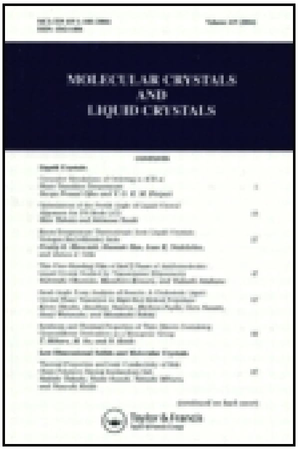

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Studies of Intermolecular Interaction in Binary Nematic Mixtures of p-Methoxybenzylidene—p′-n-Butylaniline and p-Cyano-p′-n-Pentylbiphenyl by Dielectric Relaxations

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Studies of Intermolecular Interaction in Binary Nematic Mixtures of *p*-Methoxybenzylidene—*p'*-*n*-Butylaniline and *p*-Cyano-*p'*-*n*-Pentylbiphenyl by Dielectric Relaxations

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Anisotropic dielectric relaxations at the nematic state under magnetic field and viscosities at the isotropic state were measured in MBBA–CPB systems with various mole % of CPB. The intermolecular interaction in the systems with different mole % of CPB was estimated by the Maier–Saupe theory from the dielectric relaxations and the viscosities. A long range–intermolecular interaction increased anomalously near the two CPB concentrations exhibiting the eutectic points (15 and 75 mole % of CPB). This was explained by some component fluctuation originating in the inversion of solvent–solute relationships at the eutectic mixing ratio.

INTRODUCTION

Our previous dielectric works[1-3] have revealed that the Meier–Saupe theory holds well in binary nematic mixtures and that an intermolecular interaction in the nematic ordering is appropriately estimated by a relation, $Q = \Delta H(L) - \Delta H(H)(\Delta H(\eta))$ [Eq. (1)], derived from the Meier–Saupe theory.[4-7] Here, $\Delta H(L)$, $\Delta H(H)$, and $\Delta H(\eta)$ are the activation enthalpies for the lower frequency relaxation (L-relaxation), the higher frequency relaxation (H-relaxation), and viscosity (η) at the isotropic phase, respectively. Q is a potential barrier for the long range–intermolecular interaction of nematic ordering,

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i.e. nematic potential. In the binary mixtures of *p*-methoxybenzylidene—*p*′-*n*-butylaniline (MBBA) and *p*-ethoxybenzylidene—*p*′-cyano-aniline (EBCA) which have the eutectic point at 15 mole % of EBCA and 14°C, a long range-intermolecular interaction in the nematic ordering increased anomalously near the eutectic concentration, c_E^2. In the binary mixtures of MBBA and non-mesogenic compound, the molecular shape of non-mesogenic compound (solute) affected the intermolecular interaction of nematic ordering in MBBA solvent; the linear shaped solute strengthened a long range-intermolecular interaction and the non-linear shaped solute did not give any influence on the intermolecular interaction.[3,8]

Recently, Park and Labes[9,10] found that MBBA—*p*-cyano-*p*′-*n*-pentylbiphenyl (CPB) system exhibits double eutectic points near 15(c_{E1}) and 75 mole %(c_{E2}) of CPB and form a charge transfer complex near 50 mole % of CPB, and they examined several electro-optic parameters such as threshold voltage, rising and decay times, and dielectric anisotropy in the system; the dielectric anisotropy deviated considerably positively from simple addition relationships with mole % of CPB and the threshold voltage increased somewhat with the formation of charge transfer complex. These results are interesting, because in usual binary nematic mixtures, the electro-optic parameters obeyed the addition rule with composition.[11–13] The purpose of this work is to examine change of intermolecular interaction in the nematic phase by mole % of CPB in the MBBA–CPB system from dielectric relaxations.

EXPERIMENTAL

MBBA was synthesized and purified by the same procedure as described previously.[2] CPB was purchased from BDH Chemicals Ltd. The binary mixtures were carefully prepared by mixing each component under a dry nitrogen atmosphere at a temperature just above the clearing temperature. The samples used are listed in Table I.

Dielectric and viscosity measurements were carried out in the way described previously.[1–3] Dielectric constant, $\varepsilon'_{\parallel}$, and the loss, $\varepsilon''_{\parallel}$, in the parallel direction to the applied magnetic field of 4 kOe were measured in the frequency range of 1 kHz to 5 MHz.

RESULTS AND DISCUSSION

Figure 1 shows frequency dependence of dielectric constant, $\varepsilon'_{\parallel}$, (a) and the loss, $\varepsilon''_{\parallel}$, (b) for C-15 at several temperatures. The *L*-relaxation is observed at 980 kHz and 21.7°C, and the increase of $\varepsilon''_{\parallel}$ at low frequencies below 10

TABLE I

List of samples

Sample	Mole % of CPB	Conductivity at 25°C (10^{-10}) Ω^{-1}. cm^{-1}	Density at 63°C g/ml
MBBA	——	9.5	1.010
C–10	10.6	6.8	1.013
C–15	14.9	3.0	1.011
C–20	19.9	5.4	1.008
C–46	46.4		1.004
C–70	69.8	18.5	0.998
C–75	75.0	12.7	0.995
C–80	79.9	11.8	0.993
CPB	100.0		0.989

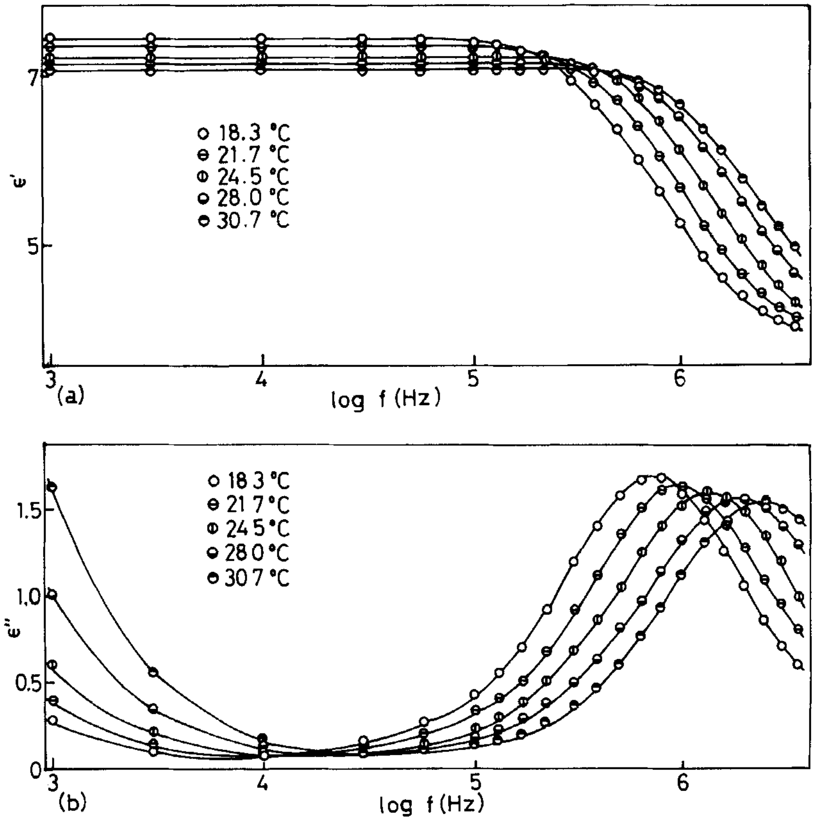

FIGURE 1 Frequency dependences of dielectric constant, $\varepsilon'_{\parallel}$, (a) and the loss, $\varepsilon''_{\parallel}$, (b) for C–15 at several temperatures.

kHz may be attributed to an ionic conduction by impurities. The Arrhenius plots of the *L*-relaxation in various samples are shown in Figure 2. The activation parameters and relaxation time, τ_L, are listed in Table II. The *L*-relaxation for C–46 was not observed in this experiment, because it existed in the higher frequency range above 5 MHz. The Arrhenius plots for η at the

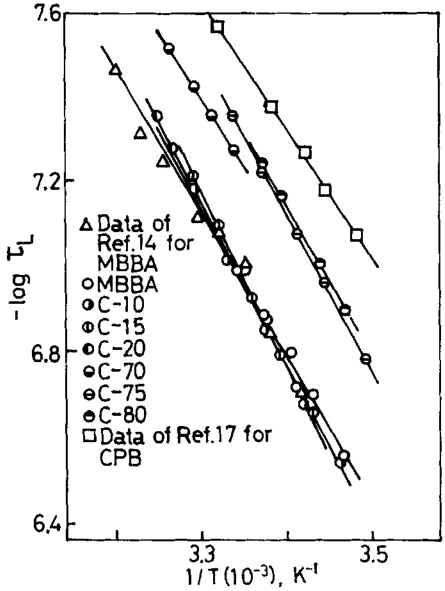

FIGURE 2 The Arrhenius plots of *L*-relaxations in various samples.

TABLE II

Relaxation parameters for *L*-relaxation, activation enthalpy for viscosity at the isotropic state, $\Delta H(\eta)$, and nematic potential, Q, in various samples.

Sample	τ_L at 26.2°C (10^{-8}) sec	$\Delta H(L)$ kJ/mole	$\Delta H(\eta)$ kJ/mole	Q kJ/mole
MBBA	10.3	63.2	33.5	29.7
C–10	10.3	68.6	32.6	36.0
C–15	9.77	76.1	33.0	43.1
C–20	10.0	71.1	32.6	38.5
C–46			31.8	
C–70	5.35	59.4	31.8	27.6
C–75	4.51	69.0	31.8	37.2
C–80	4.47	65.3	31.8	33.5
CPB	3.09	56.5	31.0	25.5

isotropic phase in various samples are shown in Figure 3. The activation enthalpies obtained from the slope are also listed in Table II. The values of Q in various samples, therefore, were calculated by Eq. (1). The values of $\Delta H(L)$, $\Delta H(\eta)$, and Q with CPB concentration are plotted in Figure 4. The

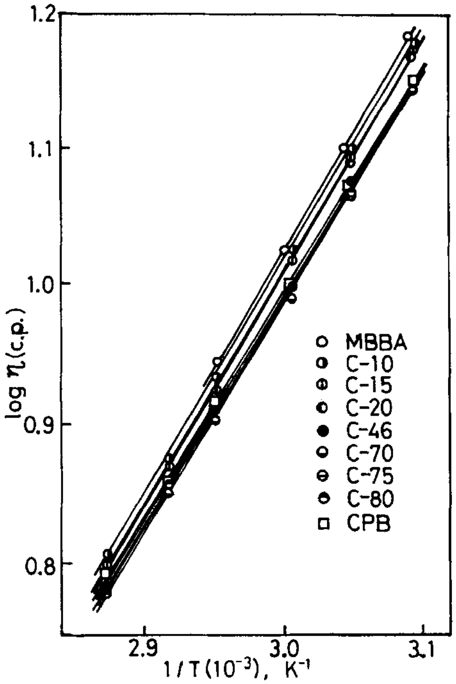

FIGURE 3 The Arrhenius plots of viscosities at the isotropic state, η, in various samples.

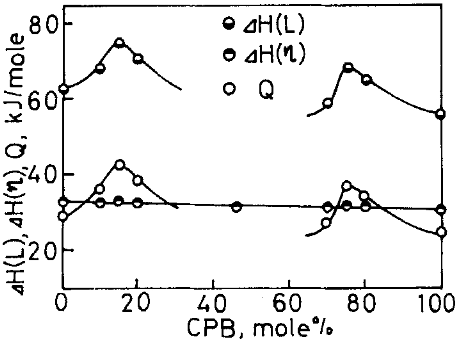

FIGURE 4 Plots of $\Delta H(L)$, $\Delta H(\eta)$, and Q vs. mole % of CPB in MBBA-CPB system.

values of Q exhibit maxima near 15 and 75 mole % of CPB, and the values of $\Delta H(\eta)$ remain constant over all CPB concentrations. Therefore, it was concluded that a long range-intermolecular interaction in nematic ordering increases near 15 and 75 mole % of CPB. These CPB concentrations correspond to the two eutectic concentrations of CPB in the binary system. From the phase diagram obtained by Park and Labes,[9,10] this system forms clearly eutectic mixtures of MBBA and charge transfer complex between 0 and 50 mole % of CPB and those of the complex and CPB between 50 and 100 mole %. Therefore, the anomalous increase of intermolecular interaction near c_{E1} and c_{E2} can be explained by a component fluctuation which would be produced by the inversion of solvent-solute relationships at the eutectic concentration. Unfortunately, we could not observe the L-relaxation around 50 mole % of CPB at which the charge transfer complex is formed, but an abnormal change of intermolecular interaction appears not to occur by the formation of the complex. Indeed, the values of $\Delta H(\eta)$ do not undergo any abnormal change near 50 mole % of CPB. This leads to the conclusion that the charge transfer complex may act as a nematogenic compound. Figure 5 shows the plots of τ_L against mole % of CPB at 0.968 of reduced temperature. The values of τ_L also exhibit a small decrease neaı c_{E1} and c_{E2}. The value of τ_L is connected with the twisted viscosity, η_t, at the nematic phase by a relation,[14,15] $\tau_L = A/kT \cdot \eta_t$. Here, A is a constant, and k and T are the Boltzmann constant and absolute temperature. Therefore, the decrease of τ_L must lead to the decrease of rising and decay times in the electro-optic effect. However, these phenomena are not obviously observed from Park–Labes' results.[10] This means that the abnormal change is too small to visualize in the electro-optic effect.

Various nematic mixtures have been developed as nematogen for electro-optic display devices during several decades.[16] Although mixing pure nema-

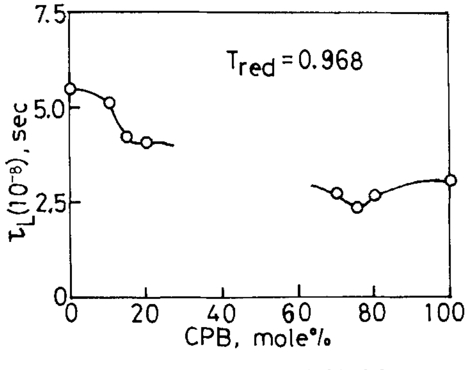

FIGURE 5 Plots of relaxation time, τ_L, vs. mole % of CPB in MBBA–CPB system.

togenic compounds broadens and lowers the nematic temperature range and compensates the characteristic physical properties of constituents each other, it scarcely afford new and distinctive properties which do not exist in pure nematogenic compounds. It is of interest to study physical properties near c_E in various eutectic mixtures for finding new electro-optic display material.

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