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CHROMATOGRAPHIC PROPERTIES OF MACROPOROUS COPOLYMERS OF 2-HYDROXYETHYL METHACRYLATE AND ETHYLENE DIMETHACRYLATE

J. HRADIL, M. KŘIVÁKOVÁ, P. STARY* AND J. ČOUPEK

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague 6 (Czechoslovakia)

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SUMMARY

The use of macroporous copolymers of 2-hydroxyethyl methacrylate and ethylene dimethacrylate as sorbents for gas chromatography was investigated. It was found by determination of ROHRSCHEIDER's constants that the materials under investigation differed in their polarities and were particularly suitable for the fractionation of polar compounds and branched hydrocarbons. Some other characteristics of these copolymers, such as specific surface area, thermal stability and analyzing effect, were also determined and compared with the corresponding properties of styrene-divinylbenzene sorbents.

INTRODUCTION

Several years ago, HOLLIS¹ described the use of organic sorbents based on a macroporous styrene-divinylbenzene copolymer for gas chromatography (GC). Since then, organic sorbents of this type (Porapak, Waters Associates Inc.; Chromosorb 101-105, Johns-Manville; Synachrom R, Research Institute of Synthetic Resins and Lacquers, Pardubice) have been used in gas-solid chromatography. If the polarities of these sorbents are compared with those of liquid phases, it can be seen that copolymers of the styrene type are phases with considerable non-polar properties whose polarities approach that of squalane (Porapaks Q and QS) and of methylphenylsilicone oils (Porapaks P, PS, R, RS and N). This low polarity results in some advantages in the separation of water from non-polar compounds when the styrene-divinylbenzene sorbent is used, but also has disadvantages in the separation of some polar compounds. It was the object of the present work to investigate the GC properties of a macroporous 2-hydroxyethyl methacrylate copolymer whose application in gel permeation chromatography has been described earlier².

EXPERIMENTAL

Preparation of macroporous copolymers

The series of copolymers investigated was obtained by suspension bead copoly-

* Present address: Institute for Ore Research, Mnšek pod Brdy, Czechoslovakia.

merization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate under the conditions for the formation of a macroporous structure³. The macroporous copolymers differed from each other in the content of the crosslinking agent and in the conditions used for the formation of the macroporous structure; they are known under the trade-name Spheron. After completion of polymerization, the copolymers were purified to remove the residual monomers and solvents by extraction with methanol, dried in a vacuum drying-box and fractionated on sieves. The 160–200- μ m fraction was used for chromatographic measurements.

Gas chromatography

A Chrom-2 apparatus (Laboratorní přístroje, Prague) with flame ionization detection and nitrogen as the carrier gas (flow-rate 3–40 ml/min) was used. A Perkin-Elmer 116E apparatus with a thermal conductivity cell was used to determine the elution characteristics of water. The macroporous copolymers were packed into glass columns about 1 m long and with I.D. 0.32 cm. The operating temperatures of the columns were ca. 150 and 175°C. The samples were injected in an amount of 0.05 μ l with a Hamilton 7101-NCH syringe.

Net retention volumes (V_N , ml) were used to calculate specific retention volumes (V_θ , ml/g) of ROHRSCHEIDER's series of adsorbates (benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine)⁴ and of the homologous paraffin series under standard conditions:

$$V_\theta = 273.16 V_N / T w \quad (1)$$

where T is the column temperature (°K) and w is the weight of the sorbent (g).

A comparison of the logarithms of the retention volumes of ROHRSCHEIDER's series of adsorbates with those of the homologous paraffin series enabled KOVÁTS retention indices to be calculated⁵. By subtracting the standard values of the KOVÁTS retention indices on squalane (I_0) from the measured values of KOVÁTS retention indices of the sorbent investigated (I), ROHRSCHEIDER's constants⁴ were calculated (the values given in Table I).

TABLE I

CHROMATOGRAPHIC PROPERTIES OF MACROPOROUS COPOLYMERS OF 2-HYDROXYETHYL METHACRYLATE AND ETHYLENE DIMETHACRYLATE

Column temperature, 150°C; carrier gas flow-rate, 20–30 ml/min.

| Adsorbent | S_θ (m ² /g) ^a | V^θ (ml/min) ^b | Rohrschneider's constants | | | | |
|--------------|---|----------------------------------|---------------------------|-------------------|-------------------|-------------------|------|
| | | | x | y | z | u | s |
| Spheron G10B | 1.54 | 0.5 | 0.78 ^c | 3.34 ^c | 1.89 ^c | 4.89 ^c | — |
| Spheron G50F | 40.90 | 2.9 | 0.73 | 3.02 | 1.41 | 5.32 | 2.58 |
| Spheron G50B | 97.27 | 13.6 | 0.87 | 2.21 | 1.91 | 2.55 | 2.36 |
| Spheron G90F | 209.0 | 91.9 | 0.28 | 1.29 | 0.82 | 1.96 | — |
| Synachrom R | — | 31.6 | 0.40 | 0.21 | 0.36 | 0.38 | 0.22 |

^a Specific surface area of adsorbents.

^b Specific retention volume of hexane.

^c Determined at 67.5°C.

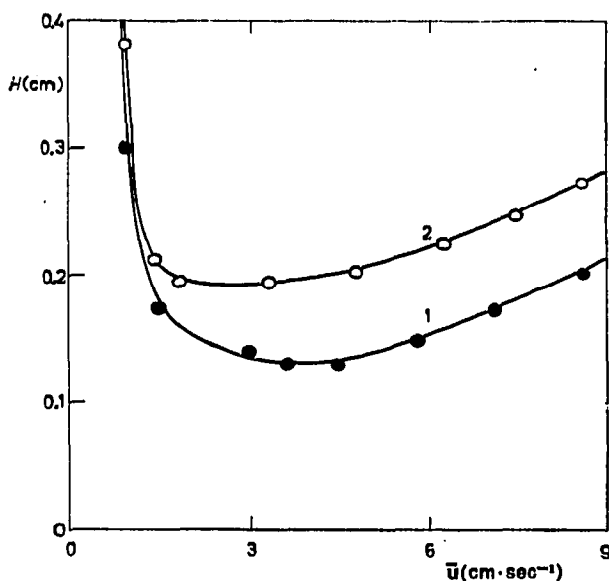


Fig. 1. Dependence of the height equivalent to a theoretical plate (H) on the average linear gas velocity (\bar{u}) of chromatographic columns packed with Spheron-type sorbents. 1, Spheron G50B; 2, Spheron G90F.

The optimum flow conditions of the carrier gas through a column packed with Spheron sorbent were determined for propanol from the dependence of the height equivalent to a theoretical plate (H , cm) on the average linear gas velocity (\bar{u} , cm·sec⁻¹) described by VAN DEEMTER'S equation⁶ (Fig. 1). The individual terms in VAN DEEMTER'S equation were calculated from the experimental data by using a method suggested by DUBSKÝ AND KREJČÍ⁷. For Spheron G50B and G90F, the equations are, respectively

$$H = -0.029 + 0.274/\bar{u} + 0.023\bar{u} \quad (2)$$

$$H = 0.036 + 0.273/\bar{u} + 0.024\bar{u} \quad (3)$$

The heights equivalent to a theoretical plate calculated from eqns. 2 and 3 are in good agreement with the experimental values (Fig. 1).

Other methods

The thermal stability of the Spheron-type copolymers was investigated by differential thermal analysis on a Du Pont Instruments apparatus in an argon atmosphere with a linear increase in temperature (20°C/min) over the range 20–500°C.

The magnitude of the specific surface was measured by thermal desorption of carbon dioxide by the method of NELSEN AND EGERTSEN^{8,9}, using titanium dioxide as a standard with a known specific surface area.

RESULTS AND DISCUSSION

As with macroporous styrene-divinylbenzene copolymers, the macroporous copolymers of 2-hydroxyethyl methacrylate and ethylene dimethacrylate (Spheron-type

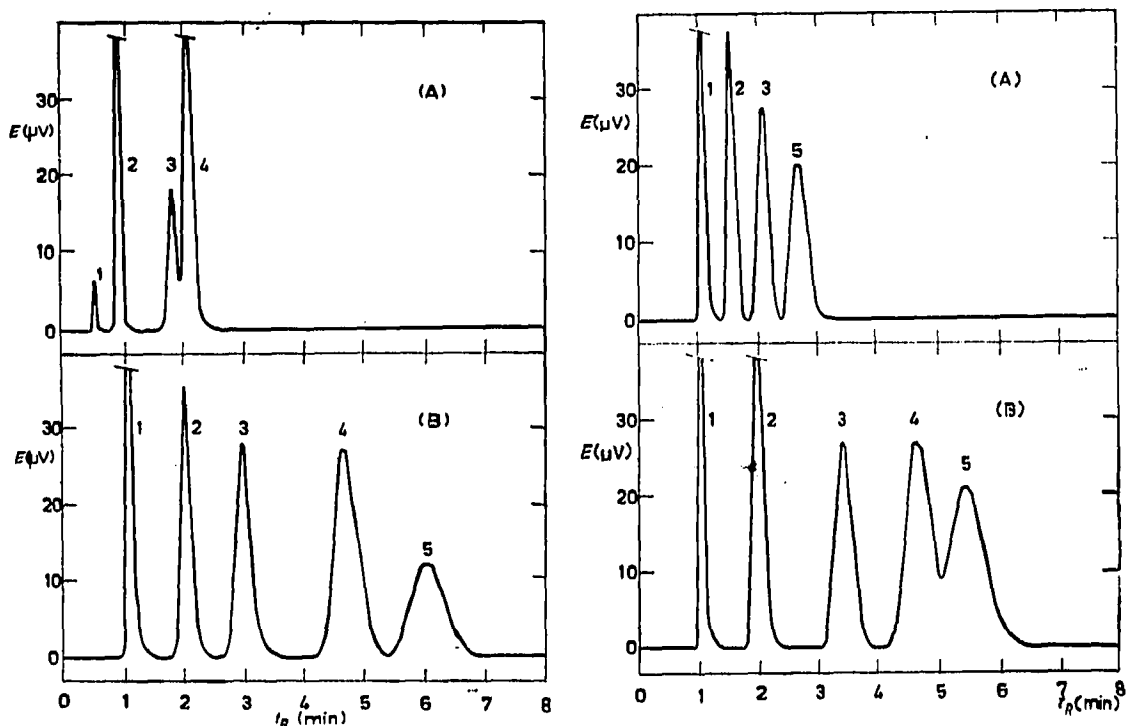


Fig. 2. Fractionation of C_2 - C_4 paraffins and polar compounds on Spheron G90F. Column, 114 cm long. (A) Column temperature, 150°C ; carrier gas (N_2) flow-rate, 25.7 ml/min. 1 = Ethane; 2 = propane; 3 = isobutane; 4 = *n*-butane. (B) Column temperature, 175°C ; carrier gas (N_2) flow-rate, 34.4 ml/min. 1 = Methanol; 2 = ethanol; 3 = acetone; 4 = propanol; 5 = ethyl acetate.

Fig. 3. Fractionation of C_1 - C_4 alcohols. (A) Spheron G50B; column, 110.1 cm long; column temperature, 175°C ; carrier gas (N_2) flow-rate, 37.3 ml/min. (B) Spheron G90F; column, 114 cm long; column temperature, 175°C ; carrier gas (N_2) flow-rate, 34.4 ml/min. 1 = Methanol; 2 = ethanol; 3 = 2-propanol; 4 = *n*-propanol; 5 = *tert.*-butanol.

sorbents) are also suitable for the fractionation of compounds with small molecules, as the adsorbate-adsorbent interactions are strong. The values of ROHRSCHEIDER'S constants (Table I) enable conclusions to be drawn on the polarity of the sorbent and practical chromatographic separations. ROHRSCHEIDER'S constants of the Spheron-type copolymers are higher in all instances than those of the styrene-divinylbenzene copolymers, which demonstrates the higher polarity of the Spheron sorbents. The high value of ROHRSCHEIDER'S constants of methyl ethyl ketone (z) indicates the separation of compounds with a branched structure; accordingly, an isobutane-butane mixture (Fig. 2A) was fractionated on a Spheron sorbent. The values of ROHRSCHEIDER'S constants for ethanol (y) and nitromethane (u), which were highest for the above copolymer, make this copolymer particularly suitable for the separation of polar compounds (Fig. 2B); the C_1 - C_4 alcohols were fractionated in accordance with this finding (Fig. 3). The higher values of ROHRSCHEIDER'S constants for benzene (x) indicate the separation of benzene from hexane and cyclohexane on the Spheron-type sorbents (Fig. 4); the above adsorbates cannot be fractionated on the styrene-di-

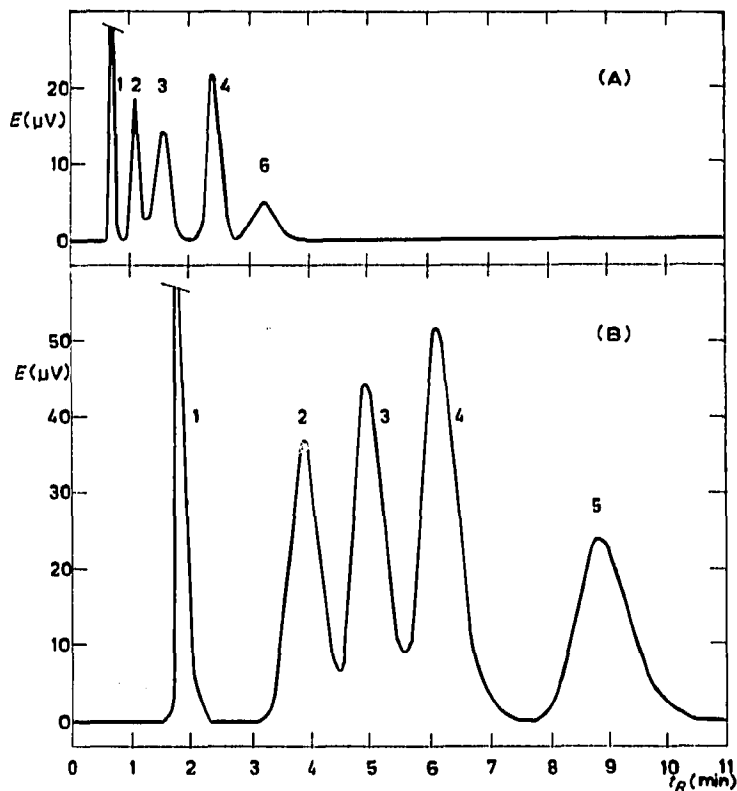


Fig. 4. Fractionation of $C_6 - C_8$ hydrocarbons. Conditions as in Fig. 3. 1 = Pentane; 2 = hexane; 3 = cyclohexane; 4 = benzene; 5 = heptane; 6 = octane.

vinylbenzene sorbents. The low value of the Kováts index⁵ for water (water on Spheron G90F: $I = 356$) permits the analysis of aqueous solutions of organic compounds on the Spheron-type sorbents in a similar manner to the styrene-divinylbenzene sorbents¹⁰.

Macroporous copolymers of 2-hydroxyethyl methacrylate and ethylene dimethacrylate contain free hydroxyl groups. In spite of this fact, however, there is no formation of undesirable "tails", even though the sorbent was not treated with trimethylchlorosilane or hexamethyldisilazane. The chromatographic peaks have a symmetrical shape over a wide range of temperatures and flow-rates of the carrier gas.

An important factor to be borne in mind when choosing an appropriate chromatographic phase is not only its polarity and activity, but also the rate of analysis, which is particularly important in series analyses. A measure of the rate of analysis is given by the specific retention volumes (V_g) of the same adsorbates. The specific retention volumes of ROHRSCHEIDER's series of adsorbates on Synachrom R vary within tens of millilitres of carrier gas relative to 1 g of sorbent (for hexane on Synachrom R: $V_g = 31.6$ ml/g, Table I). On the other hand, the specific retention volumes of ROHRSCHEIDER's series of adsorbates on the Spheron-type sorbents increase, depending on the specific surface area, from tenths to hundreds of millilitres of the car-

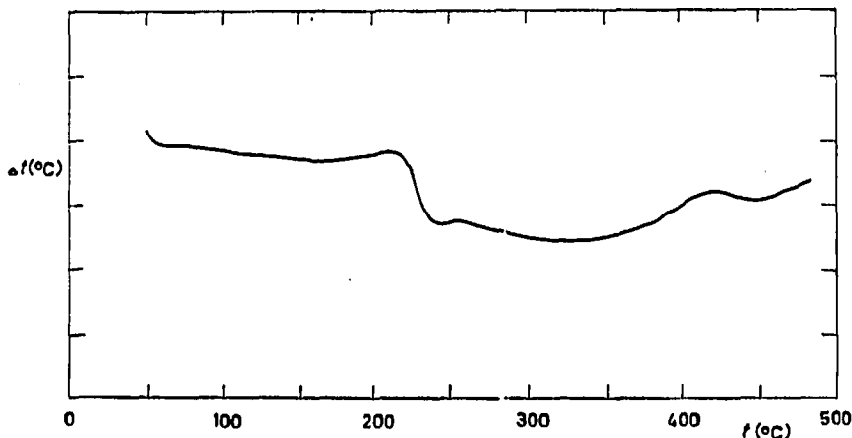


Fig. 5. Differential thermal analysis of Spheron G50B. Du Pont Instruments apparatus was used in an argon atmosphere (20 ml/min), heating rate 20°C/min, temperature range 20–500°C.

rier gas relative to 1 g of sorbent. From this viewpoint, the copolymers based on 2-hydroxyethyl methacrylate make possible not only the choice of a sorbent with the required polarity, but also a reduction in the time required for analysis.

The effectiveness of a column packed with the macroporous 2-hydroxyethyl methacrylate copolymer remains unchanged over a wide range of flow-rates of the carrier gas in terms of the flatness of the minimum on the graph of the height equivalent to a theoretical plate ($H_{\min.} = 0.131$ cm) against the linear flow-rate of the carrier gas (Fig. 1) (eqns. 2 and 3); it is comparable with the effectiveness of columns packed with Synachrom R (ref. 10).

The sorbents based on 2-hydroxyethyl methacrylate investigated are mechanically stable and thermally stable up to 250°C, as demonstrated by the results of differential thermal analysis (Fig. 5) and also by the fact that high detection sensitivities (1:100) could be used in chromatographic measurements. Styrene-divinylbenzene copolymers are thermally stable up to 350°C (ref. 10), but they are mainly used at column temperatures up to 175°C when copolymers based on 2-hydroxyethyl methacrylate can also be successfully used.

It should be stressed, in conclusion, that the macroporous copolymers of 2-hydroxyethyl methacrylate and ethylene dimethacrylate are a type of polar organic sorbent whose individual chromatographic applications will require further investigation.

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REFERENCES

- 1 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309.
- 2 J. ČOUPEK, *Meeting of Czechoslovak Chemical Society, Vysoké Tatry, October, 1971.*
- 3 J. ČOUPEK, M. KRIVÁKOVÁ AND S. POKORNÝ, *IUPAC International Symposium on Macromolecules, Helsinki, 1972.*
- 4 L. ROHRSCHEIDER, *J. Chromatogr.*, 22 (1966) 6.
- 5 E. KOVÁTS, *Z. Anal. Chem.*, 191 (1961) 359.
- 6 J. J. VAN DEEMTER, F. J. ZUIDERWEG AND A. KLINKENBERG, *Chem. Eng. Sci.*, 5 (1956) 271.
- 7 A. DUBSKÝ AND M. KREJČÍ, *Collect. Czech. Chem. Commun.*, 29 (1964) 1706.
- 8 F. M. NELSEN AND F. T. EGERTSEN, *Anal. Chem.*, 30 (1958) 1387.
- 9 J. VOLKOVÁ, M. KRIVÁKOVÁ, V. PATZELOVÁ AND J. ČOUPEK, *J. Chromatogr.*, 76 (1973) 159.
- 10 O. DUFKA, J. MALINSKÝ AND J. VLADYKA, *Chem. Prum.*, 21/48 (1971) 459.