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Original Citation:

SANS analysis of perfluoropolyether water in oil microemulsions by hard spheres and adhesive hard spheres potentials / GAMBI C. M. C.; GIORDANO R.; LAURATI M.; LANZI L.; PINI F.; P. BAGLIONI. - In: APPLIED PHYSICS. A, MATERIALS SCIENCE & PROCESSING. - ISSN 0947-8396. - STAMPA. - 74:(2002), pp. s377-s379.

Appl. Phys. A 74 [Suppl.], S377–S379 (2002) / Digital Object Identifier (DOI) 10.1007/s003390201548

Applied Physics A
Materials
Science & Processing

SANS analysis of perfluoropolyether water-in-oil microemulsions by hard sphere and adhesive hard sphere potentials

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Received: 26 July 2001/Accepted: 13 November 2001 –

Abstract. Ternary water-in-oil microemulsions formed from an ammonium carboxylate PFPE surfactant of molecular weight 710 and a PFPE oil of molecular weight 900, leading to microemulsions that show a dynamic percolation phenomenon, were investigated by SANS to characterize the microstructure. Hard sphere and adhesive hard sphere potentials were used to model the droplet–droplet interactions assuming polydispersed droplets with a Schultz distribution of sizes.

PACS: 61.12.E; 68.05.C; 82.70.D

Perfluoropolyether (PFPE) surfactants can lead to water-in-PFPE oil microemulsions [1–5]. This paper reports the study by SANS of a ternary water-in-oil microemulsion composed by an ammonium carboxylate PFPE surfactant of molecular weight 710 and a PFPE oil of molecular weight 900 leading to microemulsions that show a dynamic percolation phenomenon [3]. The monophasic region of the phase diagram [1] extends from very low water to surfactant ratio up to 22 (W/S, molar ratio) at the temperature of 20 °C. The samples are characterized by the W/S ratio and ϕ, volume fraction of the dispersed phase (water plus surfactant over total), assuming the dispersed phase composed of water droplets coated by surfactant molecules.

Previous structural investigations by light scattering and SANS [2, 4, 5] gave an insight into the microstructure of the system. To have a better insight an analysis by SANS of samples at $W/S = 15$ and 20 is presented here, assuming a model of particles interacting via a sticky hard-sphere potential. This potential, or Baxter's potential has found applications in characterising the structure and thermodynamic properties of sterically stabilized silica colloidal particles [6], microemulsion systems [7, 8] and non ionic micellar solutions [9]. All these systems consist of particles interacting via very short-range attractive potentials.

1 Materials

The fluorinated compounds were from Ausimont S.p.A. (Milan,Italy). The water was taken from a Millipore Milli-Q system. The compounds properties and the samples preparation were described in references [1–3].

2 Methods

The SANS measurements have been performed on the PAXE spectrometer of the Laboratoire Léon Brillouin at Saclay (France) using a wavelength of 5 Å with a wavelength spread of ±5%. The Q range investigated, for all the samples, was from 0.02 to 0.28 Å^{-1} (sample-to-detector distance fixed at 2.515 m). Samples of thickness 1 mm were contained in flat quartz cells, the temperature, 20 °C, was controlled within ±0.1 °C. The intensity was corrected for the empty cell contribution and normalized to absolute scale by means of a secondary standard of known cross section [10]. Thereafter, in each spectrum, the solvent contribution was subtracted for the PFPE oil spectrum.

3 Results

Typical SANS spectra of samples belonging to the lines $W/S = 15$ and 20 at a temperature of 20 °C are shown in Fig. 1. For all the spectra, the background was subtracted by means of the Porod's law [4]. The coherent part of the spectra was analysed assuming for the form factor $P(Q)$ the relationship of polydispersed spheres with a Schultz distribution of sizes [7] and for the structure factor $S(Q)$ that of adhesive

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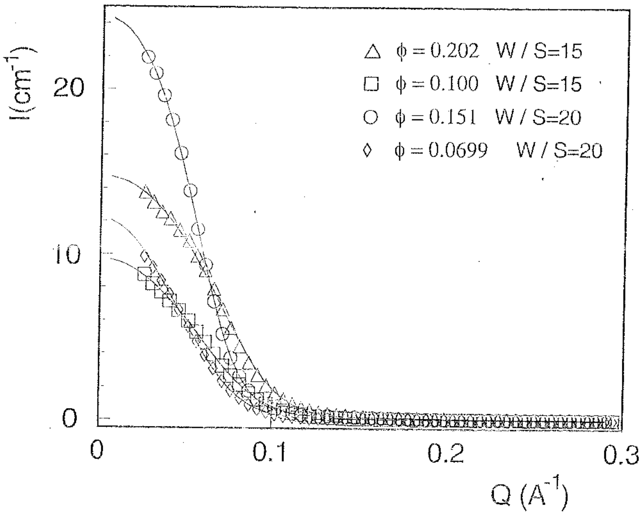

Fig. 1. Experimental scattered intensity values at $T = 20\,°\mathrm{C}$ of PFPE water in oil microemulsions at $W/S = 15$ and $W/S = 20$ and fitted curves as obtained by the adhesive hard sphere model

Table 1. SANS results at 20 °C obtained by the five parameters model (adhesive hard spheres) and the four parameters model (hard spheres)

ϕ	$\Delta\rho^2$ cm^{-4}	D (Å)	poly	Δ (Å)	E_0 K_BT	η
$W/S = 20$						
0.0318	15	56	22	0.5 ± 5	0 ± 1	0.0149
	15	56	21			0.0158
0.0699	19	68	21	8 ± 4	-1.9 ± 1.5	0.046
	18	68	20			0.0338
0.151	21	73	21	7 ± 1	-9 ± 6	0.0949
	16	74	19			0.0903
$W/S = 15$						
0.0303	19	54	23	8 ± 2	-7 ± 2	0.0191
	16	55	22			0.0146
0.100	20	57	22	8 ± 1	-7 ± 2	0.0596
	21	58	21			0.0456
0.202	21	60	22	7 ± 1.5	-1.9 ± 0.4	0.1161
	17	57	21			0.1009

hard spheres, with the square-well Baxter's potential [8]. The scattered intensity is given by:

$$I(Q) = \Delta\varrho^2\phi_{\mathrm{w}}\left(\frac{\pi}{6}D^3\right)\frac{(Z+6)(Z+5)(Z+4)}{(Z+1)^3}P(Q)S(Q) \quad (1)$$

where $\Delta\varrho^2$ is the contrast between the aqueous and the oily phases, ϕ_{w} is the aqueous hard sphere volume fraction (value obtained by the sample composition assuming the hard sphere composed by water), D is the droplets average diameter, Z is the parameter related to the droplet Schultz's polydispersity [7]. The contrast between the aqueous core and the oily continuous medium, evaluated on the basis of the composition, is $18.3 \times 10^{20}\,\mathrm{cm}^{-4}$. The free parameters of the above relationship are the contrast (because we cannot a priori exclude a composition at variance with that hypothesised), the average hard core diameter D, the Z value and the square-well potential parameters, depth E_0 and width Δ. A non-linear fitting procedure by means of the Minuit program of the CERN library was performed between the experimental spectra and the above $I(Q)$ relationship in the form of a Fortran function written by us. The five free parameters obtained by the fitting procedure are reported in Table 1. The volume fraction η of the hard sphere plus adhesive regions, evaluated by the D and Δ values is also reported in Table 1 for each sample. χ^2 values close to 1 were found except at $W/S = 15$ with $\phi = 0.202$ ($\chi^2 = 6$).

The results lead to the following considerations. For the samples of Table 1 the contrast value is similar to the calculated value. The average aqueous hard sphere diameter D apparently increases with ϕ at constant W/S ratio. The polydispersity is ~20% for all the samples. Δ and E_0 are different from zero only for $\phi = 0.151$ at $W/S = 20$ and at $W/S = 15$. The adhesion parameter [8] $\frac{1}{\tau} = \frac{12\Delta}{a}\exp(E_0/K_BT)$ is lower than 0.2. Because of the low adhesion, the spectra were also analysed by using the hard sphere potential. The results are also reported in Table 1 for each sample. The contrast, the average diameter, the Schultz polydispersity and the hard sphere volume fraction η represent the four fitting parameters. In relation to the findings of the previous analysis, contrast, average diameter and polydispersity are very similar, for each sample. χ^2 values close to 1 were found except for the samples $W/S = 20$ with $\phi = 0.151$ ($\chi^2 = 9$), $W/S = 15$ with $\phi = 0.100$ and 0.202 ($\chi^2 = 4$ and 13 respectively). Because of the lower χ^2 values, the adhesive hard spheres model is more appropriate to describe the system investigated.

Thus from the body of the results we conclude that at $\phi < 0.22$ the microemulsion system is composed of polydispersed spheres with an aqueous hard core of average diameter 60–70 Å at $W/S = 20$ and 55–60 Å at $W/S = 15$, in both cases with a polydispersity of 20%. Excluding the $\phi = 0.0318$ sample at $W/S = 20$ that does not show adhesion, all the other samples are adhesive with $\Delta \sim 7$ Å and E_0 of few K_BT units. The investigation of the system microstructure, previously performed by light scattering [2], led to a hydrodynamic radius of 44 Å at $W/S = 16$ (second virial coefficient −2) and of 57 Å at $W/S = 22$ (second virial coefficient zero). The hydrodynamic radius is that of the whole aggregate, inner water core and interfacial layer composed by surfactant and oil molecules, thus the hydrodynamic diameter must be larger than the average aqueous hard sphere diameter of Table 1. Furthermore, the light scattering second virial coefficients suggested the presence of an attractive part in the inter-particles potential. The results of this paper are in good agreement with the light scattering results and give a better insight into the microstructure of the system. In fact, the average size of the aqueous core of the particles is known for each sample as well as the extent of the adhesive region around the particle that represents a region of surfactant molecules linked to the interface. Furthermore, the attractive interaction energy between particles, due to the adhesion of the surfactant molecules, is also measured.

Acknowledgements. We thank J. Teixeira for very helpful suggestions and criticisms and A. Chittofrati for very helpful discussions. We also acknowledge Ausimont for having provided the fluorinated compounds, the EC for support via the 'Human Capital and Mobility – Access to Large Scale Facilities' Program, Contract No. ERB CHGECT920001, and the Italian MURST, INFM and CSGI for financial support.

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