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Surface Shear Viscosity and Phase Transitions of Monolayers at the Air-Water Interface

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Abstract. — The canal method has been employed to measure the in-plane steady shear viscosity of monolayers of bolaform lipids extracted from the membrane of the thermophilic microorganism Sulfolobus solfataricus. Monolayers were formed with the polar lipid extract (PLE), which is a mixture of several bolaform lipids, each one endowed with two nonequivalent polar headgroups. Viscosities were obtained from the measured flows by using the equation introduced by Joly; this equation contains a semiempirical parameter $A$, which takes into account the monolayer-subphase mechanical coupling. Measuring the flows for two different substances (PLE and oleic acid) and channel widths, the monolayer viscosities and the parameter $A$ were determined at the same time. The analysis of the viscosity data according to the free area model shows evidences of the molecular conformational changes matching monolayer phase transitions.

Introduction

Monolayer films at the air-water interface are resistant to an applied shear stress in the plane of the surface. Analogously to bulk viscosity of three-dimensional matter, they exhibit a two-dimensional surface viscosity. Surface viscosity measurements are useful in the investigation of monolayer properties: for instance, the behaviour of surface viscosity as a function of temperature and surface pressure can indicate the presence of phase transitions in the monolayer and can provide information about miscibility of different compounds [1]; surface viscosity also plays an important role in the Langmuir-Blodgett deposition process [2].

A monolayer moving under the effect of a surface pressure gradient carries some of the underlying water with it, as a consequence of lack of slippage between monolayer molecules and the subphase. When measuring monolayer shear viscosity, it is important to separate the inherent surface resistance to flow from the contribution due to the subphase friction, in order to obtain absolute measurements. Although it has even been proposed to redefine surface shear viscosity neglecting completely the subphase effect [3], several treatments have been worked out in which this effect is taken into account, particularly in the case of measurements performed by means of the canal method, which is the two-dimensional analog of the Ostwald viscometer.

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used for bulk liquids. The canal method turns out to be particularly appropriate for films of low Newtonian viscosity, since it is about two orders of magnitude more sensitive than other methods [4].

In this work we use the canal method to obtain the surface viscosity of monolayers of archaeal bolaform lipids. Following the approach introduced by Joly [5], the measurable surface flow is related to monolayer viscosity and to a term describing the mechanical coupling between the monolayer and the subphase. Both these terms are unknown and are evaluated performing parallel measurements on oleic acid and archaeal bolaform lipids extracted from the thermophilic microorganism Sulfolobus solfataricus.

Sulfolobus solfataricus pertains to the domain of Archaea, which comprise halophilic, methanogenic and thermophilic microorganisms thriving in extreme conditions such as very high salt concentration, lack of oxygen or very high temperatures. On the ground of phylogenetic and structural arguments, they have been classified as the third domain of life, besides Bacteria and Eukarya [6]. Their peculiarity is reflected also in the structure of their membrane lipids, which are mainly composed of saturated isoprenic chains ether-linked to glycerol or more complex polyols. In the case of Sulfolobus solfataricus, membrane lipids are derivatives of caldarchaeol (GDGT, glycero-dialkyl-glycerol-tetraether) and nonitolcaldarchaeol (GDNT, glycero-dialkyl-nonitol-tetraether) and are characterized by the presence of a polar head at each end of a double C40 chain. Monolayers formed with these bipolar lipids at the air-water interface have been characterized by means of pressure-area isotherms [7,8] and epifluorescence microscopy [9]; however, no information about their surface viscosity has been provided so far. Our results are compared with the corresponding viscosities of fatty acids and monopolar phospholipids.

Recently it has been proposed that the relationship between surface viscosity and molecular area is given by the two dimensional analog of the Doolittle equation [10], which is based on the free volume model for diffusion [11,12]. We show that employing this treatment it is possible to obtain indications about the occurrence of molecular conformational changes in the presence of a monolayer phase transition.

Experimental Procedures

The polar lipid extract (PLE) was obtained from the membrane of Sulfolobus solfataricus by an overnight cold extraction in chloroform/methanol (1:1, v/v). PLE is a mixture of several bolaform fractions, each one consisting of two nonequivalent polar headgroups ether-linked to each end of a double C40 alkylc chain [13]. PLE can be assigned a mean molecular weight of 1781. It was dissolved in a mixture of Aristar chloroform (purity 99.4%; BDH Ltd., UK), HPLC grade methanol (purity 99.8%; Inalco, Milan, Italy), and purified water in the ratio 65:25.4 (v/v/v).

Oleic acid (purity 99%) was purchased from Fluka Chemie (Buchs, Switzerland) and was dissolved in Aristar chloroform.

Water was purified by means of a Millipore Milli-Q system including a terminal 0.22 μm filter. The specific resistivity of purified water was greater than 18.2 MΩ·cm.

Monolayers were formed in a circular teflon multicompartment trough of a RCM2-T Monofilmmeter (Mayer Feintechnik, Göttingen, Germany) put in a laminar air flow hood (Steril, Milan, Italy) with a filter for class 10 air quality. From 10 to 25 μl of a 1 mM lipid solution were spread on purified water (pH 5.6) with the aid of a Hamilton microsyringe. At least five minutes were allowed for the spreading solvent to evaporate. Since in principle methanol is soluble in the water subphase, it was checked that the amount of methanol employed as a solvent did not affect the surface properties of the subphase. To this purpose, surface tension measurements were performed. It was found that spreading 40μl of methanol – more than
six times the amount added during the monolayer spreading procedure – on the water surface (200 cc) does not result in any measurable change of the surface tension.

Usually, during compression the film area changed from 323 to 40 cm². The Wilhelmy plate was placed about 1 cm away from the still teflon barrier and 3 cm away from the trough rims. The monolayer was compressed at a barrier speed of 0.2 ÷ 0.5 Å²/(molecule · s). The temperature of the trough was kept at 20 °C.

Surface viscosity measurements were performed employing a procedure referred to as the canal method [5]. The movable barrier of the monofilmmeter was provided with a slit of variable width. After reaching a given monolayer surface pressure on compression, the slit was opened and the film, while keeping constant the surface pressure, was allowed to flow through the slit into the other part of the trough, where the surface pressure remained negligible (Π < 0.1 mN/m). The surface pressure was kept constant by means of a gradual reduction of the film area $S$, carried out by the movable barrier. Recording the area reduction as a function of time, the flow across the mouth of the canal:

$$Q = \frac{\Delta S}{\Delta t}$$

(1)

can be obtained. Surface viscosities were then calculated according to the Joly equation, which is commented in the following section.

Solution of the Flow Equations

For clarity’s sake the main lines of the Joly model are reported. A monolayer flowing at speed $u$ under the pressure gradient $\Delta \Pi$ through a canal of width $D$ and length $l$ (oriented parallel to the $x$-axis, the $z$-axis being normal to the film plane) can be described by the equation:

$$\eta \left( \frac{\partial^2 u(x,y)}{\partial y^2} \right)_{z=0} - \lambda \left( \frac{\partial u(x,y)}{\partial z} \right)_{z=0} + \frac{\Delta \Pi}{l} = 0$$

(2)

where $\lambda$ is the bulk viscosity of the subphase and $\eta$ is the film surface viscosity. The $(x,y)$ plane is the monolayer plane and the film-water interface is at $z = 0$. The solution of equation (2) must satisfy at the same time the Navier equation for the subphase together with appropriate border conditions. In this case the border conditions are: $u(x,D/2,0) = u(x,-D/2,0) = 0$, that is the flow speed is zero at the canal borders. As the problem is rather complex to be solved, usually approximations to equation (2) are considered. Joly [5] assumed that the subphase friction is proportional to the film speed:

$$\frac{\partial u(x,y,0)}{\partial z} = Au(x,y,0)$$

(3)

$A$ is a semiempirical parameter, which is assumed to be independent of the substance, but it is supposed to be a function of the channel width. From the physical point of view, $A$ can be considered as the reciprocal of the thickness of the water layer dragged by the film. Using equation (3), equation (2) yields:

$$u = \frac{\Delta \Pi}{A \lambda l} \left[ 1 - \frac{\text{ch} \left( \sqrt{\frac{\lambda A}{\eta}} y \right)}{\text{ch} \left( \sqrt{\frac{\lambda A}{\eta} D} \right)} \right]$$

(4)
and the flow is given by:

\[ Q = 2 \int_0^\frac{D}{l} u(y) \, dy = \frac{\Delta \Pi}{A \lambda l} \left[ D - 2 \sqrt{\frac{\eta}{A \lambda}} \, \text{th} \left( \sqrt{\frac{A \lambda D}{\eta}} \frac{1}{2} \right) \right] \]  

(In 5)

In the limit of large channels, equation (5) becomes:

\[ Q = \frac{\Delta \Pi}{l} \left[ D \frac{\lambda}{A \lambda} - 2 \sqrt{\frac{\eta}{A^3 \lambda^3}} \right] \]  

(6)

On the other hand, if the subphase drag is completely neglected in equation (2), the two-dimensional analog of the Poiseuille equation is obtained:

\[ Q = \frac{\Delta \Pi D^3}{12 \eta l} \]  

(7)

It is worth noting that the same relationship can be derived from equation (5) in the limit of very narrow channels. Equation (5) and equation (7) were employed to determine surface viscosities from the measured flows.

In principle, in order to apply equation (5), a knowledge of the parameter \( A \) is required. Our approach allows to determine monolayer surface viscosity provided that two surfactants \( \alpha \) and \( \beta \) and two channel widths \( D_1 \) and \( D_2 \) are considered at the same time. No a priori knowledge of \( A \) is required, the only assumption being that \( A \) is independent of the surfactant, but it is a function of the channel width. With these hypotheses, the following set of equations holds:

\[ Q_{ij} = \frac{\Delta \Pi}{A_i \lambda l} \left[ D_i - 2 \sqrt{\frac{\eta_j}{A_i \lambda}} \, \text{th} \left( \sqrt{\frac{A_i \lambda D_i}{\eta_j}} \frac{1}{2} \right) \right] \quad i = 1, 2 \quad j = \alpha, \beta \]  

(8)

Therefore, measuring \( Q_{1\alpha}, Q_{1\beta}, Q_{2\alpha}, Q_{2\beta} \), it is possible to obtain at the same time \( \eta_\alpha, \eta_\beta, A_1, A_2 \). The above relations constitute a set of non-linear equations which was solved by iteration from an initial guess. The iterative procedure has been carried out to a convergence of less than \( 10^{-5} \). The equations for \( Q_{1\alpha} \) and \( Q_{2\beta} \), in which viscosities were chosen as unknown quantities, have a solution provided that the following condition is fulfilled:

\[ Q < \frac{\Delta \Pi D}{A \lambda l} \]  

(9)

From the physical point of view, this inequality means that the flow cannot exceed the flow obtained in the limit of a large channel (Eq. (6)), neglecting the term involving surface viscosity. The equations for \( Q_{2\alpha} \) and \( Q_{1\beta} \), in which \( A \) was chosen as unknown quantity, have a solution if this inequality holds:

\[ Q < \frac{\Delta \Pi D^3}{12 \eta l} \]  

(10)

The physical meaning of this relationship is that surface viscosity cannot exceed the value obtained neglecting the subphase drag (that is, the value yielded by Poiseuille equation).
Results

Figure 1 shows the surface pressure area isotherm of PLE, which displays a behavior similar to that of DPPC. The large inflection, beginning at 150 Å²/molecule and 16 mN/m could indicate the presence of a phase transition [9].

The canal method has been employed to measure the surface viscosity of PLE monolayers formed on distilled water (pH 5.6) at 20 °C. Figure 2 shows the monolayer flows as a function of the surface pressure along the canal and compares them with the flows obtained from DPPC [14] and oleic acid. For PLE, each point is the mean value of at least five different measurements; error bars are calculated according to Student's statistics, assuming a confidence level of 95%. A linear dependence of $Q$ on $\Delta \Pi$ can be observed at pressures as high as $\sim 15$ mN/m.

The set of equations (8) was solved starting from several set of flows ($Q_{1\alpha}, Q_{1\beta}, Q_{2\alpha}, Q_{2\beta}$), which were measured at $\Pi = 5$ mN/m and $T = 20$ °C for $D_1 = 1$ mm and $D_2 = 2$ mm. Oleic acid was considered as surfactant $\alpha$, PLE as surfactant $\beta$. The bulk viscosity $\lambda$ of the water subphase was assumed equal to 0.0100119 poise [15].

The mean values of the resulting parameters are:

$$\eta_{\alpha} = (2.1 \pm 0.3) \cdot 10^{-4} \text{ poise } \cdot \text{cm}$$

$$\eta_{\beta} = (6 \pm 2) \cdot 10^{-5} \text{ poise } \cdot \text{cm}$$

$$A_1 = 18 \pm 3 \text{ cm}^{-1}$$

$$A_2 = 21 \pm 1 \text{ cm}^{-1}$$

Figure 3 shows PLE surface viscosities obtained from equation (5) assuming $A_1 = 18 \pm 3 \text{ cm}^{-1}$.
Fig. 2. — Surface flows as a function of the surface pressure. (●) PLE, $T = 20$ °C, $D = 1$ mm; (△) oleic acid, $T = 20$ °C, $D = 1$ mm; (○) DPPC, $T = 25$ °C, $D = 1.6$ mm (data from Ref. [14]). Monolayers were formed on distilled water (pH 5.6).

Fig. 3. — Surface viscosity of PLE monolayers as a function of the surface pressure. The results obtained from the Poiseuille and Joly equations (Eq. (5) and Eq. (7), respectively) are compared. (●) Joly, $D = 1$ mm; (○) Poiseuille, $D = 1$ mm; (△) Joly, $D = 2$ mm; (△) Poiseuille, $D = 2$ mm. The error bars indicate the 95% confidence interval of the $t$-Student statistics on the measurements.
and \( A_2 = 21 \pm 1 \text{ cm}^{-1} \), as determined previously; these values are compared with the corresponding values calculated according to the Poiseuille law; it can be observed that the former are shifted downwards with respect to the latter of approximately the same amount. This correction, which is \( 1.7 \times 10^{-4} \) poise \( \cdot \) cm for \( D = 1 \) mm, represents the effect of the subphase drag. A comparison of data obtained at different canal widths (Fig. 3) shows that the corrective factor works properly at low pressures, where the corrected data for different canal widths coincide. On the other hand, at higher pressures the correction seems to be insufficient.

On the analogy of the semiempirical law introduced by Doolittle for bulk liquids [11], it has been proposed that monolayer viscosity is governed by the following equation [10]:

\[
\ln \eta_s = \ln \eta_s^0 + B \frac{a_0}{a_f}
\]

where \( a_f = a - a_o \), with \( a \) a molecular area and \( a_o \) occupied molecular area, while \( \eta_s \) and \( B \) are constants whose value is typical of the system examined. Experimentally, for a wide range of bulk liquids, \( B \) turns out to be in the range \( 0.1 \div 1 \) [12]; the free volume theory predicts \( 0.5 < B < 1 \) [11], in good agreement with experiments, in spite of the simplicity of this theoretical approach.

The surface viscosities data obtained using the Joly equation were analyzed in terms of the free area model, according to equation (11). The molecular area \( a \) and the occupied molecular area \( a_o \) were obtained from the pressure-area isotherm of PLE (Fig. 1). Considering as occupied molecular area the collapse area (51.3 \( \text{Å}^2/\text{molecule} \)), two distinct linear regions are found in the plot of \( \ln \eta \) versus \( a_o/a_f \) (Fig. 4a), corresponding to surface pressures \( \Pi < 15 \) and \( > 15 \) \( \text{mN/m} \), respectively. The change of slope occurs around \( a = 150 \) \( \text{Å}^2/\text{molecule} \), which corresponds to the beginning of the large inflection in the pressure-area curve; this inflection had been interpreted, on the ground of epifluorescence microscopy, as the onset of a conformational phase transition [9]. Table I collects the parameters \( B \) and \( \ln \eta_s \), obtained from a linear fit of the data with equation (11). The fit of the data corresponding to surface pressures \( \Pi > 15 \) \( \text{mN/m} \) is shown in Figure 4b. For \( \Pi < 15 \text{ mN/m} \), however, the values obtained taking \( a_o \) as the collapse area have no physical meaning, since \( B \) turns out to be much greater than one and \( \eta_s \) is exceedingly low (Tab. 1). But if in this surface pressure range \( a_o \) is taken equal to the area corresponding to the onset of the inflection (and not to the collapse area), then the parameters obtained lied in the expected ranges. The corresponding fit is shown in Figure 4c. This result is particularly interesting, since it indicates the presence of two different occupied molecular areas as a function of surface pressure, and it constitutes a further evidence in favour of a phase transition in PLE monolayers.

A similar behaviour can be found also for DPPC, which is known to undergo a liquid-expanded to liquid condensed phase transition. Viscosity data and the pressure-area isotherm were obtained from the literature [14] and analyzed with the free area model. Figure 5a shows the free area plot assuming \( a_o \) as the collapse area; the linear fits of the data with equation (11) in the two different regions are reported in Figure 5b (assuming \( a_o \) equal to the collapse area) and in Figure 5c (assuming \( a_o \) equal to the area corresponding to the onset of the inflection in the pressure-area curve). The fitted parameters are reported in Table I, while Table II collects and compares surface viscosities of different amphiphiles.

**Discussion**

The model proposed by Joly describes the flow of a viscous monolayer in a canal assuming that the monolayer is a newtonian two-dimensional fluid. As a consequence, equation (5) predicts a linear relation between \( Q \) and \( \Delta \Pi \). Figure 1 shows that the flows linearly depend on \( \Delta \Pi \) only
Fig. 4. — Analysis of the viscosities of PLE monolayers in terms of the free area model: a) Natural logarithm of the surface viscosity as a function of the ratio between the occupied molecular area, \(a_o\), and the free area, \(a_f\). \(a_o\) was taken equal to the collapse area (51 Å²/molecule); b) as in a) but for values of \(a_f\) in the region \(\Pi > 15\) mN/m. The solid line is the linear regression of the experimental data. The fitted parameters are reported in Table I; c) as in b) but for values of \(a_f\) in the region \(\Pi < 15\) mN/m and \(a_o\) equal to the area before the inflection (149 Å²/molecule).
Fig 5. — Analysis of the viscosities of DPPC monolayers in terms of the free area model: a) Natural logarithm of the surface viscosity as a function of the ratio of the occupied molecular area $a_0$ and the free area, $a_f$. $a_0$ was taken equal to the collapse area (41 Å²/molecule); b) as in a) but for $a_f$ values corresponding to the region $\Pi > 10$ mN/m. The solid line is the linear regression of the experimental data. The fitted parameters are reported in Table I; c) As in b) but for $a_f$ values in the region $\Pi < 10$ mN/m and $a_0$ equal to the area before the inflection (62 Å²/molecule).
Table I. — *Analysis of the surface viscosity of PLE and DPPC monolayers according to the free area model*. The parameters $B$ and $\ln \eta_0$ obtained from a linear fit of the data with equation (11) are reported. In the surface pressure range below the inflection in the $\Pi$—$a$ curve the results obtained for two different $a_0$ values are compared.

<table>
<thead>
<tr>
<th></th>
<th>PLE</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Pi$ (mN/m)</td>
<td>$\eta_0$ (poise cm)</td>
<td>$a_0$ (Å²/mol)</td>
<td>$B$</td>
<td>$\ln \eta_0$</td>
</tr>
<tr>
<td>&gt; 15</td>
<td>1.8 × 10⁻⁴</td>
<td>51</td>
<td>0.25</td>
<td>-8.6</td>
</tr>
<tr>
<td>&lt; 15</td>
<td>8.3 × 10⁻⁷</td>
<td>51</td>
<td>12</td>
<td>-14</td>
</tr>
<tr>
<td>&lt; 15</td>
<td>3.7 × 10⁻⁵</td>
<td>149</td>
<td>0.16</td>
<td>-10</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>DPPC</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Pi$ (mN/m)</td>
<td>$\eta_0$ (poise cm)</td>
<td>$a_0$ (Å²/mol)</td>
<td>$B$</td>
<td>$\ln \eta_0$</td>
</tr>
<tr>
<td>&gt; 10</td>
<td>5.4 × 10⁻⁴</td>
<td>41</td>
<td>0.058</td>
<td>-7.5</td>
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<tr>
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<td>1.5</td>
<td>-10</td>
</tr>
<tr>
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<td>1.8 × 10⁻⁴</td>
<td>62</td>
<td>0.16</td>
<td>-9.0</td>
</tr>
</tbody>
</table>

for relatively low $\Delta \Pi$. The flow curves of DPPC, PLE and oleic acid, which form liquid films, bend towards the pressure drop axis as "dilatant" fluids do [16], that is, the apparent viscosity increases as the shear stress increases. In three-dimensional fluids, this type of behaviour is observed in suspensions of solids at high solid content.

In our experimental system the pressure at the outlet of the canal is kept approximately equal to zero; therefore the pressure gradient $\Delta \Pi$ is equal to the film pressure $\Pi$. For this reason the non linearity between $Q$ and $\Delta \Pi$ (Fig. 2) could be due to the dependence of viscosity on the state of the film, determined by its surface pressure. Following other authors [10], we have considered DPPC, PLE and oleic acid films as two-dimensional Newtonian fluids also at high pressures, assuming that the surface viscosity does not depend on the rate of shear ($du/dy$) but only on the state of the film. There are no direct proofs of the validity of this assumption and,
Table II. — Comparison between the surface viscosities of PLE, DPPC and oleic acid monolayers at the air-water interface ((*) present work).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Subphase</th>
<th>T (°C)</th>
<th>Π (mN/m)</th>
<th>η (poise · cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLE</td>
<td>dist. H₂O</td>
<td>20</td>
<td>5</td>
<td>0.6 × 10^{-4}</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14</td>
<td>1.7 × 10^{-4}</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19</td>
<td>2.4 × 10^{-4}</td>
<td>*</td>
</tr>
<tr>
<td>DPPC</td>
<td>dist. H₂O</td>
<td>25</td>
<td>5</td>
<td>2.4 × 10^{-4}</td>
<td>[14]</td>
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<td></td>
<td></td>
<td>10</td>
<td>4.2 × 10^{-4}</td>
<td>[14]</td>
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<td>14</td>
<td>5.8 × 10^{-4}</td>
<td>[14]</td>
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<td>25</td>
<td>8.4 × 10^{-4}</td>
<td>[14]</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>26</td>
<td>1.7 × 10^{-3}</td>
<td>[10]</td>
</tr>
<tr>
<td>oleic acid</td>
<td>dist. H₂O</td>
<td>20</td>
<td>5</td>
<td>2.1 × 10^{-4}</td>
<td>*</td>
</tr>
<tr>
<td>oleic acid</td>
<td>HCl 0.01 N</td>
<td></td>
<td>2</td>
<td>1.7 × 10^{-4}</td>
<td>[5]</td>
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<td></td>
<td></td>
<td>8</td>
<td>1.5 × 10^{-4}</td>
<td>[5]</td>
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<td></td>
<td></td>
<td>15</td>
<td>3.9 × 10^{-5}</td>
<td>[5]</td>
</tr>
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</table>

Furthermore, this point is not thoroughly discussed in the literature. Experiments designed to separate the effect of Π from that of ΔΠ are now in progress and will be the object of a future work.

In his model, Joly assumed that A only depends on the canal width and it is independent of the surfactant. Comparing the values of A obtained at different pH, it seems that there is a dependence of A on the pH, that is, on the ionization state of the polar head of the surfactant. In fact, for oleic acid monolayers on 0.01 N HCl (pH 2), assuming the viscosity of oleic acid as 1.5 × 10^{-4} poise · cm [5], equation (5) gives \( A_1 = 4.6 \pm 0.3 \text{ cm}^{-1} \) and \( A_2 = 15.8 \pm 0.8 \text{ cm}^{-1} \), while for oleic acid on distilled water we obtained \( A_1 = 18 \pm 3 \text{ cm}^{-1} \) and \( A_2 = 21 \pm 1 \text{ cm}^{-1} \). Furthermore, the plot of Figure 3 could suggest a dependence of A on the surface pressure; in fact, at high surface pressure the viscosities calculated with the Joly equation from flows through a 1 mm and 2 mm canal do not match, while they match at low surface pressure. In this case, a possible non-Newtonian behaviour of the film could play an important role. Notwithstanding these limitations, the measured viscosities provide a good indication of the state of the film, as shown by the comparison with the DPPC data.

Table II shows that surface viscosity of PLE monolayers turns out to be smaller by a factor of four when compared with that of DPPC. This finding seems to disagree with results obtained from fluorescence depolarization measurements which indicate a restricted lateral mobility for bolaform lipids in liposomes, when compared with egg PC [17]. Generally monolayer surface viscosity is found to increase with increasing chain length [2], but it is known that it is more
dependent upon molecular packing than upon the number of carbons in the chains [18]. It is likely that in monolayers at the air-water interface the molecular packing is more disordered than in liposomes. In liposomes both polar interfaces of the membrane are exposed to water, and a straight configuration of molecules is favoured. In monolayers at the air-water interface there would be polar heads on the air side; for this reason some molecules could have the tendency to orient both polar groups in contact with water.

Conclusions

The behaviour of surface viscosity of archaeal lipid monolayers as a function of surface pressure was studied with surface flow measurements, using the Joly equation to take into account the subphase drag effect. The validity of this method is confirmed at low pressures, where the film is surely a Newtonian two-dimensional fluid. The method seems to fail at high surface pressures, either because the two-dimensional liquid is no more Newtonian or because there is a dependence of \( A \), the parameter describing the coupling of the monolayer with the subphase, on the surface pressure. Notwithstanding this limitation, the measured viscosities, also those at high pressures, follow the two-dimensional Doolittle relation and indicate the presence of two distinct phases, characterized by two different limiting areas per molecule. The viscosity of PLE monolayers turns out to be significatively smaller than DPPC monolayer viscosity, indicating a more disordered structure of the film.

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