CHROM. 8280

GAS–LIQUID CHROMATOGRAPHY ON FLUORINATED STATIONARY PHASES

I. HYDROCARBONS AND FLUOROCARBONS

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(Received January 21st, 1975)

SUMMARY

Four fluorinated stationary phases have been examined for their retention behaviour towards hydrocarbons and their fluorinated derivatives. It is seen that the customary way of determining stationary phase polarities gives little information on the retention characteristics of highly fluorinated solutes. Of the phases examined, Krytox AC, a fluorinated polyether whose gas–liquid chromatographic properties have not previously been reported, demonstrated an exeptionally high affinity for fluorinated solutes enabling hydrocarbon–fluorocarbon separations to be carried out efficiently. Fluorolube oil proved an efficient phase for the separation of fluoro compounds of different degrees of fluorination, whilst Kel F oil proved to be the best stationary phase for the separation of compounds having an equal degree of fluorination and for which boiling point differences were the main criteria for separation.

INTRODUCTION

The gas–liquid chromatographic (GLC) behaviour of fluorinated compounds has received little attention as yet, there being but few published papers on the subject. Most of the work has been on the development of efficient stationary phases for fluorocarbon separations or on the separation and analysis of the low-boiling fluorine-containing compounds used in anaesthetics or aerosols. As early as 1955, Evans and Tatlow[1] separated 1H:3H-decafluorocyclohexane, the monohydroperfluorocyclohexenes and perfluorocyclohexadienes on a preparative column containing dinonylphthalate, the column was 16 ft. long for the preparative work but identification of peaks had been achieved on a 6-ft. column. These authors made the valuable suggestion that "other high-boiling liquids such as the chloro–fluoro oils and silicones..." would be useful stationary phases for fluorocarbon analysis. Hall *et al.*[2] used columns containing di-isodecyl phthalate or benzyl ether for the separation of fluothane (2-bromo-2-chloro-1,1,1-trifluoroethane) from diethyl ether but Reed[3] had previously investigated fluorocarbon separations on fluorine-containing stationary phases. He

used three fluorocarbons, perfluoropentane, -heptane and -nonane, studying their chromatographic behaviour on perfluorokerosine, on Kel F-90 grease which is a chlorofluorocarbon polymer, and on the ethyl ester of Kel F acid 8114. Reed stated that a fluorocarbon stationary phase gives better separations of fluorocarbon mixtures than does a hydrocarbon stationary phase; furthermore for some mixtures, chlorofluorocarbons (Kel F) have a better resolving power than the fluorocarbon stationary phases.

Reed's work led to Campbell and Gudzinowicz[4] comparing the stationary phase properties of Apiezon L, a methyl phenyl ether, di-isodecyl phthalate and a Kel F oil during an investigation into the pyrolysis of commercial PTFE. For the GLC of the mixture of fluoroalkanes and -alkenes obtained, the authors found that the three non-fluorinated stationary phases gave poor performance and suggested that Kel F oil was superior for the separation of high-boiling fluorocarbons.

Greene and Wachi[5] have studied the separation of low-molecular-weight fluorocarbons at 0° and recommend a (decafluoroheptyl) acrylic ester as the optimum stationary phase. Brown et al.[6] have studied several stationary phases and their behaviour towards fluorocarbons and fluoroalcohols. Considerable information on fluorocarbon retention on Apiezon L and on poly(ethylene glycol succinate) is given and, as the authors were concerned primarily with electron acceptor types, two useful electron acceptor phases (a fluoro ester and a fluoro phosphonitrilate) are described and their properties discussed.

In this work four fluorinated stationary phases have been examined against a squalane reference. Three of the phases, Kel F-90, Fluorolube 2000, and silicone QF-1, have been used as such for some time and information is available to a limited extent about their GLC properties. The fourth phase studied, Krytox 240 AC, is a fluorinated grease produced by DuPont as a high temperature lubricant and has not previously been used as a GLC stationary phase.

A range of aromatic fluorocarbons, fluorobenzenes and fluorotoluenes, have been studied chromatographically on the five stationary phases together with the parent hydrocarbons and the results are compared from the viewpoint of the Kováts retention indices obtained. A perfluoroparaffin and a perfluoroolefin, together with their parent hydrocarbons, have also been studied and the effects of introducing π-electron characteristics and chain branching into the solutes is seen on the various stationary phases and the solute–stationary phase interactions explained in terms of molecular structure. The concept of column efficiency is also examined in terms of the degree of fluorination of the solute and the results augment Reed's conclusions that fluorinated stationary phases are superior for fluorocarbon analysis but, as retention increments show, considerable versatility is demonstrated by the comparatively few fluorinated stationary phases studied here.

EXPERIMENTAL

All measurements were made on a Pye series 104 gas chromatograph with flame ionization detector. Columns were 1 m × 6 mm O.D. tubing packed with 20% w/w of stationary phase coated on acid-washed, DCMS-treated Celite, 80–100 mesh partical size. The carrier gas was nitrogen, the flow-rate 20 ml/min.

Phases

(1) Kel F-90 oil, a chlorofluorocarbon polymer (poly(chlorotrifluoroethylene)), obtained from Phase Separations, Queensferry, Great Britain.

(2) Fluorolube 2000 oil, chlorofluorocarbon, Phase Separations.

(3) Silicone QF-1, poly(methyl-3,3,3-trifluoropropyl siloxane), Phase Separations.

(4) Krytox 240 AC, a perfluoroalkyl polyether oil thickened with Vydax 1000 fluorocarbon telomer solids, obtained from DuPont Petroleum, Chem. Div., Wilmington, Del., U.S.A. As this material is completely insoluble in all common solvents, the column packing was prepared by making a slurry of the Celite with a solution of Krytox in perfluoro 1,3-dimethylcyclohexane and evaporating under vacuum in a rotary evaporator.

RESULTS AND DISCUSSION

Table I compares the efficiencies of the five columns studied in terms of HETP at 80° using benzene and perfluorobenzene. Using the hydrocarbon for evaluation shows that squalane is the most efficient and Krytox the least efficient column, with silicone QF-1 and Kel F-90 having similar and intermediate values. With perfluorobenzene however, the situation changes remarkably when squalane shows slightly lower efficiency and Krytox, now having almost twice the efficiency, being comparable to squalane. The silicone and Kel F oil columns are no longer equivalent, Kel F showing improved efficiency with the fluorocarbon whilst the silicone efficiency decreased. To complete the picture, the Fluorolube oil shows no change in efficiency from hydrocarbon to fluorocarbon. These results suggest which stationary phase would be best suited for certain applications. Thus, for the separation of hydrocarbon–fluorocarbon mixtures Krytox and Kel F should give high resolutions with preferential retention of fluorocarbon, the silicone will display preferential retention for the hydrocarbon whilst Fluorolube would separate in order of boiling points irrespective of the fluorine content of the compound.

TABLE I

A COMPARISON OF COLUMN EFFICIENCIES AS DETERMINED BY BENZENE AND PERFLUOROBENZENE AT 80°

Stationary phase	HETP (cm)	
	Benzene	Perfluorobenzene
Krytox	0.35	0.22
Silicone QF-1	0.33	0.41
Kel F-90	0.32	0.23
Fluorolube 2000	0.22	0.21
Squalane	0.16	0.19

Table II gives the McReynolds[7] constants for the stationary phases where X', Y', Z', U' and S' are column constants given by ΔI values for benzene, n-butanol, 2-pentanone, nitropropane and pyridine, respectively. All phases are of low polarity with Krytox the least polar and silicone QF-1 having the highest polarity. Krytox, with its low X' value, will separate hydrocarbons rapidly from molecules containing

TABLE II

McREYNOLDS CONSTANTS FOR THE STATIONARY PHASES

Stationary phase	X'	Y'	Z'	U'	S'
Krytox	4	148	86	147	93
Kel F-90	41	135	134	153	111
Fluorolube 2000	75	192	148	200	158
Silicone QF-1	130	225	336	432	281

TABLE III

RETENTION INDEX (I) VALUES OF HYDROCARBONS AND FLUOROCARBONS AT 100°

Compound	Retention index				
	Krytox	Silicone QF-1	Kel F-90	Fluorolube 2000	Squalane
Benzene	668	782	698	730	650
Fluorobenzene	716	817	725	752	643
1,2,4,5-Tetrafluorobenzene	815	859	767	744	604
Pentafluorobenzene	842	848	769	716	589
Perfluorobenzene	861	827	771	687	571
Toluene	767	889	818	839	756
o-Fluorotoluene	824	919	842	858	757
m-Fluorotoluene	829	939	848	864	756
p-Fluorotoluene	829	939	846	866	756
Cyclohexane	680	700	659	679	671
Methylcyclohexane	747	758	734	743	738
Perfluoro-1,3-dimethyl-cyclohexane	978	568	698	340	462
1-Octene	772	806	797	799	784
2-Methylpentane	591	618	604	570	573
2-Methylpent-2-ene	597	611	624	616	595
Perfluoro-2-methylpent-2-ene	704	454	498	225*	185*

* Approximate values.

a functional group and the high Y' value suggests that the phase may selectively retard alcohols. Silicone QF-1, with its high Z' value, selectively retards ketones hence its usefulness in steroid analysis.

Aromatics

Table III lists the Kováts retention indices of all hydrocarbons and fluoro-carbons studied, whilst in Table IV an assessment of the degree of interaction between stationary phase and solute is made on the basis of solute retention increments on the fluorinated stationary phase as compared with squalane. The predictions made from Table I can be seen to be borne out, on Krytox benzene is rapidly eluted, the fluorin-ated benzenes having increasing retention indices as the percentage of fluorine present increases. This is not a regular increase but varies as expected, with substitution of the first fluorine into benzene giving rise to an increase of 48 units whereas introduction of the last fluorine (into pentafluorobenzene) gives a retention increase of only 19 units. Table III shows quite clearly that for the separation of unreacted benzene from

TABLE IV

SOLUTE-STATIONARY PHASE INTERACTIONS. RETENTION INCREMENTS, ΔI
($I_{\text{stationary phase}} - I_{\text{squalane}}$), FOR HYDROCARBONS AND FLUOROCARBONS AT 100°

Compound	ΔI			
	Krytox	Silicone QF-1	Kel F-90	Fluorolube 2000
Benzene	12	132	48	80
Fluorobenzene	73	174	82	109
1,2,4,5-Tetra-fluorobenzene	211	255	163	140
Pentafluorobenzene	253	259	180	127
Perfluorobenzene	290	256	200	116
Toluene	11	133	62	83
o-Fluorotoluene	67	162	85	101
m-Fluorotoluene	73	183	92	108
p-Fluorotoluene	73	183	90	110

its fluorination products, Krytox is the most efficient stationary phase. This effect is also seen when toluene and the three monofluoro derivatives are considered. Kel F oil is seen to have similar characteristics towards fluoroaromatics, however the effects are not as pronounced as with Krytox and a smoothing out is noted for this phase, the retention increment for substituting the first fluorine being 27 units and for the sixth fluorine a mere 2 units. This is seen clearly in Table IV where the solute–stationary phase interactions involving Kel F are relatively high for benzene but show a smaller increase to perfluorobenzene.

Fluorolube oil shows rather an unusual degree of interaction with the various fluorocarbons, the retention indices in Table III reflect both solute–stationary phase interaction and boiling point characteristics of the solutes so that monofluorobenzene has the highest retention increment. Consideration of Table IV however, where the boiling point characteristics have been eliminated, bears out the initial prediction that solute–stationary phase interactions on this phase will be of the same order of magnitude —in fact all the fluorobenzenes are included in the increment range 109–140.

Silicone QF-1 behaviour also follows that predicted from Tables I and II. The high retention of benzene relative to perfluorobenzene means that this would be the least effective stationary phase for such a separation. As this is the most polar phase, the highest retention indices are found on the silicone but a saturation, in terms of fluorine, is soon achieved by the solute molecule so that —as seen in Table IV— solute–stationary phase interactions involving tetra-, penta-, and perfluorobenzenes are very similar.

On considering the toluene and fluorotoluene data in the tables, it can be seen that no separation of parent hydrocarbon or three fluoro isomers is possible on squalane. As stated, the toluene could be separated from the fluorinated products on Krytox and silicone QF-1 would appear to be the most suitable phase for isolation of the *ortho* derivative. However, none of the phases examined could separate *meta* and *para* fluorotoluenes and the results indicate that a selective phase such as a Bentone or a metal stearate could be necessary to achieve this isomer separation.

Table V presents information on solute–stationary phase interactions on sub-

TABLE V

INFLUENCE OF SUBSTITUTING F FOR H IN THE SOLUTES. RETENTION INCRE-
MENTS, ΔI ($I_{\text{solute}} - I_{\text{parent hydrocarbon}}$), FOR FLUOROCARBONS AT 100°

Compound	ΔI				
	Krytox	Silicone QF-1	Kel F-90	Fluorolube 2000	Squalane
Fluorobenzene	48	35	27	22	− 7
1,2,4,5-Tetrafluorobenzene	147	77	69	14	−46
Pentafluorobenzene	174	66	71	−24	−61
Perfluorobenzene	193	45	73	−43	−79
o-Fluorotoluene	57	30	24	19	1
m-Fluorotoluene	62	50	30	25	0
p-Fluorotoluene	62	50	28	27	0

stituting one or more fluorine atoms for hydrogen in the solutes. This information is
complementary to that in Table IV and it can be seen that whilst fluorine substitution
makes a large positive contribution to interactions on Krytox, the effects after the
fourth fluorine is introduced are negligible on Kel F, and are actually negative on
Fluorolube and silicone QF-1. The largest negative contributions on fluorine substi-
tution are, of course, on the hydrocarbon stationary phase squalane. Again, for the
three monofluorotoluenes, Table V reveals that positional effects by the substituent
are very small and, in the case of the *meta* and *para* isomers, are almost certainly too
small to allow separation.

    Table VI lists the number of theoretical plates required for unit resolution of
three pairs of aromatic solutes using the Purnell[8] formula. Krytox is seen to be the
best stationary phase for benzene–perfluorobenzene separation, Fluorolube however
proving slightly more efficient than Krytox for the fluorobenzene–perfluorobenzene
separation whilst Kel F is the optimum phase for a fluorobenzene–fluorotoluene sepa-
ration.

TABLE VI

NUMBER OF THEORETICAL PLATES (n) REQUIRED FOR UNIT RESOLUTION OF
TWO-COMPONENT MIXTURES AT 100°

Mixture	n			
	Krytox	Silicone QF-1	Kel F-90	Fluorolube 2000
Benzene–perfluorobenzene	108	426	199	250
Fluorobenzene–perfluorobenzene	153	>10,000	429	118
Fluorobenzene-p-fluorotoluene	244	94	40	53

Paraffins

    The effect of chain branching is seen for 2-methylpentane in Table III where
Krytox and Fluorolube behave in a manner similar to non-fluorinated stationary
phases, showing a slight decrease in retention index when a branch point is incorpo-
rated into the paraffin. Kel F and silicone QF-1 behave uncharacteristically, a small

increase in retention being apparent. The changes in retention on cyclisation can be regarded as normal, Krytox giving a retention increment for cyclohexane over that for *n*-hexane of +80 units. In fact, the behaviour of Krytox for hydrocarbons generally is very close to the theoretical predictions obtained by the Kováts retention index system, thus the increment (ΔI) for introduction of $-CH_2-$ into benzene is +99 units, the increment for cyclisation of hexane is only slightly higher than the value obtained on squalane columns, and the increment for introduction of $-CH_2-$ into cyclohexane, +67 units, is also the value obtained using squalane. The effects of fluorinating 1,3-dimethylcyclohexane can be seen in Table III although the parent hydrocarbon was not available for study. By comparison of the fluorocarbon retention data on the fluorinated phases with that on squalane it is apparent that perfluoro paraffins show a high degree of interaction with Krytox, lower but significant degrees of interaction with Kel F and silicone QF-1 whilst perfluoro paraffins are rejected by Fluorolube oil in that their retention increments over squalane are negative.

Olefins

The availability of π-electrons to the fluorinated stationary phases upon introduction of a double bond into the solute is seen as enhanced retention. Krytox again demonstrates its indifference to the parent hydrocarbon, 2-methyl pent-2-ene, whereas the other three phases show enhanced retention. The effects of molecular structure on retention index are found not to be additive for this class of compound. From consideration of 1-octene and 2-methyl pentane results in Table III, increments for chain-branching and double bond introduction may be determined and theoretical retention indices for 2-methyl pent-2-ene calculated on the additive principle. The experimental values are considerably higher than the calculated values for three of the fluorinated phases and, even allowing for a large experimental error in the determination of such numerically low retention indices, this variation between experimental and calculated values is significant. Silicone QF-1 is the unusual phase in this respect, although the McReynolds constants in Table II show it to be the most polar phase studied and, in agreement with this, the retention index of 1-octene is higher than on the other phases, the value for 2-methyl pent-2-ene at 611 is lower than the values obtained on Kel F or Fluorolube. Furthermore, the calculated value of 624 is considerably higher than the experimental value obtained on this phase. The perfluoro analogue retention data shows close agreement with that predicted from the perfluoro paraffin data with the highest retention being on Krytox and retention indices decreasing in the order Kel F, silicone QF-1, Fluorolube, squalane. In perfluoro-olefins the factor contributing most to the retention is obviously the degree of fluorination and not the presence of the double bond as fluoro-olefins are much more similar to fluoro-paraffins than to fluoroaromatics.

CONCLUSIONS

Of the four low-polarity fluorinated stationary phases examined, the polarities increased in the order shown in Table II. However, a more important criterion for the selection of a stationary phase for the chromatography of fluorinated hydrocarbons would appear to be the extent of substitution of hydrogen by fluorine. Thus, for the three perfluorocarbons studied, Krytox, which has the lowest polarity, gives rise

to the highest retention indices —that is to say that it shows the highest degree of interaction with these solutes.

A mathematical treatment which is only an approximation nevertheless enables the performance of each stationary phase, towards substitution by fluorine into the solute, to be studied. If the retention index of each perfluorocarbon on squalane is subtracted from the retention index on each fluorinated stationary phase, the residual increment represents total solute–stationary phase interaction. This interaction, however, would seem to be dominated by the extent of fluorine substitution so, ignoring other contributions and making the broad assumption that all fluorine atoms in the molecule are equivalent (which they certainly are not), this increment may be divided by the number of fluorine atoms in the molecule to give an incremental effect on solute–stationary phase interaction of the substitution of a fluorine atom. The results of such a treatment are shown in Table VII.

TABLE VII

ΔI EFFECT, ON SOLUTE-STATIONARY PHASE INTERACTIONS, OF SUBSTITUTING ONE F FOR H IN THE SOLUTE (AVERAGED VALUES)

Solute	ΔI			
	Krytox	Silicone QF-1	Kel F-90	Fluorolube 2000
Aliphatic fluorocarbons (saturated)	32	6	15	—8
Olefinic fluorocarbons	44	21	24	2
Aromatic fluorocarbons	45	21	28	6

It can be seen that all values increase in the order aliphatic, olefinic, aromatic due to the ignored π-electron interaction. In the table, however, the similarities of the three classes of fluorocarbon on each stationary phase are apparent. Thus fluorine substitution has the largest effect on chromatographic retention on Krytox followed by Kel F, silicone QF-1 and Fluorolube in order of decreasing effect. There is such a wide spread between the large effects on Krytox and the almost negligible effects on Fluorolube that choice of one of these four stationary phases should allow most of the hydrocarbon–fluorocarbon–fluorinated hydrocarbon separations which may be necessary to be carried out efficiently.

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