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## Liquid Crystals

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## Determination of molecular diffusion coefficients in liquid-crystalline cholesteryl myristate using gas chromatography

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The molecular diffusion coefficients of xylene and picoline isomers have been determined at different temperatures in the three phases (smectic, cholesteric and isotropic) of cholesteryl myristate by gas chromatography. The results obtained are discussed in terms of molar volume, polarity and length-to-breadth ratio of the isomers.

### 1. Introduction

Liquid crystals are frequently used in gas chromatography for the separation of isomers (benzene and naphthalene derivatives, polynuclear aromatic hydrocarbons, steroids, etc.). If conventional stationary phases are used the separation is based on the different volatility and polarity of solutes, whereas employing liquid-crystalline stationary phases the separation also relies on the molecular shape of the solutes. The ordering of the different phases (smectic, nematic or cholesteric) influences the efficiency of the separation. The compounds with high length-to-breadth ratio are retained to a greater extent in the stationary phase than the more compact molecules. In addition, planar molecules are retained more than non-planar molecules. If the structure of the solute molecules is similar to those of the liquid crystal, they are dissolved more easily and the retention time in the chromatographic column is longer. The three types of liquid crystal have been used as stationary phases in gas chromatography but nematic phases have more applications because they lead to better separations.

Besides their analytical applications, liquid crystals have been used with chromatographic columns to determine thermodynamic properties such as activity coefficients, excess enthalpies and entropies, and enthalpies and entropies of solution at infinite dilution. In this way, it has been possible to determine the thermodynamics of the solution processes in the different liquid-crystalline phases to provide information about their ordered structure.

However, there is not much information about the solution processes from the point of view of solute diffusion in the liquid phase of a chromatographic column. Grushka and Solsky [1, 2] have determined molecular diffusion coefficients of *o*-xylene in 4,4'-dimethoxyazoxybenzene (PAA) and *p*-xylene in *p*-(*p*-ethoxyphenylazo)phenylundecylenate (EPAPU). In this work, molecular diffusion coefficients of *ortho*, *meta* and *para*-xylene, and alpha, beta and gamma-picoline have been determined in the smectic, cholesteric and isotropic phases of cholesteryl myristate.

### 2. Experimental

#### 2.1. Apparatus

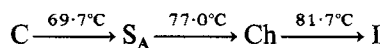
A Hewlett-Packard model 5750B gas chromatograph equipped with a thermal conductivity detector was used in this work. The oven temperature was controlled to a

precision of  $\pm 0.1^\circ\text{C}$ . The injection chamber and detector temperatures were kept  $10^\circ\text{C}$  above the oven temperature. The inlet pressures were measured with a mercury manometer. All of the experiments were carried out with 99.998% helium as the carrier gas. Flow rates were measured at the detector outlet (at room temperature and atmospheric pressure) with a soap bubble flowmeter. The chromatograms were recorded on a Hewlett-Packard recorder, model 7127A. The retention times were measured to a precision of  $\pm 0.1$  s.

## 2.2. Solvent

The liquid crystal employed as the liquid phase, cholesteryl myristate (CM), was obtained from Eastman-Kodak (Rochester, N.Y., USA). It was recrystallized three times from ethanol before use. The liquid crystal was dissolved in chloroform and coated on to the solid support (60/80 mesh glass beads) using the rotating-evaporator method. Glass beads were used because their surface is very smooth and geometrically well defined. An average loading of 0.4 wt% was obtained. The weight percentage of liquid phase in the packing was determined by the careful ashing of two samples at  $600^\circ\text{C}$ . The stationary phase was packed in a glass column (170 cm  $\times$  0.2 cm i.d.) which had been previously rinsed with acetone and dried by passing a stream of nitrogen through it. The column was conditioned overnight in the gas chromatograph at  $95^\circ\text{C}$ .

The transition temperatures ( $^\circ\text{C}$ ) were determined by gas chromatography, by plotting the retention time of ethylbenzene versus temperature with a precision of  $0.1^\circ\text{C}$  [3]; the values observed were



The transition temperatures observed are lower than those obtained in a previous work using an average loading of 13.8 wt% CM and 60/80 mesh acid-washed Chromosorb W as the solid support [4], and those obtained by other authors who worked with higher loadings [5, 6]. In addition, the transition temperatures obtained by differential scanning calorimetry for the bulk liquid crystal are different [7, 8]. The lower transition temperatures can be attributed to the low weight percentage of the liquid phase used as well as the solid support used (glass beads). Witkiewicz and Waclawczyk [9] found that the type of support used has a considerable effect on the characteristics of the liquid crystal-support system.

The glass column was inspected visually at the end of the experiments and no deterioration or darkening of the packing was observed.

## 2.3. Solutes

The organic solutes used in this work were reagent grade and were obtained from Fluka. Sample injection volumes of  $0.07 \mu\text{l}$  were added using a Hamiltonian syringe of  $0.5 \mu\text{l}$ .

## 3. Results and discussion

Numerous techniques are available in the literature for measurement of diffusion coefficients. Experimental diffusivities in the liquid phase were obtained here using the chromatography method. Van Deemter *et al.* [10] derived an expression for the height

equivalent to a theoretical plate ( $H$ ). Their equation was modified to include other effects [11, 12] which gave

$$H = \frac{Bf}{P_o v_o} + C_G P_o v_o f + C_L v_o j, \quad (1)$$

where  $v_o$  is the gas velocity at the outlet of the column,  $P_o$  is the outlet pressure,  $f$  is the Giddings compressibility factor,  $j$  is the James–Martin compressibility factor,  $B$  is the longitudinal diffusion coefficient at unit pressure,  $C_G$  is the mass transfer resistance in the gas phase and  $C_L$  is the mass transfer resistance in the liquid phase.

The resistances to mass transfer in the gas and liquid phases are given by

$$C_G = (0.63 - 0.2R)d_p^2/D_G \quad (2)$$

and

$$C_L = \frac{k d_p^2}{120 D_L (1+k)^2} \left( \frac{\rho_g}{18.75 \rho_l} \right)^{1/2}, \quad (3)$$

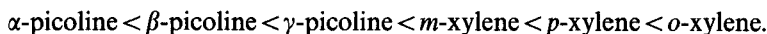
where  $d_p$  is the bead diameter,  $D_G$  is the molecular diffusion coefficient of the sample in the gas phase at unit pressure,  $R$  is the ratio of zone velocity to average gas velocity,  $k$  is the column capacity ratio,  $\rho_g$  is the density of the glass beads,  $\rho_l$  is the density of the liquid phase, % is the weight of the liquid phase in the stationary phase and  $D_L$  is the molecular diffusion coefficient in the liquid phase. Considering the average gas velocity as  $\bar{v} = v_o j$  and rearranging equation (1) the equation used to determine the molecular diffusion coefficients in the liquid phase is obtained as

$$\frac{H\bar{v}}{jf} - \frac{C_G P_o \bar{v}^2}{j^2} = \frac{B}{P_o} + \frac{C_L \bar{v}^2}{jf}. \quad (4)$$

The molecular diffusion coefficient  $D_L$  can be determined by adjusting the data on the left hand side of equation (4) against  $(\bar{v}^2/jf)$ . Thus  $C_L$  is obtained, and equation (3) allows the calculation of  $D_L$ .  $D_G$  was calculated from the Fuller, Schettler and Giddings equation [13].  $\rho_l$  of cholesteryl myristate was taken from the literature [14] and  $\rho_g$  was determined by pycnometry.

At least eight runs were performed at each velocity and temperature to determine the height equivalent to a theoretical plate  $H$  and then the resistance to mass transfer in the liquid phase  $C_L$ . At the same temperature six different flows were selected (20, 25, 30, 35, 40 and 45 cm<sup>3</sup> min<sup>-1</sup>).  $H$  was determined from the solute retention times, that of an inert gas (nitrogen) and the peak widths at 0.607  $h_{\max}$ . The peak widths were always greater than 1 cm and they were measured with a cathetometer ( $\pm 0.001$  cm). The retention times of different solutes in the three phases of CM with a flow of 20 cm<sup>3</sup>/min of helium carrier gas are shown in figure 1. Clear transitions are observed when the temperature increases and changes the ordered structure of the liquid crystal. The retention times increase when the new phase is obtained by heating. The variation of retention times with temperature is more obvious in the isotropic phase.

The solutes are eluted, in all phases, in the same order



The picolines are eluted first because they are more polar compounds. With conventional non-polar stationary phases the solutes are eluted in the order of increasing boiling points. With liquid crystals as stationary phases the order of elution of compounds with similar boiling points depends on the shape of the molecule.

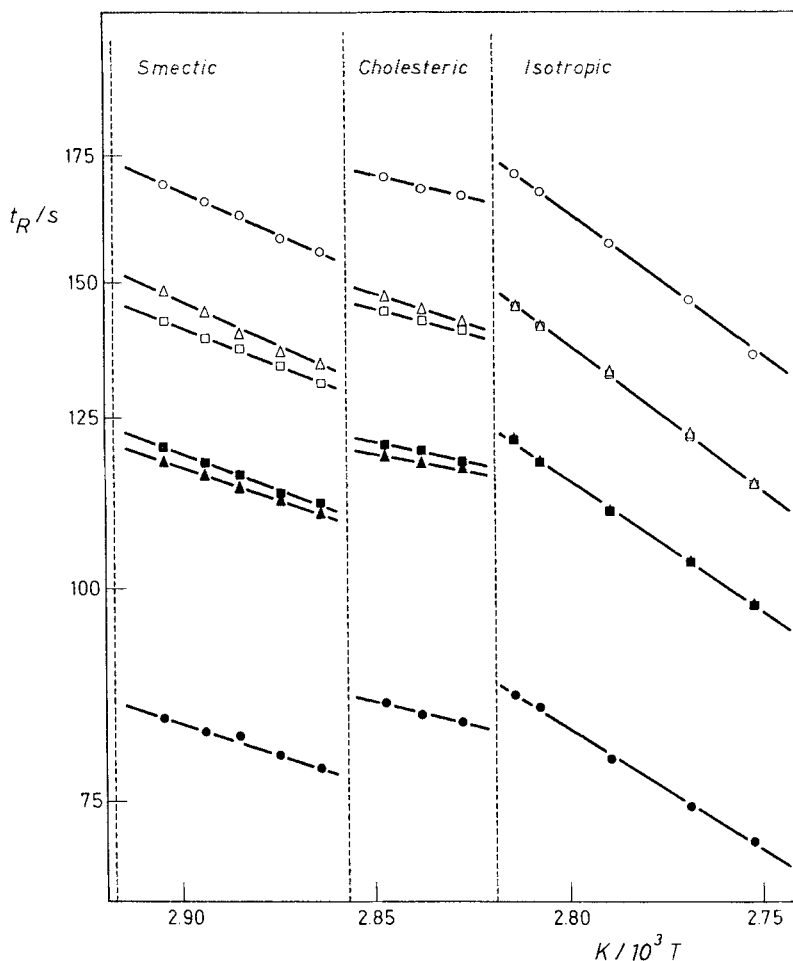


Figure 1. Retention times of xylenes and picolines in the three phases of cholesteryl myristate (flow rate:  $20 \text{ cm}^3/\text{min}$ ).  $\circ$  represents *o*-xylene,  $\square$  *m*-xylene,  $\triangle$  *p*-xylene,  $\bullet$   $\alpha$ -picoline,  $\blacksquare$   $\beta$ -picoline and  $\blacktriangle$   $\gamma$ -picoline.

Compounds with high length-to-breadth ratio are more retained than those with lower length-to-breadth ratio. Thus, the order of elution of the xylene isomers is *meta* < *para* < *ortho*. If the loading of the chromatographic column was larger the separation of *m*-xylene–*p*-xylene and  $\beta$ -picoline– $\gamma$ -picoline would be better. The chromatographic column used in this work is useful to determine diffusion coefficients but analytical separations are carried out on columns with higher loadings.

Molecular diffusion coefficients determined from equation (3) are shown in figures 2 and 3. The values obtained were in the same range as those obtained by Butler and Hawkes [15] for *m*-xylene in Carbowax 400 and 20M, and those obtained by Kong and Hawkes [16] for the three xylenes in cyanosilicones. The values of the diffusion coefficient increases with increasing temperature and they change sharply as the structure of the liquid phase changes with temperature. Xylenes diffused better than picolines in the cholesteric and isotropic phases and their diffusivities were similar in the smectic phase. In all phases the diffusivity of picolines showed the same trend:

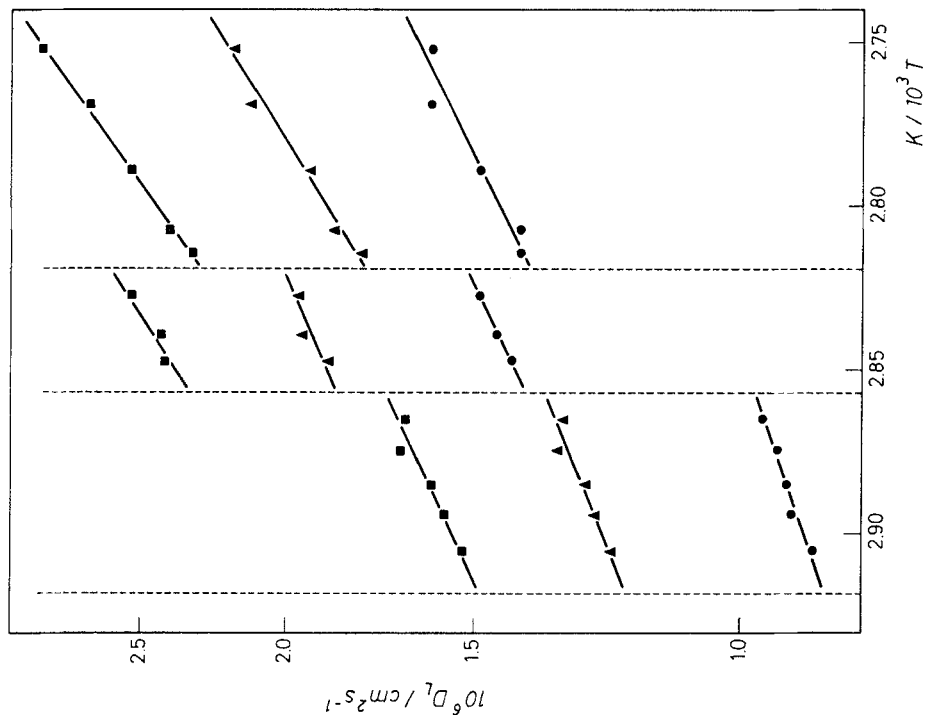


Figure 3. Molecular diffusion coefficients of the picolines in cholesteryl myristate. ● represents  $\alpha$ -picoline, ■  $\beta$ -picoline and ▲  $\gamma$ -picoline.

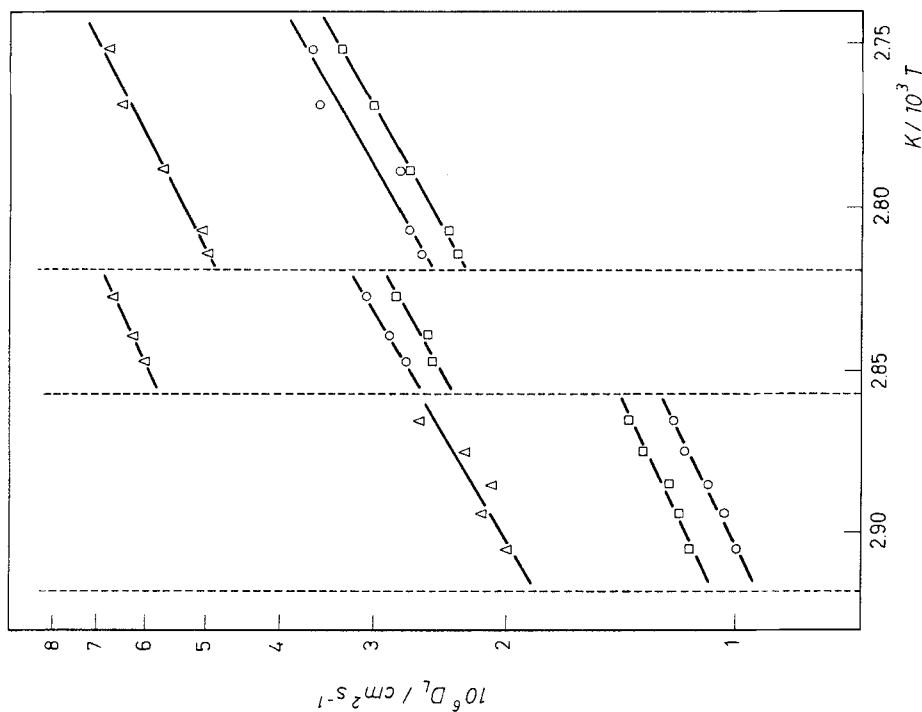


Figure 2. Molecular diffusion coefficients of the xylenes in cholesteryl myristate. ○ represents *o*-xylene, □ *m*-xylene and △ *p*-xylene.

$\beta$ -picoline  $>$   $\gamma$ -picoline  $>$   $\alpha$ -picoline. The diffusivity of the xylenes followed the order:  $p$ -xylene  $>$   $o$ -xylene  $>$   $m$ -xylene in cholesteric and isotropic phases and in the smectic phase the order was  $p$ -xylene  $>$   $m$ -xylene  $>$   $o$ -xylene.  $p$ -Xylene clearly diffuses better than the other xylene isomers in all of the phases.

The values of diffusion coefficients depend on a number of factors: the viscosity and density of the solvent, the path the molecule must follow during the diffusion process, the size and shape of the solute molecule and the interactions between solvent and solute. The diffusion coefficients are lower in the smectic phase because this phase has the highest degree of order. In fact it is a compact arrangement of molecules in layers. The solute molecules presumably penetrate into the layers with great difficulty. In the isotropic phase, the solution process is more favourable due to its disordered structure. The high values in the cholesteric phase could be explained as follows. Although solute molecules must diffuse across the ordered layers they can diffuse without many difficulties in the helical cholesteric structure.

The values observed for the xylenes can be explained in terms of the size, shape and polarity of the isomers. The size is related to the molar volume and the shape to the length-to-breadth ratio. This information was obtained from the literature [17–20]. These factors operate in opposite directions. According to polarity and length-to-breadth ratio, the diffusion coefficients should keep the order *para*  $>$  *meta*  $>$  *ortho*, but considering their molar volume the order should be *ortho*  $>$  *meta*  $>$  *para*. The values observed show which factors are more important in the different phases. In the smectic phase, the most ordered structure, the length-to-breadth ratio is an important aspect and therefore the diffusivity of  $m$ -xylene is greater than the diffusivity of  $o$ -xylene. The diffusion coefficients of the picolines are lower than the values observed for the xylenes because they are more polar compounds. The diffusion coefficients show the same order in all phases:  $\beta > \gamma > \alpha$ . There are no significant differences in the length-to-breadth ratio and the values observed can be explained on the basis of their molar volume and polarity. The  $\beta$  isomer showed the highest value of diffusivity because it has the lowest polarity and molar volume. The  $\gamma$  isomer diffused better than the  $\alpha$  isomer because its lower molar volume has more influence than the lower polarity of the  $\alpha$  isomer.

The relation between diffusivity and temperature can be expressed as

$$D_L = D_L^* \exp(-E/RT), \quad (5)$$

where  $E$  is the energy of activation and  $D_L^*$  is a fitting parameter. There were few points with too much dispersion to give reliable values of  $D_L^*$  and  $E$ . Activation energies of xylenes are higher than those of picolines and generally they are quite elevated [15]. Activation energies are clearly lower in the smectic phase and slightly higher in the isotropic than in the cholesteric phase. Activation energies increase as the ordering in the liquid crystal decreases.

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