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USE OF SMECTIC LIQUID CRYSTALS FOR THE GAS–LIQUID CHROMATOGRAPHIC SEPARATION OF POSITIONAL ISOMERS

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SUMMARY

The smectogenic compounds terephthal-bis-*n*-butylaniline and 4-(4-*n*-hexyloxybenzylideneamino)azobenzene were prepared and used as stationary phases for the gas–liquid chromatographic separation of positional isomers of dibromobenzenes, chloroacetophenones, chloronaphthalenes and methybiphenyls. These solute isomers cannot be sharply separated in the smectic B state whereas a complete separation was achieved in both the smectic A and C phases. It is suggested that the unique selectivity of the smectic A and C states relative to the smectic B state can be explained by the difference in the molecular packing in the layer between the smectic B and the smectic A or C state.

INTRODUCTION

Liquid crystals exhibit interesting solvent properties because of the rod-like shape and the ordered arrangement of their molecules. In addition, liquid crystals are a unique liquid stationary phase in gas–liquid chromatography (GLC) in that they show long-range orientational order in which the rod-like molecules tend towards a mutually parallel alignment[1–3]. It is also well established that the solutes are separated on the basis of molecular shape in GLC using liquid crystals as the stationary phase. Roughly, the more rod-like a solute molecule is, the easier it should fit into the liquid crystal lattice and hence the greater its solubility should be. These unique solvent properties of liquid crystals were applied for the first time to the separation of the positional isomers of various disubstituted benzenes[4]. Recently several reports on the separation of alkylnaphthalenes[5], polycyclic aromatic hydrocarbons[6–9], steroid epimers[10], polychlorinated biphenyls[11], azaheterocyclic compounds[12] and monochlorobiphenyls[13] using liquid crystalline stationary phases have appeared.

Most GLC studies reported so far have been carried out with the use of nematic liquid crystals. Except for a few reports[14–16], another liquid crystalline phase, a smectic liquid crystal, has not been used for the GLC separation of positional isomers. In addition, it has been reported that the separation factor in the temperature range of the stable smectic phase is worse than that in the nematic range in spite of the lower working temperature[1].

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It is well established that the smectic phases can be further subdivided into at least seven modifications, denoted by the letters A–G[17]. From a structural point of view, all of the smectic phases are stratified, the molecules being arranged in layers with a well defined interlayer spacing. Thus, the smectic states are more ordered than the nematic state and always exist at temperatures lower than the nematic state. Hence, it is unlikely that none of the smectic modifications has a selective affinity towards the solute molecules. It seemed interesting to study the GLC separation of various positional isomers in the different smectic states. In this paper we describe a study of the separation of various isomeric disubstituted benzenes, naphthalenes and biphenyls in the smectic A, B and C phases, which are the most frequently observed with smectic liquid crystals.

EXPERIMENTAL

Materials

The two smectogenic compounds used, terephthal-bis-4-*n*-butylaniline (TBBA) and 4-(4-*n*-hexyloxybenzylideneamino)azobenzene (HBAA), were synthesized according to known methods[18,19]. The crude compounds were purified by successive recrystallization from hot ethanol to give constant transition temperatures. The transition temperatures and the purities of the compounds were estimated with a Rigaku differential scanning calorimeter which was calibrated in terms of the temperature and energy. The phase transitions and the liquid crystal textures were determined by using an ordinary polarizing microscope and a Mettler FP microfurnace for sample temperature control. The determined liquid crystalline phases and their transition temperatures are as follows:

TBBA:

$$\begin{tikzcd}
K \arrow[r, "113^\circ C"] & S(B) \arrow[r, leftrightarrow, "144^\circ C"] \arrow[d, leftrightarrow, "87^\circ C"] & S(C) \arrow[r, leftrightarrow, "172^\circ C"] & S(A) \arrow[r, leftrightarrow, "200^\circ C"] & N \arrow[r, leftrightarrow, "236^\circ C"] & I \\
S(V) \arrow[u] \arrow[r, leftrightarrow, "74^\circ C"'] & S(IV) & & & &
\end{tikzcd}$$

HBAA:

$$\begin{tikzcd}
K \arrow[r, leftrightarrow, "107^\circ C"] & S(B) \arrow[r, leftrightarrow, "127^\circ C"] & S(A) \arrow[r, leftrightarrow, "148^\circ C"] & N \arrow[r, leftrightarrow, "174^\circ C"] & I
\end{tikzcd}$$

in which K denotes the solid phase, S( ) the smectic phase, N the nematic phase and I the isotropic liquid.

The solutes chosen were *m*- and *p*-dibromobenzenes, *m*- and *p*-chloroacetophenones, α- and β-chloronaphthalenes and 3- and 4-methybiphenyls. Individual positional isomer samples which were obtained from Tokyo Kasei (Tokyo, Japan) were GC pure and were used without further purification.

Apparatus and procedure

The support material employed was 100–120-mesh Chromosorb W HP. The support was coated with the liquid crystalline compounds by using chloroform as solvent, followed by gradual elimination of the solvent by evaporation on a hot water-bath. The concentration of liquid phase in the packing of the coated support was 2.5% (w/w). The packing was re-sieved to 100–120 mesh and then packed into 1.5 m × 3 mm I.D. glass columns. Prior to use the columns were conditioned for 2 h at 10°C above the nematic–isotropic transition temperature of the liquid stationary phase with the carrier gas flow-rate set at 30 ml/min.

A Hitachi 163 gas chromatograph equipped with a flame-ionization detector and a linear temperature programmer was used. A 1-mV recorder with a chart speed range of 2.5–80 mm/min was used to record chromatograms from which retention times were determined. The flow-rate of the carrier gas (nitrogen) was measured using a soap-bubble flow meter. Methane was used in the determination of the dead time. The solute mixtures to be separated were dissolved in benzene and were injected with a Hamilton 701 10-µl syringe, using the smallest detectable sample volume.

RESULTS AND DISCUSSION

Fig. 1 shows a typical chromatogram of mixtures of isomeric dibromobenzenes, chloroacetophenones, chloronaphthalenes and methylbiphenyls observed for the smectic B phase on a TBBA column. It should be noted that isomeric pairs of chloroacetophenone and methylbiphenyl can be separated on the smectic B phase whereas no separation of dibromobenzenes or chloronaphthalenes is achieved. In addition, it should be borne in mind that the retention time for the isomer with the more rod-like shape (*p*-isomer) is longer than that for the *m*-isomer. Such a separation behaviour between *meta*- and *para*-positional isomers is essential for GLC using a

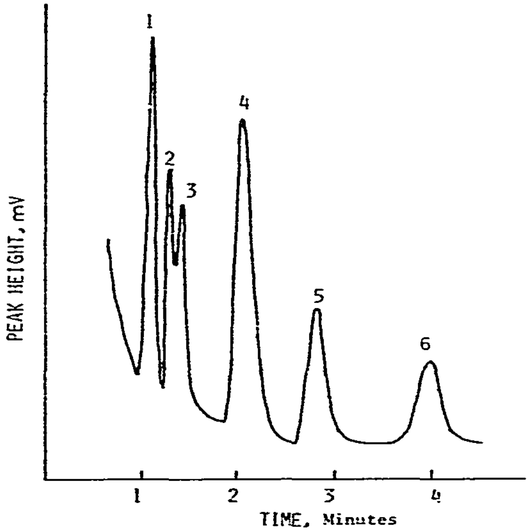

Fig. 1. Gas chromatogram of a mixture of dibromobenzenes, chloroacetophenones, chloronaphthalenes and methylbiphenyls observed in the smectic B phase on a TBBA column. Oven temperature, 125°C; injection temperature, 220°C; flame-ionization detector; nitrogen flow-rate, 25 ml/min. Peaks: 1 = *m*- and *p*-dibromobenzenes; 2 = *m*-chloroacetophenone; 3 = *p*-chloroacetophenone; 4 = α- and β-chloronaphthalenes; 5 = 3-methylbiphenyl; 6 = 4-methylbiphenyl.

liquid crystalline column. It is well recognized that a liquid crystal shows a selective affinity towards linear, rod-like solutes, as these should be able to fit better into its lattice with parallel molecular alignment.

On heating, a drastic increase in the retention volume is observed on passing from the smectic B to the smectic C state. In Fig. 2 a plot is shown of log V_R of dibromobenzene solute molecules *versus* the reciprocal temperature. As shown in Fig. 3, it should be also stressed that all of the solute molecules studied can be separated in this smectic C state, including the isomers of dibromobenzene and chloronaphthalene, which could not be separated in the smectic B state. A sharp increase in the retention volume at the phase transition from the smectic B to the smectic C state indicates that the solubility of the solutes in the smectic C state is much greater than that in the smectic B state. This fact can easily be understood by taking account of the difference in the molecular order in layers between the smectic B and smectic C state. It has been accepted that in the smectic B phase there is high degree of order in a layer and that the molecules form a local three-dimensional hexagonal structure which extends over several smectic layers[20,21]. On the other hand, the molecules in the smectic C state are disordered within the layer but tilted. Such a striking difference in molecular packing in the layer between the smectic B and C states will apparently cause a large change in solubility, and thus a sharp increase in the retention volume occurs on going from the smectic B to the smectic C state.

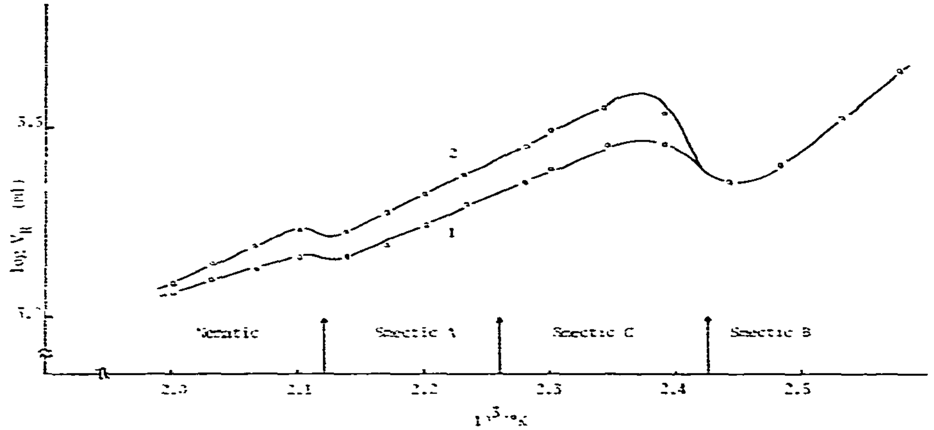

Fig. 2. Relationship between the logarithm of the corrected retention volume (V_R) and the reciprocal of the absolute temperature for *m*-dibromobenzene(1) and *p*-dibromobenzene(2) on a TBBA column.

As shown in Fig. 2, no apparent change in the retention volume can be observed at the smectic C–A phase transition. It is also noteworthy that a substantially continuous change in the retention volume is found at the smectic C–A transition for all of the other solute molecules studied. This behaviour in the change in retention volume with temperature is reasonably expected on the basis of the molecular arrangements of the smectic A and C phases. It is well known that both the smectic C and A phases have a molecular arrangement such that the molecules in each layer are uncorrelated with respect to the centre of mass position. The difference in the molecular alignment between the smectic A and C states consists solely of whether the long

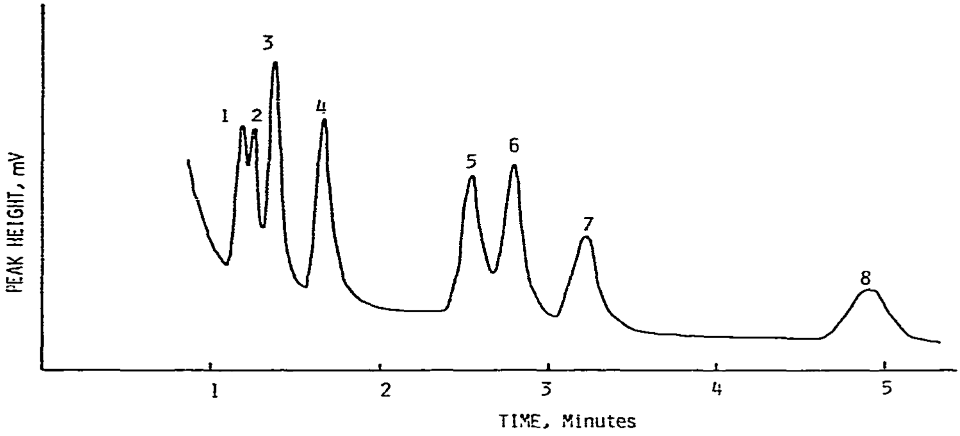

Fig. 3. Gas chromatogram of a mixture of solute molecules observed in the smectic C phase on a TBBA column. Peaks: 1 = *m*-dibromobenzene; 2 = *p*-dibromobenzene; 3 = *m*-chloroacetophenone; 4 = *p*-chloroacetophenone; 5 = α-chloronaphthalene; 6 = β-chloronaphthalene; 7 = 3-methylbiphenyl; 8 = 4-methylbiphenyl.

axis of the molecules lies perpendicular or tilted to the layer. Therefore, the transition energy associated with the smectic A–C phase transition is generally small[22]. It should be noted that log V_R varies nearly linearly with $1/T$ over the mesomorphic range of both the smectic A and C phases, as shown in Fig. 2.

On further heating, the retention volume is gradually changed on passing from the smectic A to the nematic phase. Further, a maximum in the graph of log V_R *vs.* $1/T$ is observed in the vicinity of the phase transition of the smectic A to the nematic phase. A similar maximum in the relationship between the retention volume and the temperature has been found so far for the temperature range of the nematic to isotropic phase transition. Such a characteristic behaviour of the retention volume has been reported by several workers to be typical of all solute species in the nematic and isotropic regions[2,14]. Further, this maximum has been regarded as being caused by a decrease in the free energy of solution of the solute on passing from the nematic to the normal liquid phase. It seems likely that the increase in the retention volume observed at the phase transition of the smectic A to nematic phase can be explained by a similar consideration to that at the nematic–isotropic transition mentioned above. Unfortunately, a more detailed discussion is impossible without other exact thermodynamic data for the solution of a solute in the smectic phase. However, it should be stressed that all of the solute isomers studied can be completely separated in both the smectic A and C states.

Fig. 4 shows the variation of the retention volume of α- and β-chloronaphthalenes with the temperature on an HBAA column. HBAA exhibits two smectic phases, A and C, as well as the nematic phase. The change in retention volume with temperature and the separation behaviour of solute isomers in each liquid crystalline state are similar to those on the TBBA column. The isomers of chloronaphthalenes and dibromobenzenes cannot be separated in the smectic B phase, in analogy with the TBBA column. A large increase in the retention volume is found on going from the smectic B

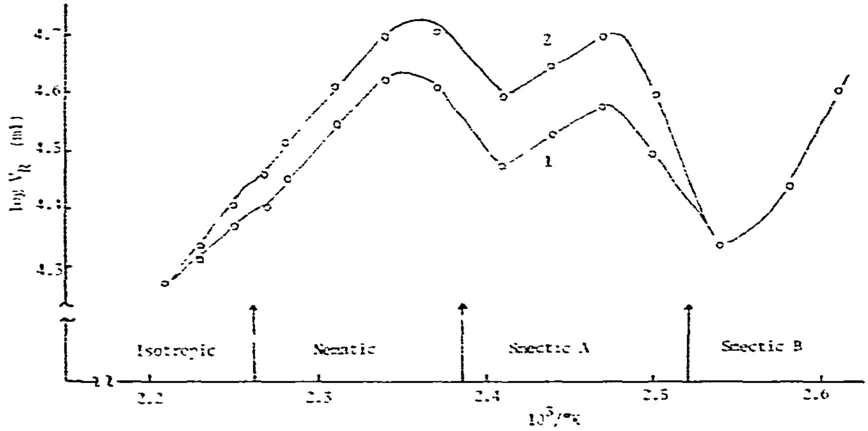

Fig. 4. Relationship between log V_R and 10^3/°K for α-chloronaphthalene (1) and β-chloronaphthalene (2) on an HBAA column.

to the smectic A state, and all of the solutes molecules can be completely separated in the smectic A state.

It has been pointed out so far that the smectic mesophase cannot be regarded as being of high value for practical GLC separations of solutes isomers because the separation efficiency of solutes obtained on the smectic liquid crystal is worse than that in the nematic state. This poor selectivity on the smectic column has been regarded as being caused by the penetration of the solute molecules between the layers in which the typical mesomorphic order does not exist. It seems that this view is in accord with the results obtained for the smectic B phase in our study. Fig. 5 shows the variation of the relative retention (α) of *p*-chloroacetophone (α = 1.0 for the *m*-isomer) with temperature using the TBBA column. It is obvious that the smectic B phase has no selective affinity towards the solutes relative to the other liquid crystalline states. At the phase transition to the smectic C there is a rapid increase in α. As is expected, α continues to decrease on further heating. It must be also stated that the

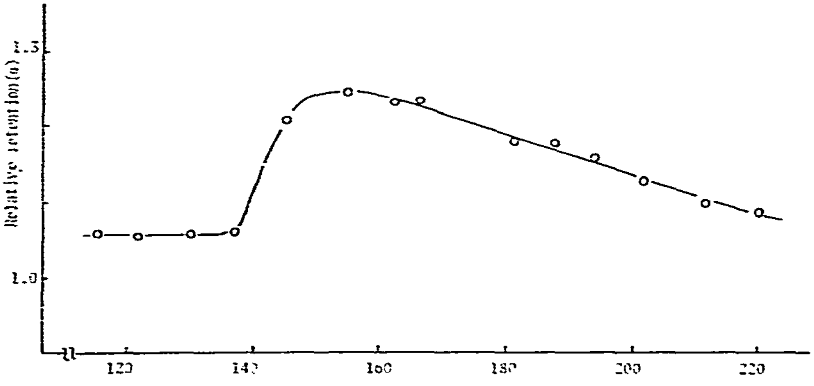

Fig. 5. Variation of the relative retention (α) of *p*-chloroacetophenone (α = 1.0 for the *m*-isomer) with temperature on a TBBA column.

other solute isomers show a variation in relative retention with temperature similar to that shown in Fig. 5. Thus, we conclude that the smectic A or C liquid crystalline phase is useful for the practical separation of positional isomers.

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