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The viscosity-pressure behaviour of some liquid crystals

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Abstract. The viscosity-pressure behaviour of certain liquid crystals is investigated with particular reference to isotropic-nematic, isotropic-cholesteric, and nematic-smectic transitions.

1 Introduction

At present a general comprehensive theory of the liquid state is still not available. The interactions between closely packed molecules in a liquid produce an intermediate state between random distribution and ideal crystalline order. This geometrical arrangement of molecules in a normal liquid is very difficult to describe by means of convenient parameters, and therefore theoretical work has largely concentrated on liquid noble gases. The arrangement of monatomic spherical molecules is described by the radial distribution function.

In the case of the usual polyatomic molecules, however, the angular distribution of neighbouring molecules in the liquid state strongly affects the physical properties. The different mesophases of liquid crystals throw light on the influence of angular distributions.

Not all degrees of freedom of unbranched molecules with a sufficiently long chain are released simultaneously at the melting point. Above it, there remain distinct arrangements of the molecules of one- or higher-dimensional orders; these are well-known as smectic, nematic, and cholesteric phases. From the theory of Maier and Saupe (1960, 1961) the angular distribution of the molecules in these mesophases is described by the second-order Legendre polynomial $S = \frac{1}{2}(3\cos^2\varphi - 1)$. The ideal crystalline order is characterised by $S = 1$, and the lack of order in an isotropic liquid by $S = 0$. At the nematic–isotropic transition point, S is usually of the order of 0·4.

Since liquid crystals are valuable model substances for liquid structures, they have been intensively studied in recent times. Their dielectric constants (de Jeu and Lathouwers 1975), optical transparence (Keyes et al 1973), dispersion of light reflection (Pollmann and Stegemeyer 1973), circular dichroism and optical rotatory power (Finkelmann and Stegemeyer 1973), and thermal conductivity (Andersson 1977) have been reported, and differential thermal analysis (Spratte and Schneider 1976) and nuclear magnetic resonance (Orrell et al 1976) studies have been carried out.

A property very sensitive to changes in liquid structure is the viscosity dependence on pressure. For such measurements up to 2·5 kbar at temperatures up to 300 °C a high-pressure falling-ball viscometer with inductive or capacitive registration of descent times, especially very long ones, was constructed (Kuss 1977). With this equipment the viscosity-pressure behaviour of MBBA (*p*-methoxybenzylidene-*p*-*n*-butylaniline), EBBA (*p*-ethoxybenzylidene-*p*-*n*-butylaniline), PBBA (*p*-phenoxybenzylidene-*p*-*n*-butylaniline), CBOOA (*n*-*p*-cyanobenzylidene-*p*-octyloxyaniline), COC (cholesteryloleylcarbonate), and some toluidines was investigated.

2 The isotropic-nematic transition

In this transition the viscosity decreases by about 25% whereas the density is changed by only 0·2 or 0·3%. Figure 1 shows the viscosity-pressure isotherms of *N*-(4-octyloxybenzylidene)-*p*-toluidine as an example. On the isotropic side—the low-pressure side— there is a sudden sharp decrease in viscosity. On the nematic side, however, the the isotherms are bent, the curvature becoming larger with increasing pressure and temperature. This behaviour indicates pretransitions in the nematic phase in the neighbourhood of the transition point.

In spite of its greater density, the nematic phase has a lower viscosity. This indicates that in the nematic phase the long axis of the molecules turns approximately in the flow direction. Therefore the molecules move more easily amongst one another than in the disordered isotropic phase.

The viscosity-pressure behaviour of MBBA differs significantly from that of EBBA. If lines are drawn through the isothermal viscosity peaks and through the minimum values, two curves are obtained, one for the upper and one for the lower viscosity along the transition line. For EBBA and the other nematic substances investigated, an increase in viscosity is found along the transition line (compare with figure 1); in contrast to this, a decrease is found for MBBA.

Along the transition line both the density and the temperature increase. To separate the influence of these two parameters, the $p-V-T$ data for the substances were determined. The compressibility of MBBA was found to be much smaller than that of EBBA. Thus the relatively small increase in the viscosity of MBBA caused by the small density increase along the transition line is overcompensated by the larger decrease in viscosity corresponding to the simultaneous rise of temperature. This effect appears only for MBBA because of its particularly small compressibility.

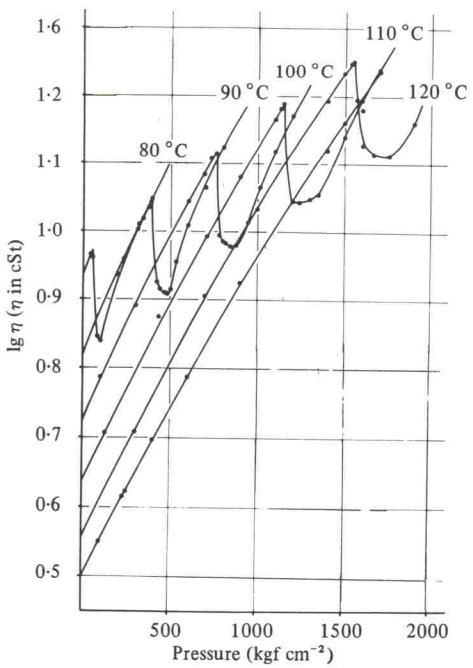

Figure 1. The viscosity-pressure behaviour of *N*-(4-octyloxybenzylidene)-*p*-toluidene.

3 The isotropic-cholesteric transition

This transition for cholesteryloleylcarbonate shows another type of viscosity-pressure behaviour. On the log η versus p diagram the isotherms are nearly straight lines for both mesophases. The viscosity in the cholesteric phase, however, is close to that in the isotropic one. The cholesteric isotherm runs only slightly higher than the extension of the isotropic isotherm. In contrast to the nematic phase, the long axis of the molecules cannot turn in the direction of flow because of the helical mutual arrangement of the nematic layers.

At the transition point itself there is a very sharp peak of viscosity, which increases slightly with increasing pressure. This seems to indicate that the coupling between the helically arranged layers is stronger than that between the molecules within the layer. The temporary appearance of a nematic phase during the dissolution of the cholesteric arrangement should result in a *decrease* in viscosity by perhaps 20-30%, which has not been found experimentally.

A temporary nematisation with a corresponding decrease in viscosity, however, appears at the temperature of compensation if the behaviour of mixtures of two cholesteric liquids with different senses of rotation at atmospheric pressure is investigated as a function of temperature (Pollmann 1972).

4 The nematic-smectic A transition point

At this point the viscosity increases by a factor of a hundred or more, as is shown for CBOOA in figure 2. Also in this case the shift of the transition point with pressure can easily be detected by the measurement of viscosity. Such measurements at high pressure provide information on the nature of the mesophase, and may throw some light on the existence of pretransitions and triple critical points.

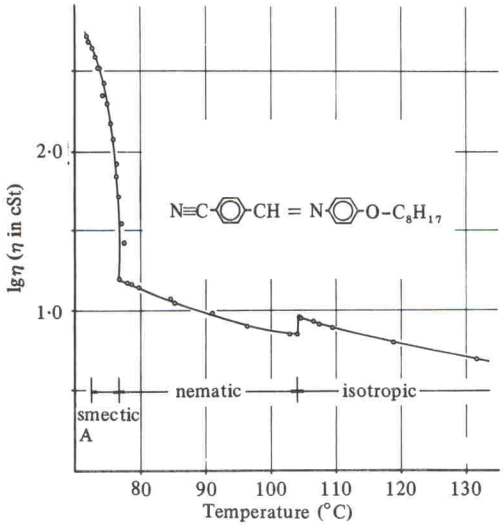

Figure 2. The smectic A-nematic and nematic-isotropic transitions of *n-p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA).

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