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GAS CHROMATOGRAPHY ON POROUS POLYMERS

IV. INFLUENCE OF THE GEOMETRIC STRUCTURE OF POROUS COPOLYMERS OF 1,4-DI(METHACRYLOYLOXYMETHYL)NAPHTHALENE WITH 1,4-DIVINYLBENZENE ON THEIR CHROMATOGRAPHIC BEHAVIOUR

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SUMMARY

Four copolymers of 1,4-di(methacryloyloxymethyl)naphthalene and 1,4-divinylbenzene were prepared with surface areas ranging from 184.5 to 342 m²/g and porosities ranging from 1.06 to 1.36 cm³/g. The chromatographic behaviour of homologous series of *n*-alkanes, *n*-alkan-1-ols, *n*-methyl ketones and *n*-alkanoic acids was similar on all four polymers.

INTRODUCTION

We recently discussed the behaviour of various aromatic compounds¹ and the peculiarities in the behaviour of *n*-alkanes² chromatographed on polymers of different polarities obtained by copolymerization of 1,4-di(methacryloyloxymethyl)naphthalene (DMN) and 1,4-divinylbenzene (DVB). An increase in the molar fraction of the polar monomer (DMN) increased the polarity of the sorbents and their selectivity towards different benzene derivatives. The relationships between the enthalpy change due to sorption of the molecules chromatographed and the corresponding entropy change for the homologous series studied indicated the existence of specific solute-sorbent interactions. We also observed linear relationships between the retention indices of benzene derivatives and the total selectivity of the sorbents, ΣI_{McR}^3 , suggesting an uniform retention mechanism, irrespective of the sorbent polarity. For the solute-sorbent interactions we considered only the chemistry of the copolymers, as the physical properties, such as the specific surface areas and total porosity, were very similar for all sorbents.

The present work considers the effects of the geometric structure of porous polymer beds (PPBs) obtained by copolymerization of DMN and DVB on the chromatographic behaviour of various homologous series of aliphatic compounds: *n*-alkanes, *n*-alkan-1-ols, *n*-methyl ketones and *n*-aliphatic acids. All the polymers studied have similar polarities, but different specific surface areas and total porosities.

EXPERIMENTAL

Preparation of copolymers

Porous copolymers of 1,4-di(methacryloyloxymethyl)naphthalene with 1,4-divinylbenzene were obtained by suspension copolymerization in the presence of a mixture of toluene and *n*-decan-1-ol used as a diluent^{4,5}. Polymers with different geometric structures were obtained by changing the proportion of toluene (v/v) to *n*-decan-1-ol. An increase in the proportion of toluene in the diluents led to an increase in specific surface areas, a decrease in the average pore radius and a modification of the pore-size distribution functions^{5,6}.

The proportion of toluene used in the syntheses of the copolymers together with some of their properties are presented in Table I.

Chromatographic measurements

Chromatography was carried out as previously¹. The bridge current was 200 mA. Measurements were performed at 185, 190 and 195°C. Samples (0.2 μ l) of *n*-alkanes, *n*-alkan-1-ols, *n*-methyl ketones and *n*-aliphatic acids were injected.

RESULTS AND DISCUSSION

The data in Table I show that changes in the composition of the diluent mixture lead to large changes in the geometric structure of the resulting copolymers. Similar effects were observed by Sederel and De Jong⁷ for styrene-divinylbenzene copolymers. On the other hand, the results of the McReynolds test (Table I) suggest that changes in the geometric structures of our copolymers are not accompanied by any important changes in the chemical structure of their surfaces. From

$$\ln k' = -\Delta H/RT + A\Delta S \quad (1)$$

where

$$k' = (t_R - t_0)/t_0 \quad (2)$$

TABLE I
PROPERTIES OF COPOLYMERS

S = Specific surface area; ΣI_{McR} = total selectivity as determined by the McReynolds test. The specific surface areas were determined by using the standard nitrogen adsorption method with help of a Sorptomatic 1806 (Carlo Erba, Milan, Italy) apparatus and the porosity was determined with help of a mercury porosimeter (Carlo Erba).

| Sample No. | Toluene conc. (% v/v) | <i>S</i> (m ² /g) | Porosity (cm ³ /g) | ΣI_{McR} |
|------------|-----------------------|------------------------------|-------------------------------|------------------|
| 1 | 20 | 184.5 | 1.36 | 624.0 |
| 2 | 25 | 222.0 | 1.24 | 618.0 |
| 3 | 40 | 281.0 | 1.10 | 602.0 |
| 4 | 65 | 342.0 | 1.06 | 609.0 |

t_R being the retention time, t_0 the dead time, ΔH the change in enthalpy, ΔS the change in entropy, R the gas constant, T the temperature and A a temperature-independent constant, characteristic of the chromatographic system, we can determine ΔH and ΔS due to the sorption of solutes. A plot of ΔH versus $A\Delta S$ for all the solutes and all the sorbents studied (Fig. 1) shows a well defined linear relationship suggesting that (i) the interactions between solutes and sorbents are non-specific and (ii) the nature of these interactions does not depend on the sorbent used. However, we do find some differences in the magnitude of the molecular interactions for each homologous series on different sorbents. This is demonstrated in Fig. 2 which shows the relationships between the enthalpy change and the number of carbon atoms, n_c , in the chain of the solute molecule. There is a linear relationship between ΔH and n_c for all homologous series considered. Similar relationships are observed for the entropy changes. These linear relationships suggest that one can consider the total changes in the enthalpy and entropy as comprised of the contributions due to the functional group in the solute molecule (ΔH_0 and ΔS_0) and to the methylene groups of the carbon chain (ΔH_1 and ΔS_1). Thus we can write

$$\Delta H = \Delta H_0 + n_c \Delta H_1$$

and

$$\Delta S = \Delta S_0 + n_c \Delta S_1$$

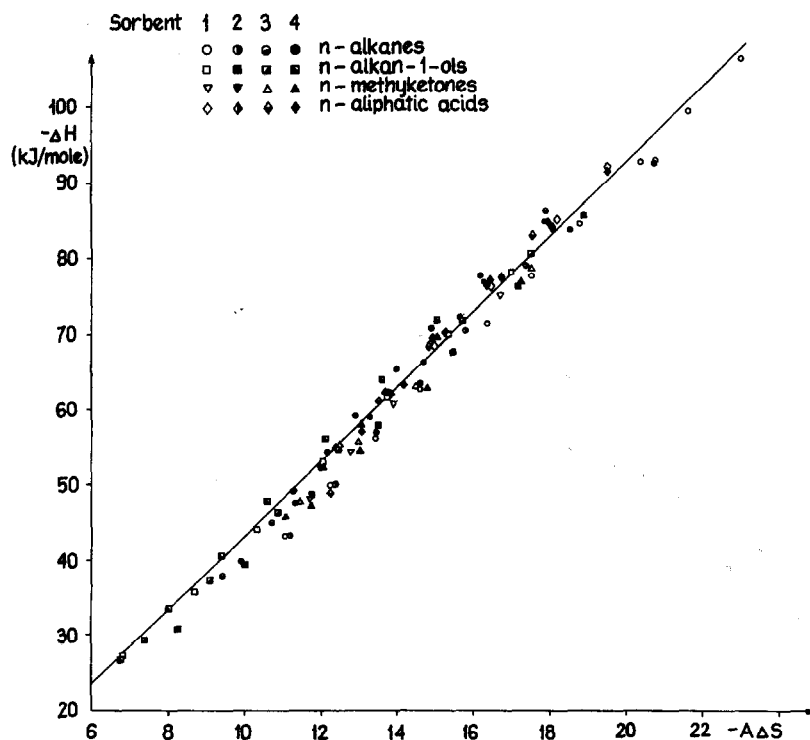


Fig. 1. Relationships between ΔH and $A\Delta S$ for various homologous series and the sorbents from Table I.

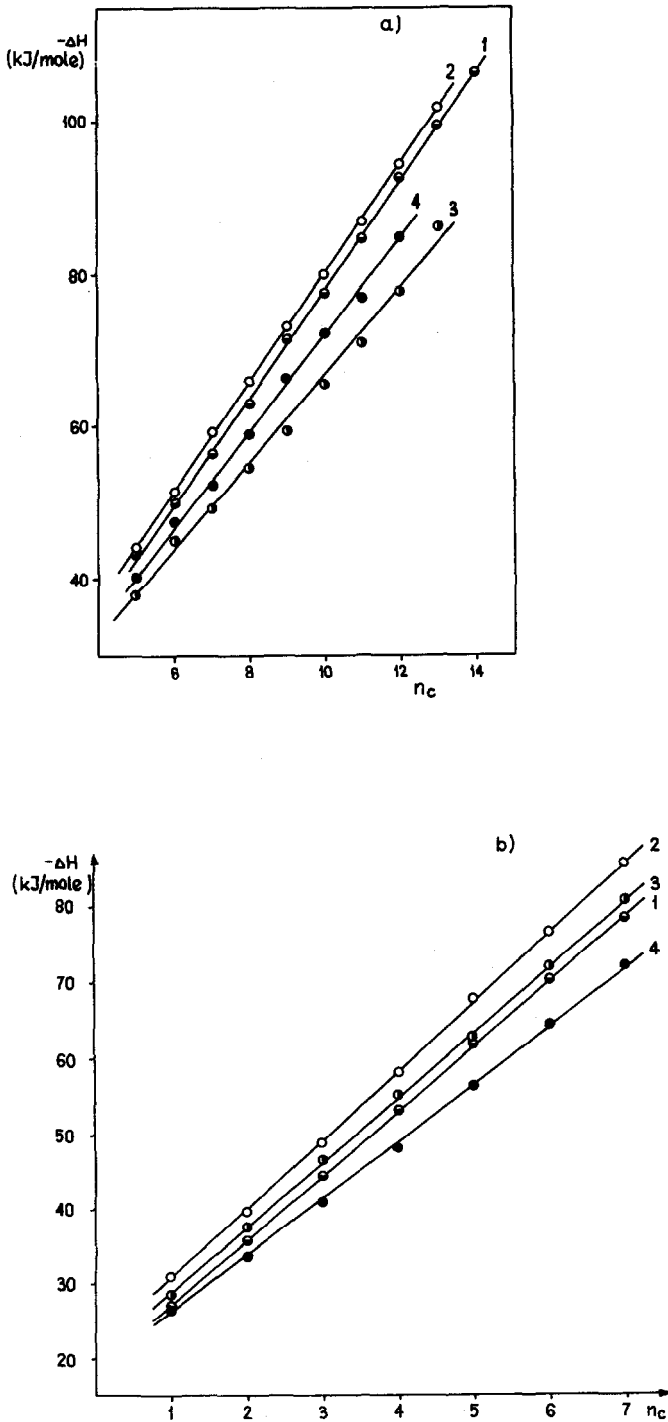


Fig. 2.

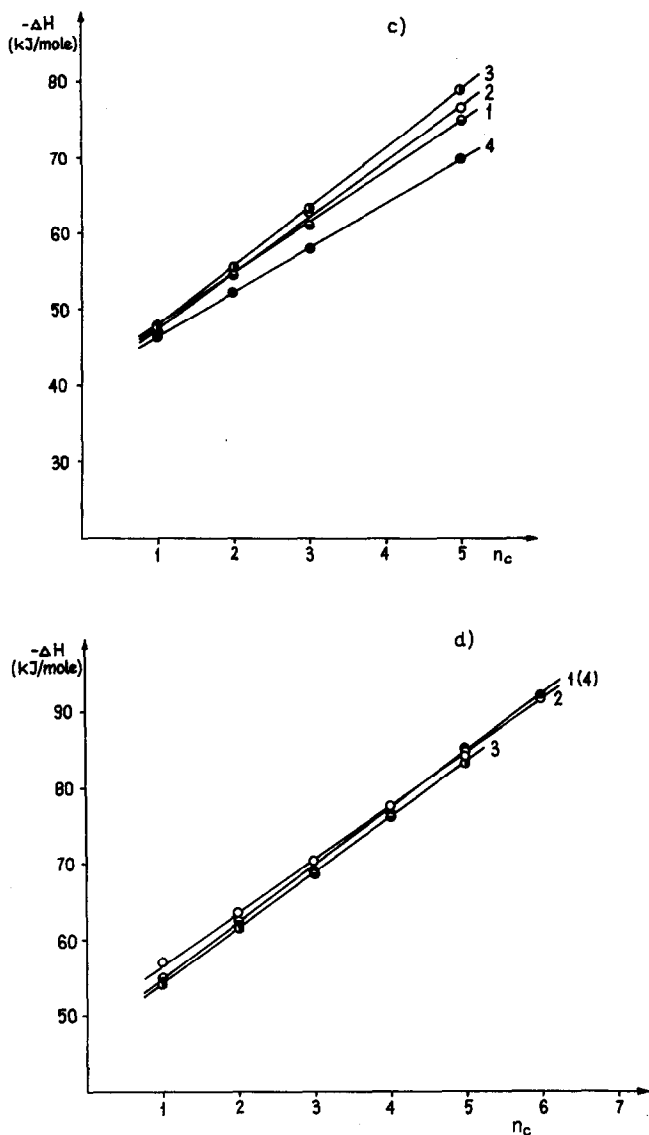


Fig. 2. Relationships between ΔH and the number of carbon atoms in the chain for various homologous series and the sorbents from Table I: (a) *n*-alkanes; (b) *n*-alkan-1-ols; (c) *n*-methyl ketones; (d) *n*-aliphatic acids.

The results in Table II demonstrate clearly that ΔH_1 and ΔS_1 remain practically constant for all homologous series considered here. On the other hand, the values of ΔH_0 and ΔS_0 increase with the polarity of the functional group in an homologous series of solute molecules, *i.e.*, these parameters characterize the chemical nature of the solute molecules. The sorbent structure seems to have little influence on the values of ΔH_0 , $A\Delta S_0$, ΔH_1 and $A\Delta S_1$.

TABLE II

THE COEFFICIENTS ΔH_1 , ΔH_0 , $\Delta \Delta S_1$ AND $\Delta \Delta S_0$ FOR VARIOUS HOMOLOGOUS SERIES OBTAINED FOR THE COPOLYMERS STUDIED

| Homologous series | Copolymer No. | $-\Delta H_1$ (kJ/mol) | $-\Delta H_0$ (kJ/mol) | $-\Delta \Delta S_1$ | $-\Delta \Delta S_0$ |
|---------------------------|---------------|---------------------------|---------------------------|----------------------|----------------------|
| <i>n</i> -Alkanes | 1 | 7.07 | 7.32 | 1.34 | 4.15 |
| | 2 | 6.90 | 8.58 | 1.28 | 4.78 |
| | 3 | 5.58 | 10.11 | 0.94 | 4.79 |
| | 4 | 6.25 | 9.12 | 1.11 | 4.49 |
| <i>n</i> -Alkan-1-ols | 1 | 8.54 | 18.76 | 1.67 | 5.31 |
| | 2 | 9.16 | 21.44 | 1.78 | 6.44 |
| | 3 | 8.61 | 20.15 | 1.65 | 5.75 |
| | 4 | 7.58 | 18.41 | 1.40 | 5.20 |
| <i>n</i> -Methyl ketones | 1 | 6.76 | 34.29 | 1.25 | 9.07 |
| | 2 | 7.37 | 32.85 | 1.37 | 9.06 |
| | 3 | 7.77 | 40.00 | 1.51 | 9.96 |
| | 4 | 5.82 | 34.73 | 0.99 | 9.40 |
| <i>n</i> -Aliphatic acids | 1 | 7.46 | 47.17 | 1.41 | 10.94 |
| | 2 | 6.89 | 43.01 | 1.24 | 10.70 |
| | 3 | 7.31 | 46.83 | 1.34 | 10.85 |
| | 4 | 7.40 | 47.48 | 1.38 | 10.95 |
| Average | | 7.28 | | 1.35 | |

TABLE III

KOVÁTS RETENTION INDICES FOR VARIOUS HOMOLOGOUS SERIES AT 190°C OBTAINED ON THE COPOLYMERS LISTED IN TABLE I

| Compound | I_R on copolymer No. | | | |
|--------------------------------|------------------------|--------|--------|--------|
| | 1 | 2 | 3 | 4 |
| Methanol | 490.7 | 439.7 | 413.2 | 422.4 |
| Ethanol | 587.0 | 546.6 | 527.3 | 536.6 |
| Propan-1-ol | 702.0 | 676.75 | 652.2 | 656.9 |
| Butan-1-ol | 816.0 | 796.3 | 777.0 | 772.8 |
| Pentan-1-ol | 922.8 | 910.3 | 889.1 | 883.2 |
| Hexan-1-ol | 1028.3 | 1016.3 | 997.7 | 987.4 |
| Heptan-1-ol | 1131.0 | 1122.9 | 1101.2 | 1092.7 |
| Acetone | 614.7 | 598.7 | 591.0 | 594.6 |
| Methyl ethyl ketone | 723.4 | 713.6 | 693.9 | 698.5 |
| Methyl <i>n</i> -propyl ketone | 818.4 | 809.5 | 784.0 | 791.6 |
| Methyl <i>n</i> -pentyl ketone | 1026.8 | 1023.1 | 985.5 | 995.3 |
| Acetic acid | 823.2 | 796.3 | 773.1 | 779.2 |
| Propionic acid | 927.1 | 906.8 | 875.4 | 883.0 |
| Butyric acid | 1036.0 | 1013.9 | 985.5 | 987.4 |
| Valeric acid | 1140.9 | 1121.0 | 1098.5 | 1101.7 |
| Caproic acid | 1245.6 | 1228.3 | 1203.3 | 1206.3 |
| Heptanoic acid | 1351.5 | 1336.3 | — | — |

TABLE IV

RETENTION TIMES FOR *n*-ALKANES AT 190°C OBTAINED ON THE COPOLYMERS LISTED IN TABLE I

| <i>n</i> -Alkane (C _n) | <i>t_R</i> (s) on copolymer No. | | | |
|---------------------------------------|---|-------|-------|-------|
| | 1 | 2 | 3 | 4 |
| C ₅ | 19.9 | 20.2 | 20.5 | 22.3 |
| C ₆ | 27.0 | 27.0 | 29.1 | 31.8 |
| C ₇ | 38.7 | 38.5 | 43.0 | 47.7 |
| C ₈ | 58.0 | 58.5 | 66.2 | 73.9 |
| C ₉ | 89.6 | 90.6 | 105.8 | 119.0 |
| C ₁₀ | 141.0 | 144.0 | 172.5 | 194.0 |
| C ₁₁ | 225.0 | 236.0 | 277.0 | 323.0 |
| C ₁₂ | 366.0 | 380.0 | 460.0 | 537.0 |
| C ₁₃ | 595.0 | — | — | — |

In Table III we give the retention indices at 190°C for *n*-alkan-1-ols, *n*-methyl ketones and *n*-alkanoic acids determined on all the sorbents used. For any substance, the values of *I_R* decrease as the proportion of toluene in the diluent mixture increases to 40% (v/v). With a still higher proportion of toluene in the diluent mixture (sorbent 4) and equal to 65% (v/v), some of the retention indices increase again. There is a gradual decrease in the difference between the retention indices obtained for different sorbents as the number of carbon atoms in the solute molecule increases, confirming that the contribution of the functional group to the retention decreases with an increase in the number of carbon atoms in the aliphatic chain. All the sorbents considered exhibit very similar interactions with the methylene groups and, hence, the retention of long-chain molecules should become similar for all the sorbents. In Table IV we give the retention times for *n*-alkanes at 190°C. It is seen that these times increase with the polarity of the sorbent.

The results presented above show that the chromatographic properties of the polymeric column packings with porosities in the range of 1.06–1.36 cm³/g are not sensitive to their geometric structure.

ACKNOWLEDGEMENT

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