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Journal of Chromatography A, 1087 (2005) 52–56
JOURNAL OF CHROMATOGRAPHY A
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# Analytical performances of two liquid crystals and their mixture as stationary phases in capillary gas chromatography

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Available online 23 June 2005

**Abstract**

Comparative gas chromatographic applications of two new liquid crystals called $LC_a$ and $LC_b$ and their equimolar mixture $LC_{a+b}$ were investigated. The thermal properties of $LC_a$, $LC_b$ and $LC_{a+b}$ were established with differential scanning calorimetry (DSC) and polarizing microscopy. Differential scanning calorimetry of $LC_{a+b}$ showed that the melting or clearing temperature was intermediate between the corresponding temperatures of the pure compounds. Polarizing microscopy showed that the liquid crystal phase of A + B was nematic. The chromatographic separation abilities $LC_a$, $LC_b$ and $LC_{a+b}$ were studied using fused silica capillary columns. Interesting analytical performances were obtained: isomeric separation of aromatics, polyaromatics, phenols.


*Keywords:* Gas chromatography; Liquid crystal mixture; Differential scanning calorimetry; Analytical performances

## 1. Introduction

The use of liquid crystals as stationary phases in gas liquid chromatography was reported in different works [1–13]. Liquid crystalline stationary phases are useful in separating close-boiling isomers which are very difficult or impossible to separate on classical stationary phases. These interesting solvent properties are due to the rode-like shape and the ordered arrangement of their molecules. The usefulness of liquid crystals stationary phases for the separation of various compounds has been reviewed by Witkiewicz [14,15]. Mixtures of liquid crystals with classical stationary phases such as silicones did not offer an essential improvement of the individual stationary phases analytical performances [16–21]. Some papers reported the use of liquid crystals mixtures as stationary phases in gas chromatography with better performances than the pure corresponding compounds [16,17,22,23].

In this paper, the analytical performances of the liquid crystals called $LC_a$, $LC_b$ (chemical structures shown in Fig. 1) and their equimolecular mixture $LC_{a+b}$ were compared. We can note that $LC_a$, $LC_b$ differ in the part 2 in their molecular structure.

## 2. Experimental

### 2.1. Reagents

All chemicals used for the liquid crystals synthesis were obtained from Janssen Chemica (The Netherlands). Compounds used in analytical study were purchased from Chrompack (The Netherlands).

### 2.2. Differential scanning calorimetry (DSC) analysis

Differential scanning calorimetry measurements were performed using TA 2920 device (TA Instruments, New Castle,

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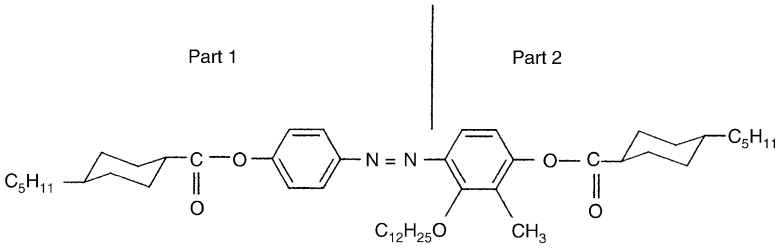
doi:10.1016/j.chroma.2005.05.022

***LC$_a$*** : 4-{(*E*)-[4-[[(*trans*-4-pentylcyclohexyl)carbonyl]oxy]-3-methyl-2-dodecyloxy phenyl]diazenyl}phenyl [(*trans*-4-pentylcyclohexyl)carboxylate]




***LC$_b$*** : 4-{(*E*)-[ 4-ethoxybenzyloxy -3-methyl-2-decyloxy phenyl]diazenyl}phenyl [(*trans*-4-pentylcyclohexyl)carboxylate]

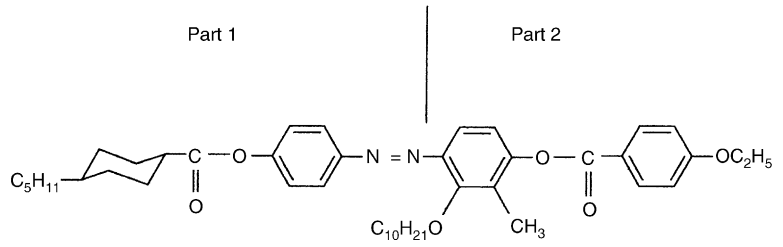



Fig. 1. Chemical structures of $LC_a$ and $LC_b$.

USA). All scans were carried out using a heating rate of 10 °C min$^{-1}$. For $LC_{a+b}$, the operation was made twice.

### 2.3. Microscopy

Heating of $LC_a$, $LC_b$ and $LC_{a+b}$ was also followed by microscopy using a polarizing microscope (Olympus) with a rate of 10 °C min$^{-1}$ beginning from the ambient to 300 °C.

### 2.4. Gas chromatography

An HP6890 series GC system gas chromatograph equipped with dual flame ionization detector and split/splitless injector was used with an HP3395 integrator. High purity nitrogen was used as carrier gas.

Fused silica column with intermediate polarity (30 m × 0.25 mm I.D.) from Supelco (Bellefonte, PA, USA) was coated dynamically with liquid crystal $LC_a$, $LC_b$ or $LC_{a+b}$ (10% in dichloromethane). Deactivation of the column inner surface was made with methylphenyl silylating reagent.

The column was then conditioned overnight at 10 °C above the nematic-isotropic transition temperature.

## 3. Results and discussion

### 3.1. DSC and microscopy results

The $LC_a$, $LC_b$ and $LC_{a+b}$ characteristic parameters of the phase transitions are collected in Table 1. The analysis of the data reveals that:

(i) There are no significant differences between the data of DSC and microscopy.
(ii) The melting or clearing temperatures of $LC_{a+b}$ were intermediate between the corresponding temperatures of $LC_a$ and $LC_b$.

Microscopy was also used to prove that the obtained liquid crystal phases are nematic.

### 3.2. Analytical applications

Table 2 reports the number of theoretical plates corresponding to the three physical states of the stationary phases. However, the efficiency is the highest in the nematic range. The columns exhibit a remarkable high efficiency, probably due to the liquid crystals molecular structures, and to the way in which the capillary was coated.

Corresponding data of the solutes eluted on $LC_a$, $LC_b$ and $LC_{a+b}$ are presented in Table 3 as relative retentions. It was difficult to compare analytical performances of $LC_a$, $LC_b$ and $LC_{a+b}$ when they were used to eluate aromatic hydrocarbons because $LC_a$ was in the nematic state and $LC_b$ and $LC_{a+b}$

Table 1
Transition temperatures (°C) of $LC_a$, $LC_b$ and $LC_{a+b}$ found by DSC and microscopy

| | Solid → Nematic | | Nematic → Isotropic | |
|---|---|---|---|---|
| | DSC | Microscopy | DSC | Microscopy |
| $LC_a$ | 58.9 | 59 | 208.3 | 209 |
| $LC_b$ | 83 | 83.5 | 211.6 | 212 |
| $LC_{a+b}$ | 62 | 62.5 | 203.6 | 203 |

Table 2
Plates numbers of $LC_a$, $LC_b$ and $LC_{a+b}$ in the anisotropic, nematic and isotropic state

| Stationary phase | State | Solutes | Temperature (°C) | Plates number (m) |
|---|---|---|---|---|
| | Solid | 1,2-Diethylbenzene | 50 | 2700 |
| $LC_a$ | Nematic | *p*-Cresol | 100 | 3500 |
| | Isotropic | Anthracene | 215 | 2950 |
| | Solid | 1,2-Diethylbenzene | 50 | 2600 |
| $LC_b$ | Nematic | *p*-Cresol | 100 | 3650 |
| | Isotropic | Anthracene | 215 | 3150 |
| | Solid | 1,2-Diethylbenzene | 50 | 2500 |
| $LC_{a+b}$ | Nematic | *p*-Cresol | 100 | 3300 |
| | Isotropic | Anthracene | 210 | 2800 |

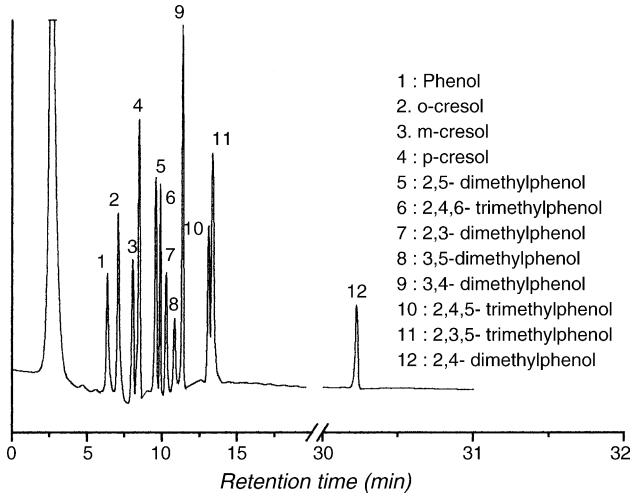



Fig. 2. Chromatogram of phenols on $LC_{a+b}$, column temperature was programmed from 70 °C at 4 °C $min^{-1}$.

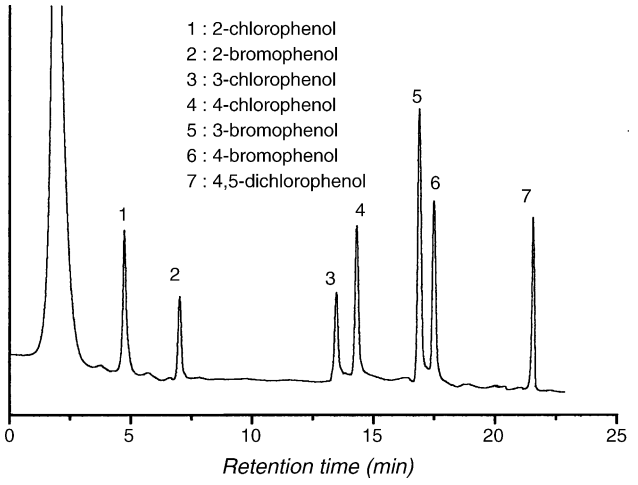



Fig. 3. Chromatogram of halophenols on $LC_{a+b}$, column temperature was programmed from 70 °C at 4 °C $min^{-1}$.

were solid. However, the three stationary phases separated positional isomers of xylenes and diethylbenzenes.

In the case of polyaromatic hydrocarbons, it was interesting to orient the discussion on the separation of phenanthrene and anthracene by the three stationary phase. The two compounds were completely separated only by $LC_a$. It is well known that, in the nematic phase, the more elongated isomer (anthracene) is more retained. Elution temperatures for the two compounds on $LC_b$ and $LC_{a+b}$ corresponded to nematic-liquid transition. $LC_{a+b}$ and $LC_b$ behaviours seem to be near.

Table 3
Relative retention times (*r*) of the tested solutes (S: solid, N: nematic, I: isotropic)

| Compound | $LC_a$ | | $LC_b$ | | $LC_{a+b}$ | |
|---|---|---|---|---|---|---|
| | State | *r* | State | *r* | State | *r* |
| Aromatic hydrocarbons[a] | | | | | | |
| Ethylbenzene | N | 0.4087 | S | 0.95035 | S | 1.75484 |
| *m*-Xylene | N | 0.54348 | S | 0.0991 | S | 0.95484 |
| *p*-Xylene | N | 0.55217 | S | 0.10853 | S | 0.97419 |
| *o*-Xylene | N | 0.70435 | S | 0.12571 | S | 0.97419 |
| Isopropylbenzene | N | 1 | S | 1 | S | 1 |
| 1,2,4-Trimethylbenzene | N | 0.92174 | S | 0.30086 | S | 1.76129 |
| 1,3,5-Trimethylbenzene | N | 0.9087 | S | 0.23046 | S | 1.48387 |
| 1,2,3-Trimethylbenzene | N | 1.33478 | S | 0.38089 | S | 2 |
| 1,2-Diethylbenzene | N | 1.41739 | S | 0.37335 | S | 2.12903 |
| 1,3-Diethylbenzene | N | 1.25217 | S | 0.32956 | S | 1.86452 |
| 1,4-Diethylbenzene | N | 1.35217 | S | 0.39996 | S | 1.71613 |
| Isobutylbenzene | N | 0.91304 | S | 0.24178 | S | 1.44516 |
| Tertiobutylbenzene | N | 0.8 | S | 0.19045 | S | 1.27097 |
| Allylbenzene | N | 1.17826 | N | 0.37712 | N | 1.76129 |

Table 3 (*Continued*)

| Compound | $LC_a$ | | $LC_b$ | | $LC_{a+b}$ | |
|---|---|---|---|---|---|---|
| | State | *r* | State | *r* | State | *r* |
| Polyaromatic hydrocarbons[b] | | | | | | |
| Naphthalene | N | 0.17953 | N | 0.04583 | N | 0.06443 |
| 1-Methylnaphthalene | N | 0.30162 | N | 0.09074 | N | 0.25129 |
| 2-Methylnaphthalene | N | 0.27648 | N | 0.10678 | N | 0.20554 |
| 1,6-Dimethylnaphthalene | N | 0.4991 | N | 0.23052 | N | 0.32539 |
| Bromonaphthalene | N | 0.614 | N | 0.32447 | N | 0.40399 |
| Phenanthrene | N | 1 | N | 1 | N | 1 |
| Anthracene | N | 1.49731 | L | 1.0802 | L | 1.0567 |
| Acenaphthene | N | 0.5781 | N | 0.31439 | N | 0.40593 |
| Acenaphthylene | N | 0.55835 | N | 0.29285 | N | 0.37371 |
| Fluorene | N | 0.85458 | N | 0.52796 | N | 0.59923 |
| Fluoranthene | I | 1.83842 | L | 1.6989 | L | 2.39755 |
| 1,2-Benzofluorene | I | 1.45422 | L | 2.28552 | N | 0.63338 |
| Pyrene | I | 1.8833 | L | 1.87672 | L | 2.94394 |
| Phenolic compounds[c] | | | | | | |
| Phenol | N | 0.88 | N | 0.94 | N | 0.88 |
| *o*-Cresol | N | 1 | N | 1 | N | 1 |
| *m*-Cresol | N | 1.27 | N | 1.21 | N | 1.18 |
| *p*-Cresol | N | 1.24 | N | 1.32 | N | 1.22 |
| 2,3-Dimethylphenol | N | 1.58 | N | 1.73 | N | 1.55 |
| 2,4-Dimethylphenol | N | 5.30 | N | 7.86 | N | 4.87 |
| 2,5-Dimethylphenol | N | 1.42 | N | 1.57 | N | 1.42 |
| 3,4-Dimethylphenol | N | 1.87 | N | 1.37 | N | 1.72 |
| 3,5-dimethylphenol | N | 1.69 | N | 1.80 | N | 1.59 |
| 2,4,5-Trimethylphenol | N | 2.00 | N | 2.39 | N | 2.01 |
| 2,4,6-Trimethylphenol | N | 1.46 | N | 1.59 | N | 1.47 |
| 2,3,5-Trimethylphenol | N | 2.12 | N | 2.44 | N | 2.02 |
| 2-Bromophenol | N | 0.95 | N | 0.66 | N | 0.99 |
| 3-Bromophenol | N | 3.02 | N | 3.39 | N | 2.64 |
| 4-Bromophenol | N | 3.04 | N | 3.49 | N | 2.74 |
| 2-Chlorophenol | N | 0.70 | N | 0.50 | N | 0.61 |
| 3-Chlorophenol | N | 2.38 | N | 2.56 | N | 2.07 |
| 4-Chlorophenol | N | 2.41 | N | 2.65 | N | 2.21 |
| 4,5-Dichlorophenol | N | 4.03 | N | 5.07 | N | 3.42 |

[a] Column temperature: 60 °C.
[b] Column temperature was programmed from 120 °C at 4 °C $min^{-1}$.
[c] Column temperature was programmed from 70 °C at 4 °C $min^{-1}$.

The comparison between the chromatographic properties of $LC_a$, $LC_b$ and $LC_{a+b}$ can be extended with the positional isomers of phenols and their derivatives. Fig. 2 shows the separation of several phenols on $LC_{a+b}$. In the conditions used, $LC_a$, $LC_b$ and $LC_{a+b}$ were nematic. Complete separation of cresols were observed with $LC_a$, $LC_b$ and $LC_{a+b}$, and the more elongated isomer (the *para*) was more retained by $LC_b$ and $LC_{a+b}$. When the halophenols were eluted $LC_{a+b}$ and $LC_b$ behaviors were similar. On the three stationary phases, the more elongated isomer *p*-bromo or *p*-chlorophenols gave higher retention times when they were compared to their corresponding *o*- or *m*-isomers. However, *p*- and *m*-bromo or *p*- and *m*-chlorophenols were not totally separated on $LC_a$, the resolution of these isomers were observed in the case of $LC_{a+b}$ (see Fig. 3) and $LC_b$.

All the shown examples demonstrated that $LC_{a+b}$ and $LC_b$ behaviors were quite similar. It seems that when $LC_a$ and $LC_b$ were mixed, the part 2 $LC_b$ influenced significantly the chromatographic properties of their mixture $LC_{a+b}$.

## 4. Conclusion

In this study, the analytical performances of two liquid crystals $LC_a$, $LC_b$ and their mixture $LC_{a+b}$ were compared. $LC_a$, $LC_b$ differ in the part 2 in their molecular structure. $LC_a$, $LC_b$ and their mixture $LC_{a+b}$ are convenient stationary phases to separate different kinds of solutes such as aromatics, polyaromatic hydrocarbons, phenols. It seems that the nematic mixture $LC_{a+b}$ had the same behavior of the pure nematic liquid crystal $LC_b$ particularly when *m*- and *p*-cresols, chlorophenols and bromophenols were chromatographied. It appeared that the part 2 of $LC_b$ influenced mainly the chromatographic properties of $LC_{a+b}$.

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