

УДК: 543.544

SOME RESULTS IN THE RESEARCH OF DIELECTRIC PROPERTIES OF LIQUID CRYSTALS. II

Kondrat'yev A.A., Kondrat'yev A.I.

О НЕКОТОРЫХ РЕЗУЛЬТАТАХ ИССЛЕДОВАНИЯ ДИЭЛЕКТРИЧЕСКИХ СВОЙСТВ ЖИДКИХ КРИСТАЛЛОВ II

Кондратьев А.А., Кондратьев А.И.

Liquid crystal research covers a wide array of disciplines. Certain capacitance measurements were taken near the phase transitions of the liquid crystal 8CB. Several measurements were taken at various temperatures to determine the relaxation behavior of the liquid crystal cell and the temperature dependence of the dielectric constant. Unlike investigations involving bulk samples of a liquid crystal, a trapped sample of 5CB produces a non-exponential relaxation process.

Keywords: liquid crystal, dielectric properties, mesophase.

Below we present article II which continue the ideas and results started in article I

Capacitance measurements. Certain capacitance measurements were taken near the phase transitions of the liquid crystal 8CB. These capacitance measurements were investigated in order to obtain an intrinsic knowledge of the dielectric relaxation time and how it was affected by variations of temperature and square wave signal amplitude. Several measurements were taken at various temperatures to determine the relaxation behavior of the liquid crystal cell and the temperature dependence of the dielectric constant. Using a PTC 10 Programmable Temperature Controller, a Tektronix TDS 724A Oscilloscope and an Agilent 20 MHz Function/Arbitrary Waveform Generator connected to the 8CB liquid crystal cell, an RC circuit with an input resistance of 50Ω was completed. Precise analysis characterizing the dielectric properties of liquid crystal over the smectic, nematic, and isotropic phases were performed. A liquid crystal cell containing 4'Octyl-4-cyanobiphenyl (8CB) was encased inside an aluminum block attached to a heating element. The sample temperature was controlled using the PTC 10 temperature controller between 25° C to 43° C

allowing for 1mK precise graduations. The frequency was fixed at 1 kHz and two separate signal amplitudes with 10 mV and 1 V square wave input signals. A non-linear dielectric relaxation was observed between the nematic, smectic, and isotropic phase transitions. Strong temperature dependence between the mesophases was also observed. The data collected was fitted to an exponential decay and the results offered insights into the behavior of the time constant as it underwent phase transitions.

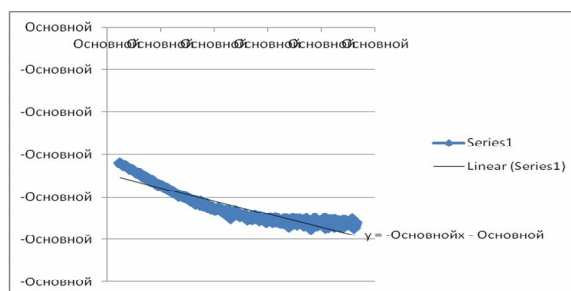


Fig. 4. 32°C with 10 mV amplitude showing a non-linear algorithmic correlation between the capacitance and the time constant

The RC time constant is defined as the time equal to the product of the resistance of the circuit measured in Ohms by the circuit capacitance measured in farads, $T = R * C$. This time is given by how long it takes to charge or discharge the capacitor, through the resistor to 63% of the difference between the initial and final value. Having a dielectric material enclosed between the plates of a capacitor allows one to take capacitance measurements of the dielectric constant of liquid crystal with values of ϵ_{\parallel} when the director is aligned normal to the plates and ϵ_{\perp} when the director is parallel to the

plates. This gives rise to the anisotropic correlation between these two values. [15] In the study by Kohji et al [2], the group examined phase transitions of the 5CB and 8CB liquid crystals through a time resolved fluorescence analysis and dielectric measurement. They found that when the lifetime of the fluorescence is shortened, this can be a signal that a strong first order phase transition will occur. In the experiment, a 5- μm thick cell with transparent electrodes was given a coating of a polyimide film. The cell temperature was stabilized between 60°C and -5°C. Measurement of the dielectric constant occurred while cooling down from the isotropic phase, with 400Hz for 5CB and 1 kHz taken through an impedance analyzer. The fluorescence was excited using a laser pulse and the time-resolved measurement utilized a picosecond time-correlated single photon counting method. From this analysis, it was determined that the dielectric constant parallel to the director ϵ_{\parallel} showed an increase when the temperature fell into the nematic phase, while the dielectric constant perpendicular to the director ϵ_{\perp} showed a decrease. It was found that 8CB exhibited a crystalline phase transition into the nematic, with ϵ_{\perp} decreasing further in the smectic phase, although ϵ_{\parallel} also showed a decrease. Furthermore, it was clearly established that the dielectric constant is temperature dependent for both the 5CB and 8CB liquid crystals. [2].

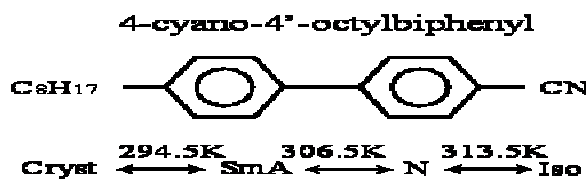


Fig. 5. The phase transitions of 8CB with cooresponding transition temperatures

(TDS) Time domain spectroscopy is used to study the complex permittivity of liquid crystals. Results enable one calculate approximations for the relaxation time distribution functions, this can be used to distinguish between domains. TDS can be used to obtain the complex permittivity of a substance over the frequency range of (100 KHz to 10GHz). Data obtained in the KHz frequency range offer insight on static permittivity. For many LC's, the dielectric relaxation

manifests in the Low Megahertz to Low Gigahertz range.

Basic principles of TDS. Composition of a TDS system entails a fast rising tunnel-diode pulse generator, a wide-band sampling oscilloscope, and a data acquisition system. Different pulses can be administered such as a step voltage pulse produced by the generator through a coaxial cable to the dielectric, with part of the signal being reflected. With TDS results obtained over the time domain, a more thorough experimental observation can be taken over the frequency domain. This is related to the Fourier transforms $R(j\omega) V_o(j\omega)$ of the reflected voltage to the incident voltage such that [5] $R(j\omega) = \rho^* V_o(j\omega)$. ρ^* being the complex reflection coefficient and the relation to the complex permittivity

$$\rho^* = \frac{1 - \epsilon^{*1/2}}{1 + \epsilon^{*1/2}}$$

in which $\epsilon^* = \epsilon' - j\epsilon''$ and

The Fourier transforms are necessarily in order to analyze the complex dielectric permittivity in the frequency range. In this case, dielectric measurements can be taken along the coaxial cable with the sample cell being the termination of the line. [10]

The study of the intrinsic properties of dielectrics requires the use of a broad frequency range in order to characterize the dielectric permittivity, although no one technique can effectively do this for the entire frequency range. This dielectric spectroscopy method covers a wide range of characteristic times. What makes this technique attractive is the way it investigates intermolecular interactions by providing a link between the structural properties and the dynamics of the complex material. Use of this technique has expanded investigations of relaxation parameters to include macroscopic, mesoscopic, and microscopic ranges. There are different ways in which most dielectric measurements are taken. These include measuring the dielectric properties through impedance or admittance. In this case, the measuring cell is assumed to be in parallel or in series circuit with a capacitor or resistor. These are also known as Lumped-Impedance Methods and can be used for frequencies in the $10^{-6} \rightarrow 10^7$ Hz and the radio frequency range up to 1GHz. Here, dielectric analyzers perform analysis along with impedance analyzers and spectrum analyzers are used in the higher RF range. [10]

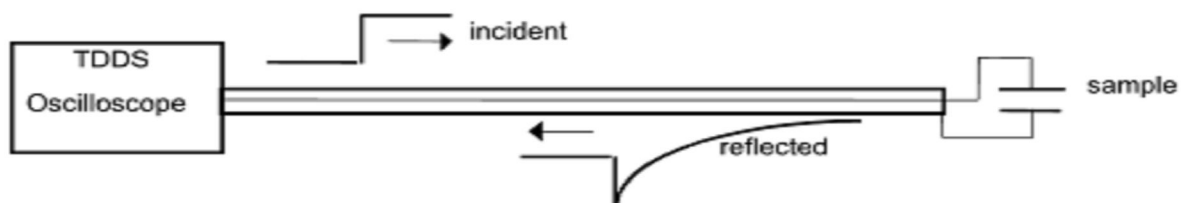


Fig. 6. Basic set up of a TDS system which includes the like coming from the oscilloscope into the sample and being reflected out of the sample

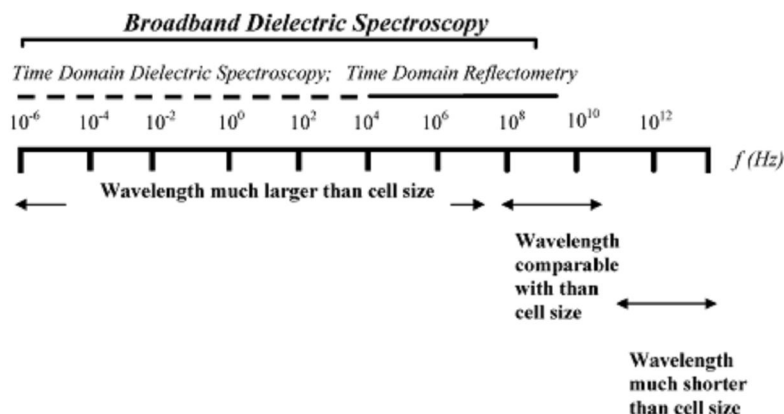
(BDS) broadband dielectric spectroscopy

Fig. 7. The wide frequency spectrum used in BDS

Calorimetry. Calorimetric measurement is used to determine the amount of energy involved in a chemical or physical process when energy is absorbed or discharged in the form of heat. Adiabatic scanning calorimetry (ASC) is an experimental analysis technique which is used to determine the enthalpy and specific heat of the substance while keeping the pressure constant. Constant power is applied to the sample and the temperature of the sample is expressed as a function of time. This technique has certain advantages over DSC experiments since liquid crystal cell is enclosed by a barrier which is kept at the same temperature as the cell. This simple change allows for heat transfer with the surroundings to be eliminated.

DTA (differential thermal analysis). The thermodynamics of materials undergoing various heating and cooling rates can be investigated using this thermal analysis technique. In the procedure, a furnace is heated with a sample cell and a reference material and the difference between the two temperatures is recorded. DTA is used to study phase transitions under different conditions. Measurement devices such as a simultaneous thermal analysis (STA) apparatus are often used in laboratory settings. An advantage that DTA has over DSC is the ability to take readings of any changes in the samples mass when taking enthalpy measurements.

DSC (differential scanning calorimetry). DSC is a powerful experimental procedure which can be used to detect phase transitions in liquid crystals by measuring the change in enthalpy associated with the transition. Its utilization is used in determining the heat supplied or extracted during a process such as a phase transition. DSC analyzes the difference in the rate of heat flowing to the sample material and a reference material while having the temperature accurately controlled. This technique needs for the mass to be constant during the enthalpy measurements.

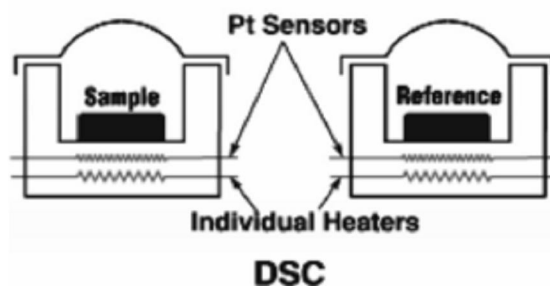


Fig. 8. The DSC setup which includes the sample and the reference sample

Non-Debye Relaxation. Materials that exhibit a single relaxation time constant can be modeled by the Debye relation; however, some liquid crystals such as 8CB do not exhibit Debye relaxation. There are certain director fluctuations which occur in dynamic light scattering experiments of the liquid crystal 5CB. The relaxation behavior in these experiments is characterized as non-Debye in nature. This relaxation behavior can be characterized by a continuous distribution of relaxation times.[3] This correlation can be described as the dynamic tendency of dielectrics in the time domain. This leads to the Havriliak-Negami relationship, which is the standard for the vast array of instances included in the dielectric spectrum. This is given by

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{[1 + (i\omega\tau_m)^{\alpha}]^{\beta}}, \quad 0 \leq \alpha, \beta \leq 1$$

During experimental studies of the dielectric relaxation of a confined liquid crystal, characteristic non-Debye relaxation behavior occurred at the molecular level. Dielectric spectroscopy examines how the relaxation behavior is induced due to the molecules change of position around the short axis. [6]

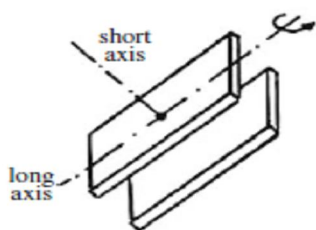


Fig. 9: Representation of the short axis and the long axis

In the study by Aliev [3], the liquid crystal 5CB was trapped in silica glass and the dielectric properties were analyzed using a broadband spectrometer and a broad band dielectric convertor. The Havriliak-Negami function was incorporated in order to further assess the nature of the dielectric spectra. Unlike investigations involving bulk samples of a liquid crystal, a trapped sample of 5CB produces a non-exponential relaxation process. This result shows a stark temperature dependent behavior present in the relaxation times. [14]

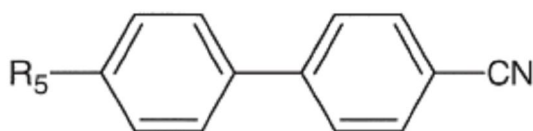


Fig. 10. The molecular structure of 5CB

References

1. Shri Singh - David Dunmur Liquid crystals: fundamentals World Scientific 2002 3-10, 50, 67, 374.
2. Abe, Kohji; Usami, Atsushi; Ishida, Kenji; Fukushima, Yoshiharu; Shigenari, Takeshi Journal of the Korean Physical Society (2005), 46, (1), 220-223.
3. F.M. Aliev "Molecular and collective relaxation in deeply supercooled confined liquid crystal" Journal of Non-Crystalline Solids, 307-310 (2002), p. 489-494.
4. Bulja S, Mirshekar-Syahkal D, James R, Day SE, Fernandez FA "Measurement of Dielectric Properties of Nematic Liquid Crystals at Millimeter Wavelength" IEEE Transactions on Microwave Theory and Techniques (2010) 58, (12) p. 3493 - 3501
5. T.K. Bose R. Chahine M. Merabet J. Thoen "Dielectric study of the liquid crystal compound ocllycyanobiphenyl (8CB) using time domain spectroscopy" J. Physique 45 (1984) 1329-1336
6. Blinov, Lev M. Structure And Properties Of Liquid Crystals Springer Verlag, 2012. p 2, 32, 164-170
7. Zidansek, G. Lahajnar, S. Kralj "Phase transitions in 8CB liquid crystal confined to a controlled-pore glass: Deuteron NMR and small angle X-ray scattering studies" Applied Magnetic Resonance March 2004, Volume 27, Issue 1-2, pp 311-319
8. Kumar S. Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions (Cambridge University Press, Cambridge) 2001. 96-106, 160
9. S. D. Gottke, David D. Brace, Hu Cang, Biman Bagchi, and M. D. Fayer "Liquid crystal dynamics in the isotropic phase" J. Chem. Phys. 116, 360 (2002)

10. Yuri Feldman, Alexander Puzenko, and Yaroslav Rrabov Fractals, Diffusion, and Relaxation in Disordered Complex Systems: Dielectric Relaxation Phenomena in Complex Materials, Advances in Chemical Physics, Part A, Volume 133
11. C. Kittel Introduction to solid state physics John Wiley & Sons – 1996 pp 381-393.
12. C. M. Roland "Characteristic relaxation times and their invariance to thermodynamic conditions" Soft Matter, 2008,4, 2316-2322
13. Grega Klančnik, Jožef Medved, Primož Mrvar "Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) as a method of material investigation" RMZ – Materials and Geoenvironment, Vol. 57, No. 1, pp. 127–142, 2010
14. Iam-Choon Khoo Liquid Crystals Hoboken, N.J: Wiley-Interscience, 2007. pp. 3-12, 23, 32.
15. Ruckmongathan, T. N., Prabhjot Juneja, and A. R. Shashidhara. "A simple technique for measurement of the voltage dependent capacitance." (2006).

Кондратьев А., Кондратьев И. О некоторых результатах исследования диэлектрических свойств жидких кристаллов II.

Исследование жидкого кристалла охватывает широкий спектр дисциплин. Некоторые измерения емкости были взяты вблизи фазового перехода жидкого 8CB кристалла. Измерения проводились при различных температурах, чтобы определить релаксационное поведение жидкокристаллической ячейки и температурную зависимость диэлектрической проницаемости. В отличие от исследований с участием объемных образцов жидкого кристалла, указанный образец 5CB производит неэкспоненциальный процесс релаксации.

Ключевые слова: жидкий кристалл, диэлектрические свойства, мезофаза.

Кондрат'єв А., Кондрат'єв І. О деяких результатах дослідження діелектричних властивостей рідких кристалів II.

Дослідження рідкого кристалла охоплює широкий спектр дисциплін. Деякі вимірювання ємності були взяті у районі фазового переходу рідкого 8CB кристалла. Виміри проводилися при різних температурах, щоб визначити релаксацийну поведінку жидкокристаллической осередку і температурну залежність діелектричної проникності. На відміну від досліджень за участю об'ємних зразків рідкого кристалла, вказаний зразок 5CB виробляє неекспоненціальний процес релаксації.

Ключові слова: рідкий кристал, діелектричні властивості, мезофаза.

Кондратьев Андрей Иванович – д.т.н., проф., профессор университета Пенсаколы США.

Кондратьев Андрей Андреевич – д.т.н., проф., профессор университета Пенсаколы США

Рецензент: **Коробецький Ю.П.**, д.т.н., проф. СЧУ ім. В. Даля.