Dielectric Studies of Tetraethylene Glycol−Bis(3-methylimidazolium) Dichloride (TEGDC) Exhibiting Large Negative Dielectric Anisotropy

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A dielectric anisotropy property of a TEGDC (tetraethylene glycol−bis(3-methylimidazolium) dichloride) is investigated as a function of frequency. TEGDC showed an extremely large negative dielectric anisotropy (−10.95 to −4753.73). Variation of dielectric anisotropy ($\Delta\epsilon$) with respect to the spot frequencies reveals that liquid crystal (LC) orientation has an n-type property at low frequencies and as the frequency increases dielectric anisotropy character shifts from negative dielectric anisotropy type (n-type) to positive dielectric anisotropy type (p-type). Consequently, the TEGDC is a liquid crystal with large negative dielectric anisotropy.

Introduction

Over the last 15 years since the isolation of the first free imidazol-2-ylidenes,[1,2] these compounds have attained enormous attention not only as surprisingly stable, isolable reactants[3,4] but also as metal-attached ligands representing a new structure principle for homogeneous catalysts.[5] Moreover, there are many other applications of the metal complexes bearing imidazolidin-2-ylidene ligands such as in the fields of bioinorganic chemistry, medicinal chemistry, and material science.

Dielectric anisotropy ($\Delta\epsilon$) is one of the most important physical properties of liquid crystalline compounds, which in essence determines the lower threshold voltages of liquid crystal displays (LCDs).[6] With the development of multimedia liquid crystal displays (LCDs), a strong demand has been created for new liquid crystalline materials with high clearing temperatures, negative dielectric anisotropy, and low viscosity. Liquid crystal mixtures with a positive dielectric anisotropy are used for most active matrix displays, currently. In contrast, the vertical alignment thin film transistor LCD (VA-TFT LCD) has been introduced, which offers a superior picture quality with a wide viewing angle (160°), high contrast, and video-compatible switching times (<20 ms). This LCD is based on a liquid mixture with negative dielectric anisotropy.[7] The image quality of liquid crystal displays (LCDs) has improved greatly with the development of new LC modes such as the in-plane switching (IPS) mode[8−11] and fringe-field switching (FFS) mode.[12−13] in the FFS mode, the electrooptical characteristics (i.e. light efficiency), driving voltage,[14] and the stability of the voltage-dependent LC dynamics[15] are strongly dependent on the dielectric anisotropy of the LC.

The aim of this study is to obtain liquid crystals exhibiting large negative dielectric anisotropy and investigate the dielectric anisotropy properties of tetraethylene glycol−bis(3-methylimidazolium)dichloride (TEGDC).

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Experimental Section

^{1}H NMR spectra were measured on a Brunker 400 MHz spectrometer. The reported chemical shifts are against TMS. Microanalyses (C, H, and N) were carried out with CHNS-932 (LECO) elemental analyzer. All organic solvents used were of puriss quality from Fluka and J. T. Baker. Teraethylene glycol, $SOCl_2$, and 1-methylimidazole were purchased from Aldrich. 1,11-Dichloro-3,6,9-trioxoundecane was synthesized using a literature procedure.[16]

Synthesis of 1,11-Dichloro-3,6,9-trioxoundecane. A mixture of 215 g (1.1 mol) of tetraethylene glycol, 1000 mL of toluene, and 193 g (2.45 mol) of pyridine was heated to 110 °C (reflux), and 290 g (2.45 mol) thionyl chloride was added dropwise with stirring in 3 h. During this period the reflux temperature of the mixture dropped from 110 to 80 °C, and a white precipitate was formed. Heating was continued overnight (16 h), and after cooling, 25 mL of concentrated hydrochloric acid diluted with 100 mL of water was added dropwise in about 10 min. The yellow colored upper phase, which contains the product, is separated from the lower phase, with black color, containing pyridinium chloride, which was thrown away. The raw product was obtained upon discarding toluene in an evaporator. To obtain a purer product the raw product was cleaned by distillation under vacuum (95 °C, 0.4 mmHg). The liquid 1,-11-dichloro-3,6,9-trioxoundecane light yellow in color was obtained (234.5 g, yield 92%). Anal. Calcd for $C_8H_{16}Cl_2O_3$: C, 41.57; H, 6.98. Found: C, 41.35; H, 6.73. ^{1}H NMR ($CDCl_3$; δ, ppm): 3.71 (t, $J = 0.016$ Hz, 4H, ClCH_2CH₂O−), 3.63 (s, 8H, −CH_2CH₂O−), 3.58 (t, $J = 0.015$ Hz, 4H, ClCH₂CH_2O−).
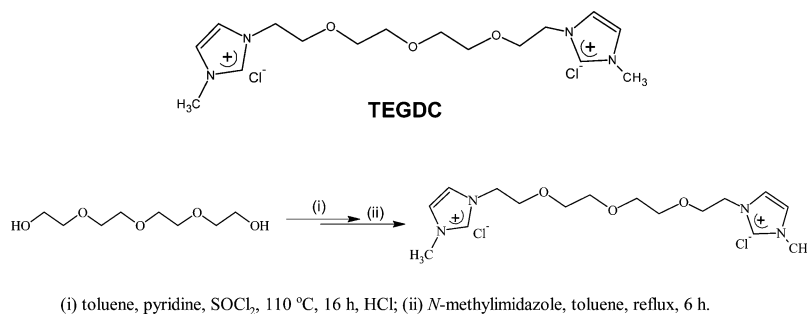
Synthesis of Tetraethylene Glycol−Bis(3-methylimidazolium) Dichloride (TEGDC). A mixture of 5 g (21.6 mmol) of 1,11-dichloro-3,6,9-trioxoundecane, 10 mL of toluene, and 3.45 mL (43.3 mmol) of 1-methylimidazole was heated to 110 °C (reflux) for 12 h. After cooling of the mixture to room temperature, the yellow colored lower phase, which contains the product, was separated from the upper phase and washed a few more times with 5 mL of toluene. After the washing step, the raw product was dissolved in CH_2Cl_2 and filtered. Then the filtrate was evaporated to dryness in a rotary evaporator and a yellowish viscous liquid was obtained at a yield of 93% (7.95

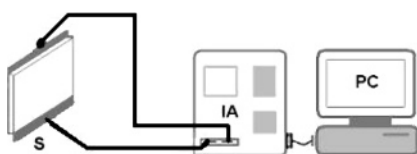TEGDC Exhibiting Negative Dielectric Anisotropy

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TEGDC

(i) toluene, pyridine, $SOCl_2$, 110 °C, 16 h, HCl; (ii) *N*-methylimidazole, toluene, reflux, 6 h.

Figure 1. Chemical structure of TEGDC.

Figure 2. Experimental setup for electrical measurements: S, sample; IA, impedance analyzer.

g). Anal. Calcd for $C_{16}H_{28}Cl_2N_4O_3$: C, 48.61; H, 7.14; N, 14.17. Found: C, 48.52; H, 7.09; N, 14.13. ^{1}H NMR (DMSO; δ, ppm): 9.06 (s, NC*H*N, 2H), 7.65 (d, $J = 0.004$ Hz, 2H, NC*H*CHN), 7.62 (d, $J = 0.004$ Hz, 2H, NCHC*H*N), 4.30 (t, $J = 0.012$ Hz, 4H, NC*H$_2$*CH$_2$O−), 3.81 (s, 6H, *H$_3$*CN−), 3.72 (t, $J = 0.012$ Hz, 4H, NCH$_2$C*H$_2$*O−), 3.48 (q, $J = 0.016$ Hz, 4H, −OC*H$_2$*CH$_2$O−), 3.42 (q, $J = 0.009$ Hz, 4H, −OCH$_2$-C*H$_2$*O−). The chemical structure of the TEGDC is given in Figure 1.

Measurements. Before the construction of the measurement cell, indium tin oxide (ITO) covered glass substrates were spin coated with poly(vinyl alcohol) (PVA) at 2000 rpm and they were cured at 50 °C for 2 h. The thickness of the coating is 100 nm, and these coating layers were exposed to a surface treatment of unidirectional rubbing with velvet to obtain the preliminary molecular orientation. The ultimate form of the constructed cell is planar with 2° rubbing tilt. The measurement cell was made up of two glass slides separated by Mylar sheets having 6.1 μm thickness assembled for parallel alignment. This cell was filled in capillary action with the TEGDC. The final cell gap is 6.2 μm. The experimental setup is shown in Figure 2. The capacitance−voltage measurements were performed by an HP 4194A impedance analyzer with a high accuracy (0.17% typ) at room temperature to determine the dielectric constants of the TEGDC.

Results and Discussion

An example of an anisotropic parameter of liquid crystals is the dielectric constant. The dielectric constant is defined as

$$\epsilon = \epsilon_r \epsilon_o \qquad (1)$$

where $\epsilon_o = 8.854 \times 10^{-12}$ F/m stands for the permittivity in a vacuum and ϵ_r is the relative dielectric constant. This means $\epsilon_r = \epsilon_{||}$ in the direction parallel to the director and $\epsilon_r = \epsilon_\perp$ perpendicular to the director leading to the dielectric anisotropy,[17]

$$\Delta\epsilon = \epsilon_{||} - \epsilon_\perp \qquad (2)$$

When a liquid crystal (LC) is placed in a sufficiently strong electric field, the director tends to align parallel or perpendicular to the electric field. Thus, the LC shows a dielectric anisotropy property. To obtain the dielectric anisotropy value of the LC
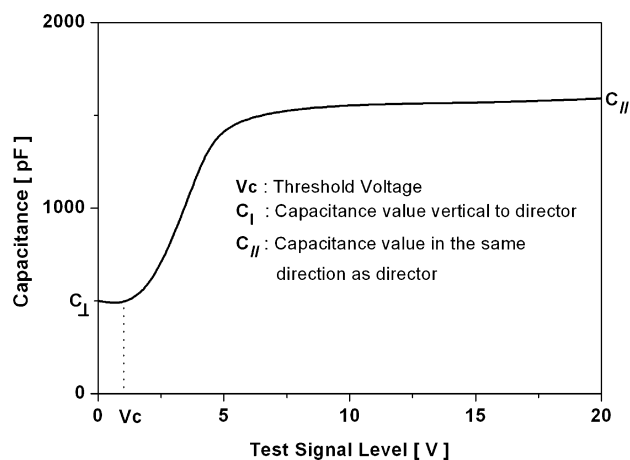
Figure 3. Example graph as to how $C_\perp$ and $C_{||}$ values are calculated for LC.

studied, the capacitance of the liquid crystal cell is measured as a function of applied voltage. Because of the energetic costs of supporting elastic deformations, below a particular voltage, the liquid crystal will not deform. The point where the cost of creating elastic distortion equals the energy cost of the applied field is called the Frederiks transition, V_{th}. At applied voltages lower than V_{th}, the capacitance measured is $C_\perp$ (since the director is perpendicular to the electric field), which gives $\epsilon_\perp$ ($C_\perp = \epsilon_0\epsilon_\perp A/d$) and where A is the cross-sectional area of the LC cell and d is the cell gap. At applied voltages much higher than the Frederiks transition ($V > 3V_{th}$), the capacitance can be plotted as a function of V_{th}/V. By a linear fitting of the data, the intercept ($V_{th}/V = 0$) gives the capacitance $C_{||}$ (i.e., the director is parallel to the electric field), which yields $\epsilon_{||}$.[18−22] An example graph plotted according to the information available in literature as to how $C_\perp$ and $C_{||}$ values are calculated is shown in Figure 3.[18−22] To calculate the $\epsilon_\perp$ and $\epsilon_{||}$ values of the LC studied, we plotted curves of ϵ versus voltage at various spot frequencies, as shown in Figure 4. The dielectric anisotropy $\Delta\epsilon$ values were determined from these figures and are shown in Figure 5. The uncertainty was calculated to be 0.02 for $\epsilon_\perp$ and $\epsilon_{||}$ values. The threshold voltages V_{th} of the Frederiks transition in TEGDC cell at various frequencies were calculated from the Figure 4. The variation of V_{th} values with frequency is shown in Figure 6. As seen in Figure 6, the influence of the frequency clearly revealed a change in the threshold voltage of the Frederiks transition. This is probably due to dielectric anisotropy property of the LC. The TEGDC exhibits extremely large negative $\Delta\epsilon$ values ranging from −4753.73 to −10.95. At low frequency, TEGDC has negative dielectric anisotropy (about −4753.73 at 100 Hz), and it changes into positive at high frequency (0.23 at 1 MHz). As seen in Figure 5, at a certain frequency called the critical frequency, the dielectric anisotropy character shifts from n-type to p-type and the critical frequency for LC was found to be
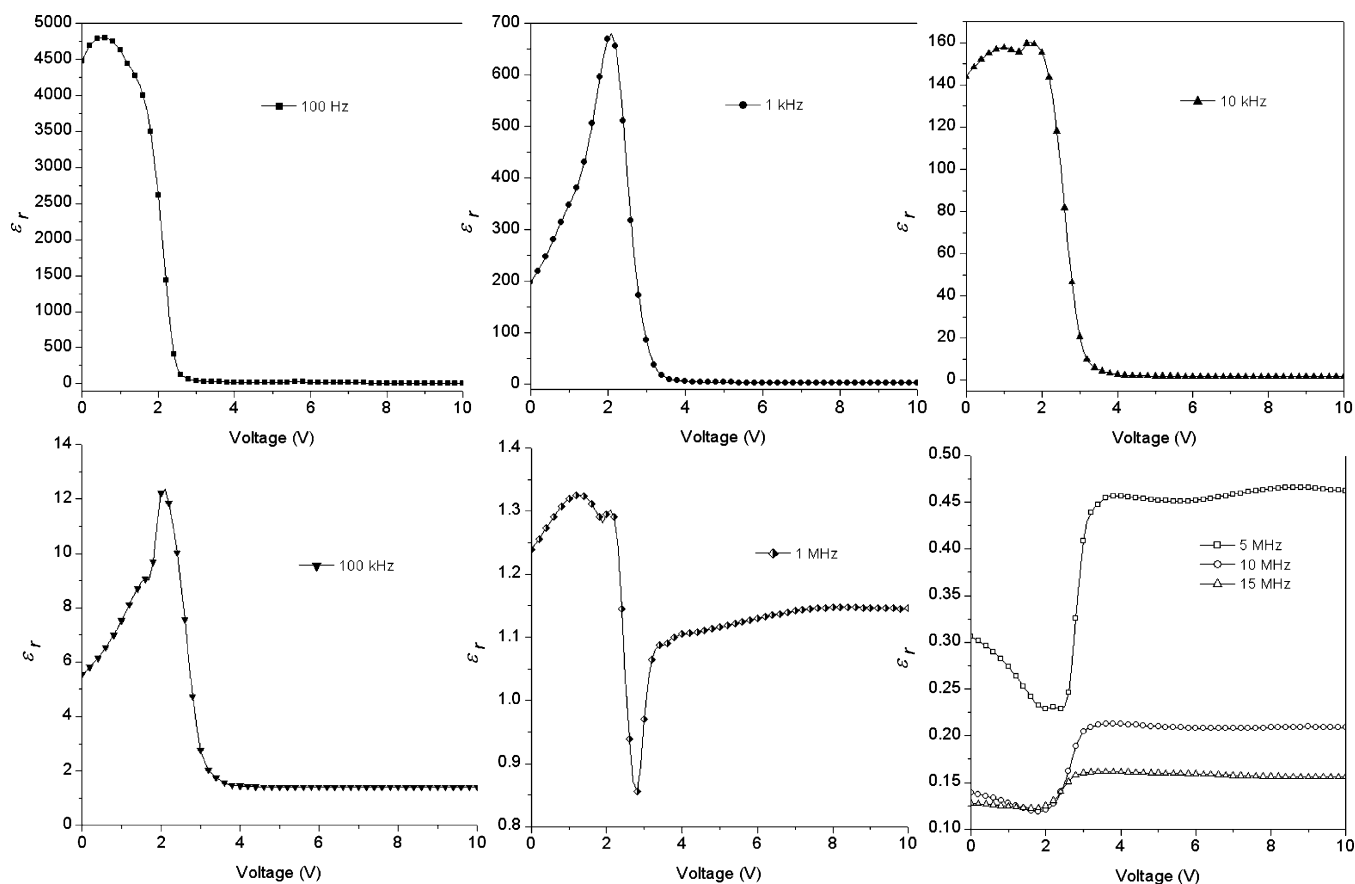
Figure 4. Dependence of real dielectric constant on ac voltage at different frequencies.
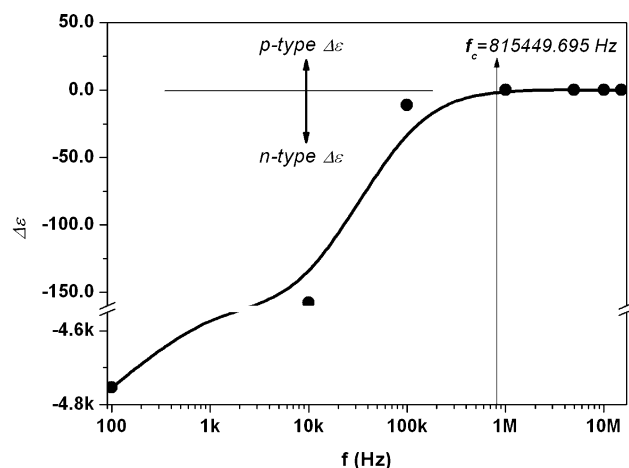

Figure 5. Variation of $\Delta\epsilon$ values with frequency.

Figure 6. Variation of V_{th} values with frequency.

815 449.695 Hz. The tetraethylene glycol−bis(3-methylimida-zolium) dichloride (TEGDC) with $\Delta\epsilon > 0$ is called a positive type; its molecules align with the director parallel to the electric field, whereas, in the negative type TEGDC with $\Delta\epsilon < 0$, they align perpendicular to the field. The electric field which is applied to the TEGDC gives rise to a dielectric torque. This torque tends to orient the director parallel or perpendicular to the electric field, according to the sign of the dielectric anisotropy. When the electric field is strong enough, the molecule will be almost perpendicular to the field. Thus, TEGDC shows an n-type dielectric anisotropy. The complex dielectric constant for LC is expressed as[23−24]

$$\epsilon^* = \epsilon_r + i\epsilon_i \qquad (3)$$

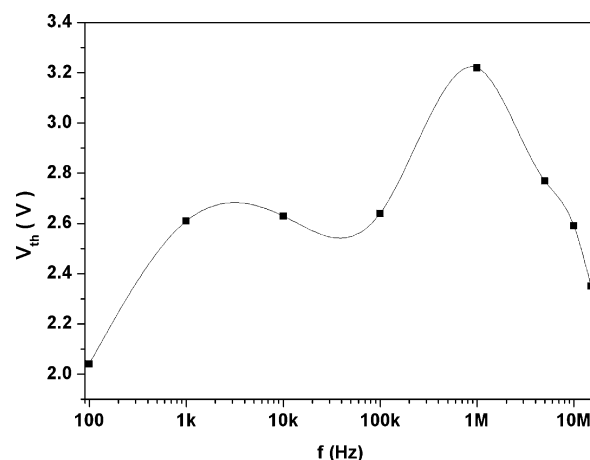where ϵ_r is the real part of the dielectric constant and ϵ_i is the imaginary part of the dielectric constant. At frequencies lower than 1 MHz, the real part of the dielectric constant increases and then decreases with increasing voltages applied and reaches nearly a constant value (see Figure 4). The change in the dielectric constant is probably due to molecular reorientation which starts by applied voltage; i.e, the dielectric constant is dependent on external effects due to the anisotropic nature of LC. The increase in the dielectric constant is probably due to molecular reorientation which starts by applied voltage. It is evaluated that a transition in the dielectric constant takes place due to the molecular reorientation. Figure 7 shows curves of the imaginary part of the dielectric constant at various frequencies. A peak in curves is observed. It is seen that intensity of the peak decreases with increasing frequencies. The imaginary part of the dielectric constant is related to the dielectric loss
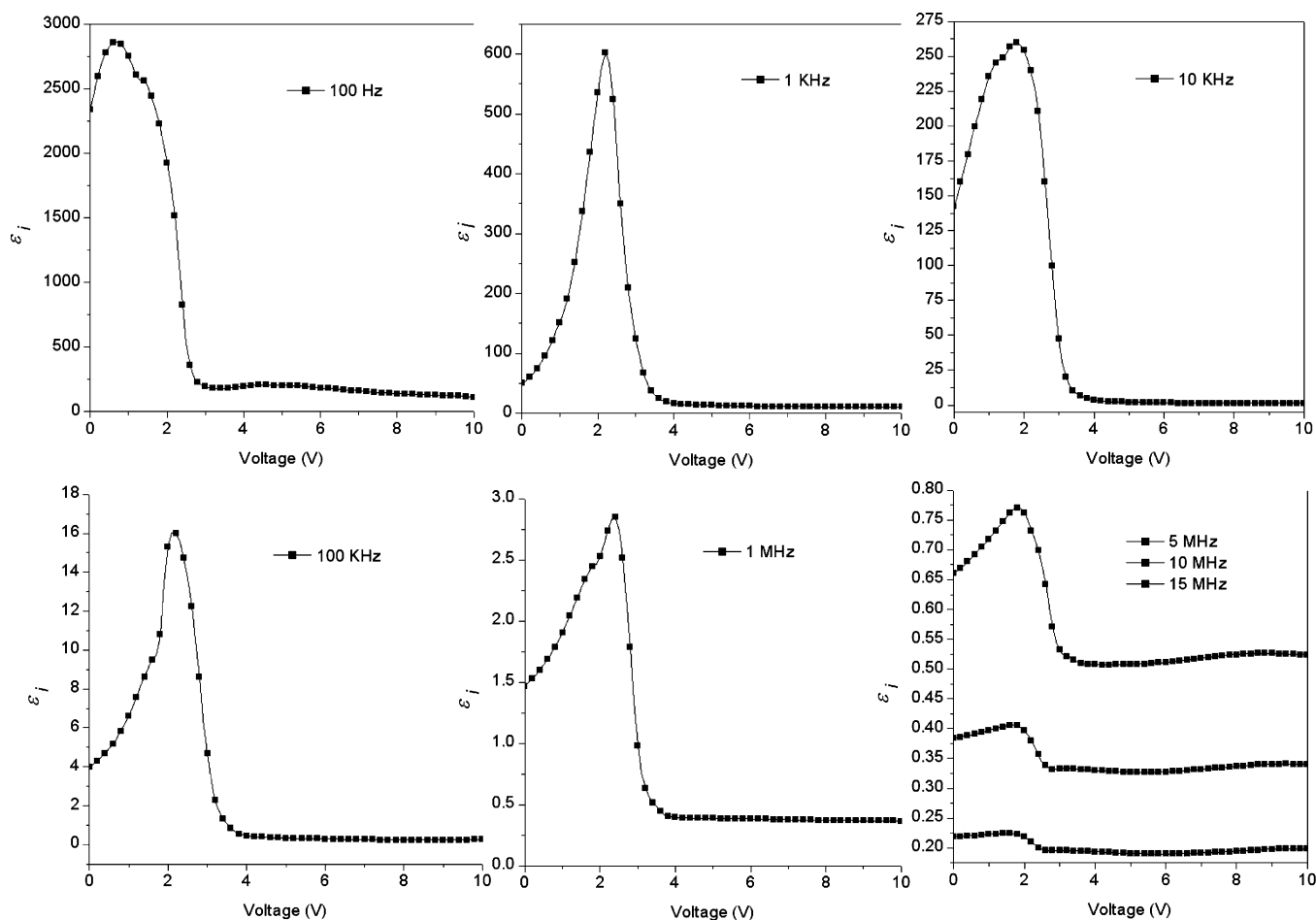
Figure 7. Dependence of imaginary dielectric constant on dc voltage at different frequencies.
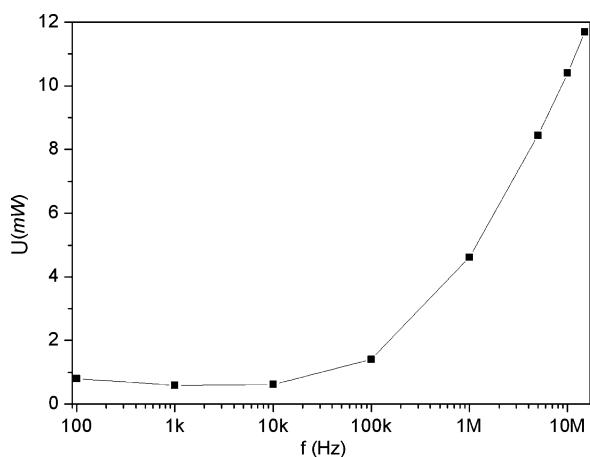

Figure 8. Variation of energy loss with frequency.

which determines the energy loss in alternating current (ac) fields. In ac fields the energy loss/(unit volume/unit time) may be expressed as[25]

$$U = \frac{\omega \epsilon_o E^2}{8\pi} \epsilon_i \qquad (4)$$

where ω is the angular frequency and E is the ac electric field. The U values were calculated from Figure 7. The variation of U values with frequency is shown in Figure 8. As seen in Figure 8, the U values increase with increasing frequencies. This suggests that the frequency of the applied voltage makes easy the orientation of molecules.

Conclusions

The dielectric anisotropy properties of a TEGDC are investigated by the dielectric spectroscopy method. TEGDC showed an extremely large negative dielectric anisotropy value (-10.95 to -4753.73); i.e, the sample is a liquid crystal with a large negative dielectric anisotropy. At a certain frequency called the critical frequency, dielectric anisotropy character shifts from n-type to p-type, and it was found to be 815 449.695 Hz. The dielectric constant of the TEGDC changes with molecular reorientation due to the anisotropic nature of LC. The increase in the dielectric constant of the LC is probably due to molecular reorientation which starts by applied voltage. The threshold voltages of the Frederiks transition in the TEGDC cell at various frequencies were determined. The influence of the frequency clearly revealed a change in the threshold voltage of the Frederiks transition. The energy loss in alternating current (ac) fields is associated with the imaginary part of the dielectric constant of LC. The energy loss values for the LC studied are calculated, and these values increase with increasing frequencies. This suggests that the frequency of the applied voltage makes easy the orientation of molecules. On the other hand, the dielectric anisotropy values of axially oriented cyclohexane derivatives have been found to be from -1.2 to -4.6.[26] The investigated *trans*-4,4′-dialkyl-(1α,1′- bicyclohexyl)-4β-carbonitrile (CCN) compounds exhibit an axial cyano group, which is responsible for the large negative dielectric anisotropy of about -9.[27] A series of liquid crystalline 2,3-bis(trifluoromethyl)phenyl derivatives have showed an extremely large negative dielectric anisotropy (-6.1 to -11.4).[28] Consequently, the

dielectric anisotropy values of TEGDC are higher than that of the liquid crystals mentioned above.

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