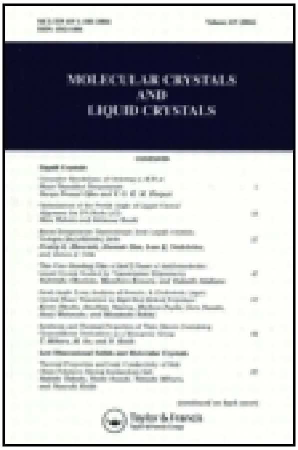

Molecular Crystals and Liquid Crystals

Attempt of Direct Measuring of Near Surface Shear Viscosity

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Attempt of Direct Measuring of Near Surface Shear Viscosity

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We offer a technique that permits the surface viscosity coefficients of LC's to be measured. The author has realized a version of the technique, distinctive feature of which is a usage of membranes having pores of submicron sizes (in the range from 40 μm down to 0.034 μm). We have found out that, at minimum diameter of pores (∼0.034 μm), the values of viscosity for the azoxy-compound based LC is larger by factor 10–15 compared to that measured with usual (∼100 μk and more) capillary tubes; the same values for LC 5CB have fond to be larger by factor of 100–350.

Keywords: LC; nano pores membrane; shear viscosity; surface viscosity

INTRODUCTION

Recently a number of publications have been devoted to viscosity properties of liquid crystals (LC's), especially to the problem of so called surface viscosity of LC's resulting from experimental findings that bulk LC viscosity is different from viscosity of LC layers adjacent to an interfacial (i.e. boundary surface between solid and LC medium). Up to now there is no a unified unambiguously treated definition of surface viscosity itself let alone techniques for its measurement.

The well known Poiseuille's law linking quantity of a liquid Q, flowing past through a capillary tube, with geometry of a capillary

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tube is known:

$$Q = P\ S\ 2T/8p\ L\ \eta,$$

where P - pressure, S - the area of a capillary tube, T - time, L - length of a capillary tube, η - viscosity of a liquid. The viscosity of a liquid is supposed by default to be the same both for liquid layers into the bulk and for a near-interfacial liquid layer.

The Poiseuille's method of shear viscosity measurements has given a good account of itself and is widely used in practice. However, we have not found any publications the method would be applied to viscosity measurements of liquids (especially LC's) that flow through capillary tubes of very small diameters (which are in the range of submicrons in value).

We clearly understand that usage of the Poiseuille's law in the case of very small diameters of capillary tubes maybe is not correct. In Poiseuille's time there was not a concept of nanotechnology and capillary tubes of submicron-in-diameter values were not available. The viscosity of liquids was supposed to be uniform through the cross-sectional area of tubes and there was no reason of not holding this rule.

With the appearance of technologies of a very small-in-size capillaries production, the question is arising whether the Poiseuille's law would hold for small capillaries and if it is possible to use the Poiseuille's law in its classical formulation for such objects. So, we've tried to analyze our experimental data obtained with submicron-sized capillaries, by Poiseuille's law in its original form and somehow to treat the result obtained.

EXPERIMENTAL SETUP

The experimental setup consists of the Bunsen volumetric flask (bulb), with the Schottky filters with pores of 40 μm and 4–4.5 μm in size, or different membranes with micron pore sizes of 3; 1; 0.6; 0.4; 0.2; 0.15; 0.074; and 0.034 μm being inserted into the bulb neck. Thus, the range of pore sizing covered 3 orders of magnitude.

The first 4 membranes (of 3; 1; 0.6; and 0.4 μm-sized pores) are obtained by heavy ions bombardment of a 15 μm lavsan film with the subsequent chemical etching and deleting of etching products out of the ions fly-over film areas. The other 4 membranes (of 0.2; 0.15; 0.074; and 0.034 μm-sized pores) are obtained by an electrochemical etching of the aluminum film, with an aluminum oxide film of 10–15 μm in thickness being formed.

The initial orientation of LC molecules inside pores was unknown to us and was out of control. Moreover, the author skeptically estimates a capability of creating a certain orientation inside the pores of less than 100 nm in size. The chemical polishing provides approximately the same sizes of surface roughness (of ~0.01 μm) as it is made with mechanical polishing of glass surfaces of the highest 14th surface condition accepted in optical engineering.

If a process of pores irritating can be considered as a chemical polishing, then the size of roughness should be comparable to a pore diameter. In the nano scale a pore represents a corrugated channel (photo of one of the samples is given below). It is difficult to imagine that there is any capability of LC molecules ordering in such a narrow and deflected channel. At the same time, after the chemical polishing of glass substrates used for preparing LC cells, the author succeeded in obtaining an excellent homeotropic orientation of LC's at the LC layer thickness in the range of 5–50 μm.

Under the operation of the vacuum pump a controllable difference of pressure up to 1 atmosphere was set in the set-up. Fixed quantity Q of reference liquids with known viscosity (ethanol, *iso*-propanol, diglycol, glycerin and an exotic liquid by a title water) was pressed through the membrane pores of the set-up, and the time of passing for each of the membranes was determined. Knowing the viscosity and the measured time of passing, the value $S^2/8\pi L$ (constant of viscosimeter) was possible to determine for the each separate membrane. That eliminated the necessity of knowing the precise size of pores, their specific quantity and the thickness of the membranes.

Then the portions of LC's studied (which bulk viscosities were known from the previous measurements with thick capillary tubes) were pressed through the same pore-sized membranes. Basically, we used LC440-mixture (a composition of azoxy-compounds) and for some comparative experiments we also used the widely known 5CB liquid crystal (belonging to the biphenyl's class of compounds).

We registered the time of the flow-passing through the viscosimeter the certain amount of tested LC's under different pressure differentials. Experimental knowledge of the viscosimeter constant for different sized-pores allowed us to estimate the shift viscosity of tested LC's and to predetermine the character of liquid flow (is it possibly Newtonian or non-Newtonian one?).

After approbation of several design versions we have accepted a design, for which the flow-passing time of 2 ml ethanol under the maximum pressure differential (~1 atmosphere) was of 10–20 sec. It allowed us to determine the time of flow-passing with an error of no more than 5% (for mobile reference liquids), and to be convinced that, at any rate, the selected reference liquids (except for water) are Newtonian ones. For tested LC's, the flow-passing times of the same quantities could be up to several hours (!), varying with the pore sizes. In the last case the measurement error may be much more, but does not exceed of 15–20% even in a rough estimation. The design of the set-up did not allow us to execute thermostatic control; therefore all the measurements were made at the room temperature (20–23°C).

RESULTS AND COMMENTS

1. It is well known that LCs are anisotropic liquids. Measured values of their viscosity coefficients depend on the viscosimeter design (that determines orientation of LC molecules with respect to the flow direction) and LC flow rate (Fig. 1a). If a flat capillary tube of 100–300 μm in thickness are used, and the certain orientation of LC molecules with respect of their flow direction and the walls of a capillary tube are provided, then, at low speed of shear movement (which does not break the initial LC orientation), it is possible to obtain the values of Gahwiller's viscosity coefficients, η_1 and η_3, and at high shear speed (and orientation of all LC molecules along the flow direction) – the value of Gahwiller's coefficient, η_2 [1]. Just by such a way we got the magnitudes of coefficients: $\eta_1 = 135\,\text{cP}$, $\eta_3 = 56\,\text{cP}$, $\eta_2 = 25\,\text{cP}$ for the reference liquid crystal LC440 [2]. If the flow rate is changed from the minimum up to the maximum, the measured values of viscosity coefficients will be ranged from the maximum (for η_1 at homeotropic orientation of molecules with respect to the boundary wall), up to the minimum (for η_2 when all LC molecules are oriented along the flow direction).

   Such situation is realized in some measurements of the present series of experiments. So, for the pores diameter down to 3–1 μm, the value of viscosity under the small difference of pressure (and the low flow speed) is of a maximum value close to η_1 (obtained in a flat thick capillary tube with homeotropic orientation of molecules (Fig. 1b). With increasing the pressure differential (and the flow rate) the measurable viscosity value drops and approaches to the minimum one for η_2. Thus, for pores of diameter down to 3–1 μm there is not any influence of near-surface LC layers on viscosity.
2. At pores diameter of 0.6 μm and at the small pressure differential, the value of viscosity is a little bit higher than for the LC bulk sample. With some increasing of the pressure differential, the viscosity magnitude levels practically by a factor of 2 times higher than that for the LC bulk sample. This is unambiguous evidence of the influence on viscosity the near-surface LC layers. At the low

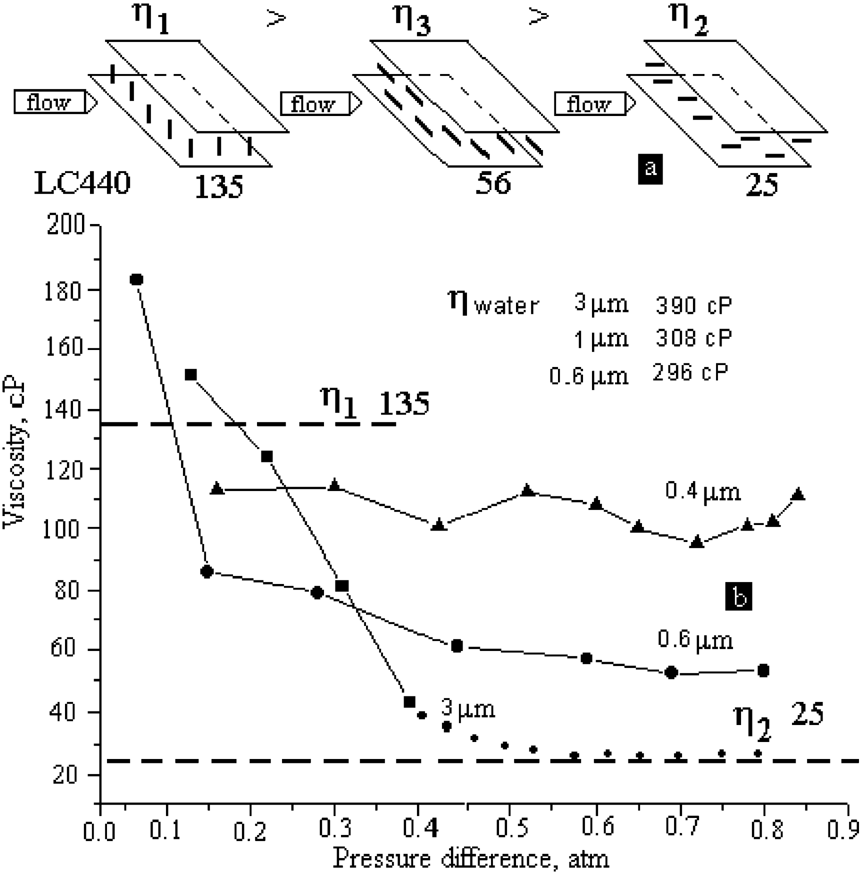

FIGURE 1 Definition of concepts of anisotropic coefficients of viscosity (a) and relation between viscosity and pressure difference (b).

shear speed, the near-surface LC layer gives the contribution to an increase of η_1. At the high shear speed (and the possibly largest degree of LC orientation along the flow direction) the contribution of the near-surface layer in the viscosity magnifies η_2-valuealmost by a factor of 2.

3. For pores of 0.4 µm in diameter, the contribution to viscosity of the near-surface layers is even larger and the LC-volume-passing-versus-time curve goes out on a plateau at a level close to the magnitude of η_1 (i.e. the maximum value of viscosity for the bulk LC sample). The practically full independence of LC viscosity from the shearing velocity of neighbor layers, as it takes place for a

classical Newtonian liquid, is amazing for us. It could mean that LC molecules do not orient along its flow direction; all moveable LC volume (both in the middle of capillary tube and adjacent to the capillary wall) flows as a single whole and there is an identical viscosity everywhere in the volume stream. Such a flow behavior is inconsistent with all early known presentations of LC flow, including the flow pattern through the 0.6 μm capillary membrane, for which the effect of LC orientation along the flow direction is undoubtedly observed. Therefore, it is obvious that the reason of such a viscous behavior is another one.

Let's imagine a cylindrical pore as a system of thick-walled concentric cylinders inserted each into other (Fig. 3). Viscosity of LC within the cylinders is different from each other and the smallest viscosity is for the central cylinder. Thus, at a small pressure differential the LC flow occurs only in the central cylinder, with a certain effective cross-section being active; the LC molecules, moving inside the central cylinder, orient along the flow direction as for the case of a common capillary tube. Owing to orientation of moveable LC molecules, the viscosity within this cylinder is reduced. So, the measured value of viscosity at small pressure differentials characterizes LC viscosity in the central cylinder. The lowering of viscosity in the central cylinder at the expense of LC orientation by the LC flow does not result in reducing the net viscosity at large pressure differentials, as the LC molecules from the adjacent larger-in-size cylinder (within which LC is more viscous) are involved in the motion.

The reduced viscosity in the central cylinder is compensated by more viscous flow within the outside cylinders. With growing the pressure differential, yet more LC molecules from outside cylinders are involved in movement (the pore effective cross-section is magnified.) Despite increasing the effective cross-section of the pore and reducing viscosity of LC molecules moving through the cross-section within the central cylinder (at the expense of LC orientation by the flow movement), the net reducing of viscosity might not be observed, since these two processes are mutually compensatory ones. Probably it explains the viscosity versus pressure-differential dependence for the pores of 0.4 μm-size in diameter.

4. Figure 2 shows dependencies of LC viscosity versus pressure-differential for membranes with the small-sized pores of 74 and 34 nm in diameter and, for the sake of comparison, with the average size pores (varying within the range of 1–0.4 μm).

   It is seen from the figure that measured with the same unified technique and for the same LC 440 mixture, the viscosity obtained

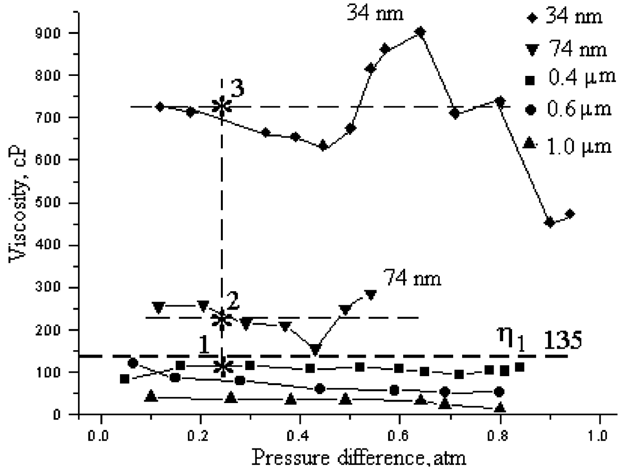

FIGURE 2 Relation between viscosity and pressure difference for some pore diameters.

for the 74 nm and 34 nm-sized pores is much larger than the maximum viscosity, η_1, measured both with the "thick" capillary tube and with the membranes of the medium-sized pores (1–0.4 μm). The measured dependencies in the figure look like broken curves and only roughly can be approximated by straight lines. For the straight-line approximation the model with a system of cylinders, given in the previous item, is still acceptable for the 74 and 34 nm-sized pores. The large values of viscosities can quite be explained by the more viscous properties of LC moving within the pore cylinders (i.e. viscosity of near-surface LC layers are higher than that of the bulk). The less the diameter of pores, the closer the pore cylinders to the boundary surface and the higher LC viscosity in each of the cylinders.

If only three points 1,2,3 for the 0.4 μm, 74 nm and 34 nm curves were taken into account, one could construct the relation of viscosity (Y) upon pore radius (X) as an exponential curve with an abrupt increase of viscosity while pore radius is decreased: $Y = A \times \exp.(-X/t) + Y_0$, where $Y_0 = 120$, $A = 2752$, $t = 11.16$ (Fig. 4).

5. The relations have an appearance of the straight-line fractures (breaks), and these fractures are not stipulated by errors of the measurements. The fractures are repeatedly observed in the measurements under increasing and reducing the pressure differential.

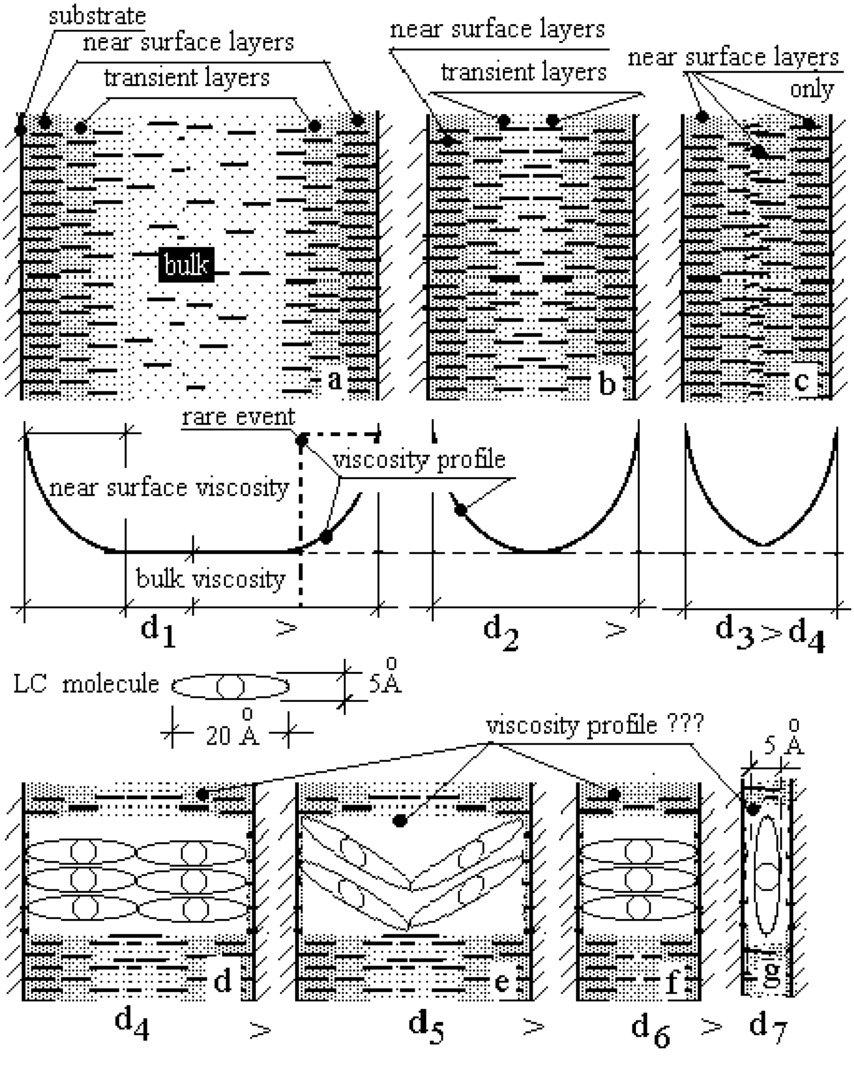

FIGURE 3 Viscosity profiles for some pores diameters.

However, the separate curves have practically never been repeated. At the pore size of 74 NM and, especially of 34 NM, the hysteresis in the dependencies takes place (Fig. 5).

It is possible to give a certain reasonable argument to this phenomenon by taking into consideration the roughness of pore walls. As already mentioned above the altitude of humps and cavities

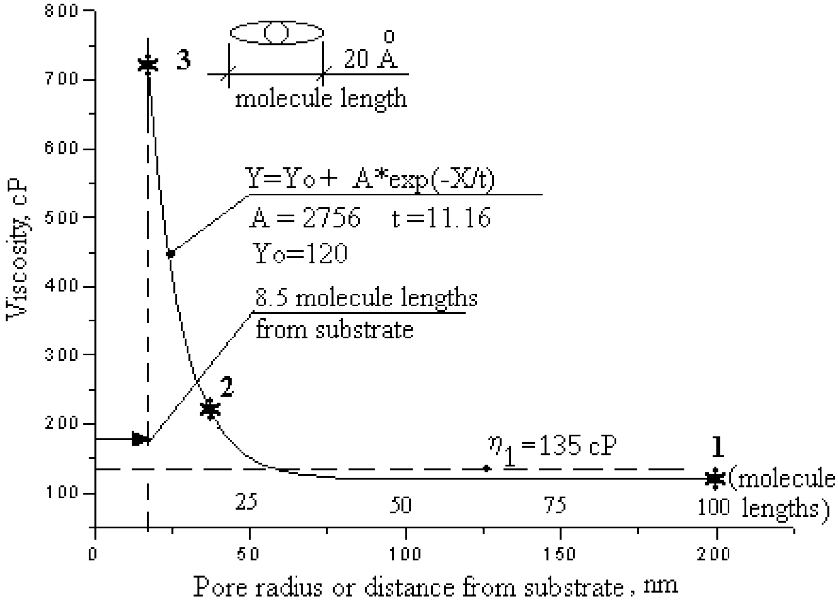

FIGURE 4 Relation between viscosity and distance from substrate.

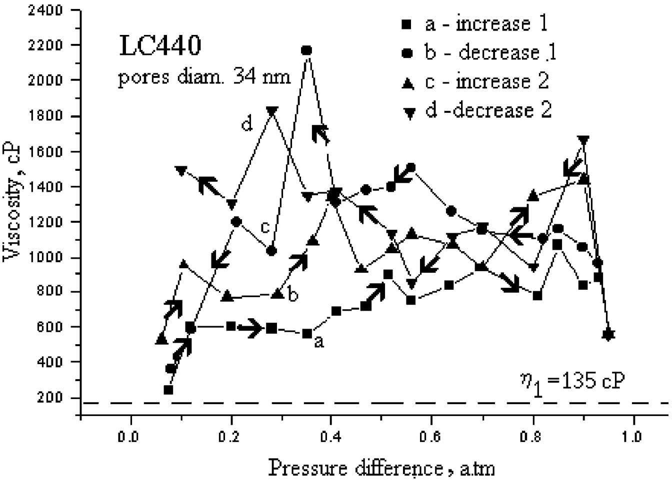

FIGURE 5 View of viscosity relations at cycling of pressure difference.

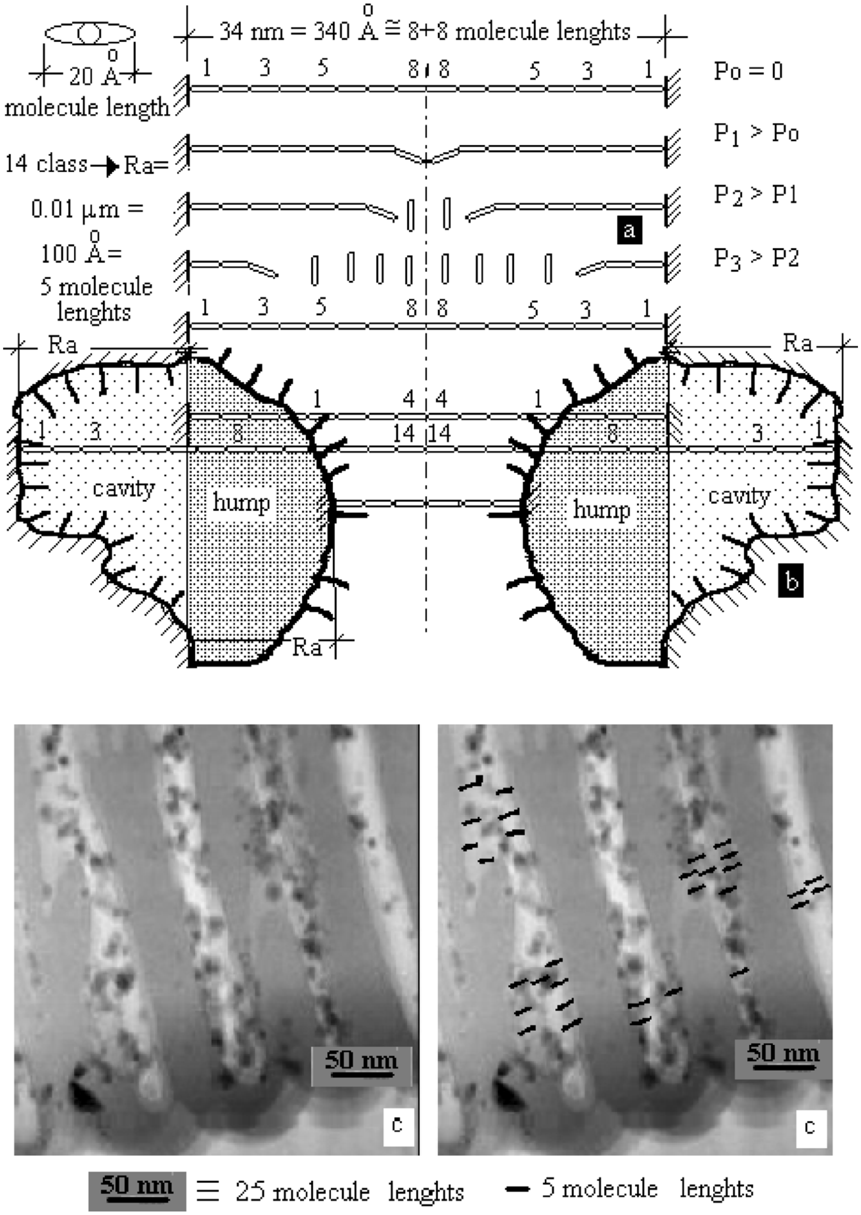

FIGURE 6 Possible distribution of molecules at different pressure in a pore with smooth walls (a), in a pore with rough walls (b) and pores photo one of membranes (c).

characterizing the roughness of the pore surface makes size of about 10 nm. If on the two opposite part of the pore wall there are the two humps of an altitude of 10 nm (or two cavities of the same depth), of the effective pore diameter in this place will be of 34–20 = 14 nm (or $34 + 20 = 54$ nm). At random relative positions of cavities and humps on the pore surface, the effective pore diameter would be of different values varying in the range from 14 nm up to 54 nm (Fig. 6). Even if it might be supposed that on the ideally smooth walls of the pores LC molecules would orient homeotropically, the homogeneous orientation of LC on the rough walls remains into question.

It is most probable the formation inside pores of micro crystalline grains with a characteristic size of about diameter of pores and with different direction of optic axes of the grains. The boundaries between crystal grains are sharp, (such as in the case of disclinations), because there is no enough LC material for smooth matching of interface orientations of adjacent micro crystal grains or of the last and the orientating wall surface (only 16 molecules keep within the size of pore diameter). If the micro crystalline grain model is valid, then the fracture kind of measured dependencies of viscosity versus pressure-differential and its nonreproductivity has the simple argumentation. In the absence of LC flow a pore may be considered as a tube filled with micro crystalline grains, which has a certain hydraulic resistance (and viscosity for liquid crystalline medium). When the flow starts, the LC molecules move from one crystal grain to the other one. So, the different system of crystal grains (having a different hydraulic resistance) is formed.

At different pressure (and flow speed) and different surface roughness with a random humps and cavities distribution, the amount of combinations of the crystalline grain forms (shapes) is enormous. It is absolutely optional, that at the same pressure (and flow speed), the absolutely identical system of crystal grains having identical viscosity would form. From this the premises follow for the presence of hysteresis loop and viscosity jumps (discontinuities, or fractures of experimental curves).

6. It is rather interesting how the dependencies of viscosity versus pressure-differential behave for the well known LC 5CB (Fig. 7).

   Similarly to the viscosity-pressure dependencies for LC 440, those for LC 5CB also have a fracture view, in particular, the hysteresis is obviously expressed for the curve of the 34 nm pore size. The measured viscosities at the pore diameter of 74 nm are by factor

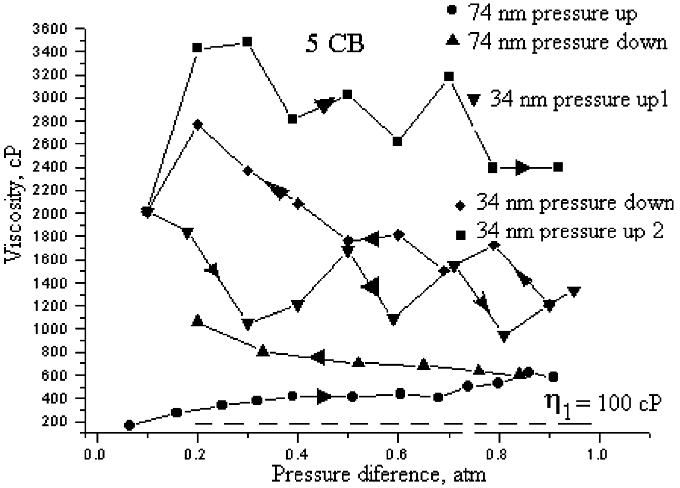

FIGURE 7 Viscosities of LC 5CB.

of 5–8 larger, than that for η_1-value, measured for the same LC 5CB with a thick capillary tube (for LC440 similar measurements give excess by factor of 2-3). At diameter of pores of 34 nm the minimum measured value of viscosity (~1000 cP) is larger by order of magnitude for η_1-value, and its maximum value exceeds the last by factor of 350 (!) (For LC 440 by factor of 5–6). So, considerable increase of viscosity can be attributed to a formation of 5CB smectic phase. The close homologues of 5CB (6-th and the higher) is known to have a smectic phase. In layers of the microns thickness, 5CB liquid crystal has not smectic phase. However, the smectic phase can occur under the influence of the pore wall on the adjacent LC molecules. The additional argument of smectic phase forming is the experimental fact that we were able to make the measurements on the freshly serviced capillary tube during the time of about 2–3 hours. After that time the flow through the capillary tube was getting impossible at the maximum pressure we could supply (we had to reject corked capillary tubes). We treat this phenomenon as a formation of a high-viscosity smectic phase which makes the pores of our viscosimeter tightly clogged. This phenomenon was observed 3 times during the viscosity measurements of 5CB, but never was observed during the viscosity measurements of LC440 (composed of azoxy-compounds), any homologue of which does not form a smectic phase.

7. Features of behavior of water in pores of small diameter.
   At the very beginning of experiments we were about to use as reference liquids water and ethanol (which viscosities are known to be of 1.0 cP and 1.2 cP, accordingly). We found that for pores of 40 μm in size and less, measured viscosity of water is substantially larger than the known tabulated value and its behavior is non-Newtonian one (there is not proportionality between the applied pressure and the speed of the water flow). We had to refuse the usage of water as a reference liquid. We were not planning studies of water viscosity in pores, but because of an extremely bright development of the effect, we were incidentally running the viscosity measurements for water. So, viscosity of water in pores of 3 μm, 1 μm and 0.6 μm in diameter size was measured to be of 390 cP, 308 cP and 296 cP, accordingly. We have not enough experimental data to state any suppositions about the nature of the observed phenomenon. The presence of clusters in water and formation of so called "Derjagin's water" might be considered as possible explanation of the phenomenon.

CONCLUSION

1. We are of opinion that the attempt of direct measurements of shear viscosity of LC's flowing through the pores of submicron sizes is quite successful. The shear viscosities of LC's, experimentally obtained for the first time for such conditions, were found to be of much larger values compared to those obtained with "thick" (~100 μk and more) capillary tubes. However these data do not contradict with common sense and are in line with the data given by other authors (for example, see [4]).
2. The data obtained and our arguments are preliminary; statistics of the conducted experiments is not too vast. It is necessary to make measurements in the larger range of flow speeds, at different temperatures, including phase transition temperature range, and with larger variety of pore sizes. The case of pores with sizes comparable to those of tested LC molecules is especially interesting for studying.
3. The performed experiments need in a good quality of theoretical understanding and refinement of some concepts. For example:

- what kind of forces are responsible for very large increasing of shear viscosity?
- what is the minimal LC amount (LC microvolume) that allows one to use the concept of mesophases?

- what are the layer thicknesses that are responsible for the anchoring energy and surface tension?
- and so forth.

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