Conductivity of an inverse lyotropic lamellar phase under shear flow

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We report conductivity measurements on solutions of closed compact monodisperse multilamellar vesicles (the so-called "onion texture") formed by shearing an inverse lyotropic lamellar L_α phase. The conductivity measured in different directions as a function of the applied shear rate reveals a small anisotropy of the onion structure due to the existence of free oriented membranes. The results are analyzed in terms of a simple model that allows one to deduce the conductivity tensor of the L_α phase itself and the proportion of free oriented membranes. The variation of these two parameters is measured along a dilution line and discussed. The high value of the conductivity perpendicular to the layers with respect to that of solvent suggests the existence of a mechanism of ionic transport through the insulating solvent.

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I. INTRODUCTION

Under shear flow, lyotropic lamellar phases present stationary states separated by dynamic transitions [1–5]. At low and high shear rates, the lamellas are generally oriented perpendicular to the shear gradient direction. For intermediate shear rates, the bilayers rollup around each other to form a closed compact assembly made of monodisperse multilamellar vesicles (referred to in literature as "onions") [1]. These vesicles are not spherical but indeed polyhedral as revealed by cryofracture images [6]. Their size that results from a balance between viscous and elastic stresses is fixed by the shear rate. It and can be tuned continuously from a tenth of a micrometer to a few micrometers by changing the shear rate [1]. This texture of L_α phases is of primary interest to investigate the properties of such phases since the density of defects is controlled and can be tuned continuously by merely changing the value of shear rate. This is why this method has already been used successfully to study the viscoelastic properties of monodisperse elastic spheres in a closed compact assembly (100% volume fraction) [7]. It is known to be experimentally difficult to determine the values of the elements of conductivity tensor corresponding to such a lamellar phase, its conductivity being very sensitive to the orientation and density of defects. Therefore, the natural way to perform such an experiment would require to avoid any defects and indeed to align the lamellas between electrodes but this is experimentally difficult to realize. However, by using a simplified version of the effective medium theory, where the system is modeled as a collection of resistors coupled in series, it has been shown that the overall conductivity of an inverse lyotropic lamellar powder can be related to $\sigma_\parallel$, the conductivity parallel to the plane of layers [8]. This element of the conductivity tensor can be also determined by measuring the conductivity of a sponge phase of same membrane composition [9]. To our knowledge, no direct determination of $\sigma_\perp$, the conductivity perpendicular to the layers, has been yet published. In the absence of permeation between layers, its value should be zero since for inverse L_α phases, the oil solvent being insulator. Therefore, determination of this quantity is very important since its value gives useful information about possible permeation mechanisms [10,11].

In the present paper, we propose a method to measure simultaneously $\sigma_\parallel$ and $\sigma_\perp$ in inverse L_α phases. The idea consists of performing conductivity measurements under shear flow. This technique has been developed a few years ago and is widely used to probe the coupling between structure and flow in complex fluids [12,13]. In the case of L_α phases, it has been used to discriminate between the different steady states of the orientation diagram [14] and more recently to study the dynamics of formation of onions [15]. Hereby, the shear flow is used to form an onion phase in its stationary state and therefore to control perfectly the defect density within the L_α phase. The conductivity is measured in the three main directions of space (flow, shear gradient and vortex directions) as a function of shear rate (i.e., onion size) and lamellar spacing. Some of us have already performed a similar experiment in a L_α phase made of sodium-di-2-ethylhexyl sulfosuccinate and salt for which the solvent is conducting [14]. This previous work has shown that the conductivity is isotropic in the onion phase region and varies linearly with the inverse of the onion size. In the present paper, we study an inverse L_α phase for which the conductivity is mainly due to the diffusion of ions in the water film inside the membrane since the solvent is now insulating. The results we obtain on this system differ considerably from those of Ref. [14]. In particular, we show that the conductivity in the onion phase region is not any longer isotropic due to the existence of some free oriented membranes along the flow. We analyze our results within a simple resistor model, which allows one to estimate the elements of the conductivity tensor of the L_α phase itself and the proportion of free oriented membranes. We derive a high value of the conductivity perpendicular to the layers (with respect to that of solvent) that suggests the existence of some ionic permeation between adjacent layers. We study these parameters as a function of lamellar spacing and evoke some possible mechanisms of permeation.

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A. Material

The lamellar phase that we studied is a quaternary system made of sodium dodecylsulfate (SDS), pentanol, dodecane, and water, with a SDS/water mass ratio of 1.55. The phase diagram of this system has been extensively studied by Roux and Bellocq [16]. SDS has been purchased from Touzart & Matignon Co. (France) and has been used without any further purification. The distilled water is filtered through millipores and its conductivity is 18 MegΩ^{-1} cm^{-1}. The dodecane and pentanol have been purchased from Aldrich and are used as received. A lamellar solution composed in weight percentage of 15.1 SDS, 23.35 water, 14.55 pentanol, and 47 dodecane is prepared. This lamellar phase can be seen as constituted of water films surrounded by surfactant molecules and separated by a solvent which here is a mixture of 91% weight fraction of dodecane and 9% of pentanol. The lamellar phase is stabilized by undulation interaction [17] and therefore the intermembrane distance can be continuously changed by dilution from 40 Å up to a few hundreds. To study the conductivity tensor along a dilution line of membranes, we have diluted the initial lamellar solution with the solvent (i.e., a mixture of 91% dodecane and 9% pentanol in weight fraction). The smectic spacing d can be varied then continuously from 100 to 300 Å. Along this dilution path, the membrane thickness, δ remains fixed and is 26 Å [16]. The solvent conductivity is extremely low so the electrical conductivity of this phase results from the diffusion of ions in the water film inside the membrane. An estimation of the conductivity of the membrane σ_{mem} is made by measuring conductivity of membrane of a sponge phase of same membrane composition [9]. Such a sponge phase can be prepared by adding slightly some dodecane to the L_α phase. The electrical conductivity of this sponge phase, σ_{L3} is then known to be two-thirds of that of the in-plane conductivity $\sigma_\parallel$ of the corresponding perfectly oriented L_α phase [9,14]. Since for an inverse L_α phase, the conductivity of solvent is extremely low above that of the membrane, the conductivity of the membrane is simply related to that of $\sigma_\parallel$ and σ_{L3} through the following relation:

$$\sigma_{\text{memb}} = \sigma_\parallel \frac{d}{\delta} = \frac{2}{3}\sigma_{L3}\frac{d}{\delta}.$$

Using this experimental procedure, we have found for the conductivity of the membrane of our system a value of 42 $\times 10^{-3}\,(\Omega\,\text{cm})^{-1}$.

B. Experimental section

1. Conductivity measurements

Conductivity measurements under shear flow have been performed in temperature controlled ($\pm 0.2\,°\text{C}$) Couette cells whose stator and rotor radii are respectively, 27 and 28 mm. Both rotor and stator are made of insulating material and equipped with electrodes. In order to access to the conductivity in the three main directions (i.e., the directions of velocity $\overline{V}$, shear gradient $\nabla\overline{V}$, and vortex $\overline{Z}$), three different set of cells have been designed. A detailed description of the cells can be found in Refs. [14,15]. The position of electrodes, which are mounted on the stator or/and rotor, is determined for each set on symmetry grounds. The electrodes are connected to a lock-in amplifier, which allows measurements of the complex impedance in the large frequency range (1 Hz–15 MHz). The impedance measured by the lock-in amplifier can then be related to that of the sample. The conductivity and dielectric constants of the sample at frequency v can be derived from the measured complex admittance $Y(v)$ of the sample

$$Y(v) = \lambda_r \sigma(v) + 2\pi v \lambda_c \varepsilon_0 \varepsilon_r(v), \tag{1}$$

where λ_r and λ_c are cell constants that have been determined measuring the complex admittance of a series of salted water and pure alcohol solutions, whose conductivity and dielectric constant are known. The conductivity of the L_α phase shows no frequency dependence in the range 1 kHz–15 MHz with or without shear flow. All measurements were made at 10 kHz. Since no frequency dependence is found, the results obtained at this frequency can be identified with the zero frequency conductivity.

The experiment has been done as follows. The L_α phase (corresponding to an intermembrane distance d) is loaded into one of the measurement cells. In order to prepare an onion phase, the material is sheared at a constant shear rate (for which the onion phase is stable) for typically an hour after a constant conductivity is reached. The value of the conductivity is then measured.

2. Small angle light scattering

A transparent Couette cell made of plexiglas cylinder was used for small angle light scattering. It consists of two concentric cylinders whose radii are 24 and 25 mm. The inner cylinder (stator) is kept fixed while the outer one (rotor) rotates. Depending upon rotor angular velocity, the shear rate can be varied from 0 to 800 s^{-1}. The incident laser beam (30-mW He-Ne laser), which is parallel to the shear gradient direction, probes scattering in the plane $\overline{q_v}$ (velocity direction) and $\overline{q_z}$ (vorticity direction). The diffusion pattern is visualized on a screen at distance L from the scattering volume. In the onion phase, the diffusion pattern is a Bragg ring whose radius is directly related to the characteristic size of the onions. We measured the onion radius size R for different shear rates of preparation and in agreement with reference [1], we have found that it varies according to: $R(\mu\text{m}) = 13.08/\sqrt{\dot{\gamma}(\text{s}^{-1})}$.

C. Results and discussion

Figure 1 shows the evolution of the conductivity in the onion phase region as a function of the applied shear rate along the three main directions. The conductivity increases with shear rate along the flow $\overline{V}$ and vorticity $\overline{Z}$ directions whereas it decreases along the shear gradient direction $\nabla\overline{V}$. This anisotropy seems to vanish if one extrapolates at zero shear rate the conductivities measured in each direction. Indeed, a closer look reveals that the conductivities along $\overline{V}$

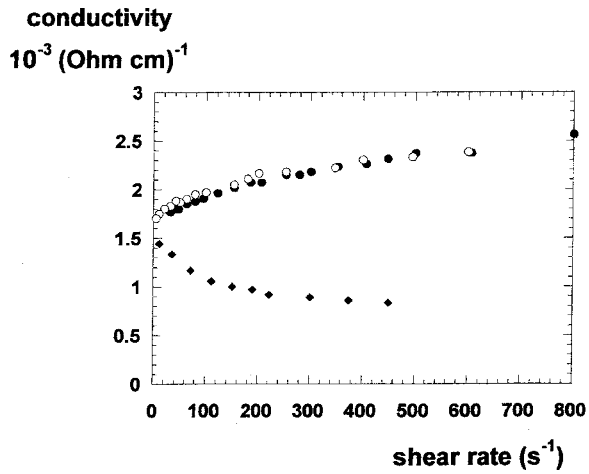

FIG. 1. Variation with applied shear rate of the conductivities measured in the three main directions. Black diamonds, open circles and closed circles represent, respectively, conductivities measured in the shear gradient, vertex and velocity directions. The composition of the lamellar phase, given in weight percent, is: 47% dodecane, 15.1% SDS, 23.35% water, and 14.55% pentanol.

and $\overline{Z}$ are almost identical and vary linearly with the inverse of the onion size [Fig. 2(a)]. In the $\nabla\overline{V}$ direction, the dependence of conductivity with shear rate is different. In this direction, it is the inverse of the conductivity that varies linearly with the inverse of the onion size [Fig. 2(b)]. In order to explain this anisotropy, we consider a simple model based on the assumption that under shear flow, the onions organize into a stack of planes perpendicular to the shear gradient direction (Fig. 3). The planes slide with respect to each other, and between them one assumes that some domains of lamellas are oriented along the flow and vorticity directions. Recall that the L_α phase of this system orientates in a similar way at high shear rates (i.e., beyond the shear rates for which the onion phase is stable) [1]. Therefore, if some lamellas are present between the onion stacking planes (i.e., monodomains), they are oriented along the flow direction since the local shear rate is likely high in these sliding planes. Let us denote D, the average thickness of sliding planes between two onion planes. Indeed, according to optical microscopy observations and small angle scattering experiments such as neutrons and x-ray, this proportion of oriented lamellas must be quite small since no noticeable anisotropy is revealed by these techniques [1]. In what follows and for sake of simplicity, one assumes that this structure is periodical along the shear gradient (see Fig. 3). Although, this last point seems at first a rather strong assumption, it does not alter the predictions of the model. In the onion planes, the structure (and therefore its conductivity) is isotropic. The conductivity related to such plane corresponds to that of a single onion: σ_{onion}. In the interstices between onion planes, the lamellas are oriented. The conductivity of these regions must be represented therefore by a tensor whose elements are: $\sigma_{\overline{v}}^{D\text{-plane}} = \sigma_{\overline{z}}^{D\text{-plane}} = \sigma_{\parallel}$ and $\sigma_{\nabla\overline{v}}^{D\text{-plane}} = \sigma_{\perp}$, where $\sigma_{\parallel}$ and $\sigma_{\perp}$ correspond, respectively, to the conductivity parallel and perpendicular to the oriented lamellas. The conductivity tensor of the solution σ can be derived from the electrical equivalent impedance of an elementary cell, Z_{cell} (Fig. 4), according to Ohm's law. In the zero frequency limit, the equivalent impedance of the elementary cell, in the shear gradient direction, is the association of two resistors in serie (Fig. 4),

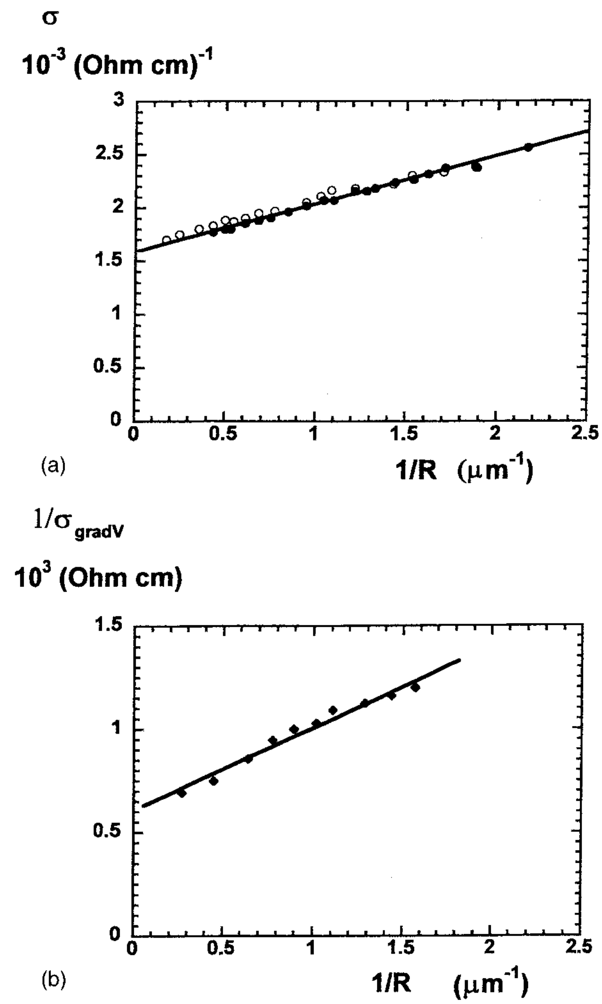

FIG. 2. (a) Variation of the conductivities measured in the flow ($\vec{V}$) and vertex ($\vec{Z}$) directions with the inverse of the onion size R. Closed and open circles represent the conductivities measured in the flow and vorticity directions. The composition of the lamellar phase is similar to that of Fig. 1. The best linear fit gives: $\sigma = 1.6 + 0.44/R$, where σ and R are, respectively, given in $10^{-3}\,(\Omega\ \text{cm})^{-1}$ and micrometers. (b) Variation of the inverse of the conductivity along the shear gradient $\nabla\overline{V}$ direction with the inverse of the onion size R. The composition of the lamellar phase is identical to that of Fig. 1. The best linear fit gives: $1/\sigma_{\text{grad } V} = 0.60 + 0.41/R$, where the conductivity and the size R are, respectively, given in $10^{-3}\,(\Omega\ \text{cm})^{-1}$ and micrometers.

$$Z_{\nabla\overline{v}}^{\text{cell}} = \mathcal{R}_{\text{onion}}(R) + \mathcal{R}(\sigma_{\perp}, D, 4R^2), \tag{1a}$$

where $\mathcal{R}_{\text{onion}}(R)$ is the equivalent resistor of a cubic onion of radius R and $\mathcal{R}(\sigma, L, S)$ is the resistance of an element of length L, surface S, and conductivity σ. In the velocity and in the vorticity directions, the equivalent impedance of the elementary cell is identical and the association in shunt of two resistors (Fig. 4),

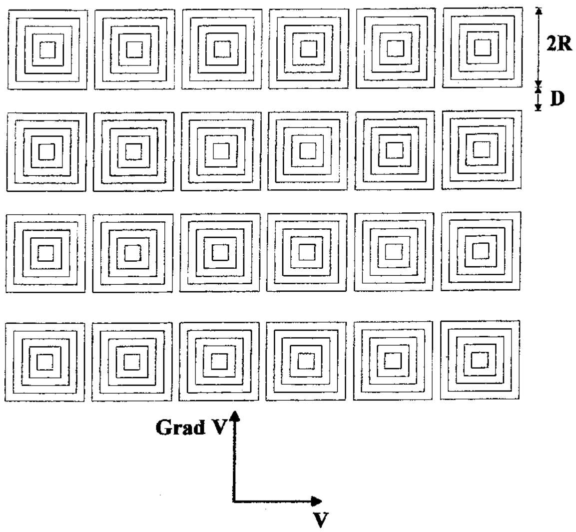

FIG. 3. Schematic representation in our model of the structure of the onion phase under shear flow. The onions organize into a stack of planes perpendicular to the shear gradient direction. These planes slide with respect to each other. The distance between two adjacent planes is D.

$$\frac{1}{Z_{\overline{v}}^{\mathrm{cell}}}=\frac{1}{Z_{\overline{z}}^{\mathrm{cell}}}=\frac{1}{\mathcal{R}_{\mathrm{onion}}(R)}+\frac{1}{\mathcal{R}(\sigma_{\parallel},2R,2RD)}. \tag{1b}$$

According to Ohm's law, it follows:

$$\sigma_{\overline{z}}=\sigma_{\overline{v}}=\frac{\sigma_{\mathrm{onion}}R+\sigma_{\parallel}D}{R+D} \tag{2a}$$

and

$$\sigma_{\nabla\overline{v}}=\frac{\sigma_{\mathrm{onion}}}{1+\dfrac{D\sigma_{\mathrm{onion}}}{R\sigma_{\perp}}}\left(1+\frac{D}{R}\right). \tag{2b}$$

Within the inequality $D/R \leqslant 1$, these equations lead respectively to

$$\sigma_{\overline{v}}=\sigma_{\overline{z}}\approx a_{\overline{v}}+\frac{b_{\overline{v}}}{R}=\sigma_{\mathrm{onion}}+\sigma_{\parallel}\frac{D}{R} \tag{3a}$$

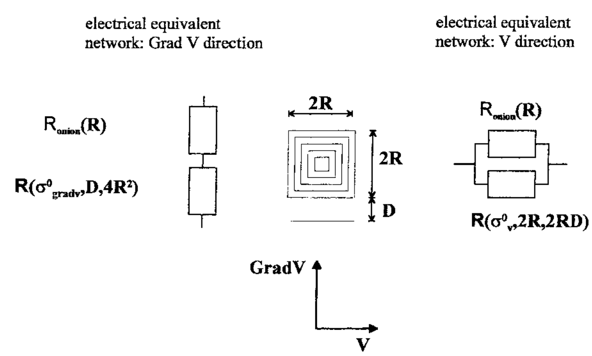

FIG. 4. Schematic representation of the elementary cell of the model described in Fig. 3 and its electrical equivalent networks along the shear gradient and the velocity direction.

TABLE I. The compositions of the different solutions and the corresponding smectic distances d.

SDS (wt. %)	Pentanol (wt. %)	Dodecane (wt. %)	Water (wt. %)	Φ_m (%)	d (Å)
15.1	14.55	47	23.35	41.0	103.7
13.75	14	50.9	21.35	37.45	115.8
12.75	13.65	53.85	19.75	34.4	127.9
11.15	13.05	58.5	17.30	29.7	152
10.20	12.70	61.25	15.85	27.0	170
9.28	12.34	64	14.38	24.3	192.5
8.4	12	66.6	13.00	21.85	218
7.4	11.65	69.5	11.45	19.1	254.9
6.25	11.15	72.9	9.70	15.9	314.8

and

$$\frac{1}{\sigma_{\nabla\overline{v}}}\approx a_{\nabla\overline{v}}+\frac{b_{\nabla\overline{v}}}{R}=\frac{1}{\sigma_{\mathrm{onion}}}+\frac{D}{\sigma_{\perp}R}. \tag{3b}$$

These predictions are in qualitatively good agreement with our measurements provided the proportion of oriented lamellas per onion plane (i.e., D) is constant [see Figs. 2(a) and 2(b)]. Extrapolating at zero shear rate (i.e., $R\to\infty$), the conductivities measured in the three main directions: $\overline{V}$, $\overline{Z}$, and $\nabla\overline{V}$, in the onion phase [Figs. 2(a) and 2(b)] yields the same value: $\sigma_{\mathrm{onion}}\approx 1.6\times 10^{-3}\,(\Omega\,\mathrm{cm})^{-1}$. At this point, it is worth mentioning that the assumption, we made in our model (assuming the conductivity in the onion planes to be isotropic), is experimentally checked. Indeed, in a more refined version of our model, taking into account an eventual anisotropy in the onion planes, the elements of the conductivity tensor are given by extrapolation of Eqs. (3a) and (3b) at zero shear rate (i.e., infinite onion size). However, these extrapolations lead experimentally to similar values of conductivity whatever the direction of measurement is. The experimental derivation of D and $\sigma_{\perp}$ [by Eqs. (3a) and (3b)] requires the determination of $\sigma_{\parallel}$ by other means. Because the solvent conductivity and $\sigma_{\perp}$ are extremely low above the membrane, this conductivity is simply related to that of the membrane, σ_{memb} by

$$\sigma_{\parallel}\approx\frac{\delta}{d}\sigma_{\mathrm{memb}}, \tag{4}$$

where δ is the membrane thickness. For the L_{α} phase studied here, we obtain a value of $10.6\times 10^{-3}\,(\Omega\,\mathrm{cm})^{-1}$. Once this value is known, D can be determined using Eq. (3a): $D=b_{\overline{v}}/\sigma_{\parallel}$ ($b_{\overline{v}}$ is determined by fitting the conductivity data of Fig. 2(a) according to Eq. (3a). The value of $\sigma_{\perp}$ can then be deduced by using Eq. (3b): $\sigma_{\perp}=D/b_{\nabla\overline{v}}$ ($b_{\nabla\overline{v}}$ is determined by fitting the conductivity data of Fig. 2(b) according to Eq. (3a). The value of $\sigma_{\perp}$, $1.2\times 10^{-4}\,(\Omega\,\mathrm{cm})^{-1}$, which is much higher than that of the solvent and about 10% of $\sigma_{\parallel}$, suggests therefore the existence of a transport mechanism of ions through the insulating solvent. Similarly, we find that on average, there are a few oriented lamellas per onion plane.

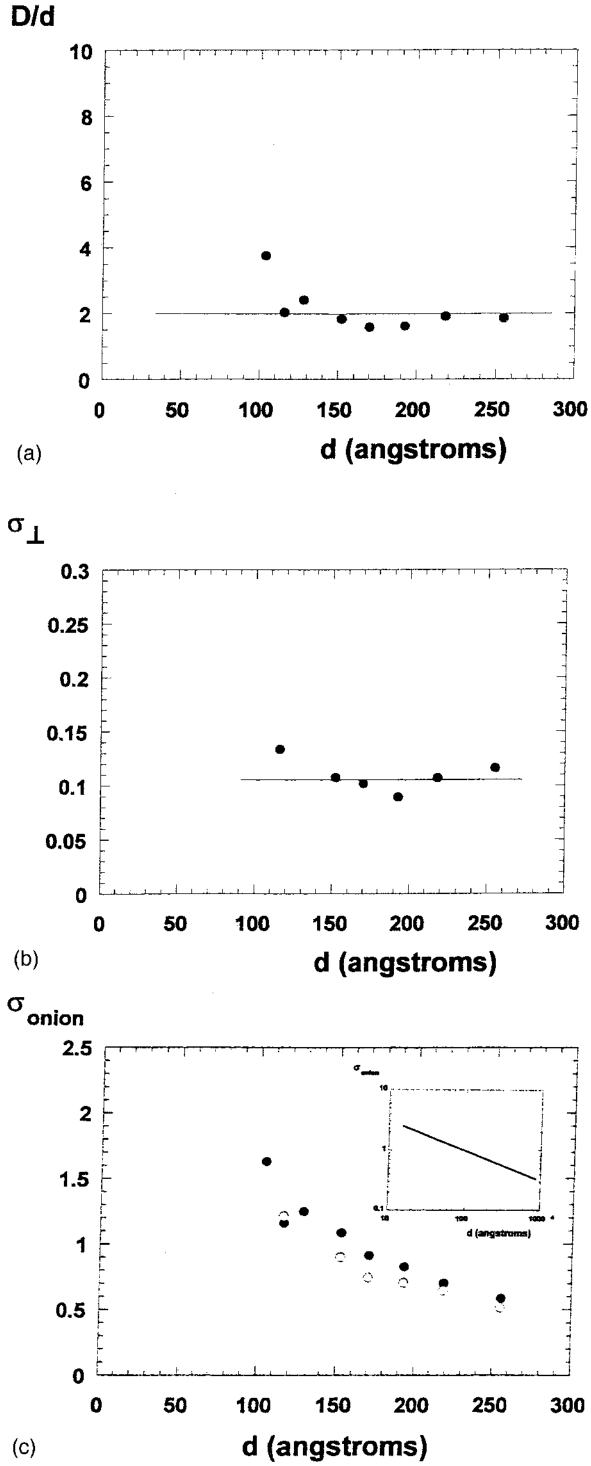

FIG. 5. (a) Variation of D (the thickness of domains of oriented lamellas per onion) with smectic distance, d. (b) Variation of $\sigma_\perp$ with d, the smectic distance. (c) Variation of the effective conductivity of onion σ_{onion} with the distance between adjacent membrane d. Units on the y axis (corresponding to conductivity) are given in 10^{-3} (Ohm cm^{-1}). Black circles correspond to the values of σ_{onion}, determined by extrapolating, for each dilution, Equations (3a) and (3b) at zero shear rate. Inset: value of the effective conductivity of the onion computed numerically from the model detailed in the Appendix.

Since R is of the order of a few micrometers and d is 100 Å, it is interesting to note that this last result confirms *a posteriori* the approximation $D/R \ll 1$ that we made previously.

We have performed a systematic study along a dilution line for the membranes. In order to do so, the initial lamellar phase (whose composition in weight fraction is: 15.1% SDS; 23.35% water; 14.55% pentanol, and 47% dodecane) is diluted with a mixture of 91% weight fraction of dodecane and 9% of pentanol. The variation of the smectic distance d with membrane volume fraction on this system has previously been measured by Freyssingeas [18] using small angle x-ray scattering. These authors have shown that for a weight fraction water/SDS$=1.55$,d varies according to

$$d(\text{Å}) = \frac{35.6 - 7.9\ln(\Phi_m)}{\Phi_m},$$

where Φ_m is the volume fraction of membrane. This relation takes into account the logarithmic correction due to the excess area surface induced by the strong thermal fluctuations [16] of the membrane. Table I gives the compositions, the membrane volume fractions and the smectic distances of the different solutions we have studied.

For each solution, we have measured the conductivities in the three main directions and the size R of the multilamellar vesicles as a function of applied shear rate. Fitting the conductivities according to Eqs. (3a) and (3b) gives the values of $a(z)$, $b(z)$, $a(\nabla_v)$ and $b(\nabla_v)$. We have calculated $\sigma_\parallel$ from Eq. (1) and have deduced the average thickness D of the sliding planes from relation (3a): $D = b(z)/\sigma_\parallel$. Figure 5(a) shows the variation of D/d (i.e., the average number of oriented lamellae per sliding planes) as a function of d. D/d seems to be independent on membrane concentration and close to 2. This result appears therefore to be an intrinsic property of the onion texture. Such a small quantity of oriented lamellas (less than 1%) has not be observed with other techniques such as small angle x-ray or small angle neutron scattering. Thus, conductivity measurements under shear flow is a very powerful technique to probe small anisotropy in low conducting materials. Combining Eqs. (3a) and (3b) permits to derive an expression for the conductivity perpendicular to the layers:

$$\sigma_\perp = \frac{b(z)}{\sigma_\parallel b(\nabla_v)}.$$

Figure 5(b) shows the variation of $\sigma_\perp$ as a function of d. The high value of $\sigma_\perp$ (compared to that of solvent) reveals the existence of an ion transport mechanism through the insulating solvent. This transport of ions may result from: (1) dynamical contacts between adjacent layers due to thermal fluctuations (the L_α phase of this system is stabilized by undulation interaction); (2) "handle" type defects connecting adjacent layers; (3) Burger's vector 2 screw dislocations [19,20]; and; (4) the presence of microemulsion droplets in the continuous phase.

Our experimental results show that $\sigma_\perp$ is almost independent on d. This likely rules out the first mechanism since the

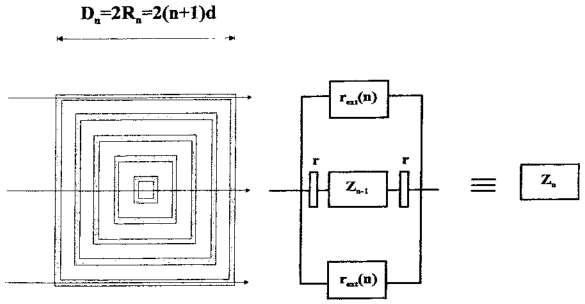

FIG. 6. Schematic representation of an onion of radius $R_n=(n+1)d$ and of its equivalent electrical network.

average distance between thermal contact is d and the conductivity should therefore vary as d^{-2}. However, it agrees conversely with the possible existence of microemulsion droplets, which should act as charge carriers through the continuous phase, or with the existence of defects: handles connecting adjacent layers or Burger vector 2 screw dislocations. If defects (handles or screw dislocations) are responsible for the ion transport between adjacent layers, the surface density of defects Φ_s can be estimated, by $\Phi_s=\sigma_\perp/\sigma_{\mathrm{mem}}$. This yields a value independent of the smectic distance d and typically of the order of 1%.

In order to check further the validity of our model, we have estimated the equivalent conductivity of an onion of size R, $\sigma_{\mathrm{onion}}(R)$, in terms of $\sigma_\parallel(d)$ and $\sigma_\perp(d)$. Qualitatively, the value of this conductivity should lie between $\sigma_\parallel$ and $\sigma_\perp$. In order to evaluate it, one derives the equivalent onion conductivity by computing the equivalent impedance of an onion of size R, modeled as a cube made of concentric layers (see the Appendix). Above a few tens of layers (therefore for onions of micrometer size), numerical evaluations show that the $\sigma_{\mathrm{onion}}(R)$ does not depend anymore on the onion size. The value of this equivalent conductivity σ_{onion} typically $10^{-3}\,(\Omega\ \mathrm{cm})^{-1}$ is in good agreement with the experimental values deduced by extrapolating at zero shear rate (or infinite onion size) the curves depicted in Figs. 3(a) and 3(b). Nevertheless, its variation with dilution shows some deviations compared to experimental results. Indeed in our model the onion conductivity varies according to $\sigma_{\mathrm{onion}}\propto 1/\sqrt{d}$ (see inset in Fig. 5(c) whereas experimental results yield a stronger variation with d (a fit leads to d^{-1}). This difference is not surprising considering the simplicity of our onion model. In particular, this model does not take into account for the variations of the smectic distance between the center of the onion and the outer layers.

II. CONCLUSION

Due to their large sensitivity, conductivity measurements performed under shear flow reveal the existence of a small anisotropy in the onion phase, contrary to small angle light, x rays or neutron scattering experiments. This anisotropy results from the existence of some oriented lamellas between onions. A simple model based on an equivalent association of resistors allows one to measure for the first time as far as we know, the conductivity perpendicular to the layers $\sigma_\perp$ and the proportion of oriented membranes. The $\sigma_\perp$ value $(10^{-4}\,(\Omega\ \mathrm{cm})^{-1})$ much higher than that of the solvent and independent on membrane concentration, reveals the existence of a conduction mechanism between successive layers likely due to the existence of microemulsion droplets or to defects in the continuous phase. Finally the proportion of free oriented membrane per onion, which is constant and independent of dilution, appears to be an intrinsic property of the onion structure under shear flow in this system.

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APPENDIX

Let us consider a cubic onion made of n successive concentric lamellas. Its size corresponds therefore (Fig. 6) to: $D_n=2(n+1)d$. To compute the effective conductivity of this onion, in terms of $\sigma_\parallel$ and $\sigma_\perp$ (the conductivity parallel and perpendicular to the layers of the constituting lamellar phase), one has to evaluate its impedance: Z_n. This calculation can be made if one notices that the onion impedance is the association of two impedances in shunt. The ions can travel by the external membrane of the onion or by inside. The impedance associated with the conduction along the external membrane is given by,

$$\frac{1}{R_{\mathrm{ext}}(n)}=\frac{2}{r_{\mathrm{ext}}(n)}=2\sigma_\parallel\left(\frac{dD_{n-1}}{D_n}+d\right). \tag{A1}$$

The impedance associated with the conduction trough the onion inside is

$$R_{\mathrm{int}}(n)=2r+Z_{n-1}=\frac{2d}{\sigma_\perp D_{(n-1)}^2}+Z_{n-1}, \tag{A2}$$

where r represents the electrical resistor associated with the ion transfer between layer n and layer $n-1$.

By combining Eqs. (A1) and (A2), one obtains the following recursive relation,

$$\frac{1}{Z_n}=2\sigma_\parallel d\left(1+\frac{D_{n-1}}{D_n}\right)+\frac{1}{Z_{n-1}+\dfrac{2d}{\sigma_\perp D_{n-1}^2}}. \tag{A3}$$

The electrical resistance corresponding to $n=0$ can be evaluated since it corresponds to that of a cubic vesicle of radius $d/2$ and membrane thickness,

$$Z_0=\frac{\delta}{\sigma_{\mathrm{mem}}(d-\delta)^2}+\frac{d}{\sigma_\perp(d-\delta)^2}. \tag{A4}$$

In order to compute the effective conductivity associated with an onion of size D_n, one uses Ohm's relation,

$$\sigma_{\text{onion}}(n) = \frac{1}{D_n Z_n}. \tag{A5}$$

We compute this value numerically taking: $\sigma_{\perp}(d) = 0.06 \times 10^{-3}\,(\Omega\,\text{cm})^{-1}$ and $\sigma_{\parallel} = \sigma_{\text{memb}}\delta/d$ with $\delta = 26\,\text{Å}$ and $\sigma_{\text{memb}} = 42 \times 10^{-3}\,(\Omega\,\text{cm})^{-1}$. When n tends to infinity, the value converges. Indeed, for $n \geqslant 100$, the effects of finite size are negligible. Therefore for smectic distances of a few tenth of angstroms, the effective conductivity of onion of micrometer size is independent of their size.

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