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# Evidence of percolative phenomena in a lecithin-based gel

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**Abstract**

The structure of the gel-phase, observed in a number of lecithin-in-oil microemulsions after addition of water, is the topic of a controversy actually taking place in the literature. In this paper, we will show how the dynamical properties of water confined in the inner core of the micelles, as investigated by QENS and INS, turn out to be inconsistent with the usually proposed model of entangled (not interconnected) polymer-like micelles. A percolated structure of branched cylindrical aggregates could agree with the presented data. 

*Keywords:* Percolation; Quasi-elastic scattering; Inelastic scattering; Surfactants

It is now well established that progressive addition of small quantities of water to a reverse micellar solution of soyabean lecithin in a number of organic solvents induces the growth of giant flexible worm-like aggregates [1,2]. The hypothesis of a close analogy with polymer solutions [3] is immediate [4], when one accounts for the finite lifetime of worm-like micelles. Theory foretells that $\langle L \rangle$ scales with the volume fraction $\phi$ of the dispersed phase as $\langle L \rangle \propto \phi^{1/2}$ [4]. However, some small angle neutron scattering experiments detected [5] a clear interference maximum at sufficiently high concentrations. Such a result, implying the existence of a well-defined correlation length in the system, is inconsistent with the hypothesis of a random entangled network of polymer-like chains. The hypothesis of a percolated sponge-like structure of branched tubular aggregates has been proposed for the first time in Ref. [5]. In addition, it was shown that the above-described scaling behavior was improperly deduced [6,7].

A definite answer is furnished by the investigation of the dynamical properties of the water confined in the micellar core. In this paper we present the results from a quasi elastic (QENS) and an inelastic neutron scattering (INS) experiments, performed on the NEAT (BENSC) and the TOSCA (RAL) spectrometers, respectively. Two systems of different compositions ($\phi = 0.1$ at $R = 5$ and $\phi = 0.2$ at $R = 10$) have been investigated ($R$ = number of water molecules per lecithin molecule). The isotopic substitution method was adopted, so as to allow the extraction, by difference, of the contributions from confined water. The half-widths of the obtained translational lines (QENS) are reported in Fig. 1a, as a function of the exchanged wave-vector, $Q$. The continuous line represents the result of the best-fit procedure with a jump diffusion model

$$\Gamma_T(Q) = \frac{D_T Q^2}{1 + D_t Q^2 \tau_0}. \quad (1)$$

The obtained residence time is very close to that typical of bulk water and exhibits a lower value at higher $R$, indicating an increasing mobility of the water molecules involved in the micellar structure. In Fig. 1b, the obtained generalized dynamic susceptibilities, $\chi(\omega)$, are reported (INS) for the systems at $\phi = 0.2, R = 10$ and $\phi = 0.2, R = 0$, normalized accounting for the sample thickness and the lecithin concentration. In the same figure, the obtained contribution from the inner core water molecules (obtained by difference between the above spectra) is also reported (continuous line), together with the corresponding spectrum from bulk water ($H_2O$ spectra are consistently normalized but are multiplied by

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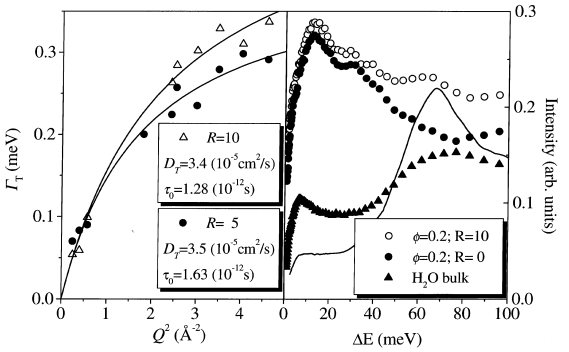


Fig. 1. (a) Half-width of the resolved translational contribution of water; continuous line: jump diffusion model. (b) $\chi(\omega)$ spectra of the dispersed phases in two systems of different compositions and in bulk water; the solid line represents the estimate for the contribution from water confined into the micellar core.

a factor 4 with respect to the others). The dramatic attenuation of the peak associated with the translational motions, around 6 meV, is interpretable as the reduction of the translational degrees of freedom upon confinement. The observed sharpening of the librational motion, centered at 70 meV, indicates a preferred local coordination for the water molecules, induced by interaction with the lecithin end groups. In summary, almost all water molecules seem to be involved at the interface with no evidence of bulky liquids. This would mean that the observed dependence of $\tau_0$ on $R$ cannot be related with a blowing-up process of the micelles. As a consequence, we remain with the hypothesis of the growth of wormlike micelles (either interconnected or not). The possibility of structural arrangement of branched interconnected cylinders seems to be more probable, if one takes into account recent results from depolarized light scattering and QENS [8], where it was shown that, at high values of $\phi$, the addition of water results in an enlargement of the rotational contribution associated with the lecithin end groups: at a branch point the interface is curved toward the water and, as a consequence, the rotational relaxation time is shifted to lower values. The same indication came from NMR measurements both in cyclohexane [9] and isooctane [10]. The occurrence that the diffusion coefficients of water measured by NMR [9] are smaller than those obtained by QENS is consistent with the hypothesis of an infinite percolated structural model. In fact, the diffusion coefficient in confined space must be a time-dependent quantity: the NMR probe furnishes a long-time and long-range diffusion coefficient that must be related to a large confinement volume.

## References

[1] Scartazzini, P.L. Luisi, J. Phys. Chem. 92 (1988) 829.
[2] P. Schurtenberger, R. Scartazzini, P.L. Luisi, Rheol. Acta 28 (1989) 372.
[3] P.G. de Gennes, J. Chem. Phys. 55 (1972) 572.
[4] M.E. Cates, Macromolecules 20 (1987) 2289.
[5] F. Aliotta, M.E. Fontanella, M. Sacchi, C. Vasi, G. La Manna, V. Turco-Liveri, Colloid Polym. Sci. 274 (1996) 809.
[6] F. Aliotta, M. Sacchi, Colloid Polym. Sci. 275 (1997) 91.
[7] F. Aliotta, M.E. Fontanella, M. Sacchi, C. Vasi, Physica A 247 (1997) 247.
[8] F. Aliotta, M.E. Fontanella, M. Pieruccini, C. Vasi, Phys. Rev. E 59 (1999) 665.
[9] R. Angelico, U. Olsson, G. Palazzo, A. Ceglie, Phys. Rev. Lett. 81 (1998) 2823.
[10] P.A. Cirkel, J.P.M. van der Ploeg, G.J.M. Koper, Phys. Rev. E 6 (1998) 6975.