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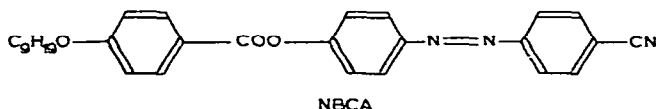
Re-entrant liquid crystals as liquid phase in gas-liquid chromatography

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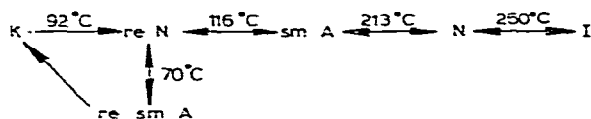
Liquid crystals are a unique stationary liquid phase in gas-liquid chromatography (GLC) because they show interesting solvent properties due to the rod-like shape and the ordered arrangement of their molecules. Solutes can be separated primarily on the basis of their length-to-width ratios and molecular planarity¹⁻³. Since the first report by Kelker⁴ a number of liquid crystalline compounds have been used as the stationary liquid phase in GLC. It is of great importance for practical application to find liquid crystals exhibiting a wide mesomorphic temperature range and a high selectivity for the solutes. Recently it has been indicated that the smectic A and C phases as well as the nematic state show a relatively high solubility and unique selective affinity for the various positional isomers⁵⁻⁷. From this viewpoint it is of interest to apply so-called re-entrant nematic liquid crystals as the stationary phase in GLC because they are structurally characterized by two thermally stable terminal groups and long alkoxy(alkyl) and cyano substituents. They also exhibit smectic A or smectic C phases as well as the nematic state over a wide temperature range⁸⁻¹¹. In this report we describe a study of the separation of some positional isomers by the use of a re-entrant nematic liquid crystal 4-(4-nonyloxybenzoyloxy)-4'-cyanoazobenzene (NBCA) as the stationary phase.



EXPERIMENTAL

Materials

The re-entrant nematic liquid crystal (NBCA) was synthesized by esterification of 4-nonyloxybenzoyl chloride and 4-hydroxy-4'-cyanoazobenzene according to the published method¹² and recrystallized twice from ethyl acetate to give constant transition temperatures. The phase transition temperatures and the liquid crystal textures were determined by using a differential scanning calorimeter and an ordinary polarizing microscope equipped with a Mettler FP microfurnace. The liquid crystalline phases and their transition temperatures were determined as follows:



The transition temperatures obtained are in good agreement with the reported data^{12,13}.

The solutes chosen were GLC pure and used without further purification.

Apparatus and procedure

The support material was 100–120 mesh Chromosorb W HP; it was coated with the liquid crystalline compound NBCA by using chloroform as solvent, followed by gradual elimination of the solvent by evaporation. The concentration of liquid phase in the packing of the coated support was 2.5% (w/w). The packing was re-sieved and then packed into 1.5 m × 3 mm I.D. glass columns. Prior to use the columns were conditioned for 2 h at 240°C, 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. The flow-rate of the carrier gas (nitrogen) was measured using a soap-bubble flow-meter. Methane was used to estimate the dead time. The solute mixtures to be separated were dissolved in benzene or carbon disulphide and were injected with a Hamilton 701 10- μ l syringe, using the smallest detectable sample volume.

RESULTS AND DISCUSSION

Fig. 1A shows a complete separation of fluorene, phenanthrene and anthracene solutes observed at 220°C in the nematic state of NBCA. A separation of mixtures of isomeric dibromobenzenes and chloroacetophenones obtained at 140°C in the smectic A state is shown in Fig. 1B. As expected, the retention time for the isomer with the more rod-like shape (*p*-isomer) is longer than that for the *m*-isomer. It is well recognized that a liquid crystal shows a selective affinity towards rod-like solutes, as these should be able to fit better into its lattice with parallel molecular alignment. The re-entrant liquid crystal NBCA exhibits a re-entrant nematic state, and another re-entrant smectic A state monotropically occurred as well as the normal nematic and smectic A phases. Fig. 2A shows a separation of three xylene isomers observed in the re-entrant nematic state. It should be noted that the order of elution of the xylene isomers observed in the re-entrant nematic state is in accord with that found on other liquid crystal columns^{14,15}, *i.e.* the more rod-like *p*-isomer is retained longer than the *m*-isomer.

Both the differential scanning calorimetry and the polarizing microscopic observations indicate that the pure liquid crystal NBCA crystallizes at *ca.* 67°C on cooling, and thus the mesomorphic temperature range of the re-entrant smectic A state is very short. However, it should be stressed that the NBCA deposited on the support can be supercooled at about room temperature. Fig. 2B shows the separation of the isomeric xylene solutes obtained at 55°C in the supercooled re-entrant smectic A state. It is also noteworthy that no separation of the xylene isomers was achieved in

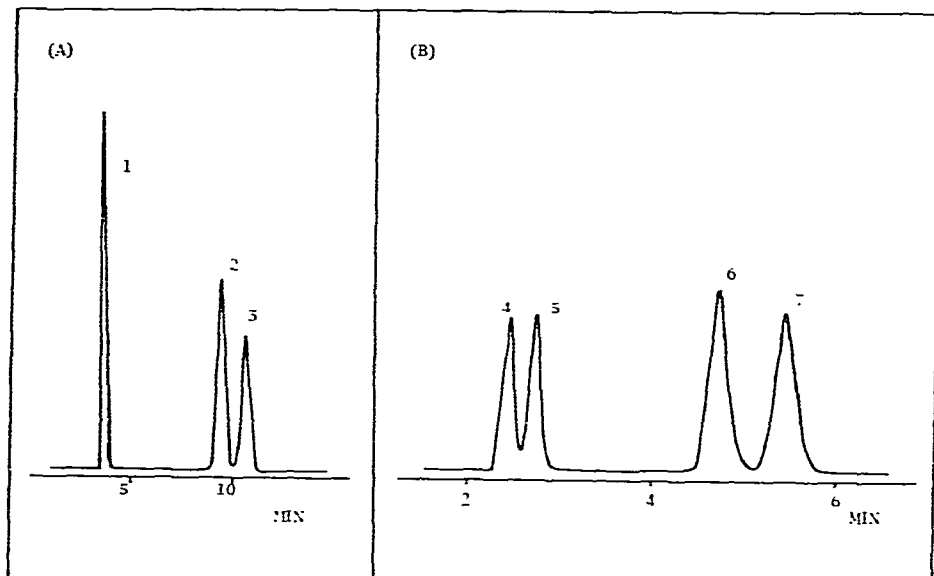


Fig. 1. Gas chromatograms of a mixture of fluorene, phenanthrene and anthracene observed at 220°C in the nematic state (A), and of dibromobenzenes and chloroacetophenones observed at 140°C in the smectic A state (B). Injection temperature, 250°C; flame ionization detector; nitrogen flow-rate, 25 ml/min. Peaks: 1 = fluorene; 2 = phenanthrene; 3 = anthracene; 4 = *m*-dibromobenzene; 5 = *p*-dibromobenzene; 6 = *m*-chloroacetophenone; 7 = *p*-chloroacetophenone.

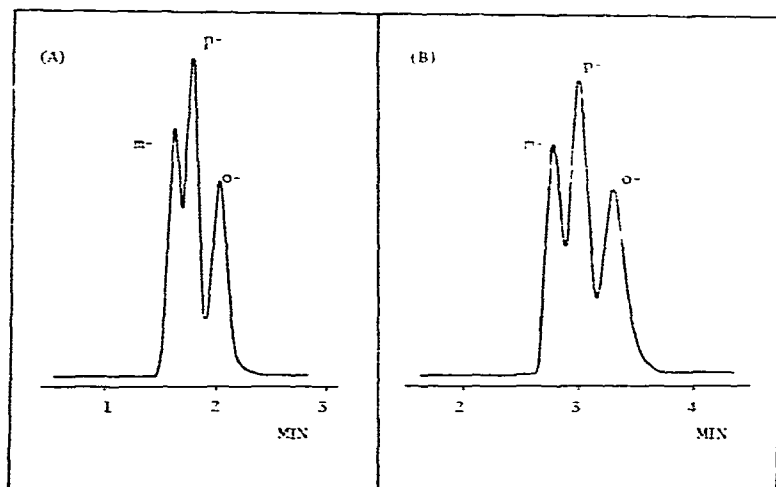


Fig. 2. Gas chromatograms of a mixture of three xylene isomers observed at 75°C in the re-entrant nematic state (A), and at 55°C in the supercooled re-entrant smectic A state (B). Injection temperature, 200°C.

the fully crystallized state, which was attained by allowing the sample to stand overnight at room temperature. The magnitude of the separation and the order of elution indicate that all four liquid crystalline states of NBCA have a relatively high solubility and a unique selectivity for several positional isomers.

Fig. 3 shows the variation in retention volume with temperature for some of the solutes studied. An almost continuous and linear change in the retention volume occurs over the whole range of mesomorphic temperatures, except for the super-cooled re-entrant smectic A state. This indicates that large variations in solubility do not occur at any of the liquid crystalline phase transitions of NBCA. This behaviour is not what is to be expected, because a maximum in the relationship between the retention volume and the temperature has been usually observed on the other liquid crystal columns in the vicinity of the mesomorphic transition, owing to a distinct change in the free energy of solution of the solutes^{2,16,17}. No abrupt change with temperature in the retention volume can be reasonably explained by taking account of the molecular order and transition heat in the case of liquid crystals showing re-entrant phases. X-Ray diffraction patterns and magnetic measurements indicate that

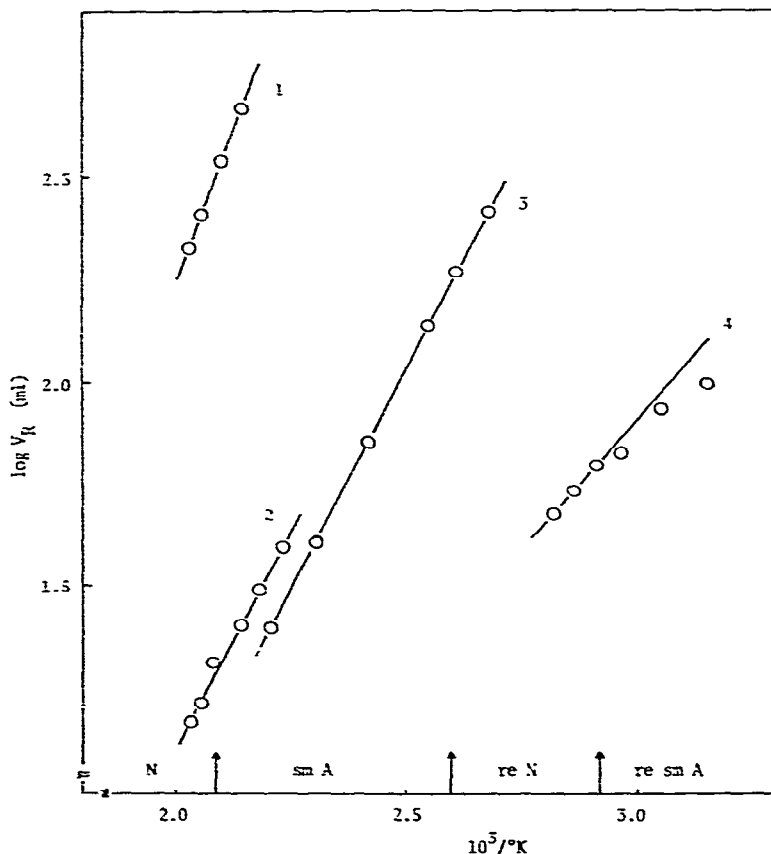


Fig. 3. Relationship between log retention volume (V_R) and $10^3/T$ for phenanthrene (1), *m*-chloroacetophenone (2), *p*-dibromobenzene (3) and *o*-xylene (4).

no abrupt change in the molecular orientational order at the phase transitions is found for the re-entrant liquid crystalline compounds, although a bilayer structure is formed owing the presence of a highly polar cyano group at one end of the molecule^{18,19}. In addition, the enthalpy change for the liquid crystalline transitions including the re-entrant phase has been found to be in general small compared with those obtained for the other mesomorphic transitions^{20,21}. Such a characteristic molecular order found for the re-entrant liquid crystals is likely to give rise to the continuous change in the retention volume with temperature that was observed in this study. The deviation of the retention volume from the linear change obtained in the supercooled re-entrant smectic A state seems to be associated with the monotropic transition.

In conclusion, we believe that the re-entrant liquid crystals are likely to be useful as the stationary liquid phase in GLC because they exhibit a wide mesomorphic temperature range and a unique selectivity for a mixture of solute molecules, as well as a linear change in retention volume with temperature.

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