Articles

Growth, Branching, and Local Ordering of Lecithin Polymer-Like Micelles

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The viscoelastic properties of lecithin organogels formed by the addition of trace amounts of water in a *n*-decane solution were studied by means of oscillatory rheology. The viscoelasticity of jelly-like phases of this sort is caused by a transient three-dimensional network consisting of entangled cylindrical reverse (polymer-like) micelles. It is shown that although the organogel properties depend on the lecithin concentration, the phase and rheological behavior is mainly regulated by the polar additive. The homogeneous jelly-like phase exists for molar ratios (n_w) of water to lecithin from 1.6–1.7 to 3.2–3.4. At n_w ratios below 2.7–2.8, the scaling exponents of the main rheological parameters—the zero shear viscosity, plateau modulus, and terminal relaxation time—are rather close to the theoretical predictions that follow from a model by Cates. This means that the lecithin polymer-like micelles are linear and flexible. At larger molar ratios the scaling behavior with the lecithin concentration is changed. The observed power law exponents for the main rheological parameters are in satisfactory agreement with those expected from a model of the branched (connected) cylindrical micelles. These findings suggest that the mechanism for the growth of cylindrical micelles changes with increasing water amount; at the initial stages there is uniaxial growth of linear micellar aggregates, and then the polar additive induces their branching. First results on an jelly-like phase that separates from the homogeneous organogel when the molar ratio n_w is over 3.2 are presented. It is established that the phase separation results in a change in the rheological behavior. An intermediate region is found in which the loss and storage moduli scale with frequency with an exponent of $1/2$. Similar scaling was previously observed only with polymers. Conceivable reasons for the square root frequency dependence of the dynamic moduli are considered. It is suggested that this scaling is caused by partial or local ordering of polymer-like micelles due to the significant decrease of the organogel volume with the phase separation.

Introduction

Lecithin in nonaqueous solutions has the ability of producing extremely extended and flexible reverse cylindrical micelles. This ability may be considered as unique because other low-molecular-weight gelators dissolved in organic media often self-organize into rigid fibers.[1–4] The formation of a flexible micellar aggregate is more typical of various surfactants in aqueous solutions. They have been extensively studied. Therefore, the main generalities are well ascertained for the aqueous systems (for reviews see, e.g., refs 5–9 and references therein). The lecithin solutions have not been adequately studied.

The phenomenology of processes in the lecithin systems was mainly ascertained by Luisi and Schurtenberger with collaborators.[10–17] By means of a combination of light-scattering and small-angle neutron scattering techniques, it was shown that the cylindrical micelles are formed from initial spherical ones under appropriate conditions. The micellar shape transformation is induced by the addition of very small quantities of water.[10,18] The spherical reverse micelles turn into rodlike micelles and then into cylindrical ones. The rodlike micelles

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have been confirmed by electron micrographs obtained in ref 19. On reaching a critical length, the cylindrical aggregates entangle in a three-dimensional transient network similar to that of flexible polymers in their semidilute or concentrated solutions. Additional supporting evidence followed from studies performed by means of an oscillatory rheology[20] and hypersound absorption technique.[21]

The formation of a three-dimensional transient entangled network by lecithin micelles leads to a sharp increase in viscosity by a factor of 10^4–10^6. As this takes place, an initial low-viscous solution with Newtonian flow behavior turns jelly-like with viscoelastic properties of a "Maxwell fluid". Such long and flexible micellar aggregates comprising the jelly-like network are often called polymer-like micelles because of the similarity of their main properties and network organization to polymers in semidilute or concentrated solutions. The names "living" or "equilibrium" polymers, "wormlike" or "threadlike" micelles can be found in the literature as well.

The polymer-like micellar aggregates, along with strong similarity, possess an essential difference from polymeric molecules; they are dynamic entities, dissociating and recombining with time. This is reflected first of all in dynamic properties. Cates[22-26] took the breakage of aggregates into account when he adapted the reptation theory developed for polymer solutions to the micellar systems. Rather numerous dynamic rheological studies have been performed on aqueous viscoelastic solutions of surfactants to test his model.[5-8,27-30] They demonstrated the validity of the main points of Cates' model for systems consisting of the polymer-like micelles.

Oscillatory rheological experiments have been carried out on nonaqueous lecithin solution, to our knowledge, in three works.[12,20,31] Theoretical scaling predictions for the zero shear viscosity and plateau modulus have been examined only. For the zero shear viscosity, an experimental value of the scaling law exponent was in marked disagreement with that expected from Cates' model.[12,20] The reasons have not been established. It is pertinent to note that rheological regimes for nonaqueous viscoelastic lecithin solutions have not been examined so far in the literature.

We consider in this article linear viscoelastic properties of lecithin solutions that will be called the jelly-like phases and organogels. Oscillatory rheology is used, to determine structural parameters and dynamic characteristics of micellar networks as well as rheological regimes. It is shown first that the rheological behavior is primarily dictated by the molar ratio of water to lecithin in the organogel. At small ratios, concentration dependencies for polymer-like micelles obey scaling relations of Cates'

model predicted for entangled long linear flexible micelles. With increasing water content, a set of measured dependencies fits predictions for branching micellar aggregates that form a three-dimensional network in which part of the entanglements is replaced by connections. This has been previously observed only for aqueous micellar viscoelastic solutions.

For the first time, we perform in this article a study on a jelly-like phase separated from a homogeneous lecithin solution with the addition of the excessive water amount. The compact organogel shows unusual rheological behavior that so far has not been observed for the systems composed of polymer-like micelles. The features established correlate well with those of semidilute solutions of polymers exhibiting chain ordering at certain conditions.

Theoretical Background

The polymer-like micelle rheology is based on a model developed by Cates [22-24] who proceeded from the reptation theory for polymers in semidilute or concentrated solutions.[32,33] It was predicted that various regimes for rheological behavior can be observed in accordance with a ratio between the lifetime of micelles τ_b and their diffusion time constant τ_{rep}. The former is defined as the average time of existence of a micellar chain of the average length $\bar{L}$ from formation to the disruption into two pieces; the latter is the time needed for a chain to completely diffuse out of a tubelike environment composed of neighboring micellar chains by the reptation mechanism (i.e., by a snakelike motion along its own contour). There are two opposite situations.

(i) $\tau_b \gg \tau_{rep}$. The micellar lifetime is very long to have an effect on the kinetics of processes on the considered time scale. A dynamic regime in this case refers to the pure reptation. Thus, the shear stress decays according to

$$\sigma(t,\gamma) = \sigma(0,\gamma) \exp(-K[t/\tau_{rep}]^{1/4}) \qquad (1)$$

where t is the time, γ the shear strain, and K the constant. The stress relaxation proceeds in a nonexponential manner or, in other words, processes are characterized by a broad spectrum of relaxation times of which the longest one is

$$\tau_t \cong \tau_{rep} \sim \bar{L}^3 \, \phi^{3/2} \qquad (2)$$

where ϕ is the volume fraction of an amphiphile. The corresponding scaling laws for the plateau modulus G_0 and zero shear viscosity η_0 in the reptation theory are in the form of[32,33]

$$G_0 \sim \phi^{9/4} \qquad (3)$$

and

$$\eta_0 \sim \phi^{21/4} \qquad (4)$$

respectively. The latter is obtained if one takes into account the following expressions:

$$\bar{L} \sim \phi^{1/2} \qquad (5)$$

and

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$$\eta_0 = \tau \, G_0 \qquad (6)$$

(ii) $\tau_b \ll \tau_{rep}$. In this regime, the fast micellar dissociation/recombination kinetics affects the relaxation processes. The shear stress decay can be described by a single-exponential function,[6]

$$\sigma(t,\gamma) = \sigma(0,\gamma) \, \exp(-[t/\tau]) \qquad (7)$$

with a new characteristic time:[22,24]

$$\tau_t = (\tau_{rep}\tau_b)^{1/2} \qquad (8)$$

Under the mixed reptation/breakage regime, the relaxation times and zero shear viscosity are characterized by the following scaling laws:[22-24]

$$\tau_b \sim \bar{L}^{-1} \sim \phi^{-1/2} \qquad (9)$$

$$\tau_t \sim \phi^{5/4} \qquad (10)$$

and

$$\eta_0 \sim \phi^{7/2} \qquad (11)$$

It should be mentioned that the above predictions hold only for *linear* and *flexible* micelles long enough to overlap each other. Polymer-like aggregates are taken as flexible if their entanglement length l_e is much larger than the persistence length l_p. The former refers to the contour length between two consecutive entanglement points; the latter can be defined as the stiff part of a cylindrical micelle.

Branched Micelles. For cylindrical aggregates having connections (branching), the model of Cates was modified in refs 34-36. A new length $\bar{L}_c$ instead of $\bar{L}$ was introduced. It is defined as

$$\bar{L}_c = \frac{n_2}{n_1 + 2n_3} l_p \qquad (12)$$

where n_1 is the concentration of ends, n_2 the number density of persistence lengths, and n_3 the concentration of connections. The concentration dependence of $\bar{L}_c$ is given by

$$\bar{L}_c \sim \phi^{-1/2} \qquad (13)$$

When taking this expression into account, one can obtain the following scaling predictions:

$$\tau_b \sim \bar{L}_c^{-1} \sim \phi^{1/2} \qquad (14)$$

$$\tau_{rep} \sim \bar{L}^3 \phi^{3/2} \sim \phi^0 \qquad (15)$$

$$\tau_t \sim \phi^{1/4} \qquad (16)$$

and

$$\eta_0 \sim \phi^{2.5} \qquad (17)$$

Values of the exponents in the scaling laws for both the regimes considered above are presented in Table 1.

Breathing and Rouse Regimes. "Breathing" and Rouse regimes refer to tube-length fluctuations and local motion of a part of a chain of order of the entanglement length l_e, respectively.[33,37] They manifest themselves on short time scales. The corresponding kinetics of a chain part in its tube can be characterized by a time τ_e. Theoretical predictions for the rheological behavior were obtained from a computer simulation and from a Poisson renewal model by Cates et al.[25,26] In a case of $\tau_e \ll \tau_b \ll \tau_{rep}$, the shear stress decay obeys eq 7 in which the relaxation time is given by[26,38]

$$\tau = \tau_{rep}^{1/4} \, \tau_b^{3/4} \, (l_e/\bar{L})^{-1/2} \qquad (18)$$

Experimental evidence has made it apparent that the Rouse modes can easily be recognized.[26,28,29,38] In a Cole–Cole representation of the loss modulus G'' versus the storage modulus G', there is an increase of G'' after a minimum in a curve at the high frequencies. The value of G'' at the dip designated as G''_{min} is determined by a ratio between l_e and $\bar{L}$. The following useful expression has been obtained:[26,38]

$$\frac{G''_{min}}{G_0} = A\frac{l_e}{\bar{L}} \qquad (19)$$

where A is a constant equal to about unity. The ratio $l_e/\bar{L}$ may be treated as a number of the entanglements per chain.

Experimental Section

Materials and Methods. Soybean lecithin, Epikuron 200, was a gift of Lukas Meyer, AG (Hamburg, Germany). The content of the main phospholipid, as declared by the supplier, was 96.7%. The lecithin was used without further purification.

n-Decane was of the purist quality from Fluka. Doubly distilled water was prepared in the common manner.

The homogeneous jelly-like phases were made up by dissolution of weighed appropriate amounts of lecithin and water into *n*-decane at about 50 °C on stirring by a magnetic stirrer. This usually proceeded over 1-3 h. To remove suspended air bubbles, the samples were heated to 70 °C for a short time. Then they were allowed to stay at ambient temperature for 1-3 days to reach an equilibrium state.

The separated jelly-like phases were prepared by the addition of a water amount as great as necessary to induce the separation of a homogeneous solution into a nonviscous upper fluid and a lower gel.[18,39,40] The two-phase mixture was set aside at 25 °C for a week to bring to equilibrium. Within 2-4 days the turbid phases became transparent. Lecithin and water concentrated almost entirely in the lower layer. The gel was separated from the upper nonaqueous solution, using a separating funnel.

Oscillatory shear measurements were made with a Bohlin CS-10 stress-controlled rheometer using a double-gap system with concentric cylinder configuration and cone-and-plate geometry. The double-gap configuration consisted of a 50.0-mm-diameter cup, 40.0-mm-diameter inner cylinder, and 44.5-mm-diameter tubelike measuring cylinder with a wall of 0.75-mm thickness. The cone angle in the cone-and-plate geometry was

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(40) It should be mentioned that specimens of the naturally occurring lecithin always contain some quantity of tightly bound water.[41] Our examination of five various samples from Lukas Meyer has shown that this is not a constant quantity. Therefore, the critical amount of water n_{cr} inducing the phase separation can be changed from one sample to another. Moreover, this parameter is sensitive to the presence of trace quantities of other phospholipids. Some of them, for example, phosphatidylethanolamine or lysolecithin (see ref 42), can even retard the formation of the organogel.

Table 1. Values of the Exponents in the Scaling Laws

model/experiment	$\bar{L}$	G_0	η_0	τ_t	ξ	G''_{min}/G_0	refs
Theoretical Predictions							
reptation theory	0.5	2.25	5.25	3	−0.77		32, 33
linear micelles	0.5	2.25	3.5	1.25	−0.77	−1.75	22−26
branched micelles	−0.5	2.25	2.5	0.25	−0.77	−0.75	34−36
Experimental Data							
$\phi \geq 0.035$; $n_w = 2.5$; n-decane		2.72 ± 0.09	3.46 ± 0.20	1.02 ± 0.22	−1.02 ± 0.04		this work
$\phi \geq 0.02$; $n_w = 3.15$; n-decane		2.41 ± 0.14	2.24 ± 0.14	0.01 ± 0.08	−0.72 ± 0.07	−0.93 ± 0.07	this work
$\phi \geq 0.05$; $n_w = 3.0$; isooctane		2.0 ± 0.1	1.9 ± 0.1				12, 20
Lecithin in isooctane or cyclohexane					−0.65 ± 0.05		12, 48
					−0.7 ± 0.1[a]		
lecithin in isooctane or cyclohexane	1.23 ± 0.08[b]						48, 50, 70

[a] The former value refers to the hydrodynamic correlation length and the latter to the static correlation length found from light-scattering measurements and small-angle neutron scattering, respectively. [b] A scaling dependence for the average molecular weight; $M_w \sim \bar{L}$ according to ref 5.
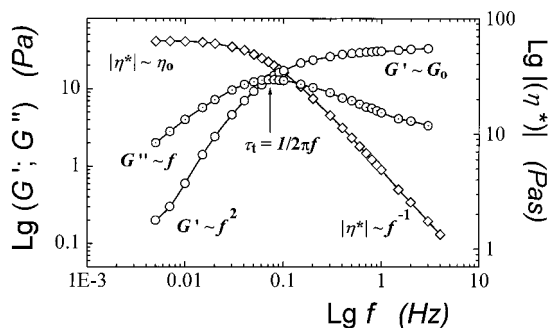

Figure 1. The complex viscosity $|\eta^*|$, storage modulus G', and loss modulus G'' vs oscillation frequency. The main features of frequency dependencies and the rheological parameters extracted from them are noted on the graph. An organogel consists of 35 mg/mL of lecithin and 3.0 water molecules per lecithin molecule in n-decane. The temperature is 25.0 ± 0.1 °C.
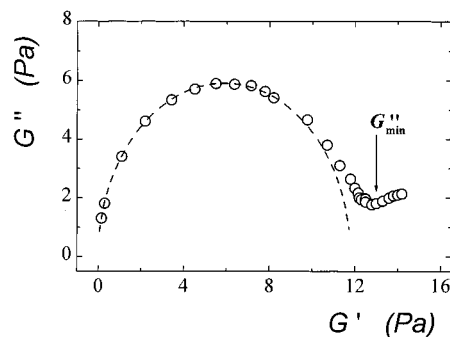

Figure 2. Cole−Cole plot for an organogel with 35 mg/mL of lecithin and $n_w = 2.85$. The dashed semicircle is the best fit in accordance with eq 20. The arrow shows the dip corresponding to the minimum value of the loss modulus in the high-frequency region.

4°, and its diameter was 40 mm. Solvent evaporation was prevented by a special chamber with a sponge soaked with alkane. The oscillatory frequency could be varied from 0.001 to 10 Hz. The temperature was controlled with an accuracy of ±0.1 °C.

Data Analysis. We begin the analysis with examination of experimentally obtained frequency dependencies of the complex viscosity $|\eta^*|$, the storage modulus G', and the loss modulus G''. Figure 1 shows a representative example. A value of $|\eta^*|$ in the low-frequency region, in which this parameter does not depend on the frequency, was taken equal to the zero shear viscosity η_0. To estimate the plateau modulus G_0, we used a Cole−Cole representation of G'' versus G'. The G_0 values were found by a fitting procedure using the equation

$$(G' - G_0/2)^2 + G''^2 = G_0^2/4 \tag{20}$$

and G_0 as an adjustable parameter. A fitting result is represented in Figure 2 as a solid semicircle curve corresponding to an ideal Maxwell behavior for viscoelastic fluids with a single relaxation time. The terminal relaxation time τ_t was calculated by eq 6, combining data for G_0 and η_0. Its value can also be estimated from the reciprocal frequency at which G' and G'' intercept in Figure 1.[6]

The data on G_0 enabled us to estimate the correlation length ξ and then the entanglement length l_e by means of the following expressions from the reptation theory:[32,33]

$$\xi = \left(\frac{k_B T}{G_0}\right)^{1/3} \tag{21}$$

and

$$l_e \approx \xi^{5/3}/l_p^{2/3} \tag{22}$$

where k_B is the Boltzmann's constant and T the absolute temperature. The correlation length scales with concentration

according to

$$\xi \sim \phi^{-3/4} \tag{23}$$

In the calculations, it was implied that the persistence length l_p of the polymer-like lecithin micelles is equal to 11 nm. This value has been determined by Schurtenberger et al.[13] by the SANS technique. Average micellar length $\bar{L}$ values were then evaluated by eq 19, but to do so we obtained first an estimate of G''_{min} from experimental Cole−Cole graphs as seen in Figure 2.

It should be pointed out that the l_e and $\bar{L}$ values estimated by the above-considered data analysis are of limited accuracy. It is caused by approximations and uncertainties in the used values of l_p and G''_{min}. Sometimes we could not obtain the reasonable precision because the ratio between G''_{min} and G_0 was not consistently less than 0.1 in accordance with the assumption of $\tau_e \ll \tau_b$ used by Granek and Cates.[26]

Experimental Results and Discussion

Frequency sweep measurements of the storage modulus G', loss modulus G'', and complex viscosity $|\eta^*|$ is shown for a typical dynamic viscoelastic behavior of a lecithin jelly-like phase in Figure 1. In the low-frequency region (the terminal zone), G' and G'' scale with frequency with exponents of 2 and 1, respectively, whereas $|\eta^*|$ is a constant and can be assigned to a zero shear viscosity η_0. At high frequencies, G' is slowly increasing; G'' first decays and then sometimes reaches a minimum; $|\eta^*|$ decreases linearly. In the intermediate region, the G' and G'' lines crossover at a frequency which is inversely related to the terminal relaxation time τ_t. The above-mentioned features are typical of transient network systems consisting of polymer-like micelles, the stress relaxation of which in the most frequency range is characterized by a single-
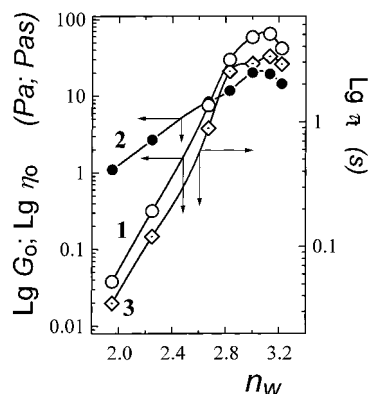
Figure 3. The zero shear viscosity (1), plateau modulus (2), and terminal relaxation time (3) vs the molar ratio of water to lecithin in organogels containing 35 mg/mL of lecithin.

Figure 4. Normalized Cole−Cole plots for organogels made up of 35 mg/mL of lecithin at n_w = 1.95 (1), 2.25 (2), 2.65 (3), 2.85 (4), and 3.15 (5). The solid semicircle is the best fit in accordance with eq 20.

exponential decay. This is also supported by a semicircle shape of Cole−Cole plots (Figure 2).

Our concern now is with the following main problems: (i) micellar growth induced by water addition, (ii) concentration dependencies of the rheological and network parameters, (iii) stress relaxation, and (iv) properties and nature of a compact jelly-like phase separated after the addition of critical water amounts. It should be mentioned that we deal with data obtained in the semidilute solutions, that is, at lecithin concentrations in excess of the threshold, one at which the entanglement of cylindrical micellar aggregates sets in.

(i) Water Effects on the Polymer-Like Micelle Formation by Lecithin. The zero shear viscosity and plateau modulus estimated for lecithin organogels containing 35 mg/mL of lecithin and varying water amounts are presented in Figure 3. The largest changes occur for the viscosity. With varying molar ratios of water to lecithin from 1.9 to 3.2, the zero shear viscosity increases more than 1000 times. The increase of the plateau modulus is as large as 20. The results are in good agreement with investigations described in the literature.[10,12,20,31,39]

The viscoelastic behavior is observed in decane solutions when about 1.5 water molecules, designated as n_w, are attached to the lecithin molecule. The homogeneous jelly-like phase can occur up to n_w equal to 3.2−3.4. This critical value n_w will be denoted n_{cr}.[40] If $n_w > n_{cr}$, there is a phase separation into a compact jelly-like phase and nonviscous solution. As followed from a comparison of the concentration regions of the organogel existence, the phase behavior of the examined *n*-decane organogels agrees very closely with that of lecithin solutions in isooctane (see, for example, both articles of Schurtenberger et al.[14,20]). This fact enables both of these jelly-like phases to be correlated to each other below.

The parameter n_{cr} is almost independent of the lecithin concentration if this is more than 15 mg/mL. At smaller concentrations, a decrease in n_{cr} was noted.[39] The zero shear viscosity and plateau modulus peak not at n_{cr}, as might be expected, but before reaching the critical water amount (Figure 3). In both the cases one can see a maximum in the curves. Subsequent slight decreases in η_0 and G_0 is followed by a phase separation of organogels and an abrupt fall in the rheological parameters of heterogeneous mixtures.[10,12,20,31,39,43]
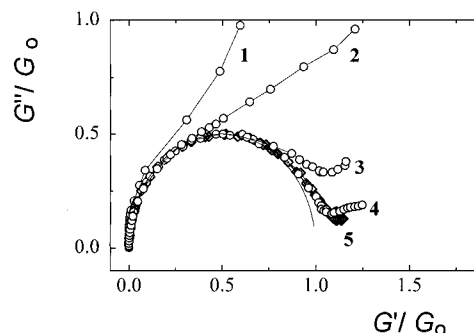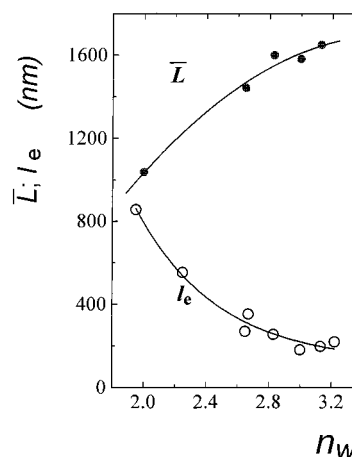

Figure 5. The average micellar length $\bar{L}$ and entanglement length l_e vs the molar ratio of water to lecithin in organogels containing 35 mg/mL of lecithin.

The increase of the water content leads also to increased terminal relaxation times. As apparent from Figure 3, the rise of τ_t may be as great as 100-fold. The curve passes a maximum, as happens with η_0 and G_0. If we now turn our attention to the Cole−Cole representation of the loss modulus against the storage modulus presented in Figure 4, it can be seen that the successive water addition into an organogel gives better and better fit of the experimental data to a semicircle curve, obeying eq 20 on the examined time scale. According to a computer simulation performed by Turner and Cates,[25] this finding gives an indication of a decrease in the ratio τ_b/τ_{rep}. In other words, a value of the reptation relaxation time rises with relation to the value of the breaking relaxation time. This would be expected to cause the increase of the terminal relaxation time (Figure 3).

The reasons for the above-mentioned changes in the rheological parameters and dynamics are being apparent if micellar and entanglement lengths are estimated. This can be done as considered in the data analysis section. It should be mentioned that the presence of a dip in the Cole−Cole plots (Figure 4) pointing to the Rouse regime at high frequencies permits one to use eq 19 for the estimations.

Figure 5 demonstrates a dependence of the average micellar length $\bar{L}$ and entanglement length l_e on the molar ratio of water to lecithin in the examined organogels. The divergence is caused by an opposite change of $\bar{L}$ and l_e with an increasing water amount. Attention is drawn to the fact that the former is a weak function of water content. Its value is varied from about 1000 to 1650 nm. By contrast, the entanglement length is decreased by a factor

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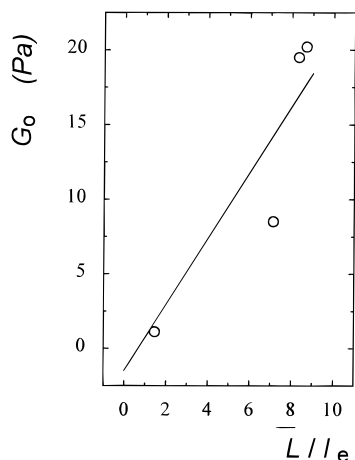
Figure 6. The plateau modulus vs the ratio of the average micellar length $\bar{L}$ to entanglement length l_e for organogels with 35 mg/mL of lecithin and n_w varied from 2.25 to 3.15.

of about 4, from 850 to 200 nm. For comparison, Schurtenberger et al.[11] found by making use of a small-angle neutron scattering of shear-aligned organogels of lecithin in isooctane that for a diluted solution $\bar{L}$ is changed from 200 nm at $n_w = 2.0$ to 450 nm at $n_w = 3.0$, respectively. These values are significantly smaller than those estimated in the present article. Our results agree better with estimations made by Schurtenberger et al. in refs 15,16. It was found by means of static and dynamic light-scattering measurements that the weight-average contour length of polymer-like lecithin micelles in cyclohexane should be in the range 400−3200 nm.

The parameters $\bar{L}$ and l_e determine respective rheological properties of jelly-like phases. In the general case (see, e.g. refs 33,37) the zero shear viscosity is dependent on the average micellar length, whereas the plateau modulus depends on the density of entangled points ν in a three-dimensional network according to

$$G_0 = \nu ART \tag{24}$$

where A is the numerical factor close to unity. To a first approximation, the value ν should be proportional to the ratio of $\bar{L}$ to l_e.

A comparison between concentration dependencies of rheological and structural parameters presented in Figures 3 and 5, respectively, shows that the plateau modulus change should be in line with the variation of the density of micellar contacts in the three-dimensional network while a correlation between η_0 and $\bar{L}$ is missing. The first suggestion is borne out by a direct relationship between G_0 and the number of entanglements per micellar chain that is made equal to $\bar{L}/l_e$ as suggested by Granek and Cates.[26] This is shown in Figure 6. In the case of the zero shear viscosity, the water addition increases η_0 more than 1000 times while the average micellar length is changed by a factor of 1.6. The lack of correlation brings up the question about reasons of the established inconsistency. A possible explanation might reside in the mechanism of the micellar growth. As shown in the next section, at large contents the water can induce branching of micelles rather than increasing their length.

(ii) Scaling Behavior with Lecithin Concentration. Double logarithmic dependencies of the zero shear viscosity and plateau modulus on the lecithin volume fraction in *n*-decane at two water concentrations are presented in Figure 7A,B, respectively. It is evident at a glance that the scaling behavior of η_0 is determined by
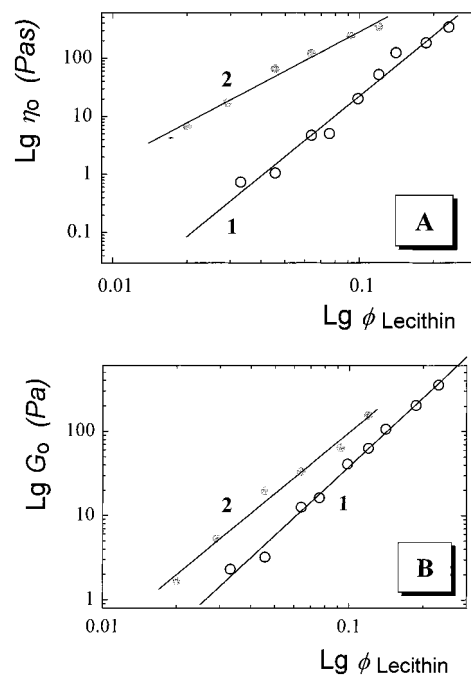

Figure 7. The zero shear viscosity (A) and plateau modulus (B) vs the volume fraction of lecithin in organogels at $n_w = 2.5$ (1) and $n_w = 3.15$ (2). Straight lines are the best least-squares fits to the experimental data. Slope values are presented in Table 1.

the molar ratio between water and the phospholipid. With increasing n_w a slope of the best linear fits to the data is varied from 3.46 ± 0.20 to 2.24 ± 0.14. For the plateau modulus a slope change is less pronounced; this is in the range 2.72 ± 0.11 to 2.41 ± 0.14.

Concentration dependencies for η_0 and G_0 were previously considered by Schurtenberger et al.[12,20] They studied organogels of the same soybean lecithin from Lukas Meyer dissolved in isooctane at one water content ($n_w = 3.0$). This value of n_w is close to n_{cr} and corresponds well with $n_w = 3.15$ in our work. Values of the scaling power law exponents presented in refs 12,20 are 1.9 ± 0.1 and 2.0 ± 0.1 for η_0 and G_0, respectively. A comparison with our results (see Table 1) shows a wholly satisfactory agreement between theirs and our estimates obtained at $n_w = 3.15$.

Schurtenberger et al.[12,20] paid attention to a notable deviation of the experimentally estimated exponent value for η_0 from the theoretical prediction of Cates' model. An extensions of the model did not enable them to improve agreement. Preliminary examination of our data has suggested *the type of micelles and their dynamics to be governed by the molar ratio between water and lecithin.* A change in the micellar growth mechanism was not considered in cited works.[12,20] To gain better insight into this problem, lets consider various models and examine additional experimental data in details. The exponent values in the scaling dependencies can be seen in Table 1. There are both theoretical predictions and experimental estimates.

Of the two above-considered parameters the experimental exponent for G_0 is the least changeable with a molar ratio of water to lecithin (Figure 7B). This is in general agreement with the same value of the exponents in various models. Moreover, the experimentally obtained exponents are comparable to the theoretical predictions.

The scaling exponent for the zero shear viscosity is decreased in a stepwise manner with an increasing molar ratio of water to lecithin (Figure 7A). The variation of the curve slopes should be indicative, as shown by Hoffmann,[7]
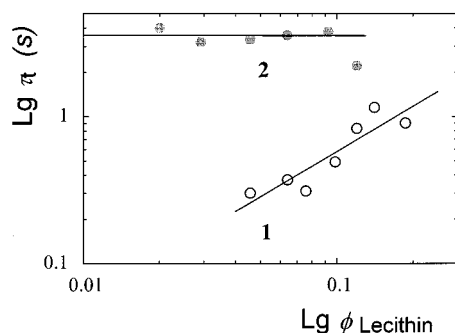
Figure 8. The terminal relaxation time vs the volume fraction of lecithin in organogels with $n_w = 2.5$ (1) and $n_w = 3.15$ (2). Straight lines are the best least-squares fits to the experimental data. Slope values are presented in Table 1.

of a change in the kinetic mechanism. If one correlates our results with the theoretical predictions of various models (Table 1), it is seen that at $n_w = 2.5$ the exponent of the power law of concentration is rather close to the theoretical value of 3.5 predicted by Cates' model for the linear extended micelles, while at $n_w = 3.15$ the power law exponent for η_0 is in good agreement with the value of 2.5 followed from the consideration of branched (connected) micelles (see Theoretical Background section). This leads us to an important suggestion that *the successive addition of water not only induces the one-dimensional growth of reverse lecithin micelles,* as believed before, *but also brings about their branching.*

The possibility of existence of branched micelles has attracted considerable interest.[7,8,34,35,44] Until the present time evidence has been found only for aqueous surfactant solutions.[28,35,36,45,46] At certain conditions branched elongated micelles of lecithin mixed with cetyltrimethylammonium chloride have been observed in water.[47] So far as we know, the branching of polymer-like reverse micelles in nonaqueous systems has not been described in the literature. It is interesting to mention that Drye and Cates suggested the possibility of this phenomenon to lecithin organogels.[44] They proceeded from the decrease in viscosity with adding water that is observed experimentally as the water critical content n_{cr} is approached (see curve 1 in Figure 3). To explain this effect without considering the branched micelles, there is a necessity to make an assumption about an improbable decrease in the micellar lifetime.[44]

The validity of the suggestion about the change in the micellar growth mechanism made from the above examination of concentration dependencies for zero shear viscosity calls for further support. Some additional confirmation can be found in associated changes of other scaling dependencies. Thus, Figure 8 presents a double logarithmic plot of the terminal relaxation time versus the lecithin volume fraction. With increasing water content, a slope of the best linear fits to the data is decreased from 1.02 ± 0.22 to 0.01 ± 0.08. The former agrees rather well with the expected value from the model of Cates considering the linear (unbranched) polymer-like micelles; the latter is consistent, but not as well as the former, with the power law exponent from the branched micelle model (Table 1). This result adds support for our suggestion about the micellar growth mechanism change.
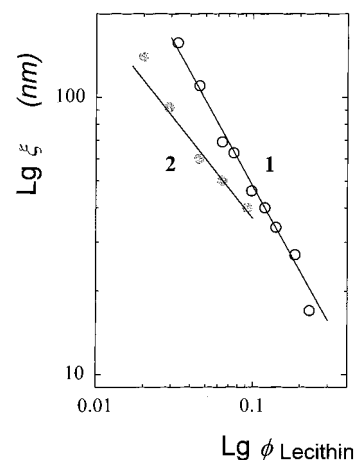
(44) Drye, T. J.; Cates, M. E. *J. Chem. Phys.* **1992**, *96*, 1367−1375.
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(47) (Silvander, M.; Karlsson, G.; Edwards, K. *J Colloid Interface Sci.* **1996**, *179*, 104−113.

Figure 9. The correlation length vs the volume fraction of lecithin in organogels with $n_w = 2.5$ (1) and $n_w = 3.15$ (2). Straight lines are the best least-squares fits to the experimental data. Slope values are presented in Table 1.

An important point is that the reptation time τ_{rep} for branched micelles is concentration-independent (Table 1). The independence of τ_{rep} on ϕ means that the reptation processes are of minor importance for the stress relaxation. The micelle dynamics is mainly dictated by the dissociation/recombination of micellar aggregates. The similar situation has been experimentally established in aqueous solutions of alkyldimethylamineoxides.[7] The kinetic mechanism for processes is not evident. This requires a sophisticated understanding.

A rather good correspondence between the observed and predicted power law exponents is seen for the correlation length (Figure 9). The slope of straight lines presented in the double logarithmic coordinates is -1.02 ± 0.04 at $n_w = 2.5$ and -0.72 ± 0.04 at $n_w = 3.15$, respectively. The exponent of the scaling law for ξ in the theory for semidilute polymer solutions is equal to -0.77.[32,37] Our result is also in good accord with measurements of Schurtenberger et al.,[13−16,48] studying polymer-like lecithin micelles in isooctane and cyclohexane by means of a static and dynamic light scattering and small-angle neutron scattering (Table 1).

(iii) Stress Relaxation. The features of the dynamical behavior of surfactant jelly-like phases are most noticeable from examination of the Cole−Cole plots representing the variation of the storage modulus versus the loss modulus measured at various frequencies.[5,25,26,38,49] For lecithin organogels corresponding plots are presented in Figures 2, 4, and 10. In the majority of cases the experimental points fit a semicircle in the low-frequency region and deviate from the semicircle at high frequencies, passing through a clear dip. These features point to several different kinetic regimes in the stress relaxation.[5,25,26,38,49]

In the region in which data follow a semicircle dependence the shear stress decay obeys a single relaxation function (eq 7). The dynamic behavior is characterized by a fast dissociation and slow diffusion of micelles (i.e., $\tau_b \ll \tau_{rep}$). With increasing oscillation frequency a situation is attained at which a frequency is approximately equal to the inverse of τ_b.[25] This reveals itself as a deviation from the semicircle that in its turn is indicative of the extension to a new kinetic regime.[5,25,26,38,49] The subsequent dip in curves (Figures 2, 4, and 10) means that the new regime is Rouse motion, corresponding to the case $\tau_e \ll \tau_b \ll \tau_{rep}$.

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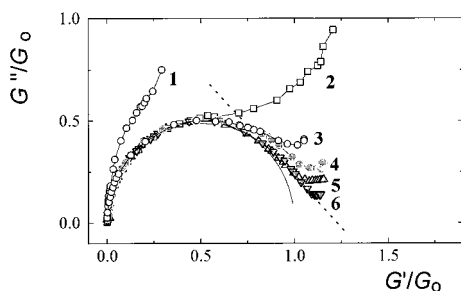
Figure 10. Normalized Cole−Cole plots for organogels at n_w = 2.5. Lecithin concentrations are 25 (1), 35 (2), 50 (3), 80 (4), 100 (5), and 220 (6) mg/mL. The solid semicircle is the best fit in accordance with eq 20. The straight dotted line shows a linear asymptote of a slope of −1.
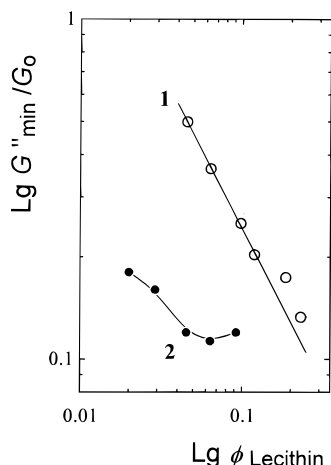

Figure 11. Ratio G''_{min} vs the volume fraction of lecithin in organogels at n_w = 2.5 (1) and n_w = 3.15 (2). Straight lines are the best fits to the experimental data. Slope value is presented in Table 1.
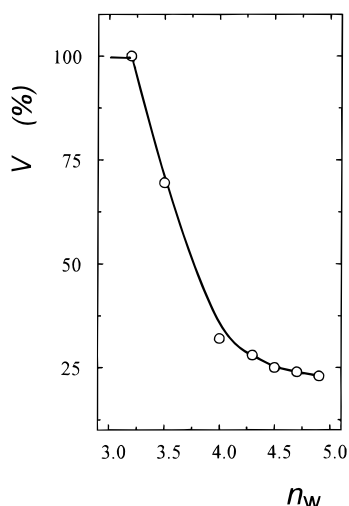

Figure 12. Equilibrium volume (in vol %) of a jelly-like phase separated after the addition of water into a n-decane solution vs the molar ratio of water to lecithin in the ternary mixture. The concentration of lecithin is 35 mg/mL. The temperature is 25.0 ± 0.1 °C.

It should be mentioned that with increasing lecithin concentration experimental points fall in increasing number on a straight line (shown as a dotted one, Figure 10) with a slope of −1. This is the high-frequency linear asymptote indicative, as predicted by Cates et al.,[25,26] of the pure reptation process. The linear scaling of G'' with

varying G' is rarely observed in practice because it is essential that a ratio $l_e/\bar{L}$ should be significantly less than unity.[25,26]

A minimum on the Cole−Cole plot at the right-hand outside of the semicircles is attained if an oscillation frequency is approximately equal to τ_e.[26,38] As this takes place, a value of the loss modulus designated as G''_{min} satisfies eq 19. For linear micelles G''_{min}/G_0 scales like $\phi^{-7/4}$ if one takes into account eqs 5, 22, 23, and the previous assumption that l_p does not depend on the concentration. The power law exponent for branched micelles is $-3/4$ because of the scaling dependence for the average micellar length given by eq 13.

This predicted scaling behavior for lecithin organogels with low (n_w = 2.5) and high (n_w = 3.15) water content is verified in Figure 11. In both the examined systems the ratio G''_{min}/G_0 decreases as the lecithin volume fraction is increased. However, this result comes only to a qualitative agreement with the prediction. For the expected linear micelles (n_w = 2.5) a least-squares fit to the experimental data (straight line 1, Figure 11) has a slope of −0.93 ± 0.07, while for the large water-to-lecithin molar ratio (n_w = 3.15) there is a smooth minimum on the curve. Our experimental observations correlate well with those of Candau et al.[28,29] who examined features of the Rouse regime in aqueous viscoelastic micellar systems. The smooth minimum on curves was related to an increase in a micellar branching degree. Their suggestion is in line with our above suggestion about the branching of the polymer-like lecithin micelles at large water contents. A disagreement between the experimental exponent of −0.93 ± 0.07 and the predicted one of −1.75 for the linear micelles might stem, in our opinion, from the used common assumption that l_p is independent of the surfactant concentration. This point is somewhat supported by recent observations of Jerke et al.[50] who performed systematic studying on lecithin organogels by a small-angle neutron-scattering technique. It was shown that the persistence length of polymer-like micelles in very diluted solutions (up to 4 mg/mL) is increased with lecithin concentration, although the authors mentioned that this effect is apparent, caused by structural factors on a local scale, not a change in the chain flexibility.

(iv) Separated Jelly-Like Phase. If the water amount is in excess of the n_{cr}, so will be the separation of a homogeneous organogel into a compact jelly-like phase and a nonviscous solution. This fact is known from the pioneering work of Scartazzini and Luisi.[18] Nonetheless, the nature, properties, and mechanism for the formation of a separated organogel, to our knowledge, still leave open questions. We have attempted to gain insight into this problem.

The volume of a transparent jelly-like phase that separates at the bottom of a flask at equilibrium after the addition of excess water amounts is shown in Figure 12 as a function of the molar ratio n_w of water to lecithin. A concentration of the phospholipid was 35 mg/mL. The subsequent water addition leads to a transformation of the jelly-like phase into a solid precipitate. Individual solid particles are found in the compact organogel even at n_w = 4.9. Thus, the formation of this new transparent and optically isotropic phase is observed in the rather narrow region of molar ratios of water to lecithin varied from 3.2−3.4 to 4.9−5.0.

The separated organogel holds almost the full amount of the phospholipid dissolved in alkane. As a result, its

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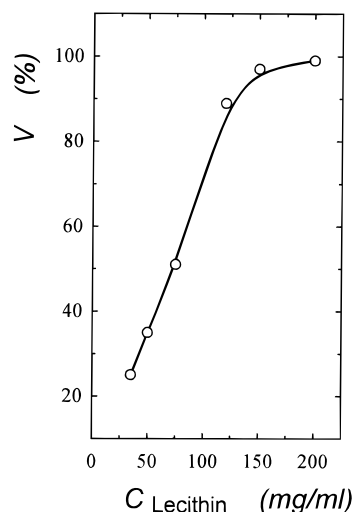
Figure 13. Equilibrium volume (in vol %) of a separated jelly-like phase vs the lecithin concentration in the ternary mixture *n*-decane−water−lecithin. Molar ratio of water to lecithin is constant (n_w = 4.5). The temperature is 25.0 ± 0.1 °C.
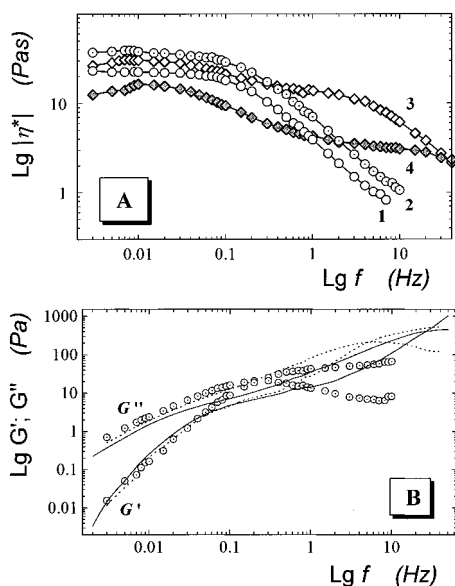

Figure 14. The complex viscosity $|\eta^*|$ (A), storage modulus G' (B), and loss modulus G'' (B) vs oscillation frequency. (A) Molar ratio of water to lecithin is 3.2 (1), 3.5 (2), 4.0 (3), and 4.9 (4). (B) Molar ratio of water to lecithin is 3.5 (data are shown by points), 4.0 (shown by dotted lines), and 4.7 (shown by unbroken lines). The concentration of lecithin is 35 mg/mL. The temperature is 25.0 ± 0.1 °C.

volume depends on the lecithin concentration. This is illustrated in Figure 13. It is worth noting that at a certain phospholipid concentration there is no phase separation with adding an excess water amount. The fact that the organogel turns into another state is made evident from studying the rheological properties.

Figure 14 demonstrates frequency sweep measurements of complex viscosity (A) and dynamic moduli (B). With increasing water content that makes a separated jelly-like phase more and more compact (Figure 14), one can find a notable change in the rheological behavior. First of all, the compactness is accompanied by a slight decrease in the complex viscosity in the low-frequency range that is attributed to the zero shear viscosity. Besides, there are other dispersions at higher frequencies followed by a lower plateau in an intermediate frequency range that expands with the water amount increase.
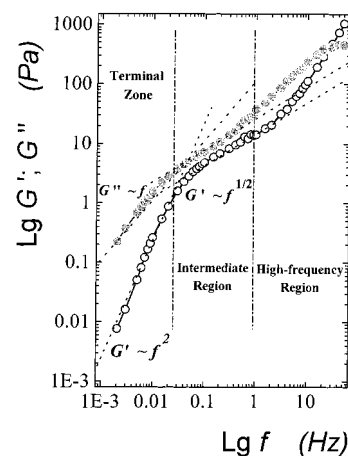

Figure 15. The storage G' and loss modulus G'' vs oscillation frequency for a mixture with 35 mg/mL of lecithin. The vertical broken lines show approximate boundaries between the various rheological regimes. Molar ratio of water to lecithin is 4.7.
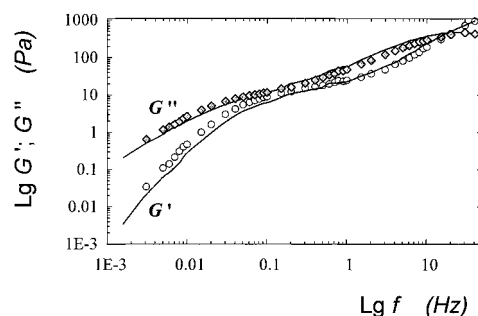

Figure 16. The storage G' and loss modulus G'' vs oscillation frequency for ternary mixtures containing 50 and 200 mg/mL of lecithin; the data are shown by points and solid lines, respectively. Molar ratio of water to lecithin is 4.5. The temperature is 25.0 ± 0.1 °C.

The dynamic loss and storage moduli exhibit also a complex behavior with frequency (Figure 14B). As long as the separated phase does not transfer into a compact organogel of small volumes (data shown by points), their behavior is typical of viscoelastic micellar systems. At molar ratios n_w > 3.5 relating to the increased compactness of the jelly-like phase (Figure 12), the point of the intersection of the G' and G'' lines is shifted into the high-frequency region (data shown by dotted and unbroken lines, Figure 14B). In the intermediate region between the terminal zone and the intersection point, a change in the dynamic moduli scaling is found. These features are better visible in Figure 15 in which boundaries between various regions are marked off by the vertical solid lines. As seen in the terminal zone the loss and storage moduli scale as $G' \sim f^2$ and $G'' \sim f$. In the intermediate region they both scale with frequency with an exponent of $^1/_2$. It is worthy to mention that with increasing molar ratio n_w the dynamic moduli approach each other in magnitude. This is achieved on account of an appreciable shift of the point of their intersection into the high-frequency region (Figure 14B).

The above-mentioned changes in the rheological behavior are governed by the molar ratio of water to lecithin in the separated organogel. A variation of the lecithin concentration at a constant n_w, as evident from Figure 16, does not change the general trend of the curves. Moreover, both the results are identical to each other. It is also notable that the solid lines in Figure 16 present data on an organogel prepared at such the concentration of lecithin at which the phase separation is not observed after the
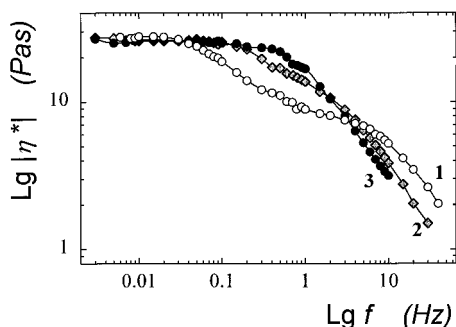
Figure 17. The complex viscosity $|\eta^*|$ vs the oscillation frequency for a ternary mixture with 120 mg/mL of lecithin and at $n_w = 4.5$. The temperature is 25 (1), 35 (2), and 40 °C (3).
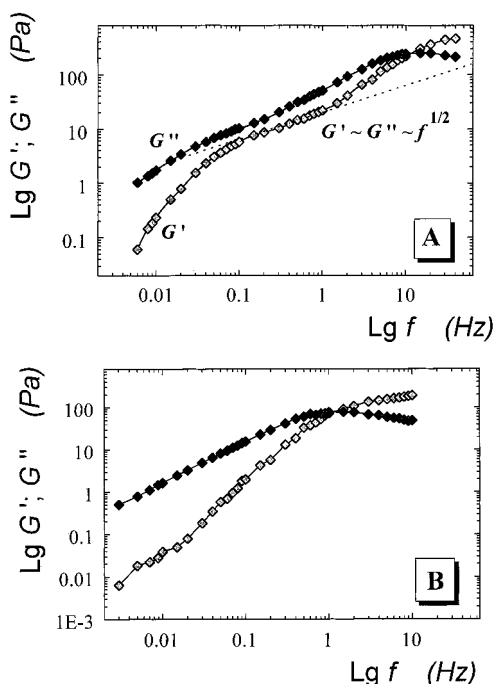

Figure 18. The dynamic moduli vs the oscillation frequency for a ternary mixture with 120 mg/mL of lecithin and at $n_w = 4.5$. Measurements were carried out at 25 (A) and 40 °C (B).

addition of water, although the polar additive amount is in excess of the n_{cr}.

A strong effect on the rheological behavior of the separated jelly-like phases, along with the molar ratio n_w, is produced by a temperature change. This is illustrated with Figures 17 and 18. By increasing temperature, one can observe a contraction of the additional plateau for the complex viscosity in the intermediate-frequency region and its disappearance at about 40 °C (Figure 17). The similar situation holds for the dynamic moduli; the regime beyond the terminal zone with $G' \sim G'' \sim f^{1/2}$ (Figure 18A) disappears, and there is a transfer to the frequency-dependent rheological properties typical of viscoelastic micellar solutions with entangled polymer-like micelles (Figure 18B).

The aforementioned characteristic features of rheological behavior with the separated lecithin organogel have not been described in the literature before. It is our opinion that nothing of this sort has been observed in aqueous viscoelastic micellar systems. Similar dynamic moduli scaling in the intermediate region with a slope of $^1/_2$ is usually exhibited by polymers of low molecular weight or in dilute solutions where entanglement effects are negligible. The rheological behavior is described in terms of

the Rouse theory.[37] A flexible randomly coiled polymeric molecule is represented as a chain of N Gaussian subchains with $N+1$ subchain junctions or ends called "beads". The energy is stored and released through subchains acting as a spring due to its length fluctuation in the stress relaxation. Hence, the model is known by the name bead-spring model. The appropriate equation is[37]

$$G' = G'' = (\pi/2\sqrt{2})\,(\omega\tau)^{1/2} \qquad (25)$$

where ω is the frequency in rad/s, and τ the terminal relaxation time.

It should be mentioned that in the event of the validity of the Rouse theory the loss and storage moduli should be equal to each other. From Figures 14B, 15, 16, and 18A it is seen that there is a gap between two lines in the intermediate region. This can be caused by hydrodynamic interactions through the surrounding solution between beads during their motions. In the limiting case considered by Zimm,[37] the G' and G'' moduli are really not equal and differ by a factor of $\sqrt{3}$. Moreover, in the Zimm model the dynamic moduli is proportional to $\omega^{2/3}$ according to

$$G' = 1.05(\omega\tau)^{2/3} \qquad (26)$$

$$G'' = 1.82(\omega\tau)^{2/3} \qquad (27)$$

Examination of our experimental results has shown that this could take place in separated organogels with molar ratios n_w of water to lecithin between 3.5 and 4.3. With increasing n_w, the difference between G' and G'' is diminished (Figure 14B). The difference lower than $\sqrt{3}$ and the intermediate power law between $^1/_2$ and $^2/_3$ are valid for partial hydrodynamic interactions.[37]

It should be stressed that the Rouse theory is valid for systems in which chains are nonentangled. In regard the lecithin organogels, it might be imagined that beyond n_{cr} the three-dimensional network from entangled polymer-like micelles is collapsed, but it is highly improbable that the micellar sharp shortening occurs with the temperature decrease (Figure 18). We suggest that the appearance of the Rouse modes in the entangled regime could be caused by short branched chains, the contribution of which into stress relaxation becomes evident with increasing network compactness.

The nature of the phase separation in the lecithin organogels is still elusive. It is difficult to perceive strong attractive interactions to be in existence between micelles. A study of interactions of surfactant-coated mica surfaces across nonpolar liquids revealed attraction that is mainly due to the van der Waals forces.[51-53] They are rather weak and short-ranging, extending up to 2−3 nm. At the distance shorter than 1 nm there is a strong repulsion.

The separation might be attributed to the micellar branching. Branches could act as chain cross-linkers, inducing the effect similar to that in the polymer solutions.

We would like to draw attention to the fact that the shrinking of the lecithin organogel occurs at the critical concentration n_{cr} at which the mesh size of the transient three-dimensional network approximates, according to our estimates, to the persistence length. If ξ approaches l_p, the polymer-like micelles are assumed to be semiflexible.[54,55] Under these conditions, a chain portion between

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neighboring entanglement points is unflexible and so incapable of moving due to bending and folding. This should lead to an entropy loss owing to restricted motions in a three-dimensional network. In other words, micellar ordering is expected. For instance, the concentration of the phase transition of polymers to a liquid-crystalline state is strongly dependent on their persistence length and insensitive to the whole chain length.[56,57] This effect has been mentioned for aqueous viscoelastic solutions.[58]

The isotropic-to-liquid crystal-phase transition is well-known for aqueous micellar systems.[59-62] This usually occurs in rather concentrated solutions. Nematic or hexagonal phases can be obtained. Sometimes the isotropic-to-nematic transition is promoted by a shear flow if a system is in close vicinity to a liquid-crystalline state.[63-66] According to current concepts,[54,55,62] alignment of micelles is coupled with their growth. Phase transformation takes place in the case of sufficiently rigid or semiflexible aggregates.

The micellar ordering gives an insight into why the compactness of the jelly-like lecithin phase after the phase separation brings about the viscosity drop, even if small, rather than an increase (Figure 14A). It should be pointed out that an orientational alignment of micelles offers an alternative explanation for the intermediate regime with $G' \sim G'' \sim f^{1/2}$ scaling (Figure 14B, 15, 16, and 18A). The similar frequency dependencies of the dynamic moduli has been found with ordered block copolymers.[67-69] It is worth mentioning that for a disordered state above the phase transition the power law exponents of 2 and 1 for G' and G'', respectively, are valid as in the case of the homogeneous organogel. The order−disorder transition presents in the respective change of the frequency dependencies of the dynamic moduli in the terminal zone. By analogy, we may assume that ordering of the polymer-like lecithin micelles commences at the critical molar ratio n_{cr} of water to lecithin that might be thought of as a phase-transition concentration. Nevertheless, it is believed that there could be only partial or local ordering. A reason for this assumption is the absence of optical anisotropy in samples of the separated organogel, although even a small shear flow induces strong birefringent. In addition, the regime with $G' \sim G'' \sim f^{1/2}$ scaling does not extend into the whole terminal zone as happens with ordered copolymers (see, e.g., ref 69). The situation with the intermediate regime for frequency dependencies of the dynamic moduli in Figures 14B, 15, 16, and 18A closely parallels that in copolymers at the phase transition at which ordered and disordered microphases coexist concurrently. Perhaps a high degree of the orientational order of polymer-like lecithin micelles is prevented by their branching.

Conclusions

The presented results have unambiguously shown that the minor component, water, plays a crucial role in the lecithin organogels. This polar additive determines the transformation of spherical reverse micelles into polymer-like ones, phase behavior, and rheological properties of ternary mixtures including *n*-alkane as the disperse media.

At the initial stages of the water addition to a non-aqueous lecithin solution, there is a uniaxial growth of reversed micellar aggregates that leads to the formation of linear flexible cylindrical micelles. The scaling behavior of the rheological parameters obeys a model of Cates. This means that the lecithin jelly-like phases are made up of a terminal three-dimensional network of entangled aggregates. The dynamical behavior is determined by micellar diffusion by the reptation mechanism and their dissociation/recombination.

With a further increasing amount of water in the jelly-like phase, one can observe a change in the mechanism of the micellar growth. This is primarily evident from the scaling behavior of the rheological parameters. The experimental power laws satisfy those followed from a model of the connected (branched) micelles. This enables us to conclude that the linear growth is substituted by the micellar branching.

At a critical molar ratio of water to lecithin in the ternary mixture, the homogeneous lecithin organogel is separated into a compact jelly-like phase and nonviscous solution. We have first established that the compactness of the organogel is accompanied with an appearance of new scaling behavior in the intermediate region beyond the terminal zone. In this region, the dynamic loss and storage moduli scale with the square root of the frequency of the mechanical oscillations. This scaling has been observed only in solutions of polymers and has not been so far noted in systems with the polymer-like micelles. It seems that the local ordering of cylindrical particles seems to be more suitable for explaining the established rheological regime.

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