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Dielectric Relaxation Studies on Two Systems Exhibiting the Induced Smectic A Phase

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Recently we reported some physical studies (layer spacings using X-ray scattering, low frequency dielectric constants) on two systems exhibiting a maximum (indicating an induced smectic A) as well as a minimum in the A–N transition boundary. In this paper we report measurements of the dielectric relaxation of $\epsilon_\parallel$ (up to 13 MHz) for a few compositions of the two systems. The activation energy in the A phase of the mixtures corresponding to the maximum in the A–N boundary is higher than that of the pure polar component. The results are discussed in relation to the molecular interactions giving rise to the induced smectic A phase.

INTRODUCTION

In an earlier study,[1] we reported the phase diagrams and some physical studies on the binary mixtures of the following systems: (i) *p*′-nitrophenyl-*p*-*n*-octyloxybenzoate (NPOOB) with (2-hydroxy)-*p*-ethoxybenzylidene-*p*′-butylaniline (OH-EBBA) and (ii) *p*′-*n*-octyloxy-*p*-cyanobiphenyl (8 OCB) with *p*-butoxyphenyl-(*p*′-pentyloxy)benzoate (40.05). The structural formulae of the compounds used are shown in Figure 1. The phase diagrams are reproduced in Figures 2 and 3. The mixtures exhibit a maximum as well as a minimum in the A–N transition boundary. The maximum indicates the formation of an induced smectic A phase[2–5] which has essentially a monolayer structure, i.e., a layer spacing corresponding to an appropriate average of the molecular lengths. The minimum in the transition boundary indicates that the partial bilayer (i.e., with layer spacing $d \leq 1.4$ times the molecular length l) of the highly polar component is not structur-

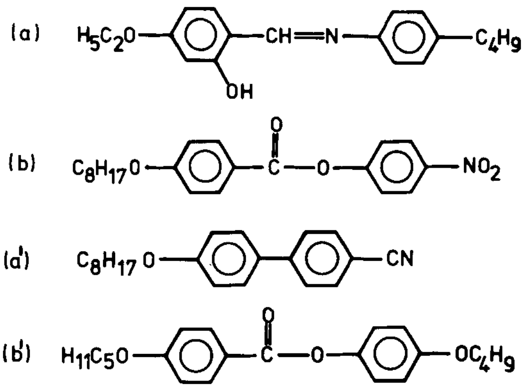

FIGURE 1 Structural formulae of (a) (2-hydroxy)-*p*-ethoxybenzylidene-*p*′-butylaniline (OH-EBBA), (b) *p*′-nitrophenyl-*p*-*n*-octyloxybenzoate (NPOOB), (a′) *p*′-*n*-octyloxy-*p*-cyanobiphenyl (8 OCB), (b′) *p*-butoxyphenyl-(*p*′-pentyloxy)benzoate (40.05).

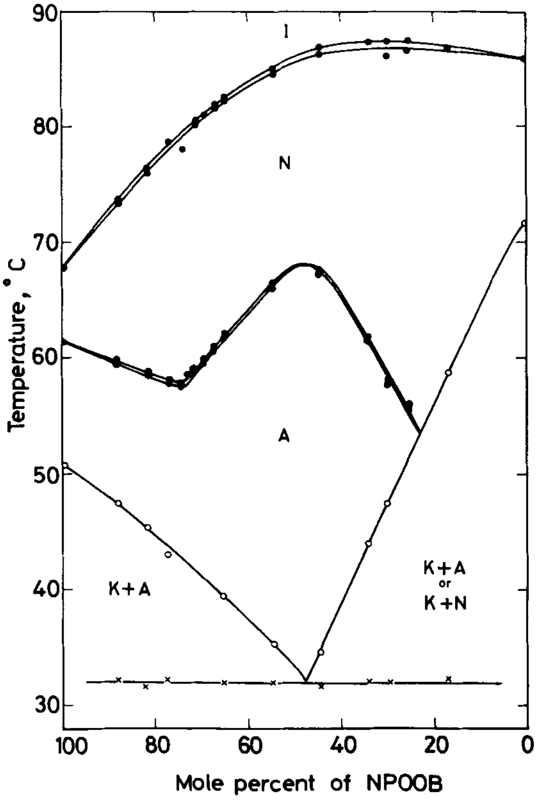

FIGURE 2 Phase diagram of mixtures of NPOOB with OH-EBBA (system I). K stands for the crystalline phase.

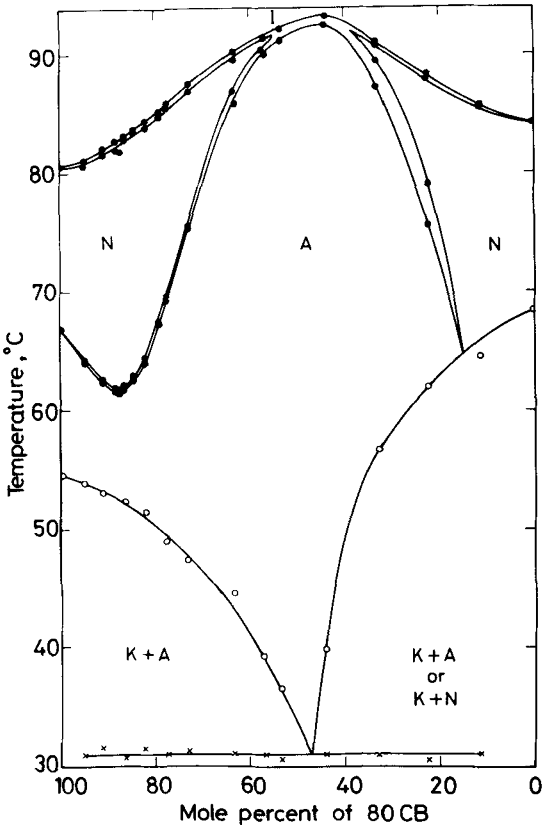

FIGURE 3 Phase diagram of mixtures of 8 OCB with 40.05 (system II). K stands for the crystalline phase.

ally compatible with the monolayer of the induced A phase. Nevertheless, the two species coexist close to the minimum in the boundary and an S_A–S_A transition could not be observed in the systems. Based on the nature of the phase diagrams and our X-ray studies on the composition and temperature dependence of the layer spacing, we concluded that in system I (see Figure 1) the mutual interactions responsible for the induced A phase are much weaker than in system II. In the present paper, we report the dielectric relaxation measurements (up to 13 MHz) on some compositions of both the systems and discuss the results in terms of the molecular interactions.

EXPERIMENTAL

The samples were taken between two aluminum coated electrodes, and aligned using a magnetic field of ~ 14 KGauss, such that the director is parallel to the applied electric field. The measurements were made using a Hewlett-Packard LF Impedance analyzer, Model 4192A.

RESULTS AND DISCUSSION

The results on NPOOB are shown in Figure 4 in the form of a Cole–Cole plot. Though the low frequency data lie on a semicircle, there are considerable deviations at higher frequencies. This result is in agreement with an earlier study on this compound[6] and indicates a higher frequency relaxation. Most probably this is analogous to the high frequency shoulder found in the $\epsilon_{\parallel}$ relaxation of 7CB and 7OCB by Buka *et al.*[7] This has been attributed by them to a partial reorientation within short range ordered groups and later reproduced in a numerical calculation on the basis of a model of Brownian motion.[8] Another possible origin for the shoulder lies in the librational and reorientational motion of the transverse dipole moment of the ester group. This relaxation frequency lies at ~ 37 MHz according to Ref. 6. The activation energies in the smectic A and nematic phases are given in Table I and are in broad agreement with the earlier results.[6] The activation energy in the A phase is much lower than that of the nematic phase. The peak value of $\epsilon''_{\parallel}$ decreases slowly with temperature in the A phase, and more rapidly in the nematic phase, due to a corresponding reduction in the orientational order. The $\mu_{\perp}$-relaxation

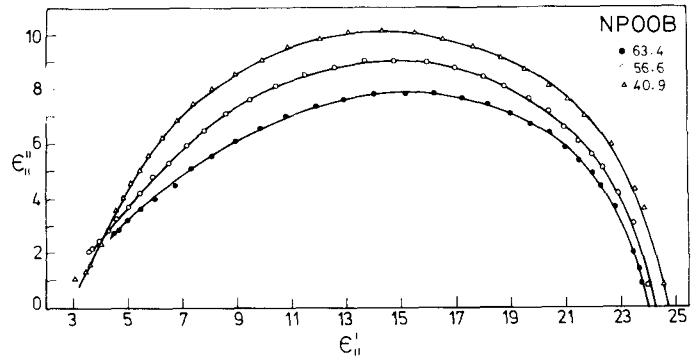

FIGURE 4 Cole–Cole plot in the case of NPOOB. In this and subsequent diagrams, the numbers against symbols indicate the temperatures in °C.

TABLE I

Activation energies in eV in smectic A and nematic phases

	Smectic A	Nematic
NPOOB	0.47	0.77
90.2% NPOOB + 9.8% OHEBBA	0.47	0.86
54.5% NPOOB + 45.5% OHEBBA	0.67	0.83
8 OCB	0.49	0.7
63.5% 8 OCB + 36.5% 40.05	increases continuously from 0.43 to 0.87 eV with decrease of temperature	—

is better visible in $\epsilon_{\parallel}$ measurements at higher temperatures for the same reason.

The Cole–Cole plot corresponding to a mixture with 90.2% NPOOB is shown in Figure 5. The peak $\epsilon''_{\parallel}$ value is slightly lower than in pure NPOOB. The Cole–Cole plot can be fitted to better semicircles at lower temperatures. The activation energy in the A phase does not change much compared to that of pure NPOOB (Table I) but that in the nematic phase shows some increase.

The results on a mixture with 54.5% NPOOB which is close to the composition corresponding to the maximum in the A–N boundary (see Figure 2) are shown in Figure 6. The fit with a semicircle is now very good indicating that a single relaxation time characterizes the

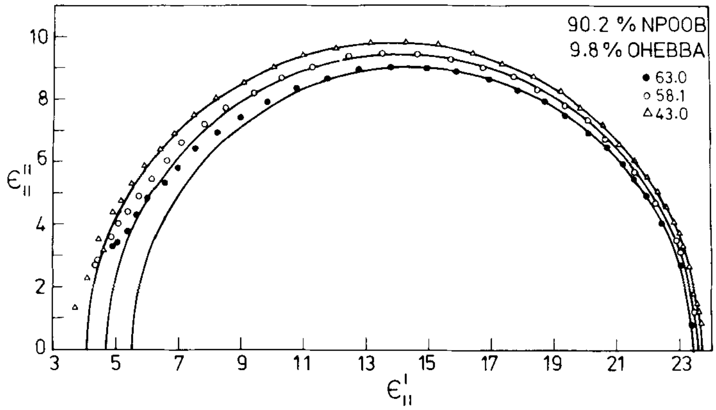

FIGURE 5 Cole–Cole plot in the case of 90.2% NPOOB and 9.8% OHEBBA. Centres of the semicircles drawn lie on $\epsilon'_{\parallel}$ axis, with the centres shifting towards the origin with decrease of temperature.

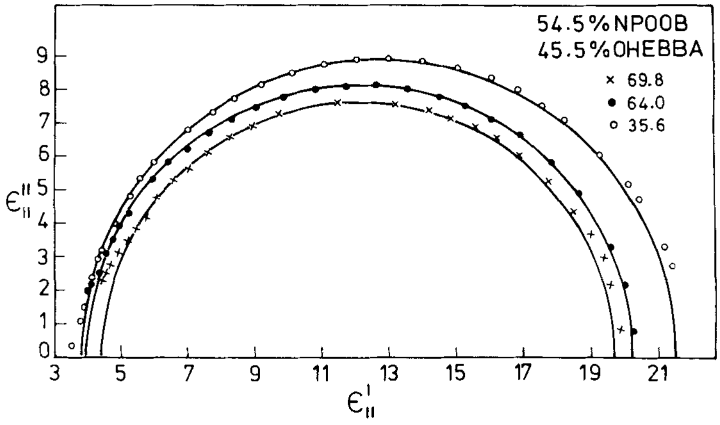

FIGURE 6 Cole-Cole plot in the case of 54.5% NPOOB and 45.5% OHEBBA. Centres of the semicircles drawn lie on $\epsilon_\parallel'$ axis with the centres shifting away from the origin with decrease of temperature.

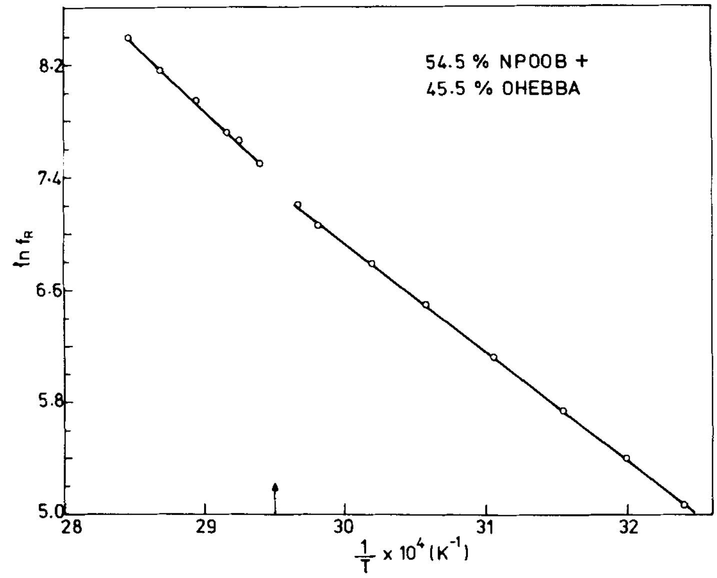

FIGURE 7 Plot of ln f_R vs. $1/T$ in the case of a mixture of 54.5% NPOOB and 45.5% OHEBBA, where f_R is the frequency corresponding to $\epsilon_\parallel''$ peak.

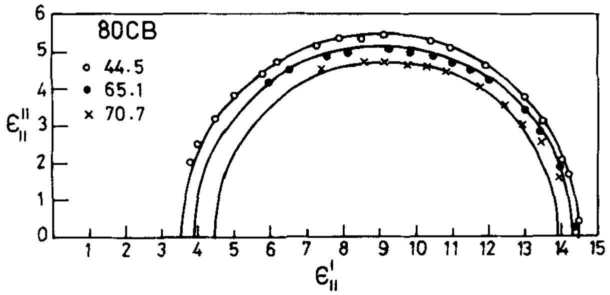

FIGURE 8 Cole–Cole plot in the case of 8 OCB. Centres of the semicircles lie on $\epsilon'_{\parallel}$ axis with centres shifting slightly towards the origin with lowering of temperature.

dispersion. The frequency of the $\epsilon''_{\parallel}$ peak at $\simeq 40\,^\circ\mathrm{C}$ is ~ 200 KHz for the 54.5% mixture while it is at ~ 900 KHz for pure NPOOB. The activation energy in the A phase has increased considerably for this mixture (Figure 7, Table I) compared to that of pure NPOOB.

The results on 8 OCB and its mixture with 36.5% of 40.05 are shown in Figures 8 and 9 respectively. In 8 OCB the Cole–Cole plots are semicircles. The amplitude is $\simeq 5.4$ at the lowest temperature, which is much lower than that in NPOOB (Figure 4). In the latter compound the ester dipole moment adds to the total dipole moment of the molecule and gives rise to a higher peak. The activation energy (Table I) in the A phase is smaller than that in the nematic phase in 8 OCB also. In the case of the mixture of 8 OCB with 40.05 (Figure 9), the Cole–Cole plot is a good semicircle with the centre lying on the $\epsilon'_{\parallel}$ axis only at lower temperatures. At higher temperatures, the centre of the

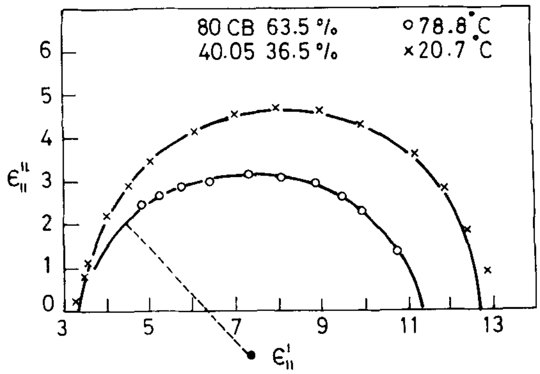

FIGURE 9 Cole–Cole plot in the case of a mixture of 63.5% 8 OCB and 36.5% 40.05. Centre of the semicircle corresponding to 20.7 °C lies on the $\epsilon'_{\parallel}$ axis while that corresponding to 78.8°C lies below the $\epsilon'_{\parallel}$ axis.

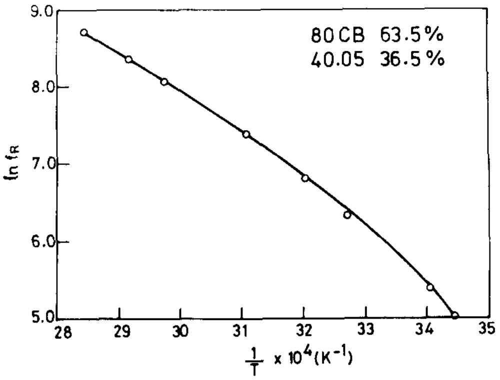

FIGURE 10 Plot of ln f_R vs. $1/T$ in the case of mixture of 63.5% 8 OCB and 36.5% 40.05, where f_R is the frequency corresponding to $\epsilon''_{\parallel}$ peak.

circular arc lies *below* the ϵ' axis, which indicates a non-Debye relaxation involving a distribution of relaxation times.[9] Indeed the plot of ln f_R vs. $1/T$ (Figure 10) does not yield a straight line as in other cases, but a line curved such that the activation energy which is ~ 0.43 eV at the highest temperature in the A phase continuously increases to ~ 0.87 eV at the lowest temperature of measurement.

As we have discussed in our earlier paper,[1] in the system I the NPOOB and OHEBBA molecules tend to form interacting pairs (due to charge transfer complex formation and other interactions) in the mixtures. The pairs are likely to break up at higher temperatures, thus allowing NPOOB molecules to form antiparallel pairs. It is fair to assume that the strongly polar NPOOB molecules contribute almost entirely to the observed dielectric relaxation of the mixtures. Thus the observed increase in the activation energy of the mixture compared to that of pure NPOOB should be attributed to the formation of NPOOB-OHEBBA pairs. This interaction is also responsible for the large reduction of the relaxation frequency itself in the mixtures. Further, the Cole–Cole plots show that at lower temperatures the mixtures deviate very little from a Debye relaxation (Figure 6). Thus the short range order effects in NPOOB-OHEBBA pairs do not lead to any tail in the high frequency region. As the temperature is increased, more NPOOB-NPOOB pairs are formed and the high frequency tail is again noticeable.

As we have argued in our earlier paper, the interactions between 8 OCB-40.05 molecules of system II leading to the formation of the induced smectic A phase are much stronger than in the case of system I (NPOOB-OHEBBA) (Figure 3). Thus the induced smectic A phase is stable over a much wider range of temperatures in system II than in system I. The interactions are strong at lower temperatures, and the activation energy has a high value. As the temperature is raised, the interactions are weakened giving a lower activation energy. Further, the relaxation takes non-Debye characteristics (Figure 9) indicating a complex mechanism. The environment of 8 OCB molecules is probably no longer as well defined as at lower temperatures.

In all the cases we have studied the activation energy in the A phase is smaller than in the nematic phase (Table I). This result has been seen earlier in many compounds exhibiting both bilayer[10-12] and monolayer[13] smectics. As we have argued elsewhere,[14] this feature can be understood as arising from two possible mechanisms.

(i) In a recent theory which takes into account the dipole-dipole correlations, Edwards and Madden[15] have shown that in a *nematic* liquid crystal the relaxation time parallel to the director can be reduced to the form

$$\tau_{\parallel} = \tau_D g_{\parallel}\left(\frac{\epsilon_{\parallel} - 1}{\epsilon - 1}\right) \tag{1}$$

where τ_D is the usual Debye relaxation time, $g_{\parallel}$ the retardation factor introduced by Maier and Meier,[16,17] which is a consequence of the nematic potential, and $\epsilon_{\parallel}$ the *static* dielectric constant parallel to the director and ϵ the mean dielectric constant. The terms in the brackets are new in this theory and reflect the effect of the dipole correlations in the medium. Assuming that this relation is valid in the smectic A phase also, the reduction in the activation energy of the A phase can be attributed to the increased antiparallel correlations brought about by the layered arrangement.[18,19] This usually leads to a lowering of $\epsilon_{\parallel}$ in the smectic A phase, or an increase in the relaxation frequency which is equivalent to lowering of the activation energy. This may partly explain the results of our study on both systems I and II. For example, we plot the static dielectric constants of the (63.5%) 8 OCB and (36.5%) 40.05 mixture in Figure 11. The $\epsilon_{\parallel}$ value first decreases in the smectic A phase and then continuously increases with decrease of temperature. Using relation (1), this effectively means that the relaxation frequency should decrease more rapidly or equivalently the activation energy is higher at lower temperatures. This effect is not very obvious in system I, perhaps due to the smaller range of temperature over which measurements could be made.

Druon and Wacrenier[20] have pointed out that in the case of partial bilayer structures in the strongly polar compounds, the mutual interaction energy between a pair of molecules is highly asymmetric as a function of the angle between their long axes. The activation energy is

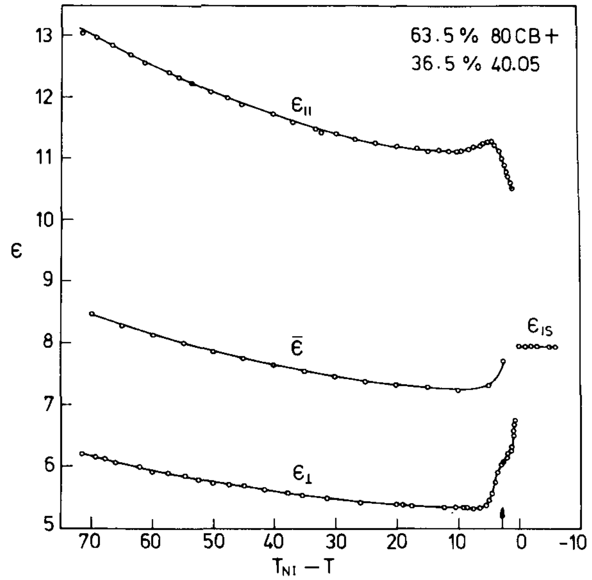

FIGURE 11 Temperature variations of static dielectric constants of a mixture of 63.5% 8 OCB and 36.5% 40.05. The arrow mark indicates T_{AN}, the nematic-smectic A transition point.

determined by the lower potential barrier. On the other hand, they assume that the asymmetry disappears in the nematic phase, the average potential barrier leading to a higher activation energy than in the A phase. This cannot be the principal mechanism in monolayer smectics in which the asymmetry of the potential function can be expected to be small.

(ii) Another possible contribution to the lowering of the activation energy in the smectic A phase may come from packing effects.[14] In many compounds, including 8 OCB[21] and NPOOB,[1] the layer spacing of the A phase hardly varies with temperature. Thus the volume expansion mainly causes an expansion in the lateral direction. For instance de Vries[22] has found that the temperature variation of the lateral dimension is larger in the smectic A phase than in the isotropic phase. In the smectic A phase, voids are pushed into the layers in which the molecules can reorient more easily, with less number of mutual collisions or a lower friction coefficient.[9] Thus the anisotropic packing effects appear to favour a lowering of the activation energy in the smectic A phase.

In conclusion, our results bring out the influence of the molecular interactions responsible for the formation of the induced smectic A phase on the dielectric relaxation of the systems studied.

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