

Lecithin Organogel with New Rheological and Scaling Behavior

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It was established from an experimental study on a lecithin organogel in *n*-decane performed by means of an oscillatory rheology that frequency dependencies for complex viscosity and storage modulus have intermediate plateaus at certain molar ratios of water to lecithin. This type of rheological behavior was previously observed for blends of homopolymers which differ significantly in their molecular weight. To mathematically describe the experimental data, a Maxwell model including two relaxation processes (i.e., two elements in parallel) was considered. Both relaxation modes were constrained according to the known interrelation between terminal relaxation time, zero-shear viscosity, and plateau modulus. The experimental results were in good agreement with the model considered. By applying a fitting procedure, two sets of values for relaxation time, zero-shear viscosity and plateau modulus, were obtained for each of the relaxation processes. When the scaling behavior was examined, a disagreement with current models for the polymer-like micelles was found. The presented results lead to a suggestion that the lecithin organogel at increased water-to-lecithin molar ratios has more complicated structural organization than that observed for surfactant based micellar aggregates before.

Introduction

The lecithin organogel represents a viscoelastic solution, the properties of which are determined by polymer-like micelles. This means that aggregates are cylindrical and long enough for overlapping and forming a transient three-dimensional network in the bulk solution.^{1–6} As a consequence of such a supramolecular structure, the micellar systems exhibit the same kind of rheological behavior encountered for semidilute solutions and/or melts of uncrossed monodisperse polymers.^{2,5,7–9} In particular, the frequency dependencies of complex viscosity and dynamic moduli in the terminal zone are well described in the framework of a simple Maxwell model with one element which characterizes a single relaxation process (hereinafter termed as one mode process, and abbreviated by 1-M).

The foregoing fully applies to the lecithin organogel. Lecithin is a naturally occurring surfactant, whose molecules are based on glycerol with attached two fatty acid residues and phosphocholine (see the structural formula in Figure 1). When being dissolved alone in a low polarity media, it forms reversed spherical micelles.^{10,11} A transition to a polymer-like system takes place after addition of small amounts of water.^{12,13} For instance, by introducing 2–3 water molecules per lecithin molecule in an alkane solution, one finds cylindrical aggregates of contour length up to 1 μm and diameter equals to about 10 nm.^{3,14,15} Their persistence length, of approximately 10 nm,¹⁶ enables one to consider the micelles as flexible entities moving in accordance with a reptation model.

The formation, growth, structure, and properties of polymer-like micelles depend mainly on the molar ratio of water to

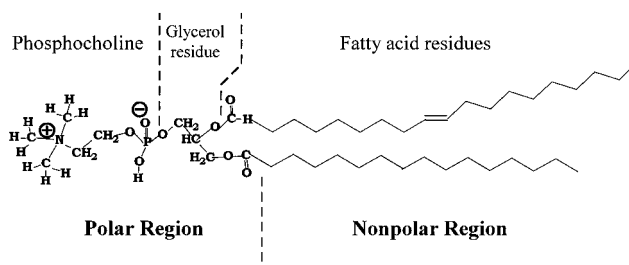


Figure 1. Structural formula of lecithin, 1,2-diacyl-*sn*-glycero-3-phosphocholine.

lecithin.^{15,17–19} The initial stage consists of a linear growth, followed by a branching of micellar aggregates.^{15,19,20} In both stages, the rheological behavior obeys the common Maxwell model characterized by a one element.^{15,21} Further increasing the water amount results in a transition to a jelly like phase, to which the 1-M model is no longer applicable. By its rheological behavior, this organogel resembles a system composed of a binary blend of monodisperse polymers with significantly different molecular weight.²² In accordance with this observation, it was suggested that the three-dimensional lecithin network in nonpolar media can be represented as a mixed supramolecular structure made up of micellar aggregates having different average size (aggregation number).²²

The paper presents a thorough study on the lecithin organogel demonstrating anomalous rheological behavior. To get a satisfactory mathematical description of this system, a more complicated Maxwell model, involving two elements, was successfully applied. This means that the organogel phase may be represented as a mixture of entities possessing various relaxation times. Their rheological parameters were extracted from experimental data after application of a standard best fitting procedure. When a dependence on the lecithin concentration

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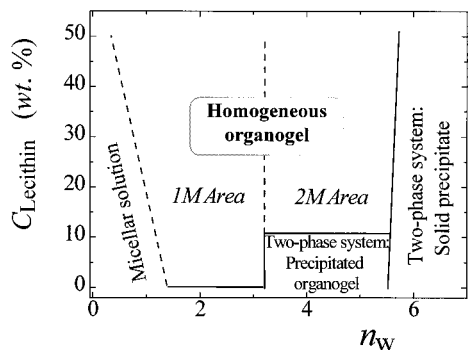


Figure 2. Phase diagram for soybean lecithin in *n*-decane presented in coordinates of lecithin concentration expressed in weight percentage against the molar ratio of water to lecithin in the system. The dashed lines show boundaries that have been determined approximately. Explanations are given in the text.

was considered, a new scaling behavior was found. The presented results suggest a new structural organization for the jelly like lecithin phase at larger water-to-lecithin molar ratios.

Materials and Methods

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

Organogels were prepared by dissolving appropriate amounts of lecithin and water in *n*-decane. To get equilibrium, they were allowed to stay at room temperature for at least 3 days. The preparation procedure is detailed in previous publications.^{17,23}

Rheological measurements were performed with a Bohlin CS-10 stress-controlled rheometer. It was equipped with a cell having cone and plate geometry. The cone diameter was 40 mm, and the cone angle was 4°. The oscillatory frequency was varied from 0.001 to 10 Hz. The temperature was fixed to 25.0 ± 0.1 °C.

Experimental Results

Partial Phase Diagram. The phase diagram for a ternary system consisting of soybean lecithin Epikuron 200 (Lukas Mayer), water, and *n*-decane at 25 °C is presented in Figure 2 in coordinates of lecithin concentration against water-to-lecithin molar ratios (n_w). It was constructed on the base of results previously obtained.^{15,17,18} A region for the homogeneous organogel is located between the left boundary (dashed line), referring to the threshold concentration for micellar overlapping, and the solid line at the right, standing for the homogeneous organogel separation into a precipitated jelly like phase and a low-viscous solution. It is significant that the dashed line is a rough approximation. The phase separation occurs when n_w is ranging from 3.2 to 3.5. This phenomenon is absent when the lecithin concentration is as much as 200 mg/mL.¹⁵ In concentrated solutions the phase region of the homogeneous organogel extends up to $n_w = 5.2$ – 5.5 .

The water added promotes not only the transition from spherical to polymer-like micelles but also a sequential change of the micellar structure and rheological properties of lecithin organogels. At the first stage, one can find linear, and then branched, polymer-like micelles (see the approximate boundary marked by a dotted line in the diagram). A micellar system with uncommon rheological behavior appears at molar ratios n_w in excess of 3.2.^{15,22} The further consideration concerns lecithin organogels prepared with varied lecithin concentration at $n_w = 3.0$ or 4.0.

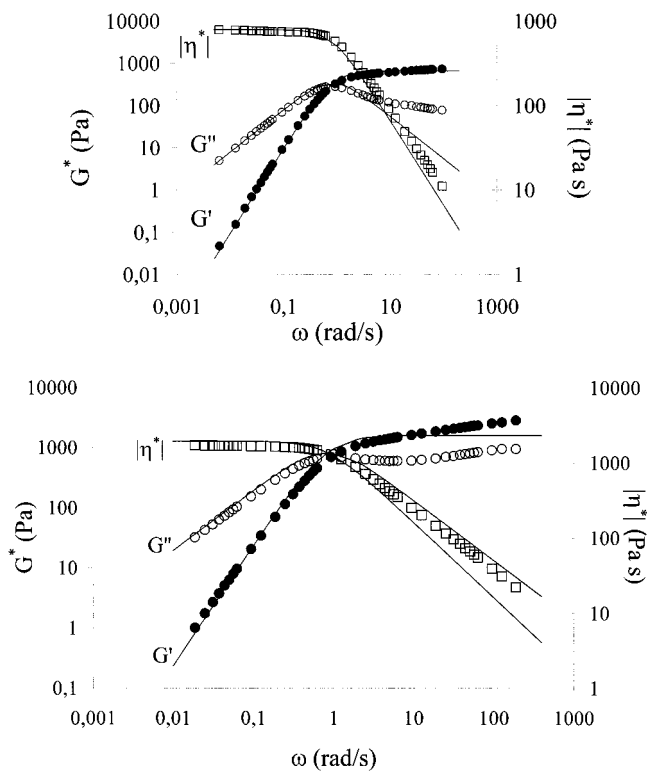


Figure 3. Complex viscosity $|\eta^*|$, storage modulus G' , and loss modulus G'' vs oscillation frequency. An organogel consisted of 17 wt. % (A) or 50 wt. % (B) of lecithin in *n*-decane. The molar ratio was $n_w = 3.0$. The temperature was 25.0 ± 0.1 °C. The experimental data are shown by points. The solid lines are the best fits in accordance with eq 1a–c for (A) $G_{01} = 660$ Pa and $\tau_1 = 1.4$ s and (B) $G_{01} = 1600$ Pa and $\tau_1 = 1.2$ s.

Rheological Behavior. Figures 3A,B and 4A,B present the experimental frequency dependencies (empty points) of the storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|$) for the two organogels mentioned above. They illustrate different viscoelastic behavior produced by changing the water-to-lecithin molar ratio. It was noted that variation of the lecithin concentration did not have a notable effect on the character of the frequency dependencies measured.

Figure 3A,B demonstrates a typical rheological behavior for micellar systems consisting of polymer-like aggregates.⁷ In the low-frequency region (the terminal zone), the storage modulus increases as ω^2 , the loss modulus as ω , whereas the complex viscosity is almost constant. When curves for G' and G'' meet each other, the storage modulus is slowly increasing, whereas the loss modulus and the complex viscosity decay. These features mentioned are typical of a 1-M relaxation process which is well modeled by a single Maxwell element in much of the experimentally measured frequency range.²⁴

Figure 4A,B shows another case, corresponding to a higher water-to-lecithin molar ratio. One can also see the terminal zone, but until when the curves for G' and G'' intersect each others in the high-frequency region, there is a portion of the curves which may be considered as an intermediate plateau. This did not allow us to describe the jelly like phase in the framework of the common 1-M Maxwell model, and yet, it suggests to take into account two relaxation processes. This feasibility is examined in the section that follows.

Analysis of Experimental Data

First, the validity of a 1-M relaxation mechanism has been checked up. The frequency dependencies of the rheological

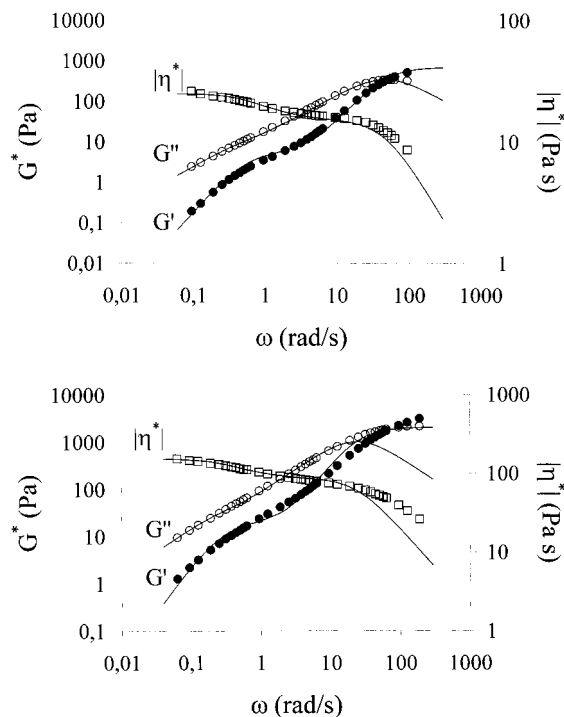


Figure 4. Frequency dependencies of the rheological parameters for an organogel with 17 wt. % (A) or 50 wt. % (B) lecithin and 4.0 water molecules per lecithin molecule in *n*-decane measured at 25.0 ± 0.1 °C. The points represent the experimental data, while the solid lines are the best fits in accordance with eqs 2a–d for (A) $G_{01} = 5$ Pa, $G_{02} = 689$ Pa, $\tau_1 = 1.9$ s, and $\tau_2 = 0.02$ s and (B) $G_{01} = 20$ Pa, $G_{02} = 2000$ Pa, $\tau_1 = 3.6$ s, and $\tau_2 = 0.04$ s.

parameters in the common Maxwell model are characterized by the following equations:²⁴

$$G'(\omega) = G_{01}\omega^2\tau_1^2/(1 + \omega^2\tau_1^2) \quad (1a)$$

$$G''(\omega) = G_{01}\omega\tau_1/(1 + \omega^2\tau_1^2) \quad (1b)$$

$$|\eta^*(\omega)| = (G'^2 + G''^2)^{1/2}/\omega \quad (1c)$$

where ω is the oscillation frequency in rad/s, G_{01} is the plateau modulus, and τ_1 is the terminal relaxation time for the only present mode 1. A result of the best fits to the experimental data is represented as solid curves in Figure 3A,B. In the most frequency range, one may see a good agreement. A deviation appears at high frequencies. This is usually observed for systems with polymer-like micelles, where a deviation from the Maxwell model is normally caused by a contribution of fast relaxation (Rouse) processes.^{25–28}

An attempt to apply the above approach to the results presented in Figure 4A,B was unsuccessful. We got a satisfactory agreement once a Maxwell model with two elements in parallel was used. It can be represented in compact form by the following equations:²⁴

$$G'(\omega) = \sum_k G_{0k}\omega^2\tau_k^2/(1 + \omega^2\tau_k^2) \quad (2a)$$

$$G''(\omega) = \sum_k G_{0k}\omega\tau_k/(1 + \omega^2\tau_k^2) \quad (2b)$$

$$\eta'(\omega) = \sum_k \eta_{0k}/(1 + \omega^2\tau_k^2) \quad (2c)$$

$$\eta''(\omega) = \omega \sum_k \eta_{0k}\tau_k/(1 + \omega^2\tau_k^2) \quad (2d)$$

with $k = 1$ and 2 , $\eta^*(\omega) = \eta' - i\eta''$, and where additional plateau modulus G_{02} and relaxation time τ_2 are introduced to

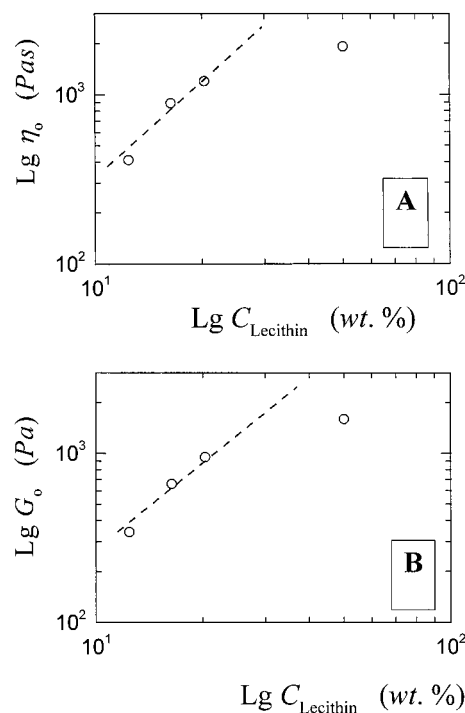


Figure 5. Zero-shear viscosity (A) and plateau modulus (B) vs the concentration of lecithin in organogel at $n_w = 3.0$. Straight dashed lines show a power law exponents equal to 2.5 (A) and 2.25 (B).

describe the presence of the second mode. For any relaxation mode (i), the terminal relaxation time, zero-shear viscosity, and plateau modulus were linked through the well-known interrelation

$$\tau_1 = \eta_0/G_{0i} \quad (3)$$

which was derived in the context of a theory of rubber viscoelasticity.^{24,29} Constrains, $G_{01} < G_{02}$ and $\eta_{01} < \eta_{02}$, were also imposed to the low-frequency region. This enabled us to reach a better agreement.

Experimental data (unfilled points) and best fits (solid lines) are shown in Figure 4A,B. As seen, the agreement is quite satisfactory, which proves that the organogel can be described in the framework of the Maxwell model accounting for two elements in parallel. The presence of two relaxation processes related to the micellar system suggests that the organogel can be conceived as a mixture of various entities.

Scaling Behavior

The developed approach enabled us to extract rheological parameters characterizing each of the relaxation processes. This gave a possibility of examining the scaling behavior of the systems under consideration.

Double logarithmic dependencies of the zero shear viscosity and plateau moduli on the lecithin concentration are presented in Figures 5 and 6 for organogels with three and four water molecules per lecithin molecule, respectively. The data for the system with the smaller n_w (Figure 5) are given for a comparison. This kind of jelly like phases was exhaustively characterized in previous works.^{15,17,18,30}

The lecithin organogel at molar ratio $n_w \approx 3$, as followed from the scaling behavior, consists of branched polymer-like micelles. Values for the extrapolated scaling exponents are given in Table 1, together with values predicted by models for linear and branched micellar aggregates. The straight lines in Figure 5 show the slope value satisfying the model of branched

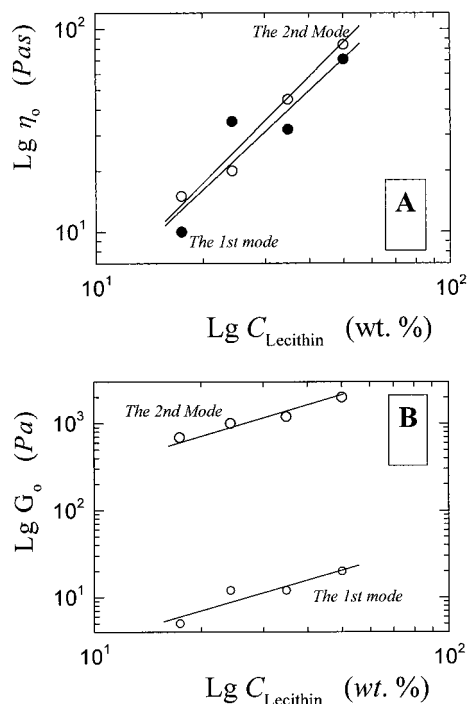


Figure 6. Zero-shear viscosity (A) and plateau modulus (B) vs the concentration of lecithin in organogel at $n_w = 4.0$. Straight solid lines are the best least-squares fits to the experimental data. Their slope values are presented in Table 1.

TABLE 1: Values of Scaling Law Exponents

model/experiment	G_0	η_0	ref
Theoretical Predictions			
reptation theory	2.25	5.25	29
linear micelles	2.25	3.5	25, 26
branched micelles	2.25	2.5	15
Experimental Data			
1-M relaxation system;	2.41 ± 0.14	2.24 ± 0.14	15
$n_w = 3.0$			
2-M relaxation system;	1.17 ± 0.34	1.63 ± 0.18	this work
1st mode			
$n_w = 4.0$	0.96 ± 0.12	1.70 ± 0.51	
2nd mode			

micelles. As is obvious, only the initial experimental points fall on it. Then there appears a deviation.

Results for the 2-M relaxation system are given for either processes in Figure 6. The straight lines present the best least-squares fits to the experimental data (see points). Table 1 summarizes the slope values obtained from the fitting procedure. It can be seen that they are in serious disagreement with the scaling law predicted by theoretical works for linear and branched micelles. A possible reason is that they were developed for 1-M relaxation processes.

Of certain interest is then the zero-shear viscosity for both of the components. The points fall practically in the same straight line (Figure 6A). As a consequence, the only difference between the two relaxation processes is caused by the plateau moduli (Figure 6B). This result leads us to the following conclusion after reasoning.

The zero shear viscosity depends mainly on the chain length.^{24,29} For polymer-like micelles, η_0 should be depending on the aggregation number. In this respect, the same order of magnitude for both the zero-shear viscosity values (Figure 6A) implies the system comprises similar micellar aggregates. On the other hand, the plateau modulus is related to the number of crossing points.^{24,29} Therefore, the difference in G_0 (Figure 6B)

leads to the conclusion the organogel at $n_w = 4$ consists of two families of entities. They have comparable aggregation numbers but different average density of crossings points within a three-dimensional network.

Discussion of the Experimental Results

It was shown that the lecithin organogel at large molar ratios of water to lecithin can be described in the framework of the Maxwell model including two elements in parallel. This provides a new insight into the structural organization of micellar system and dynamics of polymer-like micelles. The first important conclusion followed from the theoretical consideration is that the progressive addition of water induces a transition from uniform micellar aggregates to a jelly like phase with 2-M relaxation processes (Figure 4).

At first glance, it would seem reasonable to represent the 2-M system as a binary mixture of monodisperse micelles having different aggregation numbers and/or sizes. Such an interpretation is based on experiments where binary blends were prepared from monodisperse polymers of various molecular weight.^{31,32} However, this is not supported by the results on scaling behavior for the 2-M systems. A conflicting point follows indeed from the same order of magnitude of the zero shear viscosity for both the modes (Figure 6A). As a matter of fact, η_0 strictly depends on the average dimensions of the entities involved in the relaxation process.^{24,29} The plateau moduli, which are different for both the modes (Figure 6B), are mainly affected by the density of crossing points. This finding would rather imply that the organogel is built up by variously packed micellar aggregates. On the basis of the model of the temporal three-dimensional network from entangled chains, it seems extremely difficult to imagine a structural organization of lecithin aggregates in the jelly like phase at $n_w > 3$. There exists now the necessity to modify the model, or even suggest a new paradigmatic approach to the description of the jelly like phases of lecithin.

The above conclusion is also supported by the obtained results on the scaling behavior reported in Table 1. The values for the scaling exponents contradict in fact with the predictions of the current models used for describing polymer-like micelles. At this stage, when a number of several features and details are lacking, it is impossible to provide a reasonable explanation. We hope that a better understanding will be reached when other physicochemical, mainly scattering, techniques will be applied in order to study the lecithin organogel structure at larger water-to-lecithin molar ratios.

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