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RELAXATION PHENOMENA IN THE NEMATIC, NEMATIC REENTRANT AND SMECTIC A PHASES STUDIED BY DIELECTRIC SPECTROSCOPY

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Abstract Dielectric properties and relaxation processes of binary mixture (MIX I) and quaternary mixture (MIX II), both composed of 4-alkylphenylcarbonyloxy-4'-cyanophenyls and -4'-cyanobiphenyls, have been studied by dielectric spectroscopy in the frequency range from 5 Hz to 10 GHz. Dielectric measurements have been done for two principal alignments of the N, SmA_d and N_R phases. In the case of MIX II the parallel component of dielectric permittivity shows a pronounced decrease in the Sm A_d phase due to dipole-dipole correlation. This anomaly is much weaker for MIX I. Low frequency spectra for both mixtures consist of two well separated absorption peaks connected, respectively, with biphenyl and triphenyl ring entities. By fitting a sum of two Cole-Cole functions it was possible to compute dielectric parameters of the relaxation processes observed. In both cases the relaxation times exhibit Arrhenius type behavior with activation energy higher in the N_R than in SmA_d and N phases. At high frequencies (from 10MHz to 10GHz) a broad spectrum, originating from a number of relaxation processes, have been observed.

INTRODUCTION

Since the discovery of nematic reentrant (N_R) phase by P.E. Cladis[1] in 1975 its existence has been proved for many compounds and for many multicomponent systems as well. The most intriguing puzzle is that the N_R phase shows up below a more ordered smectic A_d (SmA_d) phase. The SmA_d phase has the layer thickness between the molecular length (l) and its double. The effect of reentrance is caused by change of equilibrium between correlated and non-correlated entities of molecules resulting from the competition between long range and short range order of molecules in the presence of thermal bath. Dielectric spectroscopy is a good tool to study both structure and molecular dynamics of the N, SmA_d and N_R phases. In this paper a dielectric study of two multicomponent mixtures is presented. Both mixtures exhibit an "island" of SmA_d phase[2] surrounded by a nematic "sea" (Figures 1a and b). As is seen the mixtures are composed of two phenyl ring (2Ph) : 4-alkylphenylcarbonyloxy-4'-cyanophenyls and three phenyl ring (3Ph): 4-alkylphenylcarbonyloxy-4'-cyanobiphenyls.

EXPERIMENTAL

Low frequency dielectric spectra of MIX I and MIX II have been measured in the frequency range from 5 Hz to 13 MHz using HP4192A impedance analyzer. The thickness of the sample layer placed in a capacitor made of two gold coated glass plates, was *36*μm . The sample was aligned homeotropically in the N (or N_R) by either magnetic field of 1.2T or electric field of 1 MV/m. Planar alignment was

obtained by the magnetic field. Time domain spectroscopy (TDS) was used to study the high frequency relaxation processes in the frequency range between 10MHz and 10 GHz.

Exemplary mixtures studied : MIX I and MIX II had compositions denoted in Figures 1a and 1b by vertical dashed lines. The phase diagrams studied by means of polarizing microscopy are as follows:

MIX I:(glassy) - N_R - 17.9 - 19°C - SmA_d - 71°C - N - 116.9°C - Is,
MIX II: (glassy)- N_R - 44°C - SmA_d - 74°C - N - 146.1°C - Is.

After some time the N_R phases go into a glassy state. The SmA_d and N_R are monotropic phases.

The dielectric spectra were analyzed in terms of two relaxation mechanisms by fitting the following model:

$$\varepsilon_{\|}^{*} = \varepsilon_{\|\infty} + \frac{\varepsilon_{\|01} - \varepsilon_{\|\infty}}{1+(i\omega\tau)^{1-\alpha}} + \frac{\varepsilon_{\|0} - \varepsilon_{\|01}}{1+(i\omega\tau')^{1-\alpha'}} \qquad (1)$$

where τ and τ' are respective relaxation times for the 2Ph and 3Ph molecules, α and α' are parameters responsible for distribution of the relaxation times, $\varepsilon_{\|0}$ and $\varepsilon_{\|\infty}$ are, respectively, the static dielectric permittivity and its high frequency limit, and $\varepsilon_{\|01}$ is the quasi-static dielectric permittivity for the high frequency process and at the same time the high frequency limit for the low frequency relaxation process.

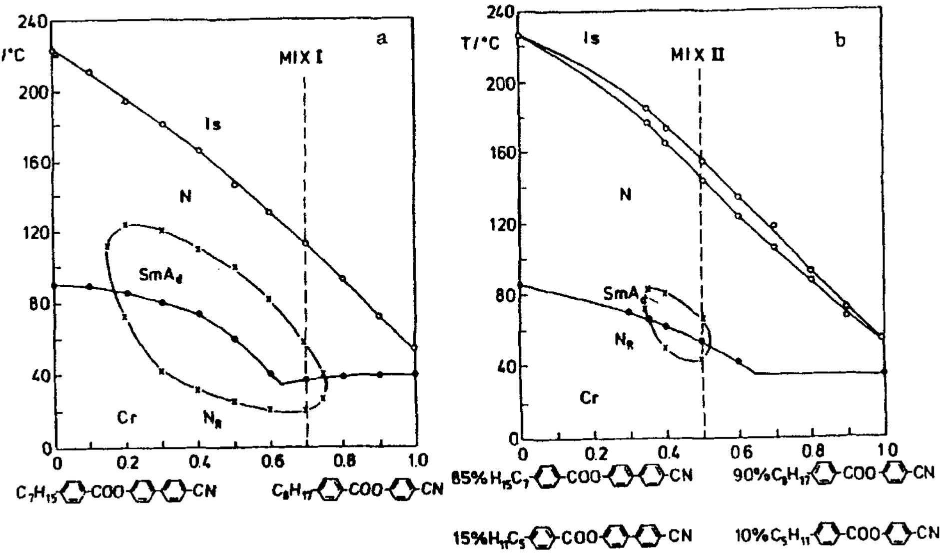

FIGURE 1 Phase diagrams for binary (a) quaternary (b) mixtures .

RESULTS AND DISCUSSION

Static dielectric permittivities measured at low frequencies for both mixtures are shown in Figures 2 and 3, respectively. In the SmA_d phases of both materials there are some anomalies seen in the temperature dependence of the $\varepsilon_{\|0}$ component of dielectric permittivity. In the case of the four component mixture (MIX II) this anomaly is pronounced and it originates from strong antiparallel dipole-dipole

correlations which are favoured in the layered structure of the SmA_d phase. Similar behavior has been reported before for $8OCB^3$ and for a mixture showing SmA_1 phase[4]. An increase of $\varepsilon_{\perp 0}$ in the SmA_d phase of MIX I is due to misalignment.

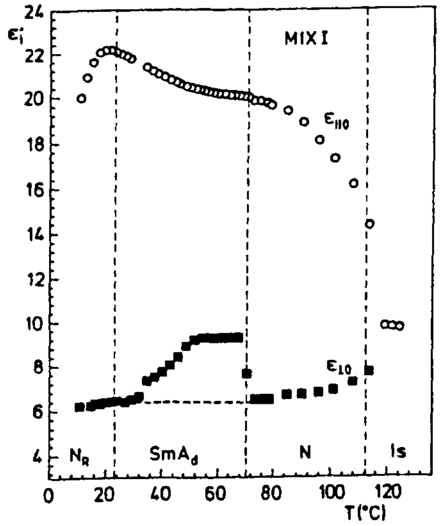

FIGURE 2 Static dielectric permittivites ($\varepsilon_{\parallel 0}$ and $\varepsilon_{\perp 0}$) obtained for MIX I .

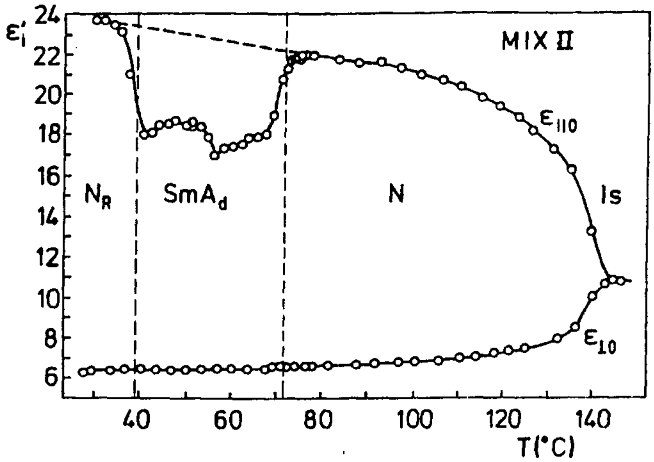

FIGURE 3 Static dielectric permittivities ($\varepsilon_{\parallel 0}$ and $\varepsilon_{\perp 0}$) obtained for MIX II .

The low frequency dielectric spectra obtained for the N_R phase of MIX I and for the N phase of MIX II are shown in Figures 4 and 5, respectively. They consist of two well separated dispersion regions coming from 180°-jumps of 2-phenyl (2Ph) and 3-phenyl (3Ph) molecules around their short axes. The splitting of the two processes is quite good in the N_R , SmA_d and in the low temperature range of the N phase, so it was possible to make decomposition of the spectrum according to Eq.(1). In the high temperature range of the N phase both relaxation processes merge in one broad spectrum which is difficult to decompose uniquely.

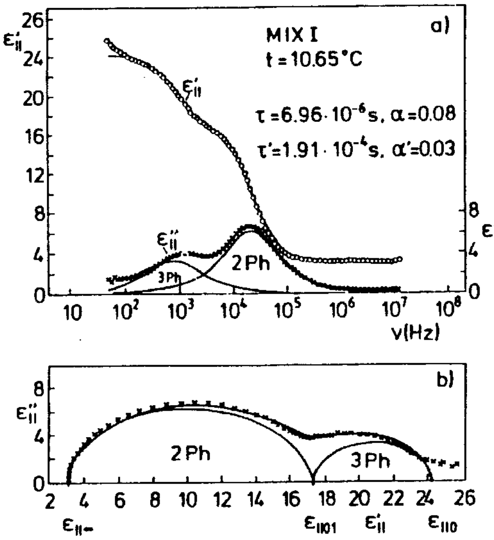

FIGURE 4 a) Dielectric spectrum for the N_R phase of MIX I. Neat solid line represents a least-square fit of Eq. (1) to the experimental points. b) Cole-Cole plots of the above spectrum. Fat solid lines represent two main contributions to the spectrum originating from two different molecular species (2Ph and 3Ph).

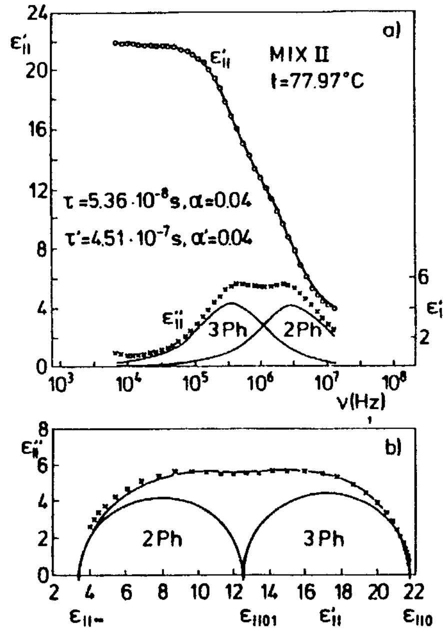

FIGURE 5 a) Dielectric spectrum of N phase of MIX II. b) Cole-Cole plot (cf.Fig.4).

The relaxation times computed for both molecular processes are presented in the Arrhenius plots (Figure 6) having distinctly different slopes in the consecutive liquid crystalline phases. One should note that the activation energies for both molecular processes are the highest in the N_R phases (Table 1) what confirms dimer formation models[6,7]. For both molecular processes the activation energies obey the following condition: $\Delta E_{NR} > \Delta E_N \geq \Delta E_{SmAd}$.

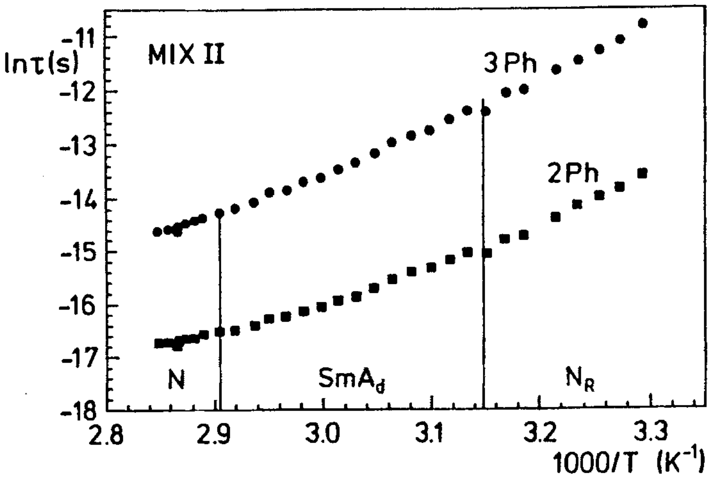

FIGURE 6. Arrhenius plots of both molecular relaxation times (τ and τ') .

TABLE I Average activation energies (Δ E in kJ/mol) obtained in different phases of MIX II for two molecular processes.

Phase	N_R	SmA_d	N
Molecule			
3Ph	(87.0 ± 3.3)	(68.3 ± 1.2)	(68.3 ± 10.2)
2Ph	(82.8 ± 2.2)	(52.2 ± 1.4)	(65.4 16.6)

As is seen from the Arrhenius plots (Figure 6) there is a reasonable splitting of the two molecular relaxation modes. This relation could be understood in view of the theoretical [6,7] and x-ray structure [8] investigations.

It is worth pointing out that generally the activation energies for 2Ph molecules are lower than those for 3Ph molecules. In addition, the activation energies for the N_R phase are distinctly higher than for the N one. This may mean that both kinds of molecules are more rigid in the N_R phase and/or dimer formation process takes place. The fact that we see separate relaxation processes coming from the molecules having distinctly different lengths of their molecular bodies shows that the low frequency dielectric process is connected with a single molecular response rather than collective one. At last one should point out that the slope of the Arrhenius plots in all liquid crystalline phases studied, increases with

decreasing temperature what supports the idea of a temperature dependent dimer formation rate. One can notice the biggest curvature in the nematic reentrant phase. Similar results obtained for MIX I will be published[10].

In the high frequency range a broad dielectric relaxation spectrum has been found with an average relaxation time of the order of 10^{-9} s. The gap between the $\varepsilon_{\|\infty}$ and the refractive index squared originates from many molecular and collective processes. They merge to one broad dielectric absorption band with a distribution parameter of 0.4.

Further studies of such systems like MIX I and MIX II are of great importance as they may lead to finding out either an antiferroelectric phase (SmA_2) with strong negative dipole-dipole correlation as described in[8] or even a ferroelectric phase with strong positive dipole-dipole correlation.

CONCLUSIONS

1. The dielectric anisotropy is positive in all liquid crystalline phases studied. However, there is a pronounced decrease of the parallel component of the dielectric permittivity in the SmA_d phase of MIX II which might be primarily due to dipole-dipole correlation present in its layered interdigitated structure. MIX I exhibits a SmA phase with very weak dipole-dipole correlation.

2. The dielectric spectra measured for the N, SmA_d and N_R phases are composed of two quite well separated dispersion regions originating from the molecular reorientation of two and three phenyl species. This indicates that both relaxation processes are non-collective in their nature.

3. The activation energy in the N_R phase is distinctly higher than in the N and SmA_d phases. The following condition is valid for activation energies:

$$\Delta E_{NR} > \geq E_N \; \Delta \; E_{SmAd}$$

found in this study for two molecular relaxation processes.

4. Temperature dependent slope of the Arrhenius plots for two molecular processes shows that the rate of dimer formation increases with decreasing temperature.

Acknowledgements

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