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Mole fraction dependence of physical properties for a binary cyanobiphenyl liquid crystal system

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The physical properties of a binary liquid crystal system were investigated, namely the transition temperatures, birefringence and viscoelastic constants measured by using thermal optical microscopy, differential scanning calorimetry and light scattering techniques with coherent laser light beams. These properties were sometimes found to exhibit linear dependence on the mole fractions of the components. Our results indicate that a required property is obtainable by the regulation of the molar ratio as if the length of the alkyl chain connected with a cyanobiphenyl core group were variable; i.e. the apparent chain length could be controlled.

1. Introduction

Physical properties, such as birefringence, elasticity and viscosity, of liquid crystals (LCs) are strongly dependent on the chemical structure of the core group, the polar end group and the flexible end group, which are associated with dielectric anisotropy, molecular interaction and excluded volume. In particular, the chain length of the flexible end group in a series of homologous LCs sometimes gives rise to a systematic variation of physical properties, such as the odd–even effect [1].

The homologous series of 4-*n*-alkyl-4′-cyanobiphenyl (*n*CB) liquid crystals are a particularly interesting and useful family of mesogens [2–5]. The lower members of the family (length of the alkyl chain, $n=2$ and 3) exhibit a monotropic nematic phase, and the higher members ($n=8$–12) are polymorphic, having some smectic phases. The middle members exhibit an enantiotropic nematic phase between the crystal and the isotropic phase.

For practical use, LC materials for display devices need to operate at a wide range of temperatures and should exhibit appropriate viscoelastic properties, which determine the switching capabilities. However, it is difficult to prepare LC display cells with a pure LC compound because of the limitation of the temperature range in which it exhibits a nematic phase with a properly short response time. In order to achieve the required physical properties for display devices, multicomponent mixtures of liquid crystals are generally used.

However, a few studies [6–8] have reported the viscosity of mixed liquid crystals while a number of studies have been made of the phase diagram, the elastic constants and the order parameters [9–11]. It is necessary to predict the properties, such as viscosity and phase transition temperature, in terms of the concentration of components for the fabrication of high-performance LC devices in practical use.

This paper presents the various properties of a binary liquid crystal system, with a view toward understanding the mole fraction dependence of these properties.

2. Experimental

2.1. *Preparation of sample cells*

2.1.1. *Liquid crystals*

The liquid crystalline materials used in this experiment were two types of 4-*n*-alkyl-4′-cyanobiphenyl having alkyl chains of C_2H_5 and $C_{10}H_{21}$, frequently termed 2CB and 10CB. Both compounds were purchased from Merck Co. Ltd and mixed at various concentrations (molar fractions) to form a binary liquid crystalline system.

2.1.2. *Substrates*

The substrates used were glass slides which had been washed sequentially with acetone, a surface active agent and pure water, cleaned with a mixture of chromic acid and sulphuric acid and soaked with pure water. For a homeotropic alignment cell the substrate surface was treated with a silane coupling agent AY-43 (Toray Silicone) which has a long alkyl chain, whereas for homogeneous alignment the surface was coated with poly(vinyl alcohol) (PVA) by the dip-coating method and rubbed with a cloth in one direction.

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2.1.3. *Sandwich cell*

The LC mixtures were assembled in sandwich-type cells constructed with two glass substrates treated for homogeneous or homeotropic alignment and with two small pieces of polyester film of thickness 25 μm placed between the two substrates as the spacer. Capillary action gives rise to a spontaneous flow of the LC into the small space between two substrates, resulting in a sample cell with an appropriate alignment of LC molecules without air bubbles.

For the measurement of the refractive indices, we used wedge-like cells constructed with two substrates and one spacer. A small angle between the two glass substrates causes an incident laser beam to be refracted at an angle associated with the refractive index of the assembled LC.

A thin layer gold electrode was formed on the glass by vapour deposition for the determination of the dielectric constants.

2.2. *Measurements*

2.2.1. *Transition temperatures*

The mesophase transition temperatures of the LC mixtures were determined by optical microscopy with a Mettler FP82HT hot stage regulated by a Mettler FP80 controller, and were confirmed by differential scanning calorimetry. Phase assignments were made by microscopic observation of the optical textures obtained on cooling from the isotropic liquid.

2.2.2. *Refractive indices*

The temperature dependence of the refractive indices of the LC mixtures were determined by the following method. The wedge-like cell filled with the LC was placed in a copper block which was maintained at a temperature with a deviation of 0·1°C. A He–Ne laser beam (632·8 nm) was incident normal to one of the interfaces of the sample cell. The beam refracted at the other surface of the cell was detected with a photodiode placed on a stage moved by a stepping motor connected to a personal computer. The system determined the refraction angle by analysing the intensity profile of the refracted beam as a function of the position of the photodiode. We calculated the refractive indices from the refraction angle via Snell's law.

2.2.3. *Dielectric constants*

Dielectric constants of the binary LCs were measured at 700 Hz using a YHP-4192A Impedance Analyser (Yokokawa Hewlett Packard). The amplitude of the applied electric field was regulated to be 12 kV m^{-1}.

2.2.4. *Viscoelastic constants*

For the determination of the viscoelastic constants we utilized the Rayleigh light scattering methods [12, 13]. The optical measurement system was similar to that used for the previous studies on the Rayleigh line intensity [14, 15]. The light sources used were the 488 nm line of an argon ion laser and the 632.8 nm line of a He–Ne laser. The signal scattered by the LCs was detected with a photomultiplier. The data of the photoelectron pulses obtained were digitized and stored in the memory of a personal computer.

Elastic constant ratios of $K_{12}=K_1/K_2$ and $K_{32}=K_3/K_2$ were determined from the angular dependence of the depolarized Rayleigh line intensity; while the ratios of K_1/η_{splay}, K_2/η_{twist} and K_3/η_{bend} were determined from the relaxation times of the polarized and depolarized Rayleigh line intensity obtained on the basis of the photon counting technique. Separation of the viscosity and elasticity contribution to the relaxation rates was achieved by application of an external electric field.

Almost ideal homodyne detection can be achieved to measure the splay and twist deformation modes by tilting the homeotropically aligned cell with respect to the incident light around the axis perpendicular to the scattering plane. We chose a scattering geometry; the polar angle $\theta'=0°$, the azimuthal angle $\Phi'=-8°$ and the scattering angle $\alpha'=8°$. The temperature dependence of the refractive indices and the dielectric constants were determined in advance.

3. Results and discussion

3.1. *Phase diagram*

Figure 1 shows a phase diagram for the binary liquid crystal system of 2CB and 10CB. It should be noted that no nematic phase can be seen for both pure 2CB or 10CB. This figure indicates that the mixing of the two liquid crystals (2CB and 10CB) induces a nematic

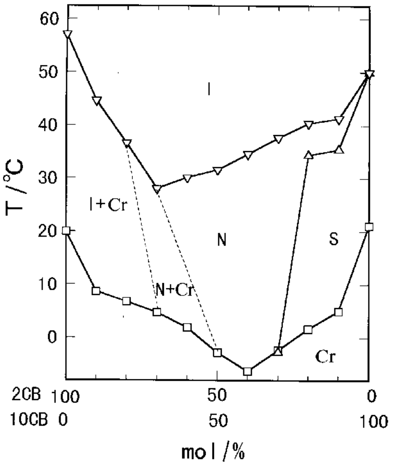


Figure 1. Phase diagram of the 2CB–10CB binary liquid crystal system.

phase at a mole fraction range between 30 and 90 per cent of 10CB. At a mole fraction around 60 per cent of 10CB, a wide temperature range of the induced nematic phase was observed (−5°C to 40°C). A smectic phase appears between the nematic and crystalline phases at a high mole fraction of 10CB, while pure 10CB exhibits only a smectic phase between the isotropic and crystalline phases.

In general, the phase boundaries defined by the I–N, N–S and S–S transitions are considered to be much more reliable than those involving Cr–S or Cr–Cr transitions at lower temperatures, because the latter transitions involving the crystal phase are subject to substantial supercooling. In figure 1, two intersecting straight lines are found for the I–N boundary with a cross-over point at 30 mol % of 10CB giving a minimum of the isotropic–nematic transition temperature (T_{NI}), whereas the crystal–liquid crystal transition temperature (melting temperature: T_m) shows minimum at 60 mol % of 10CB. The linear dependence of T_{NI} on the mole fraction allows us to predict the transition temperatures of the mixtures using a linear extrapolation of the individual T_{NI} values weighted by the mole fraction.

In other words, the transition temperatures can be controlled by mixing two cyanobiphenyl compounds having different chain lengths, as if we could obtain a required chain length of the alkyl group in pure *n*CB.

It should be noted that the phase diagram could not be complete in view of thermodynamics, because observation of the phase diagram was performed over several hours. If the transitions or the phase separation occurs slowly, the correct phase diagram may differ from our results. Actually, the phase showing coexistence of the crystal and the nematic liquid crystal disappeared within a week at room temperature; consequently a new phase of mixed crystals emerged.

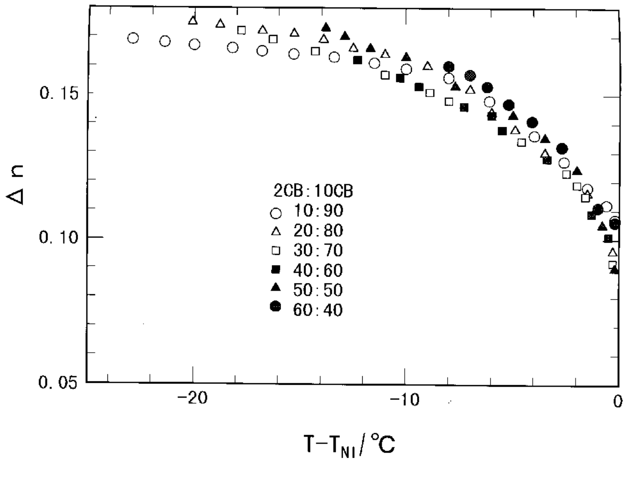


Figure 2. Birefringence of the binary LC system as a function of reduced temperature defined as T_{NI}-T.

3.2. *Birefringence*

Figure 2 shows the temperature dependence of the birefringence for binary mixtures, plotting against the reduced temperature which is defined as $T - T_{NI}$. The birefringence seems not to be strongly dependent on the molar ratio because both components in the mixture exhibit almost identical values of birefringence. For a more precise discussion we plotted the birefringences at several reduced temperatures against the molar ratio, as shown in figure 3. For 40–60 per cent of 10CB, the birefringence decreases with an increase in the mole fraction of 10CB at any reduced temperature, whereas it increases for high mole fractions of 10CB. The decrease in birefringence may be associated with a decrease in the density since the longer alkyl chain length generally reduces the degree of molecular packing in the nematic phase. On the contrary, the increase at high mole fraction

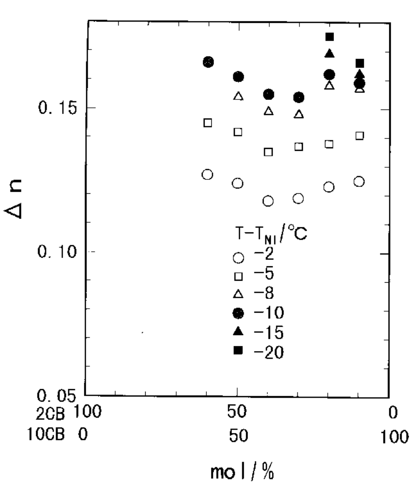


Figure 3. Mole fraction dependence of the birefringence for various reduced temperatures.

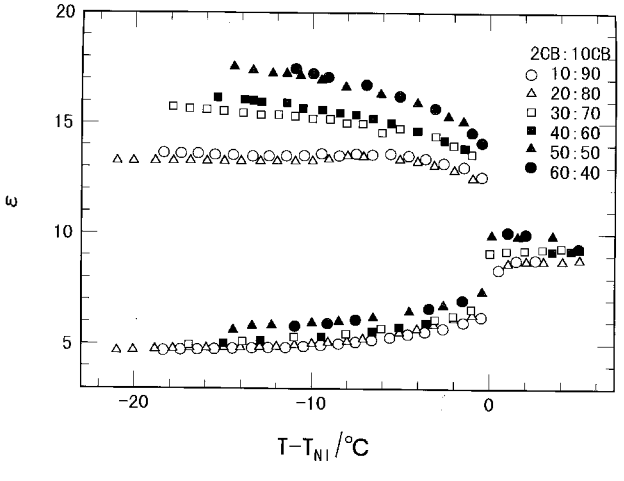


Figure 4. Dielectric constants of the binary LC system measured at 700 Hz as a function of mole fraction.

of 10CB can be caused by the existence of a smectic phase which gives a high order parameter associated with the dense packing of the LC molecules.

3.3. *Dielectric properties*

Figures 4 and 5 show the dielectric constants and the dielectric anisotropy of the LC mixtures. A higher mole fraction of 2CB gives rise to higher dielectric constants associated with the higher density of polar groups (such as the cyano group) because the volume of 2CB is smaller than that of 10CB in the system at various reduced temperatures. The dielectric anisotropy also decreases with an increase in mole fraction of 10CB as shown in figure 6, except for high mole fraction of 10CB, associated with the nematic phase as well as the refractive indices.

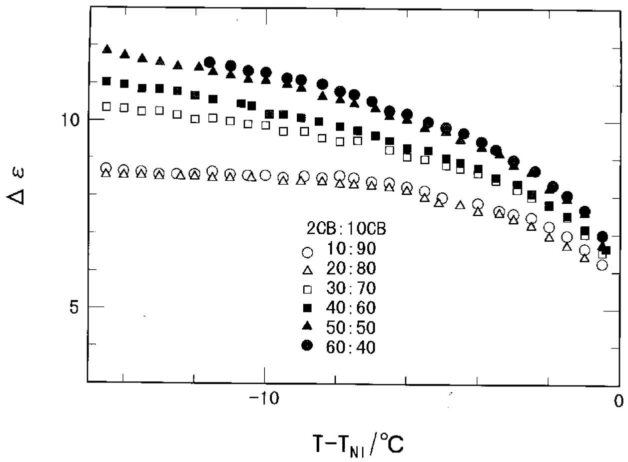


Figure 5. Dielectric anisotropy as a function of reduced temperature.

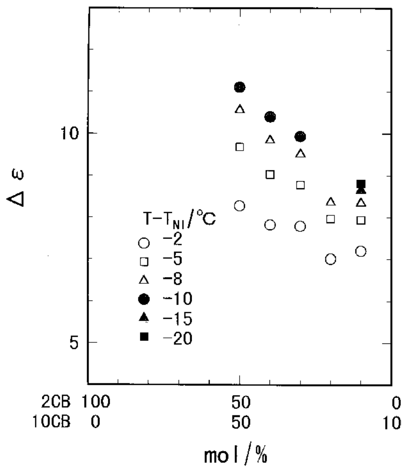
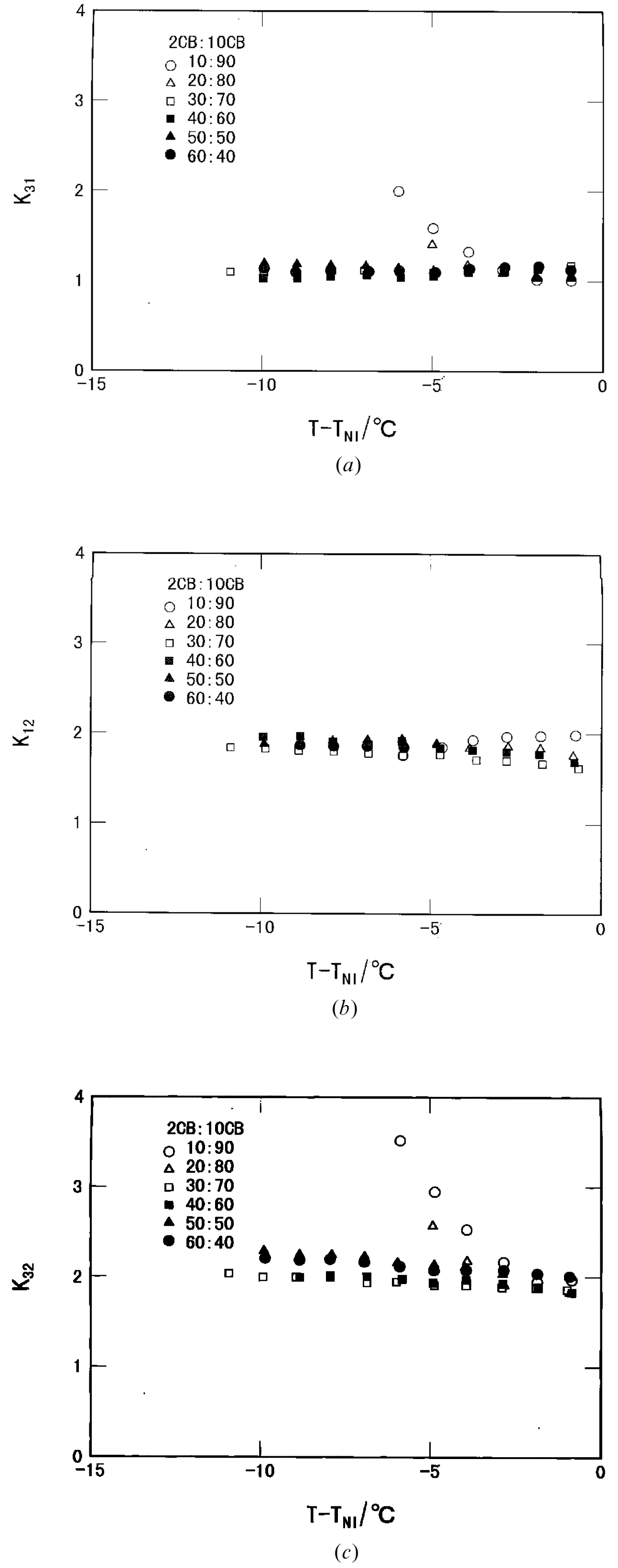


Figure 6. Dielectric anisotropy as a function of mole fraction.



(*a*)

(*b*)

(*c*)

Figure 7. Elastic constant ratios as a function of reduced temperature; (*a*) K_{31}, (*b*) K_{12} and (*c*) K_{32}.

3.4. *Elastic constants*

Three components of elastic constant ratio K_{ij} are shown in figure 7 as a function of the reduced temperature for various concentrations of the LC mixture. Each component is not strongly dependent on the reduced temperature except for high mole fractions of 10CB showing an increase in K_{31} and K_{32} at lower temperatures. This increase is associated with the existence of a smectic phase below the nematic phase at a high mole fraction of 10CB.

Figure 8 shows the variation of K_{31} measured at $T = T_{\rm NI} - 2{\cdot}0$°C with the mole fraction of 10CB; in the experimental conditions all mixtures exhibited a nematic phase. This plot indicates that the higher concentration of 10CB gives a smaller elastic constant ratio. It has been reported that for homologous series of 4-*n*-alkyl-4-cyanobiphenyl (*n*CB), the elastic constant ratio K_{31} decreases with an increase in the chain length of alkyl group. Thus the concentration of 10CB can be associated with the apparent chain length defined as an average chain length calculated from the mole fraction and the chain lengths of pure 2CB and 10CB as well as the phase transition temperatures. The curves exhibit small negative deviations from linearity. It should be noted, however, that the dependence of K_{31} on chain length is not consistent with the following empirical formula [16]: $K_{31} = kL/W$, where L is the length of the molecule, W is the width and k is a constant. This conflict could be resolved by the fact that the molecules are aggregated to pretend a larger size of molecule in the nematic phase.

Three components of elastic constants K_i are shown in figure 9 as a function of the reduced temperature for various mole fractions. The LC mixtures at high concentrations of 10CB (80–90 per cent) exhibit large values

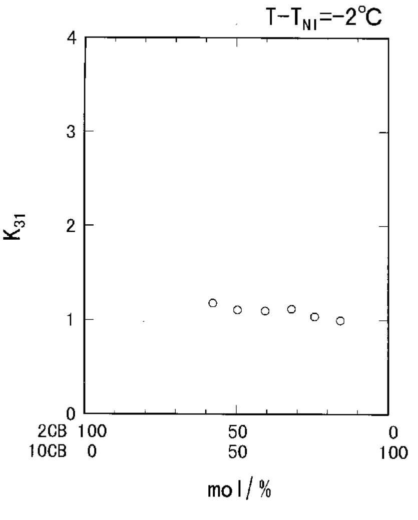
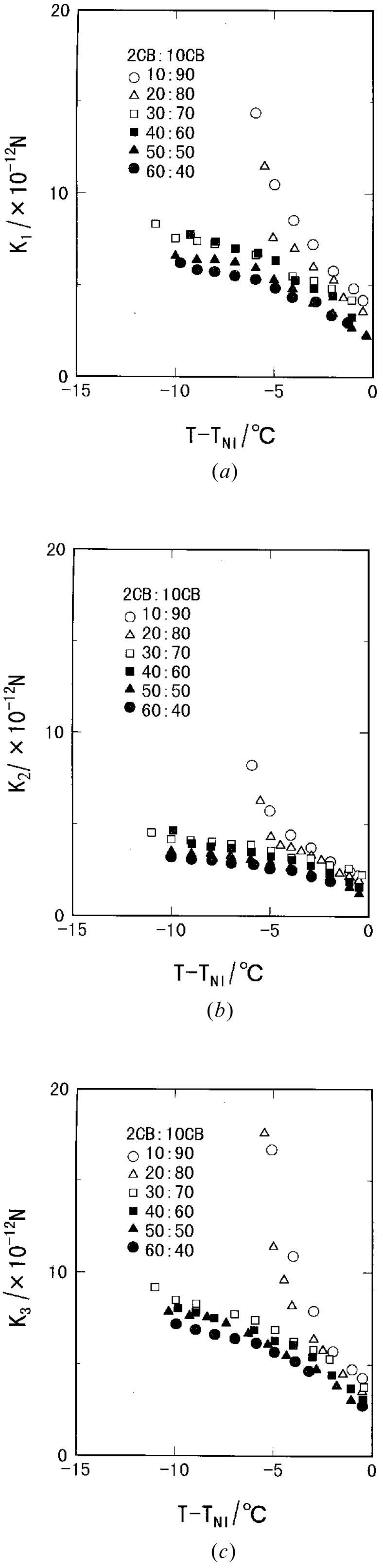


Figure 8. Mole fraction dependence of the elastic constant ratio K_{31}.



(*a*)

(*b*)

(*c*)

Figure 9. Elastic constants as a function of reduced temperature; (*a*) K_1, (*b*) K_2 and (*c*) K_3.

of K_i at lower temperature because of the effect of the smectic phase appearing below the nematic phase.

Figure 10 shows the elastic constants K_i measured at $T_{NI}-3°C$ as a function of mole fraction. In the experimental conditions, all the LC mixtures exhibited a nematic phase. Each elastic constant increases with an increase in the concentration of 10CB corresponding to the apparent chain length. At all concentrations, K_1 is nearly equal to K_3 and larger than K_2.

3.5. *Viscoelastic constant ratio*

Figure 11 shows the three components of the viscoelastic constant ratios K_1/η_{splay}, K_2/η_{twist} and K_3/η_{bend} as a function of temperature for various mole fractions. For splay and twist deformations, the ratios decrease with an increase in the reduced temperature, whereas the K_3/η_{bend} ratio increases near the transition temperature T_{NI}.

Figure 12 depicts three components of the ratios measured at $T_{NI}-2°C$ as a function of concentration. With an increase in the concentration of 10CB, all the components increase slightly. The ratio for the bend deformation is much larger than those for the splay and twist deformations.

3.6. *Viscosity coefficients*

Three components of viscosity η_{splay}, η_{twist} and η_{bend} are plotted against the reduced temperature in figure 13. For all of the deformation modes, the concentration dependence of the viscosity is similar to that of the elasticity described in the previous section; monotonous increases are found with an increase in the reduced temperature. Moreover, as well as that for the elasticity, rapid increases in the viscosity coefficients at lower temperatures for the mixtures of large concentration of

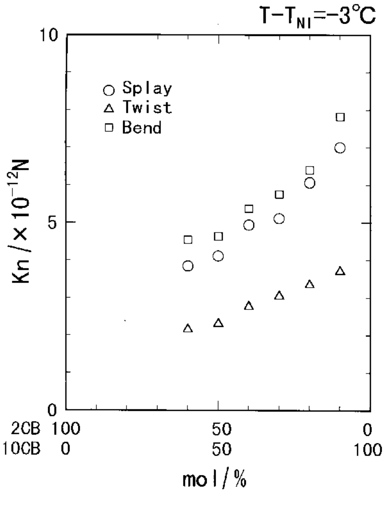
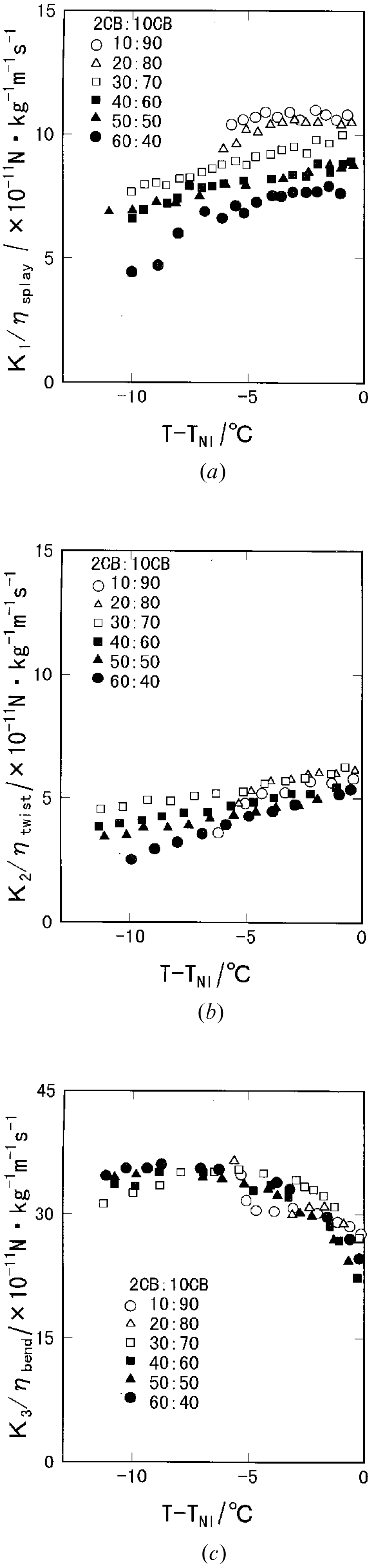


Figure 10. Mole fraction dependence of elastic constants; (*a*) K_1, (*b*) K_2 and (*c*) K_3.



(*a*)

(*b*)

(*c*)

Figure 11. Ratio of the elastic constant to the viscosity for the respective deformation mode as a function of reduced temperature; (*a*) K_1/η_{splay}, (*b*) K_2/η_{twist} and (*c*) K_3/η_{bend}.

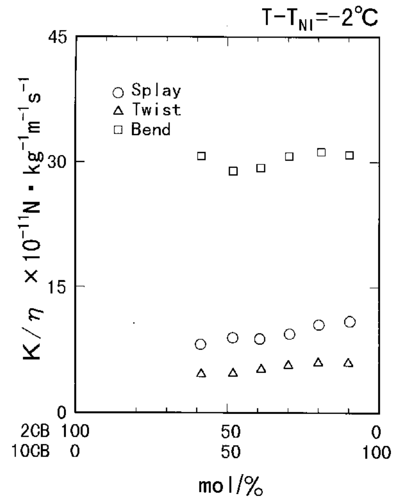


Figure 12. Ratio of the elastic constant to the viscosity for the respective deformation mode as a function of mole fraction; (*a*) $K_1/\eta_{\mathrm{splay}}$, (*b*) $K_2/\eta_{\mathrm{twist}}$ and (*c*) K_3/η_{bend}.

10CB are associated with the smectic phase which exists below the nematic phase.

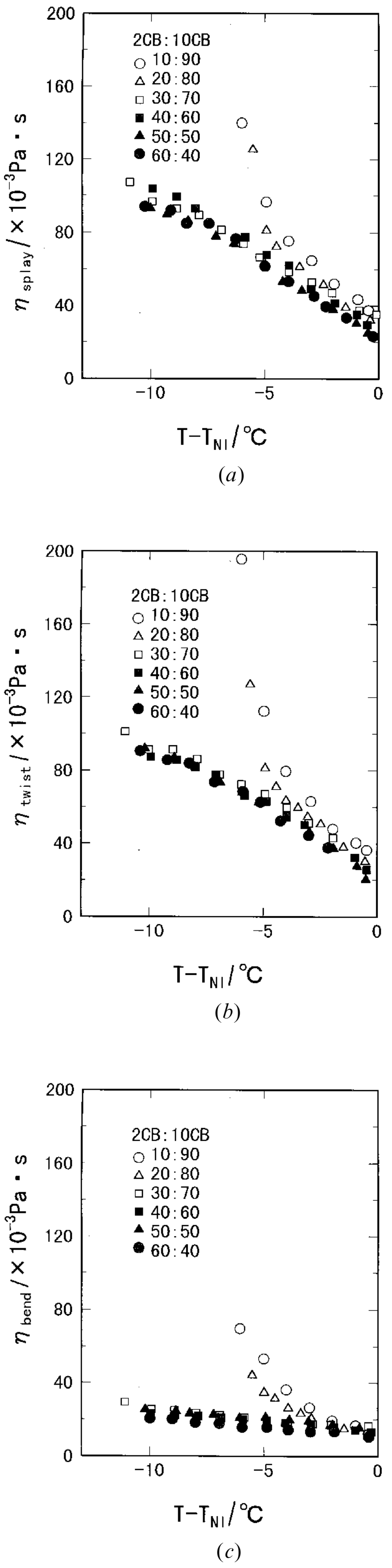
Figure 14 shows the viscosity coefficients measured at $T_{\mathrm{NI}}-3{\cdot}0$°C as a function of concentration. The concentration dependence is almost the same as for the elastic constants. However, the relations of the three components are different from that found for the elastic constants. Namely, the viscosity for the splay mode is almost identical with that for the twist mode and is much larger than that for the bend deformation. This result indicates that the Leslie coefficient μ_3 can be neglected in the nematic phase of the 2CB/10CB binary system.

It should be noted that any component of the elastic constants and the viscosity coefficients show similar dependence on the temperature, whereas for the ratio K_i/η_j, variations in the temperature dependence are found, as shown in figure 11. This result indicates that the slopes in the plots of K_i or η_j versus the reduced temperature may determine the variations in the temperature dependence of K_i/η_j, which is associated with the switching properties of LC display devices.

4. Conclusions

Physical properties of the LC mixture consisting of 2CB and 10CB are measured as a function of temperature and mole fraction. Mixing of the pure LCs gives an induced nematic phase with a wide temperature range around room temperature.

Some of the physical properties were found to exhibit a linear dependence on the mole fraction of the component. These results indicate that a required property is obtainable by the regulation of the mole fraction as if the length of the alkyl chain connected with a



(*a*)

(*b*)

(*c*)

Figure 13. Three components of the viscosity coefficient as a function of reduced temperature; (*a*) η_{splay}, (*b*) η_{twist} and (*c*) η_{bend}.

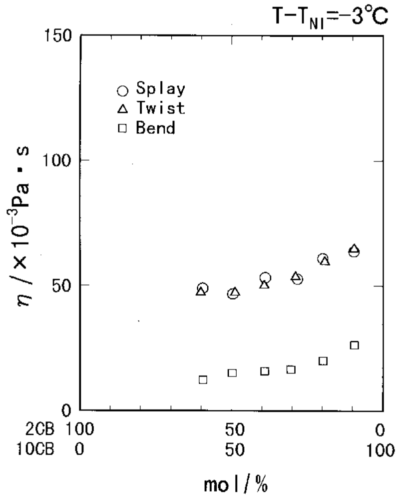


Figure 14. Three components of the viscosity coefficient as a function of mole fraction; (*a*) η_{splay}, (*b*) η_{twist} and (*c*) η_{bend}.

cyanobiphenyl core group could be controlled as far as neglecting the odd–even effect.

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