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Anisotropic Thermal Diffusion in Nematic APAPA

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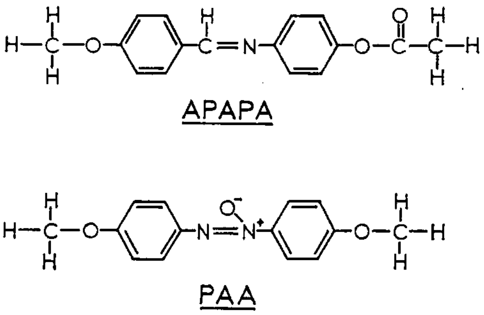
Abstract—The influence of the proximity to an interface on the thermal conduction in nematic *p*-anisylidene *p*-aminophenylacetate (APAPA) is analyzed using the experimental data on the thermal conductivity. The ordering influence of the interface extends to a distance of 143.3μ which is considerably greater than values previously obtained for PAA.

A comprehensive review of the literature on the anisotropic transport properties of nematic mesophases can be found in Refs. 2–5. The object of this paper is *to report the thermal conductivity data on* nematic *p*-anisylidene *p*-aminophenylacetate or *p*-[*p*-methoxybenzylidene] phenylaminoacetate (APAPA) which exhibits nematic behaviour between 82 and 110 °C.(1) The commercial sample used in this work was nematic from 79.5 to 102 °C.(4) Thermal conductivity data on nematic *p*-*p*-di-*n*-methoxyazoxybenzene or paraazoxyanisole (PAA) has been reported earlier.(3) Figure 1 gives the structure of these two substances.



APAPA

PAA

Figure 1. Structure of PAA and APAPA.

Rajan and Picot(3) analyzed the interfacial orientation effect on the nematic molecules using the concept of "swarm continuum"—i.e., continuous variation of the orientation of molecular aggregates in space. The mean orientation of the spheroidal swarm axis at a "point" is given by the anisotropy tensor (Cartesian) defined as follows:

$$\mathbf{A}(x) = \langle r(x)r(x)\rangle - \frac{\mathbf{I}}{3} \qquad (1)$$

where

r = orientation vector ≡ $-r$ (transverse isotropy)

x = position vector

$\mathbf{I}$ = Idem factor

$\langle\ \rangle$ = ensemble average over all possible orientations given by a suitable distribution function

For the parallel plate system used, it was shown(3) from the one-dimensional equation that

$$k_e = \frac{k_o}{\displaystyle\int_0^1 \frac{d\xi}{[1+\lambda_1 \mathbf{A}_{33}(\xi)]}} \qquad (2)$$

where

$\xi = \dfrac{x_3}{L} = \dfrac{\text{distance normal to the surface}}{\text{gap between the plates}}$

k_o = thermal conductivity in the randomly oriented state far away from the interface

k_e = effective thermal conductivity

λ_1 = material constant or conductivity anisotropy = $(k_{\parallel} - k_{\perp})/k_0$

By solving the equation of change for A,(5) Eq. (2) can be integrated(3) to give:

$$k_e = \frac{k_o\sqrt{1-b^2}}{2\sqrt{\mathscr{D}}} \Bigg/ \ln\left(\frac{1+b+\sqrt{1-b^2}\tanh(1/4\sqrt{\mathscr{D}})}{1+b-\sqrt{1-b^2}\tanh(1/4\sqrt{\mathscr{D}})}\right) \qquad (3)$$

where

$$\left.\begin{aligned} b &= \left(\frac{k^\circ}{k_o} - 1\right)\Bigg/\cosh\frac{1}{2\sqrt{\mathscr{D}}} \\ \mathscr{D} &= \frac{\lambda\tau}{L^2} \end{aligned}\right\} \qquad (3a)$$

λ = diffusion constant for the propagation of the interfacial orienting influence

τ = orientational relaxation time

k° = effective interfacial thermal conductivity

The relaxation of orientation results from the rotational Brownian motion of r. This as well as the concept of interfacial orientational diffusion is different from and new to the principles of continuum theory for liquid crystals.(6) The term $\sqrt{\lambda\tau}$ was characterized(3) as an interfacial layer thickness δ_c where A_{33} is 36.8% of the value A_{33}° at the interface. From Eq. (3), it is clear that $k_e \rightarrow k_0$ as $L \rightarrow \infty$ and $k_e \rightarrow k^\circ$ as $L \rightarrow 0$. The orientation at the interface is perfect but the exact nature, i.e. parallel or perpendicular to the surface is decided by the nature, purity and preparation of the surface and the sample.

Equation (3) is fitted to the k_e data of Patharkar(4) as suggested in Ref. 3 to estimate the unknown constants k_0, k° and $\sqrt{\lambda\tau}$. Figure 2 is a plot of k_e against $1/L$ giving the fitted curve and data points for purified (> 99.9% pure) PAA at 125–6 °C and commercial APAPA at 80–81 °C. The estimated parameters are listed in Table 1, along with those for commercial PAA.(3)

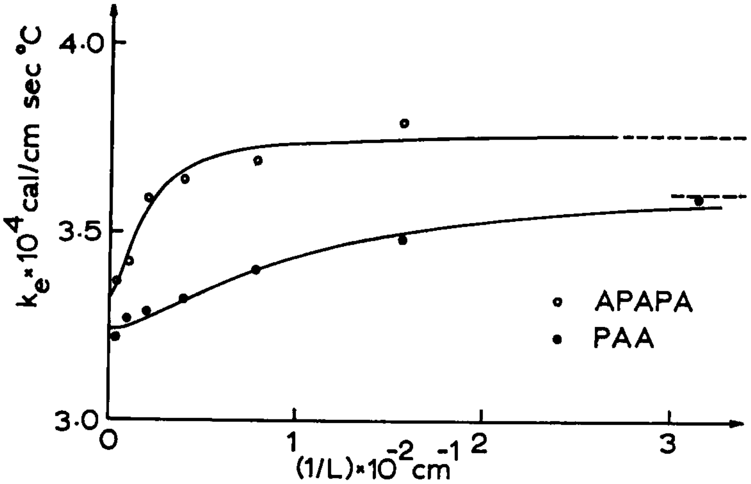


Figure 2. Experimental data (k_e vs $1/L$) for commercial APAPA (80–81 °C) and purified PAA (125–6 °C). Solid lines are the fitted curves per Eq. (3). Dotted lines represent the limit as $L \rightarrow 0$.

Table 1

Estimated parameter	Purified PAA 125–6 °C	Commercial PAA 125–6 °C	Commercial APAPA 80–81 °C
$k_0 \times 10^4$ cal/cm sec °C	3.24	3.14	3.33
$k^\circ \times 10^4$ cal/cm sec °C	3.60	4.94	3.75
δ_c microns	28.8	31.9	143.3

If τ can be measured experimentally by some optical or other means using external fields to orient the swarms, λ may be determined easily which would be of use in situations involving interfaces. Yun(7) has listed the different values of τ reported in the literature including his own observations. The mean value of τ for PAA is of the order of 2 seconds.

The striking difference in the extent of interfacial orienting influence for PAA and APAPA is clear from the values of δ_c. A long range ordering by the interface is indicated for APAPA. This is attributed to the differences in the λ and τ values for the two chemicals because of different molecular structures.

Further analysis by measuring the different properties using optical techniques such as light scattering is under investigation.

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REFERENCES

1. Anon., *Chem. & Eng. News*, **49**, 45, 20–23 (1971).
2. Brown, G. H., *et al.*, " Liquid Crystals ", Technical Report, AFML-TR-71-20, NTIS, Springfield, Virginia (1971).
3. Rajan, V. S. V. and Picot, J. J. C., *Mol. Cryst. and Liq. Cryst.*, in press (1971).
4. Patharkar, M. N., Ph.D. Thesis, University of New Brunswick, Canada (1971).

5. Fisher, J. and Fredrickson, A. G., *Mol. Cryst. and Liq. Cryst.*, **8**, 267–284 (1969).
6. Sullivan, J. T., Ph.D. Thesis, University of Minnesota, U.S.A. (1966).
7. Yun, C. K., Ph.D. Thesis, University of Minnesota, U.S.A. (1970).