Percolative phenomena and electrorheological structures in reverse micelles

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Abstract
Structural relaxations in AOT (sodium bis(2-ethylhexyl) sulphosuccinate) and
lecithin reverse micelles are investigated by means of dielectric relaxation and
conductivity measurements. The different behaviours exhibited by the two
systems are interpreted in terms of the different kinds of interaction between
the water and the surfactant molecules. In the case of lecithin, the application
of an external electric field induces the establishing of some electrorheological
structure. The temperature dependence of the observed electrorheological
effects agrees with the hypothesis of a structural arrangement consisting in a
percolated network of branched cylindrical micelles. The experimental results
are compared with other literature data and discussed within the framework of
the current theories.

1. Introduction

The gel-forming character exhibited by a number of lecithin reverse micelles was historically
ascribed to the existence of giant cylindrical aggregates that are able to entangle at sufficiently
high values of the concentration [1]. However, some criticisms have been recently made of
such a polymer-like approach. First of all, the theoretical prediction of a micellar contour
length exponentially scaling with the concentration in the diluted regime was revealed not to
be borne out [2]. In addition, the results from a small-angle neutron scattering experiment [3]
performed on a concentrated system do not agree with the hypothesis of a random entangled
network. Some recent dielectric relaxation experiments [4] on analogous systems seem to
suggest a percolated network of branched cylindrical aggregates. However, the role played by
the water molecules in determining the macroscopic viscosity of the system requires further
investigation.

In this paper we try to gain further insight into this point by investigating the concentration
and temperature dependence of the electrical properties of the system. The experimental results
for lecithin-based systems are juxtaposed with those for spherical AOT reverse micelles.

AOT is a synthetic anionic surfactant while lecithin is a natural phospholipid that can be extracted from cellular membranes (of soya beans, 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 [5], the observed specific macroscopic properties of the two kinds of system.

2. Experimental procedure

The soya bean lecithin (Epicuron 200) was a gift from Lucas Meyer and was used as received. Sodium bis(2-ethylhexyl) sulphosuccinate (AOT), D_2O (100% D) and d_{12}-cyclohexane (99.5% D) were purchased from Aldrich Chemicals. Water was deionized and bidistilled. 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. 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 10. The formation of structures induced by an external electric field was monitored visually by means of a schlieren optical system. A home-made optical cell was used, consisting of two concentric stainless steel cylinders, electrically connected to a Trek 664 high-voltage amplifier; two fused quartz windows are used as the basis. The cell was put at the confocal point of the first two lenses of the schlieren optical system and was aligned with the optical axis of the system passing between the electrodes. 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. 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^{-1}. 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 high-frequency-response analyser SI 1255; the dielectric spectra were recorded at room temperature with an applied field of 6 V cm^{-1} and in the frequency range 0.01 Hz–1 MHz, using the above-described cylindrical cell.

3. Results and discussion

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. The experimental data are reported in figure 1 for the systems at $R = 0$ (top) and 10 (bottom). The values of the conductivities, σ, are easily extracted. The results are reported in the inset of figure 1, both for the system at $R = 0$ and for that at $R = 10$. The conductivity of the 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} Ω^{-1} cm^{-1}). The addition of water induces a further increase by two orders of magnitude. The observed conductivity can be in any case associated with the continuous process of coalescence and subsequent separation of droplets, which occurs in ∼0.1% of all droplet encounters [6]. The conductivities of the $R = 0$ and 10 systems both behave linearly with ϕ, ensuring that no structural process is taking place other than the above-described kinetic equilibrium. The result agrees with those from a number of studies on the phase diagram of the system [7, 8] 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 figure 2 (top). In
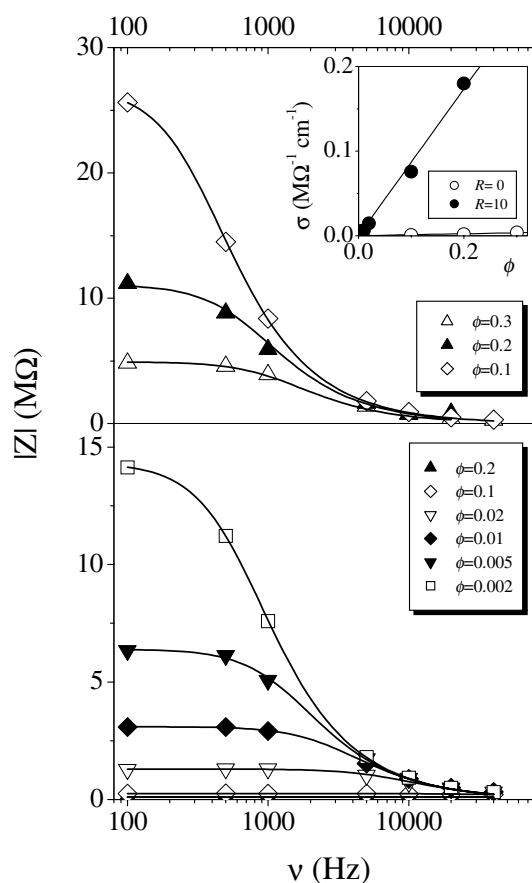
Figure 1. The frequency dependence of the experimental impedance of AOT reverse micelles at $R = 0$ (top) and at 10 (bottom) at different values of the volume fraction. Inset: the extracted ϕ-dependence of the conductivity.

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. In this case also, the values of the conductivity remain very low (at the same order of magnitude of 10^{-9} Ω^{-1} cm^{-1}), and show an almost linear dependence on ϕ. As a consequence, the same picture as for AOT-based systems can be deduced for the mechanisms underlying the observed conductivity. The situation turns out to be much more complicated in the case of lecithin–cyclohexane–water systems at $R = 10$ (see figure 2, (bottom)). In attempts to rationalize the nature of the relaxation processes revealed in the lecithin–cyclohexane–H_2O systems, the results from dielectric measurement can be of some help. In figure 3 (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 the same figure 3 (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:

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\omega\tau)^\beta} \tag{1}$$
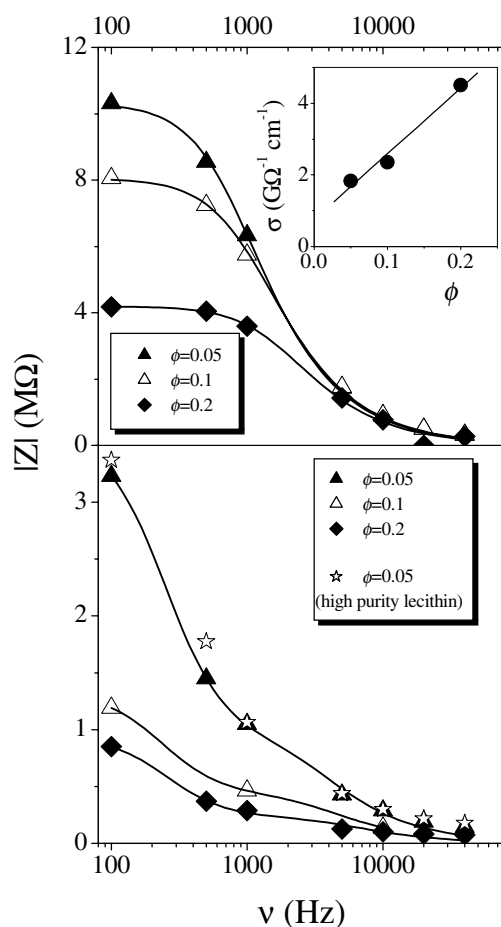
Figure 2. Top: the frequency dependence of the experimental impedance of lecithin reverse micelles at $R = 0$ and at different values of the volume fraction. In the inset the ϕ-dependence of the conductivity is reported. Continuous curves are the results of fitting with equation (3). Bottom: the frequency dependence of the experimental impedance of lecithin reverse micelles at $R = 10$ and at different values of the volume fraction. Continuous curves are guides for the eye.

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 continuous curves reported in figure 3 represent the results of the fitting with equation (1).

The calculated values of the fitting relaxation parameters, τ and β, are reported as a function of ϕ in the inset of figure 3 (top). It is quite clear how the increasing of the volume fraction of the dispersed phase is reflected in the shift of the relaxation process toward higher frequencies and in the narrowing of the relaxation times distribution. These results can be rationalized in terms of the relaxation process of percolated dynamical structures spanning larger sample volumes at higher values of the volume fraction. There is no indication of a similar fast relaxation process in lecithin-based systems at $R = 0$ or in AOT-based systems, but this should not be surprising if one looks at the difference between AOT- and lecithin-based systems. In AOT the first few water molecules are strongly bonded to the sulphonate and the sodium
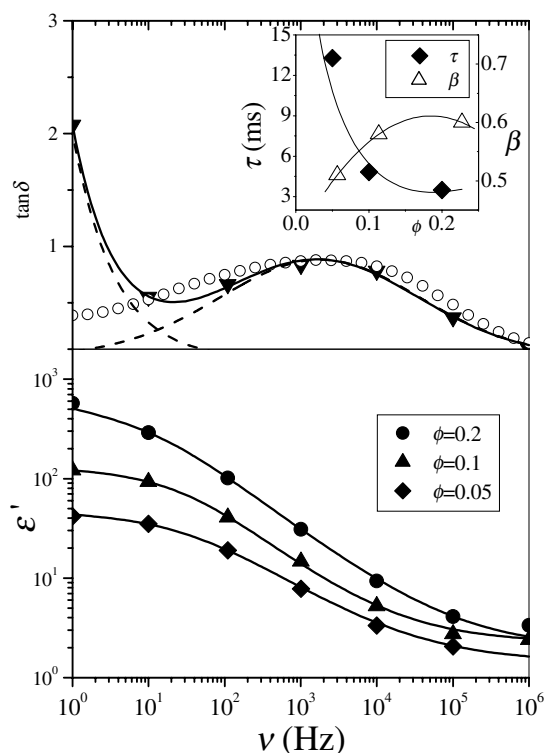
Figure 3. Top: the frequency dependence of $\tan \delta$ for the dielectric relaxation process at $\phi = 0.1$ and $R = 10$. Triangles: samples prepared with Epicuron 200; circles: high-purity lecithin; continuous curves: results of the fitting with a Cole–Cole model (see the text); inset: fitting parameters obtained. Bottom: the Cole–Cole fitting of ε' at $R = 10$ and at different values of the volume fractions.

ions [9, 10] but, after this first hydration shell is completed, any additional water molecule does not interact significantly with the AOT carbonyl group or with the alkyl chains, and remains localized in core water pools. Conversely for lecithin micelles, it was proposed [11] that, at low hydration levels ($R \leqslant 4.8$), water associates with the phosphate group and, remaining confined in the head groups region, cannot coalesce into core pools. In such a picture, the phosphate group plays for the lecithin the same role as the sulphonate groups play in AOT, it being the initial site of hydration. However, the larger volume occupied by the lecithin head groups makes a difference, and water added once the phosphate group is hydrated can still hydrate the head groups, without leading to the formation of any core pool.

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, so driving the formation of an interconnected extended structure.

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 figure 4, 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
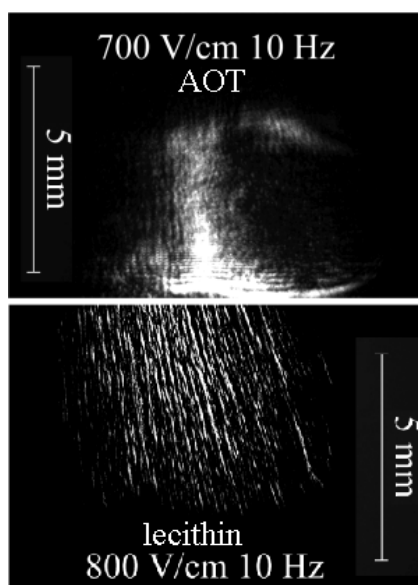
Figure 4. Schlieren images of systems exposed to an electric field. Top: AOT/cyclohexane/water ($\phi = 0.2$, $R = 10$). Bottom: lecithin/cyclohexane/water ($\phi = 0.2$, $R = 10$).

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 are also taking place, so the higher viscosity of the system could be associated with a lower mobility of the charges, but the main mechanism responsible for the charge transport is different from that for 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 together 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 (see figure 3). 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.

The same conclusions can be drawn from the observation of the schlieren images obtained when an electric field is applied to our samples. When a field at relatively low frequency is applied to the AOT-based system, some weak electrorheological structure is observed at very short times, but it is soon destroyed by the establishing of convective motions in the fluid (see figure 5 (top)). In contrast, in the case of lecithin a well defined ordered structure is observed in a transient of several minutes (see figure 5 (bottom)). After enough time the regular columnar aggregates slowly move, collapsing into larger aggregates, and becoming rather disordered as time goes on.

This effect can be understood by looking at the temporal behaviour of the system conductivity under different electric fields. At low field strength the conductivity of the system increases over time, suggesting that the applied field induces the formation of a connected
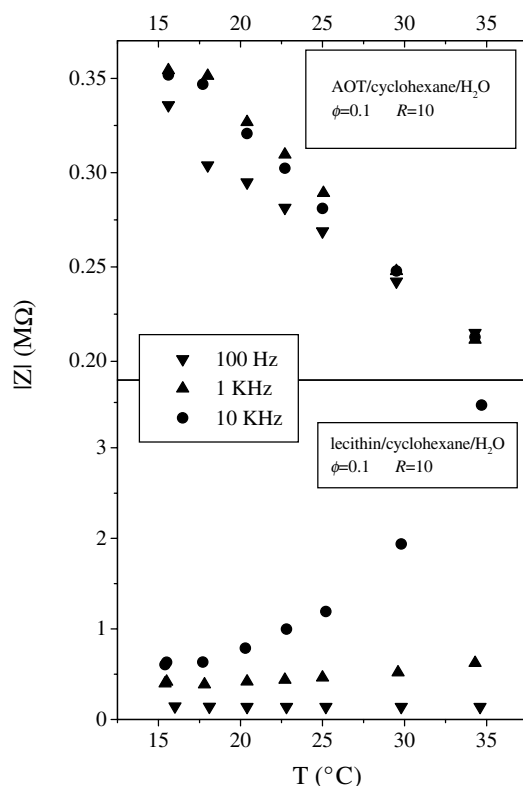
Figure 5. Temperature evolution of the measured impedances for AOT/cyclohexane/water (top) and lecithin/cyclohexane/water (bottom) systems.

structure bridging the electrodes, in a similar fashion to that apparent for conventional electrorheological fluids. At high field strength, the applied field induces a non-negligible current through the sample, and the temperature of the system increases, destroying the interconnectivity.

The observation that the more structured (and the more viscous) sample is characterized by a higher conductivity confirms our working hypothesis of the existence of a structure built up through the formation of branch points.

4. Conclusions

Our experimental results show that the sol–gel transition observed, after addition of water, in lecithin reverse micelles above a critical value of the volume fraction is due to the formation of a percolated structure of branched wormlike micelles. The branching process is triggered by the addition of water that interacts with the head groups of lecithin, promoting the necessary inversion of the micellar surface curvature.

References

[1] Scartazzini R and Luisi P L 1988 *J. Phys. Chem.* **92** 829
[2] Aliotta F, Fontanella M E, Sacchi M and Vasi C 1997 *Physica* A **247** 247–64

[3] Schurtenberger P, Scartazzini R, Magid L J, Martin E L and Luisi P L 1990 *J. Phys. Chem.* **94** 3695

[4] Cates M E 1987 *Macromolecules* **20** 2289

[5] Cevc G and Marsh D (ed) 1987 *Phospholipid Bilayers; Physical Principles and Models* vol 5 (New York: Wiley)

[6] Robinson B H, Fletcher P D I and Howe A M 1987 *J. Chem. Soc. Faraday Trans.* **1** 83

[7] Kotlarchyk M, Huang J S and Chen S H 1985 *J. Phys. C: Solid State Phys.* **89** 4382

[8] Di Biasio A, Cametti C, Codastefano P, Tartaglia P, Rouch J and Chen S H 1993 *Phys. Rev.* E **47** 4258

[9] Christopher D J, Yarwood J, Belton P S and Hills B P 1992 *J. Colloid Interface Sci.* **152** 465

[10] Moran P D, Bowmaker G A, Cooney R P, Bartlett J R and Woolfrey J L 1995 *Langmuir* **11** 738

[11] Willard D M, Riter R E and Levinger N 1998 *J. Am. Chem. Soc.* **120** 4151