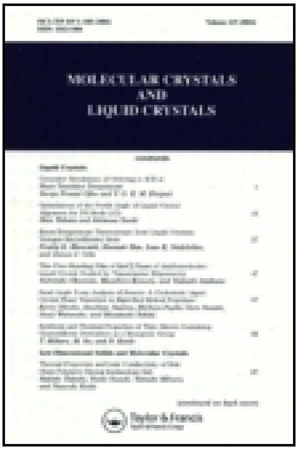

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

QUANTITATIVE AND QUALITATIVE ANALYSIS OF COMPLEX DIELECTRIC PERMITTIVITY OF THE FERROELECTRIC LIQUID CRYSTAL ON THE BASIS OF THE NORDIO-RIGATTI-SEGRE THEORY

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Version of record first published: 24 Sep 2006

To cite this article: W. Otowski & D. Demus (2001): QUANTITATIVE AND QUALITATIVE ANALYSIS OF COMPLEX DIELECTRIC PERMITTIVITY OF THE FERROELECTRIC LIQUID CRYSTAL ON THE BASIS OF THE NORDIO-RIGATTI-SEGRE THEORY, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 366:1, 533-546

To link to this article: http://dx.doi.org/10.1080/10587250108023994

Mol. Cryst. and Liq. Cryst., 2001, Vol. 366, pp. 533-546
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Gordon and Breach Science Publishers imprint,
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Printed in the USA

Quantitative and Qualitative Analysis of Complex Dielectric Permittivity of the Ferroelectric Liquid Crystal on the Basis of the Nordio-Rigatti-Segre Theory

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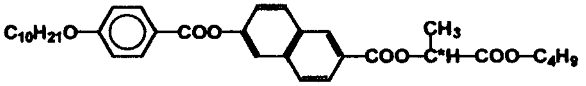
This paper presents the results of broadband dielectric studies of the dielectric relaxation of a macroscopically oriented ferroelectric liquid crystal. The Nordio-Rigatti-Segre theory is used to calculate some dielectric values and to compare with the experimental results. However, a few essential values have been calculated previously using the quantum chemical program MOPAC/7, with the AM1 Hamiltonian.

Keywords: ferroelectric liquid crystal; Nordio-Rigatti-Segre theory

INTRODUCTION

The synthesis of new liquid crystalline compounds is still an important topic for the applications of liquid crystals in displays. The prediction of the physical properties of the compounds, without performing experiments, could save a considerable amount of the manpower and materials needed for the synthesis of new compounds. Among the most important properties of liquid crystals are their dielectric constants. On the other hand any theoretical predictions should be verified by the experimental results.

This paper presents the results of broadband dielectric studies of the dielectric relaxation of a macroscopically oriented ferroelectric liquid crystal. Due to the anisotropy of the molecular structure, different contributions of the longitudinal and transversal components of the permanent dipole moment to the dielectric spectra can be observed. The Nordio-Rigatti-Segre theory is used to calculate some dielectric values and to compare with the experimental results. However, a few essential values have been calculated previously. Using the quantum chemical program MOPAC/7, with the AM1 Hamiltonian, the dipole μ and polarizability matrixes $\alpha_{\alpha\beta}$ with respect to the major axes of the isolated molecule have been calculated. For the calculation of dielectric anisotropy of nematics the knowledge of the order parameter is necessary. Using Maier-Saupe order parameters can be a poor approximation (depends on the size and shape of the molecules). We have proposed a different procedure[1]. The complex dielectric permittivity of our sample was measured over 11 decades of frequency from 10^{-2}Hz to 10^{9}Hz. For this purpose impedance analyser HP 4191A and a frequency response analyser Schlumberger 1260 were used. The measurements were done at Departamento de Fisica Aplicada II, Facultad de Ciencias, Universidad del Pais Vasco in Bilbao[2]. The chemical formula and the phase sequence of the investigated compound on cooling is as follows[2]:



I-[69.9°C]-N*-[65.3°C]-SmA-[33.0°C]-SmC*-[-31.2°C]-glass(SmC*), and the space-filling model of the molecule is presented in Figure 1.

FIGURE 1 The space-filling model of the investigated molecule. See Color Plate X at the back of this issue.

THEORY

The dielectric behaviour of liquid crystals reflects the collective response of mesogens and their molecular properties through a coupling between the macroscopic polarization and the internal electric field. So, the molecular description of the dielectric properties of liquid crystal phases requires the specification of the internal electric field in anisotropic media that is difficult. The electric permittivity ε determines the polarization in a material by an electric field. However, if the applied internal electric field is alternating, then the electric permittivity is frequency dependent $\varepsilon(\omega)$. In general, any time-dependent response may not be in-phase with the applied field. Thus to describe the frequency-dependent dielectric response of liquid crystal, the complex notation must be used[3]:

$$\varepsilon^{*}(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega) \tag{1}$$

where ε' (real) measures the in-phase response, and ε'' (imaginary) measures the out-of-phase response. The effective response of a molecule to an alternating field of frequency ω, assuming a single molecular dipole relaxation, can be described through the complex permittivity as:

$$\varepsilon^*(\omega)-1=(1+i\omega\tau)^{-1}\frac{N\mu_d^2}{3\varepsilon_0 k_B T} \tag{2}$$

where τ is the relaxation time for dipole reorientation in an electric field, N is the number density, ε_0 is the dielectric permittivity of vacuum, T is the temperature and k_B is the Boltzman constant. The molecular dipole moment μ_d is given by[4]

$$\mu_{d\lambda}=\mu_\lambda\cdot\left(1-\frac{1}{\varepsilon_0}N\cdot\alpha_\lambda\cdot\Omega_\lambda^{sh}\right)^{-1}=\mu_\lambda\cdot K_\lambda \quad (\lambda\equiv l,t) \tag{3}$$

where α_λ are polarizabilities parallel ($\lambda\equiv l$) and perpendicular ($\lambda\equiv t$) to the long molecular axis and Ω_λ^{sh} are shape factors depending on the molecular shape only.

If the variable $\omega\tau$ is eliminated from Equation 2, one obtains the representation of the real and imaginary parts of the electric permittivity known as a Cole-Cole plot. When the Cole-Cole plot is a semicircle arc Debye's theory of dipole relaxation assumes that rotational motion can be described in terms of a single relaxation time – so called Debye process. Due to anisotropic properties of a liquid crystal system, several reorientational processes can be observed. Fluctuations in the local structure of a molecule or its environment may result in a distribution of relaxation times. One can assume that the relaxation processes contribute additively to the permittivity so that the complex permittivity can be written[3]:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \sum_j \frac{(\varepsilon_s - \varepsilon_\infty)_j}{1 + i\omega\tau_j} \tag{4}$$

where (ε_s - ε_∞) is a weighting factor (an amplitude) for each Debye relaxation process with $\varepsilon_s = \varepsilon(\omega = 0)$ and $\varepsilon_\infty = \varepsilon(\omega = \infty)$. Above approach to the frequency dependent permittivity has been based on the Debye rotational diffusion model. However, the understanding of any relaxation process requires the knowledge of the correlation function of the time-dependent variables associated with the process. The correlation function approach does not simplify the analysis. It is useful, because experimental correlation functions can be compared with the theoretical one. Using Kubo's linear theory, it has been shown[3] that the relation between the dielectric spectrum and the motions of the molecular dipoles can be written as

$$\frac{(\varepsilon^*(\omega) - \varepsilon_\infty)}{(\varepsilon_s - \varepsilon_\infty)} \cdot F(\varepsilon^*(\omega), \varepsilon_s, \varepsilon_\infty) = 1 - i\omega \int_0^\infty C(t) e^{i\omega t} dt \tag{5}$$

where $C(t)$ is the dipole moment time correlation function. The function F can be often approximated by 1, and in a first approximation the cross correlation terms in $C(t)$ can be ignored. Thus $C(t)$ is defined by:

$$C(t)=\frac{\langle\mu_d(0)\mu_d(t)\rangle}{\langle\mu_d^2(0)\rangle}. \tag{6}$$

In an orientationally ordered fluid the electric permittivity becomes a second rank tensor $\varepsilon_{\alpha\beta}$. Thus the number of independent components of the permittivity tensor will depend on the symmetry of liquid crystal phase. For uniaxial liquid crystal phases of symmetry $D_{\infty h}$ such as nematic, a unique symmetry axis can be defined, parallel to the director. Thus, there are only two independent components of $\varepsilon_{\alpha\beta}$: parallel ($\varepsilon_{||}$) and perpendicular ($\varepsilon_{\perp}$) to the symmetry axis. For a uniaxial molecule with two independent moments of inertia in nematic potential Araki et al.[5] deduced a formula for the correlation functions, independent of any assumed model for reorientation:

$$C_{||}(t)=\frac{1}{3\langle\mu_d^2\rangle_{||}}\left[\langle\mu_d^2\rangle_l(1+2S)\Phi_{00}(t)+\langle\mu_d^2\rangle_t(1-S)\Phi_{01}(t)\right] \tag{7a}$$

$$C_{\perp}(t)=\frac{1}{3\langle\mu_d^2\rangle_{\perp}}\left[\langle\mu_d^2\rangle_l(1-S)\Phi_{10}(t)+\langle\mu_d^2\rangle_t\left(1+\frac{S}{2}\right)\Phi_{11}(t)\right] \tag{7b}$$

where $(\mu_d)_l$ and $(\mu_d)_t$ are longitudinal and transverse components of the molecular dipole respectively (given by Equation 3), modified into anisotropic form by Bordewijk's internal field factor[4]. $\Phi_{ij}(t)$ are functions expressing the four relaxation modes involving the motion of the molecular axes (longitudinal and transverse) in Euler space. Each components of $\varepsilon_{\alpha\beta}$ (parallel ($\varepsilon_{||}$) and perpendicular ($\varepsilon_{\perp}$)) contains two contributions from the molecular dipole moment, and each can have different relaxation time. For the model of small-step rotational diffusion, Nordio et al.[6] have shown by solving the Smoluchowski diffusion equation that $\Phi_{ij}(t)$ can be written in terms of a single relaxation time[7] $\Phi_{ij}(t)=\exp\left(-\frac{t}{\tau_{ij}}\right)$. Thus, $\Phi_{00}(t)$ is related to the reorientations around the short molecular axis, $\Phi_{01}(t)$ is connected with pure reorientational movements about the long axis of the deflected molecule, $\Phi_{10}(t)$ is related to a stochastic precessional movement of the long molecular axis about the director and the last $\Phi_{11}(t)$ originates from the rotation about the long axis of the precessing molecule.

By taking the one-sided Fourier transform of the dipole correlation functions, we obtain for the nematic phase

$$\left(\varepsilon^*(\omega)-\varepsilon_\infty\right)_{||}=\frac{G_{00}}{1+\omega\tau_{00}}+\frac{G_{01}}{1+\omega\tau_{01}} \tag{8a}$$

$$\left(\varepsilon^*(\omega)-\varepsilon_\infty\right)_{\perp}=\frac{G_{10}}{1+\omega\tau_{10}}+\frac{G_{11}}{1+\omega\tau_{11}} \tag{8b}$$

with

$$G_{00}=\frac{\left(\mu_d^2\right)_l(1+2S)(\varepsilon_s-\varepsilon_\infty)_{||}}{\left(\mu_d^2\right)_l(1+2S)+\left(\mu_d^2\right)_t(1-S)} \tag{9a}$$

$$G_{01}=\frac{\left(\mu_d^2\right)_t(1-S)(\varepsilon_s-\varepsilon_\infty)_{||}}{\left(\mu_d^2\right)_l(1+2S)+\left(\mu_d^2\right)_t(1-S)} \tag{9b}$$

$$G_{10}=\frac{\left(\mu_d^2\right)_l(1-S)(\varepsilon_s-\varepsilon_\infty)_{\perp}}{\left(\mu_d^2\right)_l(1-S)+\left(\mu_d^2\right)_t\left(1+\frac{S}{2}\right)} \tag{9c}$$

$$G_{11}=\frac{\left(\mu_d^2\right)_t\left(1+\frac{S}{2}\right)\left(\varepsilon_s-\varepsilon_\infty\right)_\perp}{\left(\mu_d^2\right)_l(1-S)+\left(\mu_d^2\right)_t\left(1+\frac{S}{2}\right)} \tag{9d}$$

Another way to estimate the amplitudes of the four relaxation modes is to apply the following procedure. If frequencies of four modes - (00), (01), (10), (11) – are well-separated, the Debye equations can be applied separately to each term. Using the Bordewijk-de Jeu equation [4]

$$\left(\varepsilon_s-\varepsilon_\infty\right)_\lambda=\frac{N}{\varepsilon_0 k_B T}g_\lambda\frac{1}{K_{\varepsilon\lambda}}\left(\mu_d^2\right)_\lambda \qquad \lambda\equiv\,||,\perp \tag{10}$$

and[8]

$$\left(\mu_d^2\right)_{||}=\frac{1}{3}\left[\left(\mu_d^2\right)_l(1+2S)+\left(\mu_d^2\right)_t(1-S)\right] \tag{11a}$$

$$\left(\mu_d^2\right)_\perp=\frac{1}{3}\left[\left(\mu_d^2\right)_l(1-S)+\left(\mu_d^2\right)_t\left(1+\frac{S}{2}\right)\right] \tag{11b}$$

one obtains:

$$\left[\left(\varepsilon_s-\varepsilon_{\infty1}\right)+\left(\varepsilon_{\infty1}-\varepsilon_\infty\right)\right]_{||}=\frac{N}{3\varepsilon_0 k_B T}\frac{g_{||}}{K_{\varepsilon_{||}}}\left[\left(\mu_d^2\right)_l(1+2S)+\left(\mu_d^2\right)_t(1-S)\right] \tag{12a}$$

$$\left[\left(\varepsilon_s-\varepsilon_{\infty1}\right)+\left(\varepsilon_{\infty1}-\varepsilon_\infty\right)\right]_\perp=\frac{N}{3\varepsilon_0 k_B T}\frac{g_\perp}{K_{\varepsilon\perp}}\left[\left(\mu_d^2\right)_l(1-S)+\left(\mu_d^2\right)_t\left(1+\frac{S}{2}\right)\right] \tag{12b}$$

where g_λ is the Fröhlich-Kirkwood dipole correlation factor. $K_{\varepsilon\lambda}$ is an internal field tensor given by

$$K_{\varepsilon\lambda} = \frac{\varepsilon_{s\lambda} + \left(\varepsilon_{\infty\lambda} - \varepsilon_{s\lambda}\right)\Omega_\lambda^\varepsilon}{\varepsilon_{s\lambda}} \tag{13}$$

where $\Omega_\lambda^\varepsilon$ is the shape factor accounting for the depolarisation field, depending on both the dielectric anisotropy and the molecular shape.

Assuming that τ_{ij} $(i,j = 0,1)$ and $\tau_{n\lambda}$ $(n=1,2\ ,\ \lambda=||,\perp)$ can be identified, one gets:

$$\text{for } \tau_{00} = \tau_{1||} \Rightarrow \left(\varepsilon_s - \varepsilon_{\infty 1}\right)_{||} = \frac{N}{\varepsilon_0 k_B T} g_{||} \frac{1}{K_{\varepsilon_{||}}} \cdot \frac{1}{3}\left[\left(\mu_d^2\right)_l \left(1 + 2S\right)\right] \tag{14a}$$

$$\text{for } \tau_{01} = \tau_{2||} \Rightarrow \left(\varepsilon_{\infty 1} - \varepsilon_\infty\right)_{||} = \frac{N}{\varepsilon_0 k_B T} g_{||} \frac{1}{K_{\varepsilon_{||}}} \cdot \frac{1}{3}\left[\left(\mu_d^2\right)_l \left(1 - S\right)\right] \tag{14b}$$

$$\text{for } \tau_{10} = \tau_{1\perp} \Rightarrow \left(\varepsilon_s - \varepsilon_{\infty 1}\right)_{\perp} = \frac{N}{\varepsilon_0 k_B T} g_{\perp} \frac{1}{K_{\varepsilon\perp}} \cdot \frac{1}{3}\left[\left(\mu_d^2\right)_l \left(1 - S\right)\right] \tag{14c}$$

$$\text{for } \tau_{11} = \tau_{2\perp} \Rightarrow \left(\varepsilon_{\infty 1} - \varepsilon_\infty\right)_{\perp} = \frac{N}{\varepsilon_0 k_B T} g_{\perp} \frac{1}{K_{\varepsilon\perp}} \cdot \frac{1}{3}\left[\left(\mu_d^2\right)_l \left(1 + \frac{S}{2}\right)\right] . \tag{14d}$$

These forms of Equations 14a÷d allow one to modify them using for example the Vuks internal field factor[9].

RESULTS AND DISCUSSION

The amplitudes of the two relaxation modes were calculated according to Equations 9c÷d and Equations 14c÷d and compared with experimental data for one temperature in the isotropic phase and one in the nematic phase. Experimental constraints made that only two modes were observed ($\Phi_{10}(t)$ and $\Phi_{11}(t)$) for the perpendicular direction[2].

The length and the breadth of the molecule, necessary to calculate the factors, were calculated for the isolated molecule, using the quantum chemical program MOPAC/7, with the AM1 Hamiltonian. The shape of the molecule was optimised. The conformation with the lowest energy had been searched. The length and the breadth were estimated (including the van der Waals radii of the hydrogens) to be 36Å and 8Å respectively. However, one should consider that sometimes the molecules are more stretched than calculated, because the environment has certain steric effect on the conformation. The value of the order parameter S was estimated from the procedure proposed by Demus and Inukai[10]. By a simple calculation one can obtain the order parameter for every temperature knowing the clearing temperature of the compound. The order parameter value was S=0.4 at t=67°C (nematic phase). The total dipole moment value obtained by MOPAC was μ=4.37D. The angles with respect to the main axes were calculated as well. To get reliable data of a dipole moment and polarizabilities the results obtained by MOPAC were further treated, in order to diagonalize them with respect to the axes of inertia, and with respect to the main polarizability. The calculated polarizibility values were diagonalize too.

We found that using the calculated dipoles, the calculated dielectric constants are too large. So, one should use effective μ_{eff} dipoles

$$\mu^2_{eff\lambda} = g_\lambda \cdot \mu^2_{d\lambda} \qquad (\lambda = \parallel, \perp) \tag{15}$$

where g is the Fröhlich-Kirkwood dipole correlation factor. There is no theoretical approach to the g factor. The only one equation presented by Dunmur and Palffy-Muhoray was criticised by Demus and Inukai[10]. However, when experimental data are available, one can estimate the g factor from Equation 12 for both, the isotropic and nematic phases or for the isotropic phase from Fröhlich-Kirkwood equation. In Table 1 we have compiled the results of calculations of the g factors.

TABLE 1 The dipole correlation factors g for the isotropic and nematic phases.

phase	*ISOTROPIC*		*NEMATIC*
g	0.60_{BJ}	0.54_{KF}	0.19_{BJ}

BJ - Bordewijk-de Jeu dipole correlation factor (Equation 12),
FK - Fröhlich-Kirkwood dipole correlation factor (FK Equation).

In order to elucidate the role of the data obtained from Equations 12a÷b, we have calculated the molecular shape factor K_λ ($\lambda=l,t$) according to Equation 3 for the isotropic phase for the calculated polarizability $\alpha_{ISO}=5.944\cdot 10^{-39}[\mathrm{Fm}^2]$. We got

$$K_l = 1.07 \quad , \quad K_t = 1.51 \tag{16}$$

For the nematic phase and for $\alpha_l=5.06\cdot 10^{-39}[\mathrm{Fm}^2]$ and $\alpha_t=10\cdot 10^{-39}[\mathrm{Fm}^2]$ we got K_λ ($\lambda=l,t$)

$$K_l = 1.06 \quad , \quad K_t = 2.40 \tag{17}$$

The internal field K_ε tensors calculated according to Equation 13 for the isotropic and nematic phases are, respectively

$$K_{\varepsilon ISO} = 0.83 \quad , \quad K_{\varepsilon\perp} = 0.87 \tag{18}$$

Using above data and Equations 9 and 14 we have calculated the dielectric relaxation amplitudes. The results of our calculations are gathered in Table 2.

As one can see the Nordio-Rigatti-Segre theory is the useful model which can be used for quantitative and qualitative analysis of the dielectric spectra for liquid crystals in the nematic and isotropic phases. This model suggests the clear physical interpretation of the molecular relaxation modes, which are active in a dielectric experiment. From the content of this paper and from Table 2 one can suppose the main process observed in the perpendicular orientation is mainly connected with the reorientation of the molecule as whole around its long axis. The quantitative description is satisfactory. The second process observed for this orientation (much weaker than the first one) is end-over-end rotation seen via longitudinal component of the dipole moment μ_l. The ratio of experimental amplitudes is equal to 0.3, however for calculated amplitudes is 0.1. The quantitative description is less satisfactory. It seems that the calculated longitudinal component of the dipole moment μ_l is too small. In the isotropic phase the spectra decomposition procedure allows to estimate the amplitudes of two processes[2]. First one, Debye-like type, is visible via the longitudinal component of the dipole moment μ_l and assigned to the end-over-end rotation. The second one, visible via the transverse component of the dipole moment μ_t is assigned to the reorientation of the molecule

TABLE 2 Theoretical [G_{10}, G_{11} (Equations 9c,d) and $(\varepsilon_s - \varepsilon_{\infty l})_\perp$, $(\varepsilon_{\infty l} - \varepsilon_\infty)_\perp$ (Equations 14c,d)] and experimental values of the dielectric relaxation amplitudes.

	NEMATIC-$\hat{n}\perp\vec{E}$		
	μ in terms of principal axes of inertia	μ in terms of principal axes of polarizability	Experimental (*)
G_{10}	0.15	0.18	0.37 (μ_l)
G_{11}	1.49	1.46	1.27 (μ_t)
$(\varepsilon_s - \varepsilon_{\infty l})_\perp$	0.18	0.15	0.37 (μ_l)
$(\varepsilon_{\infty l} - \varepsilon_\infty)_\perp$	1.46	1.52	1.27 (μ_t)
	ISOTROPIC		
	μ in terms of principal axes of inertia	μ in terms of principal axes of polarizability	Experimental (*)
G_{10}	0.65	0.79	0.72 (μ_l)
G_{11}	1.80	1.66	1.74 (μ_t)
$(\varepsilon_s - \varepsilon_{\infty l})_\perp$	0.82	0.67	0.72 (μ_l)
$(\varepsilon_{\infty l} - \varepsilon_\infty)_\perp$	1.53	1.24	1.74 (μ_t)

(*) From [2]

around long molecular axes. As one can see from Table 2 the agreement of the calculated data with experimental values is satisfactory. Equations 12 a,b show that any theory of molecular dynamics of liquid crystals should include dipole-dipole interactions (see for instance [2]). The results given in Table 1 show that the g_λ factors are less then unity, which means that in both phases the perpendicular components of the dipole moments show a tendency to anti-parallel correlations. Especially in the nematic phase anti-parallel correlations are very strong. However, taking into account that discussed molecules form the ferroelectric phase, the calculated value seems to be reasonably good.

In summary, we propose a method for the calculation of dielectric data for nematic liquid crystals, without the need for experimental data and with sufficient accuracy for quantitative and qualitative analysis of the dielectric spectra.

D.D. is indebted to Chisso Corporation for permanent support.

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