Relaxation Intensity Estimation of the Nematic Mixture-E-24 using KITA-KOIZUMI method

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ABSTRACT
This paper deals with the analysis of the dielectric for nematic mixture E-24 in order to evaluate the relaxation intensity using the method suggested by Kita Koizumi. The relaxation intensity of a commercially important nematic liquid crystal mixture E-24 was calculated using the method suggested by kita and koizumi and the results are reported in this paper. The relaxation intensities as calculated using the Kita Koizumi method are found to be in good agreement with the observed values for the sample, which shows Davidson-Cole type of relaxation. This method can be used as a versatile tool for estimating the relaxation intensity.

1. INTRODUCTION
Normally the materials have been divided into the solid, fluid and the gaseous state. But often in nature, the borders between the different categories are not well defined. Ordinary fluids are isotropic in nature; they appear optically, magnetically and electrically to be the same from any perspective. Although the molecules, which comprise the fluid, are generally anisometric in shape, this anisometry plays little role in anisotropic macroscopic behaviour (aside from viscosity).

Nevertheless, there exists a large class of highly anisometric molecules which gives rise to unusual, fascinating, and potentially technologically relevant behaviour. There are many interesting classes of materials for study, including polymers, micelles, microemulsions, and materials of biological significance, such as DNA and membranes. Although all of them are very interesting materials but we have focused here on liquid crystals. Liquid crystals have the ordering properties of solids but they flow like liquids.

Liquid crystals are materials which have unusual, fascinating and often beautiful properties. Liquid crystals are best known for their use in displays which became common in the early 1980's and are now used extensively in other areas also. Liquid crystal displays (LCDs) can be found in objects as diverse as watches, calculators, information display boards, aeroplane cockpits, laptop computers and mobiles etc. For the successful use of liquid crystals in various devices, need arises for the thorough investigation of dielectric, optical and thermo-dynamical properties.

LIQUID CRYSTAL
The term 'liquid crystal' is both intriguing and confusing; while it appears self-contradictory; the designation really is an attempt to describe a particular state of matter of great importance today, both scientifically and technologically. Thermodynamic phases of condensed matter with a degree of order intermediate between that of the crystalline solid and the simple liquid are called liquid crystals or mesophases. They occur as stable phases for many compounds; in fact one out of approximately two hundred synthesized organic compounds is a liquid crystalline material. The typical liquid crystal is highly anisotropic – in some cases simply an anisotropic liquid, in other cases solid-like in some directions. Liquid-crystal physics, although a field in itself, is often included in the larger area called 'soft condensed matter', including polymers, colloids, and surfactant solutions, all of which are highly deformable materials. This property leads to many unique and exciting phenomena not seen in ordinary condensed phases, and possibilities of novel technological applications. In a crystalline solid, molecules are ordered in both the above ways, i.e. they are constrained to occupy specific sites in a lattice and to point their molecular axes in specific

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directions. On the other hand, molecules in a liquid diffuse randomly throughout the sample without any orientation order. Thus, a crystal has orientation and three-dimensional positional order, whereas a liquid has none (Figure 1).
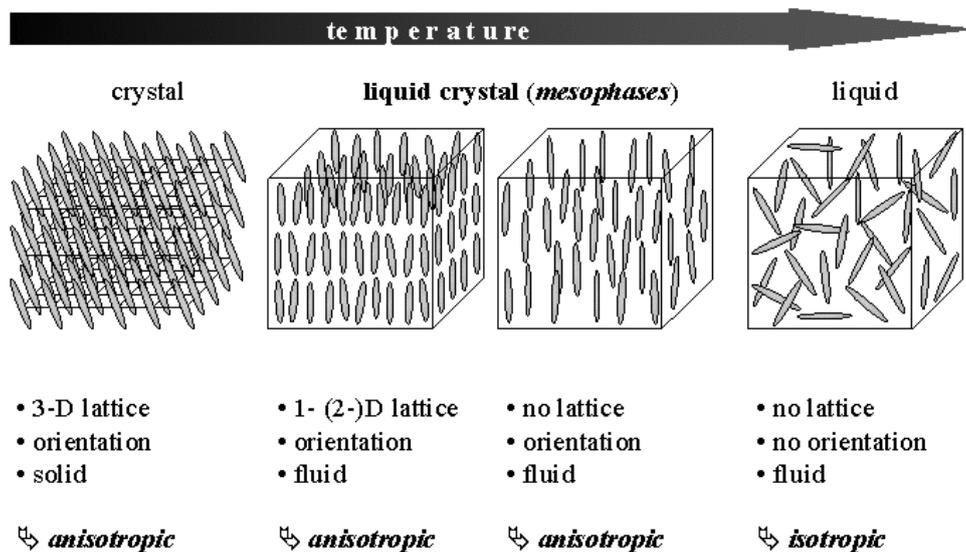

temperature

crystal	liquid crystal (*mesophases*)		liquid
• 3-D lattice	• 1- (2-)D lattice	• no lattice	• no lattice
• orientation	• orientation	• orientation	• no orientation
• solid	• fluid	• fluid	• fluid
⇨ *anisotropic*	⇨ *anisotropic*	⇨ *anisotropic*	⇨ *isotropic*

Figure 1. Solids, liquid crystals and liquids - the molecular picture.

Liquid crystalline phases occur most readily in systems whose molecules have shapes that favour parallel packing. A few representative shapes are shown in figure 2.The dielectric relaxation intensity or the magnitude of dielectric dispersion ($\Delta\varepsilon$) provides valuable information regarding the effective dipole moments associated with the relaxation process and molecular motions of polar molecules [1,2]. The relaxation intensities are easily evaluated from the measurements of the static dielectric constant at low frequency (ε_0) and limiting dielectric constant at very high frequency (ε_∞) for the molecules exhibiting Debye type relaxation [3] with a single relaxation time or a narrow distribution of relaxation times. The Cole-Cole [4] plots of complex permittivity are among the widely used methods for the evaluation of the relaxation intensity. The relaxation intensity may be evaluated by integrating the dielectric loss data over the entire frequency range in case of a broader distribution in relaxation times. However, difficulties arise in the evaluation of the relaxation intensity when dielectric loss data are available in a limited frequency range around the loss maximum. Also, in case of multiple relaxation processes in which two or more loss peaks take place and portions of the loss peaks may overlap with each other in the frequency range of measurements neither the Cole-Cole plots nor the integration of dielectric loss gives good accuracy in estimating the relaxation intensity, unless an appropriate procedure to separate a particular loss peak is established for such cases. Kita and Koizumi [5] have developed an empirical formula based on the evaluation of the area of a triangle which is product
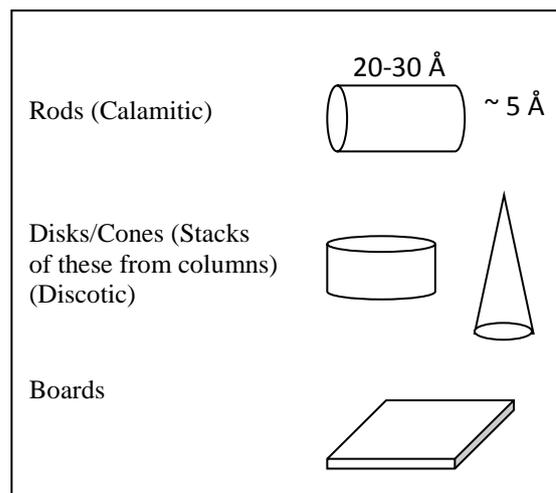

Figure 2. Shape anisotropies of liquid crystalline molecules.

of half width $W_{1/2}$ and the maximum value of the normalized dielectric loss ε_M''. The area remains constant within ±3% with the half width, and roughly estimates the relaxation intensity. In calorimetric loss measurement [6], where the dielectric constants are not available, the method seems to be adequate for the estimation of $\Delta\varepsilon$. Earlier method for estimating the dielectric increment was suggested by Frohlich [13] by considering the loss curve as a trapezoid with sides approximated by tangents at the half width points. This method however does not give very accurate results for $\Delta\varepsilon$. The accuracy of the triangle approximation was examined by Kita and Koizumi [5], Chauhan et al. [7] and Gupta et al. [8, 9] for Cole-Cole [5], Cole-Davidson [10] and Williams-

Watts [11] type of distribution. The maximum error in the evaluation of the relaxation intensity was found to be around ±1%. With a view to investigate further the validity of Kita and Koizumi method for evaluating the relaxation intensities of liquid crystals the data of commercially important nematogen E-24 [12] were analyzed using above method. An excellent agreement between the observed and the calculated values of $\Delta\varepsilon$ has been found. The dielectric relaxation intensity or the magnitude of dielectric dispersion provides information on effective dipole moments associated with relaxation processes and molecular motions of polar molecules. The relaxation intensity $\Delta\varepsilon$ is expressed by the Kramers Kronig [13] relation as

$$\Delta\varepsilon = \frac{2}{\pi}\int_0^\infty \frac{\varepsilon''}{\omega\tau}d(\omega\tau) = S\frac{2}{\pi}\ell n10 = 1.4659S \quad \cdots (1)$$

where ε'' is the dielectric loss, ω the angular frequency, τ the relaxation time and S is the area under ε'' versus log $(\omega\tau)$ curve.

The area $S/\Delta\varepsilon$ under the $\varepsilon\forall/\Delta\varepsilon$ versus $\log(\omega\tau)$ curve can be roughly by the product of half-width $W_{1/2}$ and the maximum value of the normalized dielectric loss, $\varepsilon\forall_M/\Delta\varepsilon$, as shown in Figure 3 for Cole-Cole type of relaxation. The normalized dielectric loss $\varepsilon\forall_M/\Delta\varepsilon$ is expressed by the following equations

$$\left.\begin{array}{ll} \dfrac{\varepsilon''}{\Delta\varepsilon} = \dfrac{\sin(\pi\beta/2)}{2[\cosh\beta y + \cos(\pi\beta/2)]}, & y = \ell n\omega\tau \quad \text{(Cole - Cole)} \\ \\ \dfrac{\varepsilon''}{\Delta\varepsilon} = \cos^\beta\theta\sin\beta\theta; \quad \tan\theta = \omega\tau & \text{(Cole - Davidson)} \\ \\ \dfrac{\varepsilon''}{\Delta\varepsilon} = \sum_{n=1}^\infty \dfrac{(-1)^{n-1}\Gamma(n\beta+1)}{(\omega\tau)^{n\beta}\Gamma(n+1)}\sin(n\beta/2) & \text{(Williams - Watts)} \end{array}\right\}$$

$$(2)$$

where β is the distribution parameter of the relaxation times $(0 < \beta < 1)$ and τ is the characteristic relaxation time in respective type of relaxation and $\Gamma(n\beta + 1)$ is the gamma function. $\beta = 1$ yields the Debye type of relaxation.

Also, we can approximate as

$$\frac{S}{\Delta\varepsilon} \approx C_1 + C_2 W_{1/2} + C_3 W_{1/2}^2 \tag{3}$$

or

$$\Delta\varepsilon = \varepsilon''_M / [(C_1/W_{1/2}) + C_2 + C_3 W_{1/2}] \tag{4}$$

where C_1, C_2 and C_3 are numerical constants whose values are to be determined by the method of least squares. The half-width $W_{1/2}$ can be determined by solving the equation

$$\frac{1}{2}\varepsilon''_M = \varepsilon''(\omega) \tag{5}$$

To evaluate $S_l/\Delta\varepsilon$, the values of $\varepsilon''(\omega)/\Delta\varepsilon$ are calculated at each frequency for a particular value of β and a graph of $\varepsilon''(\omega)/\Delta\varepsilon$ versus log $\omega\tau$ is drawn. The value of normalized dielectric loss

maximum ε_M'' / $\Delta\varepsilon$ evaluated from the plot may also be calculated by the following relation
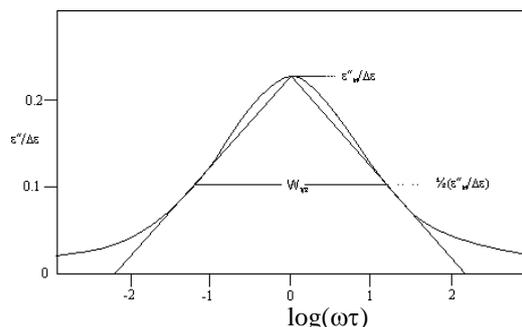

Figure 3. Plots of $\varepsilon 22/\Delta\varepsilon$ versus $\log(\omega\tau)$ for the Cole-Cole relaxation with $\beta = 0.6$ and tringle of the area $W_{1/2}\,\varepsilon_M 22/\Delta\varepsilon$.

$$\frac{\varepsilon_M''}{\Delta\varepsilon} = \cos^\beta\left(\frac{\pi}{2\beta+2}\right)\sin\left(\frac{\beta\pi}{2\beta+2}\right) \tag{6}$$

which comes out to be same as the value obtained from the plot .

Using the Newton−Raphson method this equation has two solutions ω_1 and ω_2. The half width is given as

$$W_{1/2} = \log\omega_1 - \log\omega \tag{7}$$

The values of $S_1/\Delta\varepsilon$ and $W_{1/2}$ may be fitted to represent a quadratic parabola, which may be approximated by a quadratic equation of $W_{1/2}$ as

$$S_1/\Delta\varepsilon = C_1 + C_2 W_{1/2} + C_3 W_{1/}^2 \tag{8}$$

which may be rewritten as

$$\Delta\varepsilon = \frac{\varepsilon_M''}{\left[\dfrac{C_1}{W_{1/2}} + C_2 + C_3 W_{1/2}\right]} \tag{9}$$

where C_1 C_2 and C_3 are numerical constants. These constants may be evaluated using the method of least squares. if the values of $S_1/\Delta\varepsilon$ and is also valid for two third and three fourth widths $W_{2/3}$ and $W_{3/4}$ which are the separations between log ω's when ε'' is two third and three fourth of the maximum value of dielectric loss ε_M''.

When the loss curve is asymmetric or skewed about the loss maximum, it is not possible to know which one of the Cole-Davidson and Williams-Watts equations fits the frequency dependence of dielectric loss, unless the loss data is available in the entire frequency range of relaxation.

An expression for $\Delta\varepsilon$ in the skewed arc losses, regardless of a particular type of relaxation, may be given by a quadratic equation similar to equation 8 as

$$\Delta\varepsilon = \frac{\varepsilon_M''}{\left[\dfrac{\overline{C_1}}{X} + \overline{C_2} + \overline{C_3}X\right]} \tag{10}$$

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where $\overline{C_1}$, $\overline{C_2}$ and $\overline{C_3}$ are numerical constants to be determined by the method of least squares and X is related with the half width $W_{1/2}$ as follows

$$X = W_{1/2} + A (\log \omega_1 - \log \omega_M) \qquad (11)$$

where ω_l has same meaning as in equation 6.6 and ω_M is the angular frequency corresponding to loss maximum.

The parameter A (A > 0) is introduced to correct for the differences in $S_1/\Delta\varepsilon$ between Williams-Watts and Cole-Davidson type relaxation. The parameter A is initially chosen arbitrarily and then $\overline{C_1}$, $\overline{C_2}$ and $\overline{C_3}$ are evaluated using the method of least squares. The value of A is then varied until a set of values of A, $\overline{C_1}$, $\overline{C_2}$ and $\overline{C_3}$ is found to give the least error in the evaluation of the relaxation intensity of a system at various values of β.

3. RESULTS AND DISCUSSION

The empirical model for the relaxation intensity proposed by Kita and Koizumi was suitably applied to the nematic liquid crystal mixture E-24. The numerical constants for evaluating the relaxation intensity are given in Table 1.

Table 1. Values of numerical constants $W_{1/2}$, $W_{2/3}$ and $W_{3/4}$.

	$W_{1/2}$	$W_{2/3}$	$W_{3/4}$
A	0.9	0.5	0.3
$\overline{C_1}$	-0.1327	2.325	-0.2592
$\overline{C_2}$	-0.1101	-3.102	0.6107
$\overline{C_3}$	0.1698	1.1121	0.0408

The values of relaxation intensity for different values of distribution parameter β are given in Table 2 along with the data theoretically evaluated and those obtained from the experimental results. Fig. 4 shows the plot of $\varepsilon''/\Delta\varepsilon$ versus log $\omega\tau$ for E - 24 with $\beta = 0.39$.

The data given in Table 2 shows that E-24 yielded the relaxation intensities of 0.529 and 0.717 for half width; 0.527 and 0.717 for two-third width, and 0.527 and 0.717 for three fourth width for β values of 0.39 and 0.41, respectively. The estimated errors are 0.18% and 0.19% for $W_{1/2}$; 0.24% and 0.19% for both $W_{2/3}$ and $W_{3/4}$ for above β values. The maximum error in the estimation of $\Delta\varepsilon$ was 0.24 %, which is very small. The nematic liquid crystal mixture E-24 exhibits an excellent agreement between $\Delta\varepsilon_{obs}$ and $\Delta\varepsilon_{cal}$ which is clear
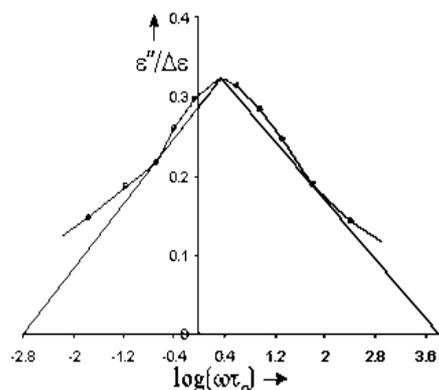

Figure 4. Plot of $\varepsilon 22/\Delta\varepsilon$ versus $\log(\omega\tau_o)$ for E-24 for $\beta = 0.4$.

from $\Delta\varepsilon_{cal}$ values 0.527 and 0.717 for β values of 0.39 and 0.41 respectively for both $W_{2/3}$ and $W_{3/4}$ the corresponding values of $\Delta\varepsilon_{obs}$ are 0.53 and 0.72. The error in determination of $\Delta\varepsilon$ was 0.24% and 0.19%. The maximum error amongst all the three widths was 0.24% for $W_{2/3}$ with $\beta = 0.44$. The maximum error is observed in the case where the data are provided in a limited frequency range about the loss maximum around the relaxation frequency. It thus seems that the empirical formula suggested by Kita Koizumi is valid for the evaluation of the relaxation intensity.

4. CONCLUSION

The relaxation intensities as calculated using the Kita Koizumi method are found to be in good agreement with the observed values for the sample, which shows Davidson-Cole type of relaxation. In fact the above-mentioned method proves to be a versatile tool for estimating the relaxation intensity in case the dielectric loss data is not provided in the entire frequency range. The present analysis on the liquid crystal E-24 also leads to the same inference.

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Table 2. Values of estimated parameters at different temperature for E-24

Temp (K).	β	$W_{1/2}$			$W_{2/3}$			$W_{3/4}$		
		$\Delta\varepsilon_{cal}$	$\Delta\varepsilon_{obs}$	% error	$\Delta\varepsilon_{cal}$	$\Delta\varepsilon_{obs}$	% error	$\Delta\varepsilon_{cal}$	$\Delta\varepsilon_{obs}$	% error
326	0.39	0.529	0.53	0.18	0.527	0.53	0.24	0.527	0.53	0.24
320	0.41	0.717	0.72	0.19	0.717	0.72	0.19	0.717	0.72	0.19

β	$W_{1/2}$	$W_{2/3}$	$W_{3/4}$	ε_∞
0.39	1.79	1.20	0.86	3.10
0.41	1.71	1.15	0.81	3.21

*Biographical Sketch

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