Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric relaxation studies of 6OCB/8OCB mixtures with the nematic-smectic A-nematic re-entrant phase sequence

Stanislaw Urban[a]; Roman Dabrowski[b]; Bo Gestblom[c]; Antoni Kocot[d]
[a] Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland, [b] Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland, [c] Institute of Physics, Uppsala University, S-75121 Uppsala, Sweden, [d] Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland,

To cite this Article Urban, Stanislaw , Dabrowski, Roman , Gestblom, Bo and Kocot, Antoni(2000) 'Dielectric relaxation studies of 6OCB/8OCB mixtures with the nematic-smectic A-nematic re-entrant phase sequence', Liquid Crystals, 27: 12, 1675 — 1681
To link to this Article: DOI: 10.1080/026782900750037257
URL: http://dx.doi.org/10.1080/026782900750037257

LIQUID CRYSTALS, 2000, VOL. 27, NO. 12, 1675–1681

Dielectric relaxation studies of 6OCB/8OCB mixtures with the nematic–smectic A–nematic re-entrant phase sequence

STANISŁAW URBAN*
Institute of Physics, Jagellonian University, Reymonta 4, 30-059 Cracow, Poland

ROMAN DABROWSKI
Institute of Chemistry, Military University of Technology, 00-908 Warsaw, Poland

BO GESTBLOM
Institute of Physics, Uppsala University, S-75121 Uppsala, Sweden

and ANTONI KOCOT
Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice,
Poland

(*Received 3 April 2000; in final form 26 May 2000; accepted 6 June 2000*)

The low frequency relaxation process was studied for 6OCB/8OCB mixtures with three concentrations (27.0, 27.3 and 27.5 wt %) exhibiting the isotropic–nematic–smectic A–nematic re-entrant–crystalline phase sequence and four mixtures (28.5, 30.0, 35.0 and 40.0 wt %) with the isotropic–nematic–crystalline phase sequence. In the liquid crystalline phases, all dielectric spectra could be excellently described by the Debye equation. The relaxation time $\tau_{\parallel}$ passes smoothly through the phase transitions separating the liquid crystalline phases. The activation barriers hindering the molecular rotations around the short axes are practically the same in the nematic and smectic phases and become larger in the re-entrant nematic phase. Smaller values of the barrier in the nematic phase of mixtures in comparison with those obtained recently for pure 6OCB and 8OCB are explained as an effect of weakening of the molecular interactions caused by increased dipole–dipole associations between molecules in mixtures in relation to pure substances. The slightly larger activation barrier in the nematic re-entrant phase indicates stronger molecular associations in this phase.

1. Introduction

In 1975 Cladis [1] discovered the appearance of the stable re-entrant nematic (N_{re}) phase in mixtures of two cyano-Schiffs base liquid crystalline (LC) compounds. Soon the same effect was observed [2] in a mixture of two *n*-alkoxycyanobiphenyls, 6OCB and 8OCB (abbreviated below as '6/8 mixture'), as well as in single compounds at atmospheric and elevated pressure (for reviews see [3, 4]). The properties of the 6/8 mixture were studied by several experimental groups [2–12]. The detailed phase diagram 'temperature versus concentration' of 6OCB in 8OCB was determined by Chen *et al.* [5] in a birefringence study, by Kortan *et al.* [6] by X-ray studies, and also by Zywociński [12] by volumetric studies. In a small range of concentration below the critical value of 28.0 wt % [5, 12], decrease in temperature leads to the following phase sequence: isotropic (I)–nematic (N)–smectic A (SmA)–nematic re-entrant (N_{re})–crystalline (Cr). A comprehensive analysis of the thermodynamic aspects of the re-entrant behaviour of the 6/8 mixtures was made by Zywociński [12]. His volumetric studies of the 26.97 wt % mixture confirmed the results of Chen *et al.* [5] that both transitions, N–SmA and SmA–N_{re}, are continuous and do not affect the continuity of the nematic phase (the same results came from measurements of the nematic order parameter [11]).

The static dielectric permittivities, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, and the low frequency (l.f.) relaxation process for one 6/8 mixture were first studied by Ratna *et al.* [7]. The static components of the permittivity tensor for the pure substances and several mixtures below and above the critical concentration were analysed by Buka and Bata [8] and then

---

*Author for correspondence; e-mail: ufurban@cyf-kr.edu.pl

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals

by Jadzyn and Czechowski [9]. Nozaki *et al.* [10] performed a dielectric relaxation study for one concentration of a 6/8 mixture (27.3 wt %) as a function of temperature in a broad frequency range (300 kHz–10 GHz) with the aid of a time-domain reflectometry (TDR) method.

Two main dynamical processes were observed in the experiments of Nozaki *et al.* [10]: the l.f. process connected with molecular rotations around the short axes, and the high frequency (h.f.) process corresponding to much faster rotations around the long axes. The authors discuss the changes of the permittivity components, as well as the relaxation times $\tau_{\parallel}$ and $\tau_{\perp}$ at the phase transitions N–SmA, SmA–N_{re} and N_{re}–Cr. However, some conclusions derived by the authors concerning the properties of the l.f. process in particular phases of the mixture seem to be doubtful. This especially concerns the value of the activation barrier hindering the molecular motions around the short axes in the smectic A phase. The authors postulated a considerable increase of the barrier at the N–SmA transition which contradicts the results obtained for many LC substances with such a phase sequence, e.g. [7, 13–15, 16–18]. Additionally, they found that the SmA phase consists of two temperature regions having different activation barriers for the motion (the same was postulated in [7]). It should be added that in figure 4 of [10] a separation of SmA phase into two parts was based on the deviation of one point only in the Arrhenius plot! Therefore, we decided to perform studies of the l.f. relaxation process in three 6/8 mixtures with smaller (27.0, 27.3 and 27.5 wt %) and four mixtures (28.5, 30.0, 35.0 and 40.0 wt %) with larger concentrations than the critical value. We used an impedance analyser (1 kHz–13 MHz) which seems to be more suitable than the TDR method for this purpose. Our results contradict the findings of Ratna *et al.* [7] and Nozaki *et al.* [10] in many respects. Additionally, a few mixtures were studied in the isotropic phase with the aid of a time domain spectroscopy (TDS) method [19].

2. Experimental

The components were synthesized and the mixtures prepared in the Institute of Chemistry, Military University of Technology, Warsaw. The measurements of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, in the LC phases were carried out with the aid of a HP 4192A impedance analyser in the frequency range 1 kHz–13 MHz. The parallel plate capacitor ($C_o \sim 50$ pF) was calibrated at room temperature by using standard liquids. Corrections due to change of the geometrical capacitance with temperature were introduced. The capacitor was filled with a mixture previously melted and shaken in order to avoid any separation of the components. A parallel orientation of the samples was achieved by applying a d.c. electric field of *c.* 3000 V cm^{-1}, whereas the perpendicular orientation was established by a magnetic field of *c.* 0.8 T. The samples were slowly cooled from the isotropic phase. During collection of the spectra, the temperature was stabilized within ±0.1 K. In the N phase both permittivity components, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, were measured alternately at T = constant. However, when the transition to the SmA phase occurred, the samples did not respond to the external fields. Therefore the measurements within the SmA phase had to be performed separately for each orientation of the sample, starting always from a well oriented nematic phase and keeping the appropriate field constant. Below the SmA–N_{re} transition, the alternation of the orientations could be obtained again. In this way both transitions, N–SmA and SmA–N_{re}, were easily detected. The observed phase transition temperatures are gathered in table 1.

Table 1. Temperatures of phase transitions T (± 0.2°C) observed in dielectric studies of 6/8 mixtures.

6/8 Mixture, wt %	I–N	N–SmA	SmA–N_{re}	N_{re}–Cr	Ref.
27.0	79.8	47.1	30.6	25.1	This work
27.3	79.4	45.0	31.0	23.0	”
27.5	79.6	45.1	31.3	26.0	”
27.3		40.3	35.7	25	[10]
35.8 : 64.2[a]	78.5	45.5	30	25	[7]
28.5	79.2			23[b]	This work
30.0	79			< 28[b]	”
35.0	79			< 28[b]	”
40.0	79			< 28[b]	”
Pure 6OCB	75.5			57[b]	[15]
Pure 7OCB	74.0			54[b]	[15]
Pure 8OCB	81.0	67.5		54.5[c]	[15]

[a] Incorrect ratio; perhaps it should correspond to *c.* 27.3 wt %.
[b] N–Cr transition.
[c] SmA–Cr transition.

The TDS measurements were carried out with a 100 ns time window which covered the frequency range from *c.* 20 MHz to *c.* 1 GHz [19]. The temperature was changed from 65 to 95°C with stabilization within ± 0.1°C.

3. Results

Typical relaxation spectra collected for particular phases are shown in figure 1 in the form of Argand diagrams. They were analysed with the aid of the well known Cole–Cole equation, $(\varepsilon^* - \varepsilon_\infty)/(\varepsilon_s - \varepsilon_\infty) = 1/(1 + i\omega\tau)^{1-\alpha}$, where ε_s and ε_∞ are the static and high frequency permittivities, respectively, $\omega = 2\pi\nu$, and α characterizes a distribution of the relaxation times τ.

In the LC phases the spectra fulfil the Debye equation with $\alpha = 0$. This is not surprising in the light of the close similarity of the values of the l.f. relaxation time $\tau_\parallel$ observed for pure 6OCB and 8OCB in the N phase [15]. (In the case of mixtures composed of two- and three-ring compounds, the dielectric spectra show two well separated dispersion regions [16]). For the spectra of the isotropic phase $\alpha \approx 0.1$; at the high frequency wing the additional relaxation process connected with molecular rotations around the long axes can be seen, similarly to pure substances [15]. The relaxation times calculated from the spectra are presented in figures 2 and 3 together with the static permittivity components $\varepsilon_\parallel$ and $\varepsilon_\perp$. In figure 2 the vertical lines correspond to the phase transitions observed clearly in the $\varepsilon_\perp(T)$ plots only. The activation enthalpy values, $\Delta H = R(\partial \ln \tau/\partial T^{-1})$ (R = gas constant), are listed in table 2. The present static permittivity values are markedly larger than those obtained by Nozaki *et al.* [10] (in an indirect way) and by Ratna *et al.* [7], whereas they agree well with the data presented in [9]. However, the discontinuity of $\varepsilon_\perp$ at the N–SmA transition observed by us and by Wróbel *et al.* [16] was not present in the results of Ratna *et al.* [7] and Jadzyn and Czechowski [9].

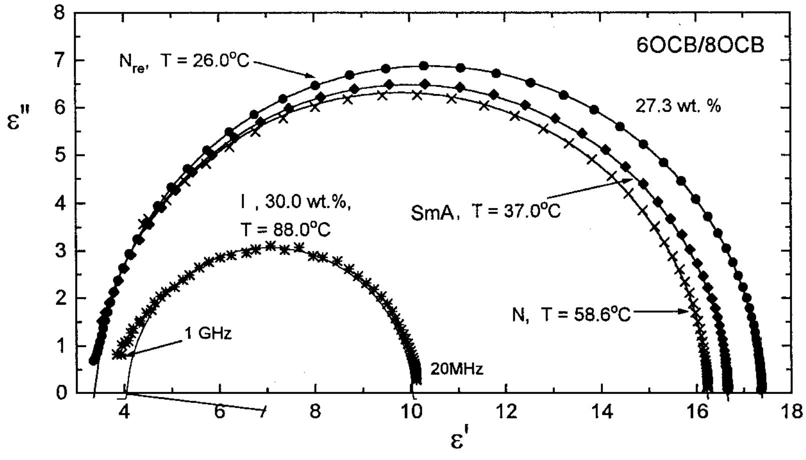

Figure 1. Argand diagrams for two 6/8 mixtures: 27.3 wt % in the N, SmA and N_{re} phases, and 30.0 wt % in the isotropic phase. The semicircles are least-square fits of the Cole–Cole equation.

Table 2. Activation enthalpy $\Delta H_\parallel$ (kJ mol^{-1}) obtained for particular phases of 6/8 mixtures and for the pure substances [20], as well as the results given in refs. [7, 10].

6/8 Mixture, wt %	I	N	SmA	N_{re}	Ref.
27.0		57 ± 2	54 ± 2	61 ± 3	This work
27.3		58 ± 2	56 ± 2	62 ± 3	”
27.5		57 ± 2	56 ± 2	62 ± 4	”
27.3		54	72 and 66	68	[10]
35.8 : 64.2[a]		79	71 and 69	165	[7]
28.5		58 ± 2	—	—	This work
30.0	47.6	60 ± 2	—	—	”
35.0	44.1	62 ± 2	—	—	”
40.0	42.9	63 ± 2	—	—	”
Pure 6OCB	41	70	—	—	[20]
Pure 7OCB	44	67		—	[20]
Pure 8OCB	50	75	56.2 ± 1		[20]

[a] See remark in table 1.

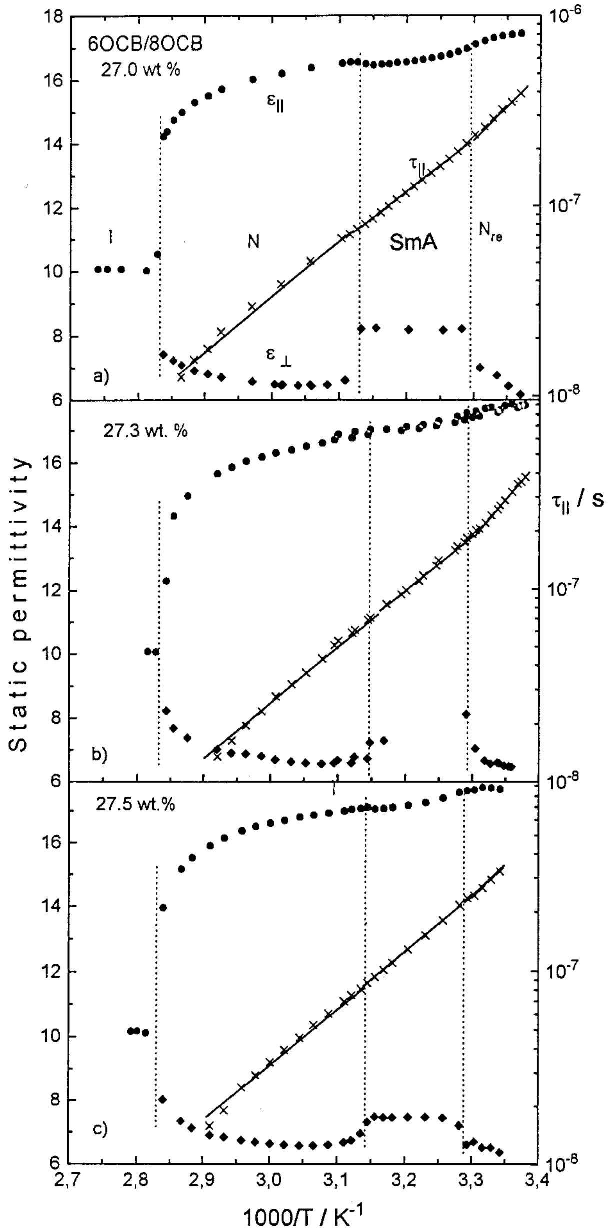

Figure 2. The static permittivity components, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, and the relaxation times $\tau_{\parallel}$ versus reciprocal temperature in the N, SmA and N_{re} phases of three 6/8 mixtures: (*a*) 27.0 wt %, (*b*) 27.3 wt % (two runs), and (*c*) 27.5 wt %. The vertical dotted lines mark the phase transitions detected in the $\varepsilon_{\perp}(T)$ measurements.

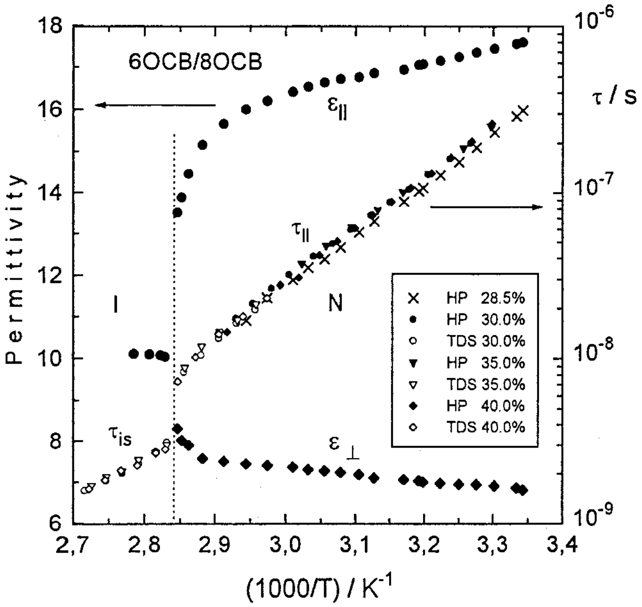

Figure 3. The static permittivity components, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, for the 28.5 wt % 6/8 mixture and the relaxation times $\tau_{\parallel}$ versus reciprocal temperature for four 6/8 mixtures exhibiting the nematic phase only (full points and crosses are measurements with the HP analyser; open points come from the TDS measurements).

4. Discussion

The cyanobiphenyl compounds form antiparallel dimers in the isotropic [17, 21] as well as in the LC phases; these influence the dielectric properties considerably [7–10, 13–16, 18, 20]. The smectic A phase of 8OCB has a layer spacing d that is incommensurate with its molecular length l: $d/l \approx 1.4$ [22] and is called the smectic A_d phase. This can be formed by pairwise overlapped associations of the aromatic cores. Therefore, it seems obvious to assume that the dimer-type associations on the molecular level are also responsible for the re-entrant behaviour in the 6/8 mixtures. According to Cladis *et al.* [3, 4] the re-entrancy in cyano compounds results from a sensitive balance between dipolar and steric factors. When dipolar forces dominate we have re-entrance from frustration, but when steric forces dominate other types of re-entrant phenomena occur. The former mechanism dominates in cyanobiphenyl compounds. The dipolar forces stabilizing the layered phase would be weakened, and eventually collapse, as the dimer population increases. Berker *et al.* [23] proposed a gas-frustrated model which mimics the N–SmA_d–N re-entrance.

The fact that the spectra of all LC phases are monodispersive (see figure 1) indicates that one is dealing with a single particle rotational motion of molecules (mostly 8OCB) around the short axes. As can be seen in figure 2, the l.f. relaxation time $\tau_{\parallel}$ changes continuously at the N–SmA and SmA–N_{re} transitions which contradicts the observations by Nozaki *et al.* [10]. Moreover, for all three mixtures studied we observed no discontinuity of the ln $\tau_{\parallel}$ vs. $1/T$ plots within the SmA phase, contrary to the other relaxation studies [7, 10]. Such a behaviour seems to be consistent with the fact—arising from the birefringence [5], NMR [11] and volumetric [12] studies—that both transitions, N–SmA and SmA–N_{re}, are continuous and they do not affect the continuity of the nematic phase.

The above discrepancies, as well as an evident difference in the values of the frequency corresponding to the maximum loss, $\nu_{max} = 1/(2\pi\tau_{\parallel})$, observed within the SmA phase of the 27.3 wt % mixture in the present study and in [10] throw doubts on the results from the time domain method. It is well known that care has to be exercised in using TDR not to evaluate spectra at frequencies much lower than the inverse of the time window used in the measurements, as discussed in [19]. Truncation of time domain line shapes can influence the results obtained via a Fourier transform calculated permittivity spectrum. Unfortunately, the time windows used in [10] are not given.

The activation enthalpy for the l.f. relaxation process in the N phase, $\Delta H_{\parallel}(\mathrm{N})$, can be divided into isotropic and anisotropic parts. The isotropic contribution is determined mainly by the activation barrier for the viscosity coefficient γ_1 (which, however, is dependent upon the order parameters [24]). The anisotropic part consists of the Maier–Saupe nematic potential q (being proportional to the order parameter S) and the dipole–dipole association energy E_{as}. From pressure studies on several cyanobiphenyls it is known [14, 17, 18] that the l.f. relaxation process is determined by volume and temperature effects to a comparable extent. The importance of volume effects in the creation of the nematic phase is clearly seen in the analysis of the entropy change at the I–N transition: the configurational and volume contributions to the total entropy change are practically the same [25]. Dielectric relaxation studies of cyanophenyls [14, 17, 18] under high pressure exhibited a lowering of the activation enthalpy with increasing pressure within the N and SmA phases which was interpreted as a weakening of the associations.

However, yet another explanation of the above effects, as well as of a decrease in the activation enthalpy on passing from the N to the SmA phase, can be suggested. The dimerization of molecules reduces the long-range dipolar interactions between a given dimer and other dimers or monomers. Moreover, it favours the interactions between the alkyl or alkoxy tails which are weaker than the interactions between the aromatic cores (this problem is discussed in a recent paper by Govin and Madhusudana [26]). Thus, the decrease in the activation enthalpy at the N–SmA transition could arise from the increase in the number of dimers in the smectic phase. If this is true, the observed decrease of $\Delta H_{\parallel}(\mathrm{N})$ and $\Delta H_{\parallel}(\mathrm{SmA})$ with pressure means that the dimers become more stable.

Let us confront this conclusion with the phase diagram for pure 8OCB established in the temperature–pressure measurements [3, 4], figure 4(*a*), and that for the 6/8 mixture obtained in the temperature–concentration studies [2–6, 12], figure 4(*b*). In these cases the SmA phase is either pressure or concentration limited. However, in some ranges of pressure and concentration, the temperature range of the SmA phase becomes considerably affected, and eventually the smectic domain forms parabolic fingers in a sea of N phase. (It should be mentioned, however, that for 8OCB the high pressure smectic A_d and N_{re} phases are observed as supercooled metastable phases, that are not always found in a high pressure experiment [27]). Thus, in some ranges of pressure and concentration the dipole–dipole associations become stronger and the number of dimers that stabilize the SmA phase markedly increases. After reaching some critical concentration of dimers, the system becomes unstable and the SmA–N_{re} transition occurs.

The X-ray studies of 6/8 mixtures by Kortan *et al.* [6] have shown that the in-plane structure factor is identical in the N, SmA and N_{re} phases, so that any transverse rearrangements of the molecules must be extremely subtle. It seems therefore that the pressure, the temperature and the concentration influence mainly the dimerization capability of the molecules which results in the observed phase sequence. The increase in the number of dimers due to pressure or concentration above

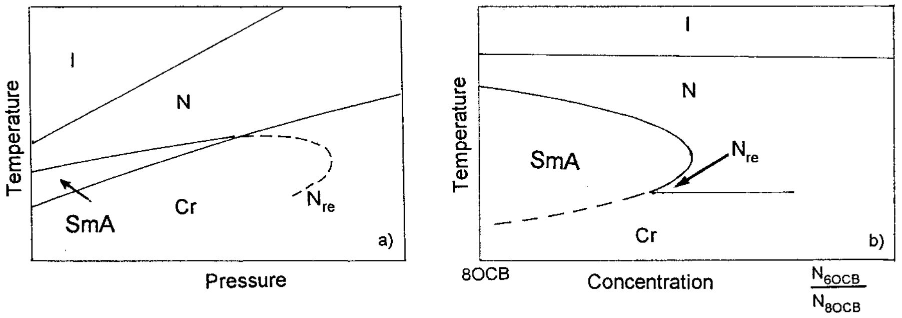

Figure 4. Schematic phase diagrams: (*a*) temperature–pressure for pure 8OCB, and (*b*) temperature–concentration for 6OCB/8OCB mixtures. I = isotropic, N = nematic, N_{re} = nematic re-entrant, SmA = smectic A_d, Cr = crystalline. Dashed lines correspond to supercooled regions.

some limiting values must destabilize the smectic order and the phase can no longer exist. Let us consider the results obtained in the light of the above remarks.

Looking at the data quoted in table 2, one has to point out the following sequences of the activation enthalpies hindering the molecular rotations around the short axes:

$$\Delta H_{\parallel}^{\mathrm{pure}}(\mathrm{N}) > \Delta H_{\parallel}^{\mathrm{mix}}(\mathrm{N}_{\mathrm{re}}) > \Delta H_{\parallel}^{\mathrm{mix}}(\mathrm{N}) \qquad (1)$$

$$\Delta H_{\parallel}^{\mathrm{mix}}(\mathrm{N}) \approx \Delta H_{\parallel}^{\mathrm{mix}}(\mathrm{SmA}) \approx \Delta H_{\parallel}^{\mathrm{pure}}(\mathrm{SmA}). \qquad (2)$$

Similar relations between barriers were also observed by Wróbel *et al.* [16] for another mixture of cyano compounds exhibiting the same phase sequence.

The relation (1) means that the dilution of the host 8OCB molecules by the shorter guest 6OCB molecules considerably weakens the molecular interactions which determine the height of the barrier. The difference $\Delta H_{\parallel}^{\mathrm{pure}}(\mathrm{N}) - \Delta H_{\parallel}^{\mathrm{mix}}(\mathrm{N}) \approx 10\,\mathrm{kJ\,mol^{-1}}$ can be compared with $\Delta H_{\parallel}(\mathrm{N}) - \Delta H_{\parallel}(\mathrm{SmA})$ in pure 8OCB (see table 2). On the other hand, close values of the barriers in the SmA phase of pure 8OCB and in the mixtures [$\Delta H_{\parallel}^{\mathrm{mix}}(\mathrm{SmA}) \approx \Delta H_{\parallel}^{\mathrm{pure}}(\mathrm{SmA})$, relation (2)] were obtained. Taking into account the previously quoted arguments, one can suppose that in the range of concentration between 27 and 40 wt % (at least) the degree of dimerization in the nematic phase is larger in the mixtures than in the pure substances. The activation enthalpy values for the isotropic phase of the mixtures show a trend which could be expected: they diminish between the values characterizing the pure substances (table 2).

Taking the relaxation times obtained for the nematic and isotropic phases of three 6/8 mixtures (figure 3), we were able to calculate the retardation factor $g_{\parallel} = \tau_{\parallel}/\tau_{\mathrm{o}}$ (τ_{o} means τ_{is} extrapolated from the isotropic to the nematic phase), the nematic potential q and the order parameter $S = \langle P_2(\cos\theta)\rangle$ according to the Kalmykov and Coffey formulae [28] (for details see [29]). Within the N phase of the mixtures, the values are: $g_{\parallel} = 2.4 \rightarrow 5.7$ and $q = 6 \rightarrow 9\,\mathrm{kJ\,mol^{-1}}$. The order parameter can be described well by the Haller formula $S(T) = 0.343\,(T_{\mathrm{NI}} - T)^{0.182}$. Thus, the nematic potential consists of *c.* 10 → 15% of the total energy barrier hindering the molecular rotations around the short axes, so the main contribution to the barrier has to be ascribed to viscosity effects.

Measurements of the viscosity coefficients for 6/8 mixtures are not known to us (results for pure 8OCB having a narrow N phase cannot give a reliable activation plot due to strong pretransitional effects [30]). Therefore the results obtained for a three component re-entrant mixture in which two cyanobiphenyls (7CB and 8OCB) consist of 91 wt % [31], can be considered for comparison. Three Miesowicz viscosity coefficients measured in the experiments have roughly the same activation energies $\Delta H_{\eta} \approx 40 - 45\,\mathrm{kJ\,mol^{-1}}$ in both the N and $\mathrm{N_{re}}$ phases (γ_1 can be expressed as a linear combination of two Miesowicz viscosities η_1 and η_2 [31]). Assuming similar ΔH_{η} values for the mixtures discussed here, one can write: $\Delta H_{\parallel} \approx q + \Delta H_{\eta} + E_{\mathrm{as}}$, with $E_{\mathrm{as}} \sim 10\,\mathrm{kJ\,mol^{-1}}$.

As already mentioned, continuity was observed in the order parameter [5, 11], the density [12] and the viscosity coefficients [31] between the N and $\mathrm{N_{re}}$ phases in spite of the discontinuity in these quantities at the N–SmA and SmA–$\mathrm{N_{re}}$ transitions. Therefore, the evident increase in the activation enthalpy $\Delta H_{\parallel}(\mathrm{N_{re}})$ with respect to $\Delta H_{\parallel}(\mathrm{N})$, observed also by Wróbel *et al.* [16], indicates that the energy of the molecular associations becomes stronger in the re-entrant nematic phase of cyano compounds.

5. Conclusions

The molecular rotational dynamics around the short axes in 6OCB/8OCB mixtures with different concentrations below and above the critical value is discussed on the basis of dielectric relaxation studies. The low frequency relaxation process is monodomain in all the LC phases. No stepped change in the relaxation time at the phase transitions between LC phases or in the activation enthalpy within the smectic A phase, suggested by other experimental groups, was observed. A substantial decrease in the activation barrier in the nematic mixtures with respect to the pure substances cancels the usual excess of the barrier in the nematic phase over the value in the smectic A phase. The change in the barrier with increasing concentration is observed for the isotropic phase only. The available data allow us to conclude that the barrier hindering the molecular rotations around the short axes in the nematic phase of mixtures consists of the nematic potential, the viscosity effects and the association energy between molecules. In spite of the continuous change in various physical parameters of mixtures between the N and $\mathrm{N_{re}}$ phases, separated by the smectic $\mathrm{A_d}$ gap, the activation enthalpy becomes larger, indicating an increase in the association energy in the $\mathrm{N_{re}}$ phase. To our best knowledge, there are no theoretical models describing the observed effects from first principles, i.e. starting from an appropriate interaction potential.

Financial support from Polish Government KBN grants Nos 25/PO3/97/13 and 168 is gratefully acknowledged.

References

[1] Cladis, P. E., 1975, *Phys. Rev. Lett.*, **35,** 48.
[2] Guillon, D., Cladis, P. E., and Stamatoff, J., 1978, *Phys. Rev. Lett.*, **41,** 1598.

[3] Cladis, P. E., 1988, *Mol. Cryst. liq. Cryst.*, **165,** 85.

[4] Cladis, P. E., 1998, in *Handbook of Liquid Crystals*, Vol. 1, edited by D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, V. Vill (Weinheim: Wiley-VCH), Chap. 6.4.

[5] Chen, N. R., Hark, S. K., and Ho, J. T., 1981, *Phys. Rev. A*, **24,** 2843.

[6] Kortan, A. R., Känel, H. V., Birgeneau, R. J., and Litster, J. D., 1981, *Phys. Rev. Lett.*, **47,** 1206; Kortan, A. R., Känel, H. V., Birgeneau, R. J., and Litster, J. D., 1984, *J. Phys., Paris*, **45,** 529.

[7] Ratna, B. R., Shashidhar, R., and Rao, K. V., 1980, in *Liquid Crystals*, edited by S. Chandrasekhar (New York: Heyden), p. 135.

[8] Buka, A., and Bata, L., 1986, *Mol. Cryst. liq. Cryst.*, **135,** 49.

[9] Jadżyn, J., and Czechowski, G., 1989, *Liq. Cryst.*, **4,** 157.

[10] Nozaki, R., Bose, T. K., and Yagihara, S., 1992, *Phys. Rev. A*, **46,** 7733.

[11] Emsley, J. W., Luckhurst, G. R., Parsons, P. J., and Timimi, B. A., 1985, *Mol. Phys.*, **56,** 767.

[12] Żywociński, A., 1999, *J. Phys. Chem. B*, **103,** 3087.

[13] Druon, L., and Wacrenier, J.-M., 1978, *Ann. Phys.*, **3,** 199.

[14] Brückert, T., Urban, S., and Würflinger, A., 1996, *Ber. Bunsenges. Phys. Chem.*, **100,** 1133.

[15] Urban, S., Gestblom, B., Kresse, H., and Dąbrowski, R., 1996, *Z. Naturforsch.*, **51a,** 834.

[16] Wròbel, S., Brodzik, M., Dąbrowski, R., Gestblom, B., Haase, W., and Hiller, S., 1997, *Mol. Cryst. liq. Cryst.*, **302,** 223.

[17] Urban, S., and Würflinger, A., 1997, *Adv. Chem. Phys.*, **98,** 143.

[18] Markwick, P., Urban, S., and Würflinger, A., 1999, *Z. Naturforsch.*, **54a,** 275.

[19] Urban, S., Gestblom, B., and Dąbrowski, R., 1999, *Phys. Chem. chem. Phys.*, **1,** 4843.

[20] Urban, S., Gestblom, B., and Würflinger, A., 1999, *Mol. Cryst. liq. Cryst.*, **331,** 113.

[21] Bradshaw, M. J., and Raynes, E. P., 1981, *Mol. Cryst. liq. Cryst. Lett.*, **72,** 73.

[22] Leadbetter, A. J., Durrant, J. L. A., and Rugman, M., 1977, *Mol. Cryst. liq. Cryst. Lett.*, **34,** 231.

[23] Berker, A. N., and Walker, J. S., 1981, *Phys. Rev. Lett.*, **47,** 1469; Netz, R. R., and Berker, A. N., 1992, in *Phase Transitions in Liquid Crystals*, edited by S. Martellucci and A. N. Chester, NATO ASI Series, Vol. 290 (New York and London: Plenum Press), Chap. 7.

[24] Zakharov, A. V., Komolkin, A. V., and Maliniak, A., 1999, *Phys. Rev. E*, **59,** 6802.

[25] Sandmann, M., and Würflinger, A., 1998, *Z. Naturforsch.*, **53a,** 233; Sandmann, M., Hamman, F., and Würflinger, A., 1997, *Z. Naturforsch.*, **52a,** 739.

[26] Govind, A. S., and Madhusudana, N. V., 2000, *Liq. Cryst.*, **27,** 215.

[27] Przedmojski, J., Jędrzejewski, J., Dąbrowski, R., Czupryński, K., Tłaczała, W., and Wiśniewski, R., 1996, *Phase. Trans.*, **56,** 119.

[28] Kalmykov, Yu. P., and Coffey, W. T., 1998, *Liq. Cryst.*, **25,** 329.

[29] Urban, S., Würflinger, A., and Gestblom, B., 1999, *Phys. Chem. chem. Phys.*, **1,** 2787.

[30] Graf, H.-H., Kneppe, H., and Schneider, F., 1992, *Mol. Phys.*, **77,** 521.

[31] Bhattacharya, S., and Letcher, S. V., 1980, *Phys. Rev. Lett.*, **44,** 414.