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# NITROGEN- AND PHOSPHORUS-CONTAINING POROUS POLYMER SORBENTS

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SUMMARY

Some new porous polymer sorbents for gas chromatography containing nitrogen and phosphorus and having very specific properties are described. The retention characteristics of different groups of organic substances on these sorbents were studied.

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In developing polymer sorbents for gas chromatography, the polarity of which can be controlled over a wide range, the study of porous copolymers of divinylbenzene and vinyl derivatives of pyridines is of great interest, owing to the presence in these copolymers of pyridine rings having a free electron pair on the nitrogen atom. Such polymers with locally concentrated negative charges should, according to Kiselev's classification[1], be referred to as specific sorbents of type III.

We have investigated some of the structural and gas chromatographic properties of the copolymers of 2-methyl-5-vinylpyridine (2,5-MVP) and divinylbenzene (DVB), obtained in benzine as an inert solvent.

Samples of copolymers (1) 16/85, (2) 40/80 and (3) 20/100 were investigated. The first figure denotes the amount of DVB and the second the amount of benzene as a percentage of the monomer mixture.

Table I presents some structural characteristics of the copolymers investigated. The surface area of the samples was determined by the B.E.T. method after the low-temperature adsorption of krypton; the total pore volume was determined by the mercury porosimetry method.

The results obtained indicate the possibility of controlling the structure of sorbents by varying the amount of the cross-linking agent and of the inert solvent used in the synthesis of the polymers. The surface area of the sorbents increases with an increase of the amount of DVB present, while the pore volume depends largely on the amount of solvent used. For the copolymers of DVB and 2,5-MVP, a wide distribution of pores according to size is characteristic (Fig. 1); the bulk of the pores (80–90 % of the total pore volume) is constituted by pores transitional to micropores.

The study of the gas chromatographic properties of the copolymers of DVB and 2,5-MVP was carried out on a gas chromatograph equipped with a thermal conductivity detector at a temperature of 150° and a carrier gas flow-rate of 30 ml/min.
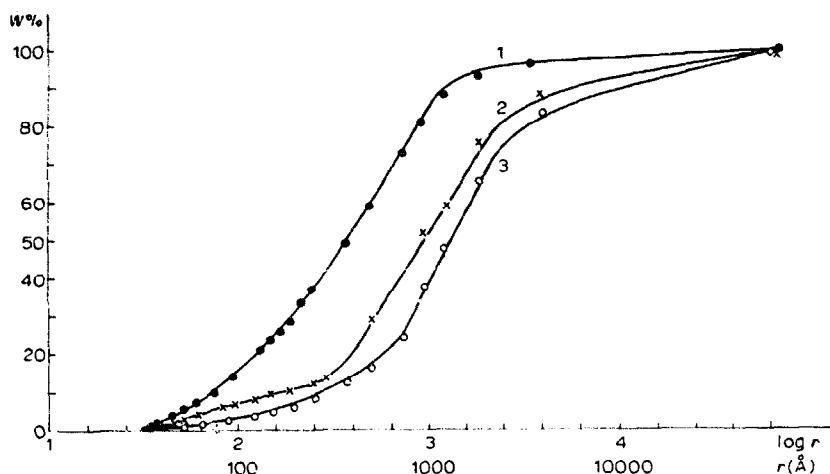
Fig. 1. Integral distribution of pores (%) according to radii: 1, copolymer 40/80; 2, 16/85; 3, 20/100.

TABLE I

SOME STRUCTURAL CHARACTERISTICS OF THE COPOLYMERS OF 2,5-MVP AND DVB

| Property | Specimen | | |
|---|---|---|---|
| | 16/85 | 40/80 | 20/100 |
| Surface area (m²/g) | 24 | 65 | 27 |
| Pore volume (cm³/g) | 0.71 | 0.99 | 1.17 |
| Average pore radius (Å) | 600 | 300 | 870 |
| Free-fall density (g/cm³) | 0.32 | 0.27 | 0.20 |

The retention of unsaturated compounds (Table II) on the sorbents used depends on the presence and number of double bonds in the molecule: stronger retention of all the olefins investigated compared with the respective alkanes was observed. Aromatic hydrocarbons are eluted considerably later than the respective alicyclic compounds. The retention of unsaturated alcohols is particularly strong.

The retention of chloromethanes on polymer sorbents based on vinyl derivatives of pyridines differs from that on Polysorb (a copolymer of styrene and divinylbenzene)[2].

The retention time of methylene chloride is three times that of *n*-pentane, while chloroform appears on the chromatogram after the heavier and higher boiling carbon tetrachloride (Table III).

The dependence of retention upon the dipole moment of the molecules is illustrated by the increase in the relative retention time from pentane to acetonitrile (Table IV), as well as by the separation of compounds with close boiling points but different dipole moments. While, for example, in the separation on Polysorb the ratio of the retention volumes $V_R$(acetonitrile)/$V_R$(cyclohexane) is 0.2, in the separation on the 40/80 copolymer it is 0.7 and on the 16/85 copolymer it is 1.1. On

TABLE II

RELATIVE RETENTION TIMES OF UNSATURATED COMPOUNDS (RELATIVE TO n-PENTANE)

| Sorbate | B.p. (°C) | M.W. | $t_R/t_R$(n-pentane) | | | |
|---|---|---|---|---|---|---|
| | | | Polysorb | 40/80 | 20/100 | 16/85 |
| Pentane | 36.1 | 72.1 | 1.0 | 1.0 | 1.0 | 1.0 |
| Pentadiene-1,3 | 44.1 | 68 | 1.2 | 1.6 | 2.1 | 2.2 |
| Hexane | 68.7 | 86.2 | 2.3 | 2.2 | 2.1 | 2.1 |
| Hexene-1 | 63.5 | 84.2 | 2.2 | 2.5 | 2.6 | 2.7 |
| Hexadiene-1,5 | 59.4 | 82.1 | 2.1 | 2.5 | 2.7 | 2.8 |
| Cyclohexane | 81.4 | 84.2 | 3.0 | 3.9 | 4.1 | 4.2 |
| Cyclohexene | 83.0 | 82.1 | 3.3 | 4.9 | 5.4 | 5.5 |
| Benzene | 80.1 | 78.1 | 2.9 | 6.8 | 7.8 | 8.2 |
| Methylcyclohexane | 100.9 | 98.2 | 5.6 | 5.4 | 6.0 | 6.0 |
| Toluene | 110.6 | 92.1 | 6.8 | 13.2 | 16.3 | 16.9 |
| Propanol | 97.2 | 60.1 | 1.05 | 7.2 | 11.5 | 12.1 |
| Allyl alcohol | 96–97 | 58.1 | 1.0 | 10.6 | 16.5 | 17.6 |
| Propargyl alcohol | 115 | 56.1 | 1.1 | 24.7 | 50.0 | 52.0 |

TABLE III

RELATIVE RETENTION TIMES OF CHLORINATED METHANES (RELATIVE TO n-PENTANE)

| Sorbate | B.p. (°C) | M.W. | Dipole moment (D) | $t_R/t_R$(n-pentane) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Polysorb | 40/80 | 20/100 | 16/85 |
| Dichloromethane | 40.1 | 84.9 | 1.62 | 0.9 | 2.9 | 3.8 | 3.9 |
| Chloroform | 61.3 | 119.4 | 1.06 | 2.1 | 6.9 | 9.8 | 10.2 |
| Carbon tetrachloride | 76.8 | 153.8 | 0 | 3.1 | 5.0 | 6.1 | 6.0 |
| n-pentane | 36.1 | 72.15 | 0 | 1.0 | 1.0 | 1.0 | 1.0 |

Polysorb, the ratio $V_R$(nitromethane)/$V_R$(n-heptane) is 0.2, and on 40/80 and 20/100 copolymers it is 1.2 and 1.6, respectively.

The retention of hydroxylated compounds on polymer sorbents based on vinyl derivatives of pyridines (referred to below as Polysorb N) largely depends on the ability of the molecules that are to be separated to form hydrogen bonds. n-Pentane on Polysorb N emerges from the column before water, methanol and ethanol (Table IV); the relative retention times of alcohols exceed those on Polysorb (Tables II–IV). Alcohols and acids having the same boiling points as those of hydrocarbons have a larger retention value on Polysorb N than the hydrocarbons; in particular, on a 40/80 copolymer, n-heptane (retention time $t_R$ = 8 min) emerges from the column before propanol ($t_R$ = 12 min) and formic acid ($t_R$ = 122 min). Also characteristic of Polysorb N is a very strong retention of acids compared with alcohols having the same number of carbon atoms in the molecule. On the 40/80 Polysorb N, the ratio $V_R$(formic acid)/$V_R$(methanol) = 34, $V_R$(acetic acid)/$V_R$(ethanol) = 20, $V_R$(propionic acid)/$V_R$(propanol) = 18, while on Polysorb these ratios are 2.1, 2.3 and 3.5, respectively. Such a high selectivity of Polysorb N towards acids seems to be due to the ability of pyridines to form salts with acids.

## TABLE IV

RELATIVE RETENTION TIMES OF POLAR MOLECULES (RELATIVE TO $n$-PENTANE)

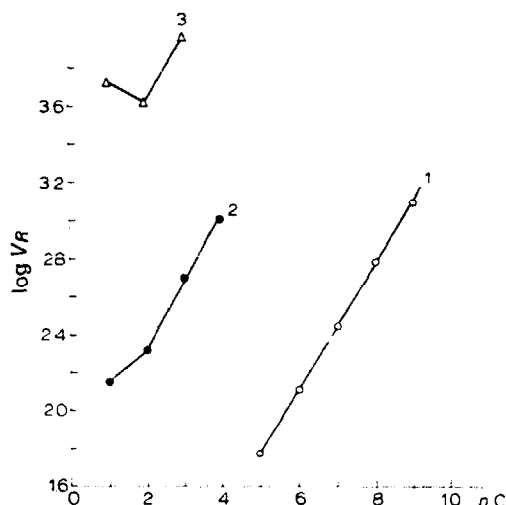| Sorbate | Polarizability $(A)$ (ref. 3) | Dipole moment (D) | $t_R/t_R(n\text{-pentane})$ | | | |
|---|---|---|---|---|---|---|
| | | | Polysorb | 40/80 | 20/100 | 16/85 |
| Water | 1.49 | 1.84 | 0.12 | 2.5 | 4.2 | 4.5 |
| Methanol | 3.23 | 1.67 | 0.19 | 2.4 | 3.7 | 3.8 |
| Ethanol | 5.06 | 1.70 | 0.40 | 3.2 | 5.5 | 5.6 |
| Acetonitrile | – | 3.91 | 0.00 | 2.9 | 4.2 | 4.5 |
| Acetone | 6.32 | 2.73 | 0.69 | 2.0 | 2.6 | 2.8 |
| Diethyl ether | 9.02 | 1.17 | 0.87 | 1.3 | 1.4 | 1.5 |
| $n$-Pentane | 9.95 | 0 | 1.00 | 1.0 | 1.0 | 1.0 |



Fig. 2. The dependence of log $V_R$ on the carbon number on Polysorb N (40/80): 1, $n$-alkanes; 2, $n$-alcohols; 3, $n$-acids.

On Polysorb N, the dependence of log $V_R$ on the carbon number is linear for alkanes and is not linear for alcohols and acids (Fig. 2).

The results presented above suggest that porous copolymers of 2,5-MVP and DVB have a highly specific molecular interaction. The specific behaviour of the sorbents investigated depends on the amount of the monovinyl monomer, in this particular instance 2,5-MVP, used in the polymerization. An examination of the results in Tables II-IV shows that with an increasing amount of 2,5-MVP (and hence a decreasing amount of the cross-linking agent, DVB) in the polymerization mixture, that is, when passing from the 40/80 to the 16/85 copolymer, there is an increase in the retention of the molecules of groups B and D in KISELEV's classification, which have a capacity for additional interactions other than dispersion. The results on the retention of the molecules considered above correspond to the amount of elemental nitrogen present in the sorbents used: copolymers 40/80, 20/100 and 16/85 contain 5.7, 7.2 and 7.6 % of nitrogen, respectively.

The Polysorb N samples investigated closely resemble, as far as the retention values of molecules of group B are concerned, such polar polymer sorbents as Porapak T and Chromosorb 104 (ref. 3), and have considerably higher retention values for molecules of group D (Table V).

TABLE V

COMPARISON OF SOME POLAR SORBENTS

| Sorbates | Relative retention time of sorbates | | | |
|---|---|---|---|---|
| | 40/80 | 16/85 | Chromosorb 104 | Porapak T |
| Cyclohexene/cyclohexane | 1.2 | 1.3 | 1.2 | 1.2 |
| Benzene/cyclohexane | 1.7 | 2.3 | 1.8 | 1.6 |
| Propanol/cyclohexane | 1.8 | 2.9 | 1.5 | 1.3 |
| Acetic acid/ethanol | 20.0 | 32.1 | 4.4 | 4.9 |



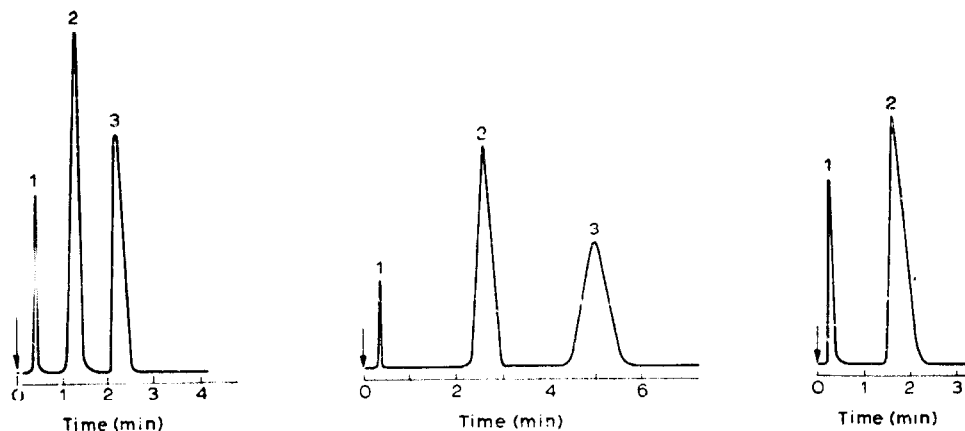Fig. 3. Separation of ethylene from acetylene on Polysorb N (16/85), 1 m × 4 mm. Column temperature 20°, helium flow-rate 30 cm³/min. 1, Air; 2, ethylene; 3, acetylene.

Fig. 4. Chromatogram obtained with Polysorb N (16/85), 1 m × 4 mm. Column temperature 150°, helium flow-rate 30 cm³/min. 1, air; 2, acetone; 3, isopropanol

Fig. 5. Determination of formaldehyde in water using Polysorb N (20/100). Column temperature 100°, helium flow-rate 40 cm³/min. 1, formaldehyde; 2, water.

The use of Polysorb N for the gas chromatographic separation of substances is very promising and enables the possible applications of gas chromatography on porous polymer sorbents to be extended by using the differences in intermolecular sorbate–polymer sorbent interactions.

Figs. 3–5 show chromatograms of mixtures, the separation of which presents some difficulties when the separation is made on the non-specific sorbent Polysorb.

The sorbents investigated, which are based on vinyl derivatives of pyridines, have a sufficient thermal stability. The results of thermogravimetric analyses carried out on a derivatograph showed that destruction of the sorbent starts at a temperature of 300° (at a rate of increase of temperature of 5°/min).

On Polysorb N, the components separated appear as symmetrical peaks. The

insufficiently high efficiency of the sorbents (HETP = 2.9–12 mm) is probably due to the peculiarities of their geometrical structure, especially to the wide size distribution of the pores. An appropriate choice of the conditions of synthesis should enable highly efficient sorbents based on vinyl derivatives of pyridines to be obtained.

It should be noted that the copolymers of vinylpyridines and DVB can be used in ion-exchange chromatography; they are anionites of low basicity with a tertiary nitrogen atom as the ionogenous group and have high mechanical strength, good kinetic properties in ion-exchange processes and high stability towards chemical, thermal and radiation attack[4,5]. This is evidence of the versatility of porous polymers, and of the possibility of using the same specimens in different types of chromatography.

A well pronounced specificity of molecular interaction is characteristic of the phosphorus-containing porous polymer sorbents produced by copolymerization of styrenephosphonic acid esters and DVB[6]. The esters have the formulae $CH_2 = CHC_6H_4P(O)(OR)_2$, where R = alkyl. This specificity is shown by the significantly greater retention values of unsaturated compounds compared with those of the corresponding saturated compounds, and by the dependence of the retention of polar molecules on the dipole moment, as well as in the sequence of elution of chloromethanes, and in the larger values of the relative retentions of alcohols and water compared with $n$-pentane (Tables VI–IX). On all the copolymers of DVB and of styrenephosphonic acid esters, water is eluted later than $n$-pentane and methanol (Table VI).

The retention on the phosphorus-containing sorbents investigated of compounds with similar boiling points, as well as of compounds with similar molecular weights, depends both on the value of the dipole moment of the molecules being separated and on the ability of the latter to form hydrogen bonds with the active sites of the sorbent surface. For instance, on Polysorb the ratio of the retention volumes of $n$-butanol and diethyl ether $V_R(n$-butanol)$V_R$(diethyl ether) is 3.2, while on the copolymers of methyl and butyl esters of styrenephosphonic acid and DVB it is

TABLE VI

RELATIVE RETENTION TIMES OF POLAR MOLECULES (RELATIVE TO $n$-PENTANE)

| Sorbate | Polariz-ability (A) (ref. 3) | Dipole moment (D) | $t_R/t_R(n$-pentane) | | |
| --- | --- | --- | --- | --- | --- |
| | | | Polysorb 1[a] | 2[b] | 3[c] |
| Water | 1.49 | 1.84 | 0.12 | 40.0 | 3.3 | 4.9 |
| Methanol | 3.23 | 1.67 | 0.19 | 21.0 | 2.8 | 3.8 |
| Ethanol | 5.06 | 1.70 | 0.40 | 14.8 | 4.8 | 5.8 |
| Acetonitrile | — | 3.94 | 0.60 | 23.1 | 5.2 | 5.5 |
| Acetone | 6.32 | 2.73 | 0.69 | 8.8 | 2.5 | 3.7 |
| Diethyl ether | 9.02 | 1.17 | 0.87 | 1.6 | 1.5 | 1.7 |
| $n$-Pentane | 9.95 | 0 | 1.0 | 1.0 | 1.0 | 1.0 |

[a] 1 = Copolymer of 60% styrenephosphonic acid butyl ester and 40% DVB; 100% isooctane.

[b] 2 = Copolymer of 60% styrenephosphonic acid methyl ester and 40% DVB, 100% isooctane.

[c] 3 = Copolymer of 70% styrenephosphonic acid methyl ester and 30% DVB, 100% isooctane.

## TABLE VII

RELATIVE RETENTION TIMES OF UNSATURATED COMPOUNDS (RELATIVE TO $n$-PENTANE)

| Sorbate | B.p. ($^{\circ}C$) | M.W. | $t_R/t_R(n\text{-}pentane)$ | | | |
|---|---|---|---|---|---|---|
| | | | Polysorb | 1 | 2 | 3 |
| $n$-Pentane | 36.1 | 72.1 | 1.0 | 1.0 | 1.0 | 1.0 |
| Pentene-2 | 36.9 | 7.1 | 1.04 | 1.4 | 1.5 | 2.0 |
| Pentadiene-1,3 | 44.1 | 68.1 | 1.2 | 2.4 | 2.5 | 2.6 |
| Hexane | 68.7 | 86.2 | 2.3 | 1.4 | 1.7 | 2.6 |
| Hexene-1 | 63.5 | 84.2 | 2.2 | 1.8 | 1.9 | 3.0 |
| Hexadiene-1,5 | 59.4 | 82.1 | 2.1 | 2.0 | 2.1 | 3.2 |
| Cyclohexane | 81.4 | 84.2 | 3.1 | 1.6 | 2.9 | 3.9 |
| Benzene | 80.1 | 78.1 | 2.9 | 2.3 | 6.1 | 8.0 |
| Methylcyclohexane | 100.0 | 98.2 | 5.6 | 1.8 | 3.4 | 5.2 |
| Toluene | 110.6 | 92.1 | 6.8 | 3.8 | 12.0 | 14.3 |
| Propanol | 97.2 | 60.1 | 1.05 | 34.0 | 10.8 | 13.6 |
| Allyl alcohol | 96–97 | 58.1 | 1.0 | 46.0 | 11.3 | 17.0 |

## TABLE VIII

RELATIVE RETENTION TIMES OF CHLORINATED METHANES (RELATIVE TO $n$-PENTANE)

| Sorbate | B.p. ($^{\circ}C$) | M.W. | Dipole moment (D) | $t_R/t_R(n\text{-}pentane)$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | Polysorb | 1 | 2 | 3 |
| Dichloromethane | 40.1 | 84.9 | 1.62 | 0.9 | 1.6 | 1.8 | 3.7 |
| Chloroform | 61.3 | 119.4 | 1.06 | 2.1 | 6.8 | 4.3 | 8.6 |
| Carbon tetrachloride | 76.8 | 153.8 | 0 | 3.1 | 5.0 | 3.4 | 6.4 |
| $n$-Pentane | 36.1 | 72.15 | 0 | 1.0 | 1.0 | 1.0 | 1.0 |

## TABLE IX

RELATIVE RETENTION TIMES OF SUBSTANCES HAVING SIMILAR BOILING POINTS (RELATIVE TO $n$-PENTANE)

| Sorbate | B.p. ($^{\circ}C$) | M.W. | Dipole moment (D) | $t_R/t_R(n\text{-}pentane)$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | Polysorb | 1 | 2 | 3 |
| Methanol | 64.7 | 32.0 | 1.706 | 0.2 | 21.0 | 2.8 | 3.8 |
| Tetrahydrofuran | 64.66 | 72.1 | | 2.3 | 4.3 | 5.2 | 6.6 |
| Ethanol | 78.4 | 46.1 | 1.68 | 0.4 | 14.8 | 4.8 | 5.8 |
| Ethyl acetate | 77.1 | 88.1 | 1.81 | 2.4 | 4.6 | 5.4 | 6.5 |
| Carbon tetrachloride | 76.8 | 153.8 | 0 | 3.1 | 5.0 | 3.4 | 6.4 |
| Acetonitrile | 81.6 | 41.1 | 3.94 | 0.6 | 23.0 | 5.2 | 5.5 |
| Benzene | 80.1 | 78.1 | 0 | 2.9 | 2.3 | 6.1 | 8.0 |
| Cyclohexane | 81.4 | 84.1 | 0 | 3.1 | 1.6 | 2.9 | 3.9 |
| Water | 100.0 | 18.0 | 1.84 | 0.1 | 40.0 | 3.3 | 4.9 |
| Propanol | 97.8 | 60.1 | 1.64 | 0.9 | 34.0 | 10.8 | 13.6 |
| $n$-Heptane | 98.4 | 100.2 | 0 | 4.8 | 1.6 | 3.2 | 3.8 |

9.7 and 36.2, respectively (Tables IX and X). The highly specific nature of the molecular interaction of porous polymer sorbents with phosphonate groups is shown particularly well in the separation of hydroxylated compounds, viz., water, alcohols and acids.

TABLE X

RELATIVE RETENTION TIMES OF SUBSTANCES HAVING SIMILAR MOLECULAR WEIGHTS (RELATIVE TO
n-PENTANE)

| Sorbate | B.p. (°C) | M.W. | Dipole moment (D) | $t_R/t_R$(n-pentane) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Polysorb | 1 | 2 | 3 |
| Ethyl acetate | 77.1 | 88.1 | 1.81 | 2.4 | 4.6 | 5.4 | 6.5 |
| 1,4-Dioxan | 100.8 | 88.1 | 0 | 4.4 | 8.0 | 14.3 | 8.6 |
| Diethyl ether | 35.6 | 74.1 | 1.17 | 0.87 | 1.6 | 1.5 | 1.7 |
| n-Pentane | 36.1 | 72.1 | 0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Tetrahydrofuran | 64-66 | 72.1 | | 2.3 | 4.3 | 5.2 | 5.0 |
| n-Butanol | 117.3 | 74.1 | 1.63 | 2.8 | 5.8 | 14.6 | 17.8 |

Fig. 6 shows the dependence of the relative retention times of isomeric C₄ alcohols on their boiling points. From these results it follows that (1) the relative retention times of isomeric C₄ alcohols are significantly greater on the sorbents investigated than on Polysorb; (2) the contribution of specific interaction increases with a decrease in the branching of the hydrocarbon chain in the molecules of isomeric C₄ alcohols; (3) the relative retention of the molecules of alcohols increases with increasing concentration of functional groups in the sorbent; and (4) the specific behaviour of the sorbent is largely dependent on the nature of the substituent in the phosphonate group, i.e., in this particular instance the relative retention times of isomeric C₄ alcohols are significantly greater on the copolymer of DVB and styrenephosphonic acid butyl ester (curve 4) than those on the copolymer of DVB and styrenephosphonic acid methyl ester (curve 2). This effect seems to be related to an increase in the excess charge on the phosphoryl oxygen from
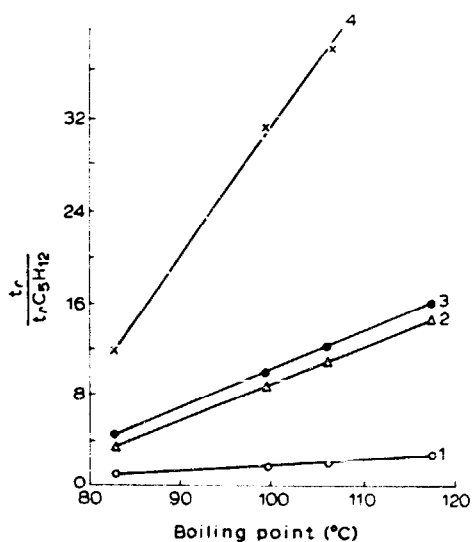


Fig. 6. Dependence of the relative retention times of isomeric C₄ alcohols on their boiling points. Column temperature 150°. 1, On Polysorb; 2, on copolymer 2 (60% styrenephosphonic acid methyl ester and 40% DVB); 3, on copolymer 3 (70% styrenephosphonic acid methyl ester and 30% DVB); 4, on copolymer 1 (60% styrenephosphonic acid butyl ester and 40% DVB).

$CH_2=CHC_6H_4P(O)(OCH_3)_2$ to $CH_2=CHC_6H_4P(O)(OC_4H_9)_2$. From their separative properties, the polymer sorbents investigated correspond to polar liquid phases.

Sorbents based on DVB and styrenephosphonic acid esters, especially the copolymer of DVB and styrenephosphonic acid butyl ester, are similar to highly polar stationary liquid phases of the polyethylene glycol type, *e.g.*, at a temperature of 150° and a helium flow-rate of 30 ml/min, the ratio of the retention volumes of *n*-butanol and *n*-pentane on PEG-2000 is 47, and on the copolymer of styrene-phosphonic acid butyl ester and DVB it is 58. The ratio $V_R$(propanol)/$V_R$(heptane) on PEG-2000 is 6.2, and on the copolymer of styrenephosphonic acid butyl ester and DVB it is 21.2.

The structural characteristics of the phosphorus-containing polymer sorbents are important. All of the sorbents are produced in the presence of an inert solvent, isooctane, and are characterized by a porous structure. This is confirmed by the results of surface area measurements (for the specimens used the surface area is 24–84 $m^2$/g) and by mercury porosimetric measurements (total pore volume = 0.57, 0.86 and 0.75 $cm^3$/g for specimens 1, 2 and 3, respectively).

The present investigation has thus shown the possibility of developing for gas chromatography porous polymer sorbents the polarity of which can be controlled over a wide range.

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