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Analytical Study of Three Liquid Crystals Used as Stationary Phases in Gas Chromatography

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The investigation of the analytical properties of three liquid crystals 5-(4-methoxyphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole (phase I), 5-(4-(carboxymethylphenyl)-azophenyl)-2-butyl-thio-1,3,4-oxadiazole (phase II) and 5-(4-(propoxyphenyl)-azophenyl)-2-butyl thio-1,3,4-oxadiazole (phase III) was carried out by gas chromatography using glass capillary columns. For this purpose, 79 solutes belonging to various families were injected. Among these compounds which have different polarities and volatilities, we studied the retention of 16 alkylbenzenes, 7 polar substituted benzenes, 24 polar and non-polar phenols, 12 substituted naphthalenes and 20 constituents of natural products. Comparison of the retention data of the studied components has shown that phase II allowed a better separation than the other phases. The three liquid crystalline materials show a good separation of the studied isomers except for xylene.

Key Words: Gas chromatography, Stationary phase, Liquid crystals.

INTRODUCTION

Liquid crystals are used as stationary phases in gas chromatography[1,2]. A large number of articles have been devoted to the analytical performances of liquid crystals in various applications, particularly for the separation of specific isomers[3-7].

These phases can either be monomeric[8] or polymeric[9], the latter being more thermally stable. The physical and chemical properties of liquid crystal polymers have been studied by various analytical techniques[10,11].

The retention mechanism on this kind of stationary phases is complex and temperature dependent. In addition to the polarity and the volatility of the solutes, their geometry and molecular structure play a role in the interactions with the liquid crystalline stationary phase.

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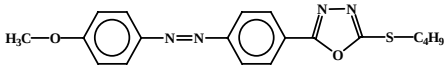
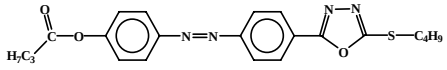
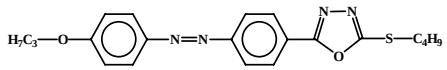
The influence of temperature on the selectivity of mesophases has been investigated by many researchers[12-14]. Soja *et al.*[15,16] showed that liquid crystals as stationary phases in gas chromatography possess shape-selective separation properties for structural and geometrical isomers of hydrocarbons. Later, Sojak *et al.*[17] studied the separation of diastereomeric C_8-C_{20} alkanes using mesogenic stationary phases in glass capillary columns. This kind of columns have been successfully used for the separation of aromatic hydrocarbons and their derivatives[18-21], phenols and their derivatives[22], volatile aroma compounds[23-25], disubstituted benzene isomers as well as various *cis*/*trans* isomers[26-30]. The present investigation aims to compare the gas chromatographic behaviour of three synthesized monomeric liquid crystals which have the same basic structure with different substituents: methoxy for phase I, butyryloxy for phase II and propoxy for phase III. This study was carried out using different temperature programmes. 79 Solutes belonging to various families having different polarities and volatilities were injected.

EXPERIMENTAL

Table-1 shows the molecular structure of the three synthesized liquid crystals used as stationary phase.

TABLE-1
NAME, FORMULA AND TRANSITION TEMPERATURES
OF THE THREE PHASES

	Name	Formula	Transition temperatures
Phase I	5-[4-(*p*-methoxyphenyl)-azophenyl]-2-butylthio-1,3,4-oxadiazole		K → N : 112°C N → I : 155°C
Phase II	5-[4-(*p*-butyloxyphenyl)-azophenyl]-2-butylthio-1,3,4-oxadiazole		K → N : 130°C N → I : 150°C
Phase III	5-(4-(*p*-propoxyphenyl)-azophenyl)-2-butylthio-1,3,4-oxadiazole		K → N : 111°C N → I : 152°C

(K: crystalline, N: nematic, I: isotropic)

Three glass capillary columns were prepared by impregnation of the three liquid crystals using the following conditions: (a) column dimension:

23 m long, 0.3 mm internal diameter, (b) inner glass surface was treated by hydrochloric acid and (c) dynamic method (carbon tetrachloride solution).

The gas chromatographic measurements were performed on a Perkin Elmer Auto System XL gas chromatograph equipped with: (i) split-splitless manual injector at 250°C in split mode (split ratio: 50), (ii) flame ionization detector at 250°C, (iii) Perkin Elmer Nelson model 1022 integrator, (iv) Okidata Microline 320 printer and (v) argon as carrier gas.

The chromatographic conditions for the three columns are listed in Table-2.

TABLE-2
OPERATING CONDITIONS

	Column I	Column II	Column III
Flow rate (mL/mn)	1.45	1.38	1.03
Inlet pressure (psi)	6.70	3.30	5.80

In order to allow the comparison between the chromatographic behaviour of the three liquid crystals, each solute was injected in triplicate on the three columns (1 µL) (Tables 3a-b).

TABLE-3a
RETENTION TIMES OF DIFFERENT COMPOUNDS ON THE THREE CAPILLARY COLUMNS

Compound	Phase 1		Phase II		Phase III	
	t_R (min)	T (°C)	t_R (min)	T (°C)	t_R (min)	T (°C)
Benzene derivatives						
m-Xylene	3.40				4.41	
p-Xylene	3.40				4.41	
Cumene	3.49		4.16		4.53	
o-Xylene	3.49				4.53	
Allylbenzene	3.76		4.16		4.53	
t-Butylbenzene	3.76	55°C (6 min) then 9°/min to 160°C	5.99	110°C (8 min) then 17°/min to 170°C	4.78	100°C (5.5 min) then 9°/min to 170°C
1,2,4-Trimethylbenzene	3.96		4.35		5.18	
iso-Butylbenzene	3.96		3.98		4.92	
pseudo-Cumene	3.96		4.35		5.18	
1,2,3-Trimethylbenzene	4.29		4.52		5.30	
1,2-Diethylbenzene	4.29		4.35		5.54	
1,3-Diethylbenzene	4.38		4.52		5.30	
1,2,4,5-Tetramethylbenzene	5.61		5.28		6.87	
Hexylbenzene	8.39		6.44		8.82	
Hexamethylbenzene	14.75		12.17		16.75	
Phenyldecane	18.55		15.40		21.33	
1,4-Dibromobenzene	9.23	60°C (6 min) then 9°/min to 170°C		130°C (10 min) then 10°/min to 170°C	27.56	80°C (5 min) then 10°/min to 170°C
Ethoxybenzene	9.23				5.75	
Nitrobenzene	9.23		8.41		8.68	
Phenylethanol	12.18		7.92		9.60	
Trimethoxybenzene	18.91		16.36		44.85	
Hexachlorobenzene	23.58		26.66		53.01	
Chlorobenzene	7.63		6.36		7.68	

Compound	Phase 1		Phase II		Phase III	
	t_R (min)	T (°C)	t_R (min)	T (°C)	t_R (min)	T (°C)
Phenols						
2,4,6-Trimethylphenol	16.25		9.47		21.90	
2,6-Dimethylphenol	16.25		9.09		16.43	
2,3,5,6-Tetramethylphenol	21.33		7.83		25.18	
2,5-Dimethylphenol	23.88		9.84		21.78	
2,4-Dimethylphenol	24.18		10.50		20.57	
2,3-Dimethylphenol	26.87		11.87		23.90	
3,5-Dimethylphenol	28.15	60°C	10.50		24.20	110°C
2,4,5-Trimethylphenol	31.24	(3 min)	13.11		30.07	(5 min)
2,3,5-Trimethylphenol	32.52	then	11.87	150°C	30.83	then
o-Cresol	9.63	2°/min	12.94		15.21	2°/min
p-Cresol	12.22	to	15.29		17.54	to 170°C
m-Cresol	12.59	130°C	16.47		17.94	
o-Ethylphenol	12.63		19.44		28.20	
p-Ethylphenol	17.37		23.61		32.70	
m-Ethylphenol	19.90		26.39		33.51	
o-Phenylphenol	27.06		18.71		46.81	
p-Phenylphenol	7.06		7.74		19.22	
m-Phenylphenol	5.88		6.45		16.47	

TABLE-3b
RETENTION TIMES OF DIFFERENT COMPOUNDS ON THE THREE CAPILLARY COLUMNS

Compound	Phase 1		Phase II		Phase III	
	t_R (min)	T (°C)	t_R (min)	T (°C)	t_R (min)	T (°C)
Benzene derivatives						
o-Nitrophenol	4.85		6.48		11.04	130°C (5 min) then 2°/min to 150°C
p-Chlorophenol	11.82	130°C	9.33		28.51	
tri-Nitrophenol	11.93	(10 min)	6.48		30.34	
4-Chloro-3-methylphenol	14.00	then	10.98	160°C	35.93	150°C (10 min) then 1°/min to 170°C
2,4-Dinitrophenol	20.74	10°/min	-		41.69	
2-Methyl-3-nitrophenol	29.47	to 170°C	-		-	
Naphthalenes						
cis-Decaline	4.59		4.86	60°C	6.28	
trans-Decaline	4.90	50°C (4	5.77	(7 min)	6.60	
1,2,3,4-Tetrahydronaphthalene	7.35	min)	10.94	then	8.82	
Naphthalene	10.72	then	14.40	5°/min	12.00	
2-Methylnaphthalene	15.39	15°/min	19.74	to	18.87	120°C
1-Methylnaphthalene	16.84	to 75°C	20.91	140°C	18.06	(10 min)
2,6-Dimethylnaphthalene	23.20		25.62		26.49	then
Chloro-Naphthalene	24.21	75°C	27.93	140°C	24.66	1.5°/min
1,6-Dimethylnapthalene	26.43	(25min)	29.46	(11min)	27.64	to 170°C
1,5-Dimethylnaphthalene	30.05	then	37.71	then	28.69	
2,3-Dimethylnaphthalene	30.05	15°/min	37.71	8°/min to	29.56	
Bromo-Naphthalene	35.99	to 170°C	39.72	170°C	35.25	

Compound	Phase 1		Phase II		Phase III	
	t_R (min)	T (°C)	t_R (min)	T (°C)	t_R (min)	T (°C)
Volatile aromatics compounds						
Camphene	3.60		6.15		5.47	
α-Terpinene	4.94		-		6.10	
Eucalyptol	5.66		6.93		5.65	
p-Cymene	5.66		7.21		6.10	
Limonene	5.66	35°C	6.93	45°C	5.65	
Fenchone	8.21	(6min)	16.57	(10	6.29	
Camphor	12.93	then	10.10	min)	7.09	
Citronellol	15.52	10°/min	15.48	then	7.09	
Linalol	19.95	to	16.57	10°/	6.29	
Decanol	20.86	150°C	25.78	min to	8.61	100°C
Menthol	29.50		21.51	90°C	10.25	
Neral	29.50	50°C	11.94		11.59	
Undecanol	31.40	(5min)	-	90°C (2	13.06	
Carvone	32.41	then	28.96	min) then	17.66	
Geranial	34.69	2°/min to	18.80	15°/min	16.15	
Nerol	40.70	110°C	27.85	to 170°C	13.06	
Geraniol	43.93		31.31		18.96	
α-Ionone	48.37		34.39		27.01	
β-Ionone	50.32		40.52		40.12	
Eugenol	56.31		41.67		47.00	

RESULTS AND DISCUSSION

Table-4 lists the injected compounds, the temperature programme used for each series and the measured retention times.

TABLE-4
RELATIVE RETENTION (α) OF *ORTHO*-, *PARA*- AND *META*-ISOMERS

Compounds	α		
	Phase 1	Phase II	Phase III
o-Cresol	1.00	1.00	1.00
p-Cresol	1.15	1.27	1.18
m-Cresol	1.18	1.30	1.27
o-Ethylphenol	1.00	1.00	1.00
p-Ethylphenol	1.16	1.38	1.21
m-Ethylphenol	1.19	1.42	1.36
m-Phenylphenol	1.00	1.00	1.00
p-Phenylphenol	1.17	1.20	1.20
o-Phenylphenol	4.60	2.90	2.84
m-Xylene	1.00	1.00	1.00
o-Xylene	1.03	-	1.03
p-Xylene	1.00	-	1.00

Benzene derivatives: For xylene isomers, *meta* and *para* homologues are not separated on the three phases while the *ortho* is more retained on phases I and III. As expected, the retention increases with the number of methyl substituents, as for xylene, trimethylbenzene, tetramethylbenzene and hexamethylbenzene, following the same order than their respective boiling points. As for xylene isomers, it can be noticed that 1,2,3-trimethylbenzene is more retained than 1,2,4-trimethylbenzene on the three columns. Comparison of tetramethylbenzene isomers shows that the retention is correlated with the substitution degree of benzene ring and the alkyl group (Fig. 1). The following order has been observed:

t-butylbenzene > *i*-butylbenzene > diethylbenzene > tetramethylbenzene

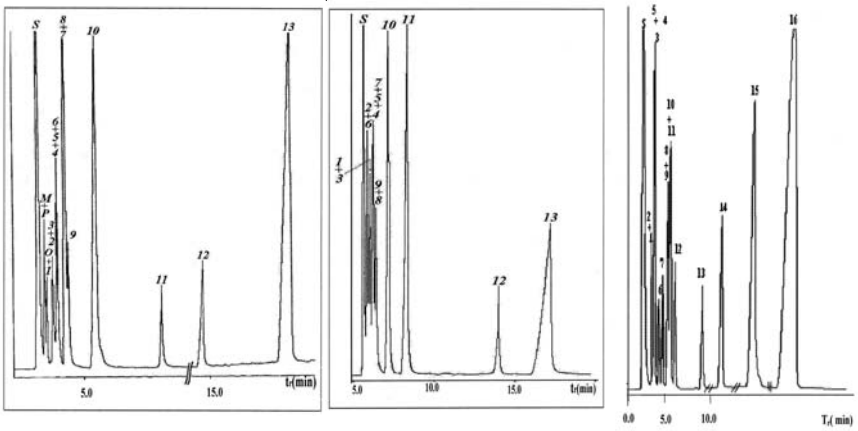


Fig. 1. Chromatograms of benzene derivatives P: *p*-xylene; M: *m*-xylene; O: *o*-xylene; 1: cumene; 2: *t*-butylbenzene; 3: allylbenzene; 4: 1,2,4-trimethylbenzene; 5: pseudo-cumene; 6: isobutylbenzene; 7: 1,2-diethylbenzene; 8: 1,2,3-trimethylbenzene; 9: 1,3-diethylbenzene; 10: 1,2,4,5-tetramethylbenzene; 11: phenylhexane; 12: hexamethylbenzene; 13: phenyldecane

The same order is obtained with hexylbenzene and hexamethylbenzene isomers, the latter being much more retained, due to its higher degree of substitution.

In the case of position isomers such as 1,2-diethylbenzene and 1,3-diethylbenzene, the former is more retained than the latter on column III while this order is reversed on columns I and II which show an abnormal behaviour. As for alkylbenzenes, the retention of polar substituted benzenes is clearly correlated to the number of polar substituents.

Phenols: Concerning the five dimethylphenol derivatives, 2,6-dimethylphenol is less retained on the three columns, while on column II 3,5-dimethylphenol is more retained and 2,4-dimethylphenol and 3,5-dimethylphenol are not separated. The retention of 2,3,5-trimethylphenol is greater then that of 2,4,5-trimethylphenol on columns I and III, while the former is eluted first on column II (Fig. 2).

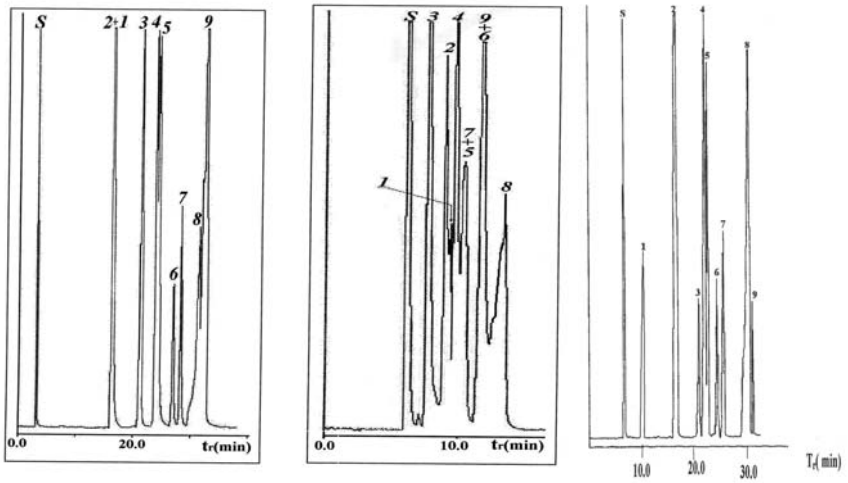


Fig. 2. Chromatograms of phenols 1: 2,4,6-trimethylphenol; 2: 2,6-dimethylphenol; 3: 2,3,5,6-tetramethylphenol; 4: 2,5-dimethylphenol; 5: 2,4-dimethylphenol; 6: 2,3-dimethylphenol; 7: 3,5-dimethylphenol; 8: 2,4,5-trimethylphenol; 9: 2,3,5-trimethylphenol

The elution order of cresol and ethylphenol isomers is also dependent on the alkyl position and is as follows : *o* < *p* < *m*. With polar substituted phenols, the retention time increases with the number of groups, such as for *o*-nitrophenol and trinitrophenol.

Naphthalenes: The mechanism of separation for methyl and dimethylnaphthalene isomers is complex[21,30,31]. For isomeric methylnaphthalenes, the main factor in determining retention is the symmetry of substitution[32]. 1-Methylnaphthalene and 2-methylnaphthalene are eluded in this order on column III and in the inverse order on the other two columns. The elution order observed for dimethylnaphthalenes on the three phases is the same:

2,6-dimethylnaphthalene < 1,6-dimethylnaphthalene <
1,5-dimethylnaphthalene < 2,3-dimethylnaphthalene

However, 1,5-dimethylnaphthalene is separated from 2,3-dimethylnaphthalene only on column III (Fig. 3).

The comparison of naphthalene with its hydrogenated homologues shows the same elution on the three liquid crystalline phases:

cis-decaline < *trans*-decaline < 1,2,3,4-tetrahydronaphthalene
< naphthalene

The influence of the molecular shape on retention is clearly noticed with *cis* and *trans*-decaline, the latter being more retained. The chromatographic behaviour of the three liquid crystals is comparable in different fields, particularly in the separation of volatile aromatic stereoisomers such as nerol and geraniol, α- and β-ionone (Figs. 4a-b).

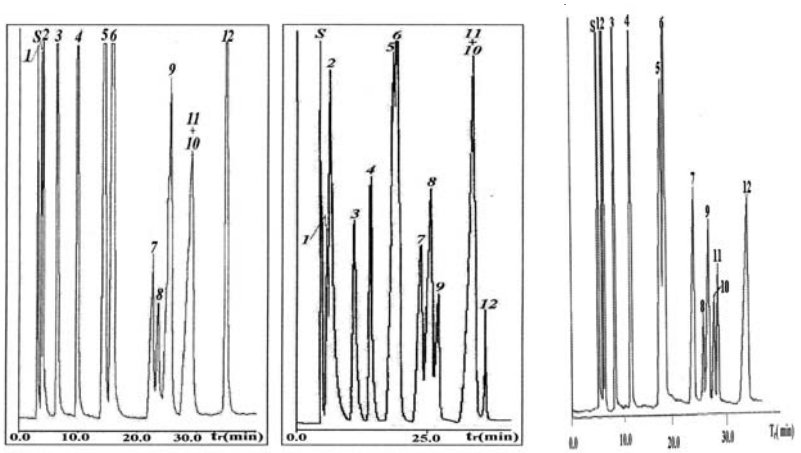


Fig. 3. Chromatograms of naphthalene derivatives 1: *cis*-decaline; 2: *trans*-decaline; 3: 1,2,3,4-tetrahydronaphthalene; 4: naphthalene; 5: 2-methylnaphthalene; 6: 1-methylnaphthalene; 7: 2,6-dimethylnaphthalene; 8: *chloro*-naphthalene; 9: 1,6-dimethylnaphthalene; 10: 1,5-dimethylnaphthalene; 11: 2,3-dimethylnaphthalene; 12: bromonaphthalene

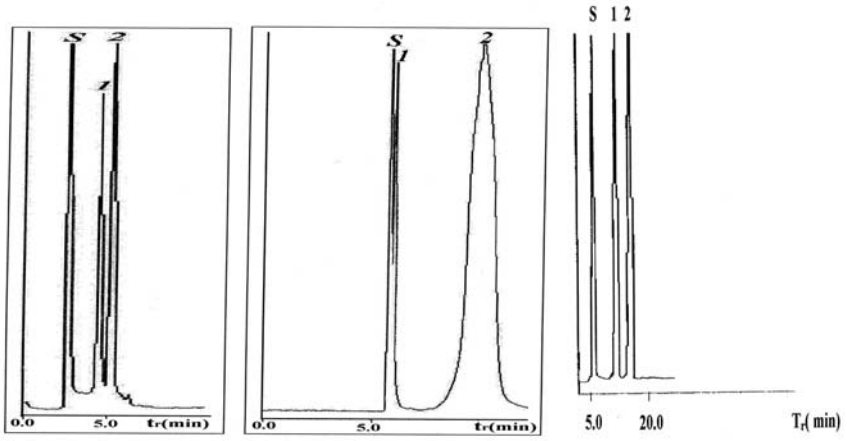


Fig. 4a. Chromatograms of citral isomers 1: neral (*cis*-citral); 2: geranial (*trans*-citral)

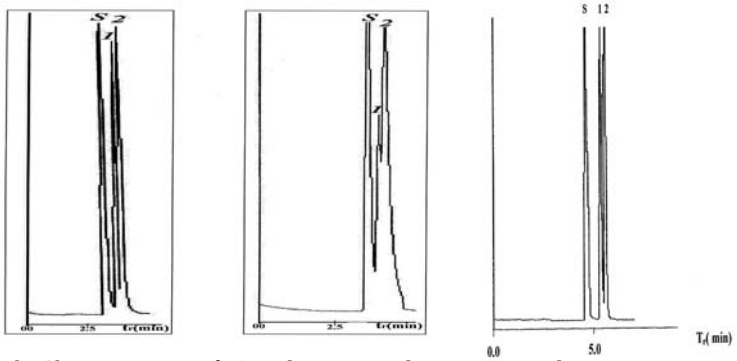


Fig. 4b. Chromatograms of *cis* and *trans*-Decaline 1: *cis*-Decaline; 2: *trans*-Decaline

Position isomers: Meta and para-cresol were partially separated in this order on the three columns while the ortho isomer is eluded first (Fig. 4c). The same behaviour was observed for ethylphenol isomers (Fig. 4d). But for the phenylphenols, the meta-phenylphenol is eluded for the para-phenylphenol and the ortho-phenylphenol.

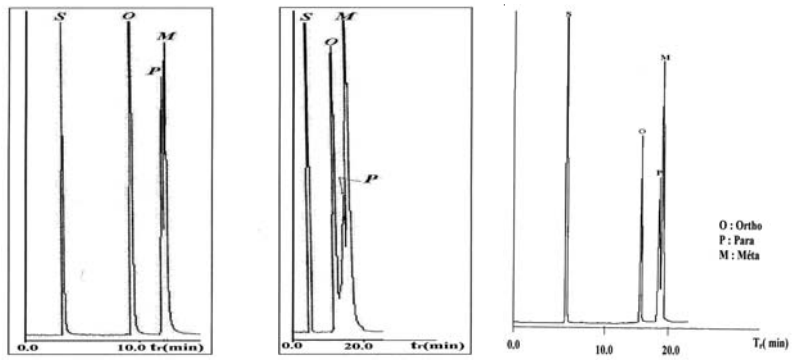


Fig. 4c. Chromatograms of cresol isomers, O: *o*-cresol; P: *p*-cresol; M: *m*-cresol

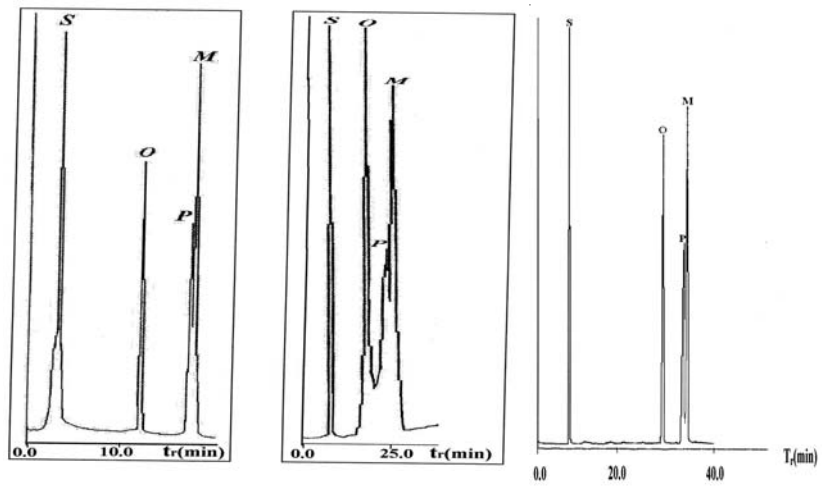


Fig. 4d. Chromatograms of ethylphenol isomers O: *o*-ethylphenol; P: *p*-ethylphenol; M: *m*-ethylphenol

No significant separation is observed between xylene isomers (Fig. 4e) while the retention measured in the case of phenol isomers is clearly different on the three liquid crystalline stationary phases. However, while the *o*-isomer is eluted first for cresol and ethylphenol, *o*-phenylphenol is more strongly retained then its *m*- and *p*-isomers This could be explained by the strong interactions between the two phenyl rings when the hydroxyl substituent is in *ortho*-position, hindering the molecule from the planar shape.

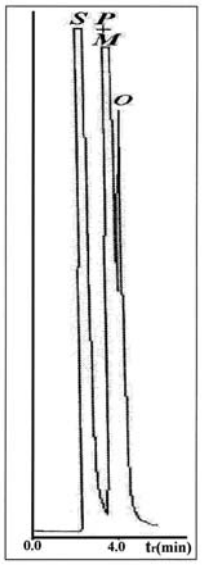


Fig. 4e. Chromatograms of xylene isomers O: *o*-xylene; P: *p*-xylene; M: *m*-xylene

Conclusion

The present work showed the comparative study of three synthesized liquid crystals used as stationary phase in capillary gas chromatography. For this purpose, 79 solutes were injected in programmed temperature. The retention times observed for the different solutes show a good efficiency for the three liquid crystalline phases which are able to separate a wide variety of compounds, such as alkylbenzenes, naphthalenes, phenols and monoterpenic components. The effect of the nature and number of substituents on the retention is clearly observed for all series. A good separation is obtained between position isomers in the case of polar substituents while the retention of alkyl-substituted compounds is closer; this fact indicates the importance of polar interactions between the solute and the studied stationary phases. The geometry of the molecule is also a determinant factor in the retention of each solute as it can be seen for several compounds such as decalines, phenylphenols and terpenic stereoisomers.

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