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Note

Gas chromatography on porous polymers

III*. Anomalies in the behaviour of *n*-alkanes chromatographed on copolymers of 1,4-di(methacryloyloxymethyl)naphthalene and 1,4-divinylbenzene

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In Part II[1], we reported the chromatographic behaviour of *n*-alkanes and aromatic compounds on porous polymers obtained by copolymerization of 1,4-di(methacryloyloxymethyl)naphthalene (1,4-DMN) and 1,4-divinylbenzene (1,4-DVB). It was shown[1,2] that by changing the molar ratio of 1,4-DMN to 1,4-DVB, polymers of varying polarity could be obtained. On the other hand, the parameters characterizing the properties of sorbents, such as the specific surface area, total porosity, the glass transition temperature and the initial temperature of decomposition, appeared to be only slightly dependent on the relative amounts of monomers.

The previous study[1] also indicated that for various aromatic compounds (methylbenzenes, chlorobenzenes, methylphenols and chlorophenols) the retention indices exhibited a nearly linear dependence on the polarity of the sorbent, expressed in terms of total selectivity determined by the McReynolds test. On the other hand, the behaviour of *n*-alkanes showed some peculiarities. The most puzzling was their behaviour on the most polar sorbent used, which corresponded to the highest molar ratio of 1,4-DMN to 1,4-DVB of 0.8.

The purpose of this work was to carry out a more detailed study of the chromatographic behaviour of *n*-alkanes on this sorbent.

EXPERIMENTAL

Chromatographic measurements were carried out on a GCHF-18.3 (Chromatron, Berlin, G.D.R.) gas chromatograph with a stainless-steel column (100 cm × 4 mm I.D.), equipped with a thermal conductivity detector. Hydrogen at a flow-rate of 50 ml/min was used as the carier gas.

The measurements of the adjusted retention times of *n*-alkanes were performed at 5°C intervals in the range 190–250°C. The samples were injected by means of a 1-μl syringe (Scientific Glass Engineering, North Melbourne, Australia). Mixtures of C_5–C_{18} *n*-alkanes were injected.

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* For Part II, see ref. 1.

RESULTS AND DISCUSSION

Fig. 1 shows plots of log [adjusted retention time, $t'_{R(n)}$] *versus* number of carbon atoms in the *n*-alkanes, n_C. The dependence can be expressed in the form

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

It can be seen that for $n_C \leqslant 9$ the slopes A are slightly different than those for $n_C \geqslant$ 10 at temperatures higher than 215°C. As we have shown previously[1], the parameters A and B are closely related to the enthalpy, ΔH_n, and the entropy, ΔS_n, of sorption
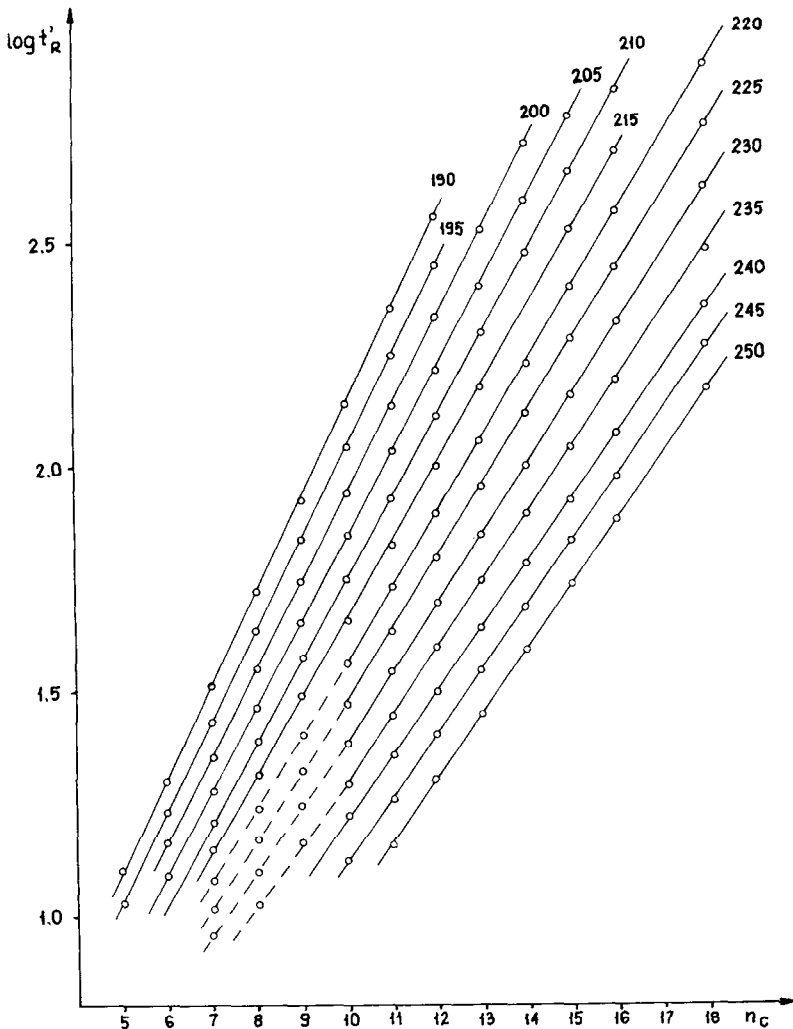

Fig. 1. Dependence of log (adjusted retention time, log t'_R) on the number of carbon atoms in *n*-alkanes, n_C.

via the following relationships:

$$A = \frac{1}{2.3}\left(-\frac{\Delta H_1}{RT} + C_1\right) \tag{2}$$

and

$$B = \frac{1}{2.3}\left(-\frac{\Delta H_0}{RT} + C_0\right) + \log t_0 \tag{3}$$

where

$$\Delta H_n = \Delta H_1 n_C + H_0 \tag{4}$$
$$C_n = C_1 n_C + C_0; \quad \Delta S_n \sim C_n \tag{5}$$

and t_0 is the retention dead time.

From eqns. 2 and 3 it follows that we can determine ΔH_1, C_1, ΔH_0 and C_0 from the plots of A and B against $1/T$. Fig. 2 shows the dependences obtained. It can be seen that at 240°C and above A is independent of temperature as observed in our earlier study[1]. This implies that $\Delta H_1 = 0$ and hence the enthalpy of sorption does not depend on the number of carbon atoms in the n-alkane molecule (see Fig. 3). Below 240°C two linear dependences between A and $1/T$ are observed one corresponding to n-alkanes containing more then nine carbon atoms (open circles in Fig. 2) and the other corresponding to lower alkanes (crosses in Fig. 2). However, both lines meet at about 210°C, and at lower temperatures only one line is observed (squares in Fig. 2a). Hence we have obtained clear evidence that at a temperature
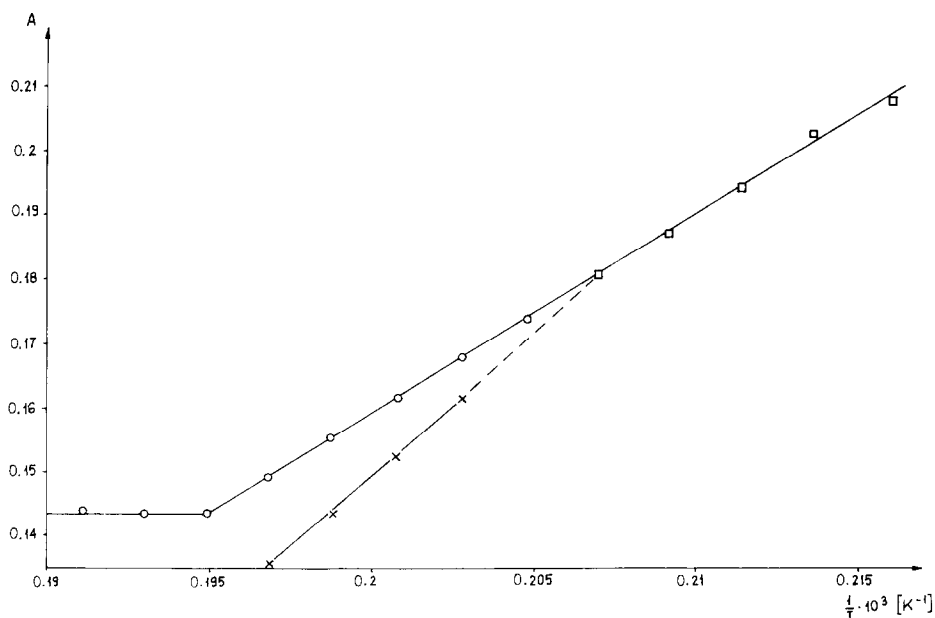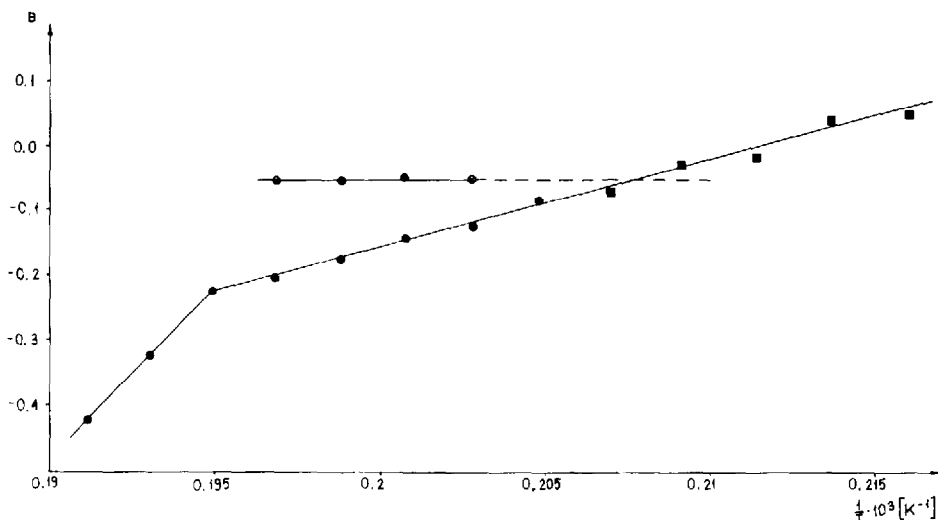

Fig. 2.

Fig. 2. Dependence of A (eqn. 2) on the reciprocal of absolute temperature, $1/T$. $\bigcirc$, $n_C > 9$; $\times$, $n_C \leqslant 9$; $\square$, any n-alkanes with $n_C \leqslant 9$ as well as with $n_C > 9$; and dependence of B (eqn. 3) on the reciprocal of absolute temperature, $1/T$. $\bullet$, $n_C > 9$; $\otimes$, $n_C \leqslant 9$; $\blacksquare$, any n-alkanes with $n_C \leqslant 9$ as well as with $n_C > 9$.
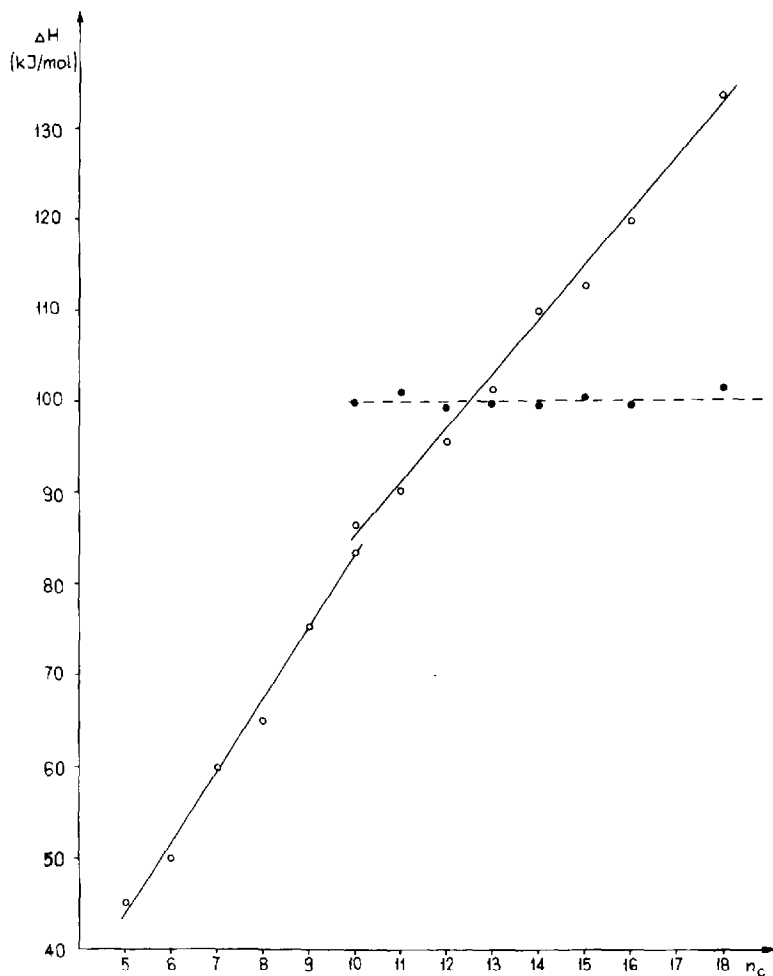

Fig. 3. Relationships between enthalpy of sorption, ΔH, and number of carbon atoms in n-alkanes, n_C. $\bigcirc$, At temperatures below 240°C; $\bullet$, at temperatures above 240°C.

close to 210°C the sorbent probably undergoes some structural change. The glass transition temperature (T_g) for this sorbent, determined by means of thermal analysis of a block polymer, is *ca.* 260°C. On the other hand, the value of T_g obtained by a chromatographic method[3] appears to be about 230–250°C. This difference in T_g is probably due to the different physical state of the porous polymer used in the chromatographic measurements compared with a block polymer. Hence the difference in the behaviour of *n*-alkanes at low (< 240°C) and high ($\geqslant$ 240°C) temperatures can be atributed to the different sorption conditions. However, we are not able to give any plausible explanation of the unusual behaviour of *n*-alkanes observed at high temperatures other than that suggested previously[1].

Fig. 2 shows that for small *n*-alkane molecules ($n_C \leqslant 9$), the parameter *B* is independent of temperature above 210°C, implying that $\Delta H_0 = 0$. Also, from the temperature dependence of *A* the contribution to ΔH of one CH_2 group is $\Delta H_1 \approx 8$.

Unfortunately, we have not been able to obtain any reliable results for *n*-alkanes with $n_C \leqslant 9$ at temperatures above 235°C, as the retention times were very short. Nevertheles, the observed differences in the behaviour of *n*-alkanes with $n_C \leqslant 9$ and with $n_C \geqslant 10$ support, at least partially, our hypothesis[1] that small molecules should interact more strongly with the sorbent.

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