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SHORT COMMUNICATION

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Percolative phenomena in lecithin reverse micelles: the role of water

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Abstract The role played by the solvation water molecules on the macroscopically observed sol–gel transition in lecithin/cyclohexane/water reverse micelles is investigated by quasielastic neutron scattering, dielectric relaxation and conductivity measurements. The experimental results are juxtaposed to those from spherical Aerosol OT reverse micelles. It is shown how the results from lecithin-based system can be interpreted only assuming that, in contrast to Aerosol OT systems, the water molecules are entrapped at the interfaces without coalescing into an inner water pool. It is suggested that, in the case of lecithin, the solvation water can induce a change in the surface curvature, in such a way promoting the formation of branch points. Such a hypothesis is supported by the temperature dependence of the conductivity which agrees with the hypothesis of an intermicellar bond percolation. The investigation of the structures imposed by an external electric field is also studied. The observed electrorheological behaviour seems to confirm the existence of a percolated transient network in the gel phase.

Keywords Living polymers · Gels · Electrorheology · Reverse micelles

Introduction

It is commonly observed that lecithin dissolved in a number of nonpolar solvents is able to form cylindrical aggregates upon the addition of small quantities of water [1]. Further addition of water determines the growth of the cylinders in giant wormlike micelles, until a maximum R value (R is the number of water molecules per surfactant molecule) is reached, above which the structure of the system changes. Above a critical concentration, the micelles entangle in a transient network [1, 2] and, from a macroscopic point of view, the system appears as a viscous gel, thermostable, thermoreversible and isotropic [3]. On this basis it became usual to describe the structure of the lecithin gels in terms of analogies with semidilute solutions of flexible polymers [4, 5]. Such an approach turns out to be able to describe many of the static properties of the systems, but the details of the microscopic role played by water molecules in promoting the observed sol–gel transition remain rather obscure [6,–8]. In addition, the nature of the intermicellar interaction characterizing the transient network of the gel phase is at present a point of controversy [2–4, 9–11].

In this work, we shall try to obtain further insight through a comparison of the peculiar properties of lecithin reverse micelles with those of the more conventional, and now well-known, Aerosol OT (AOT) reverse micelles. AOT is a synthetic anionic surfactant, while lecithin is a natural phospholipid that can be extracted from cellular membranes (of soybean, in our case) and, unlike AOT, it has a zwitterionic head group. Our aim is to show that this difference could well determine, through the local configurations established by the actual water–surfactant interaction [12], the observed specific macroscopic properties of the two kinds of system.

Experimental

Soybean lecithin (Epicuron 200) was a gift from Lucas Meyer and was used as received. AOT, D_2O (100% D) and d_{12}-cyclohexane (99.5% D) were purchased from Aldrich Chemicals. Water was deionized and bidistilled.

Epicuron 200 is not a high purity (only 96%) product but, owing to the cost of higher-quality materials, it has been used in almost all the experiments reported in the literature. We decided to use the same product in order to obtain a set of data which is fully consistent with the whole body existing. However, in order to test how much the impurities affect experimental results relevant to the present situation, some measurements were performed on samples prepared with pure (about 99%) soybean lecithin purchased from Sigma-Aldrich.

The samples were prepared by weight, first dissolving the surfactant (either lecithin or AOT) in d_{12}-cyclohexane and then adding the appropriate amount of water. The weight fractions of the dispersed phase were converted to volume fractions assuming 1.014 and 1.1 g/cm^3 for the densities of lecithin and AOT at 25 °C, respectively. For each value of the volume fraction, ϕ, samples were prepared with water contents ranging from $R=0$ to $R=10$.

AOT reverse micelles were investigated with the NEAT spectrometer at BENSC, using an incident wavelength of 5.1 Å and an instrumental resolution of $\Delta E=217$ μeV (vanadium, at room temperature (25 °C). The exchanged wave vector (Q) spanned between 0.3 and 2.2 Å^{-1} (at zero energy transfer). In order to separate the water contributions from those of the other components, the isotopic substitution method was adopted: AOT/(d_{12}-cyclohexane)/water systems of different compositions ($\phi=0.2$, $R=10$ and $\phi=0.2$, $R=5$) were prepared both with H_2O and with D_2O. In addition, a measurement was carried out on the lecithin/(d_{12}-cyclohexane)/H_2O system at $\phi=0.2$, $R=10$, in order to check the consistency with previous results [13]. Spectra from pure d_{12}-cyclohexane were also taken. All time-of-flight spectra were preliminarily translated into an energy scale and were corrected for the empty-cell contribution. Then, the quasielastic neutron scattering (QENS) spectra of the water confined in the micellar core were obtained from the difference between the corresponding, isotopically substituted samples.

The formation of structures induced by an external electric field was monitored visually by means of a schlieren optical system. A homemade optical cell was used, consisting of two concentric stainless steel cylinders, electrically connected to a Trek 664 high-voltage amplifier; two fused quartz windows were used as the top and bottom. The height of the cell was 3.2 cm and the diameters of the two cylinders were 3.535 and 2.490 cm, respectively: in such a way a fixed gap of 0.523 cm between the electrodes is obtained. The cell was put in the confocal point of the first two lenses of the schlieren optics and was aligned with the optical axis of the system passing between the electrodes. A beam stop was set at the confocal point of the second section of the optics, so that each zero-order image was stopped. Any variation of the average refractive index of the fluid was then well evidenced on a translucent screen, and the images obtained were collected by a digital camera. Preliminary calibration measurements were performed on the empty cell and on the cell filled with different nonpolar liquids, namely cyclohexane, carbon tetrachloride and diethyl ether. The experiments were performed in the frequency range 100 Hz–20 KHz and with different intensities of the applied field from 50 to 6000 V/cm. The values of the static relative dielectric constant, ε_0, of the three fluids, obtained as the ratio between the measured capacitance of the cell filled with the liquid and that of the empty cell, turned out to be in agreement with the literature values within 2%, if one takes into account an instrumental capacitance (parallel coupled) of 5.62 pF. The capacitance of the empty cell was 5.57 pF, not much larger than the value of 5.08 pF calculated on the basis of the geometrical sizes. In order to test the effects of the temperature on the conductivity of our micellar systems, the same cell was used in a thermostatic bath. Care was taken in order to avoid unwanted thermal fluxes through the sample: the field strength was kept lower that 100 V/cm in order to maintain the intensity of the current lower than 200 μA. The results are reported in Fig. 1 both for an AOT/cyclohexane/water micellar solution and for a lecithin/cyclohexane/water micellar solution.

In addition, impedance spectra of the lecithin/cyclohexane/water systems were recorded by means of a Chelsea dielectric interface CDI5/L4 coupled with a Schlumberger SI 1255 high-frequency response analyser; the dielectric spectra were recorded at room temperature with an applied field of 6 V/cm and in the frequency range 0.01 Hz–1 MHz, using the cylindrical cell described previously.

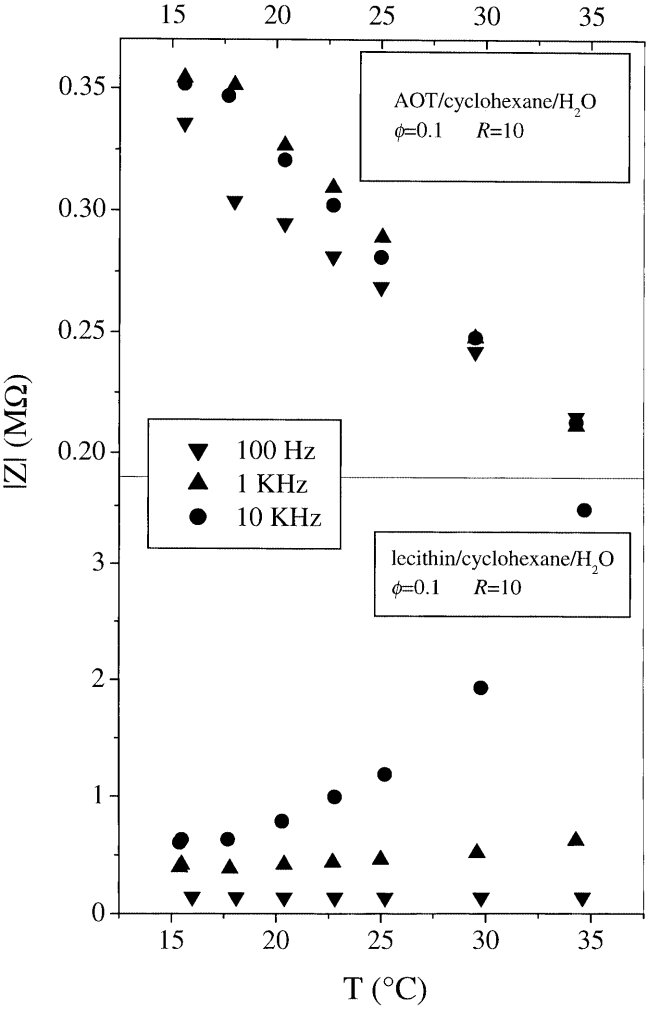

Fig. 1 Temperature evolution of the measured impedances for Aerosol OT (*AOT*)/cyclohexane/water (*top*) and lecithin/cyclohexane/water (*bottom*) systems

Handling of the data and results

QENS spectra

The contribution from the water confined in the AOT micellar core was analysed under the assumption of the Sears [14] model. A fitting procedure was adopted which is able to resolve, after convolution of the scattering law with the instrumental resolution function $R(\mathbf{Q},\omega)$, the n independent Lorentzian contributions, $L_n(\mathbf{Q},\omega)$, to the obtained QENS spectra:

$$S(\mathbf{Q},\omega) \propto \left[\sum_n L_n(\mathbf{Q},\omega)\right] \otimes R(\mathbf{Q},\omega) \quad . \tag{1}$$

Both a translational and a rotational line were detected. The average half width at half-maximum (HWHM) of the rotational line was about 1.2 meV, very close to that of the bulk water [15]. The HWHMs, Γ_T, of the resolved translational lines obtained are reported in Fig. 2 as a function of Q^2 together with previous results on lecithin-based systems [13]. All the data show a typical jump-diffusion behaviour

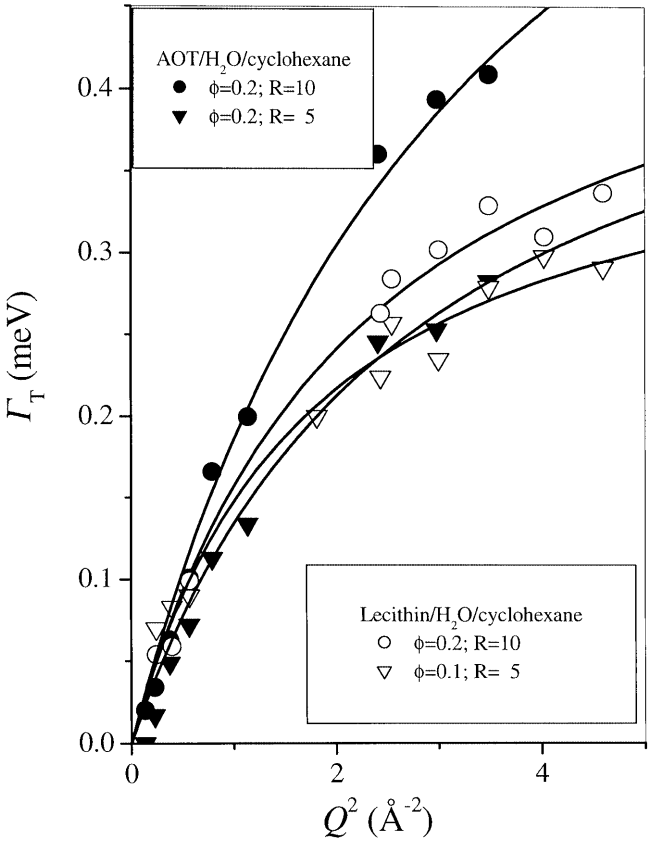

Fig. 2 Half-width at half-maximum of the resolved quasielastic neutron scattering contributions from translational motions of water molecules confined in the micellar cores. The *continuous lines* are the fitting results with a jump-diffusion model

$$\Gamma_T(Q) = \frac{D_T Q^2}{1 + D_T Q^2 \tau_0} \quad , \tag{2}$$

with D_T the diffusion coefficient and τ_0 the residence time before the jump. The solid lines in Fig. 2 are best fits of Eq. (2) with the data; the parameters determined are reported in Table 1, together with literature data for lecithin/(d_{12}-cyclohexane)/water systems and for bulk water. Note that the errors reported in Table 1 are only statistical: the fact that the diffusion coefficient for confined water turns out to be higher than that for bulk water is probably due to a not complete correction of multiple scattering effects (a 2-mm sample thickness was adopted both for lecithin and AOT micelles, to which a transmission coefficient of 0.85 corresponds) that could be reflected in a systematic broadening of the measured line. In any case, this is not relevant as long as relative changes in D_T are considered.

Impedance measurements under high field

The impedance measurements from AOT reverse micelles are well reproduced by a model consisting of a resistive circuit connected in parallel with the cell capacitance according to

$$\frac{1}{|Z|} = \sqrt{\frac{1}{R_c^2} + (\omega C)^2} \quad , \tag{3}$$

with $\omega = 2\pi\nu$. The experimental data are reported in Fig. 3 for the systems at $R = 0$ and $R = 10$. Taking into account the finite value of R_c, the parameter C was held fixed at the value obtained for the cell filled with pure cyclohexane (the value of C is essentially imposed by the solvent and the presence of the dispersed phase affects it only by a few percent). For these reasons, we will not try to undertake any discussion about the concentration dependence of ε_0; on the other hand, a number of accurate experimental determinations of this quantity can be found in the literature [16, 17]. In contrast, the

Table 1 Extracted jump-diffusion parameters for water confined in the inner core of Aerosol OT (*AOT*) reverse micelles. Previous results for lecithin-based systems and literature data for bulk water are also reported for comparison. The errors reported do not take into account possible systematic errors due to multiple scattering (see text)

Surfactant (composition)	D_T (10^{-5}cm^{2}s^{-1})	τ_0 (ps)
AOT (ϕ = 0.2 R = 5)	2.3 ± 10%	1.6 ± 16%
AOT (ϕ = 0.2 R = 10)	3.4 ± 11%	0.7 ± 13%
Lecithin [14] (ϕ = 0.1 R = 5)	3.5 ± 13%	1.6 ± 8%
Lecithin [14] (ϕ = 0.2 R = 10)	3.4 ± 8%	1.3 ± 8%
Bulk water [15]	2.3	1.1

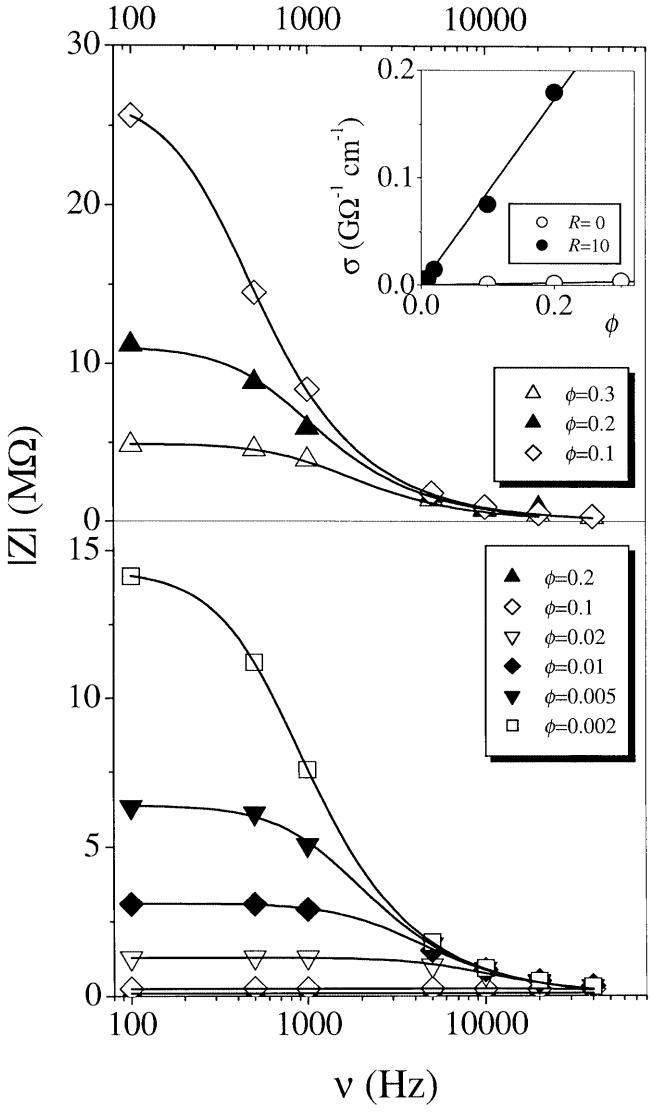

Fig. 3 Frequency dependence of the experimental impedance of AOT reverse micelles at $R=0$ (*top*) and at $R=10$ (*bottom*) at different values of the volume fraction. *Inset*: Extracted ϕ dependence of conductivity

values of the ohmic contributions can be accurately determined and the values of the conductivities, σ, are easily extracted. The results are reported in the inset of Fig. 3 both for the system at $R=0$ and for that at $R=10$. The conductivity of pure cyclohexane is negligible; the addition of AOT slightly increases the conductivity of the solution which, however, remains very low (of the order of 10^{-9} $\Omega^{-1}\text{cm}^{-1}$). The addition of water induces a further increase by 2 orders of magnitude. The observed conductivity can in any case be associated with the continuous process of coalescence and subsequent separation of droplets, which occurs in about 0.1% of all droplet encounters [18]. Both the conductivities of the $R=0$ and $R=10$ systems behave linearly with ϕ, ensuring that no other structural process is taking place besides the previously described kinetic equilibrium: any structural change (spheres to bicontinuous or droplet aggregation) is known to determine a dramatic variation of the conductivity which, in some cases, may increase up to 4 orders of magnitude [19]. The result agrees with a number of studies on the phase diagram of the system [20, 21] indicating that, at the volume fractions explored here, the system can be assumed to be formed by spherical droplets.

A similar result is obtained for lecithin-based systems at $R=0$. The experimental behaviour of the measured impedance as a function of the frequency of the applied field is reported in Fig. 4, where the continuous lines represent the results of the fitting with Eq. (3). In the inset of the same figure the extracted values of the conductivity are plotted as a function of the volume fraction of the dispersed phase. Also in this case the values of the conductivity remain very low (at the same order of magnitude of 10^{-9} $\Omega^{-1}\text{cm}^{-1}$) and show an almost linear dependence on ϕ. As a consequence, the same picture as for AOT-based systems can be drawn for the mechanisms underlying the observed conductivity.

In all the measurements, the current versus applied field plot never deviated from the straight line, up to fields of 8 kV/cm for the AOT and lecithin micelles at $R=0$ and of 2 kV/cm for AOT reverse micelles at $R=10$. This means that no change in the transport properties is induced by the electric field.

The situation turns out to be much more complicated in the case of lecithin/cyclohexane/water systems at $R=10$ (Fig. 4, bottom). In fact, as shown in Fig. 5, a steady-state current is reached after rather long transients with opposite behavior depending on the field strength.

Note that in Fig. 4, bottom, the stars refers to a sample at $\phi=0.05$ and $R=10$, prepared with pure (99%) lecithin: the effect of the impurities turns out to be negligible.

Schlieren imaging

The structural evolution of the systems under an electric field shows up depending on the shape of the micelles (spherical for AOT-based systems and for lecithin in cyclohexane micelles; cylindrical in lecithin/cyclohexane/water systems), while the kind of surfactant does not appear itself to be critical. In Fig. 6 we report some pictures of the schlieren images obtained from AOT/cyclohexane/water and lecithin/cyclohexane/water solutions, at different strengths of the applied field. The two walls (electrodes) of the cell are localized at the top and bottom of each picture and roughly correspond to the boundaries between light and dark. The application of a

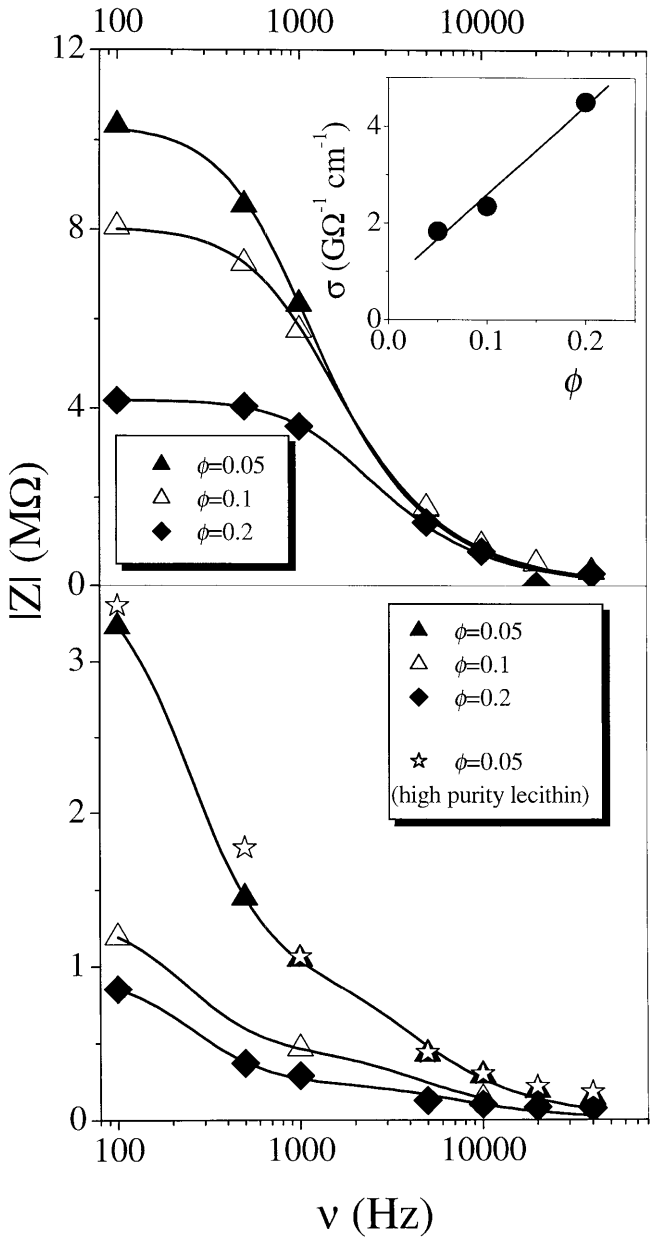

Fig. 4 *Top*: Frequency dependence of the experimental impedance of lecithin reverse micelles at $R = 0$ and at different values of the volume fraction. *Inset*: The ϕ dependence of the conductivity. The *continuous lines* are the fitting results with Eq. (3). *Bottom*: Frequency dependence of the experimental impedance of lecithin reverse micelles at $R = 10$ and at different values of the volume fraction. The *continuous lines* are guides for eye

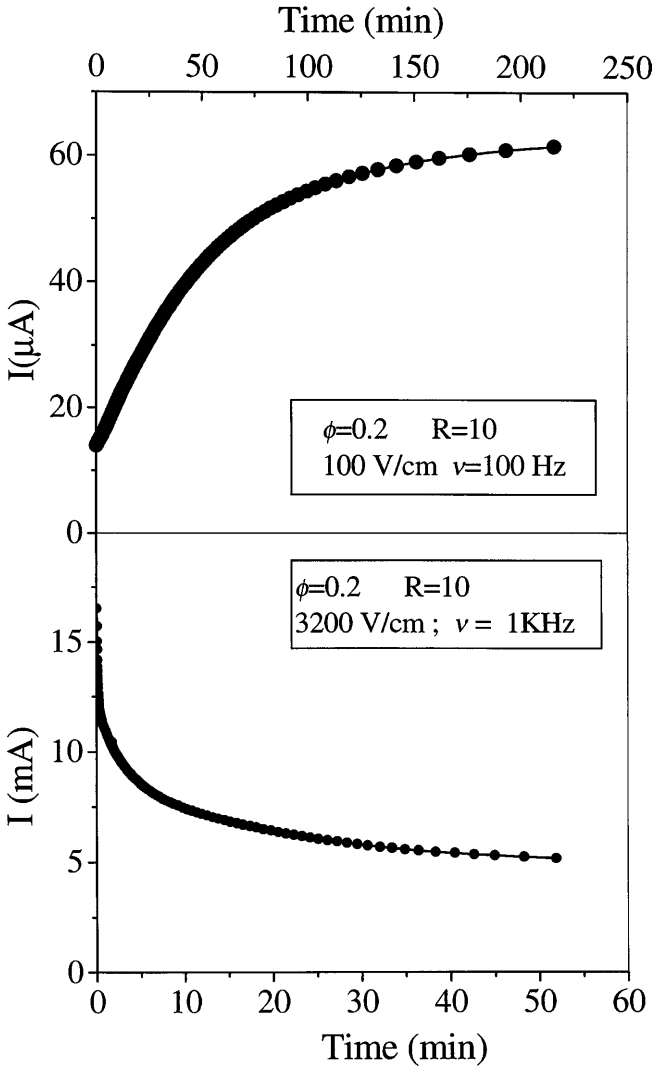

Fig. 5 Lecithin/cyclohexane/water system: time dependence of the current intensity at different values of the applied field

field of 700 V/cm at a frequency of 10 Hz to the cyclohexane/AOT/water system (Fig. 6, first frame) induces a stationary convective motion of charged particles between the two electrodes; no effect is observed at higher frequencies. On increasing the field strength the motion becomes chaotic. At frequencies of some kilohertz the turbulence is essentially localized in the proximity of the electrodes (second frame), while at lower frequencies all the sample volume is involved (third frame). Any image disappears within a few seconds when the field is switched off. Analogous behaviour was revealed for all the spherical micelles. A different result was obtained for the lecithin/cyclohexane/water system. At a field strength of 800 V/cm and at a frequency of 10 Hz, some columnar aggregates bridging the two electrodes are observed (Fig. 6, bottom, first frame). These structures become stable after some tens of seconds, while a much longer time is required to reset the system after the field is switched off. At high field strength the columnar aggregates are observed only during a transient regime; however, the shape of the columns is not so regular and the sizes of the sections of the aggregates appear to be distributed over a wide range of dimensions (Fig. 6, bottom,

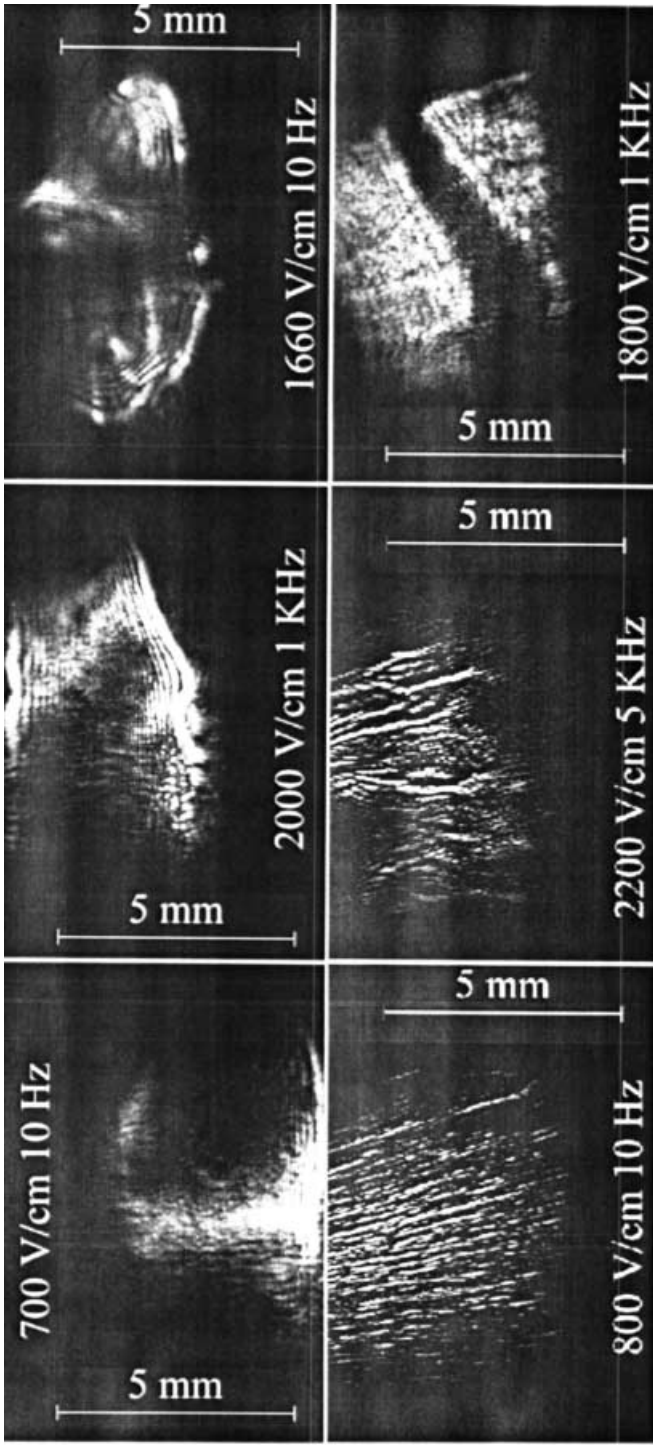

Fig. 6 Schlieren images of AOT/cyclohexane/water (*top*) and lecithin/cyclohexane/water (*bottom*) systems under an electric field. The structuring effect of the applied field is clearly evident in lecithin-based systems, at least at relatively low field strengths and within a short time after the field is switched on

middle). As time goes on, the columns move slightly across the sample volume and disappear until only a density gradient remains from the electrodes to the middle of the cell (Fig. 6, bottom, third frame). After some minutes a diffusion of small aggregates superimposed on the image that becomes faster and faster is observable. At the end the situation approaches that observed in the third picture at the top of Fig. 6. The time evolution of the system becomes faster as the strength of the field increases and the frequency lowers. When the field is switched off, a long time is required before the system fully resets (from some tens of minutes to some hours). During this time, the observed image does not differ too much from the last image in Fig. 6. The observed motions within the bulk sample agree with the temporal evolution of the viscosity under high field, observed in lecithin/(*n*-decane)/water systems [22]. The decreasing of the zero-frequency shear viscosity was interpreted as due to the polarization and subsequent realignment of the cylindrical micelles: the induced ordering would reduce the micellar entanglement coupling and perturb the transient network structure.

However, we observed some Joule heating of the sample when an electric field was applied to the lecithin/cyclohexane/water ternary systems. As an example, when an electric field of about 1000 V/cm is applied (at a frequency of 100 Hz), the current reaches a value of about 4 mA and we found a temperature rise of about 5 °C after 30 min when the field was switched on. The experimentally observed structural changes could be driven by the superimposing effects of the applied electric field and of the temperature change. Since our experimental conditions are not much different from those reported by Shchipunov and Schmiedel [22] we are confident that the same considerations can be applied to the results reported in that work.

Dielectric relaxations

In order to rationalize the nature of the relaxation processes revealed in the lecithin/cyclohexane/water systems, the results from dielectric measurement can be of some help. In Fig. 7 (top) we report, as an example, the tan $\delta = \varepsilon/\varepsilon'$ spectra obtained for systems at $\phi = 0.1$ and $R = 10$. The open circles represent the result for the system of the same composition prepared with pure lecithin (99%). In Fig. 7 (bottom) the behaviour of ε' is reported for systems at $R = 10$ at three different values of the volume fraction.

We adopted a Cole–Cole dispersion function as a suitable dispersion model able to fit our experimental data:

$$\varepsilon = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (j\omega\tau)^\beta} \quad , \tag{4}$$

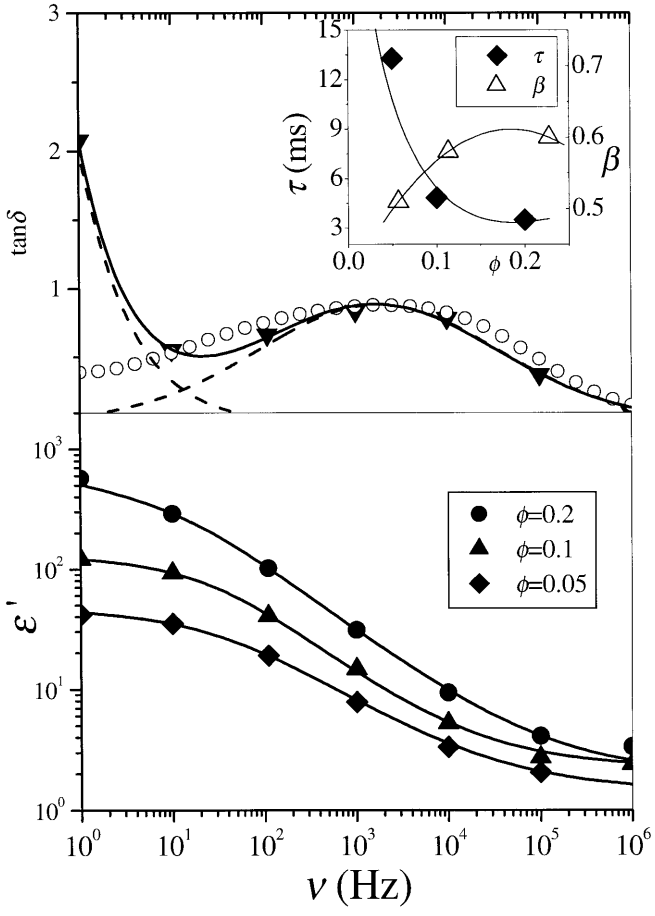

Fig. 7 *Top*: Frequency dependence of tanδ of the dielectric relaxation process at $\phi = 0.1$ and $R = 10$. Samples prepared with Epicuron 200 (*triangles*); high-purity lecithin (*circles*); results of the fitting with a Cole–Cole model, see text (*continuous lines*). *Inset*: Fitting parameters: obtained. *Bottom*: Cole–Cole fitting of ε' at $R = 10$ and at different values of the volume fraction

where ω is the angular frequency, τ is the characteristic relaxation time, ε_0 and ε_∞ are the permittivities at $\omega\tau \ll 1$ and $\omega\tau \gg 1$, respectively, and β is a parameter describing the broadness of the distribution. The value of β ranges from 0 to 1, describing narrower distributions of relaxation times as its values approach unity, corresponding to a single relaxation process (the Cole–Cole model collapses to the Debye model). The model adopted is adequate for the case in which the distribution of relaxation times is smooth and not too broad. The continuous lines reported in Fig. 7 represent the results of the fitting with Eq. (4). In addition, measurements have been taken at a fixed value of the volume fraction ($\phi = 0.1$) and at different R values ($R = 0$, 3 and 6). However, the polarization contribution of the electrodes, that we can observe at $\nu \leq 10$ Hz (exponential component in Fig. 7, top), becomes too high at $R = 0$ and $R = 3$ and completely masks the contribution of the relaxation process, which shifts towards lower frequencies as the water content decreases ($\tau = 0.05$ s at $R = 6$). The same contribution from the polarization of the electrodes was revealed in other dielectric experiments on lecithin/isooctane/water systems [9, 23]. It has been imputed to the diffusion of charged particles over a distance comparable with the electrode spacing [9, 23]. The values of the fitting relaxation parameters, τ and β, are reported as a function of ϕ in the inset of Fig. 7 (top). It is quite clear how the increasing of the volume fraction of the dispersed phase reflects in the shift of the relaxation process towards higher frequencies and in the narrowing of the relaxation time distribution. The results obtained are consistent with our previous finding for lecithin/isooctane/water systems [24]. In contrast to what was revealed by Cirkel and coworkers, in lecithin/isooctane/water systems, it is possible to fit our data with a symmetric distribution of relaxation times; however, this is not a discrepancy, if one takes into account that the system we are dealing with here is characterized by a different solvent. In addition, also in that work the distribution function becomes asymmetric only at the higher concentrations explored.

Discussion

First of all, we consider the impact of impurities in the commercial soybean lecithin we used. One of them, namely β-carotene, is known to decrease the end cap energy of the micelles [25], with a significant modification of the viscoelastic properties owing to its influence on the breaking and recombination processes of the micelles.

Here, the impurity/surfactant ratio is a constant and we are confident that R is a real controlling parameter in our system. In fact, impurities affect essentially the conductivity below 10 Hz (Figs. 4, 7), so any discussion for shorter time scales can be safely undertaken. Moreover, small-angle neutron scattering (SANS) results [10, 11] show that, from the static point of view, the effect of the impurities is a moderate shift towards larger sizes of the micellar cross-sectional radius. In any case, the percolation process observed does not appear to be significantly altered by β-carotene.

QENS clearly shows that the mobility of water molecules confined in the micellar core has a stronger dependence on R when the surfactant is AOT rather than lecithin. In fact, a significant percentage of free (bulk) water is present at high enough R values in water-in-oil AOT reverse micelles [26–28]. In AOT the first few water molecules are strongly bonded to the sulfonate and the sodium ions [29, 30], but after this first hydration shell is completed any additional water molecules do not interact significantly with the AOT carbonyl group or with the alkyl chains and remain localized in core water pools. This starts to be detectable

already from $R = 5$ [28]. Conversely for lecithin micelles, it was proposed [8] that at low hydration levels ($R \leq 4.8$) water associates with the phosphate group and remaining, confined in the head-group region, cannot coalesce into core pools. In such a picture, the phosphate group plays for the lecithin the same role that the sulfonate groups play in AOT, being the initial site of hydration. However, the larger volume occupied by the lecithin head groups makes the difference, and water added once the phosphate group has been hydrated can still hydrate the head groups, without formation of any core pool. This is also indicated by SANS experiments [10, 11], which show an almost constant cross-sectional radius (about 30 Å) over the whole hydration range explored in this work. The narrow cross-section of the tubular aggregates and the lack of indications for any blowing-up process under addition of water suggest that there is significant penetration of the water molecules into the interfacial region. This is fully consistent with some recent results from inelastic neutron scattering [13], where no evidence of bulk water was observed, even in samples with a high hydration level ($R = 10$). The observed (QENS) small increase of the water mobility with R can be understood, within the previously described framework, by considering the formation of branch points (see later) and does not seem to be correlated with the macroscopic change of the viscosity observed at $R \geq 4.8$ in the semidilute regime. On the one hand, this would mean that water molecules are not directly involved in the extended structure of the gel network; on the other, there is evidence that the increase of R above 4.8 induces some local structural modification of the lecithin head-group palisade, responsible for the observed sol–gel transition.

Very recently, the formation of branch points has been considered in order to describe the observed dependence of the conductivity on ϕ and to rationalize dielectric relaxation measurements in lecithin/isooctane/water systems [9]. In that work, a maximum at $\phi \simeq 0.04$ of the low-frequency relaxation time was pointed out. This is consistent with the hypothesis of a percolation threshold, ϕ_c, at that concentration: for $\phi < \phi_c$ the rotational correlation time increases with increasing average size of the clusters; at ϕ_c the largest cluster spans the whole sample volume and on further increasing ϕ the relaxation time decreases again because only the smaller clusters still contribute to the spectrum (see top of Fig. 7). Of course, the same results should be expected in the case of an entangled network in which wormlike micelles either stick together at the entanglement points or form junctions with the water channels fusing: in both cases the same kinds of reorienting aggregates are observed. The former, however, is not consistent with a conductivity percolation threshold.

A further indication comes from the observation that the self-diffusion and rotational dynamics of lecithin molecules slightly increase upon addition of water [13]. It was proposed that the presence of water molecules at the interface is able to promote a change in the curvature which can induce the formation of branch points. At each of them the interface is curved towards the micellar core, the mobility of the lecithin end groups increases and the corresponding rotational relaxation shifts towards shorter times. The same conclusion has been drawn from the existence, at high R values, of a fast dielectric relaxation process which becomes faster and faster as the concentration increases above ϕ_c [9]. The existence of a fast relaxation process, beyond the high-frequency limit of our experiment, can be deduced by the fact that the high-frequency best fit value of ε obtained here is definitely higher than $\varepsilon_\infty = n^2$ (where n is the refractive index). There is no indication of this fast relaxation process in systems at $R = 0$: at low water contents, the lecithin molecules are tightly bonded among them and so form the micellar interface and, as a consequence, no relaxation process connected with the reorientation of the dipoles of the end groups can be observed.

This picture is consistent with some previous results from dielectric measurements on lecithin/isooctane/water reverse micelles performed at a fixed composition as a function of the temperature [24]. In that work, a linear increase of the tanδ peak frequency with the inverse temperature was observed, while the distribution of the relaxation times narrows as the temperature is raised. So one retrieves the result to be expected for a system where the percolation transition is driven by the interaction among aggregates whose average size is determined by the kinetic equilibrium between (thermally activated) breaking and reforming processes, since very similar behaviour is observed when either the concentration or the temperature are used as the experimental parameters.

The low-frequency conductivity measurements further indicate the existence of a percolated structure of interconnected aggregates in lecithin-based systems at high enough values of the volume fraction and water content. The situation is well depicted in Fig. 1, where the temperature dependences of the impedances for AOT and lecithin reverse micelles are compared. In the case of AOT, the conductivity is essentially due to the free diffusion of ions and/or to the charge exchange among diffusing aggregates during a collision. As the temperature increases the viscosity of the system decreases, the breaking and reforming processes of the micellar aggregates become faster, while their size distribution function narrows around smaller values. All these effects assist the diffusion of charges within the fluid and, as a consequence, the sample conductivity increases. In the case of lecithin the conductivity lowers by an order of magnitude. Probably the mechanisms described for AOT also take place, so the higher

viscosity of the system could be associated to a lower mobility of the charges, but the main mechanism responsible for the charge transport is different from AOT-based systems. This can be understood assuming that the main channel of charge transport is an (infinite) cluster spanning the whole sample volume in the gel phase. Under this hypothesis the conductivity should scale exponentially with the number of branching points with the temperature. This is, in fact, confirmed by the loss-tangent data obtained from dielectric measurements at a frequency of 10 kHz (Fig. 7). As the frequency decreases, the lifetime of the extended structure shortens, the system cannot follow the field oscillations and the role played by the exchange processes between colliding aggregates becomes important again. At a frequency of 100 Hz the different mechanisms roughly balance and the system conductivity remains practically temperature independent.

We now discuss the images of the structures induced by an external electric field. When a relatively low voltage at low frequency is applied to AOT reverse micelles some weak electrorheological structure is observed but it is soon destroyed by the establishment of chaotic diffusive motions. In the case of lecithin, at the same values of applied field and frequency, a well-defined ordered structure is revealed during a transient of some minutes. The situation is represented by the first frame at the bottom of Fig. 6. The picture was taken under experimental conditions very similar to those used for the second photograph reported in Fig. 5 of Ref. [22]. During such a transient the image appears to be static; after several minutes the regular columnar aggregates slowly move, collapsing into larger aggregates and becoming rather disordered as time goes on. At the end, the original structured image is substituted by a smooth field of light over which fast motions of small particles can be observed. The time evolution becomes faster and faster as the field strength and the frequency are increased (see the second and the third pictures at the bottom of Fig. 6). The situation does not seem to be much different from that depicted by the time variation of the shear viscosity reported in Fig. 3 of Ref. [22]. Here, however, in the light of the low-frequency conductivity measurements, we are led to assert that no anomalies exist in the electrorheological properties of the system. When the external field is applied, the formation of columnar aggregates probably induces an increase of the apparent viscosity. However, since the intensity of the current is not negligible, the temperature of the system slowly increases, the interconnectivity is destroyed (as above reported) and the shear viscosity decreases.

This structural destructive effect could be avoided with a low enough field strength. The results reported in Fig. 5 (top) (obtained with a relatively low field of 100 V/cm) support our hypothesis about the main mechanism responsible for the electric conductivity, and the structuring effect of the electric field in our system. Further accurate measurements of the apparent shear viscosity under low applied fields are required in order to obtain a definitive picture of the situation.

However, the observed time dependence of the conductivity (Fig. 6, bottom) and shear viscosity (Fig. 3 of Ref. [22]) and the dramatic structural changes induced by the external electric field seem to be strongly correlated.

Conclusions

The results show that both AOT and lecithin reverse micelles exhibit the same behaviour at low R values. An increase in R is accompanied by increasing the water mobility, but only for AOT may this be attributed to a blowing-up process of the micelles, resulting in bulklike properties of the water confined in the micellar inner core. In lecithin reverse micelles the formation of a second hydration shell is observed, but in any case all water molecules remain entrapped at the micellar surface without formation of bulk water pools. This means that when the second hydration shell is fully developed, a structure of the micellar cross-section is obtained which is highly stable against changes in the volume fractions, as recent SANS experiments have demonstrated [10, 11]. At first sight, one could assume that water molecules are only involved in the inner structure of the micelle and that no correlation exists between their dynamics and the sol–gel transition observed above a critical volume fraction. However, the experimental observation that such a sol–gel transition takes place only above a minimum R value ($R \leq 4.8$) suggests that the role played by water on the local structural arrangement is important in determining the macroscopic viscosity of the system. The idea that the addition of water molecules could promote the formation of branch points above a critical volume fraction value is a very appealing one, because it seems to be able to explain a number of experimental results, not otherwise rationalizable in terms of an entangled network of noninterconnected giant cylindrical micelles. IR measurements [7] have shown that water molecules can interact simultaneously with phosphate groups of neighbouring lecithin molecules via hydrogen bonding; as a consequence, lecithin and water molecules can self-arrange in a hydrogen-bonding network. The further addition of water to the previously described structure lowers the packing of the lecithin molecules, thus enhancing the rotational rearrangements. This may explain the observed trend towards higher mobility for the lecithin and the water in the gel phase: such a mechanism could be able to promote the changes in the micellar curvature which allows the formation of branch points, as proposed earlier. The same suggestion has

recently been advanced to rationalize the results from a dielectric measurement performed in lecithin/isooctane/water systems [9]. The experimental observation that the orientational relaxations of the dipoles of the lecithin end groups shift towards higher frequencies as the concentration increases seems to be consistent with such a point of view. As a last point, the different behaviour of AOT- and lecithin-based systems with regard to the conductivity as a function of the temperature unambiguously indicates that besides the usual exchange processes among colliding particles other mechanisms are responsible for the charge transport in lecithin/cyclohexane/water systems. The lowering of the viscosity with increasing temperature induces an increasing of the conductivity; on the other hand, the hydrogen-bonding network responsible for the establishment of an infinite cluster of branched cylindrical micelles is more and more unstable as the temperature increases, so the conductivity decreases. On the path towards equilibrium, one effect or the other will dominate, depending on the instantaneous value of the temperature. The instantaneous value of the current through the sample represents the feedback effect responsible for the opposite time evolutions that the system exhibits depending on the field strengths (Fig. 5) (an increasing of the current induces an increase in the temperature, which in turn causes a decrease in the current and then in the temperature, and so on). The idea that the formation of branch points could be responsible for the high viscosity observed at high values of the volume fractions as common behaviour for these kinds of systems is actually taking place in the literature. Just as an example, besides the results reported for lecithin/isooctane/water systems [9], we mention that recent rheological measurements on lecithin/(*n*-decane)/water micelles have pointed out that no correlation exists between the observed increasing of the shear viscosity and the growth process of the micellar aggregates [31]. Also in that work the authors tried to overcome the interpretative difficulties assuming that at high enough R values the formation of branch points between micelles becomes more probable.

At the moment, in our opinion, the picture presented in this work remains the only one able to describe, at least qualitatively, the role played by water molecules on the establishment of the gel structure together with the observed higher orientational mobility of the lecithin end groups crossing the sol–gel transition. In addition, also the electrorheological anomalies reported in the literature can be removed if one takes into account the existence of branch points whose number density is a function of the temperature.

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