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Detailed study of a two component smectic 4TPB–8OCB system with a nematic gap

Phase diagram and viscosity study

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The phase diagram of a two component system composed of two smectic compounds: 4-octyloxy-4′-cyanobiphenyl (8OCB) and 4-isothiocyanatophenyl 4-butylbenzoate (4TPB) was investigated. Three Miesowicz viscosity coefficients η_1, η_2, η_3 and the refractive indices at different temperatures as well as the enthalpies of the phase transitions were measured. It was stated, that the properties of the induced nematic phase, for example, the nematic phase existing between two smectic regions, are the same as the ones observed in the case of low viscosity nematic mesogens.

1. Introduction

The phenomena involving the destabilization of smectic phases leading to the full separation of the smectic regions by a nematic gap have been investigated for some years [1–3].

The main aim of this investigation was to discover what conditions are necessary and responsible for such behaviour. The properties of the nematic phase which were formed by depressing the smectic stability have not been studied as yet in detail. In order to understand better the properties of such nematic systems we have carefully studied two component 4TPB–8OCB mixtures which, as we have found already, have a very broad nematic phase range [4]. In this paper we present the phase diagram and the Miesowicz viscosity coefficients η_1 ($V_\perp n$ and $\nabla V_\| n$); $\eta_2(V_\| n$ and $\nabla V_\perp n)$; $\eta_3(V_\perp n$ and $\nabla V_\perp n)$, the refractive indices and the enthalpies of phase transitions measured for different concentrations.

2. Experimental

The phase diagram was established by a single concentration method. The temperatures of the phase transitions of the compounds and their mixtures were measured by a THM-600 LINKAM programmable hot stage with a polarizing microscope, ‘Biolar’ PZO, and DSC-92 ‘SETARAM’ microcalorimeter. The Miesowicz viscosity coefficients were measured using a vibrating plate viscosimeter built at Jagiellonian University [5]. The refractive indices were measured by means of a refractometer. The X-ray patterns were obtained in a way similar to the Laue transmission method using the sample freely hanging in a circular aperture 2 mm in diameter [6].

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3. Results and discussion

The isobaric phase diagram of the two component 4TPB–8OCB mixture, with concentration and temperature as the axes, is shown in figure 1. The nematic phase is observed in a very broad concentration range (from 0·23 to 0·9 mole ratio of x_{8OCB} at 20°C). In the concentration range $x_{8OCB} < 0·3$ mole ratio the nematic phase is monotropic and this causes some experimental difficulties during the viscosity measurements. However, the fact that all the interesting phase transition points are in the temperature range of 0–85°C justifies the choice of this system.

The temperatures of the N–I phase transition change with concentration in a linear way. The temperatures of the S_{A_1}–N phase transition decrease quickly with increasing concentration of 8OCB and the enthalpy decreases, also quickly, in a continuous way, falling to 0 for the concentration x_{8OCB} of 0·3 mole ratio, the change from a first order transition to a second order one is observed ($\Delta H_{S_{A_1}-N}$ for $x_{8OCB} = 0·1, 0·2, 0·3$ mole ratio is respectively 2·1, 0·55, 0 J g^{-1}). On the other side of the diagram, the smectic A_d phase disappears rapidly with increasing 4TPB concentration in the mixture, such that for $x_{8OCB} = 0·9$ mole ratio only the nematic phase is observed and for $x_{8OCB} = 0·91$ mole ratio the smectic A_d phase exists in a narrow temperature range of 28–32°C, and at lower temperatures a nematic reentrant phase is observed. The S_{Ad}–N phase transition is a second order transition for the concentration region 0·9–1·0 mole ratio of 8OCB. The dependence of the enthalpy of the N–I phase transition upon concentration is shown in figure 2. The enthalpy of the N–I phase transition for the composition $x_{8OCB} = 0·9$ mole ratio is two times higher than for the composition $x_{8OCB} = 0·1$ mole ratio. This may be the result of the fact that for $x_{8OCB} = 0·9$ mole ratio some additional energy is needed to destroy this partially dimer structure at the clearing point. A similar relation was observed for the mixture 5BT–12OCB [7].

The Miesowicz coefficients for the individual mixture compositions change with temperature exponentially see figures 3 (*a*)–(*c*) and the energies of viscosity activation for the different compositions are shown in the table. The dependence of the Miesowicz

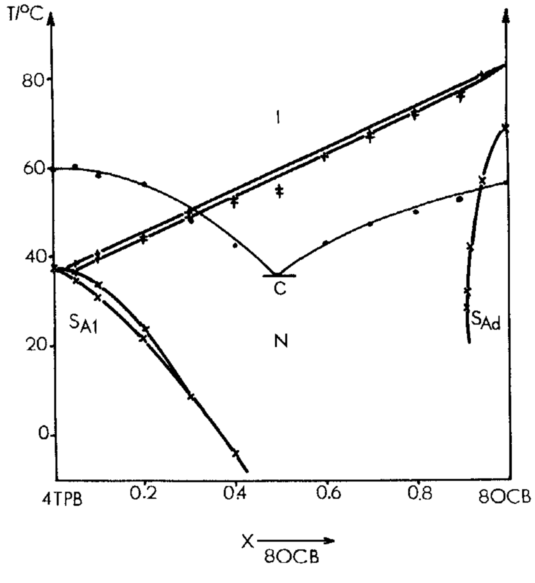


Figure 1. The phase diagram for the 4TPB–8OCB mixture.

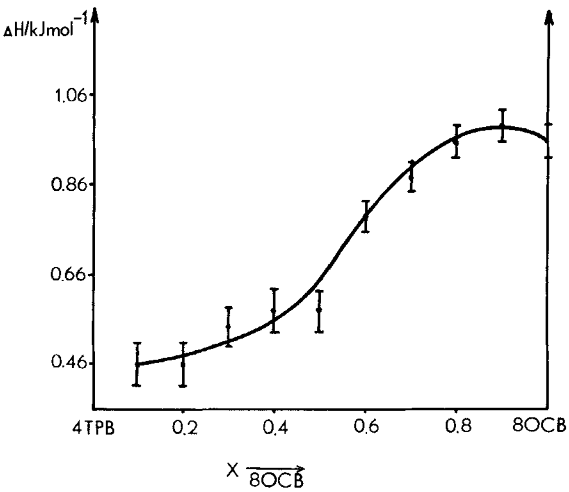
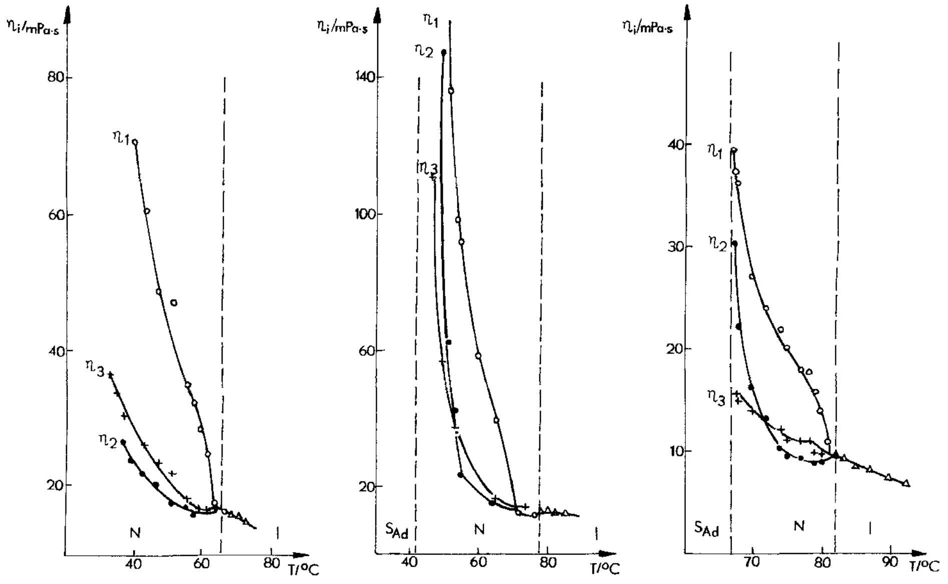


Figure 2. The dependence of the clearing enthalpy versus concentration for the component 4TPB–8OCB system.



(*a*) (*b*) (*c*)

Figure 3. The dependence of the Miesowicz viscosity coefficient versus temperature for the 4TPB–8OCB system; $x_{8OCB} = 0{\cdot}6$ (*a*), $x_{8OCB} = 0{\cdot}92$ (*b*) and pure 8OCB (*c*).

viscosity coefficient upon temperature for the $x_{8OCB} = 0{\cdot}6$ mole ratio is shown in figure 3 (*a*). This mixture is taken from the central region of the nematic gap. The viscosity coefficients increase in the order $\eta_2 < \eta_3 \ll \eta_1$. This sequence is typical for classic nematic compounds, for example MBBA or *p*-azoxyanisole [8]. The same character for the change in viscosity is also observed for other mixtures with the concentration of 8OCB in the range of 0·3–0·8 mole ratio. In quite another way the viscosity coefficients change with temperature for pure 8OCB which has smectic A_d and nematic phases and for the composition $x_{8OCB} = 0{\cdot}92$ mole ratio which is in the

Miesowicz viscosity activation energies for the system 4TPB–8OCB.

Composition mole ratio of 8OCB	E/eV		
	η_1	η_2	η_3
1·00	0·60	1·51	0·40
0·92	0·97	1·59	1·27
0·90	0·55	0·40	0·46
0·60	0·49	0·31	0·34

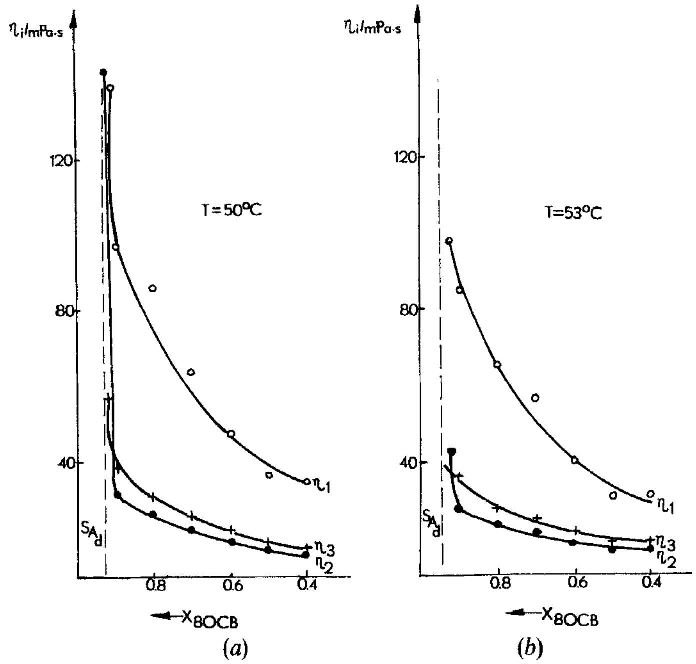


Figure 4. The dependence of the Miesowicz viscosity coefficient versus the concentration for the 4TPB–8OCB system at 50°C (*a*) and at 53°C (*b*).

neighbourhood of the smectic A_d phase (see figures 3 (*b*) and (*c*)). Near to the S_{Ad}–N phase transition a rapid increase in the η_2 coefficient is observed. At the temperature 10°C above the S_{Ad}–N phase transition the sequence of the viscosity coefficient changes. The sequence $\eta_3 < \eta_2 < \eta_1$ is observed, i.e. the same as for the mixture near the nematic–smectic phase transition [9]. It is not possible to measure the viscosity near the smectic A_1 phase because of crystallization. The character of the change of the viscosity coefficient near the S_{Ad}–N phase transition with concentration allows us to deduce how far the smectic ordering is preserved from the S_{Ad}–N borderline (see figures 4 (*a*) and (*b*)). The η_2 and η_3 coefficients are nearly independent of concentration in the x_{8OCB} mole ratio range 0·4 to 0·8 and η_1 coefficient increases monotonically with the increase of the concentration of 8OCB. In the neighbourhood of N–S_{Ad} phase transition a rapid increase of the η_2 coefficient occurs. It is interesting to note that this change takes place directly (0·02 mole ratio) before the phase transition to the smectic A_d phase, i.e. the smectic order is very quickly destroyed by the introduction of the 4TPB compound. In figure 5 the optical anisotropy Δn versus concentration is shown.

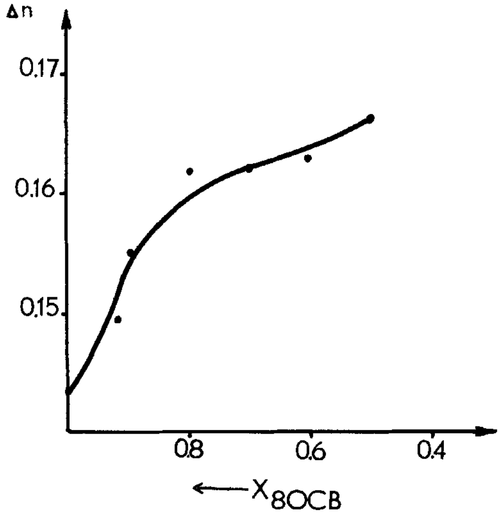


Figure 5. The dependence of optical anisotropy versus concentration 10°C from the N–I phase transition temperature.

In this case it is also observed, that a change of the optical anisotropy is much higher in the concentration range 0·98–0·8 mole ratio of 8OCB (for $T_{NI} - T = 10°C$) than in the rest of the concentration range in the gap.

X-ray investigation of the nematic phase in the gap shows the absence of cybotactic groups or other spaces. The X-ray pattern for the entire nematic gap is the same as for the common nematic phase.

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