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 (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.

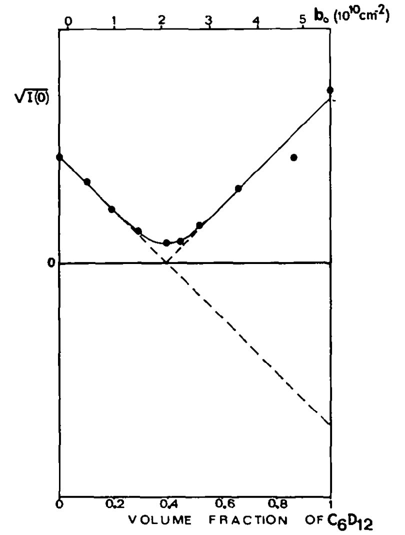

Fig. 3. The square root of the extrapolated zero-angle scattering intensity of microemulsion is plotted *versus* the volume fraction of C_6D_{12} of mixture C_6H_{12}/C_6D_{12}. b_0 is the mean coherent scattering length of the solvent.

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*.

References

Jacrot, B. (1976). *Rep. Prog. Phys.* **39**, 911–953.

Marshall, W. & Lovesey, S. W. (1971). *Theory of Thermal Neutron Scattering*. Oxford Univ. Press.

Stuhrmann, H. B. (1974). *J. Appl. Cryst.* **7**, 173–178.

Zimm, B. (1948). *J. Chem. Phys.* **16**, 1093–1099.

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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 ultrarapidly 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_c of ~1200 °C at ~20 mol% Al_2O_3). Of particular interest to us

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was the possible occurrence of a spinodal mode of decomposition.

The above quenched compositions were aged at temperatures from 200 to 850°C and the small-angle spectra were followed isothermally. To a first approximation spinodal behavior was observed for a number of compositions and temperatures (*e.g.* for 30 mol% Al_2O_3 at 200 and 600°C), though the mode of decomposition could not with certainty be specified as linear. There was, however, indication of a non-shifting cross-over point and an increasing integrated intensity for the SANS experiments, which indicates that a spinodal process is occurring. For example, an examination of the $R(\beta)$-*vs*-β plot for 30 mol% Al_2O_3 for the 0–5 min interval of aging at 200°C gives $\beta_c/\beta_m = 2{\cdot}68$ and $\lambda_m = 175$ Å, indicating that this composition is within the spinodal region at 200°C. On the other hand, aging at 850°C for only 1 and 5 min showed a clear decay in the scattering curves, indicating that the glass was homogenizing. A new miscibility gap was, thus, constructed from the region of the experimentally determined spinodal line.

The large observed SAXS scattering noted for this system is an indication that considerable changes of density are occurring concurrently with decomposition (Si and Al have closely similar atomic scattering factors, and, thus, are not expected to yield a strong SAXS intensity). This was confirmed with density and refractive index measurements, which enabled us to conclude that the observed density fluctuations, *e.g.* as observed by SAXS, result from alumina densification. Thus, density and composition fluctuations are one and the same.

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Study of the Colloidal Nature of Petroleum with an Automated Bonse–Hart X-ray Small-Angle Scattering Unit

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A Bonse–Hart small-angle X-ray diffractometer was interfaced to an automated X-ray diffraction system and used to study the colloidal nature of crude oil. Asphaltic colloids, which have a radius of gyration of 20 to 40 Å in many oils, were found to grow in size to several thousand Å on addition of straight and branched-chain aliphatic hydrocarbons. Addition of cyclic and aromatic hydrocarbons produced little change in colloid size. Two types of large colloids, having radii of gyration of several hundred to several thousand Å, were found in some crude oils in addition to the mentioned asphaltic ones. One of the larger colloids is wax. The other seems closely associated with the asphaltene colloids and is present in the asphaltene fraction on precipitation of the asphaltene with pentane. The use of ultracentrifugation, deasphalting, and temperature variation allowed mixtures of colloids to be studied in more detail than could be single oil samples.

Introduction

Previous small-angle X-ray scattering studies (Dwiggins, 1965) indicated that many crude oils contain colloids rich in asphaltic material, that the size of the colloids can be determined, and that some information about polydispersity can be obtained. Earlier references are given in that paper. Intense scattering at very low scattering angles reported in the previous paper for one crude oil, Rhodes, indicated that colloids much larger than the usual asphaltic colloids might be present. Since the Guinier region of the curve was not studied in that work, studies at very small scattering angles were needed to provide good radii-of-gyration estimates. Moreover, studies of the colloidal nature of petroleum have a considerable bearing on petroleum production, because many additives and colloidal materials are now being introduced into petroleum formations in attempts to increase production, and the effect that such substances could have on the colloidal nature of crude oil may be considerable, as viscosity and other properties that influence the rate of production might be changed.

Although small-angle scattering studies of various high-molecular-weight fractions separated from petroleum have been made and may be of considerable importance in understanding such substances, the treatment of the oil was kept to the minimum for this study, to avoid possible change to the colloids. Thus only solvent addition, heating, and ultracentrifugation were used.

The first objective was to automate fully data collection and data reduction. Because scattering data down to a few seconds of angle were needed with monochromatic radiation, a Bonse–Hart type of diffractometer (Bonse & Hart, 1965, 1967) was used.

The second objective was to study the effect of adding various types of hydrocarbons and alcohols to crude oil, because some hydrocarbons produce colloid growth (Dwiggins, 1965).

The third objective was to determine what types of colloids might be present in crude oils in addition to the known asphaltic colloids.

Equipment

The basic automated diffractometer unit used was the Philips Electronic Instruments* APD 3500 (Jenkins, Haas & Paolini, 1971). The basic Bonse–Hart camera was the Advanced Metals Research Corporation Model 6-220 (Koff-

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* Reference to brand names is made for information only and does not imply endorsement by the US Department of Energy.