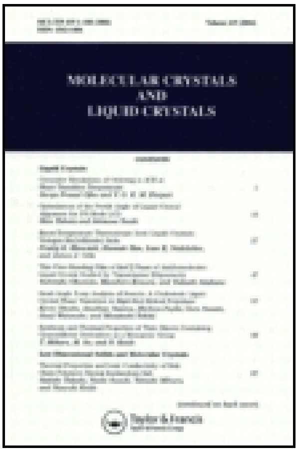

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Dynamic Light Scattering Studies on Lecithin Polymer-Like Gels

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DYNAMIC LIGHT SCATTERING STUDIES ON LECITHIN POLYMER—LIKE GELS.

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Abstract Depolarized light scattering (DRS) and ultrasonic measurement on isooctane/lecithine/water gel are reported as a function of temperature. The analysis of the DRS data reveals a fast contribution connected to the pure isooctane. The ultrasonic normalized absorption data clearly show a relaxation process. A tentative interpretation of the results is performed on the basis of existing models.

Keywords: lecithin, gels, light scattering

GENERAL CONSIDERATIONS

Very recently a lot of attention was devoted to a new family of organogels from water in oil microemulsions[1,2,3]. The interest in this field arises from some peculiar properties of such kind of gels that make them of primary importance for biochemistry, pharmaceutical and medical applications. In particular, they are able to solubilize and to trap guest molecules like drugs. Furthermore lecithin gels are of great importance in biomimetic chemistry because they can be connected strictly to gellike lipidic aggregates existing in vivo. Soybean lecithin is able to form a clear and optically isotropic microemulsion when small quantities of water are added to a solution of lecithin in organic solvents[1]. Generally speaking, it was proposed the existence in microemulsion systems, of a polymer–like phase induced by the presence of giants flexible and cylindrical micelles. In particular a description of the growth process of the micelles as a function of the surface active agent concentration and temperature was successfully developed by Blankschtein[5]. Very recently, from Small Neutron Scattering[3] experiment on the system soybean lecithin/iso-octane/water, a gyration radius was obtained of ~15 Å to which correspond a radius of ~20 Å for the micelles. Such values suggest a radial distribution of water throught a very extended lecithin headgroup region. It was shown that the addition of a very small amount of water (~3 water molecules for each surfactant molecule) causes a dramatic increase in the zero shear viscosity up to a factor 10^6. The observed viscoelastic properties of such aqueous micellar solutions could be connected with a water induced aggregation of lecithin molecules into flexible cylindrical reverse micelles and the subsequent formation of a transient network of entangled micelles above an overlap concentration[6,7] Φ^*. At the same time the system was investigated by quasi elastic light scattering from which the hydrodynamic correlation length was estimated. It turned out a dependence of such a quantity upon the lecithin volume fraction Φ, in the range $0.014 \leq \Phi \leq 0.145$, according to a power law with an exponent of -0.65 and in good agreement with the proposed structural model[3].

In this paper we present some preliminary results, by Depolarized Rayleigh Scattering (DRS) and ultrasonic techniques, performed in order to obtain a better insight on the not yet clarified structural and dynamical properties of such organogels, that however promise to be good model systems for the experimental investigations of the entanglement networks formed by non–permanent objects.

EXPERIMENTAL SECTION

Samples were prepared starting from soybean lecithin purchased by Sigma. According to ref. 1 it is to be stressed that lecithin of not enough purity is not able to form gel. As a consequence the commercial product was subjected to purification with a silica gel column by applying CH_2Cl_2/CH_3OH (1:1 v/v) as the eluant and collecting the resulting material with an $R_f=0.22$ following the indications from Thin Layer Chromatography in order to obtain a high degree of purity (~ 97%). The solution obtained from the chromatografic column was dried by a Rotovapor and the obtained lecithin was put under vacuum in order to remove each trace of eluant. The lecithin was dissolved in isooctane (Baker Chemical), at room temperature, to obtain a ~100 mM solution (corresponding to a Φ value of about 0.072). Then the appropriate amount of water was added to reach a water/lecithin ratio value ~3 following the usual procedure described in ref. 1.

DRS measurements (Rayleigh wing) were performed in a 90° geometry, using a SPEX Ramalog 5 triple monochromator and the 4880 Å line of an unimode Ar^+ laser working at a mean power of ~500 mW. The experiment tested both pure isooctane and the gel at temperatures of 10, 15, 20, 30, 40 and 50°C. To obtain the better compromise between intensity and resolution three spectra with a pass–band of 0.3, 0.6 and 1.0 cm^{-1}, in the spectral ranges $-2\div2$, $-5\div5$ and $-50\div50$ cm^{-1} respectively, were recorded for each run and then numerically matched. In fig. 1 the spectrum for the gel at T=50°C is shown as an example.

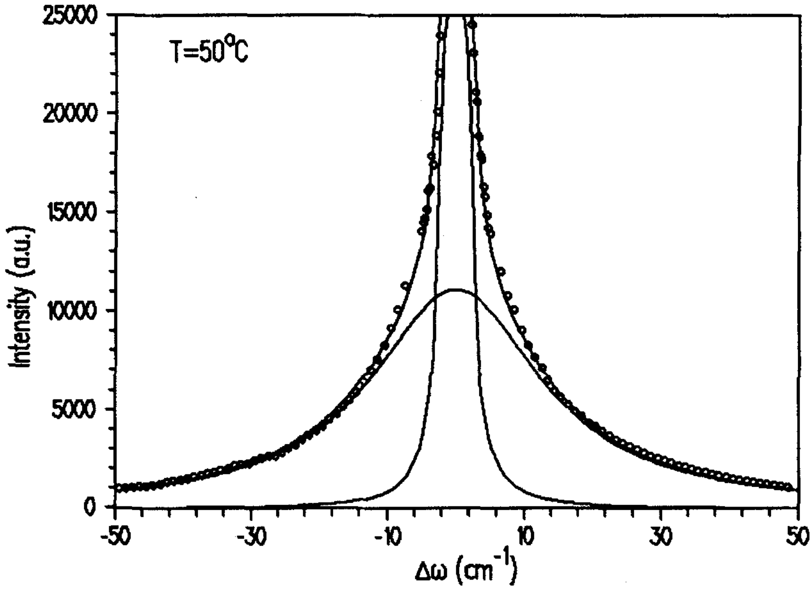

FIGURE 1 DRS spectrum for the soybean/lecithin/water gel at T=50°C. Circles: experimental points. Continuous lines represent the two components revealed by the deconvolution procedure and the total fitting.

Ultrasonic measurements were performed, by a standard Matec pulse echo apparatus, in the same temperature range, at the frequencies of 5, 6, 10, 14, 15, 25 and 35 MHz. The obtained normalized absorption (α/f^2) data for soybean lecithin gel at different temperatures are reported in fig. 2 as a function of frequency.

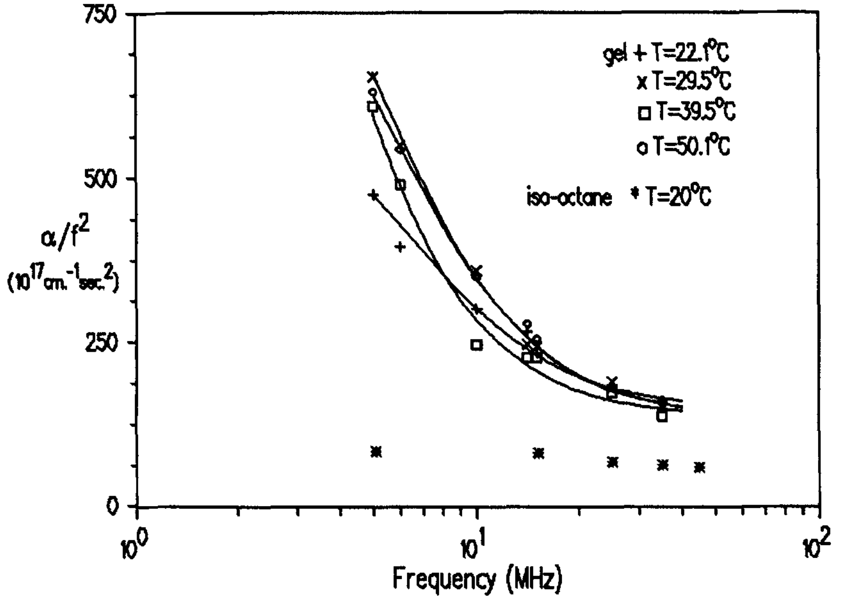

FIGURE 2 Normalized ultrasonic absorption as a function of frequency, for soybean lecithin gel, at various temperatures. Isooctane data are reported for comparison.

DISCUSSION AND CONCLUSIONS

It is well known that the not–shifted depolarized light scattering is connected to the density–density correlation function characterized by various contributions depending by the different mechanisms contributing to the scattering process, namely rotational and diffusional traslations, collisional interactions, hydrodinamic collective motions and, in the case of highly viscous fluids, also coupling effects between the above mentioned processes. To obtain informations on the various contributions to the DSR, we analyzed the experimental spectra by a suitable deconvolution procedure according to[8]:

$$I_{anis}^{total}(\omega)=S(\omega)+\sum_i L_i(\omega)+I_{anis}^{vibr}(\omega) \qquad (1)$$

where S(ω) represents an ultraslow symmetric contribution, resolution enlarged, which could be originated by the traslational diffusion mechanisms and, in the case of gel, by the slow reorientational dynamics of the micelles or/and to the coupling with transverse spectral contributions. The second term represents the superpositions of symmetrical lorentzian lines arising from the occurrence of more fast relaxation process in the system, happening within a time scale accessible to our experiment. The last term, cooperative in character, is the low frequency contribution of the vibrational spectral density and, in any case, behaves like a constant background in the explored low frequency region. Really our fitting procedure by eq. 1 evidenciated only the presence of two contributions both in the pure isooctane and in the gel. The first one, resolution enlarged (HWHM≃0,15 cm.$^{-1}$), is originated by slow processes whose dynamics is not accessible by our experiment. The second contribution gives evidence of a fast process taking place in the 10^{-13} sec time scale. In fig. 1 the two above described contributions and the total fitting result are represented by continuous lines. In fig. 3 we report, in an Arrhenius plot, the obtained relaxation times τ ($\tau=1/2\pi c\Gamma$) as a function of reverse temperature both for the pure solvent and for the gel. As it can be seen the revealed processes in the two investigated systems are taking place on the same time scale. This evenience make us confident in hipothesizing that, in both the cases, we are observing the dynamical evolution of the same reorientational mechanism and that this is strictly connected with the dynamics of the bulk isooctane. The straight lines in fig. 3 represent the result of the fitting procedure of the experimental data by an Arrhenius law, from which the activation enthalpy values ΔH=2.5 Kcal/mol and ΔH=1.4 Kcal/mol are derived for gel and isooctane respectively. Such a result gives some indications of a more hindered character, for the observed process, when the gel network is present. At the same time, it is to be observed that the relaxation process turns out to be faster in the gel, at least at high temperatures. Such experimental indications could give arise to the hypothesis that some interactions are taking place between isooctane and the entanglement of micelles in the gel. Our feeling is that the network established by the interactions between micelles induces a more stable equilibrium position for the isooctane molecules trapped into the cages: in such a way one could rationalize both the higher activation enthalpy for the process and the faster reaching of a new equilibrium position. Such hypothesis could be supported by the trend to increase of the integrated areas of the fast contributions with temperature, from which, using a two states model[9], a binding energy ΔG≃1.8 Kcal/mol and ΔG≃2.7 Kcal/mol are estimated for isooctane and gel respectively.

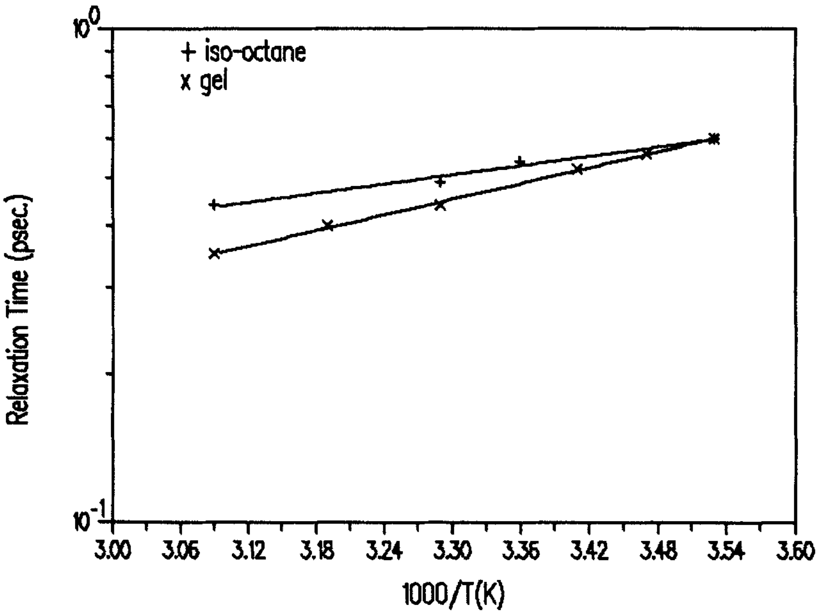

FIGURE 3 Relaxation time for the fast process in isooctane (+) and soybean lecithin gel (x) as a function of 1/T. Continuous lines represent the results of a best fit by an Arrhenius law.

In summary, our idea is that what we are observing is the effect on the solvent dynamics of some although complicated structural evolution with temperature. Such effects could be influenced by micelles reorientation and reptation dynamics and by the growth process of the polimer–like network triggered by the interaction among micelles[3,6,7]. Unfortunately such effects take place on a long time scale and, in our experiment, are collapsed and masked into the resolution enlarged contribution.

The ultrasonic results reveal a temperature dependence of the sound velocity, with a trend to decrease when T increases, while the obtained values (~1050 m/sec) do not change significatively passing from the pure isooctane to the gel. The more interesting effect is observed in the absorption behaviour as a function of the ultrasonic frequency reported in fig. 2. The data clearly show that some relaxation effect is taking place whose frequency, obtained by a fitting procedure with a single relaxation process

$$\frac{\alpha}{f^2} = \frac{N}{1 + \left(\frac{f}{f_c}\right)^2} + M \qquad (2)$$

where N, f_c and M are the strenght of the relaxation, the relaxation frequency and the relaxed value of the absorption respectively, turns out to be almost temperature independent with a mean value of ~5 MHz. It is evident, from an inspection of fig. 2, that the relaxed value for the observed process is about the same revealed for the pure isooctane. Really what we are observing is the tail of the relaxation process and, as a consequence, we are not able to distinguish between a single relaxation or a distribution. In our case both the hypothesis could be assumed. In fact a distribution of relaxation times, due to the hierachy of structures present in the system could be reasonable[10]. In the hypothesis of a single relaxation process, this could be connected to some interactions between lecithin and water molecules.

In order to better clarify the effects lying on the basis of the observed phenomena and to have a better understanding of the gel formation process, new DRS, photon correlation spectroscopy and ultrasonic measurements, as a function of temperature and of the water/lecithin ratio, are actually in planning in our laboratories.

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