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SANS study of a fluorinated water-in-oil microemulsion¹

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SANS study of a fluorinated water-in-oil microemulsion¹

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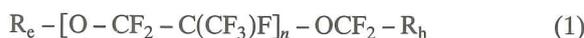
Abstract

The experimental results of a SANS analysis of fluorinated water-in-oil microemulsions with perfluoropolyether oil and surfactant are shown at $T = 20^\circ\text{C}$ and $T = 35^\circ\text{C}$ for samples with a constant water-to-surfactant molar ratio $W/S = 11$. Under the hypothesis that the system is composed of interacting droplets, by a Guinier analysis of the dilute samples, a droplet radius of 23 Å is found for the two temperatures studied. Furthermore, all the samples studied follow the Porod law, as expected for dispersed particles with a sharp interface. For the two temperatures studied, a microemulsion interfacial area per surfactant molecule of 50 \AA^2 is found in the dilute region and about 35 \AA^2 in the concentrated region.

Keywords: Small angle neutron scattering; Microemulsions

1. Introduction

In this work we present some preliminary results of a SANS study on fluorinated water-in-oil microemulsions. The microemulsion is composed of water (W), fluorinated surfactant (S) and fluorinated oil (O). The oil and the surfactant are perfluoropolyether compounds of general formula



The oil chain ends (R_e and R_h) are a mixture of $-CF_3$, $-CF_3CF_2$ and $(CF_3)CF$ groups, and the surfactant polar head group R_h is $-COO^- NH_4^+$. The oil has a molecular weight (MW) of 900, density 1.8 g

cm^{-3} and viscosity 6.2 cP. The surfactant has MW 710 (MW distribution 95% by gas chromatographic analysis). The ternary system studied in this work shows a large monophasic domain at $T = 20^\circ\text{C}$ (transparent, not birefringent samples) for a water content of less than 17 wt% and a surfactant to oil ratio in the range 0.05–4.8 (w/w) which decreases towards the S–O side at higher temperatures [1]. Water and oil are insoluble in any proportions; water and surfactant give liquid crystalline phases [2,3]; the surfactant and the oil solubilize each other only at temperatures above 30°C . A previous light scattering investigation [4,5] gave reliable results for the dilute microemulsions. Water droplets on the nm scale were identified at water to surfactant (W/S) molar ratios higher than 6. It was experimentally established that, for the dilute system, the droplets maintain a constant radius at constant W/S. Spherical shapes were

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hypothesized in the dilute region, as no experimental evidence of depolarized light was found and the polydispersity was very low (10%). The dilute region corresponds to ϕ values lower than 0.05 at W/S = 6.5 (molar ratio), and ϕ values lower than 0.10 at W/S = 11 and 16, where ϕ is the volume fraction of the dispersed phase, $\phi = (\text{water} + \text{surfactant}) / \text{total}$, assuming that the dispersed phase consists of water droplets coated by surfactant molecules. The hydrodynamic radius increases from 30 to 50 Å as the W/S ratio increases: it is 27 Å at W/S = 6.5, 31 Å at W/S = 11 and 44 Å at W/S = 16. The second virial coefficient α was found to be below -20 at W/S = 6.5, -8 at W/S = 11 and -2 at W/S = 16. The increase in the radius follows the increase in the water to surfactant ratio, as for the majority of water-in-oil microemulsions. The interactions between droplets are more attractive for the lowest W/S ratio (smaller droplets) and less attractive for larger droplets, approximating the hard-sphere behavior ($\alpha \approx 0$). This trend is opposite to that usually observed in hydrocarbon water-in-oil microemulsions. A dielectric study on the system at W/S = 11 has recently shown a percolation phenomenon of mainly dynamic nature [6,7] which also represents indirect 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 in the number density of the aggregates themselves or for a temperature increase. By dielectric investigation it is possible to distinguish between samples composed of interacting droplets and those composed of continuous channels of water and oil, namely bicontinuous structures. The fluorinated microemulsions of this work show the behaviour of interacting droplets.

In this paper we report the experimental data for a SANS study performed on a microemulsion system with a water to surfactant molar ratio W/S = 11 studied at temperatures of 20°C and 35°C, and also some considerations of the system structure. The light scattering study is difficult because of the poor contrast between the water core (index of refraction 1.33) and the fluorinated external medium (index of refraction 1.28). On the other hand, the contrast in neutron scattering K , i.e. the difference between the coherent scattering length densities of the droplet water core ($-6.21 \times 10^9 \text{ cm}^{-2}$) and of the oil medium ($3.88 \times 10^{10} \text{ cm}^{-2}$) is high, $K = -4.50 \times 10^{10} \text{ cm}^{-2}$.

2. Experimental

The fluorinated compounds were obtained from Ausimont S.p.A. (Milan, Italy). The water was taken from a Millipore Milli-Q system. The sample preparation was described in ref. [1].

The SANS measurements were performed on the PAXE spectrometer at the Laboratoire Léon Brillouin at Saclay (France) using a wavelength of 5 Å with a wavelength spread of 10%. The Q range investigated for all the samples was $0.02\text{--}0.28 \text{ \AA}^{-1}$ (sample-to-detector distance fixed at 2.515 m). Samples of thickness 1 mm were contained in flat quartz cells temperature controlled to within $\pm 0.1^\circ\text{C}$. The intensity was corrected for the empty cell contribution and normalized to the absolute scale by means of a secondary standard of known cross section [8].

3. Results and discussion

In Fig. 1 and Fig. 2 the experimental scattered intensity as a function of Q , $I(Q)$, is shown for samples of the dilution line W/S = 11 at $T = 20^\circ\text{C}$ (ϕ values in the range 0.6–0.02) and $T = 35^\circ\text{C}$ (ϕ values in the range 0.5–0.2), respectively. For each curve the contribution of the oil scattered intensity has been subtracted. The principal characteristic of the spectra of Fig. 1 is the presence of a peak at $Q = 0.1 \text{ \AA}^{-1}$ for $\phi =$

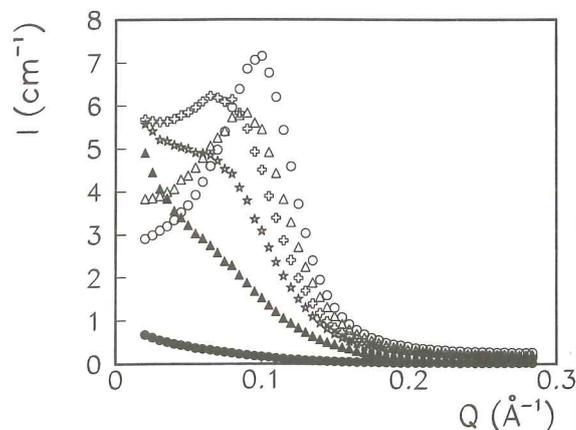


Fig. 1. Experimental scattered intensity of fluorinated microemulsions with W/S = 11 and ϕ values: 0.600 (open circles), 0.501 (open triangles), 0.408 (open crosses), 0.327 (open stars), 0.205 (filled triangles) and 0.0205 (filled circles). $T = 20^\circ\text{C}$.

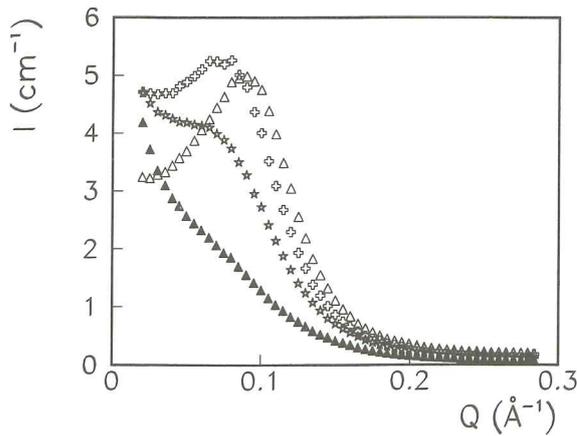


Fig. 2. Experimental scattered intensity of fluorinated microemulsions with W/S = 11 and ϕ values: 0.501 (open triangles), 0.408 (open crosses), 0.327 (open stars) and 0.205 (filled triangles). $T = 35^\circ\text{C}$.

0.6 and 0.5, and the shift of the peak to lower Q values as a function of the decrease in the volume fraction of the dispersed phase. Similar behaviour is observed in Fig. 2.

The curves corresponding to $\phi = 0.0208$ and 0.208 in Fig. 1 and to $\phi = 0.208$ in Fig. 2 have been analysed in the low Q region ($QR < 1$) by the Guinier relationship $I(Q) = K^2 V^2 \exp(-Q^2 R_g^2/3)$, where K is the contrast, R_g is the radius of gyration of the particle and V is its volume [8]. The plots are reproduced in

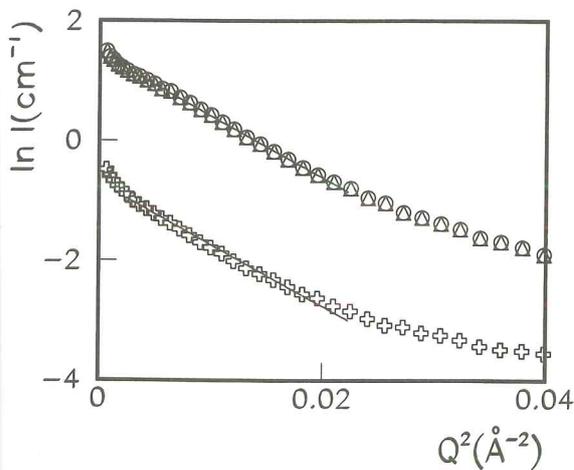


Fig. 3. Scattered intensity vs. Q^2 for the samples with $\phi = 0.205$ at $T = 20^\circ\text{C}$ (open circles) and $T = 35^\circ\text{C}$ (open triangles) and with $\phi = 0.0205$ at $T = 20^\circ\text{C}$. The solid lines represent the Guinier plots.

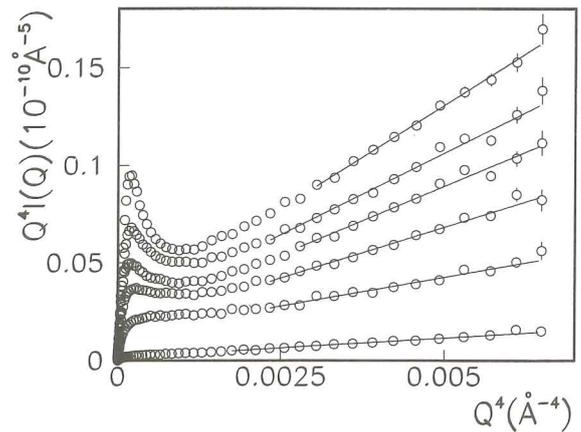


Fig. 4. $Q^4 I(Q)$ as a function of Q^4 for the samples of Fig. 1 at $T = 20^\circ\text{C}$. ϕ varies from top to bottom in the range 0.600-0.0205.

Fig. 3 for the three samples. The trend is linear in the low Q region and the radius of the dispersed particles can be obtained from the relationship $R = R_g \sqrt{5/3}$. The values are: 23 Å for samples with $\phi = 0.0205$ and 0.205 at $T = 20^\circ\text{C}$, and 22 Å for the sample with $\phi = 0.205$ at $T = 35^\circ\text{C}$.

In the ideal case, where the interfacial region is sharp, for QR values higher than 5 (R is the radius of the particle), the Porod law applies: $I(Q) = 2\pi K^2 C_s \Sigma Q^{-4}$, where C_s is the number of surfactant molecules per unit volume of the microemulsion sample, and Σ is the area per polar head group of the surfactant molecules. This law can be written in the following form [9]: $Q^4 I(Q) = 2\pi K^2 C_s \Sigma + BQ^4$, where a term B is introduced to

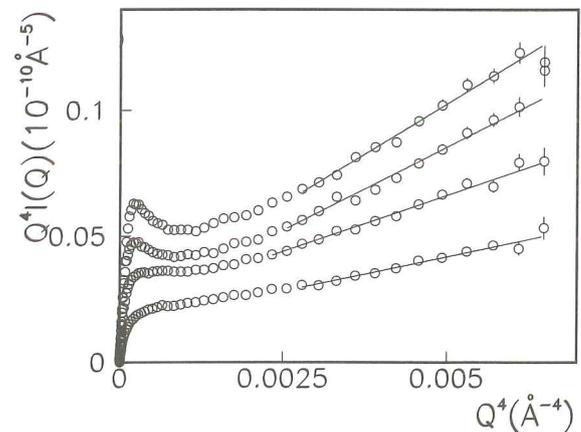


Fig. 5. $Q^4 I(Q)$ as a function of Q^4 for the samples of Fig. 2 at $T = 35^\circ\text{C}$. ϕ varies from top to bottom in the range 0.501-0.0205.

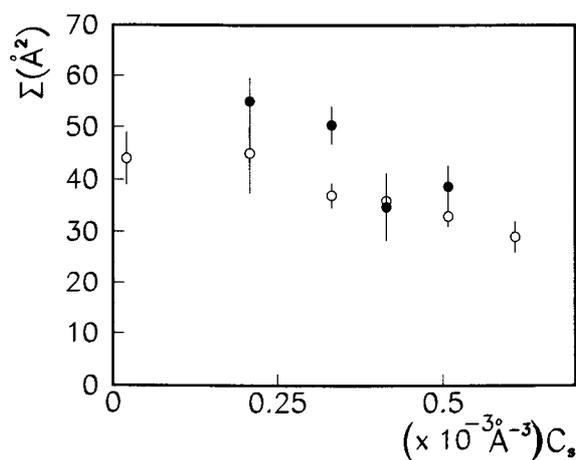


Fig. 6. The microemulsion interfacial area per surfactant molecule deduced by the Porod analysis. Open circles correspond to values calculated for the samples of Fig. 1 ($T = 20^\circ\text{C}$); filled circles to values calculated for the samples of Fig. 2 ($T = 35^\circ\text{C}$).

interpret the incoherent contribution of the hydrogen atoms of the sample and of any other incoherent part. The fitting of the experimental data to this last relationship allows the calculation of $A = 2\pi K^2 C_s \Sigma$ (the intercept of the straight line with the ordinate axis at $Q^4 = 0$) and B (the slope of the straight line). Once the contrast K and the C_s value are known, Σ can be deduced from A . In Fig. 4 the family of curves at $T = 20^\circ\text{C}$ and in Fig. 5 the family of curves at $T = 35^\circ\text{C}$ demonstrate that the Porod law is followed by all the samples studied, thus a sharp interface exists in the

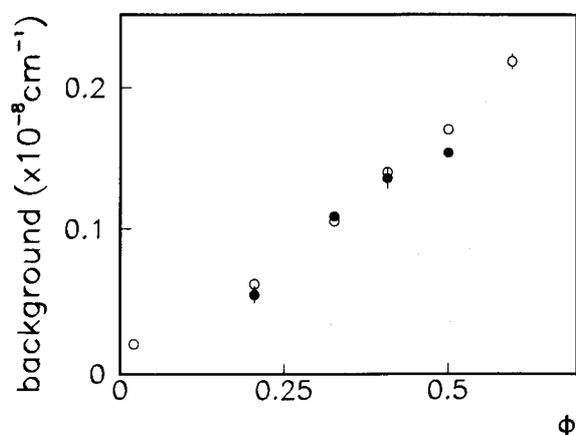


Fig. 7. The background as a function of ϕ deduced by the Porod analysis. The meaning of the symbols is as in Fig. 6.

system. The straight lines drawn in Fig. 4 and Fig. 5 represent the best fit of the experimental points to the equation reported above. The error bars (standard deviation) are drawn except when they are smaller than the symbol used. In Fig. 6 and Fig. 7, Σ and B as a function of concentration are reported for all the samples studied. We should point out that the area per polar head of the surfactant molecule, obtained by measuring the air–water interfacial tension after surfactant addition, is 50 \AA^2 [10]. The values of Fig. 6 at surfactant concentrations up to $\phi = 0.327$ agree with the value of ref. [10]. An increase in ϕ produces a decrease in the interfacial area per surfactant molecule. Similar results are shown at $T = 35^\circ\text{C}$. The increase in the background as a function of the increase in ϕ (see Fig. 7) is compatible with the increased contribution of the hydrogen atoms due to the increase in water content. The temperature does not affect this result.

In conclusion, under the hypothesis that the system is composed of interacting droplets, the droplets have a radius of about 23 \AA , which is presumably constant in the range $20\text{--}35^\circ\text{C}$. The interface is sharp and the interfacial area per surfactant molecule is $\approx 50 \text{ \AA}^2$ for ϕ values in the range $0.0205\text{--}0.327$, and decreases to $\approx 35 \text{ \AA}^2$ for higher ϕ values.

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