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RETENTION BEHAVIOUR DURING SEPARATIONS ON POLAR SORBENTS CONTAINING ETHER GROUPS

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SUMMARY

The retention of various classes of compound on polar polymer sorbents containing ether functional groups was investigated and correlation was made between the retention values obtained and those obtained on non-polar polymeric sorbent and on polar stationary phases.

INTRODUCTION

As well as using non-polar polymeric sorbents in gas chromatography great use is made of polar sorbents—Porapacks R, N, S, T, and Chromosorbs 103–105 which are obtained by the polymerisation of styrene, divinylbenzene and polar monomers. By introducing monomers containing various functional groups into the polymerisation mixture it is possible to control the chemical properties of the surface of the sorbents obtained and thus to influence the nature of the intermolecular interactions of the surface of the sorbent with the components of the mixture being separated. The use of porous polymer sorbents containing polar functional groups in gas chromatography makes it possible to change the position of water and other polar compounds relative to non-polar ones and also to lessen the widening of the rear limit of the peak of a number of components—in particular amines, diamines, aldehydes.

Some data concerning the retention of polar molecules, water, unsaturated compounds on Porapacks R, N, S, T have been discussed in a number of works^{1–5}. However, functional groups are not known to exist on the surface of these sorbents which makes it difficult to correlate the laws of retention of these components on Porapacks R, N, S, T with the nature of the functional groups on the surface. The development and study of polymer sorbents having certain chemical and functional composition must become of great practical and theoretical importance.

Comparative studies of the laws of retention of various classes of molecules on Polysorb-6 (styrene and *p*-divinylbenzene copolymer*) and Polysorbate-2**

* Polysorb-6 corresponds to Porapack Q, Chromosorb-102 and Polysorb-1.

** The authors' opinion is that polymer sorbents can be called "polysorbs" for convenience¹⁰, but for polar sorbents it would be somewhat more useful to change this term so that it characterises the presence of the respective functional group. Thus polymer sorbents containing ether groups are called "polysorbates" by the authors.

(methyl acrylate and *p*-divinylbenzene copolymer) were carried out, and the correlation was studied between the values of retention obtained and the respective values, obtained in the case of dinonyl phthalate and polyethylene glycol (PEG)-2000 which were coated onto a teflon support—Polychrome-1.

The structure of the surface can be seen on the photographs taken by means of a scanning electronic microscope (Fig. 1) (see also ref. 9).

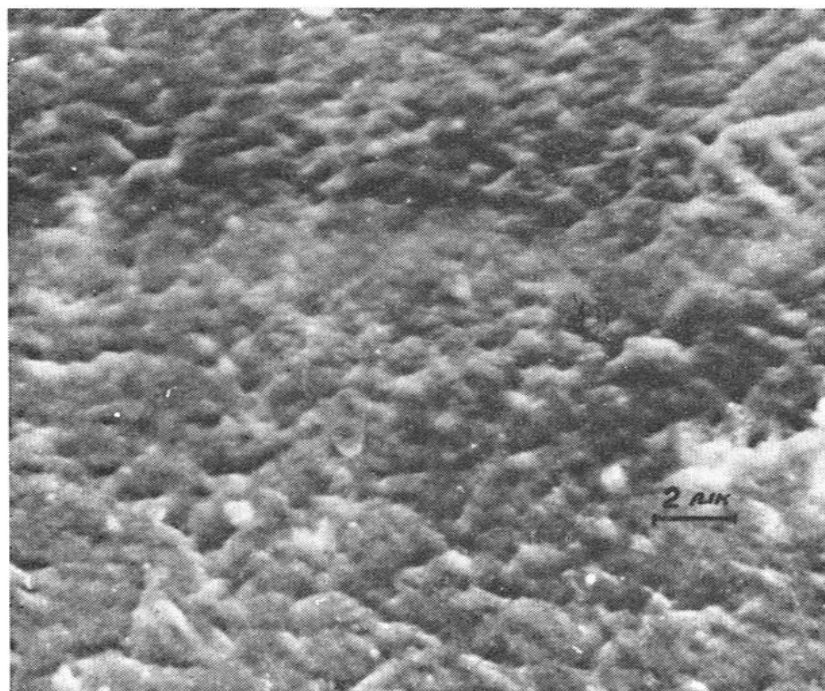


Fig. 1. Photograph ($\times 5000$) of the surface structure of Polysorbate-2, taken by a scanning electron microscope (JSM-2 JEOL, Japan).

Gas chromatographic studies were carried out by means of an instrument having a column 1 m long and 4 mm in diameter. The operating temperature was 150° ; the flow rate of the carrier gas (helium) was 30 ml/min, detection was by means of a katharometer. The principal differences in behaviour, during separation, of molecules having various bonds and functional groups on Polysorbate-2 are compared with that for the non-polar Polysorb-4.

THE DEPENDENCE OF RETENTION VOLUME ON BOILING POINT, ETC.

Polysorb-6

We have found a linear dependence between the corrected retention volume logarithm ($\log V_R$) and the number of carbon atoms in the molecule for homologous series of: *n*-alkanes, aromatic hydrocarbons, *n*-alcohols, ketones and fatty acids⁶. For the homologous series of the above classes of compounds $\log V_R$ is also a linear function with respect to boiling points, standard entropy (Fig. 2), molecular weights of the compounds and to the general polarisability of molecules and this linearity holds for the whole range of temperature studied, 120° – 180° .

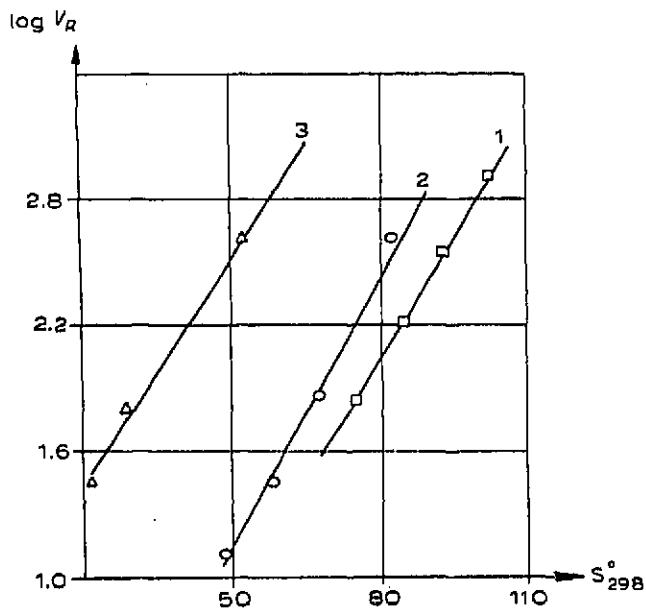


Fig. 2. Dependence of the log of the corrected retention volume upon the standard entropy of molecules on Polysorb-6. 1 = *n*-alkanes C_5-C_8 ; 2 = *n*-alcohols C_1-C_6 ; 3 = *n*-acids C_1-C_4 .

Polysorbate-2

The dependence of $\log V_R$ on the number of carbon atoms (boiling point, molecular weight, standard entropy, general polarisability of molecules) in the molecules is linear for homologous series of *n*-alkanes but is non-linear for alcohols and acids (Fig. 3).

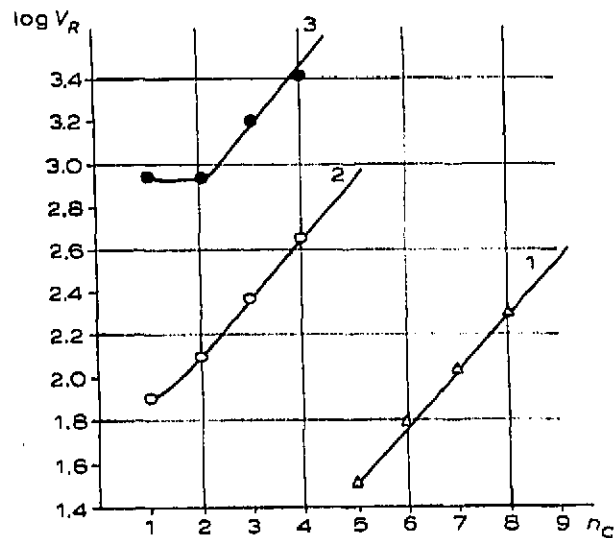


Fig. 3. Dependence of the log of the corrected retention volume upon the number of atoms of hydrogen in molecules on Polysorbate-2. 1 = *n*-alkanes C_5-C_8 ; 2 = *n*-alcohols C_1-C_6 ; 3 = *n*-acids C_1-C_4 .

THE SEPARATION OF UNSATURATED COMPOUNDS

Polysorb-6

The local electronic structure of unsaturated compounds does not appear to provide any features which would contribute to their ability for specific interaction. The elution of unsaturated compounds occurs in accordance with their boiling points, and does not depend on the presence of the double bonds in the molecules (see Table I). This applies in the case of hydrocarbons as well as alcohols and acids.

TABLE I

RELATIVE RETENTION TIME OF UNSATURATED COMPOUNDS

 t_R of *n*-pentane taken as a standard.

Sorbate	<i>b.p.</i> (°C)	<i>M.W.</i>	t_R/t_R of <i>n</i> -pentane			
			<i>Poly-sorb-6</i>	<i>Polysorbate-2</i>	10% of dinonyl phthalate on <i>Poly-chrome-1</i>	10% of PEG-2000 on <i>Poly-chrome-1</i>
Pentane	36.1	72.1	1.0	1.0	1.0	1.0
Pentene-2	36.9	70.1	1.04	1.4	1.1	1.4
Pentadiene-1,3	44.1	68.1	1.2	2.3	2.6	2.6
Hexane	68.7	86.2	2.3	1.9	2.0	2.1
Hexene-1	63.5	84.2	2.2	2.3	2.1	2.4
Hexadiene-1,5	59.4	82.1	2.1	2.7	2.1	2.9
Cyclohexane	81.4	84.2	3.0	3.9	3.7	4.0
Cyclohexene	83.0	82.1	3.3	5.5	4.2	6.3
Benzene	80.1	78.1	2.9	8.8	5.1	13.3
Heptane	98.4	100.2	4.8	3.4	3.7	3.9
Heptene-3	95.6	98.2	4.6	4.2	3.9	4.3
Methylcyclohexane	100.9	98.2	5.6	5.2	5.2	5.0
Toluene	110.6	92.1	6.8	15.1	9.6	25.7
Propanol	97.2	60.1	1.05	7.1	2.8	24.1
Allyl alcohol	96-97	58.1	1.0	8.9	3.0	36.9
Propionic acid	141.1	74.1	3.9	49.5	—	—
Acrylic acid	141.0	72.1	3.8	69.1	—	—

Polysorbate-2

Separation depends on the local electronic structure of the unsaturated compounds. Their elution is determined by the presence and the number of unsaturated bonds in a molecule rather than by the boiling point. Aromatic hydrocarbons are retained much better than the respective cyclic compounds on this sorbent; this is particularly true in the case of unsaturated alcohols and acids (see Table I).

THE EFFECT OF DIPOLE MOMENT AND GENERAL POLARISABILITY

Polysorb-6

The molecular retention is independent of the value of the dipole moment for the series of compounds: pentane, diethyl ether, methanol, ethanol, water, acetone, acetonitrile.

The retention volumes increase with the general growth of the polarisability of the adsorbate molecules (Table II); the rapid elution of water (before methanol and pentane), is the result of the small value of the polarisability of the water molecules.

TABLE II

RELATIVE RETENTION TIME OF POLAR MOLECULES

 t_R of *n*-pentane taken as a standard.

Sorbate	α (Å^3)	μ , D	t_R/t_R of <i>n</i> -pentane			
			<i>Poly-sorb-6</i>	<i>Poly-sorbate-2</i>	10% of dinonyl phthalate on <i>Poly-chrome-1</i>	10% of PEG-2000 on <i>Poly-chrome-1</i>
Water	1.49	1.84	0.12	3.5	1.1	41.1
Methanol	3.23	1.67	0.19	2.7	0.9	14.3
Ethanol	5.06	1.70	0.40	3.8	1.3	17.5
Acetonitrile	—	3.94	0.60	7.4	2.3	26.7
Acetone	6.32	2.73	0.69	3.7	1.6	8.7
Diethyl ether	9.02	1.17	0.87	1.7	1.2	2.5
<i>n</i> -Pentane	9.95	0	1.0	1.0	1.0	1.0

Polysorbate-2

The elution of the compounds: water, methanol, ethanol, acetonitrile, acetone, diethyl ether, pentane, is determined not only by the value of general molecular polarisability, but also by the value of molecular dipole moment (the retention time of pentane is less than that of acetone and acetonitrile). It is also influenced by the ability of the compounds to form hydrogen bonds with the polar-polymer surface: better retention of water and methanol than that of *n*-pentane is observed as compared to the retention on *Polysorb-4*.

THE RETENTION OF CHLOROMETHANES

Polysorb-6

The retention of chloromethanes is independent of the value of the dipole moment, and their elution from the *Polysorb-6* column occurs in parallel with the increase of their molecular weights and boiling points (Table III).

Polysorbate-2

The retention of the chloromethanes depends on the value of the molecular dipole moment and on the ability of molecules to form hydrogen bonds. Chloroform

TABLE III

RELATIVE RETENTION TIME OF CHLORINATED METHANES

 t_R of *n*-pentane taken as a standard.

Sorbate	M.W.	b.p. (°C)	μ	p of saturated vapours at 150° (atm)	t_R/t_R of <i>n</i> -pentane			
					Poly-sorb-6	Poly-sorbate-2	10% of dinonyl phthalate on Poly-chrome-1	10% of PEG-2000 on Poly-chrome-1
Dichloromethane	84.9	40.1	1.62	—	0.9	4.8	2.3	10.8
Chloroform	119.4	61.3	1.06	9.6	2.1	8.5	4.2	19.7
Carbon tetrachloride	153.8	76.8	0	5.8	3.1	6.5	4.1	9.1
<i>n</i> -Pentane	72.1	36.1	0	15.5	1.0	1.0	1.0	1.0

is retained better on Polysorbate-2 than the heavier and higher-boiling CCl_4 , while retention time for methylene chloride is about 5 times greater than that of pentane (Table III).

THE RETENTION OF COMPOUNDS WITH SIMILAR BOILING POINTS

Polysorb-4

The retention of the substances with similar boiling points on porous styrene and divinylbenzene copolymers is practically independent of the value of molecular

TABLE IV

RELATIVE RETENTION TIME OF SUBSTANCES HAVING SIMILAR BOILING TEMPERATURES

 t_R of *n*-pentane taken as a standard.

Sorbate	b.p. (°C)	M.W.	μ	p of saturated vapours at 150° (atm)	t_R/t_R of <i>n</i> -pentane			
					Poly-sorb-6	Poly-sorbate-2	10% of dinonyl phthalate on Poly-chrome-1	10% of PEG-2000 on Poly-chrome-1
Methanol	64.7	32.0	1.7	13.6	0.19	2.7	0.9	14.3
Tetrahydrofuran	64-66	72.1	—	—	2.3	6.5	3.6	8.9
Ethanol	78.4	46.1	1.68	9.7	0.4	4.2	1.3	17.5
Ethyl acetate	77.1	88.1	1.81	6.8	2.4	5.9	2.9	9.5
Carbon tetrachloride	76.8	153.8	0	5.8	3.1	6.5	4.1	9.1
Acetonitrile	81.6	41.05	3.94	—	0.6	7.4	2.3	26.7
Benzene	80.1	78.12	0	5.8	2.9	9.2	5.1	13.3
Cyclohexane	81.4	84.16	0	5.2	3.1	3.9	3.7	4.0
Water	100	18	1.84	—	0.12	3.8	1.1	41.1
Formic acid	100.7	46.03	1.67	—	0.4	28.5	—	—
Nitromethane	101	61.0	3.54	—	—	14.1	6.2	62.5
1-Dioxane	100.8	88.1	0	—	4.4	11.6	6.0	30.1
<i>n</i> -Heptane	98.4	100	0	3.6	4.8	3.4	3.7	3.9

dipole moment, the geometrical structure and the molecule's classification relating to groups (A, B, D) and their differing ability to perform molecular interactions; the retention value is primarily determined by the differences in the molecular weights of compounds and in the pressure of saturated vapours of the components at the separation temperature of 150° (Table IV).

Thus, ethanol (dipole moment = 1.68) elutes earlier than carbon tetrachloride ($\mu = 0$), and benzene (planar configuration) is retained on Polysorb-4 column for a shorter time than cyclohexane (mainly "chair" configuration); formic acid and *n*-propanol (molecules of the D-group capable of specific interaction with the sorbent surface), appear on the chromatogram much earlier than *n*-heptane (molecules of A-group, with σ -bonds).

Polysorbate-2

The retention of compounds with similar boiling points on Polysorbate-2 differs from that on Polysorb-6 and depends both on the dipole moment of the molecules being separated and on their ability to form hydrogen bonds with the active sites of the sorbent surface (Table IV). For example, water, *n*-propanol, nitromethane are retained on Polysorbate-2 better than *n*-heptane, in spite of their molecular weights being well below that of *n*-heptane, while all the boiling points are close.

THE SEPARATION OF COMPOUNDS WITH CLOSE MOLECULAR WEIGHTS

Polysorb-6

The main factor which determines the separation of components having close molecular weights is the difference in the boiling points of the compounds and in the pressure of their saturated vapours; due to this *n*-butanol (b.p. 117.5° and $p = 2.6$ atm), for instance, is retained in the Polysorb-4 column better than diethyl ether (b.p. 35.6°, and $p = 16.8$ atm) (t_R *n*-butanol/ t_R diethyl ether = 3.1). Tetrahydrofuran (b.p. 64–65°) is retained better than cyclopentane (b.p. 49.3°) and *n*-pentane better than furan (Table V).

Polysorbate-2

The retention of compounds with close molecular weights depends both on the dipole moment of the molecules being separated and on their ability to form hydrogen bonds with the active sites of the sorbent surface (Table V). Thus, *n*-butanol is retained much better than diethyl ether (t_R *n*-butanol/ t_R ether = 7.8), and furan better than *n*-pentane.

The observed differences in the retention behaviour of components on these sorbents result from the changes in the chemical nature of the surface of the Polysorbate; *viz.* the transition from an aromatic polyhydrocarbon (Polysorb-6) to a sorbent containing ether functional groups (Polysorbate-2).

The results obtained show that Polysorbate-2 is characterised by specific molecular interactions and according to the classification of KISELEV AND YASHIN for types of sorbents, one containing ether functional groups should be regarded as a specific sorbent of type III⁷.

The interaction of the components being separated with the surface of such

TABLE V

RELATIVE RETENTION TIME OF SUBSTANCES HAVING SIMILAR MOLECULAR WEIGHTS

 t_R of *n*-pentane taken as a standard.

Sorbate	M.W.	b.p. (°C)	μ	p of saturated vapours at 150° (atm)	t_R/t_R of <i>n</i> -pentane			
					Poly- sorb-6	Polysor- bate-2	10% dinonyl phthalate on Poly- chrome-1	10% of PEG-2000 on Poly- chrome-1
Hexane	86.2	68.7	0	—	2.3	2.4	2.0	2.1
Ethyl acetate	88.1	77.1	1.81	6.8	2.4	5.9	2.9	9.5
1,4-Dioxane	88.1	100.8	0	—	4.4	11.6	6.0	30.1
<i>n</i> -Amyl alcohol	88.1	138.0	1.65	—	5.6	26.7	9.1	85.4
Butyric acid	88.1	163.5	0.93	0.5	5.7	84.2	—	—
Furan	68.1	32.0	0.72	—	0.7	3.4	0.9	4.7
Diethyl ether	74.1	35.6	1.17	16.8	0.9	1.7	1.2	2.5
<i>n</i> -Pentane	72.1	36.1	0	15.6	1.0	1.0	1.0	1.0
Cyclopentane	70.1	49.3	0	—	1.4	2.3	2.0	—
Tetrahydrofuran	72.1	64-65	—	—	2.3	6.5	3.6	8.9
<i>n</i> -Butanol	74.1	117.5	1.63	2.6	2.8	13.2	5.9	4.7
Propionic acid	74.1	141.1	1.74	1.4	3.9	49.5	—	—
Acetone	58.1	56.2	2.85	11.5	0.7	3.7	1.6	8.7
Nitromethane	61.0	101.0	3.54	—	1.0	14.1	6.2	6
Acetic acid	60.1	118.1	1.70	2.4	1.0	28.0	—	—

sorbents depends essentially on the value of the dipole moment of the compounds, on their ability to form hydrogen bonds with the sorbent and on the strength of these bonds. In the case of Polysorbate-2 this can be demonstrated by the retention of fatty acids as compared to alcohols, both having a similar number of carbon atoms in the molecule. Far greater retention of formic acid is observed compared to methanol and of propionic acid as compared to propanol.

The ratio of the retention volumes of *n*-acids and *n*-alcohols having an equal number of atoms of carbon in molecules is given in Table VI. From Table VI it can be seen that the ratio of V_R of the acid to V_R of the alcohol decreases with an increasing number of carbon atoms in the respective molecules, which, probably, results from the lessening of the contribution of the specific interaction to the total

TABLE VI

RATIO OF THE RETAINED VOLUMES OF *n*-ACIDS AND *n*-ALCOHOLS HAVING EQUAL NUMBER OF CARBON ATOMS IN A MOLECULE

Components being separated	Polysorb-6	Polysorbate-2
1 HCOOH/CH ₃ OH	2.1	10.0
2 CH ₃ COOH/C ₂ H ₅ OH	2.3	7.4
3 C ₂ H ₅ COOH/C ₃ H ₇ OH	3.5	7.0
4 C ₃ H ₇ COOH/C ₄ H ₉ OH	2.0	5.8

TABLE VII

THE RETENTION OF STRUCTURAL ISOMERS
 t_R of *n*-pentane taken as a standard.

Sorbate	M.W.	b.p. (°C)	t_R/t_R of <i>n</i> -pentane			
			Poly-sorb-6	Poly-sorbate-2	10% of dinonyl phthalate on Polychrome-1	10% of PEG-2000 on Polychrome-1
Pentane	72.1	36.1	1.0	1.0	1.0	1.0
Isopentane	72.1	27.9	0.8	0.8	0.8	0.9
Cyclopentane	70.1	49.3	1.4	2.3	2.0	2.0
Hexane	86.2	68.7	2.3	1.9	2.0	2.1
Cyclohexane	84.2	81.4	3.1	3.9	3.7	4.0
Hexene-1	84.2	66.5	2.2	2.3	2.1	2.4
Cyclohexene	82.1	83	3.3	5.5	4.2	6.3
Heptane	100.2	98.4	4.8	3.4	3.7	3.9
Methylcyclohexane	98.2	100.9	5.6	5.2	5.2	5.0
Octane	114.2	124.7	11.9	6.3	6.2	9.5
Isooctane	114.2	99.2	6.0	5.6	4.4	3.3
<i>tert.</i> -Butanol	74.1	82.8	1.2	4.5	2.2	10.4
<i>sec.</i> -Butanol	74.1	99.5	1.3	8.5	3.6	22.7
Isobutanol	74.1	107	2.2	10.0	4.5	2.7
<i>n</i> -Butanol	74.1	117.5	2.8	13.2	5.9	47.0

energy of molecular interaction—sorbate (group D molecule)—polar polymer sorbent—as the number of carbon atoms in the molecules of the alcohols and acids increases.

The retention of structural isomers was studied on the sorbents mentioned above (see Table VII).

Like Polysorb-6, Polysorbate-2 gives a more rapid elution of isomeric alkanes and better retention of cyclic hydrocarbons as compared to the respective *n*-hydrocarbons. Isomeric alcohols are characterised by better retention of molecules of normal structure compared to branched molecules, on Polysorbate-2, similar to that on Polysorb-6, *i.e.* the retention time of *n*-butanol is longer than that of isobutanol, *sec.*-butanol, and *tert.*-butanol, although the relative retention values of alcohols on Polysorbate-2 considerably exceed the respective values on Polysorb-6 (Table VII).

Fig. 4 shows the dependence of the relative retention time of C₄ isomeric alcohols on polymer sorbents upon their boiling point. The relationship is linear, but during chromatographic analysis on Polysorbate-2 the relative retention of alcohols and the slope of this relationship as compared to the respective relationship on Polysorb-6 increases.

These data indicate the specific interaction of alcohols with the ether functional groups of Polysorbate-2 and the growth of importance of hydrogen bonds between sorbate and Polysorbate-2 when the structure of the carbon chain in molecules of alcohols having the same number of hydrogen atoms becomes less branched. The

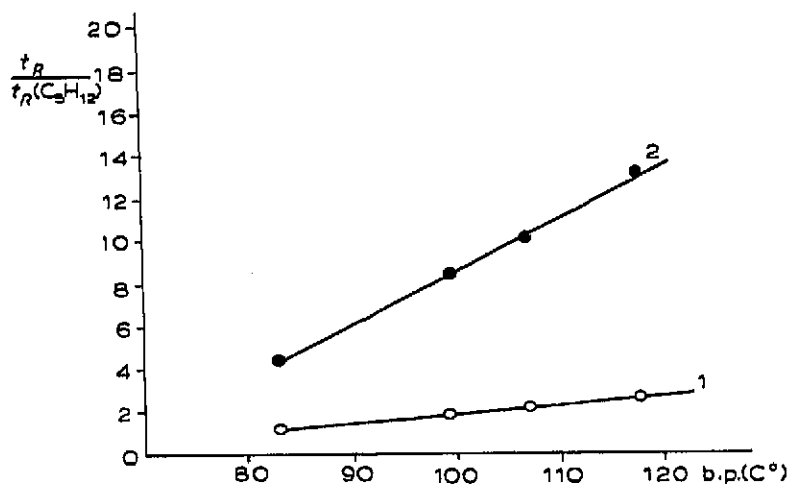


Fig. 4. Dependence of the relative retention time of isomeric C_4 alcohols upon the boiling point. (1) On Polysorb-6; (2) on Polysorbate-2.

similar values of the relative retention volumes of branched alcohols and alcohols of normal structure having similar boiling points, in particular *sec.*-butanol and *n*-propanol, *tert.*-butanol and isopropanol, during their separation on Polysorbate-2 proves the same point.

For instance, in the case of Polysorb-6 the ratio of the retention volumes V_R *sec.*-butanol/ V_R *n*-propanol = 1.8; for Polysorbate-2 it is 1.2 and the ratio of the retention volumes V_R *tert.*-butanol/ V_R isopropanol equals 1.7 and 1.1, respectively for Polysorb-6 and Polysorbate-2.

The peculiarities of the retention behaviour of components pointed out in the case of Polysorbate-2 can also be observed in the case of Porapack T⁷—the most polar of the known polymeric sorbents—the Porapacks.

A comparison was made between the retention values of various types of compounds on Polysorbate-2 and on the stationary liquid phases, dinonyl phthalate and PEG-2000, applied over an inert Teflon support—Polychrome-1⁶. Some similarity was observed in the retention of the components on the Polysorbate-2 and on these phases, although the values of the relative retention time of polar molecules on Polysorbate-2 exceed those for dinonyl phthalate, but are lower than for PEG-2000, which, probably, is the result of different concentrations in the functional groups in these sorbents.

Thus, methyl acrylate-divinylbenzene base polymer sorbent—Polysorbate-2—possesses separating properties which are similar to those of stationary polar phases.

The value of relative polarity found by the ROHRSCHEIDER method⁸ was 41% for Polysorbate-2, *i.e.* Polysorbate-2 is identical with stationary phases of average polarity and the value of its relative polarity somewhat exceeds that of Porapack T ($P = 34\%$).

Still more polar sorbents (polarity according to ROHRSCHEIDER 60–90%) can be obtained by using other polar monomers as a base.

Thus polymer sorbents having various degrees of polarity according to the limits of ROHRSCHEIDER scale for stationary phases can be developed.

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