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Gas Chromatographic Separation of Phenol Derivatives by Schiff-Base Liquid Crystalline Stationary Phases

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The chromatographic behaviour of liquid crystalline compounds benzylidene-p-aminobenzoic acid and 4-(p-methyl benzylidene)-p-aminobenzoic acid as stationary phases for the separation of dimethylphenol isomers was investigated. These isomers were analysed on benzylidene-p-aminobenzoic acid within a nematic range of 169-194 °C with a temperature interval of 5 °C. Better peak resolution was at a column temperature of 190 °C. The analysis was repeated on a 4-(p-methyl benzylidene)-p-aminobenzoic acid column at a nematic temperature of 256 °C, which represented the end of the nematic range, and gave the optimum peak resolution. It was found that isomer better separation was obtained at 20% loading for both liquid crystal materials. Other columns of different liquid crystalline percentages (15% and 25%) were used. A chromatogram with unoverlapped peaks was only obtained in both cases at 20% column loading. The order of elution isomers under the applied chromatographic conditions is discussed. The separation of these isomers is also discussed on the basis of stereo chemical confirmations.

Introduction

Liquid crystalline compounds as new stationary phases in gas liquid chromatography have been widely used recently[1−4]. A variety of solute molecules can be separated with high accuracy, especially those of isomeric character.

A considerable number of liquid crystalline solvents have been investigated. These studies showed that the necessary condition for a good separation power of the liquid crystal is a large persistence range of mesophase[5,6]. The mixtures of different isomers have been separated on liquid crystalline stationary phases and the results obtained so far have been superior to those obtained on conventional stationary phases[7,8]. Among these mixtures were isomers of disubstituted benzene (xylene isomers)[9−12]. However, the separation of meta and para xylene presents a convenient test for the effectiveness of a column packing material[13]. The separation of xylene isomers by gas chromatography using liquid crystal as a stationary phase is of reliable technical importance, since these isomers have about equal retention in most ordinary phases. The use of saturated cyclic compounds is thought to be superior to the use of xylene in measuring the shape-selective

properties of liquid crystal stationary phases as they are less polar than xylenes and their selectivity factors are more sensitive to selectivity changes[14]. The liquid crystalline stationary phases were very suitable for the isomer separation of phenol derivatives[15−17], esters[17], pyridine derivatives[18] and methyl ester of fatty acids[17].

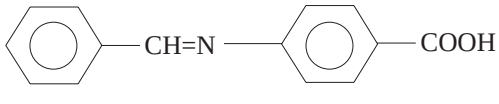
Increasing attention has been focused on important pollutants and phenols introduced into the environment through the discharge of industrial waste and the decomposition of various pesticides and herbicides[4,16,19]. The determination of isomeric phenol by ordinary stationary phases presents some difficulties, since these isomers have similar boiling points and polarities. A stationary phase able to separate on a basis other than boiling point or polarity is essential. The selectivity shown by liquid crystal phases is a consequence of the high degree of molecular order found in the liquid crystal mesophases. This selectivity is dependent on several factors including molecular shape, polarity and the flexibility of the solute molecule[13−17].

In this work gas chromatographic behaviour using liquid crystals benzylidene-p-aminobenzoic acid and 4-(p-methyl benzylidene)-p-aminobenzoic acid as liquid crystalline stationary phases for the separation of disubstituted dimethylphenol isomers was investigated. The loading percentages of liquid crystal as well as the effects of the stereo confirmation of stationary phase and solute molecules on the sequence of separation are discussed.

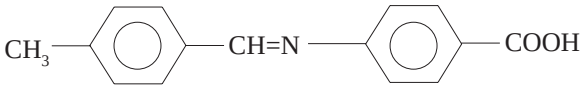
Experimental

All chemicals and solvents were of analar grade and were used without further purification. A Shimadzu GC-9A gas chromatographer equipped with a flame ionization detector (FID) linked to a data processor (Shimadzu C-R6A) capable of plotting a chromatogram and printing data on the same recording thermal chart paper was used. High purity nitrogen gas (99.99%) was used as a carrier gas. The flow rate was measured with a soap bubble flowmeter. The FID and injector port were maintained at 240 °C. Samples of 0.5-1.0 μL were injected into the column by calibrated hypodermic syringes.

The liquid crystals benzylidene-p-aminobenzoic acid



and 4-(p-methyl benzylidene)-p-aminobenzoic acid



were prepared according to well-defined procedures for the liquid crystal preparation of the Schiff base structure[20]. The identities of the prepared compounds were confirmed by the measurement of their infrared spectra (Pye-Unicam SP 105 Infrared spectrometer) and mass spectra (Shimadzu QPMS-1000A GC-MS spectrometer, using a direct inlet probe). The transition temperatures were recorded by differential scanning calorimeter (DSC Mettler-3000A) and also by hot stage polarised microscope (Litez-Labrolux 12. Pol). The preparation of liquid crystalline columns was performed by dissolving the liquid crystalline compound in chloroform and mixing with solid support Chromosorb W/AW(80-100 mesh) for around 2 h. The solvent

was removed and the solid residue was dried in an oven. The procedure was repeated for the preparation of three loading percentages: 15%, 20% and 25% w/w (liquid crystal:support). Glass columns (2.1 m × 3.2 mm i.d.) were packed with the prepared stationary phases and were conditioned overnight in GC-oven at temperatures 10 °C below the melting point of the used liquid crystal with a flow of carrier gas. Samples were injected into the columns at the measured nematic transition temperature ranges with column temperature intervals of 5 °C under specified chromatographic conditions (Figures 1 and 2).

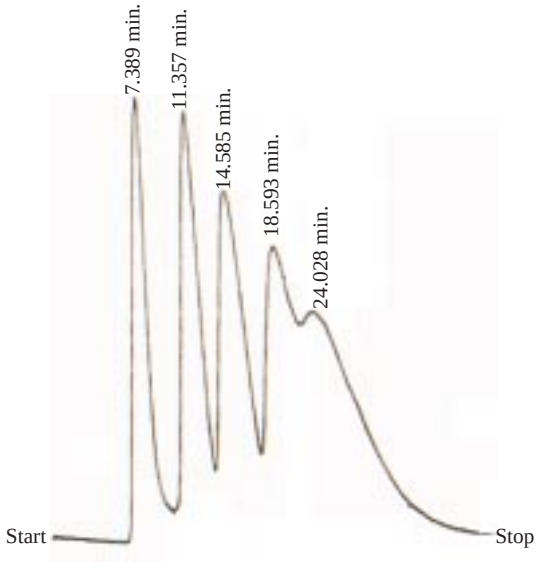


Figure 1. Gas Chromatogram of phenol isomers mixture on 20% benzylidene-p-aminobenzoic acid Conditions: Oven Temp. = 190 °C, Flow rate = 40 mL/min, Det. and Inj. = 240 °C. Sample size 1 μL. Peaks: 1 = Ethanol (solvent), 2 = 2,6-dimethyl phenol, 3 = 2,5-dimethyl phenol, 4 = 3,4-dimethyl phenol, 5 = 3,5-dimethyl phenol.

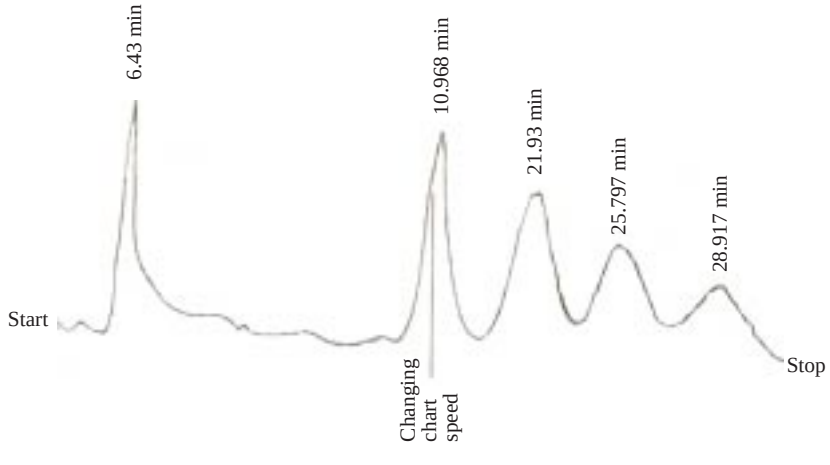
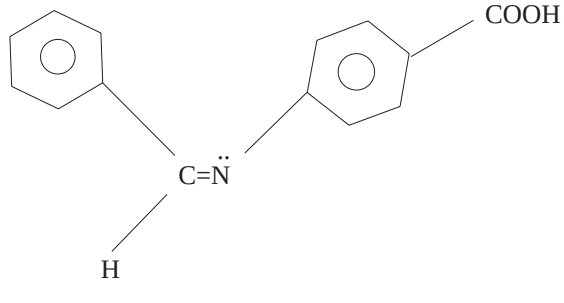


Figure 2. Gas Chromatogram of phenol isomers mixture on 20% p-methyl benzylidene)-p-aminobenzoic acid Conditions: Oven Temp. = 256 °C, Flow rate = 30 mL/min, Det. and Inj. = 270 °C. Sample size 1 μL. Peaks: 1 = Ethanol (solvent), 2 = 2,6-dimethyl phenol, 3 = 2,5-dimethyl phenol, 4 = 3,4-dimethyl phenol, 5 = 3,5-dimethyl phenol.

Results and Discussion

Gas chromatographic analyses were carried out for a mixture of phenol isomers in ethanol that consisted of 2,5-dimethyl phenol, 3,4-dimethyl phenol, 3,5-dimethyl phenol and 2,6 dimethyl phenol, by using columns packed first with benzylidene-p-aminobenzoic acid and then with 4-(p-methyl benzylidene)-p-amino benzoic acid. The phenol isomers were analysed on benzylidene-p-aminobenzoic acid within the nematic ranges of the liquid crystalline compound 169-194 °C with a temperature interval of 5 °C. The same analysis was repeated on 4-(p-methyl benzylidene)-p-aminobenzoic acid at a nematic column temperature of 256 °C. In both cases the best resolution was obtained from a 20% loading column. On the other hand, better selectivity for the separation of phenol isomer mixtures was obtained at column temperature 190 °C for the liquid crystal benzylidene-p-aminobenzoic acid (Figure 1). The separation by such selectivity at 20% loading could be attributed to the type and quantity of the liquid crystalline compound. Similar cases using stationary phases of different liquid crystalline materials have been reported[14,15,21]. Separation with a 15% loading column gave only one overlapped peak for the mixture, which indicates the inability of this loading percentage to achieve separation. In addition, upon increasing the loading percent to 25%, some peaks were combined with each other. This may be explained by the increase in the sites of interaction between solute molecules and stationary phases[17] which retained the analysed components longer and hence the coeluation of their peaks. The order of elution for these isomers under the applied chromatographic conditions was (1) 2,6-dimethyl phenol b.p. 212 °C, (2) 2,5-dimethyl phenol; b.p. 211.5 °C, (3) 3,4-dimethyl phenol; b.p. 225 °C and (4) 3,5-dimethyl phenol; b.p. 219.5 °C (Figure 1). A small amount of interference the last peak (Figure 1) is observed with the 3,4-dimethyl phenol isomer peak. This could be overcome by using a longer column.

It is clear that the order of elution for these isomers does not depend on their boiling points as is usually expected in ordinary stationary phases[16−17]. It also seems that the linear and symmetrical molecules are retained longer on the liquid crystalline column as in 3,5-dimethyl phenol[13−17]. The behaviour of phenol isomers and their order of elution from the column could also be explained on the basis of stereo confirmation In this respect, the stereo confirmation of benzylidene-p-aminobenzoic acid is



An interhydrogen bond is formed between the nitrogen pair of electrons and the proton of the OH group in the phenol molecule.

The steric effect from the presence of bulky methyl groups in positions 2,6-is expected. This means that the methyl groups do not allow bond formation with the nitrogen electron pair in the stationary phase, so the retention of 2,6-dimethyl phenol is the lowest and is eluted first.

In the case of 2,5-dimethyl phenol the steric effect of the methyl groups is reduced, since only one methyl group is adjacent to the OH group and is consequently retained longer in the column, compared

with 2,6-dimethyl phenol. For 3,4-dimethyl pheno, no methyl groups are in the vicinity of the OH group and this compound has more freedom to form an intermolecular hydrogen bond. The 3,4-dimethyl phenol derivative has a good symmetrical structure, which permits the formation of an intermolecular hydrogen bond. In addition, the symmetrical structure allows the molecules to be aligned parallel with stationary phase molecules, which are therefore retained longer than all the above phenol derivatives. This agrees well with all previously results mentioned for the separation of these derivatives[15,16]. The separation and resolution factors were calculated and are shown in Table. The isomeric 3,4-dimethyl phenol and 3,5-dimethyl phenol (Figure 1) are partially separated. A separation factor of 1.461 (Table) indicates poor separation[22].

Table. Separation and resolution factors of phenol isomers on 20% benzylidene-p-aminobenzoic acid column.

Compound	Column Temp.	Separation Factor (α)	Resolution (Rs)
2,5-dimethyl phenol/ 2,6-dimethyl phenol	190 °C	1.709	4.362
3,4-dimethyl phenol/ 2,5-dimethyl phenol	190 °C	1.515	5.605
3,5-dimethyl phenol/ 3,4-dimethyl phenol	190 °C	1.461	4.36

It is worth mentioning that an attempt was made to separate the phenol isomers mixture on an ordinary column (3% OV-17 and 5% SE-30) under the same chromatographic conditions used in liquid crystalline stationary phases and unresolved overlapped peaks were obtained.

The phenol isomers mixture was gas chromatographed on a column packed with liquid crystalline compound 20% 4-(P-methyl benzylidene)-p-aminobenzoic acid on Chromosorb W-AW 80-100 mesh at a column temperature of 256 °C (isothermal), which represents the end of the nematic range (228-256 °C). No resolved peaks were observed for other column loadings (15% and 25%) for the rest of the nematic range. Fairly good separation was observed (Figure 2) with 20% loading and at 256 °C. The elution order of phenol derivatives is the same as in the previous column in which the results here could be explained according to that previously mentioned for the a benzylidene-p-aminobenzoic acid column.

Broad peaks for 2,5-dimethyl phenol, 3,4-dimethyl phenol and 3,5-dimethyl phenol were obtained (Figure 2) with poor resolution and efficiency. In other words the column is less efficient compared with a the benzylidene-p-aminobenzoic acid column. This may be attributed to the effect of-p-methyl group substituent as weak electron donating in enhancing electronic density on the nitrogen atom through hyper double bond conjugation and hence increasing intermolecular hydrogen bonding with phenol isomers[23].

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