

CHROMSYMP. 911

GAS CHROMATOGRAPHY ON POROUS POLYMERS

II. RETENTION–STRUCTURE CORRELATIONS FOR AROMATIC SUBSTANCES, CHROMATOGRAPHED ON SORBENTS OF DIFFERENT POLARITIES

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SUMMARY

The retention mechanism of *n*-alkanes and aromatic compounds, in gas chromatography on polymeric sorbents of different polarities, has been studied. The sorbents were copolymers of 1,4-divinylbenzene and 1,4-di(methacryloyloxymethyl)naphthalene with various compositions. It has been found that *n*-alkanes behave differently on each sorbent, and a retention mechanism has been proposed. Concerning the retention of aromatic compounds, solute–sorbent interactions are specific. The retention indices for various aromatic compounds change linearly with the total selectivity (determined by the McReynolds method), suggesting that the retention mechanism remains the same for all the polymers used. The effect of temperature on the retention indices has also been studied.

INTRODUCTION

Among the most important factors determining the usefulness of porous polymeric beads (PPBs) as column packings in gas chromatography (GC) are the degree of cross-linking and the “polarity”^{1,2}. The degree of cross-linking is responsible for their thermal and mechanical stability and also determines the internal structure and porosity of porous polymers³. In general, an increase in the degree of cross-linking leads to an increase in both the thermal and mechanical stability. Besides, it was found⁴ that the glass transition temperature, T_g , increases with the degree of cross-linking. On the other hand, the internal structure and the porosity of beads are not simple functions of the degree of cross-linking but also depend strongly upon the synthesis conditions⁵.

The polarity of PPBs depends mainly on the chemical nature of the monomers used and their relative amounts in the polymer⁶.

The complexity of PPB structure makes very difficult a study of the retention mechanism. It is commonly accepted^{7,8} that both surface adsorption and bulk absorption may contribute to retention. Which of these two phenomena prevails depends upon the details of the PPB structure and the chemical nature of both the

TABLE I
 PROPERTIES OF THE POLYMERIC SORBENTS USED

In each case: $T_g \approx 260^\circ\text{C}$; initial temperature of decomposition, $\approx 330^\circ\text{C}$.

Sorbent No.	Mole fraction of monomers		Surface area (m^2/g)	Porosity (cm^3/g)	McReynolds constants			Total selectivity ΣI
	1,4-DVB	1,4-DMN			x	y	z	
1	0.8	0.2	161.0	1.84	72	176	134	382
2	0.5	0.5	169.0	1.34	130	263	231	624
3	0.2	0.8	135.0	1.59	255	381	343	979

sample molecules and the polymer, as well as on the temperature^{9,10}. In particular, at temperatures below the glass transition temperature it seems reasonable to assume that retention is dominated by absorption, whereas at higher temperatures (greater than T_g) the contribution due to bulk absorption may be important. Also, bulk adsorption occurs when the sample is a good solvent for the polymeric sorbent¹¹.

The influence of sorbent polarity upon the retention behaviour is expected to differ for various classes of samples. In this paper we consider the retention of various mono- and disubstituted benzene derivatives, chromatographed on a series of copolymers of 1,4-divinylbenzene (DVB) and 1,4-di(methacryloyloxymethyl)naphthalene (1,4-DMN). Both monomers are known cross-linking agents¹² and, therefore, we expected to obtain PPBs of high thermal and mechanical stability. On the other hand, by changing the relative amounts of the monomers we can obtain polymers of different polarities, as determined by chromatographic tests^{13,14}.

In this work, we discuss the effects of the polymer polarity on the selectivity towards various aromatic compounds, and the correlations between the retention data and the structure of solute molecules. The behaviour of *n*-alkanes is also considered in some detail.

EXPERIMENTAL

Preparation and properties of the sorbents

Porous copolymers of 1,4-divinylbenzene with 1,4-di(methacryloyloxymethyl)naphthalene were obtained by suspension copolymerization in the presence of a mixture of toluene and *n*-decanol as a diluent. By changing the molar fractions of the monomers, sorbents of different polarities have been obtained. Inasmuch as both monomers are cross-linking agents, the copolymers obtained exhibit high thermal as well as mechanical stability and do not undergo swelling in various solvents. In Table I the properties of the three sorbents used in this work are summarized. Details of the synthesis conditions and a physico-chemical study of these polymers will be published elsewhere.

Chromatographic measurements

Chromatographic measurements were carried out on a GCHF 18.3 gas chromatograph (Chromatron, Berlin, G.D.R.) equipped with a thermal conductivity detector. Hydrogen at a flow-rate of 50 ml/min was used as the carrier gas; the bridge current was 150 mA. The stainless-steel columns measured 100 cm × 4 mm I.D. The diameter of the sorbent beads was always 0.15–0.20 mm. Columns (packed with PPBs) were heated till the retention times for *n*-alkanes were constant. The measurements were performed at 240, 245, 250 and 255°C. The samples were injected by means of a 1- μ l syringe (Scientific Glass Engineering, North Melbourne, Australia). In the case of liquid substances, trace amounts were injected by dipping the needle (at the zero position of the piston) into the sample for 1 s. Solid substances, in trace amounts, were injected in the form of benzene solutions.

RESULTS AND DISCUSSION

It is known that the logarithm of the adjusted retention time for *n*-alkanes, t'_{R} , is a linear function of *n*, the number of carbon atoms, *i.e.*:

$$\log t'_{R(n)} = An + B \quad (1)$$

The parameters A and B are functions of temperature and also depend on the properties of a given sorbent. The relationship between the capacity factor, $k' = t'_R/t_0$, where t_0 is the dead-time, and the enthalpy, ΔH , and entropy, ΔS , of sorption is given by

$$\ln k' = -\frac{\Delta H}{RT} + C, \quad C = K\Delta S \quad (2)$$

where K is a constant independent of sample properties. Assuming that both ΔH and ΔS are also linear functions of the number of carbon atoms for n -alkanes, we can write

$$\Delta H_n = \Delta H_1 n + \Delta H_0 \quad (3)$$

and

$$\Delta S_n = \Delta S_1 n + \Delta S_0 \text{ or } C_n = C_1 n + C_0 \quad (4)$$

where $C_1 = K\Delta S_1$ and $C_0 = K\Delta S_0$. Thus, from eqns. 1-4 we obtain:

$$\begin{aligned} \log t'_{R(n)} &= \frac{1}{2.3} \cdot \ln k'_n + \log t_0 = \frac{1}{2.3} \left(-\frac{\Delta H_n}{RT} + C_n \right) + \log t_0 \\ &= \frac{1}{2.3} \left(-\frac{\Delta H_1}{RT} + C_1 \right) n + \frac{1}{2.3} \left(-\frac{\Delta H_0}{RT} + C_0 \right) + \log t_0 \end{aligned} \quad (5)$$

From eqns. 1 and 5 we obtain

$$A = \frac{1}{2.3} \left(-\frac{\Delta H_1}{RT} + C_1 \right) \quad (6)$$

and

$$B = \frac{1}{2.3} \left(-\frac{\Delta H_0}{RT} + C_0 \right) + \log t_0 \quad (7)$$

When t_0 can be assumed to be temperature-independent, eqns. 6 and 7 imply that both A and B are proportional to the reciprocal of the temperature.

The Kováts retention index for any sample, I_x , is given by

$$I_x = 100 \left[n + \frac{\log t'_{R(x)} - \log t'_{R(n)}}{\log t'_{R(n+1)} - \log t'_{R(n)}} \right] \quad (8)$$

where $t'_{R(x)}$ is the adjusted retention time of the sample x . Since eqn. 2 is valid for any sample, inserting it into eqn. 8 gives

$$\begin{aligned} I_x &= -\frac{100}{2.3ART} \cdot \Delta H_x + \frac{100}{A} \left(\frac{1}{2.3} C_x - B + \log t_0 \right) \\ &= \alpha_1 \Delta H_x + \alpha_2 C_x + \alpha_3 \end{aligned} \quad (9)$$

where

$$\alpha_1 = -\frac{100}{2.3ART}, \alpha_2 = \frac{100}{2.3A}, \alpha_3 = \frac{100}{A} (\log t_0 - B) \quad (10)$$

Differentiating eqn. 9 with respect to temperature, we obtain:

$$\partial I_x / \partial T = (\partial \alpha_1 / \partial T) \Delta H_x + (\partial \alpha_2 / \partial T) C_x + \partial \alpha_3 / \partial T \quad (11)$$

Let us consider three situations that can occur in real systems: (1) both A and B change with temperature; (2) A is temperature-dependent, whereas B is constant; (3) A is temperature-independent and B changes with temperature. We have excluded the situation when both A and B are temperature-independent, as it does not seem experimentally accessible. Situations 1 and 2 differ only slightly: when B is temperature-independent, then ΔH_0 vanishes. This means that the lines given by eqn. 1 and corresponding to various temperatures meet when $n=0$. In both cases, $\partial I_x / \partial T$ depends on both the enthalpy and entropy of sorption. The constancy of the parameter A (situation 3) leads to more serious consequences. Now, $\Delta H_1 = 0$ and, hence, $\Delta H_n = \Delta H_0$ is independent of the number of carbon atoms in n -alkanes. Besides, eqn. 11 is reduced to

$$\partial I_x / \partial T = (\partial \alpha_1 / \partial T) \Delta H_x + \partial \alpha_3 / \partial T \quad (12)$$

since $\partial \alpha_2 / \partial T$ vanishes.

The above argument is purely mathematical and does not involve any considerations of the properties of real chromatographic systems. In particular, we have not attempted to correlate the behaviour of the parameters A and B with the retention mechanism.

Now, we turn to our measurements of retention of n -alkanes on polymeric sorbents. For all PPBs studied, linear dependences between the logarithm of the adjusted retention time and the number of carbon atoms have been found. In fig. 1 we present results for sorbents 1 and 3, whereas in Table II the parameters A and B for all systems are summarized. In Figs. 2 and 3 we show plots of A and B , respectively, against reciprocal temperature. It is seen that for sorbent 1 the parameter B is nearly temperature-independent and A is proportional to $1/T$. In the case of sorbent 2, both A and B depend upon the reciprocal of the temperature, as predicted by eqns. 6 and 7, whereas for sorbent 3 we observe that A is constant. These results illustrate our foregoing argument very well. However, we must expect the retention mechanism of n -alkanes to show some peculiarities for each PPB studied.

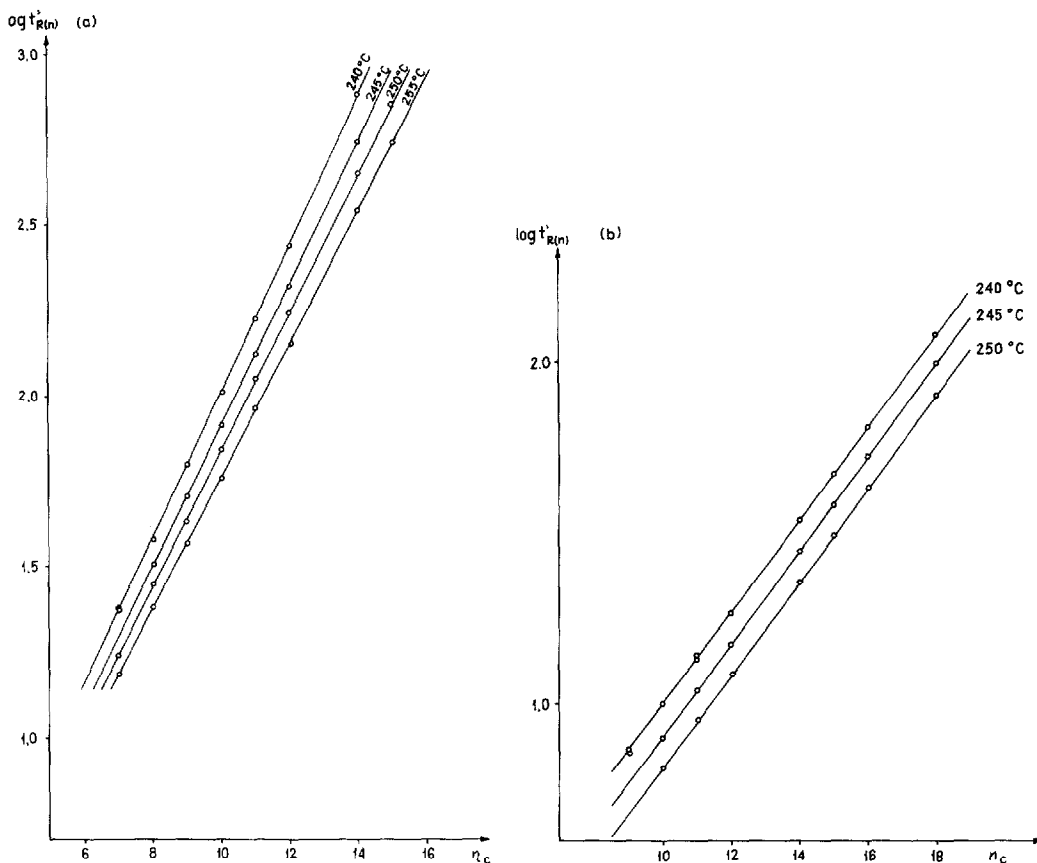


Fig. 1. The dependence of the logarithm of the adjusted retention time on the number of carbon atoms for *n*-alkanes on (a) sorbent 1, (b) sorbent 3.

From Fig. 3 and the results given in Table II, we can conclude that the slopes of the lines representing the dependence of B on $1/T$ increase with increasing sorbent polarity. Thus, the value of ΔH_0 is expected to increase with the sorbent polarity. In Table III we give the values of ΔH_n and C_n for the *n*-alkanes used here, as well as the values of ΔH_0 , ΔH_1 , C_0 and C_1 , calculated from eqns. 3 and 4. It is seen that the value of ΔH_0 does increase with the sorbent polarity. In particular, for sorbent 1 the value of ΔH_0 is practically equal to zero. The most surprising result is the observed temperature independence of the parameter A for sorbent 3, which implies that ΔH_n is independent of the number of carbon atoms (*cf.*, also Table III). Moreover, in this case we observe a gradual decrease in the loss of entropy resulting from sorption with increasing number of carbon atoms. In general, the entropy loss should increase with the number of carbon atoms in *n*-alkanes, as is observed for sorbents 1 and 2. The differences in the behaviour of our polymers towards *n*-alkanes cannot be explained in terms of differences in their polarities.

To find an explanation for the observed constancy of the sorption enthalpy and the changes in sorption entropy for *n*-alkanes sorbed on the polymeric sorbent

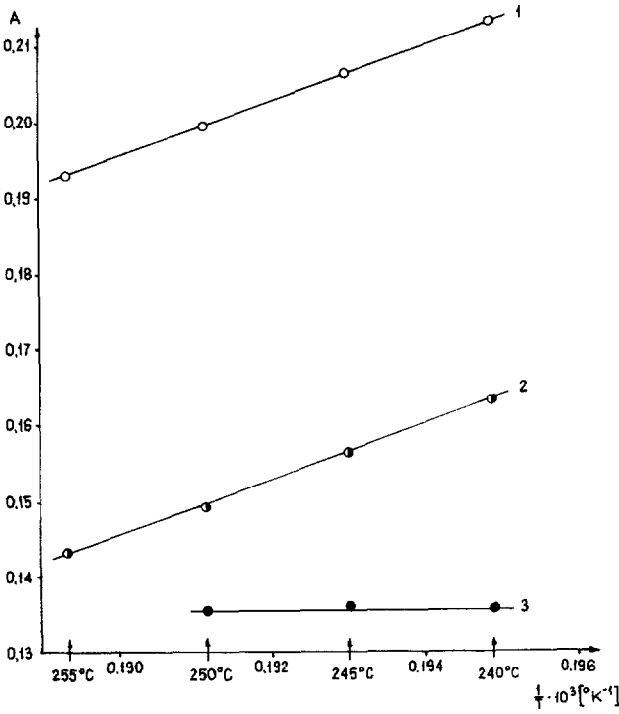


Fig. 2. The dependences of the parameter *A* of eqn. 1 on the reciprocal of the temperature for sorbents 1 (○), 2 (○) and 3 (●).

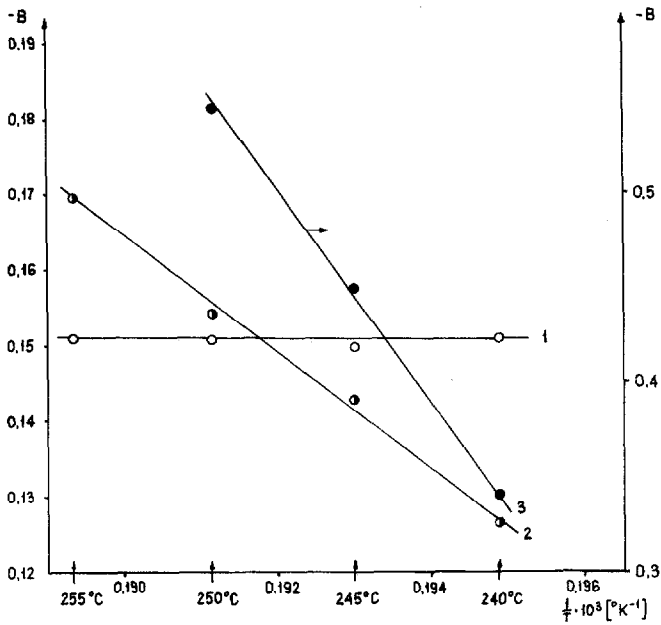


Fig. 3. The dependences of the parameter *B* of eqn. 1 on the reciprocal of the temperature. Sorbents as in Fig. 2.

TABLE II

PARAMETERS OF EQN. 1 FOR *n*-ALKANES, OBTAINED ON VARIOUS SORBENTS AND AT DIFFERENT TEMPERATURES

Temperature (°C)	Sorbent 1		Sorbent 2		Sorbent 3	
	A	B	A	B	A	B
240	0.213	-0.151	0.161	-0.126	0.135	-0.340
245	0.206	-0.150	0.156	-0.143	0.136	-0.450
250	0.199	-0.151	0.149	-0.154	0.135	-0.545
255	0.193	-0.151	0.143	-0.169	-	-

3, we must consider the structure of the beads. Taking into account that our PPBs show the glass transition at temperatures of about 260°C, *i.e.*, higher than those used in our chromatographic measurements (see Table I), we can assume that surface adsorption dominates the retention mechanism. Next, we assume that only part of the alkane molecule can interact with the sorbent. This can happen when the surface has only very small "flat" elements or when the sorbent exhibits ultramicroporous structure (see Fig. 4).

Taking into account that our measurements were performed for *n*-alkanes with greater than ten carbon atoms (on sorbent 3), we assume that the interacting part of the adsorbed molecule contains less than ten carbon atoms. Both situations, shown in Fig. 4, are conceivable and both explain the observations. The constancy of ΔH_n results from the fact that, regardless of the actual length of the adsorbed molecule, the number of carbon atoms interacting with the surface remains the same. Next, considering the decrease in the entropy loss resulting from sorption when the number

TABLE III

THE VALUES OF ΔH_n (kJ/mol) AND C_n FOR *n*-ALKANES ON DIFFERENT SORBENTS AND THE PARAMETERS ΔH_0 , ΔH_1 , C_0 AND C_1 OF EQNS. 3 AND 4

<i>n</i> -Alkane	Sorbent 1		Sorbent 2		Sorbent 3	
	$-\Delta H_n$	$-C_n$	$-\Delta H_n$	$-C_n$	$-\Delta H_n$	$-C_n$
Heptane	48.8	10.4	-	-	-	-
Octane	55.8	11.6	67.6	15.6	-	-
Nonane	62.7	12.7	74.3	16.8	-	-
Decane	69.7	13.9	81.0	18.0	104.0	24.0
Undecane	76.6	15.0	87.6	19.3	104.1	23.7
Dodecane	83.6	16.1	94.3	20.5	104.0	23.4
Tetradecane	97.4	18.4	107.0	22.9	103.9	22.7
Pentadecane	-	-	114.3	24.1	104.2	22.4
Hexadecane	-	-	120.9	25.4	104.0	22.0
Octadecane	-	-	134.3	27.8	104.1	21.4
$-\Delta H_0$ (kJ/mol)	0.19		14.36		104.04	
$-\Delta H_1$ (kJ/mol)	6.95		6.66		0.0	
C_0	-2.47		-5.80		-27.40	
C_1	-1.14		-1.22		0.345	

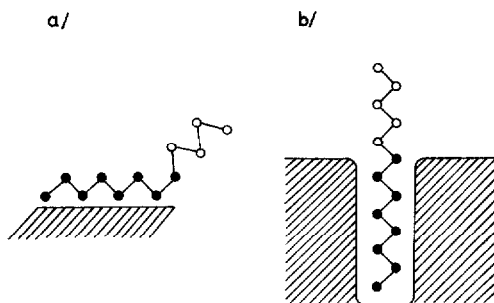


Fig. 4. Two possible locations of an n -alkane molecule adsorbed on sorbent 3. The filled circles denote segments of the chain contributing to sample-sorbent interaction.

of carbon atoms increases, we find that the model presented also works, *i.e.*, the entropy loss results from the suppression of various degrees of freedom of a molecule. According to the above model, the number of the degrees of freedom suppressed due to sorption decreases with increasing length of a molecule. Taking into account that the values of $\Delta H_n (= \Delta H_0)$ for n -alkanes sorbed on sorbent 3 are relatively high, the situation shown in Fig. 4b seems more probable. Unfortunately, we could not make measurements for n -alkanes with a smaller number of carbon atoms due to difficulties with the accurate determination of retention times; this could be done only at considerably lower temperatures. Such measurements are underway, and the results will be published later. If the above model is true, a determination of the enthalpies and entropies of sorption for smaller molecules should confirm it. That is, for molecules with sufficiently short chains we should observe changes in both ΔH_n and C_n , as for sorbents 1 and 2. Besides, the lines representing the dependence of the logarithm of the adjusted retention time *versus* the number of carbon atoms should not be parallel for small molecules, *i.e.*, the parameter A should become temperature-dependent.

We now consider the behaviour of mono- and disubstituted benzene derivatives, chromatographed on three sorbents. Tables IV and V contain the retention indices, the enthalpies and entropies of sorption as well as the temperature coefficients of the retention indices, $\partial I_x/\partial T$, obtained. Inasmuch as we have observed an anomaly in the retention mechanism for n -alkanes chromatographed on sorbent 3, it is of immediate interest to see whether this also occurs for other substances. In Fig. 5 we show plots of the retention indices for various benzene derivatives against the total selectivity, $\sum I_{McR}$. These plots exhibit surprisingly good linearity, suggesting a uniform retention mechanism. The increase in retention indices with $\sum I_{McR}$ results from the increasing strength of the sample-sorbent interaction (relative to n -alkanes). However, taking into account that the molecules of the benzene derivatives used are rather small, the above result does not contradict the proposed model of retention for n -alkanes.

In Figs. 6-8 we show the correlations between the retention indices and the boiling points, obtained for benzene derivatives chromatographed on different polymers at $T = 245^\circ\text{C}$. With increasing sorbent polarity, the selectivity towards samples of different chemical nature also increases. It is seen that on all polymers the relationship between the boiling points and the retention indices for isomeric compounds is linear. However, the results given in Table IV show that the separation of *m*- and

TABLE IV

RETENTION INDICES, I_x , OF AROMATIC COMPOUNDS, OBTAINED AT VARIOUS TEMPERATURES AND ON DIFFERENT SORBENTS

No.	Substance	Sorbent 1			
		240°C	245°C	250°C	255°C
1	Benzene	690.5	700.2	705.5	713.1
2	Toluene	798.4	807.6	807.9	812.1
3	<i>o</i> -Xylene	927.6	930.5	931.2	931.8
4	<i>m</i> -Xylene	897.4	903.4	907.0	916.7
5	<i>p</i> -Xylene	895.4	901.4	905.1	915.5
6	Chlorobenzene	893.4	900.1	905.0	916.0
7	<i>o</i> -Dichlorobenzene	1067.9	1082.9	1093.6	1097.2
8	<i>m</i> -Dichlorobenzene	1032.7	1049.4	1053.5	1062.2
9	<i>p</i> -Dichlorobenzene	1043.2	1059.2	1064.3	1071.6
10	Phenol	1050.3	1067.8	1074.5	1084.4
11	<i>o</i> -Methylphenol	1115.2	1132.0	1138.5	1148.1
12	<i>m</i> -Methylphenol	1141.3	1158.9	1167.2	1175.0
13	<i>p</i> -Methylphenol	1141.3	1157.7	1164.4	1170.7
14	<i>o</i> -Chlorophenol	1081.4	1090.6	1097.7	1107.0
15	<i>m</i> -Chlorophenol	1288.1	1301.3	1311.1	1320.0
16	<i>p</i> -Chlorophenol	1288.1	1301.3	1311.5	1320.1
		Sorbent 2			
1	Benzene	800.0	813.0	821.1	834.1
2	Toluene	904.1	916.3	928.1	940.6
3	<i>o</i> -Xylene	1045.5	1060.8	1076.0	1080.0
4	<i>m</i> -Xylene	1006.5	1015.4	1025.7	1034.7
5	<i>p</i> -Xylene	1006.5	1015.3	1025.7	1034.8
6	Chlorobenzene	1031.1	1047.3	1062.7	1075.2
7	<i>o</i> -Dichlorobenzene	1260.7	1278.6	1287.4	1302.9
8	<i>m</i> -Dichlorobenzene	1212.3	1229.8	1243.5	1255.8
9	<i>p</i> -Dichlorobenzene	1227.0	1242.8	1257.9	1271.8
10	Phenol	1318.9	1335.6	1353.0	1370.2
11	<i>o</i> -Methylphenol	1366.8	1382.9	1397.8	1412.4
12	<i>m</i> -Methylphenol	1406.6	1418.7	1438.8	1449.4
13	<i>p</i> -Methylphenol	1406.6	1418.7	1438.5	1449.6
14	<i>o</i> -Chlorophenol	1302.5	1323.2	1344.0	1365.2
15	<i>m</i> -Chlorophenol	1601.0	1615.5	1631.2	1646.2
16	<i>p</i> -Chlorophenol	1605.1	1620.9	1637.2	1653.2
		Sorbent 3			
1	Benzene	989.3	1022.7	1047.0	
2	Toluene	1066.2	1107.0	1135.0	
3	<i>o</i> -Xylene	1220.3	1254.8	1279.7	
4	<i>m</i> -Xylene	1155.4	1184.9	1214.2	
5	<i>p</i> -Xylene	1161.3	1191.6	1219.2	
6	Chlorobenzene	1242.5	1275.6	1299.5	
7	<i>o</i> -Dichlorobenzene	1500.3	1528.7	1554.5	
8	<i>m</i> -Dichlorobenzene	1448.0	1471.4	1494.7	
9	<i>p</i> -Dichlorobenzene	1463.8	1486.5	1508.0	
10	Phenol	1638.4	1647.8	1663.7	
11	<i>o</i> -Methylphenol	1666.8	1674.8	1692.5	
12	<i>m</i> -Methylphenol	1721.2	1726.2	1737.7	
13	<i>p</i> -Methylphenol	1717.7	1722.1	1732.7	
14	<i>o</i> -Chlorophenol	1596.1	1613.0	1631.9	
15	<i>m</i> -Chlorophenol	1959.3	1967.9	1976.6	
16	<i>p</i> -Chlorophenol	1968.3	1976.1	1983.5	

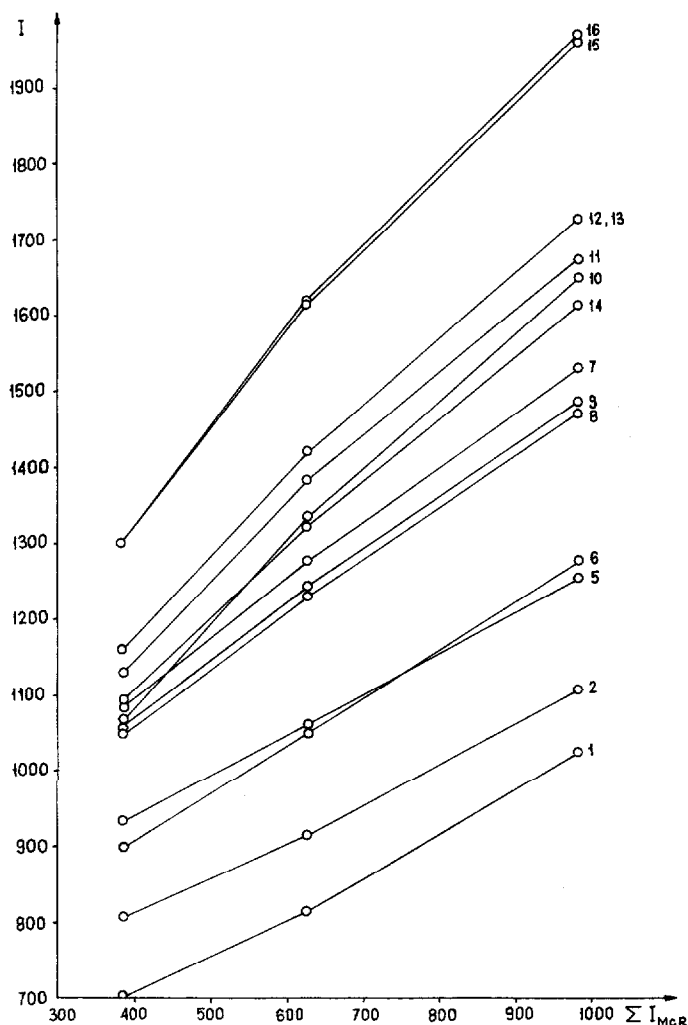


Fig. 5. Correlations between the retention indices for aromatic compounds and the total selectivity of our sorbents. The numbers correspond to the substances in Table IV.

p-isomers is rather difficult. Besides, the values of $\partial I_x/\partial T$ are also very similar for isomeric compounds and on all polymers (see Table V). Thus, one cannot improve the separation by changing the temperature. On the other hand, the values of $\partial I_x/\partial T$ become more and more specific for functional groups attached to aromatic rings when the polarity of the PPB increases. This may be helpful in the separation of chemically different compounds.

In our previous paper¹⁵ we discussed the retention of benzene derivatives on the commercial PPB, Polichrom A¹⁶. This sorbent was also found to be specific for functional groups attached to an aromatic ring. On the other hand, we have observed a linear relationship between the enthalpy and entropy of sorption that was independent of the chemical nature of the sample molecules. Such behaviour is charac-

TABLE V

THE VALUES OF ΔH , (kJ/mol), C AND $\partial I_x/\partial T$ FOR THE AROMATIC COMPOUNDS LISTED IN TABLE IV OBTAINED ON DIFFERENT SORBENTS

Substance No.	Sorbent 1			Sorbent 2			Sorbent 3		
	$-\Delta H$	$-C$	$\partial I_x/\partial T$	$-\Delta H$	$-C$	$\partial I_x/\partial T$	$-\Delta H$	$-C$	$\partial I_x/\partial T$
1	47.94	10.21	1.51	53.43	11.85	2.20	43.01	9.51	7.40
2	61.67	12.90	0.92	58.06	12.55	2.43	46.19	10.26	6.89
3	77.20	15.90	0.29	66.86	14.09	2.25	51.77	11.09	5.93
4	64.74	13.14	1.29	67.44	14.37	1.89	52.59	11.49	5.89
5	64.07	12.99	1.35	67.44	14.37	1.89	53.22	11.62	5.79
6	62.47	12.63	1.43	61.12	12.80	2.90	53.24	11.37	5.70
7	80.69	16.19	1.22	74.07	14.98	2.76	53.39	10.61	5.43
8	68.05	13.23	1.29	70.92	14.42	2.84	59.06	12.10	4.67
9	69.42	13.50	1.24	70.71	14.32	2.97	60.69	12.43	4.42
10	66.13	12.70	1.66	72.22	14.34	3.43	72.64	14.70	2.53
11	71.57	13.65	1.61	77.52	15.40	3.03	72.12	14.49	2.58
12	72.66	13.78	1.61	76.62	15.10	2.88	78.24	15.75	1.65
13	75.49	14.44	1.30	76.62	15.10	2.88	79.26	16.00	1.50
14	65.98	12.56	1.75	61.18	11.82	4.04	65.62	13.18	3.58
15	77.33	14.19	1.84	89.74	17.40	3.02	76.03	14.50	1.73
16	77.26	14.17	1.84	88.42	17.08	3.22	77.46	14.80	1.52

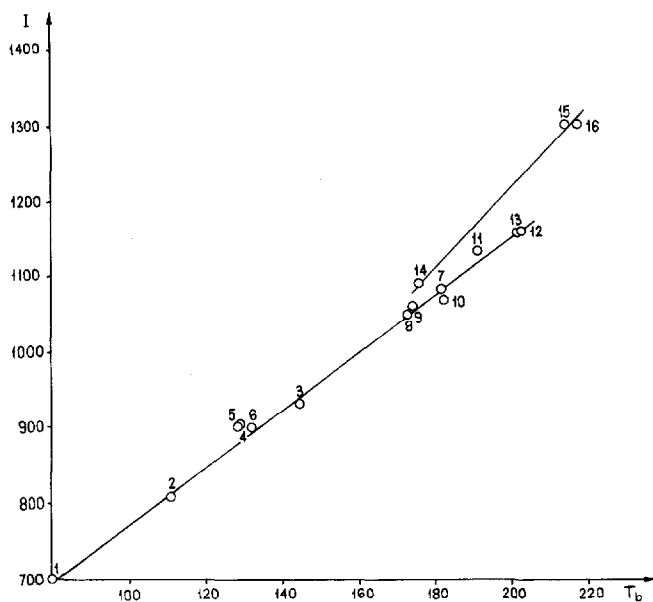


Fig. 6. Dependence of the retention indices for aromatic compounds on their boiling points, obtained on sorbent 1. The numbers correspond to the compounds in Table IV.

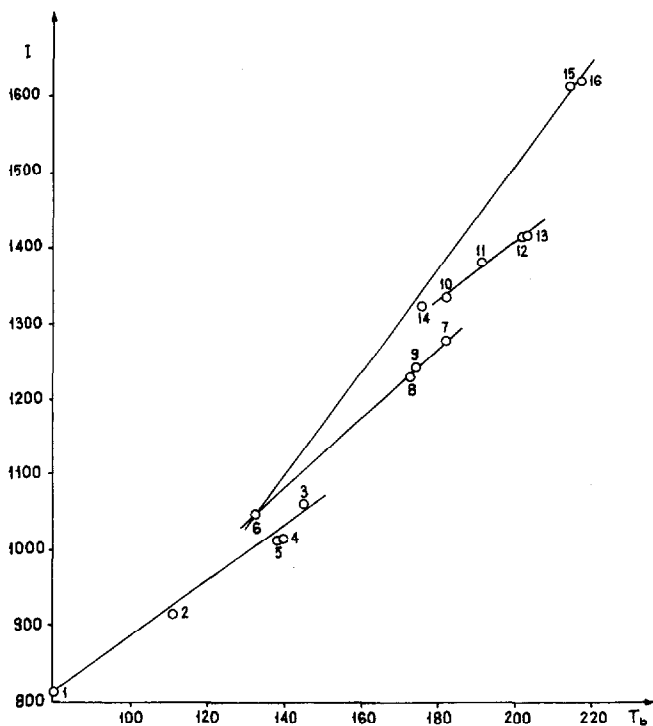


Fig. 7. Dependence of the retention indices for aromatic compounds on their boiling points temperatures, obtained on sorbent 2. The numbers correspond to the compounds in Table IV.

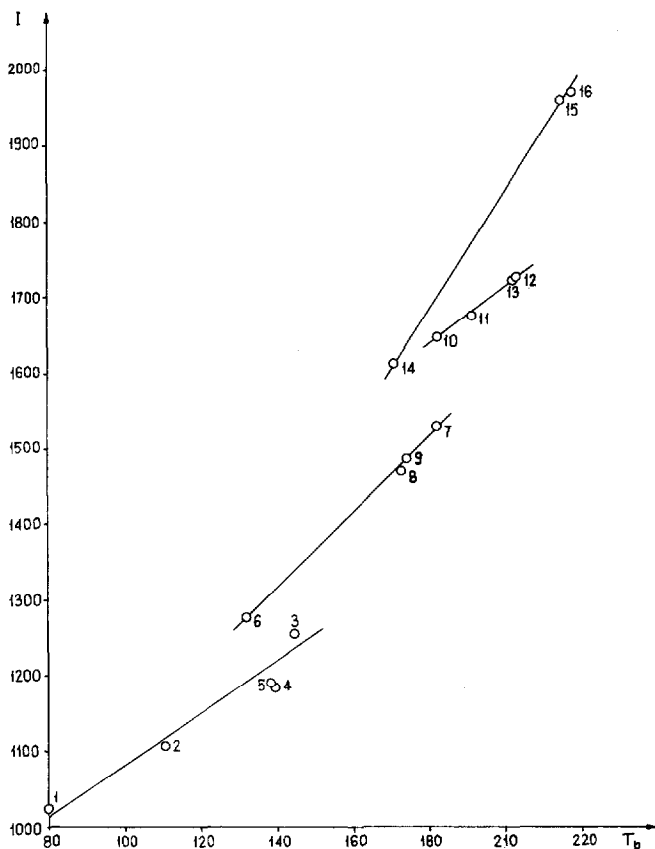


Fig. 8. Dependence of the retention indices for aromatic compounds on their boiling points, obtained on sorbent 3. The numbers correspond to the compounds in Table IV.

teristic for non-specific sample-sorbent interactions. In Figs. 9-11 we present plots of ΔH versus C for various compounds, determined from our measurements. It is seen that the deviations from linearity are quite large. Thus, in all cases, there are specific interactions between the samples and sorbent. However, it is a little surprising that the deviations become less pronounced on highly polar sorbents. This may be due to purely quantitative effects, *i.e.*, the contributions due to specific interactions may become relatively smaller on highly polar sorbents, as compared to other contributions to the sample-sorbent interaction.

Now, we return to the problem of correlations between $\partial I_x/\partial T$ and the enthalpy and entropy of sorption, as predicted by eqns. 11 and 12. For sorbents 1 and 2, plots of $\partial I_x/\partial T$ versus ΔH or C (ΔS) do not give any well defined dependences. However, according to eqn. 11, the term

$$(\partial I_x/\partial T) - (\partial \alpha_1/\partial T) \Delta H \quad (13)$$

should be linearly dependent upon C , if the parameter $\partial \alpha_1/\partial T$ was properly chosen.

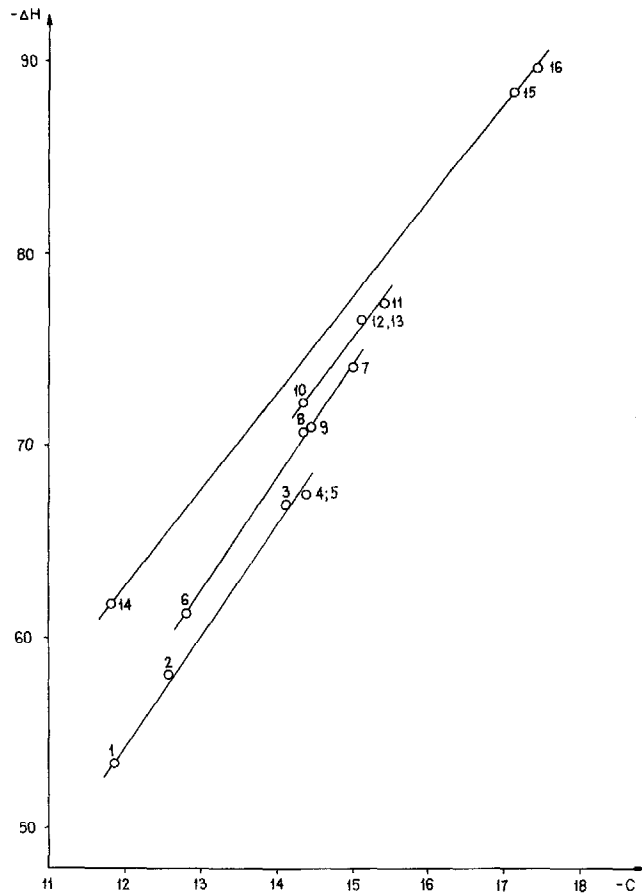
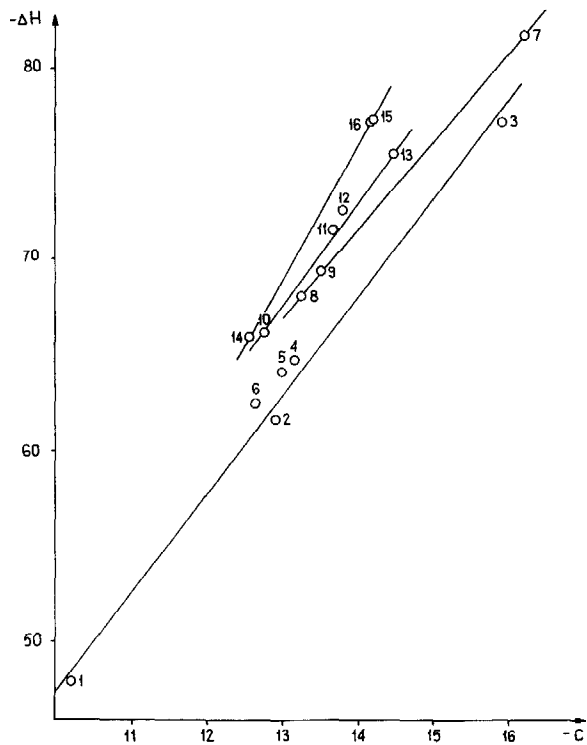


Fig. 9. Dependence of ΔH (kJ/mol) on C for aromatic substances chromatographed on sorbent 1. The numbers correspond to the compounds in Table IV.
 Fig. 10. Dependence of ΔH (kJ/mol) on C for aromatic substances chromatographed on sorbent 2. The numbers correspond to the compounds in Table IV.

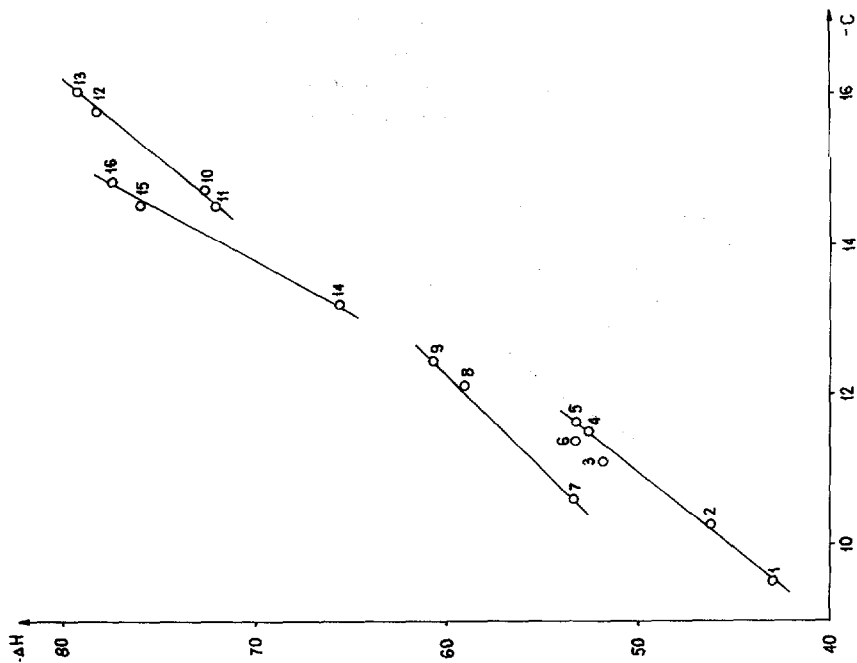


Fig. 11. Dependence of ΔH (kJ/mol) and C for aromatic substances chromatographed on sorbent 3. The numbers correspond to the compounds in Table IV.

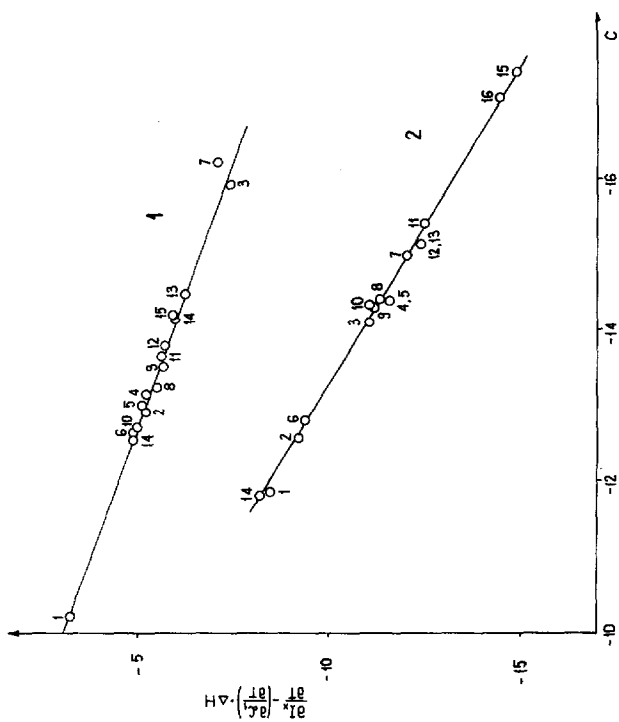


Fig. 12. Dependences of $(\partial I_n / \partial T) \Delta H$ on C for aromatic compounds in Table IV, obtained on sorbents 1 and 2.

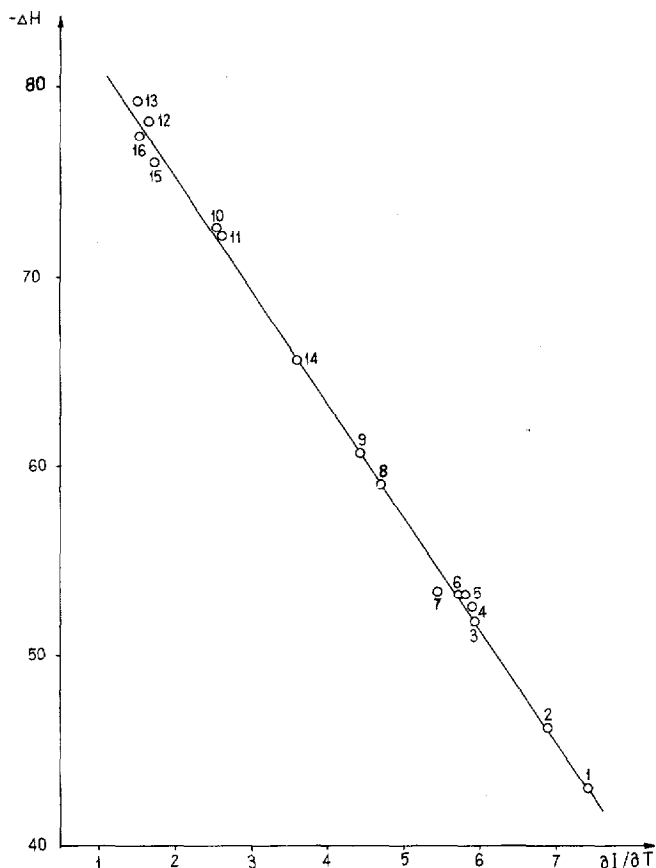


Fig. 13. Dependence of ΔH (kJ/mol) on $(\partial I_x/\partial T)$ for aromatic compounds in Table IV, obtained on sorbent 3.

Indeed, Fig. 12 confirms this. For sorbent 1, we have found $\partial\alpha_1/\partial T \approx 0.1$, whereas for sorbent 2, $\partial\alpha_1/\partial T \approx 0.2$. In the case of sorbent 3, we expected to obtain a linear dependence between $\partial I_x/\partial T$ and ΔH , because A was found to be temperature-independent. According to our earlier discussion, eqn. 12 should hold in such a case. Fig. 13 confirms this prediction very well.

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