

Lecithin organogel

A micellar system with unique properties

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Abstract

Lecithin self-assembles in nonaqueous media into reversed giant cylindrical micelles when small amounts of water, glycerol or formamide are added. The micellar aggregates, much like the polymer molecules, overlap, interpenetrate, entangle, thus forming a temporal three-dimensional network that brings about viscoelastic properties. For this reason, the micellar system is in a jelly-like state. This review article considers key results on the phase behavior, molecular interactions, properties, structure and dynamics of the lecithin organogels as well as current models for the polymer-like micelles. Much attention is given to rheological behavior. The effects of a shear flow, electric field and added surfactants, that cause a significant change in the structure and properties of the micellar system, are also discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The first description of the lecithin organogels was given in an article published by Scartazzini and Luici in 1988 [1]. They found that an addition of trace amounts of water into nonaqueous solutions of naturally-occurring lecithin caused an abrupt rise in the viscosity (10^4 – 10^6 times, Fig. 1), producing a transition of the initial nonviscous solution into a jelly-like state. A list of the nonpolar media in which the phenomenon was observed includes more than 50 solvents [1,2]. This fact

allows one to consider the organogel formation by the water addition as a common phenomenon, being inherent in the nonaqueous solutions of lecithin.

In the same year an article [3] was independently published that was devoted to a jellification occurring in layers of a nonaqueous lecithin solution adjacent to the aqueous phase. These layers were separated to study their behavior under the action of an electric field, since it was established that the external field influenced strongly the interfacial processes associated with the organogel formation. As shown in further publications [4–7], the interfacial jellification is caused by a transfer of water from an aqueous phase into the nonpolar solution that inherently represents the same phenomenon as described by Scartazzini and Luici.

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It should be mentioned that the gel formation in natural oils separated from plant seeds (soy beans, sunflower or rape seeds, etc.) by the water addition was well-known long before the first publication on the lecithin organogels. This procedure forms the basis for the purification of oils from lipids. The addition of water induces a separation of a gum-like mass that is why the corresponding technological process is called *degumming* [8].

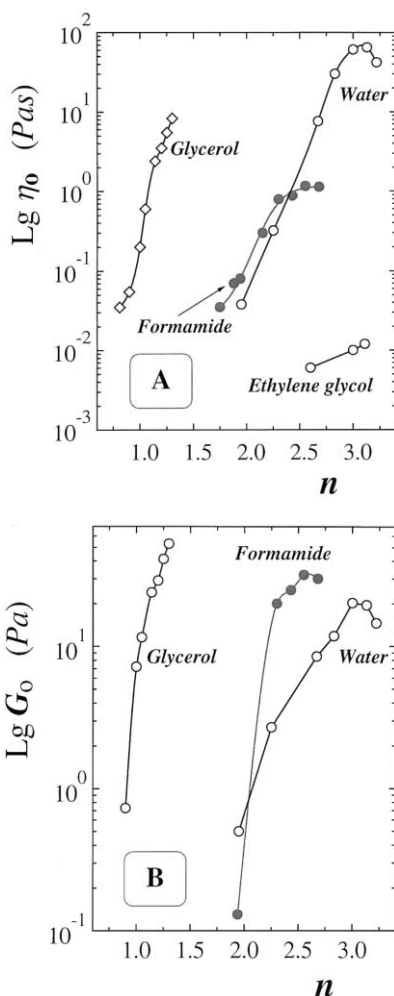


Fig. 1. The zero shear viscosity η_0 (A); and plateau modulus G_0 (B) versus the molar ratio of a polar additive (shown close to curves) to lecithin in organogels containing 35 mg ml^{-1} of lecithin. The temperature was $25.0 \pm 0.1^\circ\text{C}$ (adapted from Refs [15,45]).

By now the lecithin organogels have been studied extensively in many laboratories worldwide. Lots of facts about this unique nonaqueous system can be found in the literature. However, a review on the lecithin organogel has not been so far published. This is a purpose of this article to give a short consideration of the main results and ideas in this progressive area.

2. Substances

The transfer into the jelly-like state has been demonstrated only for nonaqueous solutions of naturally-occurring lecithins [1,2,9]. They are mainly separated from soy bean and egg yolk. Poorly purified substances did not possess gel-forming properties [1]. When synthetic lecithins containing residues of saturated fatty acids were examined, the organogel formation was not observed [10]. This has also failed when hydrogenated soybean lecithin has been taken (author's unpublished results). The gelation takes place only in a case of derivatives having a portion of unsaturated fatty acid residues that is why naturally-occurring lecithins are suitable.

Lecithin is a trivial name for 1,2-diacyl-*sn*-3-phosphocholine. Its structural formula is shown in Fig. 2. It belongs to a biologically essential class of substances termed *phosphoglycerides* or *phospholipids*. They form the lipid matrix of biological membranes and play a key role in the cellular metabolism [11]. Lecithin amounts among the phospholipids frequently account for 50–60% [12]. As a biocompatible surfactant, it is widely used in every day life, including human and animal food, medicine, cosmetics and manifold industrial applications [8].

A list of organic solvents, in which lecithin is capable of forming the organogel, comprises more than 50 items [1,2]. Among them are linear, branched and cyclic alkanes, ethers and esters, fatty acids and amines. The exceptions are represented by aromatic and chlorinated solvents. In their case the thickening effect is not observed with the addition of water because of its inclusion into micelles through a distinctive mechanism [4,13].

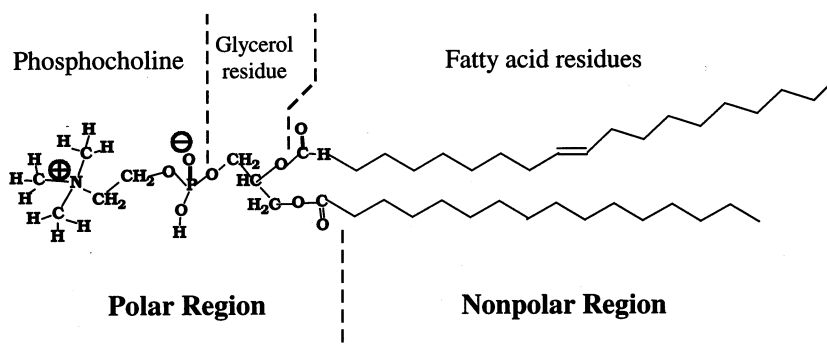


Fig. 2. Structural formula of lecithin. Its molecule includes residues of choline, phosphoric acid, glycerol and two fatty acids. They all are marked. Hydrocarbon chains of the fatty acid residues form the nonpolar part of a lecithin molecule. The rest residues constitute the polar region. The lecithin molecule is zwitterionic because of positively charged choline and negatively charged phosphate group. Naturally-occurring lecithins bear usually a saturated fatty acid residue at the *sn*-1 position and unsaturated ones at *sn*-2 position.

The third component crucial for the organogel formation is water. This polar solvent is added in trace or small amounts that depends on the organic media [1,2]. It was also established that water can be substituted for such polar organic substances as glycerol, ethylene glycol and formamide [9,14]. They also have a capability of transferring an initial nonviscous lecithin solution into a jelly-like state, given rise to the zero shear viscosity and plateau modulus [15] (Fig. 1).

3. Supramolecular structure

In the first publication Scartazzini and Luici suggested that the sharp increase in the viscosity of nonaqueous lecithin solutions after the water addition is caused by a micellar change [1]. In succeeding years their suggestion was confirmed by applying small angle scattering techniques [16–22]. Lecithin, when being dissolved alone in the nonpolar media, forms spherical reversed micelles [4,13]. Water added induces an uniaxial growth of the micelles. As a result, one will find cylindrical aggregates instead of the initial spherical ones. After reaching threshold length, the extended micelles begin overlapping, forming a temporal three-dimensional network. This supramolecular structure from entangled micellar aggregates bears resemblance with that of uncrossed polymers in semidilute or concentrated solutions. For this rea-

son, they are often called *polymer-like* micelles. The terms *living* or *equilibrium* polymers, *wormlike* or *threadlike* micelles can be also met in the literature. They account for various structural features of such the micellar aggregates.

4. A molecular model

A model has been suggested in [9,23]. Attention was drawn to the fact that the transition to polymer-like micelles is accompanied with a formation of hydrogen bonds between the phosphate group of a lecithin molecule (Fig. 2) and water. This was established with the help of IR and ^{31}P -NMR spectroscopies [9,14,24]. An ultimate insight into the mechanism of their interactions was provided by experiments with homologous series of polar organic solvents [9,14]. This is illustrated by the example of a formamide-dimethylformamide pair in Fig. 3 (left side). The former induces the organogel formation (Fig. 1), whereas the latter is incapable to do the same. Meanwhile, they both form hydrogen bonds with the phosphate group of lecithin, but the bondings are stronger for formamide then for dimethylformamide [24]. It was related to the known ability of a formamide molecule to form up to four hydrogen bonds and three-dimensional networks from them in the bulk [25]. In particular, it can be concurrently linked, as shown in Fig. 3, with two phosphate groups of

neighboring lecithin molecules. The other gel-inducing solvents—water, glycerol and ethylene glycol—possess in much the same ability. Dimethylformamide interacts only with a one phosphate group because its amino group is protected from interactions by two attached methyl groups (Fig. 3). By taking this difference into account, it was suggested [9,14,23] that the stabilization of extended cylindrical micelles is brought about by linking neighboring phospholipid molecules through a polar solvent molecule which acts as a linking bridge between them. Water, formamide, glycerol or ethylene glycol molecules, together with phosphate groups, create linear networks from hydrogen bonds (Fig. 3, right side).

It was shown in recent article [26] devoted to a thorough study on the successive filling of hydration shell of lecithin by means of the FT-IR spectroscopy that about three first water

molecules are attached to a phosphate group through hydrogen bonds. At this molar ratio H_2O molecules begin also coming to the carbonyl groups. They interact with each other, also forming hydrogen bonds. With increasing further the solvent amount, water molecules are found adjacent to a choline group. The sequence of the established stages is in agreement with that observed in the process of the hydration of lecithin being in the solid state [13].

5. Rheological properties

The lecithin organogel is an optically transparent isotropic phase. In its appearance it looks like the initial solution before the water has been added. The main difference between them is in the increased viscosity (Fig. 1). The viscoelasticity

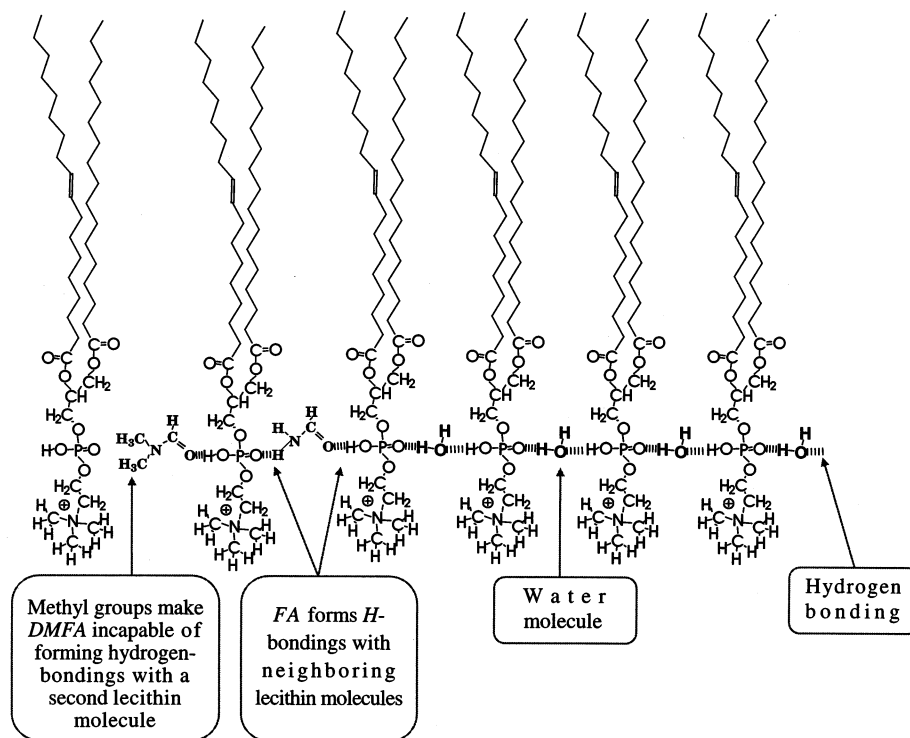


Fig. 3. A two-dimensional schematic representation of arrangement of molecules within the polymer-like micelles, illustrating the main points of the molecular model (details are in the text). The left side shows the key difference between dimethylformamide (DMFA) and formamide (FA) in their interactions with phosphate groups of neighboring lecithin molecules. The right side presents a hydrogen bonding network formed by water molecules and phosphate groups (adapted from Refs [9,14,23]).

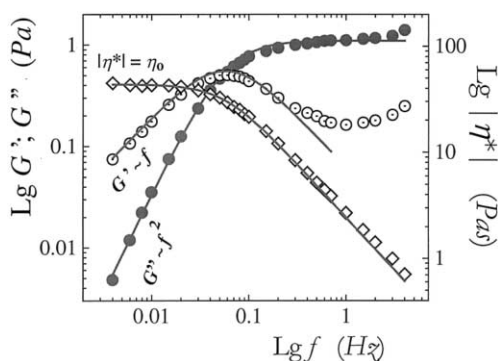


Fig. 4. The complex viscosity $|\eta^*|$, storage modulus G' and loss modulus G'' versus oscillation frequency f . The experimental results are shown by points. The solid curves are the best fit in accordance with Eqs. (1)–(3). An organogel consists of 35 mg ml^{-1} of lecithin and 2.7 water molecules per lecithin molecule in *n*-decane. The temperature was $25.0 \pm 0.1^\circ\text{C}$.

represents a distinctive macroscopic property inherent in the lecithin organogels. Therefore, studies on the rheological properties have received much attention.

Fig. 4 presents typical experimental dependencies (points) of the storage modulus (G'), loss modulus (G'') and complex viscosity ($|\eta^*|$) on the frequency (f) of mechanical oscillation applied to a lecithin organogel. In the low frequency region, called the *terminal zone*, the storage modulus increases as the square of the frequency and the loss modulus, directly with f , whereas the complex viscosity is almost constant [15,27,28]. This value of $|\eta^*|$ is set equal to the zero shear viscosity η_0 [29,30]. When curves pertaining to G' and G'' meet each other, the storage modulus is slowly increasing, while the loss modulus and the complex viscosity decay. These features are typical of rheological behavior obeying a Maxwell model [31]. In this model spring and dashpot are in series, forming an element that represents the main features of the viscoelastic behavior. The frequency dependencies of the complex viscosity and shear moduli are described by the following equations [31]:

$$G'(\omega) = G_0 \omega^2 \tau_1^2 / (1 + \omega^2 \tau_1^2) \quad (1)$$

$$G''(\omega) = G_0 \omega \tau_1 / (1 + \omega^2 \tau_1^2) \quad (2)$$

$$|\eta^*(\omega)| = (G'^2 + G''^2)^{1/2} / \omega \quad (3)$$

where G_0 is the plateau modulus, τ_1 the terminal relaxation time, ω the frequency in rad s^{-1} ; $\omega = 2\pi f$. The best fits in accordance with these equations are given as solid lines in Fig. 4. One can see a good agreement between experimental data and calculated curves. This means that the rheological behavior of the lecithin organogels is in line with the Maxwell model. Notable deviations are usually seen in the high frequency region. They are caused by manifestation of fast relaxation (Rouse) processes and extension to new kinetic regimes [32,33].

The Maxwell model holds for systems with certain supramolecular organization [29–31,34,35]. They should consist of a temporal three-dimensional network of entangled interpenetrating chains. The chains are uncrossed or slightly crossed. Their interactions are mainly caused by physical contacts. Each of the chains is localized within an imaginary tubelike space arising by virtue of topological restrictions for its movement from the neighboring chains. Its diffusion proceeds similar to a snakelike motion along its own contour. This mechanism, known as a *reptation* one, was developed by De Gennes for semidilute or concentrated solutions of uncrossed polymers and their melts [34–36]. A model for the micellar systems of polymer-like micelles has been suggested by Cates [37,38]. He proceeded from the reptation theory, taking into account a principal distinction between polymer molecules and micelles. This lies in dissociation/recombination of the latter that complicates additionally the dynamic behavior of the micellar system. In any case the viscoelastic properties of the lecithin organogels, if they obey the Maxwell model (Fig. 4), result from the three-dimensional network of entangled interpenetrating polymer-like micelles [29,30,39–43].

6. Phase behavior

A whole phase diagram for the lecithin-cyclohexane-water system has been recently published in Ref. [44]. This article is devoted to the phase behavior in a restricted region in which the organogel formation was noted. Furthermore, the

nonpolar media is presented with *n*-decane. In this case one may find some notable differences from the system based on cyclohexane.

The phase behavior in the ternary system, as observed with varying water and lecithin concentrations, is shown in Fig. 5. As seen, it is mainly determined by a water-to-lecithin molar ratio (n_w). A homogeneous organogel region is rather narrow. The left boundary, that represents the threshold concentration for the micellar overlapping, is shown approximately because of severe difficulties with its precise determination. The line is slightly tilted to the region of smaller molar ratios. The position of the right boundary, which refers to a separation of the homogeneous organogel into a precipitated jelly-like phase and a nonviscous solution, is more definite. This happens at $n_w = 3.2\text{--}3.5$ [9,14]. The phase separation is absent when the concentration of lecithin is as much as 200 mg ml^{-1} [45]. At its greater concentrations, the homogeneous organogel phase region extends up to $n_w = 5.2\text{--}5.5$. This molar ratio represents the commencement of precipitation of solid particles. Similarly, one can observe the formation of solid particles in the separated organogel obtained at the lecithin concentrations smaller than 200 mg ml^{-1} [45]. At the bottom the organogel phase region is restricted by a lecithin concentration equal to about 7 mg ml^{-1} [9,14]. A diluted solution is composed, as shown for isooctane system [46], of rodlike micelles. Their length is not enough to overlap and form a three-dimensional network.

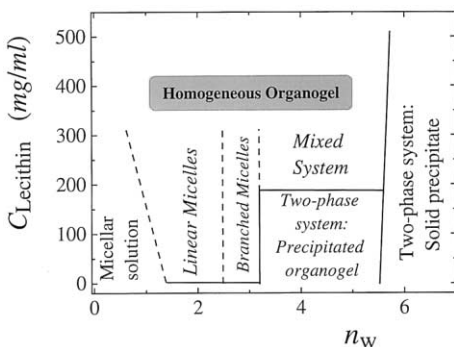


Fig. 5. A quasiternary phase diagram of lecithin-*n*-decane-water system. The area of a homogeneous organogel phase is only presented.

It is worth mentioning that the position of the boundaries and the width of the organogel phase region depends strongly on the dryness of a lecithin sample. The fact is that water is difficult to remove completely from lecithin [47]. Therefore, its well-dried samples always contain about one water molecule per lecithin molecule. The variation in the water content leads to a shift of the phase boundaries. The presented phase diagram in Fig. 5 is valid for soybean lecithin *Epikuron 200* manufactured by *Lukas Mayer* (Hamburg, Germany). It should be taken into account that lecithin is hygroscopic [4,13]. Water vapor is easily absorbed from the air that results in a change of water content and, as a consequence, a shift of phase boundaries into the region of low molar ratios n_w .

The water addition into a lecithin solution induces not only the polymer-like micelles formation, but their modification as well. This does not lead to a phase transition. There is only a sequential change of micellar structure and rheological properties of the lecithin organogel. When adding successively water, one can find linear and then branched polymer-like micelles [45], and in the closing stage a mixed system from micellar aggregates differing in their relaxation times [48]. The subregions relevant to these micellar systems are marked by dashed vertical lines in the phase diagram in Fig. 5. The various types of the polymer-like lecithin micelles are considered more comprehensively in the following section.

7. Linear and branched micelles

When introduced into a solution, the initial portions of the gel-forming additives-water, glycerol, ethylene glycol or formamide-provide the uniaxial growth of micelles. In place of spherical aggregates, there are cylindrical ones. This transition was confirmed by means of various physicochemical techniques [16–19,21,49,50]. In addition, the system consisted of polymer-like micelles demonstrates particular rheological behavior. This is easily revealed by examining scaling dependencies [45].

Table 1
Values of the exponents in the scaling laws

| Model/experiment | G_o | η_o | τ_t | References |
|-----------------------------------|-----------------|-----------------|-----------------|------------|
| <i>Theoretical predictions</i> | | | | |
| Reptation theory | 2.25 | 5.25 | 3 | 35, 36 |
| Linear micelles | 2.25 | 3.5 | 1.25 | 37, 38 |
| Branched micelles | 2.25 | 2.5 | 0.25 | 45, 51 |
| <i>Experimental data</i> | | | | |
| Small water amounts; $n_w = 2.5$ | 2.72 ± 0.09 | 3.48 ± 0.20 | 1.02 ± 0.22 | 45 |
| Large water amounts; $n_w = 3.15$ | 2.41 ± 0.14 | 2.24 ± 0.14 | 0.01 ± 0.08 | 45 |

In the framework of the Cates' model, the zero-shear viscosity, plateau modulus and terminal relaxation time are characterized by the following scaling laws [37,38]:

$$\eta_o \sim \phi^{7/2} \quad (4)$$

$$G_o \sim \phi^{9/4} \quad (5)$$

$$\tau_1 \sim \phi^{5/4} \quad (6)$$

where ϕ is the volume fraction of lecithin. It should be mentioned that the terminal relaxation time does not refer, as in the reptation theory [34–36], to a single relaxation process. The micellar kinetics is complicated by dissociation/recombination processes. Cates introduced a new constitutive equation for the terminal relaxation time [37,38]:

$$\tau_t \sim (\tau_{\text{rep}}\tau_b)^{1/2} \quad (7)$$

where τ_{rep} is the relaxation time characterizing the movement of micelles in accordance with the reptation mechanism, τ_b is the lifetime of micellar aggregates between two dissociation events. It is essential that the Eqs. (4)–(6) are valid for a regime at which $\tau_{\text{rep}} \gg \tau_b$. Otherwise, the scaling behavior obeys the reptation model [29,37,38]. The corresponding values of the exponents in the scaling laws for this regime are presented in Table 1. There are also experimental data for lecithin organogels prepared at various amounts of water. By comparing them with theoretically expected values, one can find satisfactory agreement with the Cates' model at the beginning stage (at small n_w) of the micellar growth. This implies the formation of linear polymer-like micelles.

Disagreement between experimental data and the model by Cates is observed with increasing the water-to-lecithin molar ratio. In addition, the steep rise in the zero-shear viscosity, as obvious from Fig. 1A, slows down and then η_o comes through the maximum, being little decreased. It was shown in Ref. [45] that the further addition of water induces a change of the micelles. The power law exponents is in agreement with those predicted in the framework of a model for the branched micelles. It is obvious from Table 1. A model for the branched micellar aggregates was developed in Ref. [51]. It was also predicted that there is an opportunity for sliding branches along the main chain that can cause a decrease in the viscosity owing to a faster relaxation process [51]. From the molecular point of view (Section 4), the branching is associated with the presence of additional water molecules at larger n_w . They provide an opportunity for the side growth of a micellar chain [26]. The idea of the branched polymer-like lecithin micelles is also shared by other researchers who arrived at it from other experimental position [52–56].

8. Organogels with a new rheological regime

A further change in the rheological behavior of the lecithin organogels prepared on the base of *n*-decane was established at $n_w > 3.2$ [45]. An illustrative example is presented in Fig. 6. By comparing the frequency dependencies of the rheological parameters with those in Fig. 4, one can easily notice a difference between two jelly-like phases. The common system composed of

polymer-like micelles (see Section 5) demonstrates rheological properties features of which obeys a Maxwell model with one relaxation time. The frequency dependencies are well-described by Eqs. (1)–(3) (Fig. 4). This model, as established in [48], is inappropriate for the results in Fig. 6. Attention was drawn to intermediate plateaus in curves. It was suggested [48] that there are at least two relaxation processes. For this case a Maxwell model with two parallel elements was applied [57]. To describe the rheological behavior, the following equations were used:

$$G'(\omega) = G_{o1}\omega^2\tau_1^2/(1 + \omega^2\tau_1^2) + G_{o2}\omega^2\tau_2^2/(1 + \omega^2\tau_2^2) \quad (8)$$

$$G''(\omega) = G_{o1}\omega\tau_1/(1 + \omega^2\tau_1^2) + G_{o2}\omega\tau_2/(1 + \omega^2\tau_2^2) \quad (9)$$

where subscripts 1 and 2 refer to the first and second relaxation processes, respectively. A result of the best-fit procedure is shown by solid lines in Fig. 6. Theoretical consideration performed in Ref. [57] confirmed the initial idea that the lecithin organogel at $n_w > 3.2$ can be represented as a binary mixture of variously relaxed entities.

The formation of mixed system from micellar aggregates varying in relaxation times was also demonstrated by another way in Ref. [48]. An interpretation of rheological data was made with the help of an approach developed in the chem-

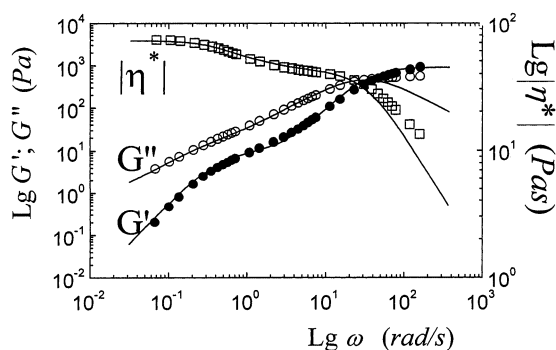


Fig. 6. The complex viscosity $|\eta^*|$, storage modulus G' and loss modulus G'' versus oscillation frequency ω . The experimental data are shown by points; the solid curves are the best fit in accordance with Eqs. (8) and (9). An organogel consists of 35 wt.% of lecithin and 4.0 water molecules per lecithin molecule in *n*-decane. The temperature was $25.0 \pm 0.1^\circ\text{C}$.

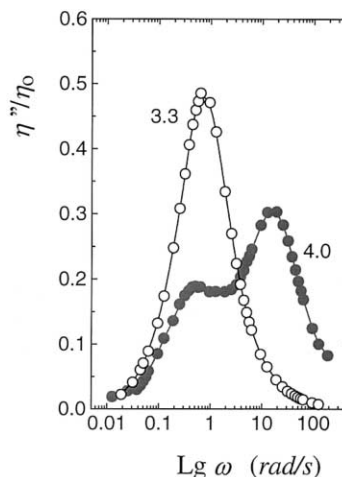


Fig. 7. The imaginary part of the complex viscosity η'' , normalized by the zero shear viscosity, versus oscillation frequency ω . An organogel consists of 250 mg ml^{-1} of lecithin. The numbers of water molecules per lecithin molecules are shown close to curves. The temperature was $25.0 \pm 0.1^\circ\text{C}$.

istry of polymer blends [58,59]. Fig. 7 shows a dependence of the imaginary part of the complex viscosity on the oscillation frequency for organogels containing 3.3 and 4.0 water molecules per lecithin molecule. As seen, a transfer from single-peaked curve to a double-peaked one happens with increasing molar ratio between water and phospholipid. Model experiments with monodisperse polymers made it apparent that the second peak appeared in the low-frequency region when a low-molecular component was introduced into a solution of polymer with higher molecular weight [58,59]. The mixing gave a system consisting of entities having various relaxation times. This difference can be easily revealed when the measured results are presented as shown in Fig. 7. It is of worthy to mention that the well-defined peaks can be obtained if polymers are monodisperse and differ significantly in their molecular weight. Otherwise, one will have a smooth curve.

Thus, the homogeneous lecithin organogel phase (see phase diagram in Fig. 5) represents a rather complicated system. Our experimental studies led us to recognize that there are at least three subsystems: (i) linear polymer-like micelles;

(ii) branched micellar aggregates; and (iii) a mixture of entities possessing various relaxation times.

9. Micellar kinetics

At present there is the only model describing the dynamics of polymer-like micelles that was developed by Cates (see Section 7) on the base of the reptation theory [37,38]. From rheological measurements it is possible to determine the terminal relaxation time. In distinct of the polymer systems, τ_t characterizes two relaxation processes (Eq. (7)). Therefore, the problem is that how to extract τ_{rep} and τ_b describing movement and dissociation of micelles.

Turner and Cates suggested [60] to use Cole-Cole plots representing the loss modulus against the storage modulus. To enhance the precision for determination of the relaxation times, a new formalistic procedure based on the Cates theory was developed in Ref. [61]. For convenience of mathematical treatment of experimental data, an auxiliary function:

$$F(G'(\omega)) = \frac{G'(\omega)^2 + G''(\omega)^2}{G'(\omega)} \quad (10)$$

was introduced. Fig. 8 illustrates the developed procedure. In case the behavior of a system obeys the Maxwell model, there is a horizontal line (Fig. 8A). The ascending branch of the curve gives an indication of the deviation from this model. This is characterized by a parameter ζ , introduced by Turner and Cates. ζ is equal to a ratio between the relaxation times of dissociation τ_b and reptation τ_{rep} [60]. Curves calculated at various values of ζ can be seen in Fig. 8B. A result of fitting into the experimental data is presented in Fig. 8A. By using the determined value of ζ and experimentally measured terminal relaxation time, one can then calculate τ_b and τ_{rep} with the help of Eq. (7).

A dependence of the relaxation times characterizing the micellar dissociation and reptation on the molar ratio of water to lecithin is shown in Fig. 9. As seen, τ_b is practically invariable with n_w . This result was explained in Ref. [61] by unchangeable interactions within the polymer-like

micelles in the examined region of molar ratios n_w . The successively added water forms hydrogen bonds with phosphate groups of lecithin molecules (see Section 4). At the same time, the relaxation time for reptation is increased in the region of linear micelles and is unchanged when the branched micelles are in existence. Such the dynamic behavior was associated with two reasons. The increase of τ_b is caused with the growth of micelles. It was shown in Ref. [45]. The subsequent plateau in the curve (Fig. 9) can be related, in accordance with the suggestion in Ref. [51], to an increased mobility of branched polymer-like micelles owing to sliding the branching points along the chain.

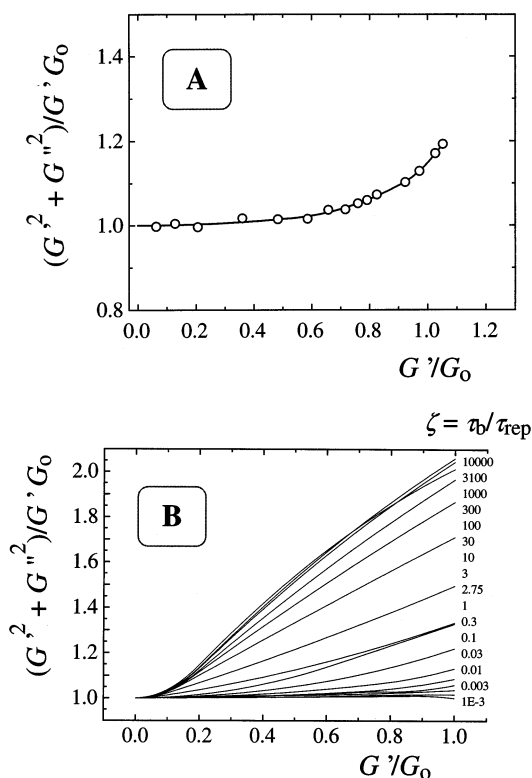


Fig. 8. Plots of $(G'^2 + G''^2)/G'G_0$ as a function of G'/G_0 that are used to find ζ (details are in text and in Ref. [61]). (A) The points present experimental data for an organogel containing 50 mg ml^{-1} of lecithin and 2.7 water molecules per lecithin molecule in *n*-decane; the solid curve is the best fit at $\zeta = 0.027$. (B) Calculated curves at various values (shown in the right side) of the parameter ζ (adapted from Ref. [61]).

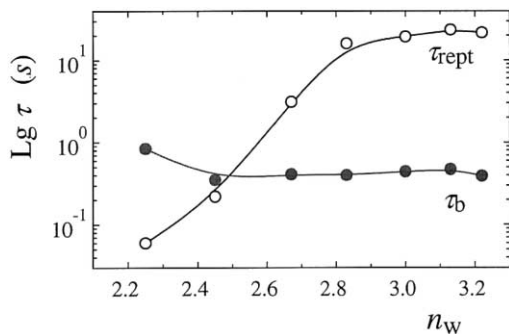


Fig. 9. The relaxation times for reptation τ_{rep} and dissociation τ_{b} of micelles versus the water-to-lecithin molar ratio in a *n*-decane organogel with 35 mg ml⁻¹ of lecithin. The measurements were performed at 25.0 ± 0.1°C (adapted from Ref. [61]).

10. The effects of external fields

The lecithin organogel demonstrates high sensitivity to external influences. A shear flow or electric field brings about a prominent change in the structure and properties of polymer-like micelles. The external fields represent also a convenient way for controlling over the structural organization of lecithin organogels.

10.1. Shear flow

The behavior of sheared lecithin organogels was studied thoroughly in Ref. [62]. Fig. 10 demonstrates a dependence of the steady shear viscosity

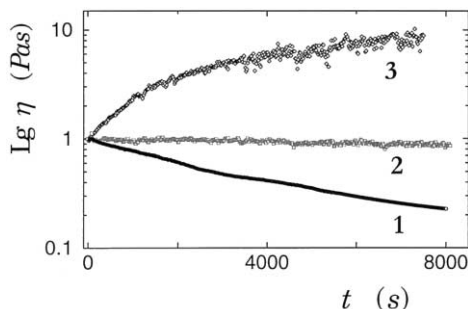


Fig. 10. The steady shear viscosity vs. the time. Measurements were performed at the shear rate of 2.25 s⁻¹. An organogel contains 250 mg ml⁻¹ of lecithin and 2.0 (1); 3.0 (2); and 5.1 (3) water molecules per lecithin molecule (adapted from Ref. [62]).

on the shear rate for organogels prepared at various water-to-lecithin molar ratios. As obvious, the effects produced by the shearing are determined by n_w . Closer inspection shows that they are dictated by the type of micelles. In the region of linear micelles (curve 1, Fig. 10) the constant shear flow led to a decrease in the steady shear viscosity (the thinning effect). The region of branched micelles featured insensitivity to the shearing (curve 2, Fig. 10). Jelly-like phases containing increased amounts of water (at $n_w > 3.2$) demonstrated a thickening effect. In their case one can see an increase in the steady shear viscosity when applying the shear flow (curve 3, Fig. 10).

The shearing effects in the regions of linear and branched polymer-like micelles, as noted in Ref. [62], bear a strong resemblance with those observed in aqueous solutions of direct micellar aggregates. Therefore, it was suggested that the same mechanisms are valid for both the systems. The thinning effect is caused by alignment of micellar aggregates along the flow direction [29,63–67]. This effect is confirmed by observations on sheared lecithin organogels made by using a small angle neutron scattering in Ref. [17]. Since the alignment leads to micellar disentanglement, the viscosity decrease takes place. As regards the branched polymer-like micelles, it was suggested [66] to consider their system as a superposition of two networks, each consisting of linear parallel aggregates which are crossed with ones of the alternative network oriented at an opposite angle to the flow direction [67]. The rheological properties are less sensitive to the shearing because of unchanged number of crossing points (branching).

It is not so easy to perceive the mechanism for the thickening effect (curve 3, Fig. 10). An important finding is presented in Ref. [62]. It was established that the shearing transferred the system into a steady state which demonstrated the rheological properties inherent in the organogel consisting of branched polymer-like micelles. The thickening effect manifested itself as a reconstruction of the state occurring at smaller water-to-lecithin molar ratios. It was suggested [62] that the shearing can induce a micellar length growth. In addition, there should be an increase in the num-

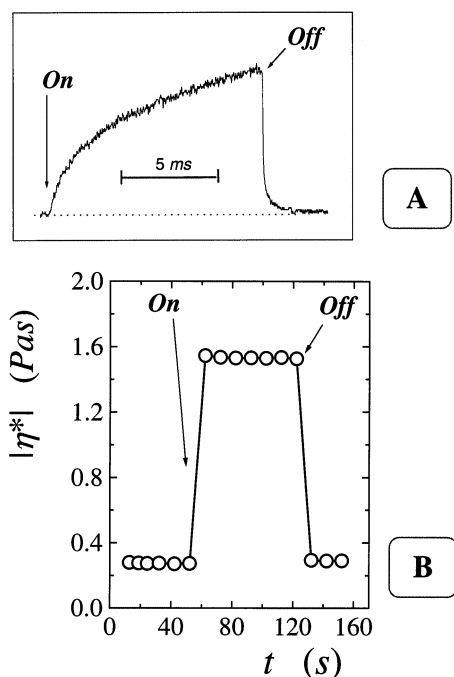


Fig. 11. (A) A transient birefringent signal. (B) Temporal changes of the complex viscosity measured at a constant frequency of 1 Hz. Arrows mark the time when an electric field of 800 V mm^{-1} strength from an external source was applied and switched off. An organogel consists of 35 mg ml^{-1} of lecithin and 0.9 glycerol molecules per lecithin molecule in *n*-decane. The temperature was $25.0 \pm 0.1^\circ\text{C}$ (adapted from Ref. [69]).

ber of entanglements within the three-dimensional network of polymer-like micelles because an increase of plateau modulus also was found.

10.2. Electric field

The first experiments were performed on a jelly-like phase collected in the close vicinity of the interfacial boundary between water and non-aqueous lecithin solution [3]. It was established that an electric field induced a birefringent effect (Fig. 11A). In addition, a formation of filament-like structures was observed. These effect and behavior were confirmed in the succeeding article [4]. It was also found [68] that the external electric field applied brought about a notable increase in the viscosity of jelly-like phase. An illustrative example is presented in Fig. 11B. The effect, as

may be seen, is reversible. These facts gave grounds to assign the established phenomenon to the *electrorheological effects*. An insight into their mechanism was provided by a detailed study on the behavior of lecithin organogels under the action of an electric field performed in Refs [69,70].

The electrorheological effects were studied on water- and glycerol-containing jelly-like phases. It was shown [69] that this behavior depended on the molar ratio of a polar additive to lecithin. The increase in the viscosity and shear moduli after the application of an electric field were absent in solutions in which a three-dimensional network from the micelles was not found. The electrorheological effects are inherent only in the polymer-like micelles [69]. Notable differences in the rheological behavior for glycerol- and water-containing organogels were established [69]. The former demonstrates a more stable and reproducible response to the applied voltage a region of which is more extended than that observed for the latter. Furthermore, the electrorheological effects for the glycerol-containing organogel were more expressed in the region of branched micelles, while in a case of the water-containing one there was a gradual growth of the response extending into the two-phase system containing solid precipitated particles (see the phase diagram in Fig. 5).

The increase in the viscoelasticity of lecithin organogels under the action of an external electric field was attended with strong birefringence [68,69] (Fig. 11A). The optical effect implies that there is orientation of the whole cylindrical micelles or, what is more likely, their portions along electric field lines. If this is the case, it is reasonable to expect that the orientation brings about the disentanglement of the micellar aggregates. This should result in decreased viscoelasticity of the organogels. In real situations the viscosity increase was found (Fig. 11B). An insight into the mechanism of processes was provided by recent experiments in Ref. [70].

Fig. 12 shows the frequency dependencies of the imaginary part of the complex viscosity for an organogel without and under the action of an external electric field. One may see notable differences between the two considered cases. The applied voltage causes an appearance of the second

peak in a curve. Important points are those its maximum is in the low-frequency region and its growth is accompanied by a decrease in the height of the initial peak. The doubled-peaked curve means, as considered previously (Section 8), that the micellar system is composed of a mixture of entities possessing various relaxation times. Based on this finding, a suggestion was made in Ref. [70] about merging of polymer-like micelles by their ends under the action of the external electric field.

11. Mixed organogels

Scartazzini and Luici mentioned in their first article [1] that the organogels were formed only from purified lecithin. The presence of impurities influenced strongly its gelling ability. For example, carotenoids, when added even in trace amounts, changed drastically, as shown in Ref. [71], the viscoelastic properties of a jelly-like phase. As a rule, any additive has an effect on the lecithin organogel. To date lecithin mixtures with phosphatidylethanolamine, its structural analogue, and sugar-containing surfactants have been studied in sufficient details.

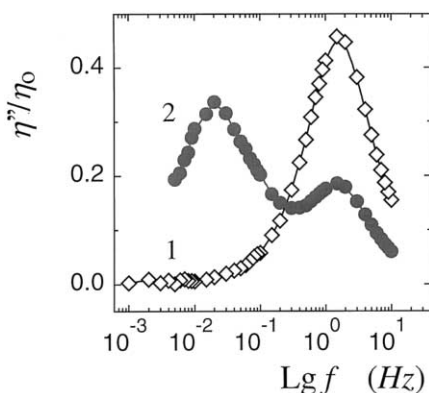


Fig. 12. The imaginary part of the complex viscosity η'' , normalized by the zero shear viscosity, versus the oscillation frequency ω . Measurements were performed without an applied electric field (1); and at 2000 V mm^{-1} strength (2). An organogel consists of 250 mg ml^{-1} of lecithin and 0.9 glycerol molecules per lecithin molecule in *n*-decane. The temperature was $25.0 \pm 0.1^\circ\text{C}$ (adapted from Ref. [70]).

A molecule of phosphatidylethanolamine has a strong resemblance with a lecithin one except for the terminal functional group. The nitrogen atom in choline is surrounded by three methyl groups (Fig. 2), whereas there are hydrogen atoms in ethanolamine. This difference, as shown in Refs [23,72], has two important consequences. The amino group can form hydrogen bondings, thus influencing the interactions between molecules within micelles. In addition, ethanolamine is smaller than choline that causes a change of the molecular geometry. The shapes of a phosphatidylethanolamine molecule can be represented as a truncated cone. A lecithin molecule has a cylindrical shape. Therefore, phosphatidylethanolamine forms predominantly a hexagonal H_{II} mesophase and lecithin, lamellar L_α one [73]. When they have been mixed, this results in structural rearrangement and a phase transition. In particular, a phosphatidylethanolamine molecule being introduced into a linear chain of lecithin molecules tends to curve it, thus inducing packing constraints and chain disruption in the end.

The modifying effects of sugar-containing surfactants, *n*-alkyl-d-glucosides and *n*-alkyl-d-lactobionamides, on the lecithin organogels are explicable on the same basis. When they are involved into the polymer-like micelles, they change intermolecular interactions and a curvature of a monolayer. There are also additional features [74–76]. *n*-Alkyl-D-glucosides and *n*-alkyl-D-lactobionamides changed the mechanism of the micellar growth. In place of linear micelles, branched aggregates were found [76]. The effect was related to a bulky polar region and the presence of several hydroxyl groups liable for hydrogen bonds.

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