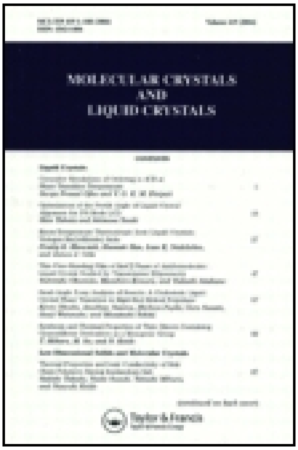

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Experimental Evidence of Permeation Effects in Induced Cholesteric Systems†

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Viscous properties of induced cholesteric systems with different steroidal and non-steroidal optically active dopants were investigated in flat capillaries. In all the systems studied, when helical pitch values were sufficiently low we observed a pronounced non-Newtonian behaviour interpreted in the terms of "permeation" model. With high pitches and high shear rates, however, properties were much more nematic-like. Comparisons are made with data obtained for mesogenic cholesterol esters and tube capillaries.

INTRODUCTION

It is a well established fact that the viscosity in the mesophase of cholesterol derivatives is markedly non-Newtonian for both tube and flat capillaries.[1–3] A generally accepted interpretation of this fact is based upon the so-called "permeation" model proposed by Helfrich.[4] The situation is not so clear, however, for induced cholesteric systems. It is often argued that, in this case, there is but a small dependence of the apparent viscosity η_{app} upon the shear rate, and that η_{app} values have the same order of magnitude as in the conventional nematics, even at low flow velocities.[5] A question then naturally arises—what are the reasons for such differences between the two classes of cho-

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lesterics at a molecular level? One may recall also[6] that in a compensated cholesteric mixture (i.e., in a mixture of two cholesterol derivatives having opposite helical pitch senses) when the pitch $P \rightarrow \infty$ the viscosity properties become quite similar to those of conventional nematics with no peculiar features that can be associated with the steroidal nature of the molecules. On the other hand, there are indications[7] that the nature of chiral molecules does, in fact, influence significantly the viscosity properties of the cholesteric mesophase. One should note that experimental data on the viscous properties of induced cholesteric systems are rather scarce and, in fact, can not provide a basis for any significant conclusions.

In order to clarify the situation we have studied a number of systems consisting of a nematic matrix with different chiral dopants, both steroidal and non-steroidal, over a broad range of concentrations.

EXPERIMENTAL

For our measurements we used a modified Tsuda viscometer with a flat capillary.[8] The scheme of experimental set-up is presented in Figure 1. The capillary dimensions were 50x5x0.4 mm; as a rule, no preliminary surface treatment of the internal wall was carried out.

The nematic matrix used was 4-butyl-4′-methoxyazoxybenzene (BMAOB) and mesogenic cholesteryl caprinate as well as non-mesogenic ℓ-menthyl-p-nitro-benzoate, ℓ-menthyl-p-methoxycinnamate and tigogenin caprinate served as optically active dopants.[9]

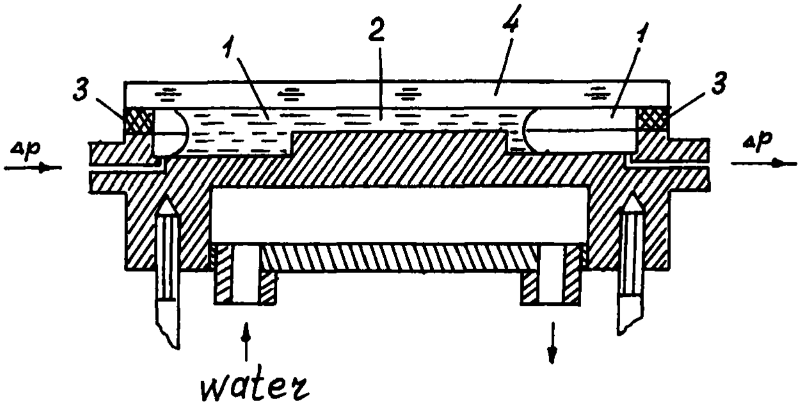

FIGURE 1 A schematic drawing of the modified Tsuda viscometer: 1—reservoirs, 2—flat capillary, 3—sealing gasket, and 4—glass lid.

The apparent viscosity values were calculated using the relationship

$$\eta_{app} = \frac{\Delta p \cdot t}{\Delta p_r \cdot t_r} \eta_r.$$

Here Δp is the excess pressure, the subscript r corresponds to the reference fluid with the known viscosity value η_r, and t is time required for a fixed volume of the fluid to flow through the capillary. Cyclohexanone and glycerine were chosen as reference fluids; their viscosities (at 30°C, η = 41.07 sP nd 622 sP, respectively) being of the same order of magnitude as those of the systems studied.

RESULTS AND DISCUSSION

The principal results are presented in Figures 2–5. When the optically active dopant concentration is small (i.e., when the helical pitch is large ~5–10 μm) η_{app} only changes slightly on varying the excess pressure (i.e., with changing shear rate). In this case the $\eta_{app}(T)$ curves are quite similar in form to those for pure BMAOB, i.e., the viscosity in the cholesteric phase is essentially lower than the value extrapolated from the isotropic phase; a minimum is clearly seen just below the isotropic transition point T_i. With higher OAD concentrations (≥10%) and, correspondingly, smaller pitches (<2 μm), η_{app} becomes very sensitive to shear rate changes, and the minimum below T_i gradually disappears; η_{app} in the cholesteric phase is always higher than the value extrapolated from the isotropic phase. It should be noted that the picture was quite similar for all the OADs tested, depending primarily upon the helical pitch value, and not upon the chemical structure of the OAD molecules.

The picture becomes clearer when the apparent viscosity is plotted as a function of inverse pitch. For all the systems studied these plots appear to be linear, and for a given Δp value the slope is essentially insensitive to the nature of the chiral dopant.

Compensated cholesteric mixtures (e.g., cholesteryl chloride + cholesteryl oleate) have been investigated[10] using a cone plate rotational viscometer at different shear rates. On increasing pitch or shear rate the form of viscosity versus temperature curves changed in a manner similar to that observed in our experiments, i.e., the minimum close to T_i gradually appeared. This leads us to the conclusion that there is, in fact, no essential difference in the rheological prop-

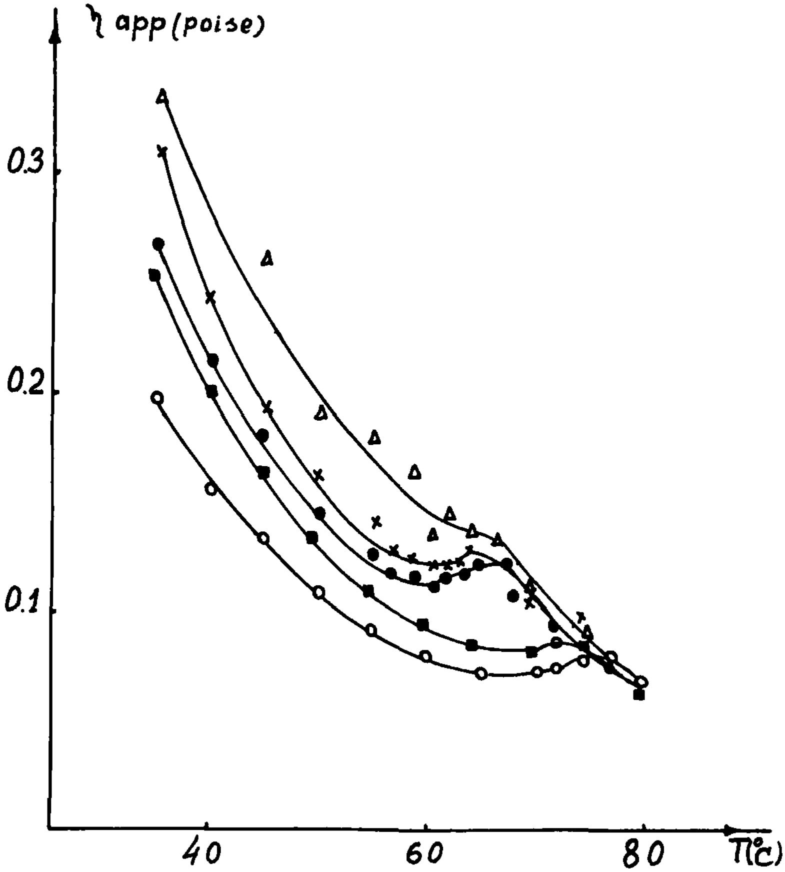

FIGURE 2 Temperature dependence of η_{app} for the 97% BMAOB + 3% *l*-menthyl-p-nitrobenzoate mixture (P = 1.3 ÷ 1.6 μm): ●—50 mm H_2O; ×—10 mm H_2O; △—2 mm H_2O. For 99.5% BMAOB + 0.5% *l*-menthyl-p-nitrobenzoate mixture (P = 7.2 ÷ 9.3 μm): ○—50 mm H_2O; ■—2 mm H_2O.

erties of the known types of cholesterics, either induced or formed by mesogenic cholesterol derivatives.

It is worth commenting on the nature of permeation effect on the systems studied. Our geometry was evidently different from that assumed in the original approach by Helfrich,[4] i.e., the flow direction was normal, and not parallel, to the helical axis. It has already been shown[11] that the temperature and shear rate dependencies of apparent viscosity are quite similar both in flat and tube capillaries (though the absolute viscosity values are larger in the latter case). The permeation effect is thus not limited to one peculiar geometry, but appears as a general property of a broad class of systems. Referring to

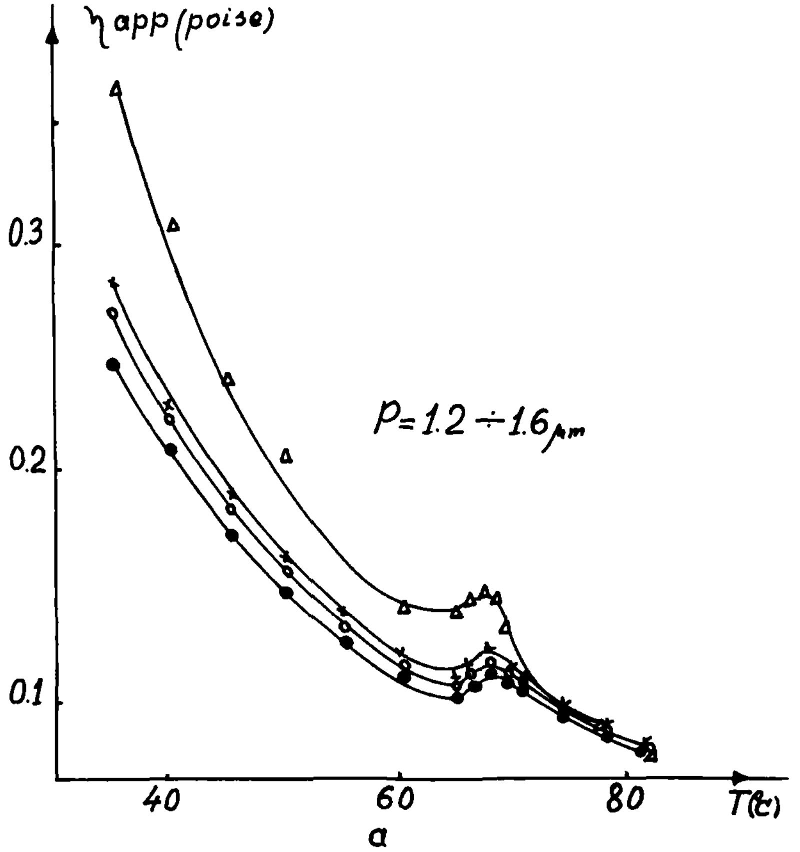

FIGURE 3 Temperature dependence of η_{app} for BMAOB mixtures with *l*-menthyl-p-methoxycinnamate (2.5%—(a) and 10%—(b)): ●—180 mm H_2O; ○—100 mm H_2O; ×—50 mm H_2O; △—5 mm H_2O.

our particular case, we note that the viscosity features determined by permeation were distinctly weakened when preliminary rubbing of the internal walls was carried out or ac electric fields were applied to the conducting walls of capillary.† This fact leads us to the assumption that disclination lines and other texture defects are of considerable importance, for the phenomenon. During the flow the capillary was observed under the miscroscope, and non-vanishing flow oriented disclination lines were clearly visible. One should also note

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†Low viscosity values were also observed in[12] when cholesterics were oriented by magnetic fields.

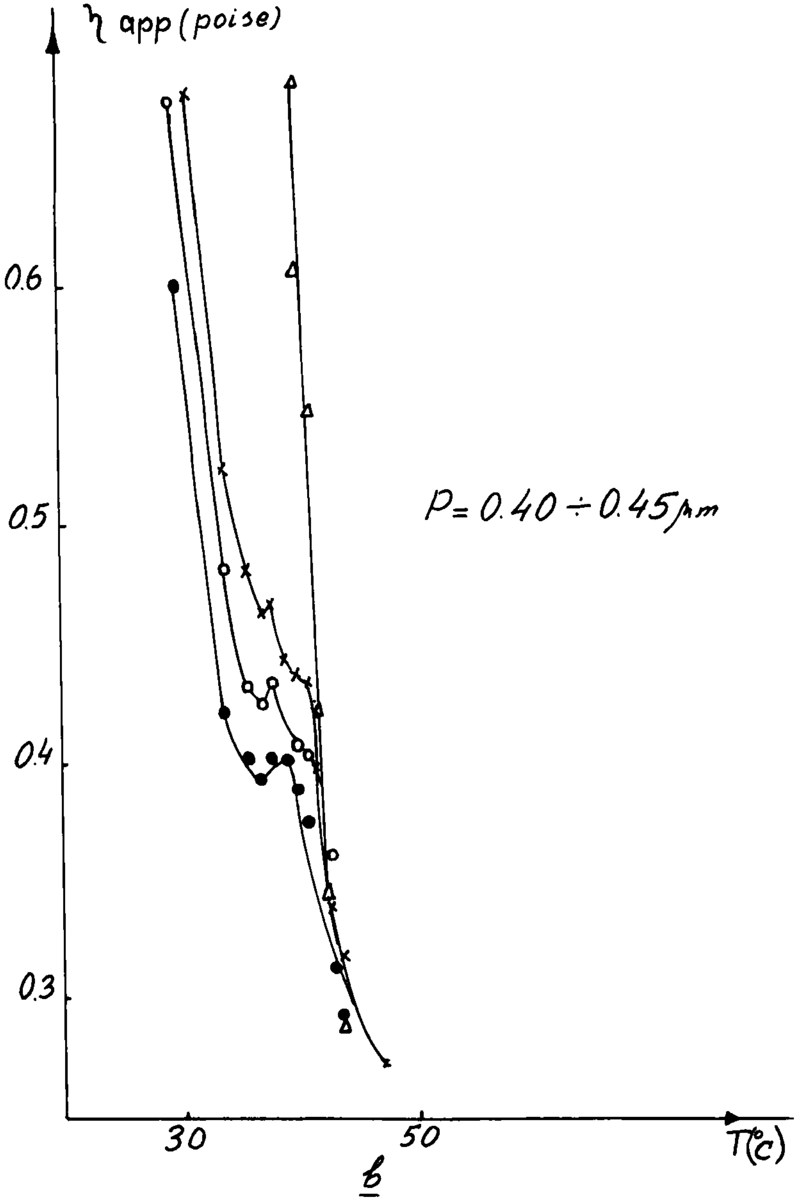

FIGURE 3 *Continued*

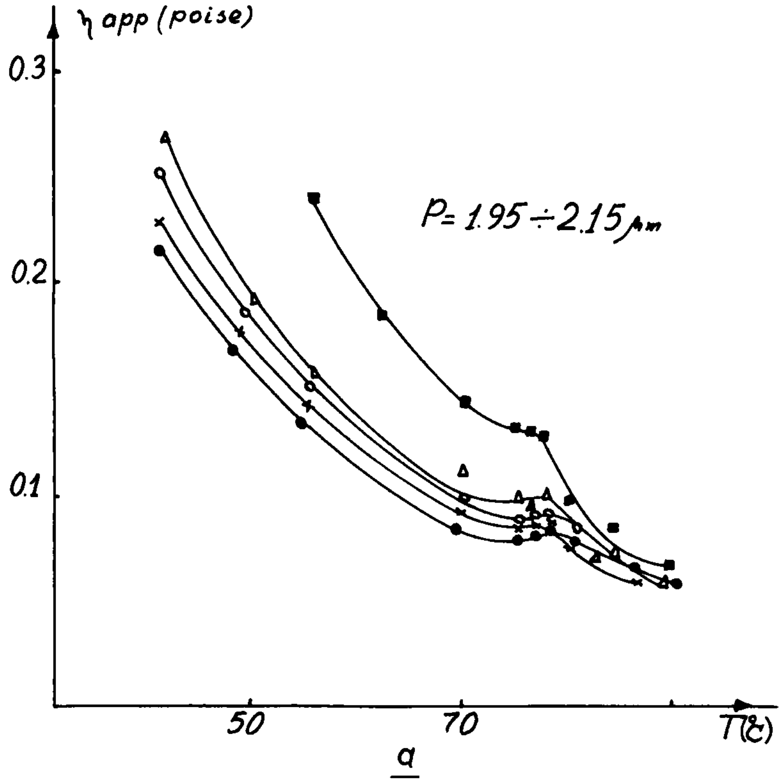

FIGURE 4 Temperature dependence of η_{app} for BMAOB mixtures doped with cholesteryl caprinate (6%—(a), and 12 %—(b)): ●—50 mm H_2O; ×—30 mm H_2O; ○—10 mm H_2O; △—5 mm H_2O; ■—2 mm H_2O.

that no change in colour was observed under flow for those systems where the pitch was sufficiently low as to bring the selective reflection band into the visible range. This implies a stable helical structure, non affected by the flow which therefore provides a source of hindrances to molecular motions which is reflected in the high apparent viscosities.

CONCLUSIONS

The present investigation shows that the viscosity behaviour of induced cholesterics in flat capillaries, with the helical axis normal to the flow direction, is quite similar to the classical "permeation" ob-

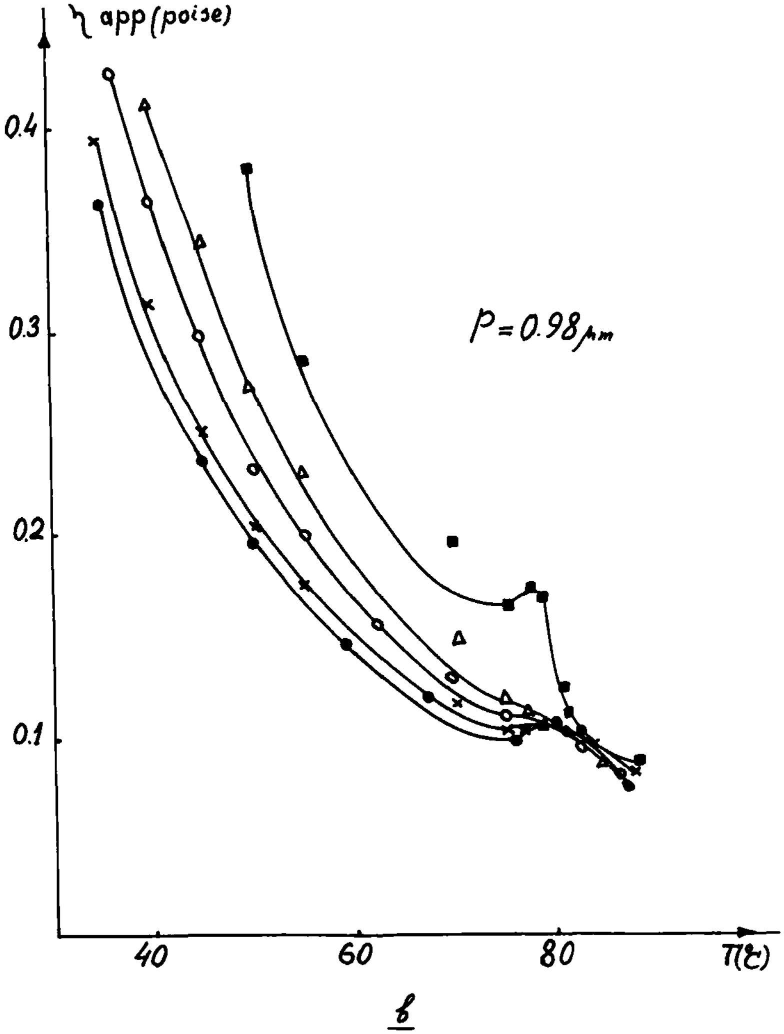

FIGURE 4 *Continued*

served in tube capillaries with the helical axis parallel to the flow direction. This effect is presumably due to non-uniformities of the planar texture which in the absence of external fields or special orientation procedures, show themselves as disclination lines oriented by flow.

Another conclusion is that there are no qualitative difference in the viscous properties between cholesteric systems of different types, e.g., between induced cholesterics and mixtures of mesogenic cho-

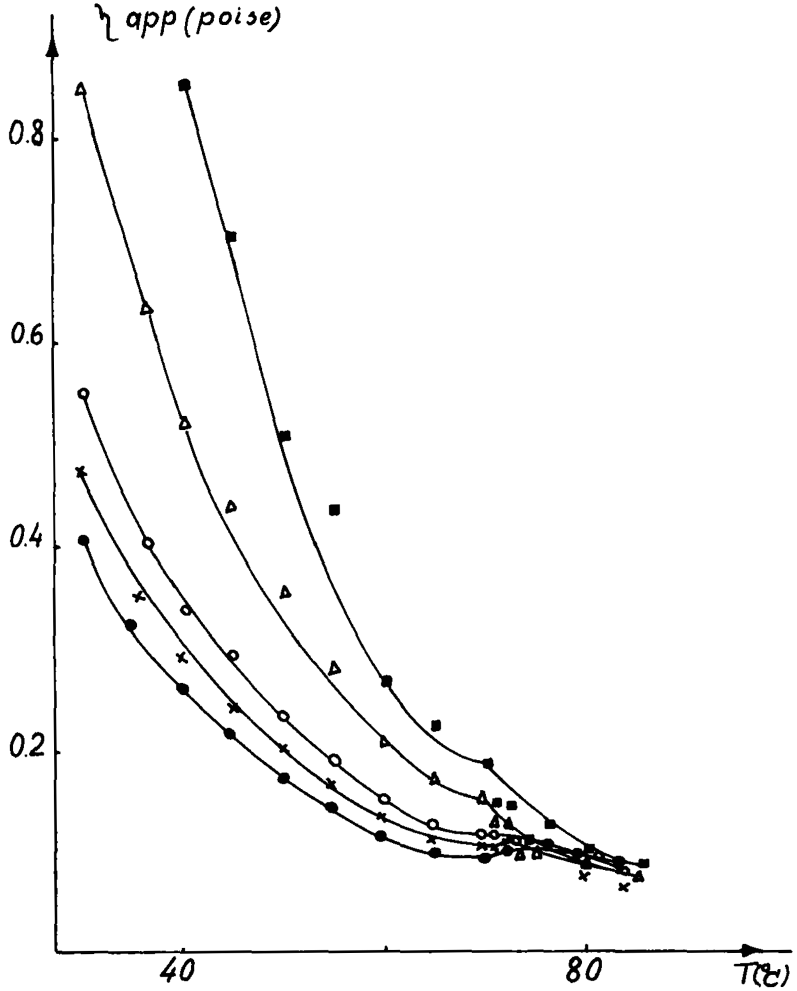

FIGURE 5 Temperature dependence η_{app} for the 93% BMAOB + 7% tigogenin caprinate: ●—100 mm H_2O, ×—50 mm H_2O; ○—30 mm H_2O; △—10 mm H_2O; ■—5 mm H_2O.

lesterol derivatives and it is the helical pitch value that is the decisive factor determining the apparent viscosity of cholesterics.

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