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GAS CHROMATOGRAPHIC BEHAVIOUR OF SOME POLYNUCLEAR HYDROCARBONS ON CADMIUM CHLORIDE COLUMNS MODIFIED WITH CARBOWAXES

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SUMMARY

The retention behaviour of some polynuclear hydrocarbons on cadmium chloride columns modified with Carbowaxes was studied and was found to be independent of the chain length of the glycol. This behaviour was not observed with other metal salts and liquid stationary phases. The sharp maxima in the absolute retention of phenanthrene and anthracene at a 4% salt coating level are surprising. Polynuclear hydrocarbons show both positive and negative retardation. Electron repulsion and slow interfacial mass transport in the micropores dictate the retention behaviour of the stationary phase.

INTRODUCTION

In gas chromatography, a compound is usually retained on a column through electronic interaction forces, which have been classified as non-specific and specific. In some instances, shape-selective properties of the stationary phase dictate chromatographic retention. In typical instances a salting effect also plays a major role in the retentive mechanism of a stationary phase.

The analytical potential of a cadmium chloride column modified with Carbowax 20M was reported recently¹. The interesting retention behaviour of this stationary phase cannot be explained in terms of the hitherto recognized concepts of retention mentioned above. In this work, we studied the behaviour in greater detail and we present here an explanation of this interesting retention behaviour.

EXPERIMENTAL

The experiments were conducted on a Perkin-Elmer 810 gas chromatograph equipped with a flame-ionization detector and a Honeywell 1-mV strip-chart recorder. The columns were made of stainless steel (182 cm × 2 mm I.D.) and were packed by a conventional technique. The support used was Chromosorb P of mesh size 80-100 μ m. In each instance, a dilute solution of the model compounds in methyl ethyl ketone was injected with a 10- μ l Hamilton microsyringe. The average linear

velocity (\bar{u}) was determined from the retention of the methane peak. The purity of the organic model compounds tested was the same as reported earlier¹.

The packing material was prepared by both one- and two-step methods. In the one-step method, the appropriate amounts of the salt and the liquid stationary phase were dissolved in aqueous methanol. The support to be coated was added to this solution and the solvent was removed by evaporation. When a suitable solvent for both the salt and the stationary liquid was not available, the two-step method was employed. In the first step the salt was coated on the support from aqueous or aqueous methanolic solution. In the second step, the liquid stationary phase was re-coated on it from a solution of the liquid stationary phase in a solvent in which the salt was insoluble (e.g., chloroform). With the cadmium chloride-Carbowax system, it was found that the gas chromatographic behaviour is the same whether the packing material was prepared by the one- or the two-step method.

RESULTS

Effect of the salt and the liquid stationary phase

A baseline separation of phenanthrene and anthracene, with the former being retained for a longer time than the latter, has been observed recently¹ on a column of cadmium chloride modified with Carbowax 20M, and also with Carbowax 1500 and 4000. Thus the behaviour is independent of the chain length of the glycol. This behaviour has not been found with other liquid stationary phases, both polar and non-polar, such as Apiezon L, SE-30 and QF-1 silicones, sorbitol and D-mannitol, or when the repeat unit of the polymeric phase contains a C=O group, e.g., butanediol adipate polyester and polyethylene glycol adipate. This pair co-elutes on columns of other metal salts, such as cadmium bromide, cadmium iodide, barium chloride, lithium chloride and calcium chloride modified with Carbowax 4000. With nickel chloride, this pair could not be eluted within 90 min. Therefore, the behaviour appears to be a characteristic feature of the cadmium chloride-Carbowax system.

Effect of coating

At a 2% level of Carbowax 20M, the retention and resolution of phenanthrene and anthracene were insensitive to cadmium chloride coatings of 20% and higher¹. However, interesting behaviour was observed at low levels of cadmium chloride coating.

Fig. 1 shows the effect of cadmium chloride coating at a level of 2% Carbowax 1500 on the retention of phenanthrene and anthracene. When cadmium chloride is incorporated into Carbowax 1500, there is a decrease in the retentions of both the compounds up to a 0.2% salt coating level and they co-elute in this region. Thereafter, although the retention of anthracene remains unchanged up to a 2% salt-level, there is a steady increase in the retention of phenanthrene. Beyond the 2% salt level there is a sharp increase in the retention of both compounds up to a 4% salt level, followed by a sharp decrease up to 6%. Thereafter the decreasing trend continues for both compounds up to a 10% salt level and beyond this level the retentions are virtually unaffected by a further increase in the salt coating. The peaks were tailed at salt coating levels between 2.0 and 10.0%, but beyond this range symmetrical peaks were found for both compounds. The sharp maxima at a 4% coating level are surprising.

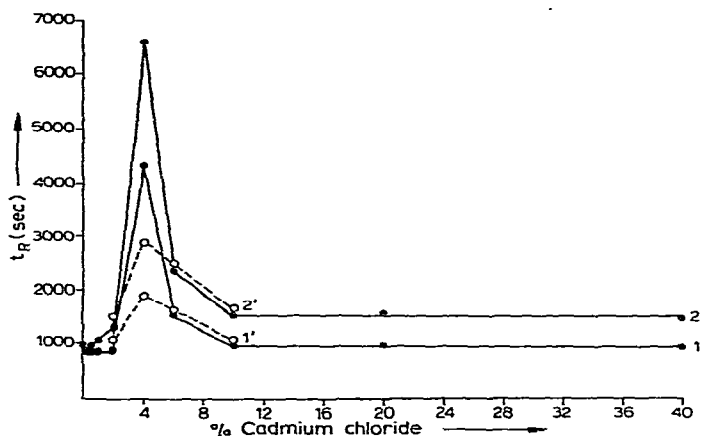


Fig. 1. Effect of cadmium chloride coating at 2% level of Carbowax 1500 (●) and Carbowax 20M (○) on the adjusted retention time (t_R) of anthracene (1, 1') and phenanthrene (2, 2'). Temperature: 190°; flow-rate: 20 ml/min.

Other Carbowaxes behave in a similar manner: the curve with Carbowax 4000 is almost superimposed on that with Carbowax 1500 and, apart from a less sharp maximum, the trace with Carbowax 20M also overlaps that of Carbowax 1500.

Fig. 2 shows the effect of coating on the relative retention (α) and resolution (R_{ij}) of phenanthrene and anthracene. Above a coating level of 0.2% there is a sharp increase in α up to a 2% level, followed by a gradual increase up to a 10% level. Thereafter it is virtually insensitive to a further increase in the salt coating level. The effect of coating on R_{ij} is slightly different. The dependence of R_{ij} on coating up to a 2% level is similar to that for α . At higher coating levels, an increase in the differential migration rate is compensated for by an increase in HETP and flattening of the R_{ij}

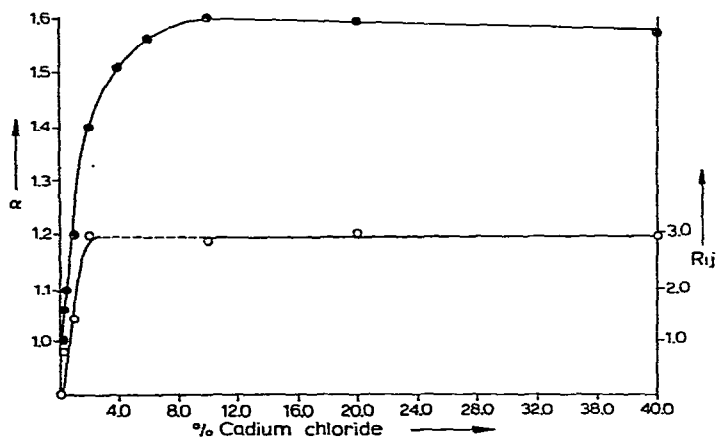


Fig. 2. Effect of cadmium chloride coating at 2% level of Carbowax 1500 on the relative retention, α , (●) and resolution, R_{ij} , (○) of phenanthrene and anthracene. Temperature: 190°; flow-rate: 20 ml/min.

trace at coating levels of 2% and higher is thus observed. The points at 2% and 10% coating levels are joined with a broken line in Fig. 2 as R_{tj} values have not been determined within this range.

Carbowax 4000 and 20M behave in a similar manner and their curves overlap with that of Carbowax 1500. At higher coating levels, a significant amount of the salt is lost during the coating procedure. However, provided that the coating level is at least 10% the overall retention behaviour is the same and comparable to that at the 2% level. Hence, for practical purposes a stationary phase with a composition of cadmium chloride-carbowax-chromosorb P of 1:1:50 is as good as the composition of 20:1:50 reported earlier¹. The separation of phenanthrene and anthracene on this stationary phase is depicted in Fig. 3.

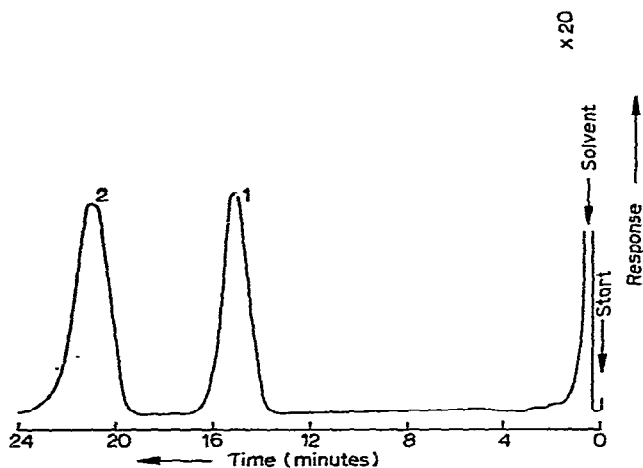


Fig. 3. Chromatogram of anthracene (1) and phenanthrene (2) on cadmium chloride-Carbowax 1500-Chromosorb P (1:1:50). Temperature: 190°; flow-rate: 20 ml/min.

Effect of carrier gas flow-rate

Fig. 4 shows the effect of carrier gas flow-rate (\bar{u}) on the HETP values of phenanthrene and anthracene measured in the mass-transfer-predominant flow-rate region. The total non-equilibrium coefficient ($C_s + C_m$) determined from the slope was found to be $57.1 \cdot 10^{-3}$ sec for the former and $29.3 \cdot 10^{-3}$ sec for the latter. The C_m coefficient for these compounds was calculated from the expression²

$$C_m = \omega d_p^2 / D_m'$$

where ω is a dimensionless coefficient of the order of unity³ and d_p is the diameter of the particle. The diffusivity (D_m') of the solute components into the carrier gas at unit pressure was calculated from Fuller-Schettler-Giddings expression⁴. The C_m coefficients for these compounds were found to be of the same order of magnitude of 10^{-3} sec. Hence the order of magnitude of C_s for both phenanthrene and anthracene is 10^{-3} sec with approximately a two-fold higher value for the former than the latter.

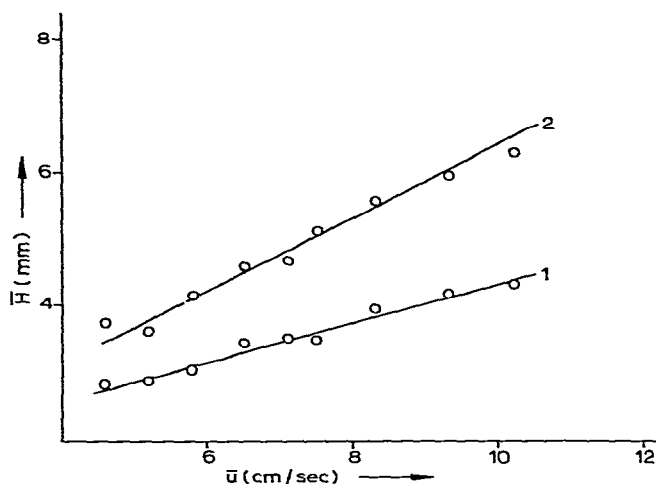


Fig. 4. Dependence of \bar{H} on \bar{u} for anthracene (1) and phenanthrene (2) at 210° on cadmium chloride–Carbowax 20M–Chromosorb P (20:1:50).

Retention behaviour of polynuclear hydrocarbons

The retention behaviour of some polynuclear hydrocarbons on a cadmium chloride column modified with Carbowax 1500 is illustrated by the values in Table I. The elution pattern of the modified stationary phase is different from that of the Carbowax 1500 column. A similar behaviour has also been observed when cadmium chloride is modified with Carbowax 20M¹. Dibenzofuran and biphenyl show negative retardation ($R_F < 1.0$), while anthracene and 2,3-dimethylnaphthalene show almost

TABLE I

RETENTION BEHAVIOUR OF SOME POLYNUCLEAR HYDROCARBONS ON A CADMIUM CHLORIDE COLUMN MODIFIED WITH CARBOWAX 1500

Columns: A, cadmium chloride–Carbowax 1500–Chromosorb P (20:1:50); B, 2% Carbowax 1500 on Chromosorb P. Column temperature: 160° (190° for phenanthrene and anthracene). Flow-rate: 20 ml/min.

Compound	Boiling point (°C)	α		R_F	$\bar{H} - \bar{H}^*$ (mm)
		Column A	Column B		
Naphthalene	218.0	1.00	1.00	1.57	7.41
2-Methylnaphthalene	241.1	1.05	1.42	1.15	7.00
1-Methylnaphthalene	244.4	2.18	1.66	2.07	8.77
Biphenyl	255.2	0.81	2.17	0.59	4.43
2,6-Dimethylnaphthalene	261.0	1.64	2.09	1.22	6.09
1,6-Dimethylnaphthalene	264.0	1.84	2.34	1.26	7.13
2,3-Dimethylnaphthalene	268.0	1.66	2.55	1.03	6.01
Acenaphthene	277.2	5.47	3.35	2.59	7.49
Dibenzofuran	287.0	2.57	4.88	0.83	4.64
Fluorene	297.9	5.81	6.05	1.51	6.38
Phenanthrene	338.4	1.00	1.00	1.60	3.00
Anthracene	339.9	0.64	1.00	1.02	2.63

zero retardation ($R_F \approx 1.00$) due to salt. The other compounds show positive retardation ($R_F > 1.0$). Here the word retardation means the increased adjusted retention time due to the salt, which follows from the definition of retardation factor (R_F)¹. 2-Methylnaphthalene and substituted 2-methylnaphthalenes are retarded less than the corresponding 1-substituted isomers. \bar{H} and \bar{H}^* are the apparent plate heights measured on the modified stationary phase and Carbowax 1500, respectively. The \bar{H}^* values lie between 0.80 and 0.92 mm. Large $\bar{H} - \bar{H}^*$ values indicate a significantly poorer efficiency of the modified stationary phase relative to a conventional liquid phase. However, a high specific selectivity of the phase outweighs this disadvantage. As a result, a good separation of several isomeric pairs that are usually difficult to separate such as 1- and 2-methylnaphthalenes, phenanthrene and anthracene, has been found.

DISCUSSION

In gas-liquid-solid chromatography, the retention of a compound is due to the confined contributions of the stationary liquid and the adsorbent. However, a different elution pattern of the modified stationary phase compared with that of the Carbowax column and large $\bar{H} - \bar{H}^*$ values suggest that Carbowax, as a partitioning liquid, does not play any significant role in the mechanism of retention. In contrast to Fig. 2, a salting-effect^{5,6} would reflect the desired resolution at a much lower salt concentration. Moreover, other electrolytes, such as lithium chloride, did not show this behaviour. Aromatic compounds are known to exhibit a salting-out effect when lithium chloride is dissolved in polyethylene glycol 400⁵. However, in this instance, both positive and negative retardation have been observed with condensed aromatic compounds. It is likely, therefore, that a solubilization process does not play any major role.

Unlike the present instance, a shape-selective property of the stationary phase lead to a longer retention time for anthracene than phenanthrene⁷. The extremes in the solute retention-binary stationary phase composition plots relate to the composition of the molecular compounds formed by interaction between the components of the stationary phase⁸. Such a possibility can be ruled out here as the IR spectra of the stationary phase did not show any band shift of the glycol¹. It is likely, therefore, that the adsorptive mechanism dictates the retention behaviour. Moreover, a significant difference between the elution pattern of this modified stationary phase and that of the cadmium chloride column⁹ indicates that the adsorptive mechanism with cadmium chloride is altered when Carbowax is incorporated.

For a sorbate molecule, affinity for the sorbent and hence the extent of penetration into the micropores depend on a net balance among the dispersion forces, electron repulsion and steric and polar effects. The peculiar retention behaviour of some condensed aromatic compounds on the modified stationary phase in Table I cannot be explained in terms of electronic interaction forces. It is likely, therefore, that electron repulsion outweighs other effects in these specific instances. The π -electron system of phenanthrene is more stabilized than that of anthracene owing to resonance effects. The former compound thus experiences a lower repulsive force than the latter during their penetration into the micropores and a greater effective surface area is therefore available to the former than to the latter owing to its greater depth of

penetration into the micropores. The greater retention of phenanthrene than anthracene can thus be explained. The effect of electron repulsion is very marked when the condensed aromatic compounds contain a hetero-atom with a lone pair of electrons, e.g., dibenzofuran and carbazole¹, both of which show a significant negative retardation ($R_F < 1.0$). In this respect, the behaviour is similar to that of certain porous organic polymer column packings. Porapak Q shows a repulsion effect with hydroxyl, ether and ketone oxygen functions¹⁰. The specificity of the branched-chain peak-broadening phenomenon¹¹ towards sorbates on Porapak P has also been attributed to this effect¹².

The C_s coefficients for sorbates on porous sorbents may originate from the sorptive-desorptive kinetics (C_k) and hindered surface diffusion, including intraparticle diffusion. A symmetrical peak on this stationary phase indicates surface homogeneity. For uniform adsorption with porous adsorbents¹³ C_k would probably vary between 10^{-6} and 10^{-8} . The order of magnitude of C_s for both phenanthrene and anthracene found here cannot be compared with the order of magnitude of C_k . It is likely, therefore, that the C_s coefficients originate mainly from the slow interfacial mass transport in the micropores. As phenanthrene penetrates deeper than anthracene into the micropores, it passes over a greater length of tortuous and constricted pathways than the latter and the effective diffusivity of the former will therefore be slower than that of the latter. The higher C_s coefficient of the former can thus be explained. The effect of slow interfacial mass transport in the micropores is also reflected in the $\bar{H}-\bar{H}^*$ values in Table I as, under identical experimental conditions, the contribution of other terms to HETP is nearly the same and almost cancels out on subtraction. The k' values of the model compounds tested were kept significantly higher to make their effect to HETP practically constant. A solute in Table I with a positive retardation always has a larger $\bar{H}-\bar{H}^*$ value than a solute with a negative retardation. This study may, therefore, open a new field of investigation of the surface of cadmium chloride modified with Carbowaxes.

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REFERENCES

- 1 O. K. Guha and A. Bhaumik, *J. Chromatogr.*, 119 (1976) 181.
- 2 J. C. Giddings, *Dynamics of Chromatography, Part I, Principles and Theory*, Marcel Dekker, New York, 1965.
- 3 N. C. Saha and J. C. Giddings, *Anal. Chem.*, 37 (1965) 830.
- 4 E. N. Fuller and J. C. Giddings, *J. Gas Chromatogr.*, 3 (1965) 222.
- 5 C. Bighi, A. Betti and F. Dondi, *J. Chromatogr.*, 39 (1969) 125.
- 6 A. Betti, F. Dondi, G. Lodi and C. Bighi, *J. Chromatogr.*, 68 (1972) 59.
- 7 G. Chiavari and L. Pastorelli, *Chromatographia*, 7 (1974) 30.
- 8 Yu. N. Bogoslovsky, V. M. Sakharov and I. M. Shevchuk, *J. Chromatogr.*, 69 (1972) 17.
- 9 O. K. Guha and A. C. Bhattacharyya, *Proceedings of the Symposium on Chemicals and Oil from Coal*, Central Fuel Research Institute, Dhanbad, 1972, p. 354.
- 10 F. M. Zado and J. Fabecic, *J. Chromatogr.*, 51 (1970) 37.
- 11 M. Dressler, O. K. Guha and J. Janák, *J. Chromatogr.*, 65 (1972) 261.
- 12 O. K. Guha, J. Novák and J. Janák, *J. Chromatogr.*, 84 (1973) 7.
- 13 J. C. Giddings, *Anal. Chem.*, 36 (1964) 1170.