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On the Dielectric and Splay Elastic Constants of Nematic Liquid Crystals With Positive Dielectric Anisotropy

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The temperature dependence of dielectric constants, the Frederiks threshold voltage, and the splay elastic constant of three pure nematic liquid crystal (NLC) compounds and one binary mixture are reported. A four-parameter model explaining temperature dependency of dielectric constants is derived. The four-parameter model can be approximated as a three-parameter model for the liquid crystals (LCs) having low dielectric anisotropy, provided the operating temperature is far from the clearing point. To validate these models, the experimental data of four NLC compounds have been taken from the literature. The results obtained using the two models are compared. Applying the four-parameter model, temperature dependencies of the Frederiks threshold voltage (V_{th}) and the splay elastic constant (K_{11}) are investigated. It is also discussed how the expression for the splay elastic constant can be written as a second-order polynomial under certain conditions. This prediction is also validated by comparing with the experimental results available in the literature. Using the dielectric anisotropy results, the orientational order parameter is also calculated. Satisfactory agreement between experimental data and fitting results is obtained.

Keywords Dielectric properties; elastic properties; nematic liquid crystals; threshold voltage

1. Introduction

Liquid crystal (LC)-based materials have received much attention owing to their manifold display applications. Nematic liquid crystals (NLC) are most commonly used in the production of LC display devices due to their unique physical properties and wide temperature range. LCs exhibit anisotropy properties, which include viscosity, elasticity, birefringence, dielectric permittivity, and magnetic susceptibility etc. Operational characteristics of LC devices depend significantly on the anisotropy of their dielectric and optical properties. Study of dielectric parameters is therefore vital for the development of electro-optic devices, and in addition, provides very useful information about the molecular structure and intermolecular forces in LCs [1–3]. A four-parameter model that describes the temperature dependence of LC dielectric constants is proposed. We also discuss how the four-parameter model can be approximated as a three-parameter model under certain conditions. Fitting results obtained from the application of both the four- and the three-parameter model to the experimental data of three different nematics and one mixture are compared.

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The elastic constants of NLCs are very important material constants from both application and fundamental research point of view. Consequently, the knowledge of elastic constants of various liquid crystalline materials is of basic importance in understanding the electro-optical effects of LCs. The Frank elastic constants have been the subject of extensive experimental [4–9] and theoretical [10–15] investigations. Information about the elastic constants can be obtained from a number of experiments. In this article, our focus is on the temperature dependency of the splay elastic constant (K_{11}). With the knowledge of dielectric constants of NLC and the Frederiks threshold voltage (V_{th}), K_{11} can be determined [9,16], provided the nematic anisotropy is positive and the surface anchoring is strong [5,17,18]. The four-parameter model is applied to describe the temperature dependence of the threshold voltage and the splay elastic constant. The expression for the splay elastic constant can be written as a second-order polynomial for low dielectric anisotropy NLC materials if the operating temperature is far from the clearing point. The orientational order is responsible for the physical properties such as refractive indices and dielectric constants to become anisotropic. The order parameter can be calculated directly from a macroscopic quantity measured in experiment, and from this idea, a simple procedure solely based on anisotropy data [19] has been applied. This procedure consists in the following steps: determination of dielectric anisotropy ($\Delta\varepsilon$), determination of $(\Delta\varepsilon)_o$ for the case of perfect order using the extrapolation method, and calculation of the order parameter. The four-parameter model is applied to fit the experimental data of the order parameter.

The experimental data of dielectric constants and the Frederiks threshold voltage of four different LC materials have been collected from the literature [20,21]. Experimental results were determined from the measurements of capacitance–voltage characteristics at a frequency of 1 kHz. Experimental data of compounds PTP4O2 (4-n-butyl-4-ethoxytolan), 3PBC^{2,4}F$_2$, and 3PBC^{3,4}F$_2$ and the binary mixture 3PBC^{2,4}F$_2$(50%): 3PBC^{3,4}F$_2$(50%) have been used to obtain the fitting results. The fluorinated PBC (phenyl-bi-cyclohexane) compounds used in this study have the same 3PBC core structure but different fluorine substituents. All these NLCs exhibit the nematic phase in a broad temperature interval. The clearing temperatures of 3PBC^{2,4}F$_2$, 3PBC^{3,4}F$_2$, 3PBC^{2,4}F$_2$(50%): 3PBC^{3,4}F$_2$(50%), and PTP4O2 were reported as 133.5, 120.9, 128.2, and 81.1 °C, respectively.

2. Theory

2.1 Dielectric Constants

Due to the dielectric anisotropy, an aligned uniaxial NLC cell exhibits two components of dielectric permittivity ($\varepsilon_{||}$, $\varepsilon_{\perp}$), which can be measured with an electric field parallel and perpendicular to the director n, respectively:

$$\varepsilon_{||} = \langle\varepsilon\rangle + \frac{2}{3}(\Delta\varepsilon), \tag{1.1}$$

$$\varepsilon_{\perp} = \langle\varepsilon\rangle - \frac{1}{3}(\Delta\varepsilon). \tag{1.2}$$

The dielectric anisotropy ($\Delta\varepsilon$) is the difference between the parallel and the perpendicular dielectric constant, i.e., $\Delta\varepsilon = (\varepsilon_{||} - \varepsilon_{\perp})$. The sign of $\Delta\varepsilon$ depends upon the permanent dipole moment of the molecules. Here, $\langle\varepsilon\rangle = (\varepsilon_{||} + 2\varepsilon_{\perp})/3$ represents the average dielectric constant. According to the available experimental data and fitting results, the average

dielectric constant ($\langle\varepsilon\rangle$) has a linear decreasing behavior with temperature:

$$\langle\varepsilon(T)\rangle = A + BT, \tag{2}$$

where $B < 0$.

On the other hand, the temperature-dependent dielectric anisotropy ($\Delta\varepsilon$), adopting Haller's approximation, can be expressed by

$$\Delta\varepsilon(T) = (\Delta\varepsilon)_{\mathrm{o}} \left(1 - \frac{T}{T_{\mathrm{c}}}\right)^{\lambda}. \tag{3}$$

In this equation, $(\Delta\varepsilon)_{\mathrm{o}}$ is the NLC dielectric anisotropy in the crystalline state (or $S = 1$), nominally the extrapolated NLC permittivity anisotropy at $T = 0$ K; the exponent λ is a material constant; and T_{c} is the clearing temperature of the NLC material under investigation. By substituting Equations (2) and (3) back to Equations (1.1, 1.2), we drive the four-parameter model describing temperature-dependent dielectric constants of NLCs:

$$\varepsilon_{||}(T) = A + BT + \frac{2}{3}(\Delta\varepsilon)_{\mathrm{o}} \left(1 - \frac{T}{T_{\mathrm{c}}}\right)^{\lambda} \tag{4.1}$$

$$\varepsilon_{\perp}(T) = A + BT - \frac{1}{3}(\Delta\varepsilon)_{\mathrm{o}} \left(1 - \frac{T}{T_{\mathrm{c}}}\right)^{\lambda}. \tag{4.2}$$

Equations (4.1, 4.2) have four fitting parameters. A and B can be obtained by the fitting of temperature-dependent $\langle\varepsilon(T)\rangle$ data, Equation (2). Similarly, $(\Delta\varepsilon)_o$ and λ can be obtained by fitting the temperature-dependent $\Delta\varepsilon$ data to Equation (3), written in logarithmic form.

Some pure LC compounds and mixtures exhibit low dielectric anisotropy. For such LCs, along with the condition $T \ll T_{\mathrm{c}}$, the $(1 - T/T_{\mathrm{c}})^{\lambda}$ term in Equations (4.1) and (4.2) can be expanded into power series. Restricting our expansion up to the third term, we drive a three-parameter model:

$$\varepsilon_{||}(T) = A_{||} + B_{||}T + C_{||}T^2, \tag{5.1}$$

$$\varepsilon_{\perp}(T) = A_{\perp} + B_{\perp}T - C_{\perp}T^2, \tag{5.2}$$

where $A_{||} = A + 2(\Delta\varepsilon)_{\mathrm{o}}/3$, $B_{||} = B - 2(\Delta\varepsilon)_{\mathrm{o}}\lambda/3T_{\mathrm{c}}$, $C_{||} = (\Delta\varepsilon)_{\mathrm{o}}\lambda(\lambda - 1)/3T_{\mathrm{c}}^2$ and

$$A_{\perp} = A - (\Delta\varepsilon)_{\mathrm{o}}/3,\ B_{\perp} = B + (\Delta\varepsilon)_{\mathrm{o}}\lambda/3T_{\mathrm{c}},\ C_{\perp} = (\Delta\varepsilon)_{\mathrm{o}}\lambda(\lambda - 1)/6T_{\mathrm{c}}^2.$$

We will see that, for low dielectric anisotropy NLC materials, when the operating temperature is far from the clearing point, the three-parameter model can be satisfactorily applied.

2.2 Threshold Voltage and Splay Elastic Constant

The splay elastic constant K_{11} is related to the Frederiks threshold voltage (V_{th}) by the following relation:

$$K_{11} = \frac{\varepsilon_{\mathrm{o}}\Delta\varepsilon}{\pi^2} V_{\mathrm{th}}^2 \tag{6}$$

if the cell has unidirectional planar configuration, strong anchoring, and $\Delta\varepsilon$ is positive.

Here, ε_{o} is the permittivity of vacuum.

To describe the temperature-dependent behavior of the threshold voltage, we use Equation (6) itself. The order parameter dependence of the elastic constant, explained by Kimura et al. [22], is given by

$$K_{ii} = K_{iio} S^2, \tag{7}$$

where K_{iio} is the extrapolated elastic constant at $T = 0$ K. By substituting Equations (3) and (7) into Equation (6), we drive an expression that describes the temperature effect on the threshold voltage of the Frederiks transition:

$$V_{\text{th}} = V_{\text{o}} \left(1 - \frac{T}{T_{\text{c}}}\right)^{\lambda/2}, \tag{8}$$

where $V_{\text{o}} = \pi (K_{11\text{o}}/\varepsilon_{\text{o}}(\Delta\varepsilon)_{\text{o}})^{1/2}$.

The value of V_{o} is obtained by plotting $\ln(V_{\text{th}})$ as a function of $\ln(1 - T/T_{\text{c}})$. The plot is linear and can be extrapolated to $T = 0$ K; the intercept at $T = 0$ K gives the value of V_{o}. Once the temperature dependence of the threshold voltage is known, we can calculate the splay elastic constant using Equation (6), which takes the following form:

$$K_{11} = (K_{11})_{\text{o}} \left(1 - \frac{T}{T_{\text{c}}}\right)^{2\lambda}, \tag{9}$$

where $(K_{11})_{\text{o}} = \varepsilon_{\text{o}} V_{\text{o}} (\Delta\varepsilon)_{\text{o}}/\pi^2$.

Under some limitations, such as low $(\Delta\varepsilon)$ and small value of fraction T/T_{c}, the splay elastic constant can be written as a second-order polynomial:

$$K_{11} = A_k - B_k T + C_k T^2, \tag{10}$$

where $A_k = (K_{11})_{\text{o}}$, $B_k = (K_{11})_{\text{o}} 2\lambda/T_{\text{c}}$., and $C_k = (K_{11})_{\text{o}} \lambda(2\lambda - 1)/T_{\text{c}}^2$.

We remark that the operating temperature must be sufficiently far from the clearing point.

2.3 Order Parameter

All macroscopic properties, e.g., the diamagnetic susceptibility, the refractive index, the dielectric permittivity, can be used to identify the macroscopic order parameter. In the present work, we deal with the dielectric anisotropy. The method of calculating order parameters is very simple, consisting in the following steps: measurements of dielectric anisotropy $\Delta\varepsilon$, determination of $(\Delta\varepsilon)_{\text{o}}$ by extrapolation, and calculation of S. Following Haller's approximation, Equations (1.1, 1.2) can be rewritten, respectively, as

$$\varepsilon_{||} = \langle\varepsilon\rangle + \frac{2}{3}(\Delta\varepsilon)_{\text{o}} S, \tag{11.1}$$

$$\varepsilon_{\perp} = \langle\varepsilon\rangle - \frac{1}{3}(\Delta\varepsilon)_{\text{o}} S. \tag{11.2}$$

Combining these two equations, we get

$$S = \Delta\varepsilon/(\Delta\varepsilon)_{\text{o}}. \tag{12}$$

Table 1. Fitting parameters of $3PBC^{2,4}F_2$, $3PBC^{3,4}F_2$, $3PBC^{2,4}F_2$(50%): $3PBC^{3,4}F_2$(50%), and PTP4O2 for four-parameter model

	$\langle\varepsilon\rangle$		$(\Delta\varepsilon)$	
LC material	A	$B(T^{-1})$	$(\Delta\varepsilon)_o$	λ
$3PBC^{24}F_2$	4.7747	-0.95×10^{-2}	1.9302	0.2704
$3PBC^{34}F_2$	6.8657	-2.12×10^{-2}	6.9671	0.2735
Mixture[a]	4.7527	-1.04×10^{-2}	3.7626	0.3900
PTP4O2	3.7410	-0.22×10^{-2}	0.1157	0.0680

[a]$3PBC^{2,4}F_2$ (50%):$3PBC^{3,4}F_2$ (50%).

3. Results and Discussion

The four parameters [A, B, $(\Delta\varepsilon)_o$, λ], in Equations (4.1, 4.2), can be easily obtained by fitting the experimental data of $\langle\varepsilon\rangle$ and $\Delta\varepsilon$ as a function of temperature. The best fit that illustrates the temperature dependence of $\langle\varepsilon\rangle$, Equation (2), gives the value of A and B. Besides, by fitting the experimental data of $\Delta\varepsilon$ to Equation (3), in logarithmic form, the values of $(\Delta\varepsilon)_o$ and λ can be obtained. Table 1 contains these fitting parameters for all investigated NLC samples. By substituting these four parameters, along with the clearing temperature T_c, in Equations (4.1, 4.2), we can calculate the temperature dependency of dielectric constants. For low-$\Delta\varepsilon$ NLC compounds or mixtures, if the operating temperature is far from T_c, the four-parameter model can be reduced to a three-parameter model. Under these conditions, the term $(1 - T/T_c)^{\lambda}$ can be written into a power series expansion. The fourth term of this expansion, depending upon the NLC material under investigation, has been found approximately from 0.95% to 4.0% of the first term. So keeping the first three terms, the four-parameter model is simplified to a three-parameter model. Table 2 lists the fitting parameters of the three-parameter model. The fitting results have been obtained by applying the four- and three-parameter models to the experimental data already quoted. Experimental data of four different NLC materials have been used in the present study.

The temperature dependency of experimental data and fitting curves of the four- and three-parameter models for dielectric constants are shown in Figures 1 and 2. The four-parameter model closely fits the experimental data during the whole nematic range for all

Table 2. Fitting parameters of $3PBC^{2,4}F_2$, $3PBC^{3,4}F_2$, $3PBC^{2,4}F_2$(50%): $3PBC^{3,4}F_2$(50%), and PTP4O2 for three-parameter model

	$\varepsilon_{\|\|}$			$\varepsilon_{\perp}$		
LC material	$A_{\|\|}$	$B_{\|\|}(T^{-1})$	$C_{\|\|}(T^{-2})$	$A_{\perp}$	$B_{\perp}(T^{-1})$	$C_{\perp}(T^{-2})$
$3PBC^{24}F_2$	6.0615	–0.0122	-7.1230×10^{-6}	4.1313	–0.0083	-3.5615×10^{-6}
$3PBC^{34}F_2$	11.5104	–0.0317	-3.1576×10^{-7}	4.5433	–0.0160	-1.5788×10^{-5}
Mixture[a]	7.2611	–0.0181	-1.8212×10^{-5}	3.4985	–0.0066	-9.1059×10^{-6}
PTP4O2	3.5481	–0.0023	-3.7205×10^{-7}	3.4324	–0.0022	-1.8603×10^{-7}

[a]$3PBC^{2,4}F_2$ (50%):$3PBC^{3,4}F_2$ (50%).

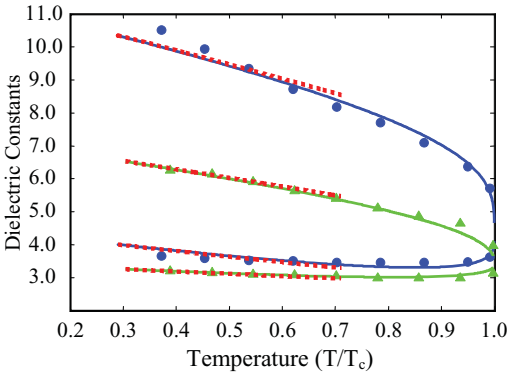

Figure 1. Temperature-dependent dielectric constants ($\varepsilon_{||}$, $\varepsilon_{\perp}$): Circles (●) represent the experimental data of 3PBC^{3,4}F$_2$ and triangles (▲) represent the experimental data of 3PBC^{2,4}F$_2$(50%): 3PBC^{3,4}F$_2$(50%). Solid lines are the fitting curves of the four-parameter model, Equations (4.1, 4.2), while dotted lines correspond to the three-parameter model, Equations (5.1, 5.2).

the NLC materials we have studied. The fitting results are in better agreement with experimental data for the NLC materials with small dielectric anisotropies, such as for 3PBC^{2,4}F$_2$, PTP4O2, and 3PBC^{2,4}F$_2$ (50%):3PBC^{3,4}F$_2$ (50%). The four-parameter model is an appropriate model to describe the temperature dependency of dielectric constants. The three-parameter model fits the experimental data satisfactorily for low dielectric anisotropy NLC materials when the operating temperature is sufficiently far from the clearing temperature. For LCs 3PBC^{2,4}F$_2$ and 3PBC^{3,4}F$_2$, in Figure 1, and for 3PBC^{2,4}F$_2$(50%): 3PBC^{3,4}F$_2$(50%), in Figure 2, the noticeable differences between four- and three-parameter models appear after half of the nematic range. PTP4O2 has extremely low dielectric anisotropy ($\Delta\varepsilon \sim 0.10$) as compared with other LC materials. For PTP4O2, in Figure 2, the three-parameter model

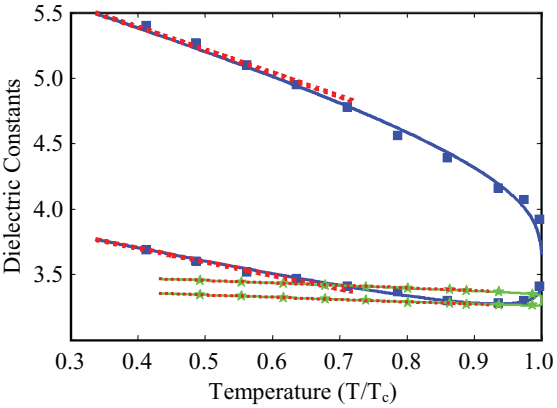

Figure 2. Temperature-dependent dielectric constants ($\varepsilon_{||}$, $\varepsilon_{\perp}$): Squares (■) represent the experimental data of 3PBC^{2,4}F$_2$ and stars (★) represnt the experimental data of PTP4O2. Solid lines are the fitting curves of the four-parameter model, Equations (4.1, 4.2), while dotted lines correspond to the three-parameter model, Equations (5.1, 5.2).

fits the experimental data equally well as the four-parameter model even when the operating temperature reaches values near to the clearing point. Since the dielectric anisotropies of $3PBC^{2,4}F_2$, $3PBC^{3,4}F_2$, and $3PBC^{2,4}F_2(50\%)$: $3PBC^{3,4}F_2(50\%)$ are higher than that of PTP4O2; therefore, the power expansion is less accurate. Thus the three-parameter model is suitable only for low-$\Delta\varepsilon$ NLCs with operating temperature much lower than T_c.

The dielectric anisotropy ($\Delta\varepsilon$) is plotted as a function of temperature, for three NLC materials, in Figure 3. Two pure $3PBC^{2,4}F_2$, $3PBC^{3,4}F_2$ and one binary mixture ($3PBC^{2,4}F_2(50\%)$: $3PBC^{3,4}F_2(50\%)$ are presented. Pure $3PBC^{3,4}F_2$ has the highest dielectric anisotropy, while $\Delta\varepsilon$ of the binary mixture is found to be slightly higher than that of pure $3PBC^{2,4}F_2$. Solid lines represent the fitting curves using the four-parameter model. For $3PBC^{2,4}F_2$ and $3PBC^{2,4}F_2(50\%)$: $3PBC^{3,4}F_2(50\%)$, the experimental data are consistent with the fitting results in the whole nematic range, whereas for $3PBC^{3,4}F_2$, having large anisotropy ($\Delta\varepsilon \sim 7.0$), the fitting results are not in as good agreement as for NLC materials with smaller dielectric anisotropies.

Based on the four-parameter model, Equation (8) describes the temperature dependence of the threshold voltage (V_{th}). Figure 4 depicts the temperature dependence of the threshold voltage. It is observed that the threshold voltage decreases nonlinearly as the temperature is increased. V_{th} shows weak temperature dependence at low temperatures, but begins to decrease rapidly near the nematic–isotropic transition. The experimental results are almost similar to the fitting curves obtained by Equation (8). Taking in the values of V_{th} and other required parameters, K_{11} can be calculated by Equation (9). Under certain conditions, such as low dielectric anisotropy and if $T \ll T_c$, the term $(1 - T/T_c)^{2\lambda}$, in Equation (9), can be written as a power series expansion. Restricting this expansion up to the third term, we formulate a second-order polynomial for the splay elastic constant, Equation (10). This expression contains three constants, which are listed in Table 3. Fitting results (obtained by Equations (9) and (10)) and experimental data of the splay elastic constant for $3PBC^{3,4}F_2$ and $3PBC^{2,4}F_2(50\%)$: $3PBC^{3,4}F_2(50\%)$ are plotted in Figure 5. Equation (9) fits well the experimental data in the whole nematic range, whereas the fitting curves of the polynomial relation start deviating from the experimental data after half of the nematic range. Thus, Equation (9) is an adequate expression to describe the temperature dependence of the splay

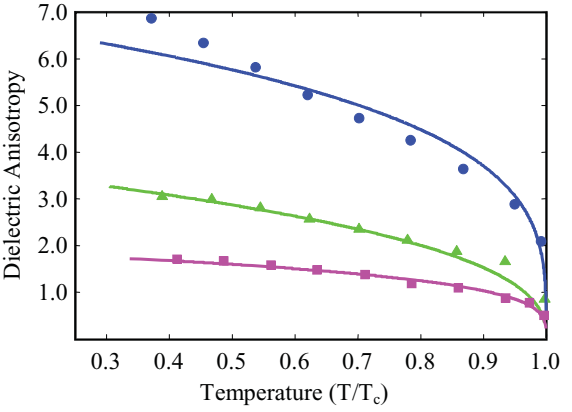

Figure 3. Temperature-dependent dielectric anisotropy ($\Delta\varepsilon$): Circles (●), triangles (▲), and squares (■) represent the experimental data of $3PBC^{3,4}F_2$, $3PBC^{2,4}F_2(50\%)$: $3PBC^{3,4}F_2(50\%)$, and $3PBC^{2,4}F_2$, respectively. Solid lines are the fitting results of Equation (3).

Table 3. Fitting parameters of $3PBC^{2,4}F_2$, $3PBC^{3,4}F_2$, and $3PBC^{2,4}F_2$(50%): $3PBC^{3,4}F_2$ (50%) for splay elastic constant

	K_{11}		
LC material	A_k(N)	B_k(NT^{-1})	C_k(NT^{-2})
$3PBC^{24}F_2$	2.2979×10^{-11}	7.7134×10^{-14}	-1.5943×10^{-16}
$3PBC^{34}F_2$	2.2546×10^{-11}	9.0362×10^{-14}	-1.9262×10^{-16}
Mixture[a]	3.1755×10^{-11}	1.4117×10^{-13}	-2.3766×10^{-16}

[a]$3PBC^{2,4}F_2$ (50%):$3PBC^{3,4}F_2$ (50%)

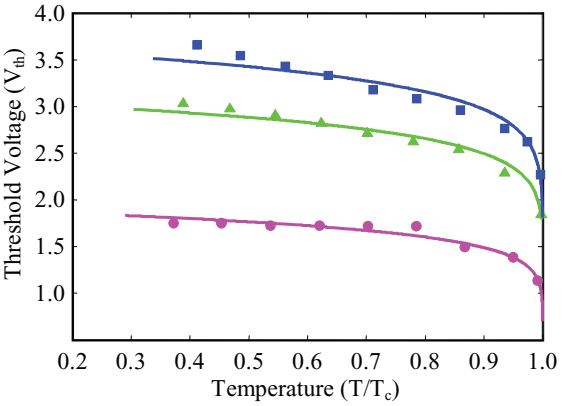

Figure 4. Temperature-dependent threshold voltage (V_{th}): Circles (●), triangles (▲), and squares (■) represent the experimental data of $3PBC^{3,4}F_2$, $3PBC^{2,4}F_2$(50%): $3PBC^{3,4}F_2$(50%), and $3PBC^{2,4}F_2$, respectively. Solid lines are the fitting results of Equation (8).

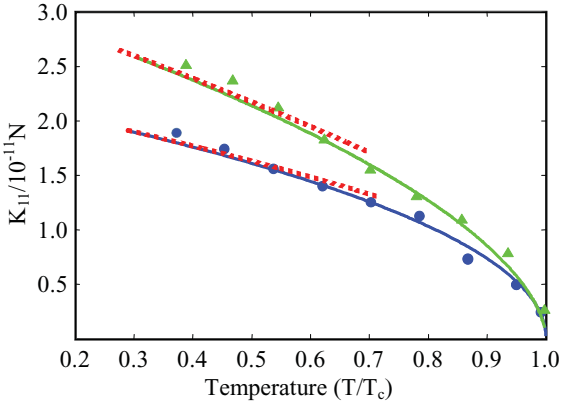

Figure 5. Temperature-dependent splay elastic constant (K_{11}): Triangles (▲) and circles (●) represent the experimental data of $3PBC^{2,4}F_2$(50%): $3PBC^{3,4}F_2$(50%) and $3PBC^{3,4}F_2$, respectively. Solid lines are the fitting results of Equation (9), while dashed lines correspond to Equation (10).

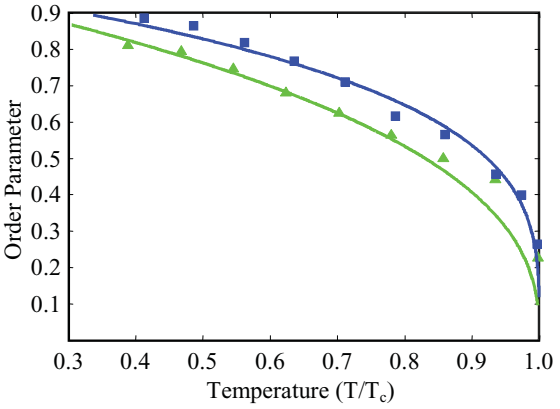

Figure 6. Temperature-dependent order parameter (S): Triangles (▲) and squares (■) represent the experimental data of 3PBC^{2,4}F$_2$(50%): 3PBC^{3,4}F$_2$(50%), and 3PBC^{2,4}F$_2$, respectively. Solid lines are the fitting results of Equation (12).

elastic constant. The polynomial expression is suitable only for the low-$\Delta\varepsilon$ NLC materials if the operating temperature is far from clearing point.

From the temperature-dependent dielectric anisotropy ($\Delta\varepsilon$), the order parameter can be calculated using Equation (12): $S = \Delta\varepsilon/(\Delta\varepsilon)_o$. Figure 6 demonstrates the temperature dependency of the order parameter for 3PBC^{2,4}F$_2$ and 3PBC^{2,4}F$_2$(50%): 3PBC^{3,4}F$_2$(50%). The order parameters of both NLC samples are almost proportional to their dielectric anisotropies. The obtained values of the order parameters for the binary mixture are higher than the ones for pure 3PBC^{2,4}F$_2$. The fitting with the experimental data is quit satisfactory in the entire nematic region.

4. Conclusion

Four- and three-parameter models describing the temperature dependence of dielectric constants of NLCs have been derived and confirmed by the experimental data. Experimental data of four NLC materials with different anisotropies are used to validate the two models. The four-parameter model satisfactorily fits the experimental data in the whole nematic range for all four NLC materials. For three PBC compounds, the three-parameter model fits the experimental data only if the temperature is far from the clearing point (up to $T \approx 0.6T_c$). However, for PTP4O2, having very low dielectric anisotropy, the three-parameter model fits well the experimental data and almost overlaps with the four-parameter model even when the temperature is not so far from the clearing point (up to $T \approx 0.9T_c$). So, it can be concluded that the four-parameter model is an appropriate model to describe the temperature dependency of NLC dielectric constants. While the three-parameter model is more suitable for low-$\Delta\varepsilon$ NLC materials if the operating temperature is not close to the clearing point. Dielectric anisotropy, the Frederiks threshold voltage, the splay elastic constant, and the order parameter are also well described by the four-parameter model. All of these properties are well explained by the three-parameter model for NLCs with small dielectric anisotropy if the operating temperature is far below the clearing point.

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