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# SANS on fluorinated water-in-oil microemulsions

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**Abstract**

Preliminary SANS results on water-in-oil microemulsions composed of water, fluorinated surfactant and fluorinated oil, indicate that the system is composed of interacting droplets in a large range of compositions. Work is in progress to find the interaction potential.

*Keywords*: Small-angle neutron scattering; Fluorinated microemulsion; Perfluoropolyether surfactant

Fluorinated water-in-oil microemulsions with perfluoropolyether compounds were recently characterised by phase diagram, conductivity, light scattering, nuclear magnetic resonance, dielectric spectroscopy, etc. (see Ref. [1] for a complete list of references). The ternary system water, fluorinated surfactant and fluorinated oil, show a large monophasic domain of homogeneous, transparent, isotropic samples [2]. Previous light scattering investigation [3] gave reliable results for the dilute microemulsions, $\phi < 0.10$ where $\phi$ is the volume fraction of the dispersed phase ($\phi = (\text{water} + \text{surfactant})/\text{total}$) assuming the dispersed phase composed of water droplets coated by surfactant molecules. Water droplets on nanometer scale were identified at water to surfactant molar ratio ($W/S$) higher than 6. The droplets maintain a constant radius at constant $W/S$ ratio. Spherical shapes were hypothesized, as no experimental evidence of depolarized light was found and the polydispersity was very low (10%). The hydrodynamic radius increases versus the $W/S$ ratio increase (27 Å at $W/S = 6.5$, 31 Å at 11, 44 Å at 16 and 57 Å at 22) for the most part of hydrogenated water-in-oil microemulsions. The second virial coefficient $\alpha$ ($< -20$ at $W/S = 6.5$, $-8$ at 11, $-2$ at 16 and $\sim 0$ at 22) indicates that the attractive component of the interaction between droplets is higher for smaller droplets. This trend is opposite to that usually observed in hydrogenated water-in-oil microemulsions for which the attractive interaction between droplets is dominated by the attraction of water cores [4]. A percolation phenomenon mainly of dynamic nature was found in the system [1], representing further evidence that the microemulsion is composed of interacting droplets. The droplets give rise to a cluster of infinite size, or percolate, either for an increase of the number density of the aggregates themselves or for a temperature increase [1].

The fluorinated compounds [1] were from Ausimont S.p.A. (Milan,Italy). The water was from a Millipore Milli-Q system. SANS experiments were performed at the spectrometer PAXE (Lab. Léon Brillouin, Saclay) with a sample-detector distance of 2.5 m and incident neutron wavelength of 5 Å with wavelength spread of 10%. Collimation was achieved by two slits of 12 and 7 mm placed 2.5 m far apart. Samples of thickness 1 mm were contained in flat quartz cells, temperature controlled within ±0.1°C.

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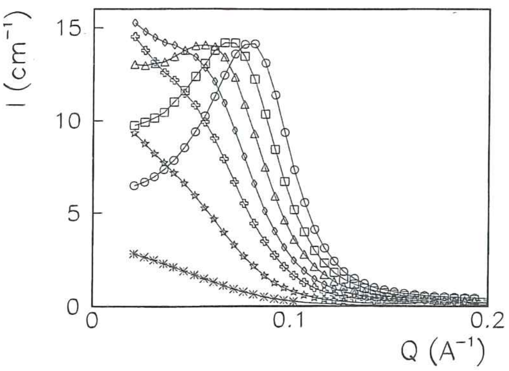


Fig. 1. Experimental scattered intensity at $T = 20°C$ of fluorinated microemulsions with $W/S = 15$ and $\phi$ values: 0.599 (circles), 0.499(squares), 0.390(triangles), 0.285(rhombuses), 0.202(crosses), 0.100(stars) and 0.0303(asterisks). The lines are guides for the eyes.

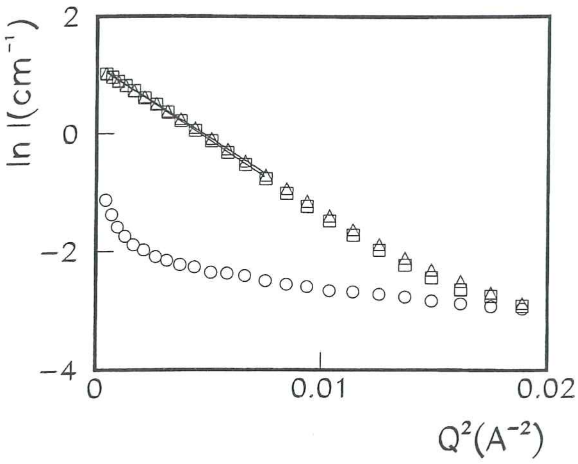


Fig. 2. Guinier plot of samples at $W/S = 15$ with $\phi = 0.0303$(triangles), at $W/S = 20$ with $\phi = 0.0318$(squares) and at $W/S = 5.6$ with $\phi = 0.0300$(circles). $T = 20°C$. The solid lines represent the fitted straight lines to the data points. $I(Q) \sim \exp(-Q^2R_g^2/3)$ where $R = R_g * \sqrt{5/3}$ is the droplet radius.

The intensity was corrected for the empty-cell contribution and normalized to absolute scale by means of a secondary standard of known cross-section [5].

In Fig. 1 the experimental scattered intensity as a function of $Q$, $I(Q)$, is shown for samples with $W/S = 15$ at $T = 20°C$ ($\phi$ values in the range 0.60 to 0.03). For each curve, the contribution of the oil scattered intensity was subtracted. The principal characteristic of the spectra of Fig. 1 is the presence of a peak at $Q \sim 0.08$ Å$^{-1}$ for $\phi = 0.599$ and the shift of the peak to lower $Q$ values as a function of the decrease of the volume fraction of the dispersed phase. The Guinier plot of the curve at $\phi = 0.0303$ is reported in Fig. 2. A radius of the particle of 35 Å is calculated, and found to be in good agreement with light scattering results. In neutron scattering, the fluorinated surfactant shell and the continuous fluorinated oily medium have the same scattering-length density thus it is reasonable that the Guinier radius is smaller than the hydrodynamic radius measured by light scattering. SANS investigation at $W/S = 11$ gave a Guinier radius of 23 Å and a similar interpretation was given in Ref. [6]. At $W/S = 20$ a data set similar to that of Fig.1 was detected; the Guinier radius of the dilute sample is 36 Å, see Fig. 2. For comparison, the dilute sample at $W/S = 5.6$ is reported in Fig. 2. The Guiner region is not observed.

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