CHROM. 12,585

LIQUID CRYSTALS AS THE STATIONARY PHASE IN GAS CHROMATO-GRAPHY

ADSORPTION PHENOMENA CAUSED BY AN ELECTRIC FIELD APPLIED ACROSS THE COLUMN

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(First received October 29th, 1979; revised manuscript received December 4th, 1979)

SUMMARY

An investigation of the direct current electric field effect on capillary column gas chromatography, in which liquid crystals were used as the stationary phase, is described. When the electric field was applied across the column axis, the peak size was reduced, to an extent that depended on the configuration of the solute molecule, the field strength and the stationary phase employed. When the field strength was increased the amount adsorbed also increased. At every injection, the amount of sample adsorbed was constant, *i.e.* independent of sample size. This phenomenon was successfully exploited in qualitative and quantitative experiments.

INTRODUCTION

Liquid crystals have the mobility of ordinary liquids and the anisotropic properties of solid crystals. In other words, the liquid crystalline state has more order in the arrangement of its molecules than the liquid state, but less than solid state. Their interesting properties have been extensively investigated, and electro-optical, thermographic, structural and other properties are being used in various fields, such as display devices, temperature indicators, solvents, etc.

In gas chromatography (GC), the use of liquid crystals as the stationary phase was first reported by Kelker[1] and Dewar and Schroeder[2]. They showed that many disubstituted benzenes (or isomers of disubstituted benzenes) could be separated much better by nematic liquid crystals than with conventional column packing materials. Thereafter, many types of liquid crystals were introduced for the separation of various kinds of compounds[3-5].

Generally, the molecular arrangement of liquid crystals is significantly affected by the conditions. An electric field may promote the molecular arrangement and/or may give rise to the molecular rearrangement. Such liquid crystals are called field effect type liquid crystals.

Rogers et al.[6] investigated a field effect type liquid crystal, Vali Light A, as a liquid phase for GC: the retention behaviour and column efficiency for several kinds of organic compounds were examined in the presence of alternating current (a.c.) and direct current (d.c.) electric fields. They reported that application of the electric field increased retention values and sharpened peaks. They also studied a cholesteric liquid crystal capillary column with an applied electric field[7,8]. The apparent capacity ratio of the liquid crystal stationary phase was increased, and the peak fronting phenomenon was a function of both the dielectric constant of carrier gas and the strength of the field.

There have been, however, no detailed investigations on the strength of the electric field. In the course of our experiments, using a d.c. electric field, we discovered that some solutes were extensively retained in the column. This "adsorption" phenomenon, which results in the reduction of peak size on application of the electric field, increased with increasing field strength. Further, we found that the peak of o-dichlorobenzene did not elute from a cholesteryl palmitate column, when a field of 500 V was applied across the column. This adsorption phenomenon may lead to a new identification technique in GC.

EXPERIMENTAL

Materials

All reagents used were analytical grade, and each sample injected into the gas chromatograph was dissolved in n-hexane (2000 ppm). Cholesteryl palmitate (cholesteric mesophase in temperature, 80–146°) and p-dianisal-3,3'-dichlorobenzidine (nematic mesophase, 144–330° dec.) were obtained from Tokyo Chemical Industry (Tokyo, Japan), and p-azoxydianisol (nematic mesophase, 116–136°) and OV-17 from Nishio Industry (Tokyo, Japan). Liquid crystals were used without further purification. Fine metal wires (0.150 mm diameter) made of stainless steel or nickel were obtained from Nishio Industry and Nippon Denkyu (Tokyo, Japan), respectively. Sealbest P-246, an electroconductive resin, which is composed of fine carbon and silver suspended in the dispersoid solvent, was obtained from Tokuriki Kagaku Institute (Kanagawa, Japan).

d.c. generator

A laboratory-made d.c. generator was used (capacity, 5 kV × 10 mA).

Gas chromatography

An F & M Model 810 gas chromatograph equipped with a flame ionization detector was modified so that a glass capillary column of special conformation could be connected.

The GC conditions were as follows: injection temperature, 200°; detector temperature, 230°; column temperature, mesomorphic temperature; carrier gas, high-purity nitrogen; flow-rate, 0.5–1.5 ml/min; sample size, 1 μl; split ratio, 1:20.

Preparation of column

     Coiled glass capillaries were made by drawing Pyrex glass tube (2.0 mm I.D. and 9.0 mm O.D.) with a Shimadzu Model GDM-1 glass drawing machine (Shimadzu Seisakusho, Kyoto, Japan). A fine metal wire for an internal electrode was inserted into the Pyrex tube during the drawing. The capillaries were washed with acetone and dried with nitrogen, then coated with a liquid crystal by passing 1–5% benzene or chloroform with a Shimadzu Model MCT-1 microcolumn treating machine. The outer surface of the capillary was painted with an electroconductive resin, Sealbest P-246, for an external electrode. The cross-section of the column is ideally as shown in Fig. 1, but it is most likely that the wire rests on the inside of the capillary. Table I lists the columns used.

     Each column was conditioned for two days at 5–10° above the upper limit of the mesomorphic temperature. The sample injection was started after the field had been applied for 4–5 h.
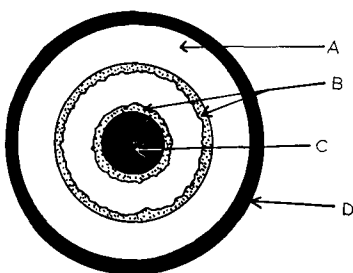

Fig. 1. Cross-section of column. A = Glass capillary; B = liquid crystal; C = metal wire electrode; D = electroconductive resin electrode.

TABLE I

LIST OF COLUMNS

	Cholesteryl palmitate	*p-Azoxy-dianisol*	*p-Dianisal-3,3'-dichloro-benzidine*
Length (m)	20	20	30
Diameter (mm)	0.25 I.D.	0.30 I.D.	0.20 I.D.
	0.75 O.D.	0.80 O.D.	0.80 O.D.
Wire electrode	stainless steel	stainless steel	nickel
	0.150 mm dia.	0.150 mm dia.	0.125 mm dia.
Column temperature	100°	120°	150°

RESULTS AND DISCUSSION

     We examined the effect of changing the strength of the electric field from 0 to 500 V, and the adsorption of o-dichlorobenzene on four stationary phases, OV-17, cholesteryl palmitate, p-azoxydianisol and p-dianisal-3,3'-dichlorobenzidine. The adsorption phenomenon was not observed on the OV-17 column, but o-dichlorobenzene was completely adsorbed on the other three columns at field strengths greater than 300 V.

We then investigated the d.c. field effect on the adsorption of halogenated aromatic hydrocarbons, o-, m- and p-methoxytoluene, m- and p-diisopropylbenzene and tridecane, using a cholesteryl palmitate column at 100°. The relationship between the amount adsorbed and the field strength is shown in Fig. 2. The adsorption of the chlorinated aromatic hydrocarbons increased with increasing field strength, and each compound was adsorbed in different extent. Hydrocarbons were not adsorbed at all, whereas dichlorobenzene and dibromobenzene were strongly adsorbed. Methoxytoluene was weakly adsorbed, and chlorotoluene moderately so. It seems that the o-isomers were more strongly adsorbed than the other two positional isomers.
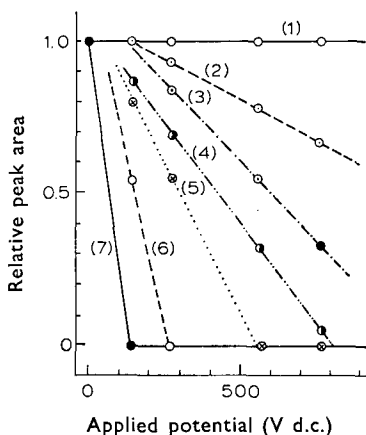

Fig. 2. Relationship between field strength and relative peak area. 1 = n-Tridecane and diisopropylbenzene; 2 = p-methoxytoluene; 3 = o- and p-methoxytoluene; 4 = o-chlorotoluene; 5 = o-dichlorobenzene; 6 = m-dibromobenzene; 7 = o-dibromobenzene. Cholesteryl palmitate column, at 100°.

The adsorption on the other two liquid crystalline phases, p-azoxydianisol and p-dianisal-3,3'-dichlorobenzidine, was also investigated, and similar relationships to that on cholesteryl palmitate were obtained.

The amounts of compounds adsorbed on these three liquid crystal columns were compared at the same field strength. The result was that the extent of adsorption depended on the liquid crystals, i.e. o-dichlorobenzene was adsorbed by 80% on p-dianisal-3,3'-dichlorobenzidine, 70% on p-azoxydianisol and only a little on cholesteryl palmitate. On the whole, cholesteryl palmitate was found to adsorb less strongly than the other two. Table II lists the critical values of electric field strength at which peaks disappeared from the chromatograms. It can be concluded from these data that cholesteryl palmitate requires a stronger field than the other two for complete adsorption.

The retention times and column efficiences were determined with electric fields of 0 and 200 V. Table III summarized the results for cholesteryl palmitate at 100°. In the presence of a field, the retention times of halogenated aromatic compounds, except o-dichlorobenzene and p-bromotoluene, were generally decreased. But the variation was always less than 15% and mostly negligibly small. The peaks were sharpened by the field and the height equivalent to a theoretical plate (HETP) values were lower in the presence of the field.

TABLE II

POTENTIALS (V) AT WHICH PEAKS DISAPPEARED ON CHROMATOGRAMS
Sample, chloroform solution, 1 μl.

Compound	Stationary phase		
	p-Azoxydianisol	p-Dianisal-3,3'-dichloro-benzidine	Cholesteryl palmitate
m-Chlorotoluene	76	56	400
o-Dichlorobenzene	70	56	270
o-Methoxytoluene	120	92	over 600
o-Dibromobenzene	28	28	150
m-Dibromobenzene	56	44	200
p-Dibromobenzene	120	92	over 600

TABLE III

EFFECT OF APPLIED POTENTIAL ON RETENTION TIME (min) AND HETP (cm)
Cholesteryl palmitate column, column temperature, 100°.

Compound	Retention time		HETP	
	0 V	200 V	0 V	200 V
p-Chlorotoluene	2.14	1.80	0.655	0.608
o-Dichlorobenzene	4.90	4.96	1.00	0.478
p-Bromotoluene	5.12	5.15	1.13	0.735
p-Methoxytoluene	3.70	3.57	1.09	0.924
m-Diisopropylbenzene	9.20	8.83	1.67	1.48

Fig. 3 shows the relationship between the amount adsorbed and sample size. The solid line was obtained without a field, and the broken line with a field of 14 V. From 30 to 660 nmol the lines are linear and parallel, which suggests that the amount adsorbed was independent of the sample size.
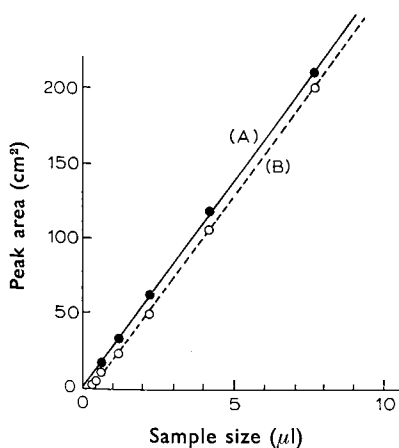

Fig. 3. Effect of sample size on adsorption. A, Without electric field; B, with d.c. electric field (14 V). Sample, methanol (8.24·10² nmol/μl). Column p-azoxydianisol, at 120°.

The time-course of the adsorption was also investigated on p-azoxydianisol at 118° under a constant field of 14 V (Fig. 4). Steady adsorption was observed over 50 h, although the amount adsorbed did not settle down until 5 h after starting. The reproducibility of this phenomenon was confirmed by exactly the same experiment.
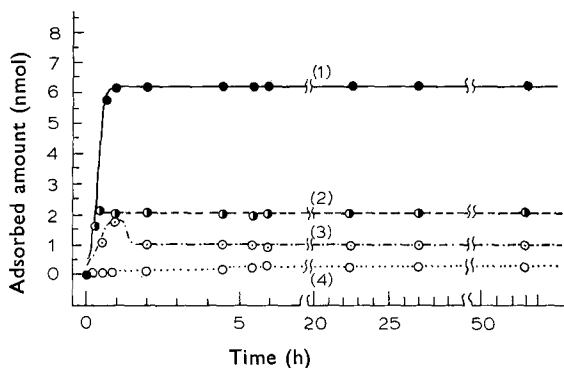

Fig. 4. Variation with time of amount adsorbed. 1 = a,3,4-Trichlorotoluene; 2 = 1,2,4-trichlorobenzene; 3 = 3,4-dichlorotoluene; 4 = o-dichlorobenzene. p-Azoxydianisol column, at 118°, under 14 V d.c.

No solvent effect on the adsorption was observed. However, as shown in Fig. 5, a portion of the amount previously adsorbed comes out of the column. This is thought to be caused by the displacement of the adsorbed compound by a polar solvent, such as methanol, ethanol, chloroform, 1,2-dichloroethane, acetone and so on. This phenomenon was not observed when non-polar solvents were used for the preparation of the sample.
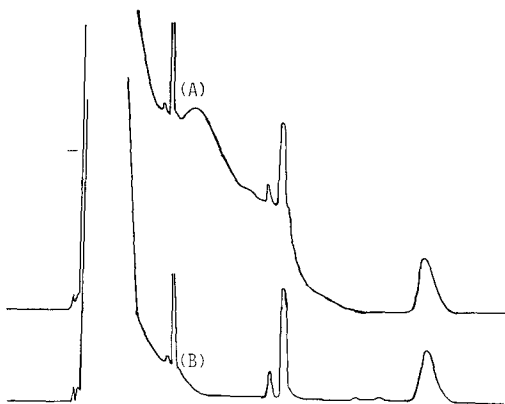

Fig. 5. Solvent effect on elution. (A), Chromatogram after over 20 injections; (B), chromatogram at an early time. Solvent, methanol; sample size, 1 μl; cholestryl palmitate column, at 114°, 200 V d.c.

Additionally, when the electric field was turned off, the adsorption gradually diminished and finally became undetectable. Though the low-level bleeding of the adsorbed compounds was predicted, no appreciable change of the base line could be observed on the chromatogram.

The features discussed above were used in the separation of multi-component samples, particularly those with overlapping peaks. Fig. 6a and b shows that application of the field results in selective adsorption and the identification of each peak. Furthermore, it is of importance that the adsorption behaviour is not affected by the coexisting compound.
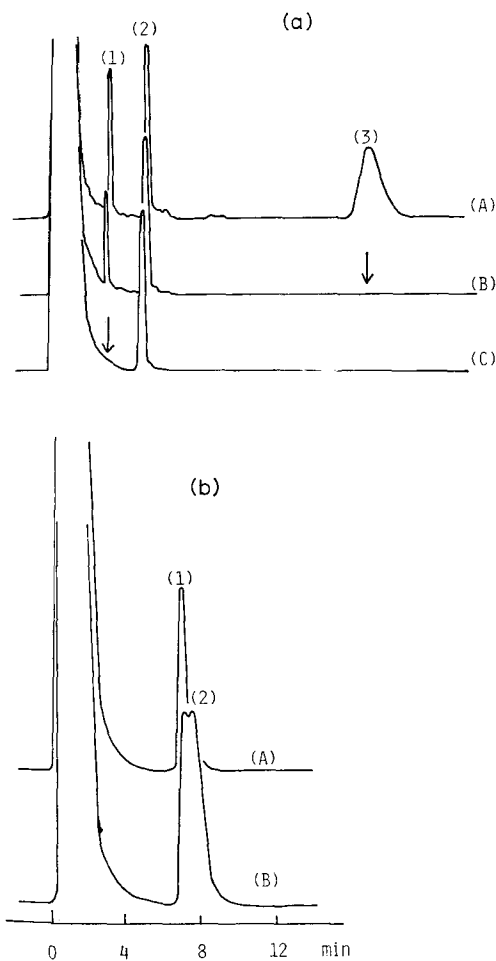

Fig. 6.(a), Chromatograms of aromatic compounds. 1 = m-Chlorotoluene; 2 = m-methoxytoluene; 3 = m-dibromobenzene. A, Without electric field; B, at 250 V d.c.; C, at 500 V d.c. Cholesteryl palmitate column, at 100°. Sample size 1 μl. (b) Chromatograms of p-methoxytoluene (1) and o-dichlorobenzene (2). A, with electric field (400 V d.c.); B, without electric field.

CONCLUSIONS

The adsorption phenomena were found only with the liquid crystal columns, and not with the ordinary liquid phase OV-17.

The amount adsorbed increased with increasing electric field strength.

The amount adsorbed was dependent on the sort of solute injected. Hydrocarbons were not adsorbed, methoxytoluene was weakly adsorbed, chlorotoluene slightly, and dichlorobenzene and dibromobenzene strongly.

Steady and constant adsorption could be maintained, reproducibly, for 50 h.

The amount adsorbed was independent of the sample size.

These adsorption phenomena are thought to be worth studying for the development of a new gas chromatographic technique, and further investigation is under way in our laboratory.

ACKNOWLEDGEMENTS

REFERENCES

1 H. Kelker, *Ber. Bunsenges. Phys. Chem.*, 67 (1963) 698.
2 M. J. S. Dewar and J. P. Schroeder, *J. Amer. Chem. Soc.*, 86 (1964) 5235.
3 H. Kelker and A. Verhelst, *J. Chromatogr. Sci.*, 7 (1969) 79.
4 D. G. Willey and G. H. Brown, *J. Phys. Chem.*, 76 (1972) 99.
5 P. J. Porcaro and P. Shubiak, *J. Chromatogr. Sci.*, 9 (1971) 690.
6 P. J. Taylor, R. A. Culp, C. H. Lochmuller, L. B. Rogers and E. M. Barall, II, *Separ. Sci.*, 6 (1971) 841.
7 R. B. Westerberg, F. J. Van Lenten and L. B. Rogers, *Separ. Sci.*, 10 (1975) 593.
8 J. E. Conaway and L. B. Rogers, *Separ. Sci.*, 13 (1978) 303.