Q)$  of each droplet and a structure factor  $S(Q)$  describing their spatial distribution:

$$I(Q) = \frac{N}{V_0} P(Q) S(Q), \quad (1)$$

where  $N$  is the number of scattering centers in the total volume  $V_0$  of the sample. In the first approximation, the position of the interaction peak in  $I(Q)$  is not very different from that of  $S(Q)$  and gives the order of magnitude of the separation  $d$  of scattering centers by  $d \approx 2\pi/Q_{\text{max}}$ . In the cases seen in Fig. 2,  $d \approx 290 \text{ Å}$  for the benzene microemulsion and 300 Å for the  $\text{CCl}_4$  microemulsion. For the toluene microemulsions discussed further below  $d = 210\text{--}240 \text{ Å}$  dependent on temperature, while for *p*-xylene and  $\text{CS}_2$  we find  $d = 260$  and  $206 \text{ Å}$ , respectively, at ambient temperature.

Information on the form factor  $P(Q)$  can be obtained by scattering from a microemulsion which is very dilute in the

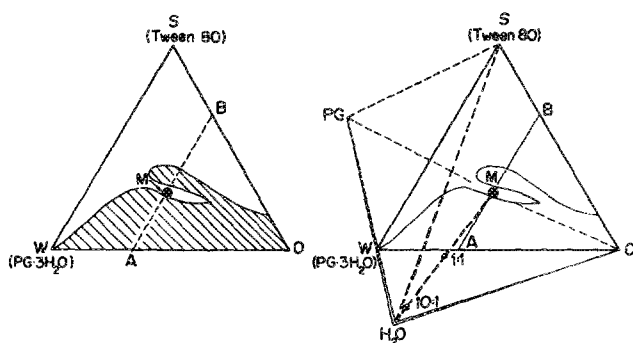


FIG. 1. Pseudoternary phase diagram for present microemulsion system showing relation of undiluted (vitrifiable) microemulsion used in present study to position of two phase regions in the system. The right-hand diagram shows relation of the pseudoternary diagram to the full quaternary system propylene glycol PG–water–oil O–surfactant S. To obtain diluted microemulsions to study droplet sizes and dilution effects, dilutions along the line  $M \cdots \text{H}_2\text{O}$  were performed.

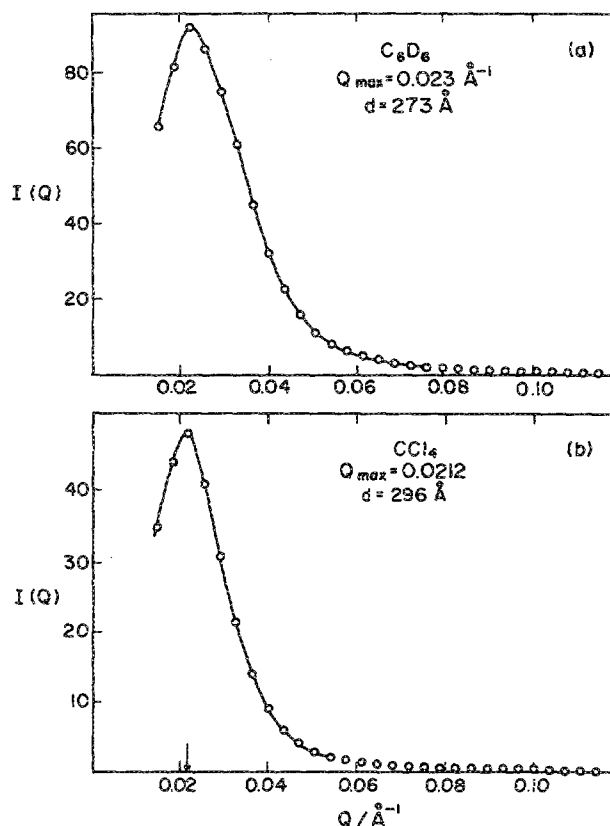


FIG. 2. Scattered neutron intensity vs wave vector (SANS spectrum) for microemulsions of (a) perdeuterated benzene, (b)  $\text{CCl}_4$ .

water phase (Fig. 1) so that the droplets, rather than being forced into a quasiordered arrangement as in hard sphere packing, are distributed at random. In this case  $S(Q) \approx 1$  (as for x-ray scattering from a gas) and  $P(Q)$  may be obtained directly.

For the diluted (100/1) cases the region of low  $Q$  can be analyzed by extrapolation to  $Q=0$  of the linear fit of  $I(Q)^{-1}$  vs  $Q^2$  to obtain a correlation length  $\xi$ .<sup>10</sup> Assuming spherical shape for the droplets, one obtains<sup>10</sup> the droplet radius from  $r = \sqrt{3}\xi$ . Figure 3 shows  $I(Q)^{-1}$  vs  $Q^2$  for the *p*-xylene and the toluene microemulsions at dilutions of 100/1. From the plots we obtain the characteristic lengths  $\xi = 125$  Å for toluene and  $\xi = 25$  Å for *p*-xylene, corresponding to the radii  $r = 280$  and  $50$  Å, and radii of gyration  $R_g = \sqrt{3}\xi$  of 220 and 40 Å, respectively. Previously, polydisperse *o*-xylene microemulsion particles of radius 10–30 Å have been seen by transmission electron microscopy of vitrified films of microemulsions of the same dilution.<sup>5</sup>

For the concentrated microemulsions, the data obtained at large  $Q$  are more useful because they show the interaction peak resulting from  $S(Q)$ . Moreover, beyond this peak they show the  $Q^{-4}$  dependence expected for particles of smooth surface in the Porod region, because  $S(Q)$  is close to unity in this region. Figure 4 shows  $\ln I$  vs  $\ln Q$  for toluene microemulsion of the original concentration 33.3 vol % oil, and for dilutions of 20/1, 50/1, and 100/1. In the Porod region, the scattered intensity is proportional to the total surface area of the droplets. We can therefore extract from the linear  $Q^{-4}$  dependence in a logarithmic plot, the ratio of surface areas per unit volume of sample. We recover the expected ratio due to dilution, confirming that the droplet radii are not changing upon dilution. These radii are consistent with the interparticle spacing suggested by the  $Q_{\max}$  values of Fig. 2. A center-to-center spacing of 290 Å implies a concentra-

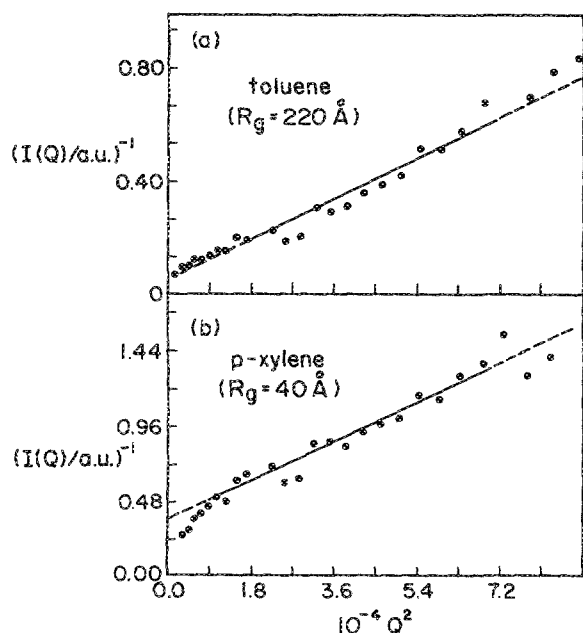


FIG. 3. Inverse scattered intensity vs  $Q^2$  for (a) diluted (100/1) microemulsion of toluene, (b) diluted (100/1) microemulsion of *p*-xylene.

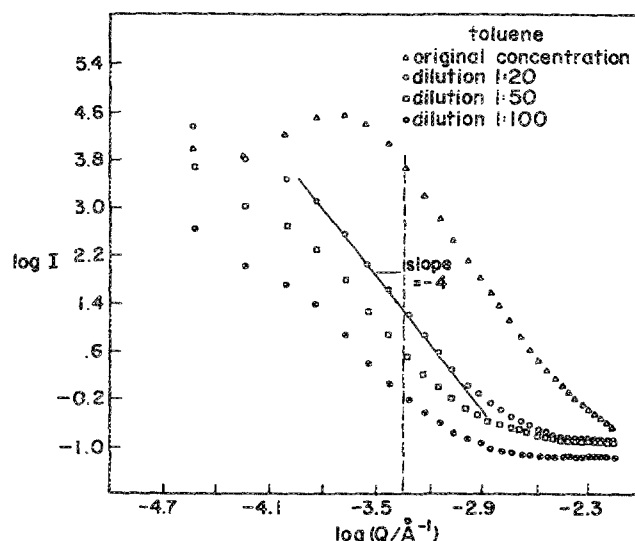


FIG. 4. Porod plot at large  $Q$  of toluene microemulsions at original 33 vol % toluene, and various dilutions with water. 20/1; 50/1; 100/1. Note that for  $q = 0.035$  Å<sup>-1</sup>, where in all cases the scattered intensity shows the  $Q^{-4}$  dependence, the ratio of intensities is the same as the ratio of dilutions, implying that the droplet size changes little with dilution.

tion of particles of  $[1/(290 \times 10^{-8})]^3$  per cc and, since there is only 0.33 cc of benzene in a cc of microemulsion, the average volume of each droplet must be about  $6.7 \times 10^{-18}$  cc and its radius must therefore be  $\sim 120$  Å.

Such radii are compatible with the result of two freeze-fracture electron microscopy studies of 27 vol % *o*-xylene microemulsions.<sup>6,7</sup> These have shown the presence of a particulate microemulsion with irregularly shaped droplets (see Fig. 5 insert) of mean radii  $\sim 200$  and  $\sim 25$  Å in different experiments. The origin of the difference in particle sizes seen in the different experiments was not known but a difference in effective quench temperatures was considered a possibility. With the present data we can make an accurate assessment of the effect of temperature on the mean particle separation hence draw semiquantitative conclusions about the effect of temperature on particle size, as follows.

Figure 5 shows SANS spectra at seven different temperatures from ambient to 100 K. The insert to Fig. 5 shows the variation of the mean particle separation  $d$  with temperature. It can be seen that  $d$  changes significantly with temperature down to 220 K and then becomes fixed. The break occurs well above the matrix glass temperature of 164 K. This is appropriate because changes in droplet size can only occur by diffusion between droplets which becomes extremely slow as the matrix viscosity increases with approach to  $T_g$ . Therefore the emulsion structure should become non-ergodic at temperatures well above  $T_g$ .<sup>12</sup> The persistence of relaxation to the lower temperature  $T_g$  for a homogeneous liquid is possible because only local ( $\sim 1$  Å) adjustments in particle positions are needed to achieve the equilibrium state. The dashed line in Fig. 5 insert shows how the particle radius would continue to change with decreasing temperature if sufficient time for diffusion between droplets were allowed so that the equilibrium state could be maintained.

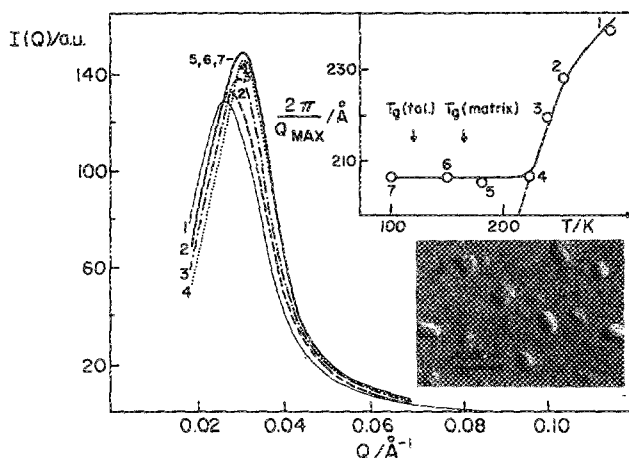


FIG. 5. SANS spectra of toluene microemulsions between ambient temperature and 100 K. Insert shows variation of  $2\pi/Q_{\max}$  with temperature showing kinetic arrest of microemulsion structure (ergodicity breaking) at  $T \gg T_g$  (matrix phase). The second insert shows freeze fracture electron micrograph of microemulsion droplet sizes and shapes, from Ref. 6.

The changes in  $Q_{\max}$  seen in Fig. 5 correspond to changes in average particle separation of no more than 30 Å, hence to changes in the number of particles (or, correspondingly, of their average diameter) of no more than a few percent. The surprising insensitivity of these pseudoternary microemulsions against change in temperature which was noted in previous work<sup>5</sup> is therefore fully confirmed. On the other hand, this finding leaves unexplained the variation in microdroplet sizes seen in the freeze-fracture electron microscopy studies.<sup>6</sup>

The weak temperature dependence of the structure is of considerable importance to the prospect of using these vitrifiable systems for detailed electron microscopy studies of subtle details of size and shape distribution of the dispersed phase in these systems. It means that the structures observed will be essentially independent of the cooling rate used during sample preparation. It also implies that the droplets do not interact strongly<sup>13</sup> and that the surface tension changes little with temperature hence that the dynamic variations in droplet shapes will be the same at all temperatures.<sup>9</sup> In this case, all that will happen on cooling will be a slowing down of the rate of change of each microdroplet shape as the viscosity of the matrix phase rises with approach to the glass transition. The characteristic time scale for microemulsion droplet shape changes, which is normally extremely short, of order  $10^{-9}$  s, can thus be brought into any time scale window of experimental interest simply by change of temperature. Since the shape change kinetics are now controlled by the sluggishness of relaxation in the *matrix* phase,  $T_g = 164$  K, rather than by the droplet phase, the shape variation time scale will be decoupled from any intrinsic time scale (shear relaxation time, dielectric relaxation time, etc.) of the droplet phase. This time scale separation could be useful in developing experimental probes of the droplet deformation modes. It means, likewise, that shape variations, which merely slow down on approach to the matrix glass transition, should be faithfully preserved in the glassy state for

electron microscope study. The shape variations already reported from electron microscopy studies<sup>6,7</sup> (see Fig. 5 insert) are therefore likely to be reliable representations of the actual higher temperature dynamic structures (hence should provide for tests of validity of theories<sup>10</sup> of microemulsion structure).

Since the results so far confirm an almost temperature-independent droplet microstructure for this type of system it will be of interest to examine further the cases of the simplest liquids  $\text{CS}_2$  and  $\text{CCl}_4$ . The former must be the simplest molecular liquid ever obtained in the glassy state, while  $\text{CCl}_4$  is a pseudospherical molecule which has been studied in great detail in all *except* supercooled and glassy conditions. While the concentrated microemulsion seen in Fig. 2(b) is a dispersed droplet phase, with particles of the order of  $r = 300$  Å, there is evidence of aggregation phenomena in the more diluted cases. A more detailed study of these cases will be presented in a future article.

## CONCLUDING REMARKS

It is worth noting that, at compositions just *out* of the clear phase (microemulsion) range of Fig. 1, a system with the present combination of vanishing, and also temperature independent, surface tension, between two liquid phases of very different fluid viscosities, should provide an excellent model system for the study of fractal patterns in viscous fingering fluid interpenetration studies, according to current theories of the phenomenon.<sup>14</sup>

## ACKNOWLEDGMENTS

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