Molecular dynamics parameters of liquid crystal mixtures with different chemical structures

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Abstract. Results of molecular parameters studies using methods of dielectric spectroscopy, acoustic spectroscopy and viscometry are compared. An influence of dipole-dipole interactions on the relaxation time, the coefficients of molecular friction and rotational diffusion of molecules has been established. An analysis of modern methods for determining the coefficient of molecular friction and rotational diffusion for liquid crystal mixtures of different composition is carried out. It is shown that currently there is no theory that can describe qualitatively and quantitatively the behavior of the molecular relaxation parameters of the liquid crystal mixtures.

1. Introduction

A study of molecular dynamics processes is an important issue in the physics of liquid crystals, since the macroscopic properties of the liquid crystals (LCs) depend on the chemical structure of the molecules [1,2], as well as on their collective behavior [3] and association due to intermolecular interactions [4,5]. This is especially true in composite materials [6–9].

In this regard, both practical and scientific interest is represented by the multicomponent nematic LC mixtures [10] consisting of compounds with positive and negative anisotropy of dielectric permittivity $\Delta \varepsilon$. As a result, the LC mixture is able to change the sign of dielectric anisotropy at a certain frequency of the external electric field. This provides an ability to control the response time in LC devices using signals of various frequencies (above or below the transition, respectively).

This paper discusses different approaches to determining molecular relaxation parameters [11–15] such as the molecular friction and rotational diffusion coefficients [16].

2. Materials

The liquid crystal mixtures based on cyanophenylpyridine, alkoxycyanobiphenyls and their derivatives were chosen as the object of the study.

Figure 1 shows the structural formulas of the ZhK-1282 mixture components [17], where 1 are alkoxycyanobiphenyls (47 wt%), 2 is a Gray ester (48 wt%), 3 is a Demus ester (5 wt%). The synergistic effect of the interaction [18,19] of individual components allows to conclude about contribution of each component into the final mixture. The mixture ZhK-1289 is similar in composition to the mixture ZhK-1282 and differs in the concentration of components.
Figure 1. Structural formulas of ZhK-1282 mixture components: 1) derivatives of alkoxycyanobiphenyls, 2) Gray ester, 3) Demus ester

The material ZhK-614 consists of a few complex esters (CFEBA) and 4'-cyanophenyl ester of cinnamic was used as a substance that increases $T_c$.

Figure 2. Structural formula of the cyanophenylpyridine

The liquid crystal mixture ZhK-1630A has a wide temperature range of the nematic liquid crystal phase (from $-70^\circ C$ to $80^\circ C$). ZhK-1630A mixture is based on cyanophenylpyridines and has the best multiplex ability (1:64) \cite{20}. The multiplex value depends on the value of the elastic constants $K_{33}/K_{11}$ and the $\Delta \varepsilon/\varepsilon_\perp$ ratio. Figure 2 shows the structural formula of cyanophenylpyridines that are a part of the ZhK-1630A.

3. Results and discussion

Based on previous experimental data of dielectric relaxation times \cite{16,21}, other parameters of the molecular dynamics of the LC can be calculated: molecular friction $\zeta$ and rotational diffusion $D$ characteristics.

There are several approaches for calculating the molecular friction coefficient $\zeta$. Various authors have obtained corresponding expressions for calculating the molecular friction coefficient \cite{11,15}

$$\zeta = kT\tau_D,$$

$$\zeta = \frac{\gamma_1}{3n\bar{f}_1(P_2)} = \frac{q + (2 + P_2)P^2_2(1 + \frac{bq}{6}) + 6P^2_2 - 1.5bP^4_2}{3nP^2_2(1 + \frac{bq}{6})},$$

$$\zeta = \frac{2(1 + 2\gamma)(1 + p)}{\gamma} \left[ 1 - \frac{5}{p^2 + 6} \right] d^4\sqrt{\pi kTmn} \exp \left( \frac{E}{kT} \right).$$
\[ \zeta = 8\pi\gamma_1 L^3 f(p) \approx \frac{16\pi\gamma_1 L^3}{6 \ln[1 + \sqrt{p^2 - 1}] - 3}, \quad (4) \]

where \( \tau_D \) is the characteristic relaxation time of molecules, \( T \) is the temperature of the molecules system, \( \gamma_1 \) is the rotational viscosity coefficient, \( P_2 \) is the order parameter, \( p = L/d \) is the ratio of the long and short axes of the molecule, \( n \) is the concentration of the molecules, \( m \) is the molecular mass, \( E \) is the potential barrier that must be overcome when a cluster of the molecules is reoriented according to the Maier-Saupe theory \[22\].

The dependence of the function \( f_1(P_2) \) on the order parameter \( P_2 \) is slightly weaker than the first degree and in the studied temperature range \( f_1(P_2) \sim 0.21 \). The parameters \( \gamma \) and \( p \) depend on the shape of the molecules and their relative position. The value of \( (1 + 2\gamma)/\gamma \) is almost independent of \( p \) and \( P_2 \), and the value of \( (1 + 2\gamma)/\gamma = 3.25 \) can be used to estimate the molecular friction coefficient \[15,23\]. The average value of the parameter \( p \) for the studied mixture should be taken equal to 3, \( d \sim 0.4 \text{ nm} \), and \( n \sim 2.04 \times 10^{27} \text{ m}^{-3} \). However, the coefficient of the molecular friction in turn is also related with rotational diffusion \( D \) by the expression \[24\]

\[ \zeta = \frac{kT}{D}. \quad (5) \]

The results of molecular parameters studies using the methods of dielectric spectroscopy \[16,21\], acoustic spectroscopy and viscometry are compared. The influence of dipole-dipole interactions on the relaxation time, the coefficients of molecular friction and rotational diffusion of molecules has been established. The analysis of modern methods for determining the coefficient of molecular friction and rotational diffusion for LC mixtures of different composition is carried out. The results of this comparison are presented in Table 1.

**Table 1.** Comparison of the molecular friction and rotational diffusion coefficients at \( T = 297 \text{ K} \) for different models

| Parameter | Values obtained | Ratna model [11] | Nentsov model and the Enskog method [12] | Belyaev-Nentsov model [15] | Bata and Buka model [14] |
|-----------|-----------------|------------------|-------------------------------------------|------------------|-------------------|
| \( \zeta \cdot 10^{27}, \text{ kg m}^2/\text{s} \) | 0.734 | 0.117 | 0.00057 | 1.97 |
| \( D \cdot 10^6, \text{ s}^{-1} \) | 5.59 | 38.35 | 7190 | 2.08 |
| \( \zeta \cdot 10^{27}, \text{ kg m}^2/\text{s} \) | 0.76 | 0.113 | 0.00062 | 1.87 |
| \( D \cdot 10^6, \text{ s}^{-1} \) | 6.01 | 34.48 | 6960 | 1.88 |
| \( \zeta \cdot 10^{27}, \text{ kg m}^2/\text{s} \) | 0.78 | 0.112 | 0.00052 | 1.94 |
| \( D \cdot 10^6, \text{ s}^{-1} \) | 5.91 | 36.24 | 7040 | 1.64 |
| \( \zeta \cdot 10^{27}, \text{ kg m}^2/\text{s} \) | 0.68 | 0.12 | 0.00048 | 2.34 |
| \( D \cdot 10^6, \text{ s}^{-1} \) | 6.09 | 34.27 | 6080 | 1.74 |

The values of the molecular friction coefficients determined by the dielectric relaxation and rotational viscosity using the Perrin function are approximately by one order of the
magnitude smaller than the values of $\zeta$ determined by the rotational viscosity according to the formula (2) [12, 13]. This value is consistent with the value $\zeta$ given for azoxic compounds, Schiff bases, pentylycyanobiphenyl, and the bicyclooctane derivative [25].

The values of the rotational diffusion $D$ calculated using different formulas are in the range $2 \cdot 10^7 \text{s}^{-1} < 7 \cdot 10^8 \text{s}^{-1}$. Both parallel and perpendicular components of the rotational diffusion $D$ for the hexyloxy-cyanobiphenyl (6OCB) are given in the Refs. [26, 27], where $D || \sim 10^8 \text{s}^{-1}$, $D \perp \sim 3 \cdot 10^7 \text{s}^{-1}$ at 312 K. For the pentylycyanobiphenyl (5CB) $D || \sim 8 \cdot 10^8 \text{s}^{-1}$, $D \perp \sim 4 \cdot 10^7 \text{s}^{-1}$ at 297 K. These data are best matched by the results in column 3 of Table 1.

Conclusions
The results obtained show that the existing theories that use acoustic and dielectric studies to determine the coefficient of molecular friction and rotational diffusion do not provide uniform values. This is due to the fact that at the moment there is no single theory that could simultaneously describe the results of acoustic and dielectric spectroscopy of liquid crystal systems. It follows that this issue is an important stage in research in this area.

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