Dielectric relaxation studies for mixtures of strongly polar and mesogenic \textit{n}-heptylcyanobiphenyl with non-polar and non-mesogenic carbon tetrachloride (CCl\textsubscript{4}) were performed. The absorption band broadening due to fractional diffusion was observed. A correlation between the non-mesogenic admixture concentration and the anomalous diffusion exponent was found.

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1. Introduction

Anomalous diffusion concerns the systems in which the transport processes are different than those occurring in case of normal Brownian diffusion. In terms of the mean square displacement of particles, the phenomenon is described by the power-law pattern [1–3]:

$$\langle x^2(t) \rangle \propto K_\alpha t^\alpha,$$

instead of the Brownian linear dependence [4–6]:

$$\langle x^2(t) \rangle \propto K t.$$

$K$ and $K_\alpha$ denote the normal and generalized diffusion coefficients, respectively.
and $\alpha$ is the anomalous diffusion exponent. The fractional values of the exponent $\alpha$ ($0 < \alpha < 1$) refer to the subdiffusion (or fractional diffusion) and for $\alpha > 1$ the superdiffusion (or enhanced diffusion) takes place. The normal Brownian diffusion ($\alpha = 1$) is located on the limit threshold between sub- and superdiffusion.

Subdiffusion reflects an existence of some traps for diffusing particle in a system, thus it can be expected in some complex and heterogeneous liquids as well as in homogeneous and isotropic liquids placed in a matrix of complex geometry. The list of systems displaying a subdiffusive behavior is quite long and among them, one can quote percolative [7], porous [8], and polymeric [9, 10] systems as well as some transport processes such as the charge transport in amorphous semiconductors [11–14], for example.

In our recent paper [15] we have shown that in the vicinity of the isotropic to nematic phase transition one observes the anomalously slow rotational diffusion, which is undoubtedly due to the microscopic heterogeneity in a form of molecular pseudo-domains, the precursors of a forthcoming new phase. Because in pure mesogenic compounds studied the effect was rather of moderate intensity ($\alpha \approx 0.95$), the anomalous diffusion is expected to be more pronounced in mixtures of mesogenic and non-mesogenic compounds, as an additional microscopic heterogeneity arises in such mixed systems. In this paper we present the results of analysis of the dielectric relaxation spectra recorded for the mixtures of mesogenic $n$-heptycyanobiphenyl and non-mesogenic carbon tetrachloride.

2. Theoretical background

The subdiffusion phenomenon can be theoretically described in numerous ways. Mostly, a generalization of the equations of normal Brownian diffusion to fractional dynamics [16–20] is used. Particularly important role was played here by a concept of the continuous-time random walk [21–25], i.e. a walk with a long-tailed (Lévy-like) distribution of the waiting times between successive elementary jumps of particles. This concept was essential in the construction of the physical basis of some empirical equations widely used for describing the anomalous dielectric relaxation in complex systems [26].

It is obvious that the relaxation way of a system returning to its equilibrium state, is governed by the type of diffusion occurring in it. In the Brownian limit, the relaxation process follows, in the time domain, a simple exponential decay:

$$f(t) = \exp \left( -\frac{t}{\tau} \right),$$

where $f(t)$ is the normalized relaxation function and $\tau$ is the relaxation time. The Brownian diffusion is well modelled by the Einstein–Smoluchowski theory [6]. The theory was applied by Debye [27] to the rotational Brownian motion of an assembly of non-interacting dipolar molecules placed in external ac electric field; Eqs. (1) and (2) concern then the angular displacement of the molecular dipole. As
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A result, the following well-known equation for the complex dielectric permittivity in the frequency domain has been obtained:

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{A}{1 + i\omega\tau},
\]

where \(\omega\) is the angular frequency of the probing electric field, \(A = \varepsilon_s - \varepsilon_\infty\) is the dielectric strength, \(\varepsilon_s\) and \(\varepsilon_\infty\) are the permittivities measured in the static and high frequency electric field, respectively. According to Eq. (4), for the systems in which Brownian rotational diffusion occurs, the real (\(\varepsilon'\)) and imaginary (\(\varepsilon''\)) parts of the permittivity, presented in the complex plane as a Cole–Cole plot, form a semicircle, the center of which is placed on the \(\varepsilon'\) axis. Experimental data on the dielectric relaxation, obtained for most of simple liquids under normal conditions fulfill Eq. (4), indicating a normal diffusional behavior.

However, for many complex liquids, the dielectric relaxation processes cannot be described by the Debye theory because the dielectric absorption bands are broadened in comparison to those predicted by Eq. (4). If the broadening is symmetric with respect to the maximum of the absorption band, the following modification of the Debye equation (4) allows one to correctly reproduce the experimental relaxation spectrum:

\[
\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_\infty + \frac{A}{1 + (i\omega\tau)^\alpha}, \quad 0 < \alpha < 1.
\]

The modification was firstly proposed by Cole and Cole in 1941 [28]. For \(\alpha = 1\), the above equation is identical to the Debye equation (4).

The Cole–Cole equation (5) was widely used as an empirical one [26] and only in the last few years the molecular basis of the equation and the physical meaning of the exponent \(\alpha\) have been given. Below, we shall give the main stages of deriving Eq. (5) from a purely phenomenological point of view. In order to accomplish this, we first recall shortly how Eq. (4) can be gained in the limit of the Brownian rotational motion.

The time evolution of the dielectric polarization \(P\) arising from the application of a dc electric field \(E\) to a dielectric liquid is governed by the following first-order differential equation:

\[
\frac{dP(t)}{dt} + \frac{P(t)}{\tau} = \frac{\varepsilon_0(\varepsilon_\infty - 1)}{\tau} E,
\]

whose solution is

\[
P(t) = \varepsilon_0 \left[\varepsilon_\infty - 1 + (\varepsilon_s - \varepsilon_\infty)e^{-t/\tau}\right] E,
\]

where \(\varepsilon_0 = 8.85\) pF/m.

In the case of a weak probing electric field, when the linear dielectric response applies, the complex dielectric permittivity, in the frequency domain, takes a form
\[ \varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \left[ 1 - i\omega L(e^{-t/\tau}) \right] = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}, \] (8)
i.e. the well-known Debye equation. The symbol “L” stands for the “Laplace transform of”.

These considerations may be easily extended to the fractional dynamics [29–36] by substituting the ordinary time derivative operator \( d/dt \) by a fractional (Riemann–Liouville) derivative operator of arbitrary order \( 0^D t^\alpha \), such that

\[ 0^D t^\alpha g(t) = \frac{d^\alpha}{dt^\alpha} g(t) = \frac{1}{\Gamma(1-\alpha)} \int_0^t \frac{g(t')}{(t-t')^\alpha} dt', \] (9)

where \( g(t) \) is some time-dependent function, and \( \Gamma(z) \) is the usual gamma function. In Eq. (9), one recognizes a memory kernel containing a power-law varying as \( t^{-\alpha} \), characteristic of a slow decay, compared to the Markovian (memory-less) process. Hence, the fractional equation

\[ 0^D_t P(t) + \frac{1}{\tau^\alpha} P(t) = 0, \] (10)

which is the transformed expression of the left-hand side of Eq. (6), is equivalent to

\[ \frac{dP(t)}{dt} + \frac{1}{\tau^\alpha} 0^D_t P(t) = 0. \] (11)
The solution of Eq. (11) is the Mittag-Leffler function \( E_\alpha[-(t/\tau)^\alpha] \) [37]. Equation (8) takes now the following form:

\[ \varepsilon(\omega) - 1 = \varepsilon_\infty - 1 + (\varepsilon_s - \varepsilon_\infty) \left[ 1 - i\omega L\{E_\alpha[-(t/\tau)^\alpha]\} \right], \] (12)

and taking into account that

\[ L\{E_\alpha[-(t/\tau)^\alpha]\} = \int_0^\infty \exp(-zt)E_\alpha[-(t/\tau)^\alpha]dt = [1 + (zt)^\alpha]^{-1}, \] (13)

the Cole–Cole expression (5) for the complex permittivity, is immediately recovered by setting \( z = i\omega \).

The Cole–Cole relaxational behavior is thus a direct consequence of the anomalously slow molecular rotational diffusion in a system under investigation. Then, the relaxation processes in a system cannot be described by the normal Brownian dynamics of the random walks with an exponential decay, as given by Eq. (3), but by the continuous-time random walk theory for a power-law distribution of the waiting times between the consecutive rotational jumps of the molecules. In the case of the fractional dynamics, the exponential way of equilibration of time-dependent quantities must be substituted by the Mittag-Leffler pattern [37] that interpolates between an initial stretched exponential and a terminal inverse power-law pattern, both of index \( \alpha \):
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\[ E_\alpha [-(t/\tau)^\alpha] \propto \begin{cases} \exp \left[ -\frac{(t/\tau)^\alpha}{\Gamma(1+\alpha)(t/\tau)^\alpha} \right], & t \ll \tau, \\ \left[ \Gamma(1-\alpha)(t/\tau)^\alpha \right]^{-1}, & t \gg \tau. \end{cases} \]  

(14)

The Mittag-Leffler function, being the solution of the temporal part of the fractional Fokker–Planck equation (11), is the exact relaxation function leading directly to the Cole–Cole equation (5). In the limit of \( \alpha = 1 \), the Mittag-Leffler function reduces to the exponential function given by Eq. (3).

The dielectric relaxation spectroscopy is then a quite simple and reliable experimental method for determining the value of the exponent \( \alpha \), a fundamental quantity representing the extension of the anomalously slow rotational diffusion in a particular polar liquid.

3. Experimental

\( n \)-heptylcyanobiphenyl, \( C_7H_{15}PhPhCN \), 7CB \( (T_{NI} = 43.3^\circ C) \) was synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. The purity of the compound, checked by chromatography, was better than 99.5\%. Carbon tetrachloride of the spectroscopic grade was purchased from Fluka. The temperature of the phase transitions of pure 7CB and of the solutions were determined with the use of the polarizing microscope. Dielectric characteristics of the mixtures were measured with a HP 4194A impedance/gain phase analyzer in the frequency region of 50 kHz–100 MHz. The measuring capacitor consisted of three plane electrodes: one central and two grounded on each side. A dc biasing electric field was applied to the capacitor for the measurements of the permittivity \( \varepsilon_\parallel (n \parallel E) \) in the nematic phase and in the two-phase region of solutions. A highly performing electrical heating of the capacitor made with a Unipan 650H controller assured a temperature stabilization better than \( 10^{-3} \) K and the possibility of varying the temperature by \( 10^{-2} \) K steps.

4. Results and discussion

The phase diagram for 7CB + CCl\(_4\) mixtures is depicted in Fig. 1. As appropriate for transitions of the first order, the two-phase region (isotropic + nematic, I + N) is observed and the isotropic to nematic phase transition temperature depresses approximately linearly with an increase in the non-mesogenic solute mole fraction (\( x \)). For \( x \) values higher than 0.16, the nematic phase in the mixtures disappears.

Figure 2 presents, as an example, the dielectric relaxation spectra recorded at different temperatures of 7CB + CCl\(_4\) solution for \( x = 0.07 \). The two-phase region between the isotropic and nematic phases (32–34.5\(^\circ\)C) is distinctly seen in the picture. It is obvious that the dielectric absorption spectra, recorded in the region where the isotropic and nematic phases coexist, contain contributions of relaxation
processes occurring in both phases. As the bands related to these contributions are quite close to each other, one resultant absorption band is observed in the spectra of the whole two-phase region. In such a situation, the resolution of this complex band into four elementary contributions (bands corresponding to the molecular rotations around the short and long axes in the two coexisting phases) with the use of the Cole–Cole equation (5), is so uncertain that the fitting parameters values obtained would not be of great importance. Therefore, we abandoned the quantitative analysis of the dielectric spectra in the I + N region.

The dielectric spectra, recorded in the isotropic and nematic phases of 7CB + CCl$_4$ mixtures, were analyzed with the use of the Cole–Cole equation (5) assuming that each spectrum is composed of the two bands corresponding to the molecular rotations around the long and short axes. However, for rod-like molecules having the dipole moment directed roughly along the long axis, as in the case of 7CB
studied here, the absorption band due to the molecular rotation around the short axis is strongly dominating in the dielectric spectrum. As the strength of the contribution from the molecular rotation around the long axis is small and only weakly depends on the temperature and the type of mesophase [38], we will not discuss it here.

Figures 3 and 4 present the temperature dependence of the dielectric strength $A$ and the relaxation time $\tau$ obtained for the band corresponding to 7CB molecules rotation around the short axis. An increase in the non-polar solute concentration in the mixture with polar mesogenic compound, leads to a gradual decrease in the dielectric strength (Fig. 3) as the consequence of the dipole density reduction. The effect is especially distinct in the nematic phase, where the permittivity was measured in the direction of the molecular dipole moment.

![Graph of dielectric strength vs temperature](image)

**Fig. 3.** Temperature dependence of the dielectric strength corresponding to the rotation of 7CB molecules around their short axis in the mixtures of different mole fractions of CCl$_4$. The two-phase (I + N) region is not analyzed.

As the solute used (CCl$_4$) was the liquid of a very low viscosity, the relaxation time of the dipolar solvent molecules becomes shorter as the mole fraction of CCl$_4$ increases. Figure 4 shows that the effect is more pronounced in the nematic phase where the viscosity difference of the two components is much higher than that in the isotropic phase. The figure shows also that the temperature dependence of the relaxation time of 7CB, both in the pure state and in the mixtures, does not fulfill the Arrhenius law

$$\tau = \tau_0 \exp \left( \frac{E_A}{RT} \right),$$

in the whole temperature range studied ($E_A$ is the activation energy, $R$ is the gas constant, $T$ is the absolute temperature, and $\tau_0$ is a constant). Then, the value of the activation energy cannot be determined in a simple way as the slope of $\ln \tau(T)$ on $T^{-1}$ dependence. For such situations, we have recently proposed [39] the procedure of the activation energy $E_A$ determination by calculating the...
Fig. 4. Arrhenius plots for the relaxation time of 7CB molecules in the mixtures with CCl$_4$.

derivative $d(\ln \tau)/d(T^{-1})$. As results from Eq. (15), that derivative leads directly to the activation energy at a given temperature, so allowing one to analyze how $E_A$ evolves with $T$. As we discussed in previous papers [39, 40], the activation energy should be, in general, temperature dependent and the tenet of its constancy has no physical basis. Of course, the proposed procedure of the determination of $E_A(T)$ dependence requires very accurate values of the relaxation time obtained for an appropriate step of the temperature, particularly in the vicinity of the phase transition. The experimental results presented in Fig. 4 fulfill these requirements: in the vicinity of the I–N phase transition, the temperature changes were adjusted by the step of $10^{-2}$ K. The temperature dependences of the activation energy obtained in this way for the rotation of 7CB molecules around their short axis are presented in Fig. 5. As can be seen in the figure, in the vicinity of the transition to the two-phase region of 7CB + CCl$_4$ mixtures, one observes an increase.

Fig. 5. Plot of the activation energy of 7CB molecules in rotation around their short axis in the isotropic and nematic phases of the mixtures 7CB + CCl$_4$, as a function of the temperature.
in the activation energy both from the isotropic and the nematic side. The effect is essentially higher in the nematic phase, similarly to that observed in pure 7CB [41]. Only relatively far from the phase transitions (more than about 10 degrees), the activation energy is temperature independent (or weakly dependent), which customarily means that the Arrhenius dependence (\(\ln \tau \sim T^{-1}\)) is fulfilled.

It is clearly seen in Fig. 6 that in the vicinity of the transition from both the isotropic and the nematic phase to the two-phase \(N + I\) region, we are dealing with a subdiffusion process. The anomalous diffusion exponent \(\alpha\) increases as the temperature approaches to the transition but the dependence shows a strong asymmetry. The asymmetry concerns two features of the dependence \(\alpha(T)\): (i) in the nematic phase, the anomalous rotational diffusion exponent \(\alpha\) decreases rapidly — within a few degrees, whereas in the isotropic phase the pretransitional changes of \(\alpha\) are extended to much larger temperature region; (ii) far from the \(I + N\) to \(N\) transition, the temperature evolution of the exponent \(\alpha\) in the nematic phase leads to a different level of the exponent value, depending on the solute concentration, whereas in the isotropic phase, independently of the solute concentration, far from the \(I\) to \(I + N\) transition, the exponent \(\alpha\) reaches the value close to 1, representing the normal rotational diffusion. In the nematic phase of the mixtures studied, the anomalous rotational diffusion extends in the whole temperature region used. Practically, only in a pure 7CB the diffusional behavior is very close to the Brownian diffusion in the whole temperature region of the nematic phase existence, with an exception of a few degrees just after the isotropic to nematic phase transition.

![Fig. 6. Temperature dependence of the Cole–Cole exponent \(\alpha\) in the isotropic (a) and nematic (b) phases of 7CB + CCl\(_4\) mixtures.](image)

The presented results confirm the expectations on the relation between an extension of the anomaly in the rotational diffusion and the degree of the liquid heterogeneity on the molecular level. An increase in the concentration of the non-mesogenic and non-polar solute in the mixture with mesogenic and strongly polar compound leads undoubtedly to an increase in this heterogeneity. As a result,
the determined value of the anomalous rotational diffusion exponent $\alpha$ decreases and in the dielectric relaxation experiment one observes the broadening of the absorption band.

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