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ANOMALOUS BULK VISCOSITY OF CHOLESTERIC SYSTEMS EXHIBITING BLUE PHASES

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Abstract: The bulk viscosity of two cholesteric mixed systems cholesteryl nonanoate/cholesteryl chloride and CB 15/ZLI 1612 has been measured using Ubbelohde capillary viscometers. A viscosity maximum close below the clearing point only has been observed in such mixtures exhibiting blue phases (BP). Cholesteric systems with larger pitches in which no BPs exist show a nematic-like capillary flow behaviour.

Introduction In a recent review Leslie (1) pointed out that the situation of viscosity of cholesterics "is disappointing, both from theoretical and experimental standpoints". Two outstanding experimental features of cholesteric viscosity η_{ch} have been reported (1, 2): i) η_{ch} assumes considerably larger values than that of the isotropic state (up to a factor of 10^6), ii) η_{ch} exhibits non-newtonian flow behaviour. In a lot of papers (3 - 5) a maximum of η_{ch} close below the clearing point T_c has been described. An attempt to explain the anomalous value of apparent viscosity of cholesterics has been made by Helfrich (6). In this model cholesterics are assumed to move through capillaries like a plug (permeation).

In the case of a non-steroid cholesteric mesophase (chiral nematic) a sharp viscosity peak at T_c has been found too (7) but the viscosity of the cholesteric phase was lower than the extrapolated one of the isotropic phase.

Some experimental observations on cholesteric "blue phases" (BP) (8) led us to the assumption that the extremely high viscosity close below T_c will be caused rather by BPs than by 'normal' cholesteric mesophases. This problem can be solved by simple experiments: It is well known that BPs only exist in cholesteric systems of considerably low pitches p. If p exceeds any critical value p_c the BPs vanish (8a, 9). Thus, in mixed systems in which p varies with composition viscosity measurements can be carried out on mixtures with and without BPs.

Results The first mixed system consists of the cholesteric chiral p-2-methylbutyl-p-cyanobiphenyl CB 15 (BDH) and a nematic phase ZLI 1612 (Merck). The phase diagram is given in fig. 1 showing considerably broad ranges of the two polymorphic blue phases BP I and BP II. At lower concentration of CB 15 ($\leq$ 46 weight %) the pitch increases rapidly ($p > p_c \sim$ 330 nm). Consequently, BPs no longer exist (cf. fig. 1). Capillary flow of five mixtures CB 15/ZLI 1612 has been investigated using two micro-viscometers (Schott KPG, viscometer constant K = 0.3 and 1.0, respectively). The capillary diameter (0.74 and 1.00 mm, respectively) as well as the length have been kept constant throughout all measurements to provide comparable average shear rates for all mixtures. Temperature constancy was better than 0.1 K.

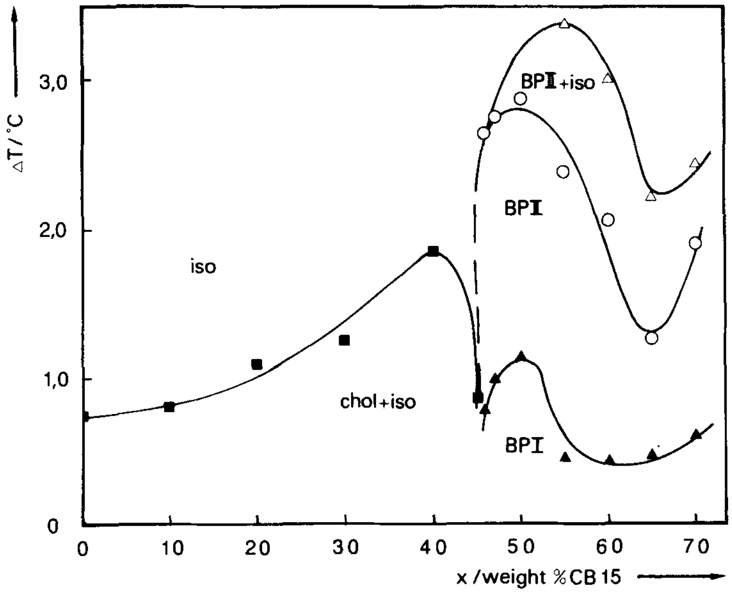

FIGURE 1 Phase diagram CB 15/ZLI 1612. Ordinate: ΔT temperature differences with respect to transition chol/BP I

The kinematic viscosity ν as a function of temperature is given in fig. 2. In all mixtures up to 55 weight % ZLI 1612 the viscosity sharply increases below T_c to extremely high values. Within a rather broad temperature span ($\sim$ 1 K) the rates of flow are so exceptionally low that ν could not be measured. At lower temperatures ($T < T_c$) ν drops to values comparable with

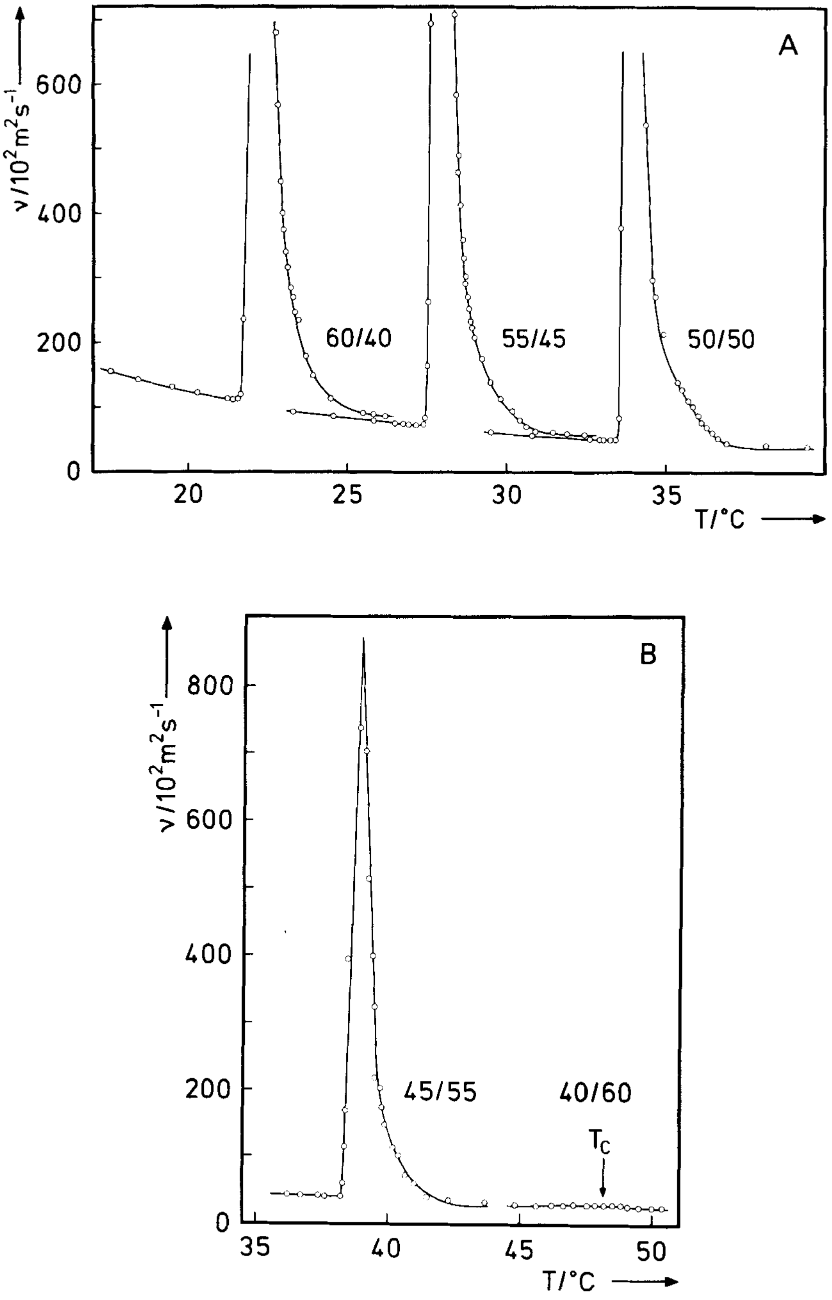

FIGURE 2 Kinematic viscosity vs. temperature of CB 15/ZLI mixtures. Parameter: weight %

those of the isotropic liquid. The rather large width of the ν peak results from the broad temperature span of BPs in this system (cf. fig. 1). The non-newtonian flow behaviour was established by varying the capillary diameter of the viscometers. The mixture CB 15/ZLI 1612 40/60 weight % exhibiting no BPs does not show any viscosity maximum at all (cf. fig. 2 B): In the curve ν (T) no discontinuity occurs at T_c .

The second system was a compensable mixture of cholesteryl nonanoate/cholesteryl chloride CN/CC. From the phase diagram (fig. 3) it can be seen that BPs onlyexist in the ranges $0 \le x_{cc} \le 0.37$ and $0.79 \le x_{cc} \le 1$ (x_{cc} mole fraction CC) because in the middle range the helical pitches exceed the critical values (p_c = 540 or 490 nm, respectively) (9).

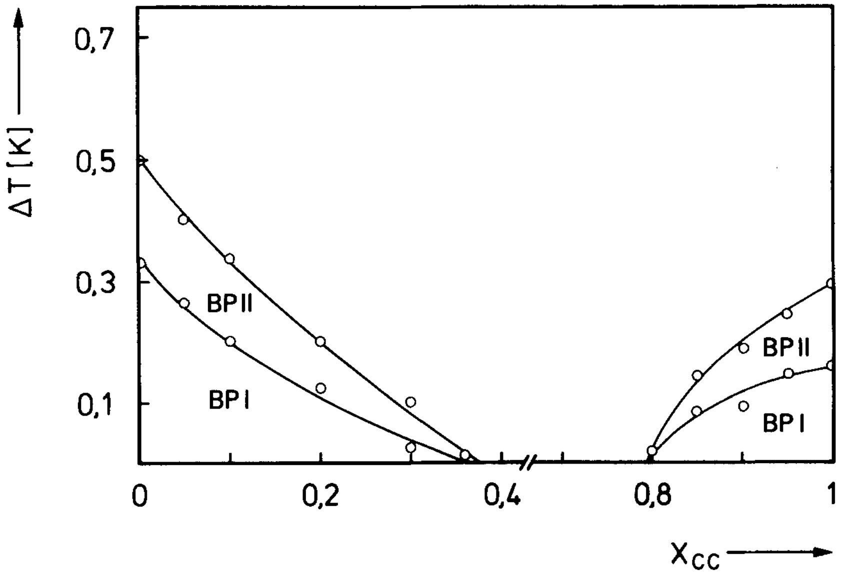

FIGURE 3 Phase diagram CN/CC; ΔT: cf. text in fig. 1

The temperature dependence of ν of two mixtures CN/CC is given in fig. 4. The BP mixture with x_{cc} = 0.15 shows the expected ν peak below T_c with a smaller width compared with that of the system described in fig. 2 which is due to the smaller BP range in the CN/CC system. In the mixture with x_{cc} = 0.50 which does not show any BP (cf. fig. 3) no viscosity maximum occurs. A small drop of ν has been found at T_c similar to that of nematic liquid crystals (5c, 10). This flow behaviour of 'normal' cholesterics is in agreement with that of compensable cholesteric mixtures as earlier found by one of us (11).

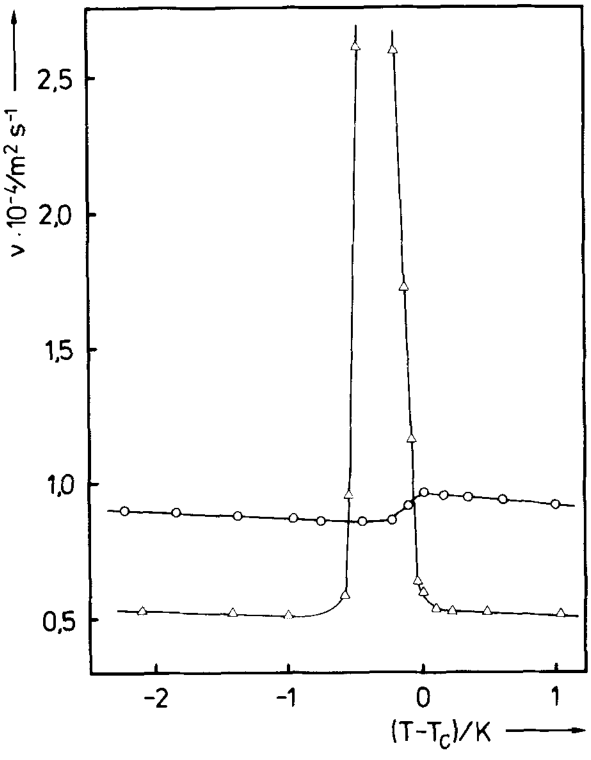

FIGURE 4 Kinematic viscosity vs. temperature of CN/CC mixtures. x_{cc} = 0.15 △ △ △ △ ; x_{cc} = 0.50 o o o o

Discussion From our experimental results it follows clearly that the extremely high viscosity of cholesteric systems actually is caused by BPs. The bulk viscosity of 'normal' cholesterics, however, is comparable to that of nematics. Thus, Helfrich's permeation theory (6) does no longer seem to be tenable in the case of cholesterics. The flow behaviour of cholesterics, however, can be understood reasonably in terms of Leslie's concept (12) since the necessity of explaining suspected high viscosity values can be cancelled out because of the experiments described above.

On the other hand, the permeation concept (6) may work with some appropriate modifications in the case of BP flow. A body-centered cubic lattice structure has been proposed for BPs (13) which was evidenced by us by obtaining liquid single crystals of cubic habitus (8b). This BP structure is expected to be rather stiff. Consequently, a plug-like flow with uniform velocity seems to be possible for BPs similar to the model of capillary flow of smectics (6). A theoretical treatment of BP flow behaviour by means of Helfrich's permeation concept taking into account the b.c.c. structure seems to be promising.

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