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Gas Chromatographic Separation of Halocarbons on Porapak Q Porous Polymer Beads

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Summary

Kováts retention indices can be used to characterize the gas chromatographic behavior of C_1 and C_2 halocarbons on Porapak Q. Within each series of halocarbons the retention index increases with chlorine content, decreases with fluorine and hydrogen content, and is directly proportional to molecular weight and boiling point. Substitution of a fluorine or a bromine atom for a chlorine atom in these compounds results in characteristic changes in the retention index. The heats of adsorption are in the neighborhood of the latent heats of vaporization for the compounds examined.

Porous polyaromatic polymer bead columns are reported to exhibit a partition process different from that encountered in conventional gas-liquid or gas-solid chromatography. According to O. L. Hollis (*1*), the compounds to be separated partition directly from the gas phase into the solid amorphous polymer, involving not just the surface but the entire particle. Janák and Kubecová reported (*2*) that in thin-layer chromatography Porapak acts as an adsorbent with a large specific surface area (10^2 m^2/g), and, since Porapak is a pure polyhydrocarbon without any polar group, the adsorbent–sorbate interactions are represented by dispersion forces only.

During a study of Porapak columns for the separation of complex halocarbon mixtures, it became of practical importance to organize the retention data obtained on these materials. Because of the unusual properties of the polymer beads and of the somewhat uncertain nature of the separation mechanism the question arose whether the Kováts retention index system could be applied.

EXPERIMENTAL

Apparatus

An Aerograph Model 1521-1B gas chromatograph (Varian-Aerograph, Palo Alto, Calif.) equipped with nickel filaments (Gow-Mac, Code Ni, Mount 9225), in conjunction with a Leeds and Northrup Speedomax W recorder (1 mV, 1 sec full travel) was used to collect retention data. The flow system of the gas chromatograph was slightly modified to decrease the dead volume of the instrument and to facilitate better carrier gas flow control and the measurement of inlet pressures. All measurements were taken with a detector temperature of 225°C, a detector current of 200 mA, and an injection port temperature of 200° to 225°C. The column and room temperatures were measured at equilibrium to the nearest 0.1°C with iron-constantan thermocouples on a Leeds and Northrup multiple-range potentiometer indicator. Retention times were measured to the nearest 0.001 min with three matched Galco stopwatches using a Meylon quick-click multiple holder. The flow rate was measured at equilibrium with a 10-cc bubble flowmeter within ±0.001 min. High purity helium, which was passed through traps containing Drierite and 5A Linde molecular sieve, was used as carrier gas.

Chemicals

The tetrahalomethanes, haloforms, chlorofluoro- and difluoromethanes, and the perhaloethanes were obtained from the Du Pont Company and were of highest purity available. All other chemicals were purchased from the Matheson Company; these materials were generally of 99+ mole % purity.

Preparation of Columns

Thin-walled, ⅛-in. o.d., 316 stainless steel tubing, which was carefully cleaned, was used to prepare 2-, 3-, and 4-m columns by vacuum-packing under gentle vibration with 80- to 100-mesh Porapak Q (Waters Associates, Inc., Framingham, Mass.). Columns were conditioned at 240°C for 14 hr under helium flow. The weight of column packing was determined by difference after conditioning.

Preparation of Samples

Gaseous sample mixtures of halocarbons and *n*-paraffins were prepared by injecting appropriate amounts of liquids into evacuated stainless steel cylinders and/or by adding measured amounts of gaseous components using a simple manifold system. All samples were diluted with helium to about 0.1 mole % concentration of each component.

Sampling System

The vacuum gas-sampling system consisted of a vacuum pump, a liquid nitrogen trap, a Helicoid 0 to 60 psia gage, and a Republic stacked double four-port sampling valve. Column inlet pressure was measured with an Ashcroft test gage with a range of 0 to 100 psig and an accuracy of 0.25%. The system was evacuated before each injection, then successively 5, 10, 15, and 20 psia of a dilute mixture were measured into the sample loop which was subsequently pressurized with helium to the column inlet pressure. The sample was injected by quickly turning the handle on the Republic valve.

Computations

The retention times at infinite dilution were obtained from linear plots of adjusted retention times vs. sample pressures. Net retention volumes at infinite dilution were calculated at various temperatures for each compound using a computer program according to well-known expressions (*3,4*). Since neither argon nor hydrogen are separated from air on the columns used at room temperature or above, dead volume corrections were based on the retention volumes of air. Retention indices were calculated from net retention volumes at infinite dilution as described by Kováts (*6,7*). Heats of adsorption were computed from plots of the logarithm of the specific retention volume at infinite dilution vs. the reciprocal absolute temperature (*5*) using the least squares method and a computer program for regression analysis.

RESULTS AND DISCUSSION

Applicability of Retention Index

There are two requirements for the use of the Kováts retention index system. One specifies a linear relationship between the logarithm of

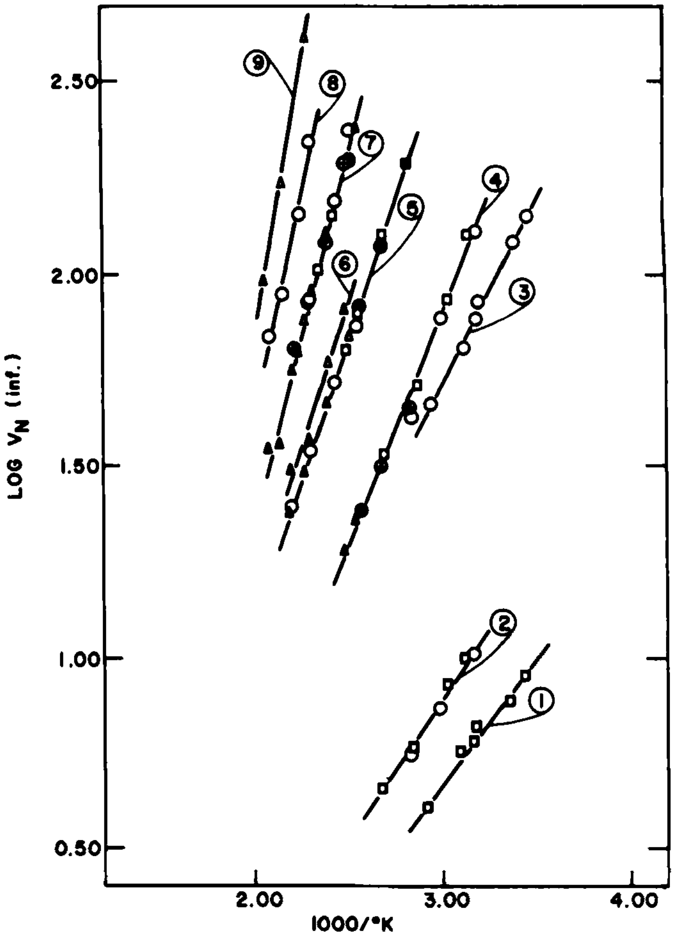

FIG. 1. Variation of the net retention volume with temperature for *n*-paraffins. (1) Methane on 3-m column; (2) methane on 4-m column; (3) ethane on 3-m column; (4) ethane on 4-m column; (5) propane on 4-m column; (6) butane on 2-m column; (7) butane on 4-m column; (8) pentane on 4-m column; (9) heptane on 2-m column.

the net retention volume and the inverse of the absolute temperature; the other, a linear relationship between the logarithm of the net retention volume at a given temperature and the carbon chain length. Both these requirements have been demonstrated for Porapak Q columns. Plots of the logarithm of the net retention volume at infinite dilution of various straight-chain hydrocarbons vs. the reciprocal absolute temperature are shown in Fig. 1, as determined on 2-, 3-, and 4-m columns. The different symbols represent data obtained at different times and/or for mixtures containing different halocarbons in addition to the hydrocarbon standards, and illustrate the good reproducibility of retention data on Porapak Q columns. As Kováts pointed out *(6,7)*, the relationship between retention volume and carbon chain length becomes more nearly linear as the carbon number increases. This is shown to be true also for Porapak Q columns, as seen in Fig. 2. Retention data for hexane and heptane were "normalized" from a 2- to a 4-m column so that they could be included in this figure.

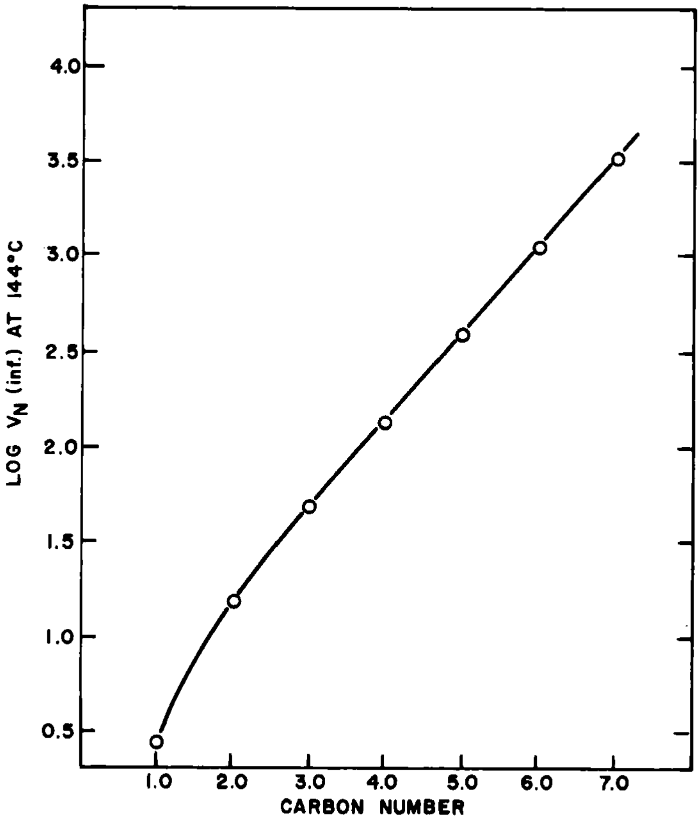

FIG. 2. Variation of the net retention volume with carbon number for *n*-paraffins.

TABLE 1

Retention Data on Porapak Q

Compound	^{130}I	dI/dT (per 10°C)	Temp. range, °C
CH_3F	174.9	−0.10	43–99
CH_3Cl	307.2	+1.2	117–157
CH_3Br	372.8	+2.0	117–157
CH_2Cl_2	446.4	+1.1	131–183
CH_2ClF	321.5	+0.10	129–183
CH_2F_2	173.1	−0.66	51–100
$CHCl_3$	550.1	−2.2	169–218
$CHCl_2F$	411.1	+0.31	162–210
$CHClF_2$	277.6	−1.1	83–127
CHF_3	160.2	−1.4	51–100
CCl_4	610.1	−3.4	169–218
CCl_3F	458.0	+1.0	162–210
CCl_2F_2	318.2	−0.34	123–183
$CClF_3$	188.9	−0.65	51–100
CCl_2FCClF_2	477.2	−0.21	131–183
$CClF_2CClF_2$	393.9	−1.1	131–179
$CClF_2CF_3$	268.0	−1.3	83–127
CF_3CF_3	161.4	−1.0	51–100
C_2H_4	181.2	+0.14	43–99
$CH_2{=}CHF$	212.6	−0.43	83–127
$CH_2{=}CHCl$	352.2	+0.79	131–179
$CH_2{=}CHBr$	417.1	+1.5	131–183
$CH_2{=}CF_2$	191.9	−0.55	43–99

Retention Indices

Kováts retention indices, I_X^T, were determined at various temperatures for a number of halocarbons and parent compounds. Table 1 shows these indices at 130°C, their temperature dependencies, dI/dT (per 10°C), and the temperature range over which the indices were determined. With the exception of methylene chloride, chloroform, carbon tetrachloride, 1,2,2-trifluorotrichloroethane, and vinyl bromide, which were run on 2-m columns because of their long retention times, all other compounds shown in Table 1 were chromatographed on 4-m columns. Additional experiments showed that the retention index did not vary significantly when determined on columns of different length. Plots of retention index vs. temperature were linear for all the compounds investigated in the temperature ranges shown in Table 1. In order to report all indices at 130°C, some of these plots had to be extrapolated. However, these extrapolations were never more than

40°C. It is interesting to note that the temperature dependencies of some of the compounds are positive while others are negative. This is related to the difference in the slopes of the log V_N (inf.) vs. $1/T$ lines of the compounds studied compared to the n-paraffin standards, resulting in an increase or decrease in the retention index with an increase in temperature.

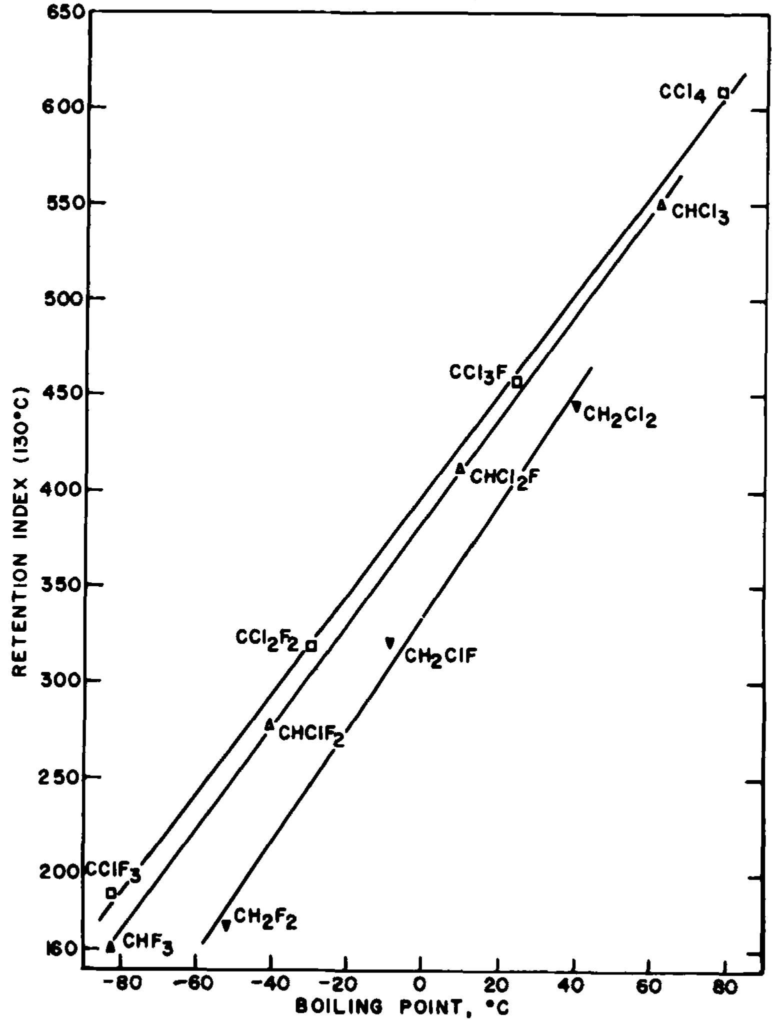

FIG. 3. Variation of retention index with boiling point for methylene halides, haloforms, and tetrahalomethanes.

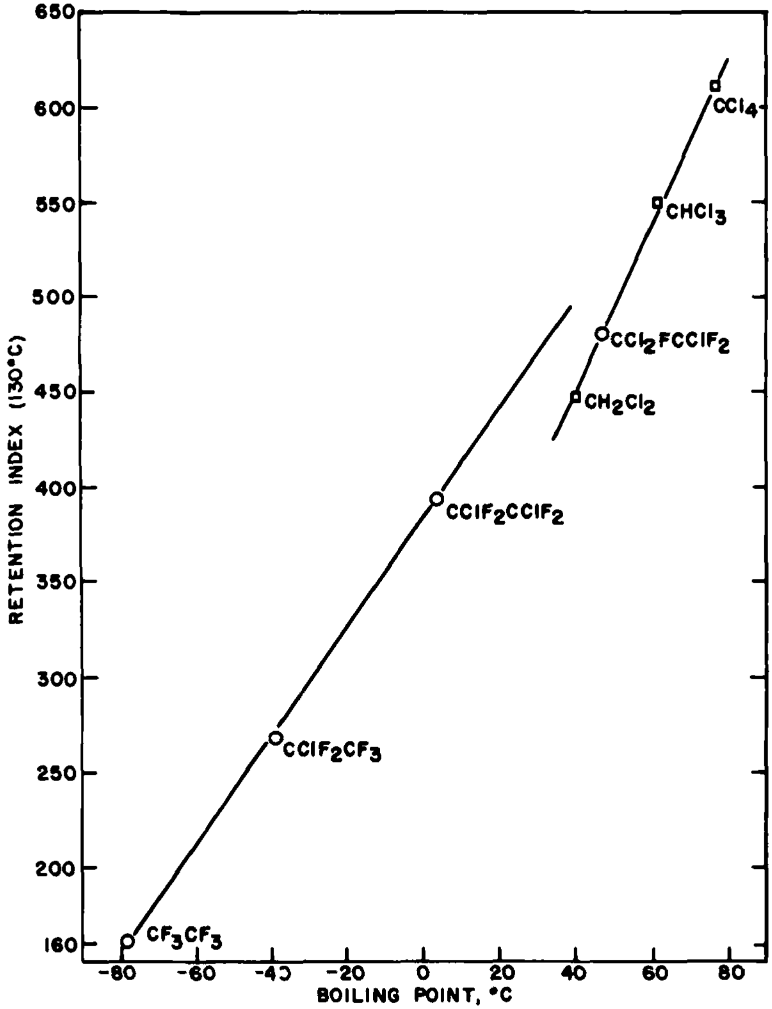

FIG. 4. Variation of retention index with boiling point for C_1 chlorocarbons and perhaloethanes.

Correlations

Kováts reported a linear relationship between the boiling point and the retention index for homologous series. A similar relationship has also been found for the more volatile members of the methylene halide, haloform, tetrahalomethane, and perhaloethane series, as shown in Figs. 3 and 4. It appears from these plots that an increase in the hy-

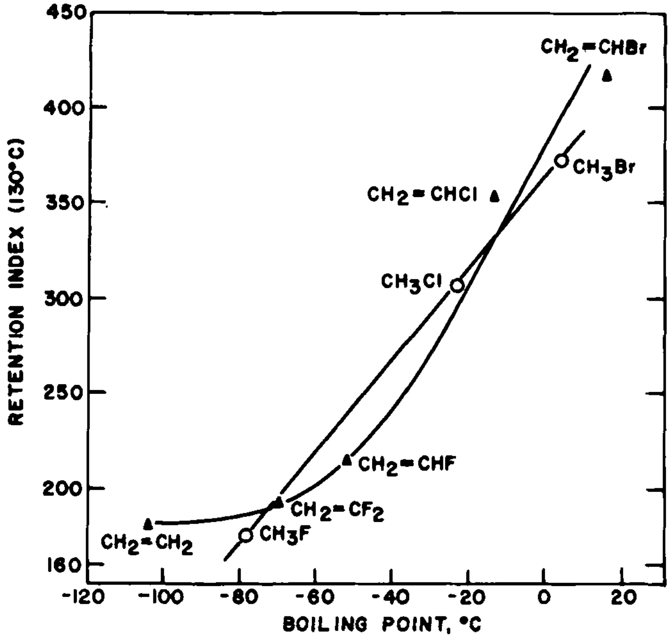

FIG. 5. Variation of retention index with boiling point for methyl halides and ethylene derivatives.

drogen content decreases the retention index of halocarbons on Porapak Q. Figure 5 shows a similar plot for the methyl halides and for various halogenated ethylenes. Again, an essentially linear relationship is noted as long as only one hydrogen atom is replaced by a halogen atom.

Plots of retention index vs. molecular weight (Fig. 6) show that the retention index of halocarbons increase with molecular weight. These plots fall into a series of straight lines similar to the homologous relationships obtained if one plots the boiling point vs. the molecular weight of these halocarbons. This straight-line relationship holds true only as long as the number of hydrogen atoms is kept constant within the series (compare the solid with the broken curves in Fig. 6). No linear relationship is obtained in a similar plot for fluoro-, chloro-, and bromomethane and for the corresponding vinyl derivatives.

Other correlations indicate that the retention indices decrease linearly with the number of fluorine atoms in the compounds (as do the boiling points and the molecular weights) but increase with the number of chlorine atoms (Fig. 7). No linear relationship exists between

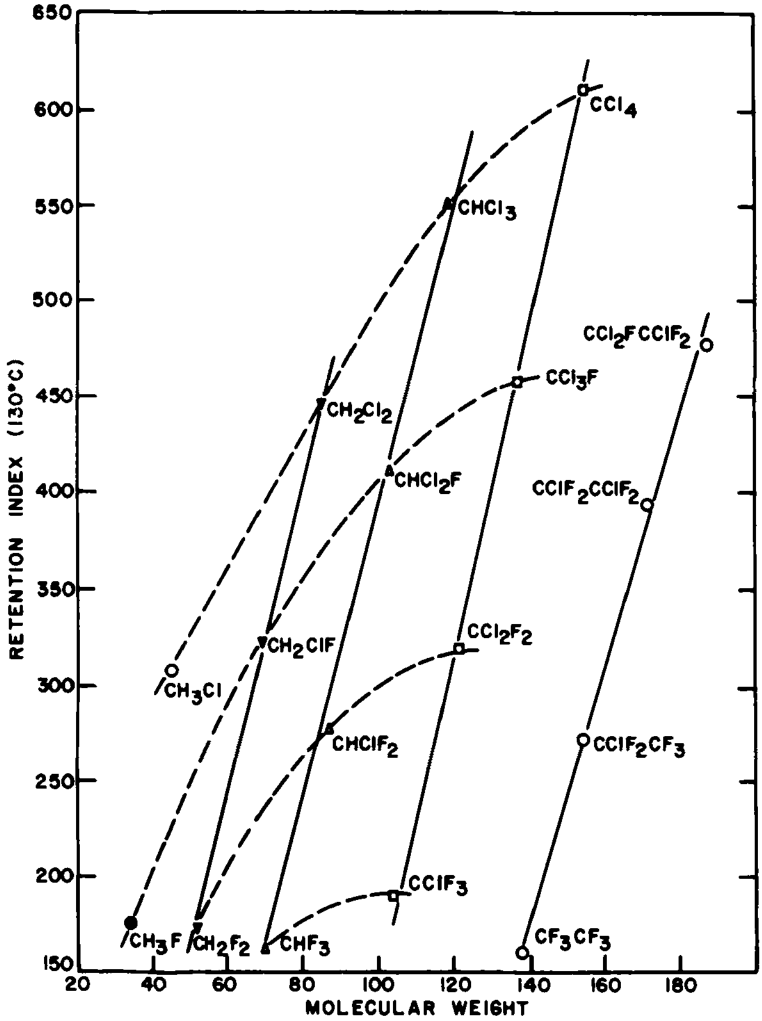

FIG. 6. Retention index vs. molecular weight for halomethanes and haloethanes.

the number of hydrogen atoms in the compounds studied and the retention index (Fig. 8). The results of these plots show that similar substitution in similar compounds produces the same change in retention index only when substituting one halogen atom for another. Thus, characteristic values for the substitution of a fluorine or a bromine atom for a chlorine atom in the fluorocarbon series can be obtained. The results are shown in Table 2. The average value of *dI* is −134 ± 17 when fluorine is substituted for chlorine and 65.2 ± 0.7 for a similar substitution by bromine.

A plausible explanation for the nonlinearity of the plots for the halocarbon series in which the hydrogen number is changed may be found in Fig. 9. Here, the retention index is plotted vs. the electric dipole moment—a measure of the polarity of the compound. Although

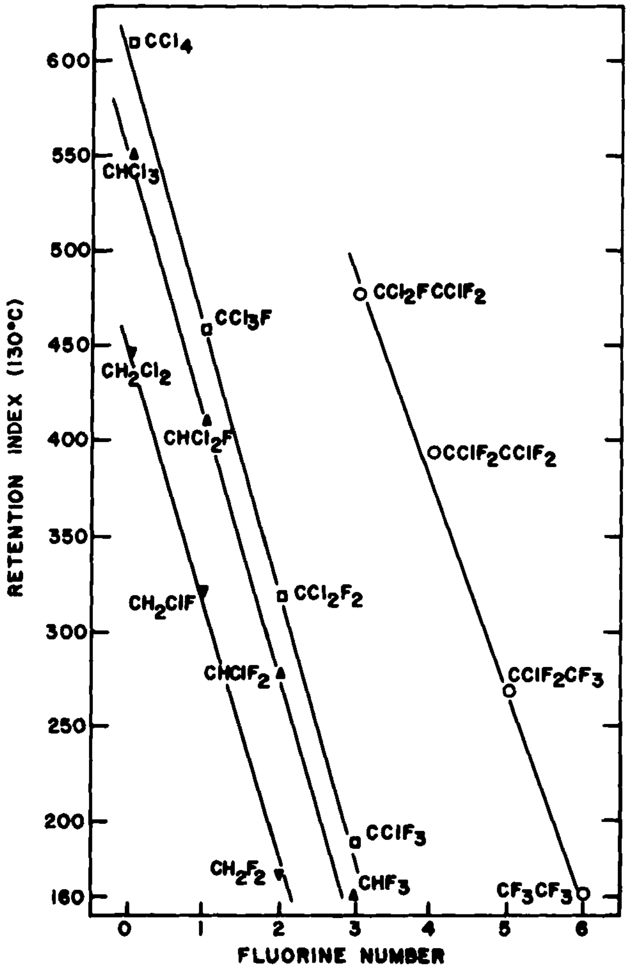

FIG. 7. Retention index vs. fluorine number.

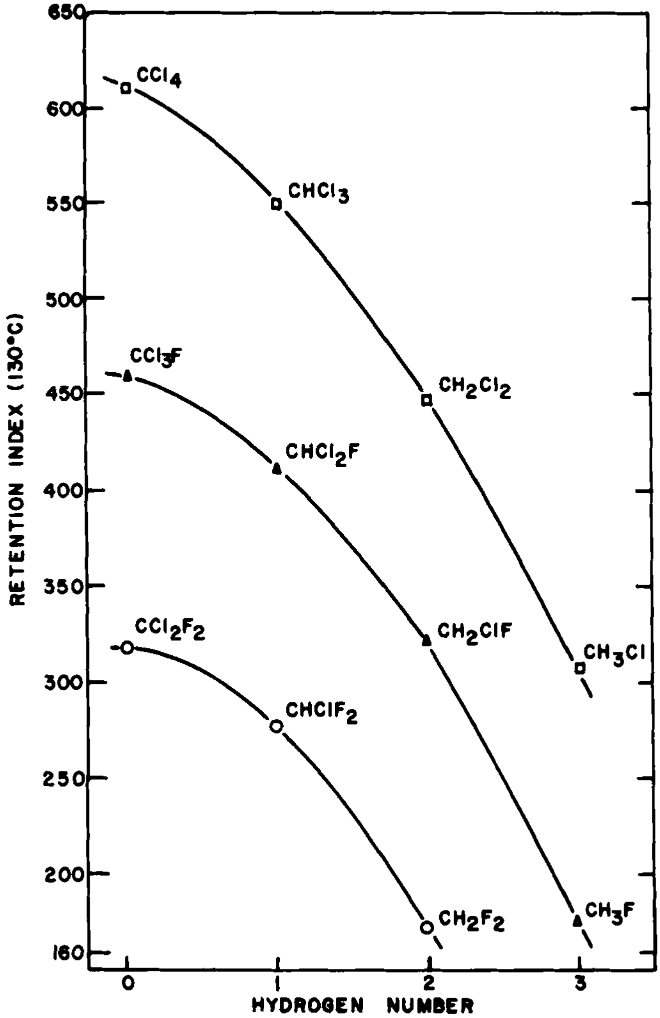

FIG. 8. Retention index vs. hydrogen number.

the polarity of the halocarbons changes relatively little within a series in which all the members have the same number of hydrogen atoms, it increases markedly as the hydrogen number is increased. This results in shorter retention times for the more polar members of the series on the essentially nonpolar Porapak Q columns. Conversely, although the molecular weight is greatly increased in going from methyl fluoride to methylene difluoride and to fluoroform, the dipole moment and the retention index change very little.

The effect of polarity on the separation of halocarbons on Porapak columns is further supported by comparison of retention values obtained in this laboratory on Porapak Q with those reported by König (*8*) who used a Porapak S column to separate components in aerosols.

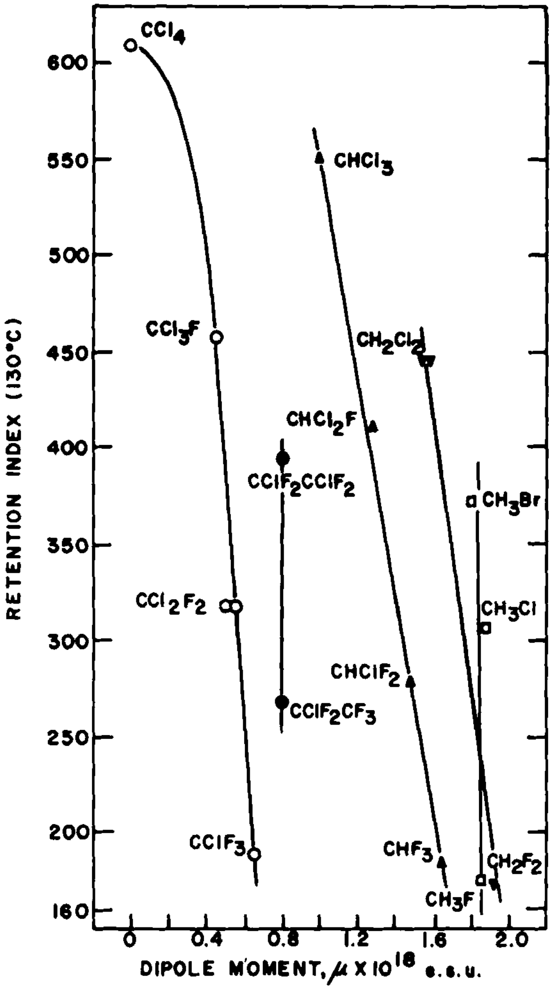

FIG. 9. Retention index vs. polarity.

TABLE 2

Changes in Retention Index upon Substitution of Fluorine or Bromine for Chlorine

Halocarbons	dI/Atom exchanged, at 130°C
CH_3F to CH_3Cl	132
$CClF_3$ to CCl_4	138
CHF_3 to $CHCl_3$	139, 134, 117
CH_2F_2 to CH_2Cl_2	125, 148
$CH_2{=}CHF$ to CH_2CHCl	140
CH_3Cl to CH_3Br	65.6
$CH_2{=}CHCl$ to $CH_2{=}CHBr$	64.9

Porapak S is somewhat more polar than Porapak Q and should retain polar compounds longer than nonpolar compounds of similar boiling points and molecular weights. Table 3 shows that the differences in the retention indices indeed increase with increasing polarity of the compound chromatographed. A plot of the ΔI values for CCl_4, $CHCl_3$, and CH_2Cl_2 vs. the corresponding dipole moments is linear.

TABLE 3

Effect of Column Polarity on Retention

Compound	^{165}I (Porapak S)[a]	^{165}I (Porapak Q)	$\Delta^{165}I$
CCl_2FCClF_2	392	391	1
CCl_2F_2	319	317	2
CCl_3F	468	462	6
CCl_4	621	613	8
$CHCl_3$	586	558	28
CH_2Cl_2	487	450	37

[a] From H. König, *Z. Anal. Chem.*, **232**, 427 (1967).

Heats of Adsorption

In the case of porous adsorbents, penetration of adsorbate to the interior may result in chemisorption at interior surfaces, in physical adsorption, or even in solution. True solution in a solid is said to be usually endothermic and is distinguished by this from adsorption which is always exothermic (*9*). Chemical bonds are usually stronger than physical forces of attraction; thus, heats of physical adsorption should be low and in the neighborhood of heats of liquefaction.

TABLE 4

Heats of Vaporization and Heats of Adsorption of Various Compounds on Porapak Q

Compound	$-\Delta H_a$, kcal/mole	ΔH_v, kcal/mole	$-\Delta H_a/\Delta H_v$
CH_4	4.1	2.06	2.0
C_2H_6	6.0	3.52	1.7
C_3H_8	7.6	4.49	1.7
C_4H_{10}	9.7	5.35	1.8
C_5H_{12}	11.6	6.16	1.9
CH_3Cl	7.1	5.12	1.4
CH_3F	5.7	4.06	1.4
CH_3Br	8.3	5.67	1.5
CH_2Cl_2	8.7	6.68	1.3
$CHCl_3$	10.5	6.84	1.5
CCl_4	11.4	7.17	1.6
CH_2ClF	8.2	5.59	1.5
CH_2F_2	6.7	4.45	1.5
$CHCl_2F$	9.4	4.96	1.9
$CHClF_2$	7.7	4.83	1.6
CHF_3	6.5	3.99	1.6
CCl_3F	10.1	5.98	1.7
CCl_2F_2	8.2	4.80	1.7
$CClF_3$	6.8	3.60	1.9
CCl_2FCClF_2	11.4	6.56	1.7
$CClF_2CClF_2$	9.6	5.60	1.7
$CClF_2CF_3$	7.7	4.65	1.7
CF_3CF_3	5.8	3.86	1.5
$CH_2{=}CH_2$	5.8	3.23	1.8
$CH_2{=}CHF$	6.2	3.97	1.6
$CH_2{=}CF_2$	6.5	3.71	1.8
$CH_2{=}CHCl$	8.3	5.20	1.6
$CH_2{=}CHBr$	9.4	5.84	1.6
HCl	6.5	3.76	1.7
CO_2	5.7	3.66 (triple point)	1.6

The heats of adsorption, ΔH_a, of various compounds on Porapak Q are shown in Table 4. Also listed for comparison are the latent heats of vaporization of these compounds at their normal boiling points. The heats of adsorption are negative and constant in the temperature ranges investigated (see Table 1). They are near the corresponding latent heats, and the ratios of $\Delta H_a/\Delta H_v$ are remarkably similar for most of the compounds shown in Table 4.

For the *n*-paraffins, the heats of adsorption increase linearly with the carbon number and molecular weight, as expected. Ethylene has a slightly lower heat of adsorption than ethane, probably because of the added polarity of the double bond. Fluorocarbons show heats of adsorption that decrease linearly with molecular weight within each series. Although polar molecules are irreversibly adsorbed on many adsorbents (*10*), this does not seem to be the case with Porapak Q. Compounds such as hydrogen chloride can be eluted wih relative ease even at room temperature.

CONCLUSIONS

Porous polymer bead columns are useful for the separation of low-boiling components in complex halocarbon mixtures. Retention data obtained on Porapak Q columns can be organized using the Kováts retention index system.

Molecular weight and boiling point seem to govern separation on these columns although polarity of sorbate and sorbent also appear to be of some influence. The magnitude of the heats of adsorption of halocarbons indicates physical adsorption rather than chemisorption of these materials on Porapak Q. Such evidence, however, is not usually enough to pinpoint sorption mechanisms (*11*), and further studies of porous polymer bead materials should be of some interest.

Acknowledgments

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