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Comments on a 'self-assembly in fluorocarbon surfactant systems'

CMC Gambi, M Carla and D Senatra

Address

Department of Physics, University of Florence and INFN, L.E.
Fermi 2, 50125 Florence, Italy

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Abbreviations

DOC	disordered-open-connected
O	oil
PFPE	perfluoropolyether
S	surfactant
SANS	small angle neutron scattering
W	water

In the paper 'Self-assembly in fluorocarbon surfactant systems', the author argues about the results gathered by small angle neutron scattering (SANS) [2] and dielectric spectroscopy [3] of some perfluoropolyether (PFPE) microemulsions. Reference is made to [2,3] (given as [13,14] in [1]). The author's comments, added as annotations, do not represent the outcomes of the cited works. In [2] SANS results at water-surfactant ($[W]/[S]$) molar ratios of 15 and 20 are reported for samples with volume fraction of the dispersed phase $\phi \sim 0.03$. The Guinier radius of the droplets was evaluated as 3.6 nm for both samples and it was never identified as hydrodynamic radius. The hydrodynamic radius was measured by quasi-elastic light scattering [4]. SANS results on the PFPE microemulsions at a molar ratio $[W]/[S] = 11$, were reported in [5] and a Guinier radius of 2.3 nm was found at temperatures of 20°C and 35°C at $\phi, 0.20$. The results of the dielectric spectroscopy measurements on the PFPE microemulsion system are reported in [3,6]. We have to point out that the annotation 'At $0.36 < \phi < 0.46$ the critical exponents typical of dynamic percolation are calculated above the thermal threshold (interacting w/o droplets), whereas at $\phi < 0.33$ and $\phi < 0.5$ the critical exponents indicate a static percolation regime, in other words a bicontinuous microstructure', is only a part of the results from the first paper on the subject [6]. As reported in the second paper [3], a further analysis of the results, leading to exponents indicating a static percolation regime was performed after having studied the frequency dependence of the dielectric complex permittivity. The latter analysis is fundamental because it does not need an *a priori* evaluation of the percolation threshold. A good summary of the whole study, which was performed at $[W]/[S] = 11$, the sentence reported in the abstract of the paper [3] '...The results show that the percolation is dynamic

throughout both the composition and the temperature range in which the samples are monophasic' is the interpretation of the results, as given by us.

To summarize our position with respect to that of Monduzzi's, we stress that the SANS and dielectric spectroscopy results already published in [2-6] point to a PFPE microemulsion system composed of aqueous droplets dispersed in oil and interacting via a hard sphere repulsive potential plus an attractive potential. At the present state of research there is a discrepancy between the dielectric and the NMR self-diffusion results on the same PFPE microemulsions [7]. The NMR results, analysed in the frame of the disordered-open-connected (DOC) cylinders model [8], describe the PFPE microemulsions as bicontinuous microemulsions at 25°C, in a large region of the phase diagram that includes the $[W]/[S] = 11$ straight line. It was also found that the bicontinuous microemulsion disconnects to form water-in-oil droplets at a higher $[W]/[S]$ ratio. The PFPE oil used in dielectric spectroscopy and SANS experiments had a molecular weight of 900, corresponding to the PFPE2 oil of [7]; in Table 1 of [7] the bicontinuous droplets transition at $Z \gg 1.3$ occurs for a water amount about twice as much as that of the $[W]/[S] = 11$ ratio. It is worth noting that the DOC model excludes dynamic percolation and assumes that the surfactant is insoluble in both water and oil. Thus, one of the questions to be answered is to what extent the PFPE surfactant is insoluble in the PFPE2 oil. In [7], the binary surfactant-oil mixtures (with PFPE1, PFPE2 or PFPE3 as oil) at 25°C are described as isotropic liquids which become turbid after 2-3 hours. In [9], the binary phase diagram surfactant-PFPE2 oil is reported in the range from 0 to 80°C. The samples with oil to surfactant (o/s) weight ratio 1.22 and 1.83 at 25°C are on the boundary line between a region of monophasic transparent isotropic samples (surfactant is totally soluble in oil) at higher temperatures, and a region, at lower temperatures, of biphasic samples (the lower phase white turbid, the upper phase transparent fluid) where the surfactant is partly soluble in oil. Only the sample with o/s = 3.00 is biphasic at 25°C. Thus, the application of the DOC model to the above samples is open to debate.

The other question to be answered is more general. Through dielectric spectroscopy it has been discovered that the PFPE microemulsion system is composed of interacting droplets. At 25°C (temperature of the NMR

measurements) the samples with o/s ratios 1.22, 1.83 and 3.0 intersecting the $[w]/[s]$ line have, respectively, $\phi = 0.552$, 0.451 and 0.334. All these samples are above the thermal percolation threshold [6], thus the droplets form more than one connected cluster of droplets and the number of connected clusters increase with ϕ . In NMR measurements interpreted by the DOC model, the connection is obtained by aqueous channels. Thus, both approaches lead to a multiconnected system. The discrepancy is therefore confined to the type of connection whether they are continuous channels or interacting droplets. A question that, in our opinion, can be clarified only by further experimental work.

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