SANS on fluorinated water - in - oil microemulsions

ELSEVIER

Physica B 234–236 (1997) 295–296

PHYSICA B

SANS on fluorinated water-in-oil microemulsions

P. Baglioni[a], C.M.C. Gambi[b,*], R. Giordano[c]

[a] *Department of Chemistry, University of Florence, v.G.Capponi 9, I-50121 Firenze, Italy*
[b] *Department of Physics, University of Florence and INFM, l.E.Fermi 2, I-50125 Firenze, Italy*
[c] *Department of Physics, University of Messina and INFM, Salita Sperone 31, I-98010S, Agata, Italy*

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 ϕ 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 α (< -20 at $W/S = 6.5$, -8 at 11, -2 at 16 and ~ 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.

* Corresponding author.

PII S0921-4526(96)00962-3

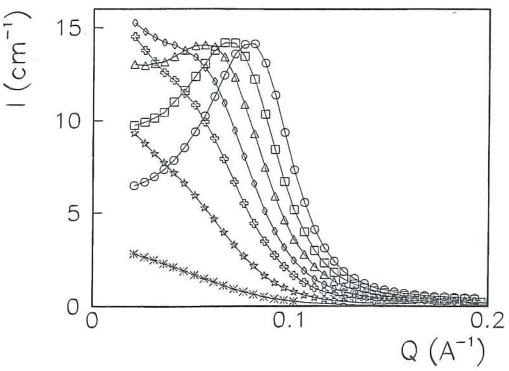

Fig. 1. Experimental scattered intensity at $T = 20°C$ of fluorinated microemulsions with $W/S = 15$ and ϕ values: 0.599 (circles), 0.499(squares), 0.390(triangles), 0.285(rhombuses), 0.202(crosses), 0.100(stars) and 0.0303(asterisks). The lines are guides for the eyes.

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 $T = 20°C$ (ϕ 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.

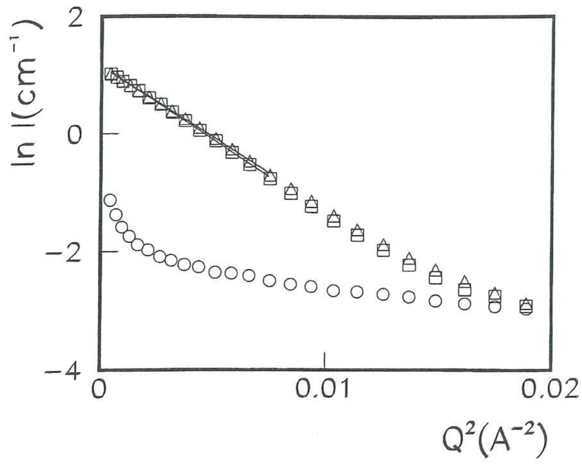

Fig. 2. Guinier plot of samples at $W/S = 15$ with $\phi = 0.0303$(triangles), at $W/S = 20$ with $\phi = 0.0318$(squares) and at $W/S = 5.6$ with $\phi = 0.0300$(circles). $T = 20°C$. The solid lines represent the fitted straight lines to the data points. $I(Q) \sim \exp(-Q^2R_g^2/3)$ where $R = R_g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

Acknowledgements are due to EC for support via the "Human Capital and Mobility – Access to Large Scale Facilities" program (Contract N. ERB CHGECT 920001) and to the italian MURST and INFM. Ausimont is acknowledged for having furnished the products. We thank A. Chittofrati for helpful discussions and J. Teixeira for very useful criticisms and suggestions.

References

[1] M.G. Giri, M. Carlà, C.M.C. Gambi, D. Senatra, A. Chittofrati and A. Sanguineti, Phys. Rev. E 50 (1994) 1313.

[2] A. Chittofrati, D. Lenti, A. Sanguineti, M. Visca, C.M.C. Gambi, D. Senatra and Z. Zhou, Progr. Colloid Polymer Sci. 79 (1989) 218.

[3] A. Sanguineti, A. Chittofrati, D. Lenti and M. Visca, J. Colloid Int. Sci. 155 (1993) 402.

[4] A.M. Cazabat and D. Langevin, J. Chem. Phys. 74(6) (1981) 3148.

[5] J. Teixeira, in: Structure and Dynamics of Strongly Interacting Colloids and Supra-molecular Aggregates in Solution, eds. S.-H. Chen et al. (Kluwer Academic Publishers, Dordrecht, 1992).

[6] P. Baglioni, C.M.C. Gambi, R. Giordano and D. Senatra, J. Mol. Struct. 383 (1996) 165.