Reply to "Comment on the Self-Diffusion in L_3 and Other Bicontinuous Surfactant Solutions"

The "Comment on the Self-Diffusion in L_3 and Other Bicontinuous Surfactant Solutions" is relative to the paper "Surfactant Self-Diffusion in L_3 Phases" [1] in which the fluorescence recovery after fringe pattern photobleaching (FRAPP) technique has been used. The NMR spin-echo technique also allows the measurement of the surfactant self-diffusion in this type of system. The authors of the comment, who are experts in the NMR technique, say that it is suggested in the paper that this technique has severe limitations. It is rather suggested that the techniques are complementary, the NMR technique allowing shorter time and distance scales to be probed. The typical length scales probed by FRAPP are between 5 and 100 μm; this range can be covered easily by simply using interference fringes as in the setup of ref 1. Smaller lengths can be studied by using a microscope and larger lengths by imaging grids on the sample. The range of length scales of the method is therefore very broad. The NMR length scales are of the order of 10 μm for surfactant diffusion, which is investigated in ref 1. In the special case of the *very dilute* L_3 phases of ref 1, previous experiments and theories suggested the presence of disconnected large aggregates (sizes up to micrometers). In order to check for this possibility, the technique to be preferred was clearly the one where the length scales are large enough compared to the predicted sizes.

The authors of the comment also discuss the importance of the self-diffusion techniques in relation to structural investigations in surfactant systems. Of course, NMR and FRAPP techniques are basically equivalent for this purpose. However, and again in particular cases, one technique can be more powerful than the other. Let us take the example of dilute surfactant phases which can either possess a microstructure with well-defined surfactant layers or simply be molecular solutions. If D_{agg} is the surfactant diffusion coefficient in the layer and D_{mon} the surfactant diffusion coefficient in the solvent, typically $D_{mon} \approx 5 \times 10^{-6}$ cm^2/s and $D_{agg} \approx 10^{-7}$ cm^2/s in lamellar and bicontinuous cubic phases.[2] However, with some surfactants like SDS, $D_{mon} \approx D_{agg}$ (ref 13 in the comment), and it becomes less easy to distinguish between molecular and organized solutions: this is for instance the case of the bicontinuous microemulsions of ref 3. In the FRAPP technique, there is a large choice of fluorescent probes, and generally, their diffusion coefficient in the surfactant layer is much smaller than in the solvents. Obviously, this makes the distinction between molecular and organized solutions easier than with NMR. The large value of D_{agg} for SDS led us to conclude that the differences between the NMR and FRAPP measurements were due to the exchanges between the layers and the solvents. The argument of ref 10 in the comment proves that this cannot be the case. In fact, the different molecular species studied in the two techniques are likely to have different diffusion coefficients in the surfactant layer. This effect is well known in lipid bilayers.[4]

In the comment, the problem of the structural perturbation due to probes is mentioned. Of course, a large probe is likely to impose major perturbations. In the FRAPP technique, however, the probe molecules are not much larger than surfactant molecules. Moreover, the sensitivity is extremely high: the technique can even be applied to a single surfactant monolayer. It is then possible to work with very small probe concentrations, even in dilute systems: typically 1 probe molecule per 100 surfactant molecules. This concentration can still be lowered by a few orders of magnitude to rule out completely the influence of eventual perturbations.

In the experiments dealing with the L_3 phases of $C_{12}E_3$ and $C_{12}E_4$ discussed in the comment, the ratio of the surfactant diffusion coefficient in the L_3 phase, D_s, and in the pure liquid surfactant, D_0, is close to $^2/_3$. Anderson and Wennerström, in a paper quoted by the authors of the comment,[5] showed that $D_s/D_1 = {}^2/_3$ when D_1 is the diffusion coefficient of a particle *confined* in the surfactant layer. One could expect that there will be another factor $^2/_3$ between the diffusion coefficients in the neat phase, D_0, and in the surfactant layers, D_1 (simply from the difference in dimensionality, if the neat phase is a fully isotropic phase). In our experiments, we were able to measure the surfactant diffusion coefficient in the lamellae of an oriented lamellar phase, and we have shown that $D_s/D_1 \approx {}^2/_3$ which is the expected theoretical result.[5]

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