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CORRELATION BETWEEN GAS CHROMATOGRAPHIC AND INFRARED SPECTROSCOPIC BEHAVIOUR IN SMECTIC PHASES

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SUMMARY

Particular smectic mesophases, namely the C and F phases of 2-(4-*n*-nonyl-phenyl)-5-(4-*n*-nonyloxyphenyl)pyrimidine (I), were used as stationary phases in gas chromatography and different solution behaviours of these smectic phases against 2-octanol, characterized by the retention volumes, were found. Parallel results were obtained by recording the variation of the OH stretching frequency of 2-octanol in I as a solvent by means of infrared spectroscopy.

INTRODUCTION

Since the work of Kelker[1], the nematic modification and the smectic modifications of liquid crystals have been used successfully as stationary phases in gas chromatography (GC). The well known fact that the different tendencies for substances to be separated by GC is based on the different interactions between the mobile and stationary phases is also valid in this instance. Such different interactions, at least in special cases, can be demonstrated independently by IR spectroscopy. This method was first used by Ecknig *et al.*[2], who measured the shift of some characteristic frequencies of the molecules acting as the mobile phase as a function of the polarity of the compound that was used as a stationary phase in GC and as a solvent in IR spectroscopy.

In this paper, we describe some extensions of the above principle to the GC behaviour of selected compounds in relation to two smectic phases of one mesomorphic compound. Of course, here there are no differences in polarity, but we expected to observe some differences as a consequence of the polymorphy of the smectic state.

EXPERIMENTAL

The substance used as a stationary phase was 2-(4-*n*-nonylphenyl)-5-(4-*n*-nonyloxyphenyl)pyrimidine (I), the synthesis and specifications of which will be described elsewhere[3]. The regions of existence and the designations of the smectic phases of interest are given in Fig. 1. The nomenclature used here follows that given by Demus *et al.*[4]. The GC work was carried out on a Chromatron GCHF 18.3 gas

chromatograph, equipped with a flame-ionization detector and inlets adapted to glass columns, which were packed with 5% of I on 80–100-mesh Varaport-30.

The spectroscopic measurements were made on a Beckman IR 12 spectrometer. A VLT-2 accessory was used, together with an automatic temperature controller. The thickness of the potassium bromide cells was 0.1 mm. About 2% of the indicator substances were dissolved in I. The very small variations of the wavenumber of the CO band of camphor were determined by a series of measurements, and in no instances were differences greater than 0.2 cm^{-1} found between different measurements.

RESULTS AND DISCUSSION

The isomers of chlorotoluene and xylene show different partial molar enthalpies of solution in the C and F phases, as is demonstrated in Fig. 1, but unfortunately the interaction between chlorotoluene or xylene and I cannot be studied by IR spectroscopy because all of the important bands of the dissolved molecules are overlapped by those of I.

In order to find an interaction that can be recognized clearly in the IR spectrum we investigated the GC behaviour of 2-octanol with the smectic C and F modifications of I as stationary phases. In this instance, a hydrogen bond should be formed between the OH group of the alcohol and the nitrogen atoms of the pyrimidine ring, which
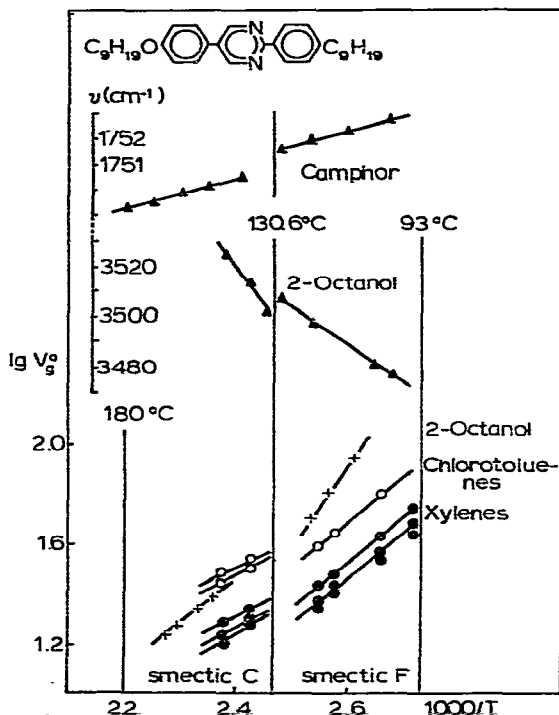

Fig. 1. IR spectroscopic (above) and gas chromatographic (below) results.

should give a clearly observable effect in the OH region of the IR spectrum. The retention volume (V_g) for this example is given as a function of the reciprocal of the absolute temperature in Fig. 1. We studied mainly the transformation point near 130 °C, because on both sides of this point there are broad regions where only one modification exists. Fig. 1 shows a clear discontinuity of the V_g curves at this transformation point for all substances. Moreover, the slopes of these curves in the regions of the C and F modifications differ considerably from each other, and consequently there is a substantial difference between the solution enthalpies of all compounds dissolved in the two modifications under discussion.

In the IR spectroscopic study we recorded the temperature-dependent IR spectra of 2-octanol dissolved in I in the OH stretching region. The wavenumbers of the associated OH bands are also given as a function of the reciprocal of the absolute temperature in Fig. 1. Here also a discontinuity at the transformation point near 130 °C occurs, amounting to about 12 cm^{-1}. We interpret this effect as a consequence of the different steric arrangements of the molecules in those smectic modifications which are in equilibrium at 130 °C. Probably the formation of the smectic F modification is connected with an arrangement of molecules that diminishes the accessibility of the nitrogen atoms of the pyrimidine ring, acting as the acceptors in the hydrogen bond under investigation here. Therefore, the hydrogen bond will be shorter in the smectic F modification.

We cannot give an exact description of the variation of the hydrogen bond in the different mesophases. Perhaps only the distances of the hydrogen bonds vary at the smectic F–C transformation point, or perhaps the angles also vary. However, in both instances the potential function of the hydrogen bond will be influenced. This explains the discontinuity of $\Delta \nu$ (OH) at the smectic C–smectic F transformation point and the changed variation of this value as a function of temperature.

We can unambigously exclude any influence of an OH–O hydrogen bond between the alcohol and the oxygen atom of the ether, as the OH wavenumber of 2-octanol in n-$C_4H_9OC_6H_5$ as a solvent at 90 °C is about 3620 cm^{-1}, which is far from the position of the OH band given in Fig. 1.

There is complete disagreement when we consider the differences in the solution enthalpies deduced from the slopes of the retention volume plots and compare them with the variations of the interaction energy that could be obtained from a tentative use of the Badger–Bauer relationship[5]. Evidently the hydrogen bond enthalpy does not play a dominant role in the interaction between the mobile and the stationary phases in this instance.

In an additional study, we used the CO stretching frequency of camphor, also dissolved in I, to examine the intermolecular interactions in the phases of interest. The spectroscopic effects here should clearly be lower, because in this instance only a dipole–dipole interaction is involved, instead of a hydrogen bond. The frequencies of this test band are also given in Fig. 1.

CONCLUSION

Overall, we obtained analogous results in GC and IR spectroscopy in the work described here. We shall extend our investigations to a variety of other compounds.

REFERENCES

1 H. Kelker, *Ber. Bunsenges. Phys. Chem.*, 67 (1963) 698.
2 W. Ecknig, H. Kriegsmann and H. Rotzsche, *Ber. Bunsenges. Phys. Chem.*, 71 (1967) 587.
3 H. Zaschke, to be published.
4 D. Demus, S. Diele, M. Klapperstück, V. Link and H. Zaschke, *Mol. Cryst. Liq. Cryst.*, 15 (1971) 161.
5 R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, 5 (1938) 839.