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GAS CHROMATOGRAPHY OF FLUORINATED COMPOUNDS ON POROUS POLYMERS

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SUMMARY

The porous polymers Chromosorb-101 and Chromosorb-102 are weakly specific adsorbents. Complete separation of organic compounds and their fluorinated analogues is possible on sorbents of this type; the fluorinated compounds usually elute first. The heats of adsorption of some substances and their fluorinated analogues on the weakly specific adsorbents Chromosorb-101 and Chromosorb-102 and the specific adsorbent Porapak T were measured.

INTRODUCTION

It has been shown earlier^{1,2} that the porous polymers Chromosorb-101 and Chromosorb-102 are weakly specific adsorbents of the III-d type³ as π -bonding phenyl groups exist on their surfaces. However, the contribution of nonspecific dispersion interactions to the total energy of the molecules of different compounds on these polymer surfaces predominates. This can be seen if the retention volumes of organic compounds of different groups (A,B,D) are compared with the retention volumes of their fluorinated analogues. When the energy of dispersion interactions is evaluated the values of the electron polarizability and the Van der Waals radii of groups of interacting molecules are very important. The polarizabilities of hydrogen and fluorine are slightly different, but the hydrogen Van der Waals radius is less than that of fluorine. Therefore the value of α/r^6 characterizing the dispersion interaction is less for F than for H. Since there is a partial or complete change of hydrogen atoms for fluorine atoms in the organic molecules studied, this must result in a decrease in the retention volumes and heats of adsorption (especially in the case of the predominant appearance of nonspecific dispersion interactions). This effect was noticed earlier⁴ in calorimetric analyses of heats of adsorption of methylcyclohexane and perfluoromethylcyclohexane (molecules of group A) on the nonspecific adsorbent graphitized carbon black and the specific adsorbent Zeolite.

EXPERIMENTAL

Measurements were made on a Zvet-3 gas chromatograph with a thermal conductivity detector. Samples were injected with a $1\text{-}\mu\text{l}$ syringe. Chromosorb-101, Chromosorb-102 (Johns Manville) and Porapak T (Waters Associates) were used as adsorbents.

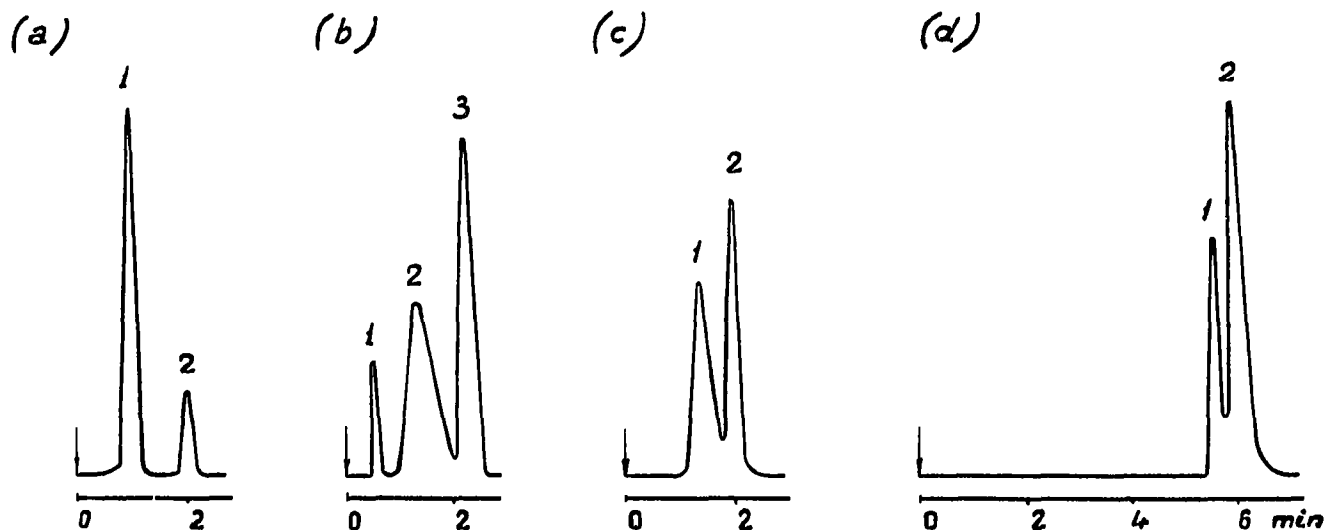


Fig. 1 Chromatograms obtained on a column, length 0.37 m, with Chromosorb-101: (a) 1 = tri-fluoromethyl acetate, 2 = methyl acetate; temperature 130° ; carrier gas (helium) rate 50 ml/min; (b) 1 = water, 2 = perfluoropropanol, 3 = propanol, temperature 130° ; carrier gas (helium) rate 50 ml/min; (c) 1 = *n*-perfluoroamyl alcohol, 2 = *n*-amyl alcohol, temperature 190° ; carrier gas (helium) rate 36 ml/min; (d) 1 = *p*-fluoroacetophenone, 2 = acetophenone, temperature 220° ; carrier gas (helium) rate 30 ml/min.

RESULTS AND DISCUSSION

Fig. 1 shows chromatograms of the separation of compounds of different classes and their fluorinated analogues on the porous polymer Chromosorb-101. In all four cases (alcohols, ester and ketone) the substitution of hydrogen atoms by fluorine atoms results in a decrease of the retention volumes (even in the case of one atom of fluorine in acetophenone). Thus, it can be seen that the contribution of the nonspecific dispersion interaction to the total energy of adsorption on Chromosorb-101, at fixed temperatures, predominates. In the case of molecules of group D, orientation interaction takes place especially at lower temperatures. In fact, the order of elution of amyl and perfluoroamyl alcohol on Chromosorb-102 is reversed in the temperature interval $100\text{--}250^{\circ}$ (Fig. 2). The chromatogram for the methyl acetates and acetophenone on this Chromosorb is analogous to that on Chromosorb-101 (Fig. 3). It was interesting to compare the behaviour of fluorinated compounds on weakly specific and specific adsorbents. Fig. 4 shows a chromatogram of the separation of propanol and perfluoropropanol on the polar porous polymer Porapak T. In this case the nonfluorinated alcohol elutes much earlier than the fluorinated one owing to the large influence of the orientation interactions. Heats of adsorption were calculated from the temperature dependences. The results are shown in Table I.

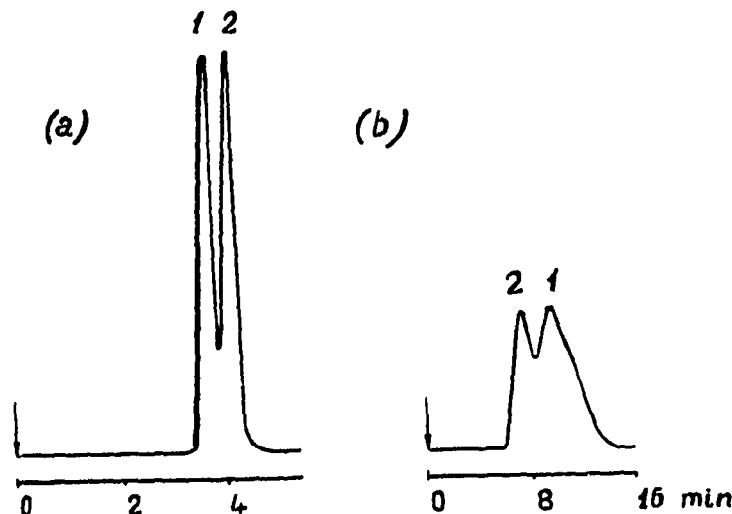


Fig. 2. Chromatograms obtained on a column with Chromosorb-102: (a) 1 = *n*-perfluoroamyl alcohol, 2 = *n*-amyl alcohol; column length 2 m; temperature 230°; carrier gas (helium) rate 30 ml/min; (b) 1 = *n*-perfluoroamyl alcohol, 2 = *n*-amyl alcohol; column 0.375 m; temperature 120°; carrier gas (helium) rate 50 ml/min.

The heats of adsorption of the fluorinated compounds on weakly specific adsorbents are generally less than those of the nonfluorinated compounds. The exception is amyl alcohol for both Chromosorbs. The fact that heats of adsorption of fluorinated compounds are less than those of nonfluorinated ones shows that the predominant contribution to the total energy of interaction is made by the nonspecific dispersion interaction which is proportional to a/r^6 .

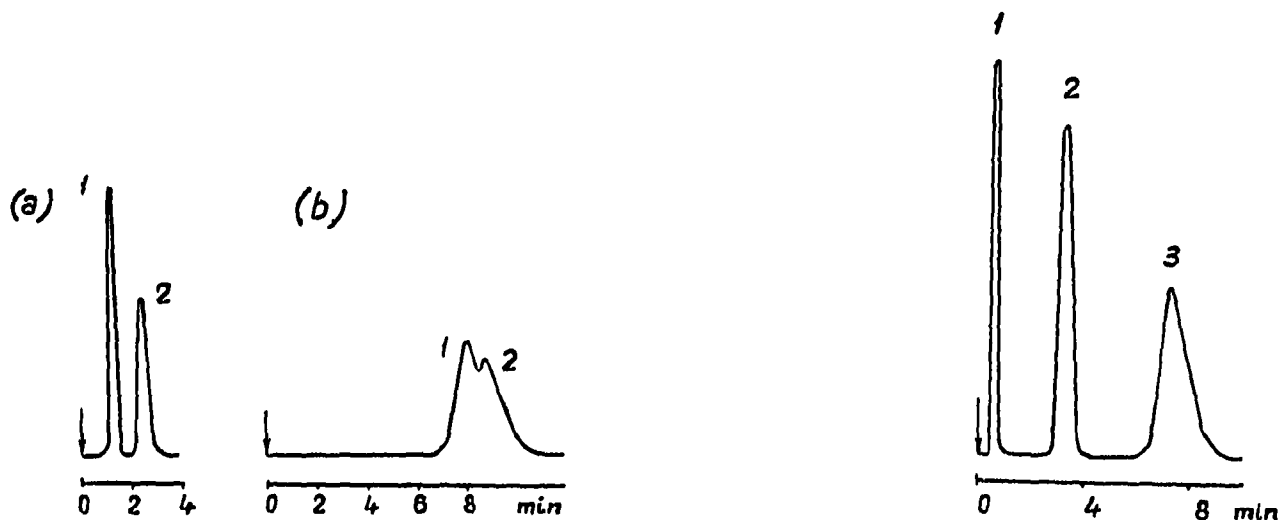


Fig. 3. Chromatograms obtained on an 0.375 m column with Chromosorb-102: (a) 1 = trifluoromethyl acetate; 2 = methyl acetate; temperature 100°, carrier gas (helium) rate 60 ml/min; (b) 1 = *p*-fluoroacetophenone, 2 = acetophenone; temperature 190°; carrier gas (helium) rate 43 ml/min.

Fig. 4. Chromatograms obtained on an 0.375 m column with Porapak T: 1 = water, 2 = *n*-propanol, 3 = perfluoropropanol; temperature 150°; carrier gas (helium) rate 45 ml/min.

TABLE I

HEATS OF ADSORPTION (Q) OF SOME ORGANIC COMPOUNDS AND THEIR FLUORINATED ANALOGUES ON THE POROUS POLYMERS CHROMOSORB-101, CHROMOSORB-102 AND PORAPAK T

	Q (kcal/mole)		
	Weakly specific		Specific
	Chromosorb-101	Chromosorb-102	Porapak T
C_3H_7OH	10.2	—	11.4
$C_3H_5F_5OH$	9.7	—	13.7
CH_3COOCH_3	9.3	10.5	11.1
CF_3COOCH_3	8.3	9.9	10.3
$C_5H_{11}OH$	12.1	11.0	15.1
$C_5H_9F_9OH$	12.8	13.2	20.8
$CH_3COC_6H_5$	13.6	15.3	—
$p\text{-}CH_3COC_6H_4F$	13.2	14.4	—

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