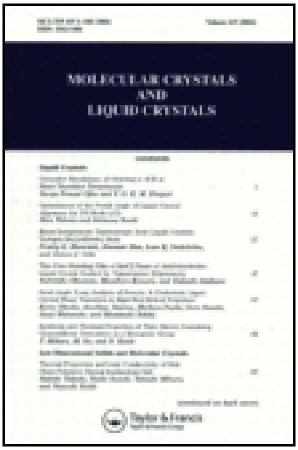

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DIELECTRIC RELAXATION OF NEMATIC LIQUID CRYSTALS WITH DIFFERENT MOLECULAR SHAPES

Hiromoto Sato [a] , Atsushi Sawada [a] , Atsutaka Manabeb [b] & Shohei Naemura [a]

[a] Atsugi Technical Center, Merck Japan Ltd., 4084 Nakatsu, Aikawamachi, Aikou-gun Kanagawa Pref., Japan

[b] Liquid Crystal Research, Business Unit Liquid Crystals, Merck KGaA, Frankfurter Strasse 250 64293, Darmstadt, Germany

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Dielectric Relaxation of Nematic Liquid Crystals with Different Molecular Shapes

HIROMOTO SATO[a], ATSUSHI SAWADA[a], ATSUTAKA MANABE[b]
and SHOHEI NAEMURA[a]

[a]*Atsugi Technical Center, Merck Japan Ltd., 4084 Nakatsu, Aikawamachi, Aikou-gun Kanagawa Pref., Japan and* [b]*Liquid Crystal Research, Business Unit Liquid Crystals, Merck KGaA, Frankfurter Strasse 250 64293 Darmstadt, Germany*

The parallel dielectric constants of several liquid crystal compounds having different core structures and polar substituents have been investigated as a function of frequency and temperature using the dilute solution by an unpolar nematic host mixture. The dielectric relaxation frequencies were found to depend roughly on the molecular length. With regard to the compounds showing a large deviation from the correlation between the relaxation frequency and the molecular length, the disagreement was explained by considering the intermolecular interaction estimated from the molecular structure.

Keywords: nematic liquid crystal; dielectric relaxation; inertia moment; activation energy

INTRODUCTION

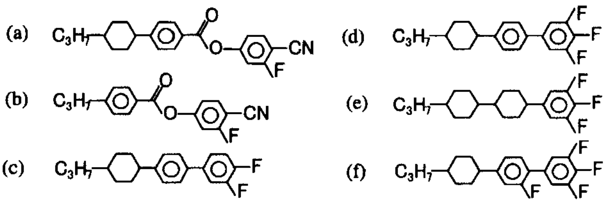
The threshold voltage (Vth) of liquid crystal display (LCD) is determined by the elastic constants and the dielectric anisotropy ($\Delta\varepsilon$) of the liquid crystal (LC) material used in LCDs. Due to a frequency dependence of $\Delta\varepsilon$, Vth varies with frequency and causes the unfavorable problems on the display quality (lowered contrast, cross-talk, etc). But the frequency dependence can also be utilized effectively for particular LCD modes. For instance, the dual frequency driven LC material which shows both positive and negative dielectric anisotropis in different frequency ranges is used for the bistable polymer dispersed liquid crystal (PDLC)[1] display. Therefore it becomes important to control the frequency dependence of the dielectric constants in LC mixture development.

The mechanism of frequency dependence of $\Delta\varepsilon$ is different in the frequency range of applied voltage [2]. In a low frequency range below 100Hz, $\Delta\varepsilon$ is correlated with the LC-resistivity and increases or decreases with frequency due to the behavior of the mobile ions in the LC material. [3] In the frequency range from 1kHz to 10MHz, dielectric relaxation of parallel dielectric constant ($\varepsilon_{||}$) of the molecules contributes the decrease of $\Delta\varepsilon$. The relaxation frequencies of $\varepsilon_{||}$ show different values among components of a LC mixture and it is an important parameter to control the frequency dependence of $\Delta\varepsilon$ of LC mixture. It is possible to roughly estimate the relaxation frequency of $\varepsilon_{||}$ from the molecular length or the inertia moment [4],[5]. However the relaxation frequency of $\varepsilon_{||}$ is affected by the multiple physical properties such as viscosity, order parameter and nematic potential, it is therefore difficult to predict it precisely due to the complicated situation. In case of evaluating the difference of the dielectric relaxation among the molecules by using their solution, the changes of the clearing point (Tni) and the viscosity from solute are not negligible. So in this study, we evaluated the dielectric relaxation of $\varepsilon_{||}$ under the condition of the dilute solution so that the properties of the Tni and the viscosity do not change significantly and studied the relationship between the molecular shape and the relaxation frequency, enabling to predict the relaxation frequency more precisely from the molecular shape.

EXPERIMENTS

TABLE I shows the compounds used in this work. As a solvent, we used ZLI-3086 (Tni=72℃ $\varepsilon_{||}=2.7, \varepsilon_{\perp}=2.7$) that is an unpolar liquid crystal mixture not showing dielectric dispersion as far as the studied range of frequency is concerned. Compound (a) and (b) were added to the solvent in the ratio of 0.5wt% and (c)~(f) were added in the ratio of 1wt%. The shift of Tni from the solvent's by adding the solute was within ±0.5℃. The dielectric constants of solution (a)~(f) were measured as a function of frequency and temperature by an impedance analyzer, Solartron1260+1296, using the parallel plate glass cell coated with a vertical alignment layer on the ITO electrodes. The distance between electrodes was 22μm. The frequency range was from 100Hz to 2MHz and the temperature range was from −20℃ to 10℃. The relaxation frequency was determined by curve fitting utilizing the Debye equation for the experimental result of the frequency dependence of the dielectric constants.

TABLE I The chemical structures of the investigated liquid crystal comounds



RESULTS AND DISCUSSION

FIGURE 1 shows the standardized frequency dependence of $\varepsilon_{\|}$ at -10℃. $\varepsilon_{\|0}$ is the constant value of the dielectric constant at low frequency region below the relaxation and $\varepsilon_{\|\infty}$ is the constant value at high frequency region above the relaxation. Although the properties of each solution (Tni, viscosity) were estimated to be almost the same, the dielectric relaxation can be observed in different frequency ranges.

Comparing the compound (d) and compound (e), the dielectric relaxation frequencies are almost the same and it is found that the phenyl or cyclohexyl ring at the center of the core structure doesn't play a significant role for the relaxation frequency. But by introducing the fluorine atom(s) on the terminal or the center of the core, the shift of the relaxation frequency can be observed. The terminally substituted trifluoro-compounds (compounds (d) and (f)) show a higher relaxation frequency than the difluoro-comound (compound(c)) and by substituting the fluoride on the center part of the core the relaxation frequency becomes even higher (compound (f)).

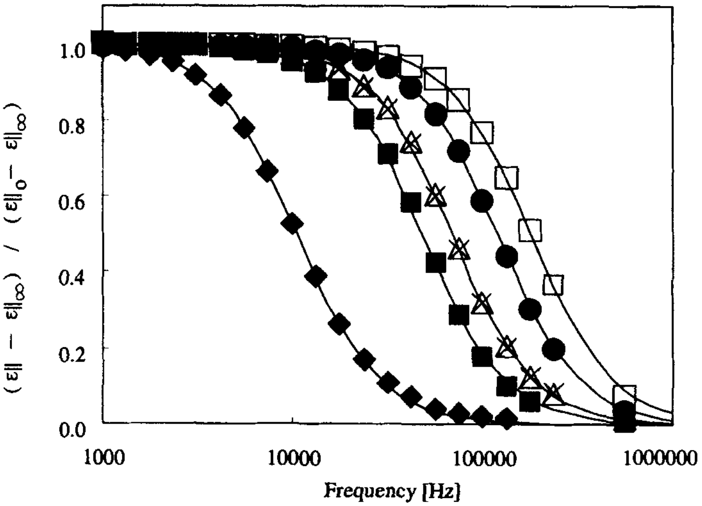


FIGURE 1 Dielectric constant $\varepsilon_{||}$ of dilution as a function of frequency
◆compound(a), □compound(b), ■compound(c)
△compound(d), ×compound(e), ●compound(f)

TABLE II Clearing temperature, relaxation frequency of $\varepsilon_{||}$ and inertia moment

	Dilution of ZLI-3086		10w% in ZLI-3086		
	Tni[℃]	f [×10^5Hz] (T=10℃)	Tni[℃]	f [×10^5Hz] (T=10℃)	I [10^{-43}kg·m^2]
(a)	72.3	0.74	83.0	0.53	1.89
(b)	71.6	8.9	65.5	7.3	0.92
(c)	72.5	2.9	77.9	2.8	1.27
(d)	72.2	4.0	73.8	3.9	1.39
(e)	72.3	3.9	73.9	4.0	1.39
(f)	71.6	5.7	69.4	5.8	1.41

TABLE II shows the dielectric relaxation frequencies of $\varepsilon_{||}$ of the dilution and the 10w% solution of ZLI-3086 at 10℃ and inertia moments which were calculated from the optimized structure by semi-empirical molecular orbital method (SPARTAN, AM1). We have reported that the relaxation frequency tends to decrease with increasing inertia moment.[4](FIGURE 2) Nevertheless the parallel relaxation frequencies among the three-rings compounds (compounds(c)~(f)) show results contrary to the order of the inertia moments. When taking into account only the results of 10w% solution of ZLI-3086, the reason why no correlation was found between the relaxation frequencies and the inertia moments among compounds (c) ~(f) may be considered to be due to the shifts of Tni or the viscosity from the solute. But even in case of using dilution which Tni and viscosity are not so different from the solvent, the same results as that of 10wt% solution were observed with respect to the order of the relaxation frequencies.

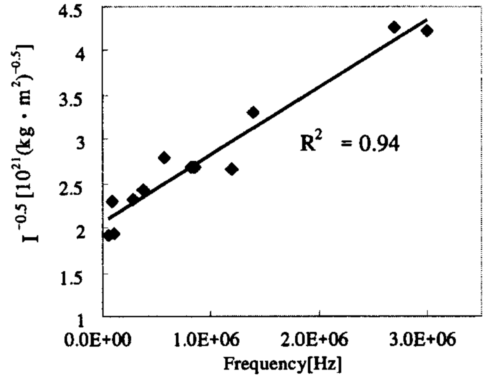


FIGURE2 [4] Correlation between the relaxation frequency of $\varepsilon_{||}$ under the solution by ZLI-3086(15mol%) and inertia moment of molecules

FIGURE 3 shows the temperature dependence of the parallel dielectric relaxation frequencies of $\varepsilon_{||}$ for compounds (a) ~ (f). Good linear relationships have been found between the relaxation frequency of $\varepsilon_{||}$ and the temperature (1/T) (Arrhenius-behavior) in all compounds from −20℃ to 10℃. From the temperature dependence of the relaxation frequencies the activation energies (q) related to the nematic potential and the viscosity [6] were calculated using the following equation.

$$f \propto \exp(-q / k_B T)$$

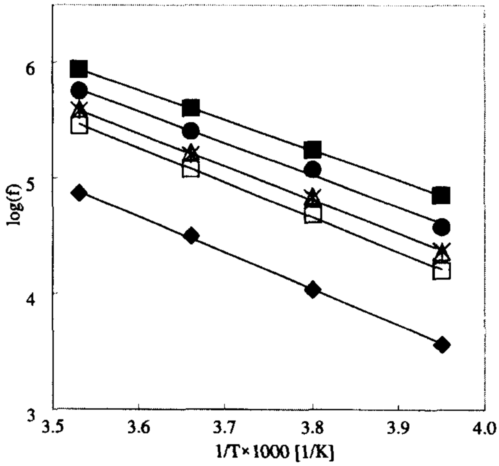


FIGURE 3 Arrhenius plots of the parallel dielectric relaxation frequency of dilution.
◆compound(a), □compound(b), ■compound(c)
△compound(d), ×compound(e), ●compound(f)

FIGURE 4 shows the correlation between the activation energies and the parallel relaxation frequencies at 10℃ for each of compounds. The larger the activation energies, the lower the parallel relaxation frequencies. The activation energy can be interpreted as the energy required to make reorientation of molecule possible and the energy necessary to make the dissociation. [7] Therefore it is considered that the large activation energy represents the large intermolecular interaction around molecules. Similar results about CN-compounds have been reported [8]. TABLE III shows the activation energies and the molecular length, width and the ratio of length-width (L/W) which were estimated from the optimized molecular structure by the AM1 calculation.

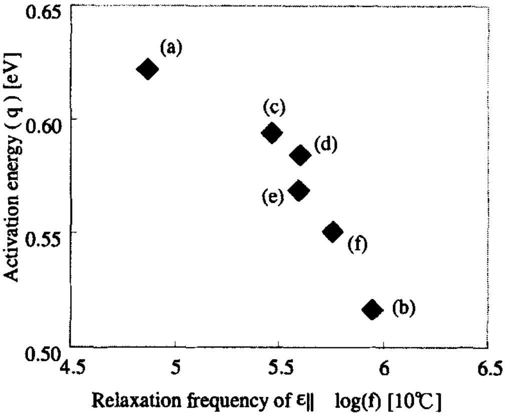


FIGURE 4 Activation energy of dilution *vs.* relaxation frequency of $\varepsilon_{\|}$

Table III Activation energy, molecular length L[Å], width W[Å] and the ratio of length-width L/W

	Activation energy of dilution [eV]	Molecular length L[Å]	Molecular width W[Å]	L / W
(a)	0.62	19.7	6.4	3.1
(b)	0.52	15.8	5.0	3.2
(c)	0.59	16.9	4.8	3.5
(d)	0.58	16.9	5.3	3.2
(e)	0.57	16.8	5.2	3.2
(f)	0.55	16.9	5.4	3.1

The relaxation frequency decreases with the molecular length, but among the three-ring compounds(c)~(f) no correlation have been found between the relaxation frequency and molecular length. But when paying attention to the L/W, a good correlation was found between L/W and the relaxation frequencies among three-ring compounds. The length-width ratio is being used to explain the molecular interaction by repulsive force and the large values of L/W correspond to the increase of the order parameter and the transition entropies related to the nematic potential. [9] Hence by considering the molecular length and L/W together, it would be possible to predict the relaxation frequency of $\varepsilon_{\|}$ more precisely.

CONCLUSION

The difference of the relaxation frequency of $\varepsilon_{\|}$ were observed among the molecules with different shapes under almost the same condition by dilute solution. The relaxation frequencies exhibit a good correlation with the activation energy of molecules. For the molecules whose relaxation frequency of $\varepsilon_{\|}$ could not be explained by molecular length, a good correlation was observed between the relaxation frequency and the length-width ratio affecting to the nematic potential. It would be possible to predict the frequency dependence of $\Delta\varepsilon$ more precisely for polar molecules by considering the length and the length-width ratio together.

Acknowledgments

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