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## Structure and dynamic properties of a polymer-induced sponge phase

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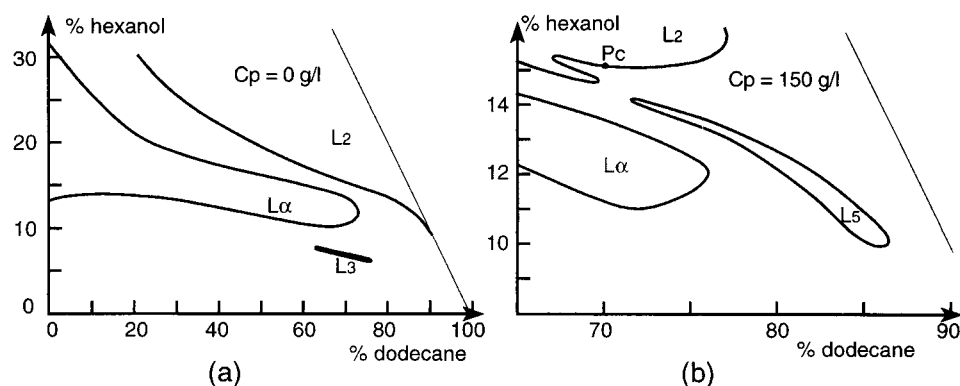
**Abstract.** The effect of polyethyleneglycol (PEG) on the phase behaviour of oil-rich sodium dodecyl sulphate, hexanol, water and dodecane mixtures has been investigated. PEG causes the disappearance of the 'sponge' phase and induces the formation of a new isotropic phase, labelled  $L_5$ , located between the microemulsion,  $L_2$ , and the lamellar,  $L_\alpha$ , phases. Small angle neutron scattering and electrical conductivity results show that at local scales the  $L_5$  phase consists of inverted bilayers, connected at larger scales. These features suggest a sponge-like structure for the  $L_5$  phase, a hypothesis which is further supported by a static and dynamic light scattering study.

### 1. Introduction

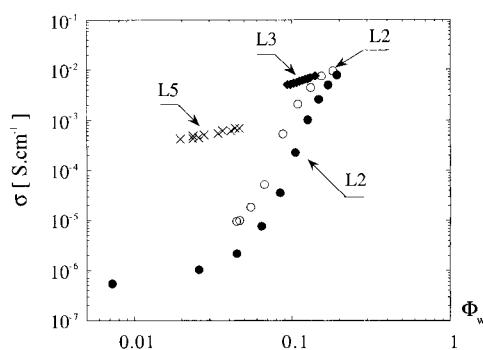
Polymers may significantly alter the thermodynamic stability and the elastic properties of self-assembled surfactant structures. Mixtures of water, oil and surfactant lead to a variety of structures corresponding to different topologies of the surfactant interfaces. Experimentally, water droplet microemulsions and inverted bilayer structures such as lamellar and sponge phases are commonly observed in oil-rich systems. The effect of the incorporation of water-soluble polymers within inverse microemulsions has been investigated [1–4]. The present study is concerned with an experimental study of a polymer-induced phase, labelled  $L_5$ , where the polymer is confined within a bilayer. Further to the phase-diagram introduction, an attempted structure elucidation is reported involving successively conductivity, static and dynamic scattering experiments.

### 2. Phase diagram

The system studied is made of sodium dodecyl sulphate (SDS), hexanol, water, dodecane and polyethylene glycol (PEG) ( $M_w = 22\,600\text{ g mol}^{-1}$ ). Figure 1 shows the oil-rich part of two cuts of the phase diagrams at constant water to SDS weight ratio 1.5 and constant PEG concentration in water,  $c_p$ . For  $c_p = 0\text{ g l}^{-1}$ , the classical microemulsion  $L_2$ , lamellar  $L_\alpha$  and reverse sponge  $L_3$  phases are observed. At very small  $c_p$  ( $\sim 0.1\text{ g l}^{-1}$ ), the reverse  $L_3$  phase disappears while no significant changes occurred in both  $L_2$  and  $L_\alpha$  phases. Increasing  $c_p$  above  $c_p = 100\text{ g l}^{-1}$  causes a critical phase separation in the  $L_2$  phase and the occurrence of a new, optically isotropic, flow birefringent phase, the  $L_5$  phase, at intermediate alcohol content between the  $L_2$  and  $L_\alpha$ . This new  $L_5$  phase with  $c_p = 150\text{ g l}^{-1}$  is studied in the following.



**Figure 1.** Phase diagrams of the SDS/water/1-hexanol/dodecane system at constant water to surfactant weight ratio 1.5 ( $W/S = 1.5$ ): (a)  $c_p = 0 \text{ g l}^{-1}$ ; (b)  $c_p = 150 \text{ g l}^{-1}$  ( $T = 25^\circ\text{C}$ ).



**Figure 2.** Electrical conductivity against water volume fraction. Reverse micelle phases: polymer-free system,  $\bullet$ ; polymer-doped system,  $\circ$ . Reverse bilayer phases: polymer-free sponge phase,  $\blacklozenge$ ;  $L_5$  phase,  $\times$ .

### 3. Electrical conductivity experiments

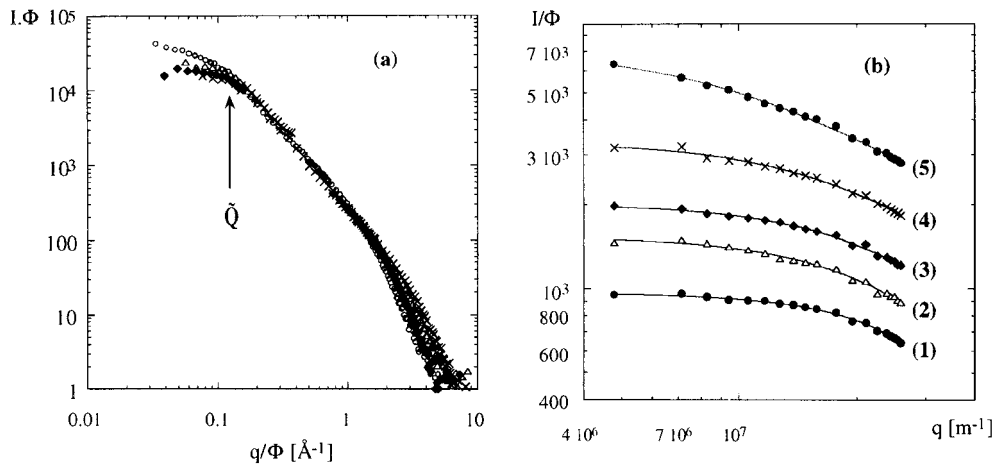
Figure 2 shows electrical conductivities  $\sigma$  measured as a function of the water volume fraction  $\Phi_w$  through two polymer-free ( $L_3$  and  $L_2$ ) and two polymer-doped phases,  $L_2$  and  $L_5$ . In the microemulsion phases, a percolation behaviour is observed. The high  $\sigma$  values for the  $L_3$  phase are consistent with the multiconnected, water-bilayer description of reverse sponge phases. The conductivity values encountered in the  $L_5$  phase are comparable to the ones collected within the  $L_3$  phase, although somewhat smaller, which suggests that water also forms a continuous channel in this phase.

### 4. Neutron scattering experiments†

In the  $L_5$  samples investigated, water was replaced by heavy water. Figure 3(a) shows for four typical samples the absolute scattering spectra in reduced coordinates ( $I(q)\Phi$  against  $q/\Phi$ ). Here,  $\Phi$  is the SDS + water volume fraction in each sample. At small wave vectors

† Neutron scattering experiments were performed at Laboratoire Léon Brillouin, Laboratoire Commun CEA-CNRS, Saclay, France.

(typically  $q/\Phi < 1$ ), the four curves merge. From a remarkable value of the reduced wave vector onwards, namely  $\tilde{Q} = 0.12 \text{ \AA}^{-1}$ , the scattering scales as  $q^{-2}$ . This  $q^{-2}$  dependence is followed by a  $q^{-4}$  one at larger wave vectors. These features are characteristic of a bilayer structure at local scales. From the  $q^{-2}/q^{-4}$  crossover, a bilayer thickness  $\delta \approx 40 \text{ \AA}$  is deduced. The observation of an unique value  $\tilde{Q}$  shows that the characteristic size of the  $L_5$  phase varies as  $\Phi^{-1}$  [5, 6]. All these results are consistent with a sponge structure for  $L_5$ . To confirm this hypothesis, static and dynamic light scattering measurements were carried out.



**Figure 3.** (a) Small angle neutron scattering spectra in reduced units for  $L_5$  samples with  $5\% < \Phi < 9.7\%$ . (b) Static light scattering for  $L_5$  samples: (1)  $\Phi = 8.9\%$ ; (2)  $\Phi = 6.3\%$ ; (3)  $\Phi = 5.4\%$ ; (4)  $\Phi = 3.7\%$ ; (5)  $\Phi = 2.9\%$ . The scattered intensity has been normalized to the volume fraction  $\Phi$ . The continuous lines are fits to equation (1).

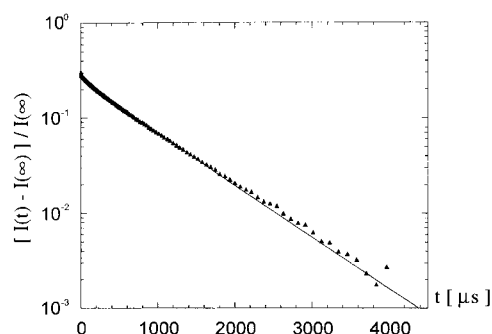
### 5. Static and quasi-elastic light scattering experiments

Figure 3(b) shows the  $q$ -dependence of the static light intensity for  $L_5$  samples with  $\Phi$  ranging from 2.9 to 8.9%. The scattering features the characteristic 'Arctangent' dependence usually encountered for a symmetric sponge phase [7]:

$$S(q) = \Gamma + B \frac{\tan^{-1}(q\xi_\eta/2)}{q\xi_\eta/2}. \quad (1)$$

In equation (1),  $\Gamma$  is the amplitude of concentration fluctuations and  $B$  that of the sponge order parameter fluctuations [8].  $\xi_\eta$  is the correlation length related to the sponge order parameter. A good quantitative description of the scattered intensities is obtained using the above expression. For the samples studied,  $\xi_\eta(\Gamma + B)$ , i.e. the product of the correlation length by the scattered intensity at  $q = 0$ , is a constant, as expected for a symmetric sponge structure [7]. The  $\xi_\eta$  values are of the same order of magnitude as  $\xi \equiv 2\pi/(\tilde{Q}\Phi)$ . Another remarkable property of our system is the small value of the ratio  $(\Gamma/B)^{stat}$  (about 0.045). This indicates that the  $\tan^{-1}(q\xi_\eta)/q\xi_\eta$  decay dominates the scattered intensities. This stresses the role of sponge order parameter fluctuations in this polymer-doped-bilayer reverse system. Such fluctuations can also be underscored by quasi-elastic light scattering.

The sponge order parameter fluctuation dynamics has been studied theoretically by Granek and Cates [9]. As the sponge order parameter  $\eta$  signals the unusual *static* scattering behaviour,

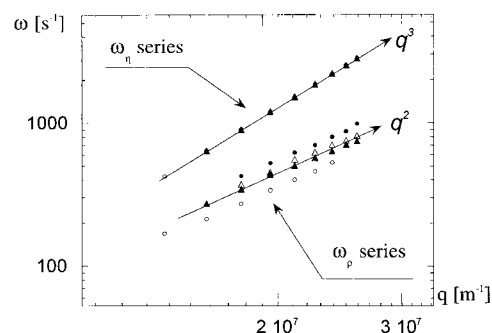


**Figure 4.** Dynamic signal at  $q = 2 \times 10^7 \text{ m}^{-1}$  for the  $\Phi = 6.3\%$  L<sub>5</sub> sample. The scattering signal has been normalized to the static intensity. The continuous line corresponds to the best fit to equation (2).

it also leaves a special fingerprint on the *dynamical* structure factor  $S(q, t)$ . According to the authors of [9] the surfactant motion is taken to be diffusive. The concentration fluctuation relaxation rate displays an *exponential* decay with a frequency  $\omega_\rho$  given by  $\omega_\rho = D_\rho q^2$ . On the other hand, the  $\eta$  motion is not diffusive. This gives rise to a *nonexponential* decay  $\tilde{F}(t)$ , with a characteristic frequency  $\omega_\eta = q^3/\tau_\eta$  and  $1/\tau_\eta = k_B T/6\pi\mu_s$  ( $\mu_s$  is the solvent viscosity). We thus use the following expression [9]:

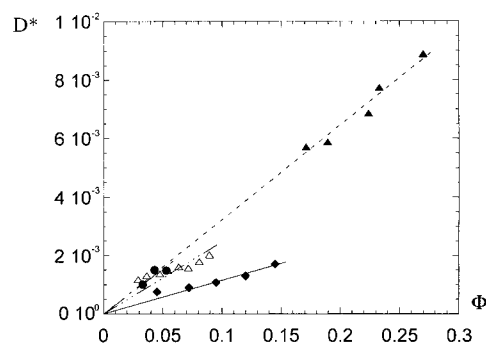
$$S(q, t) = \Gamma e^{-\omega_\rho t} + B \frac{\tan^{-1}(q\xi_\eta/2)}{q\xi_\eta/2} \tilde{F}(t) \quad (2)$$

for the dynamic structure factor. The L<sub>5</sub> sample dynamic autocorrelation functions were collected and normalized to the static intensity. The time decay of the scattering signal is definitely nonexponential, for all the studied samples and whatever the scattering wave vector ( $q\xi_\eta \gg 1$ ) (see figure 4). As also illustrated in figure 4, the above test function—equation (2)—yields a good fit to the data. The two experimental frequencies  $\omega_\rho$  and  $\omega_\eta$  extracted from the analysis scale respectively as  $q^2$  and  $q^3$  according to the model [9], see also figure 5. The order of magnitude of the  $(\Gamma/B)^{\text{dyn}}$  mean ratio extracted from the data is also small (0.14), though somewhat larger than the  $(\Gamma/B)^{\text{stat}}$  ratio. The  $\omega_\eta$  frequencies are independent of the volume fraction  $\Phi$ , as expected. Conversely,  $\omega_\rho$  varies with  $\Phi$ , as previously observed in many sponge systems [10–12].



**Figure 5.** Log–log plot of  $\omega_\rho$  and  $\omega_\eta$  relaxation frequencies against  $q$ :  $\Phi = 8.1\%$ ,  $\bullet$ ;  $\Phi = 6.3\%$ ,  $\Delta$ ;  $\Phi = 5.4\%$ ,  $\blacktriangle$ ;  $\Phi = 3.5\%$ ,  $\circ$ .

This dependence appears clearly introducing the diffusion coefficient in reduced units  $D^* = \mu_s \delta D_p / k_B T$ . In figure 6,  $D^*$  is plotted as a function of the membrane volume fraction  $\Phi$  for the four following systems: AOT/brine system (Porte *et al* [10]),  $C_{12}E_5$ /hexanol/water system (Freysingéas *et al* [12]), SDS/hexanol/water/dodecane system and SDS/hexanol/water + PEG ( $c_p = 150 \text{ g l}^{-1}$ )/dodecane. In all sponge systems,  $D^*$  scales linearly with  $\Phi$  but with different slopes, indicating that  $D^*$  is still system dependent as suggested in [12].



**Figure 6.** Reduced relaxation frequencies  $D^*$  as a function of  $\Phi$ .  $C_{12}E_5$ /hexanol/water system,  $\bullet$ ; AOT/brine system,  $\blacklozenge$ ; SDS/hexanol/water/dodecane system,  $\blacktriangle$ ;  $L_5$  phase,  $\triangle$ .

## 6. Conclusion

The new polymer-induced  $L_5$  phase exhibits a reverse sponge-like structure. Conductivity and small-angle neutron scattering experiments taken together indicate an inverted bilayer structure connected in a random way to build a continuous water path. The results of static light scattering demonstrate the presence of very strong sponge order parameter fluctuations. The relaxation of these fluctuations was studied using quasi-elastic light scattering and the two characteristic frequencies measured. Their orders of magnitude and scaling properties are nicely compatible with the ‘sponge’ description. It remains that encountering a sponge phase ‘sandwiched’ between  $L_2$  and  $L_\alpha$  phases is uncommon, and unexplained up to date.

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