

Indicative Evidence for Coexistence of Long and Short Polymer-like Micelles in Lecithin Organogel from Rheological Studies

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A jelly-like phase, which is separated from the homogeneous lecithin organogel after exceeding the critical amount of water, has been studied by an oscillatory rheology. An interpretation of rheological parameters taken from the chemistry of polymer blends enabled us to suggest that the separated organogel consists of a mixture of at least two types of rather monodisperse polymer-like micelles differing by their length.

Introduction

The polymer-like micelles of lecithin are formed with an addition of small amounts of water^{1,2} or some organic polar solvents^{3,4} into its nonaqueous solution. The polar additives induce the transformation of initial spherical aggregates into extended cylindrical ones of 20–25 Å radii and up to several micrometers in length.^{5–7} The extended micelles entangle, forming a three-dimensional network that is the cause of viscoelastic properties of the solutions.^{8,9} The solutions behave like jelly-like phases, called often organogels.

The polar additives bring about also a lesser known second phenomenon; they induce a phase separation of the initially obtained homogeneous organogel into a compact jelly-like phase and a nonviscous solution when their concentration is in excess of the critical one.^{1,3} Of interest is the separated organogel. This has been first examined in our previous publication.¹⁰ A new rheological regime was observed in the intermediate region in which the shear moduli scale as the square root of oscillation frequency. This dependence is suggestive of local ordering of micellar aggregates. However, the reasons for the phase separation and why the polymer-like micelles become more closely packed are still unclear.

The paper presents a new interpretation of rheological data that gives an indication of a partial disintegration of micellar aggregates as soon as the homogeneous organogel is separated. The compact jelly-like phase

consists of no less than two types of polymer-like lecithin micelles: long and short ones. This is the first indicative evidence that aggregates of various length can coexist in the organogel.

Materials and Methods

Soybean lecithin, Epikuron 200, from Lukas Meyer AG (Hamburg, Germany) was used as supplied. *n*-Decane was of puriss quality from Fluka. Water was purified by double distillation.

To prepare jelly-like phases, weighed appropriate amounts of lecithin and water were dissolved in *n*-decane and then allowed to stay at ambient temperature at least for 3 days. A precipitated jelly-like phase in two-phase systems was separated from the above nonviscous solution by means of a separating funnel. The detailed procedures have been described in our previous publications.^{3,10,11}

Rheological measurements were made with a Bohlin CS-10 stress-controlled rheometer in an oscillation regime. A measuring cell with a cone and plate geometry (a diameter of 40 mm and a cone angle of 4°) was used. The oscillatory frequency was varied from 0.001 to 10 Hz. The temperature was 25.0 ± 0.1 °C.

Experimental Results and Discussion

Parts A and B of Figure 1 show a frequency dependencies of the storage G' and loss G'' moduli for a homogeneous lecithin organogel and separated jelly-like phase, respectively. The graph in Figure 1A is typical of systems made up of an entangled network of long flexible cylindrical micelles or polymer molecules of which the dynamical behavior satisfies a reptation theory.^{12,13} Furthermore, in most of the frequency range accessible for measurements the dependencies in Figure 1A obeys a Maxwell model wherein¹⁴

$$G'(\omega) = 4\pi^2 G_0 f^2 \tau_t^2 / (1 + 4\pi^2 f^2 \tau_t^2) \quad (1)$$

$$G''(\omega) = 2\pi G_0 f \tau_t / (1 + 4\pi^2 f^2 \tau_t^2) \quad (2)$$

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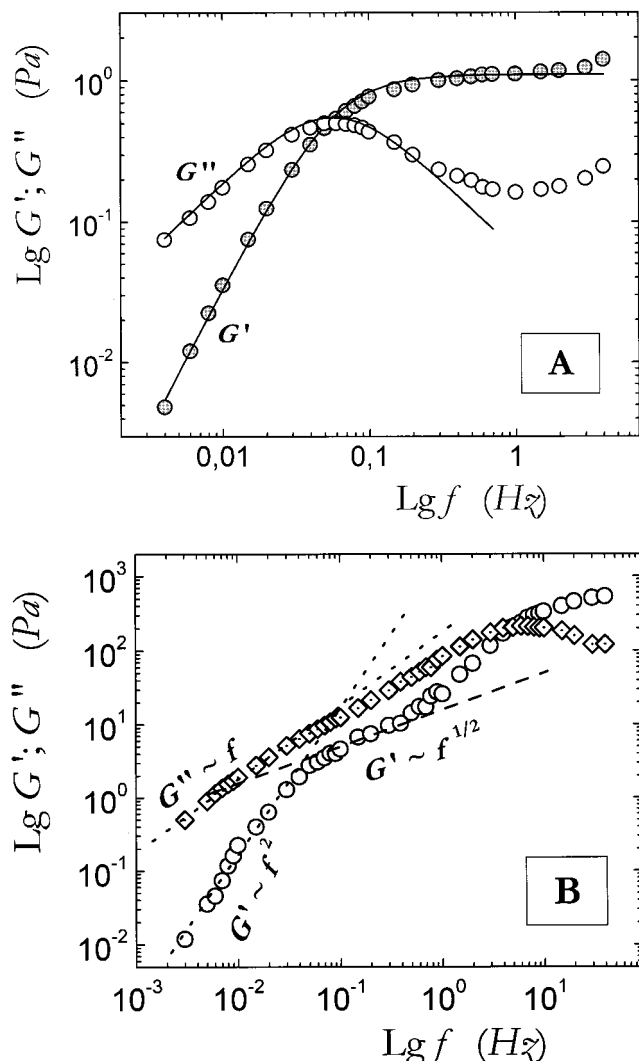


Figure 1. The storage modulus G' and loss modulus G'' vs oscillation frequency. The experimental data are shown by points: The solid lines in (A) are the best fits in accordance with eqs 1 and 2. The straight dotted and dashed lines in (B) show the corresponding slopes. An organogel consists of 35 mg/mL lecithin and 2.6 (A) or 4.0 (B) water molecules per lecithin molecule in *n*-decane. The temperature was 25.0 ± 0.1 °C.

Here G_0 is the plateau modulus, f the frequency in Hz, and τ_t the terminal relaxation time. The solid lines in Figure 1A represent best fits to eqs 1 and 2 where G_0 and τ_t have been used as adjustable parameters.

In the second case being considered (Figure 1B) there is only a short terminal zone in the low-frequency range in which the rheological behavior can be characterized within the framework of the Maxwell model. The main distinction from the previous system is in an intermediate range where G' and G'' scale like $f^{1/2}$. This scaling behavior, as shown in our recent article,¹⁰ should be caused by ordering of polymer-like micelles at the local level. The features of the system at the whole frequency range accessible for measurements have not been so far examined.

We have resorted to the procedure that is usually used for examining polydisperse polymers.^{15–19} Figure 2 shows

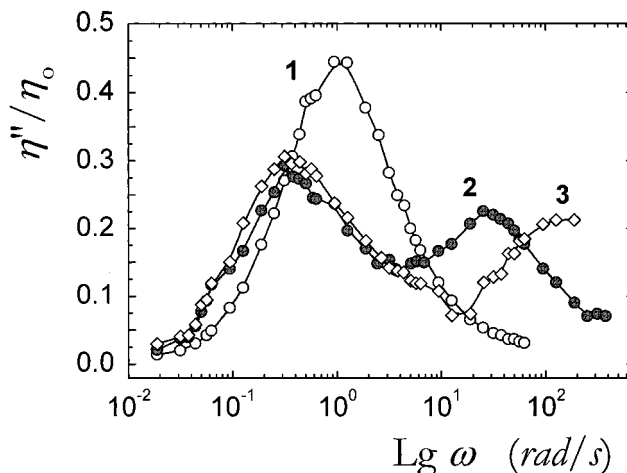


Figure 2. The imaginary part of the complex viscosity vs oscillation frequency. An organogel consists of 35 mg/mL lecithin and 3.2 (1), 4.0 (2), or 4.3 (3) water molecules per lecithin molecule in *n*-decane.

a frequency dependence of the imaginary part (η'') of the complex viscosity. The η'' values are normalized by the zero-shear viscosity. Commonly used is the loss modulus in place of η'' , but we follow an approach by Montfort et al.^{18,19}

One can see that there is one peak in curve 1. The corresponding data refer to a homogeneous organogel in which the molar ratio of water to lecithin is equal to 3.2. In going to separated jelly-like phases (curves 2 and 3), the peak decreases in height and shifts somewhat into the low-frequency region. Furthermore, there appears a second peak in curves 2 and 3 at high frequencies. With increased water, this peak shifts further into the high-frequency region.

Similar behavior has been previously observed in a model system composed of binary blends of linear monodisperse polymers.^{15,18} The polymer molecules were long enough to entangle into a three-dimensional network. Therefore the molecules of both the types move in accordance with a reptation mechanism. By use of such a model system to clear up the effects of polydispersity, it was established that the addition of the low-molecular component resulted in appearance of the second peak in a curve in the high-frequency region in graphs of loss modulus or imaginary part of the complex viscosity against the frequency of mechanical oscillations. The similarity observed with dependencies in Figure 2 offers a new approach for the interpretation of our data.

A jelly-like phase separated from the homogeneous organogel at a large molar ratio of water to lecithin consists of no less than two types of polymer-like micelles: short and long ones. A possibility of forming additional micellar aggregates with relaxation times outside the frequency range accessible for our measurements, must not be ruled out.

The length of the shorter micelles is well above the entanglement threshold; therefore, they form a three-dimensional network.

The polymer-like micelles of both types should be with rather narrow-distributed aggregation numbers. This follows from the well-defined peaks in curves in Figure 2. A difference in micellar lengths, as inferred from a

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comparison with the polymer model systems, can be as much as 10 times.

The interpretation considered above implies our attempt to understand the experimental results that are not consistent with the present views on viscoelasticity of solutions of polymer-like micelles. The micellar systems represent a more complicated object for the experimental study than polymers because of the dynamic nature of aggregates. It is impossible to create a formulation from micelles, for example, with prearranged lengths. Therefore, the correlation of properties of micellar solutions with

those of model polymer systems provides a good means for understanding the experimental data. The approach considered in the article can potentially yield useful insight, but this calls for the further supporting evidence.

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