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CHEMICALLY MODIFIED POLYMERIC SORBENTS FOR GAS CHROMATOGRAPHY

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SUMMARY

The gas chromatographic properties of some chemically modified polymeric sorbents have been studied. The sorbents were based on macroporous styrene and divinylbenzene, 2-methyl-5-vinylpyridine and divinylbenzene copolymers and obtained by using polymer-analogous reactions, in particular, chloromethylation, nitration, amination, sulphation, phosphorylation, oxymethylation and N-oxidation reactions. The specificity and selectivity of the sorbents are estimated. It is shown that chemical modification allows a larger group of sorbents to be obtained with a diversity of functional groups on their surfaces.

INTRODUCTION

Porous polymeric sorbents are of great interest, since they possess suitable properties for separating the majority of classes of organic compounds; their structures and chemical nature of the surface can be controlled. They comprise macromolecular organic compounds capable of chemical transformations, which allows the production of new types of sorbents based on known ones and the variation of their properties (and, correspondingly, their application) over wide ranges. The development of a set of methods for chemical modification of porous polymeric sorbents represents a new technological advance.

EXPERIMENTAL

The sorbents are listed in Table I, together with their method of preparation and the type of functional groups attached.

Gas chromatographic (GC) measurements were carried out on a Tsvet-132 chromatograph equipped with a thermal conductivity detector and 1 m × 3 mm I.D. columns at 150°C and a carrier gas (helium) flow-rate of 30 cm³/min. The basic retention parameters determined included the relative retention times, t_R^{rel} (with respect to *n*-pentane), and the retention indices.

TABLE I

<i>Sorbent</i>	<i>Method of preparation</i>	<i>Attached functional groups</i>
Polysorb-1	Copolymerization of styrene (60%) and divinylbenzene (40%)	
Chloromethylated polysorb-1	Treatment of polysorb-1 by chloromethyl ether	CH ₂ Cl
Polysorb-2	Copolymerization of styrene (80%) and divinylbenzene (20%)	
Sorbent with ethylenediamine groups	Treatment of polysorb-2 by chloromethyl ether, subsequent amination by ethylenediamine	CH ₂ NCH ₂ CH ₂ NH ₂
Sorbent with diethylenetriamine groups	Treatment of polysorb-2 by chloromethyl ether, subsequent amination by diethylenetriamine	CH ₂ N $\begin{array}{l} / \text{CH}_2\text{CH}_2\text{NH}_2 \\ \backslash \text{CH}_2\text{CH}_2\text{NH}_2 \end{array}$
Nitropolysorb-1	Nitration of polysorb-1 by a mixture of potassium nitrate and concentrated sulphuric acid	NO ₂
Nitropolysorb-2	Nitration of polysorb-2 by a mixture of potassium nitrate and concentrated sulphuric acid	NO ₂
Aminopolysorb-1	Nitration of polysorb-2 with subsequent reduction of nitric groups to amino groups by a mixture of tin (II) chloride and concentrated hydrochloric acid	NH ₂
Aminopolysorb-2	Nitration of polysorb-2 with subsequent reduction of nitric groups to amino groups	NH ₂
Sulphopolysorb-1	Sulphation of polysorb-1	SO ₃ H
Sulphopolysorb-2	Sulphation of polysorb-2	SO ₃ H
Phosphopolysorb-2	Phosphorylation of polysorb-2	PO(OH) ₂
Polysorb N	Copolymerization of 2-methyl-5-vinylpyridine (85%) and divinylbenzene (15%)	
Polysorb N with carboxyl groups		
Specimen 2	Oxymethylation with subsequent oxidation by nitric acid	COOH and pyridine rings
Specimen 4	N-oxidation with subsequent acetylation	

RESULTS AND DISCUSSION

Tables II and III give the retention indices and t_R^{rel} values for various classes of compounds on the chemically modified sorbents. It is seen that the attachment of various functional groups to one polymeric matrix (80% styrene and 20% divinylbenzene copolymer of porous structure), as a result of polymer-analogous transformation reactions, influences the retention and the order of elution of the compounds.

TABLE II

RELATIVE RETENTION TIMES FOR VARIOUS COMPOUNDS ON CHEMICALLY MODIFIED SORBENTS BASED ON STYRENE AND DIVINYLBENZENE COPOLYMERS

Sorbate	Functional group of sorbent						
	CH_2Cl	Ethylene diamine	Diethyl- enetriamine	NO_2	NH_2	SO_3H	PO_3H_2
Cyclohexene	3.1	3.3	3.8	6.2	3.0	2.0	2.9
Benzene	3.9	4.6	4.9	10.3	12.9	15.0	3.1
Toluene	5.4	5.6	10.3	15.9	19.0	20.7	4.8
Acetone	1.4	1.8	1.1	8.4	7.3	66.3	7.7
Methyl ethyl ketone	2.6	3.2	3.3	14.1	9.9	94.3	10.2
Acetonitrile	1.6	2.1	2.3	13.4	16.9	26.0	13.5
Propionitrile	2.1	3.2	3.4	17.8	28.8	30.3	27.6
Nitromethane	2.4	3.0	3.6	20.0	18.2	34.3	11.6
Ethyl acetate	2.6	2.9	3.5	6.4	15.1	30.2	11.2
Pyridine	15.3	12.8	13.1	49.4	63.7	—	20.0
Water	0.6	1.2	1.3	3.9	9.4	51.3	9.9
Thiophene	3.8	4.4	4.8	11.4	16.3	19.6	6.9
Dichloromethane	1.7	2.4	3.9	5.1	3.0	6.9	6.2
Chloroform	2.6	3.6	4.4	9.6	10.5	11.0	4.0

TABLE III

RETENTION INDICES FOR COMPOUNDS OF VARIOUS CLASSES

NE = not eluted.

Sorbent	Sorbate					
	Benzene	Methyl ethyl ketone	Nitromethane	Pyridine	Acetonitrile	Ethanol
Nitropolysorb-1	735	775	780	920	720	580
Nitropolysorb-2	1140	1235	1320	1460	1210	995
Aminopolysorb-1	640	705	635	855	540	555
Aminopolysorb-2	1250	1195	1300	1485	1295	1180
Sulphopolysorb-1	1000	1400	1030	NE	1120	NE
Sulphopolysorb-2	920	1800	1400	NE	1450	NE
Sulphonitropolysorb-1	690	730	680	NE	680	NE
Polysorb-1	660	584	520	726	475	432

The sorbents with SO_3H functional groups yield the highest retention values, I , t_R^{rel} , indicating the specificity of the molecular interaction. These sorbents are highly selective with respect to compounds capable of donor-acceptor interactions *e.g.*, hydroxyl and nitrocompounds, nitriles, ketones and aromatic compounds, and they are suitable for separating polar and non-polar compounds, substances of various classes with similar physical and chemical properties, for selective retention of some compounds.

The sorbents with chemically attached amino groups, namely ethylenediamine, amine and diethylenetriamine, whose retention characteristics depend on the electronic and geometric structures of the attached amino groups, possess a lower specificity of molecular interaction. Table II shows that an increase in the number of aminogroups, due to the use of diethylenetriamine instead of ethylenediamine as a modifying agent, results in an increase in the specificity of the sorbents.

The sorbents which contain amino groups directly coupled with carbon atoms of a benzene ring in the aminopolysorb possess higher specificity of molecular interaction. The retention indices for polar compounds on aminopolysorb are considerably higher than those on sorbents containing amino groups coupled with a benzene ring via the carbon chain¹. In this case, the direct influence of the benzene ring on the electron-density distribution in the sorbent is probably significant.

Sorbents with NO_2 - and $-\text{PO}_3\text{H}_2$ functional groups are highly specific.

Of great importance in the chemical modification of polymeric sorbents is the polymeric matrix to which the functional groups are attached. By employing polymeric matrices (the initial sorbents) of the same chemical nature but different porous structures, sorbents with different GC properties can be obtained. This is clearly seen by comparing the retention indices of compounds on nitropolysorb-1, aminopolysorb-1, and sulphopolysorb-1 whose polymere matrix comprises 60% styrene and 40% divinylbenzene (DVB) copolymer obtained in the presence of 100% isooctane, as well as on nitropolysorb-2, aminopolysorb-2 and sulphopolysorb-2 whose polymeric matrix is 80% styrene and 20% divinylbenzene copolymer obtained in the presence of 100% isooctane (Table III).

The data in Table III indicate that the use of polymers with lower contents of cross-linking agent (20% instead of 40% DVB) makes it possible to obtain sorbents with higher specificity. Thus, the sum of the retention indices for test compounds of the Rohrscheider series on nitropolysorb-1 is equal to 3790, whereas on nitropolysorb-2 it is 6150, on aminopolysorb-1 it is 3395 and on aminopolysorb-2 it is 6410. With polymeric matrices of less rigid structure (20% instead of 40% cross-linking agent), a larger number of functional groups can probably be introduced into the initial sorbent.

The chemical modification, while changing the chemical nature of the surface of the initial sorbent, in some cases causes a change in the type of polymeric sorbent. So, if the sorbents with NO_2 functional groups are, in accordance with Kiselev's² classification, those of type III with the local electron density concentrated on the periphery, then the sorbents with NH_2 groups, obtained as a result of the reduction of nitropolysorbs, as well as those with ethylenediamine and diethylenetriamine groups, are of type II with a concentrated positive charge.

The polymer-analogous transformation method allows two types of functional groups to be introduced simultaneously into the initial sorbent, and GC enables the

variation of the surface chemistry to be examined. We have studied the GC properties of a polymeric sorbent based on styrene and divinylbenzene copolymers-polysorb-1 with NO_2 and SO_3H functional groups. This sorbent differs in its retention characteristics from the initial copolymer and from the sorbents with one type of functional group (Table III).

By employing for chemical modification the sorbents whose chemical nature differs from that of styrene and divinylbenzene copolymers, *i.e.*, those which already contain some functional groups, one may use other polymer-analogous reactions for chemical modification and, thus, attach functional groups of different chemical nature to the initial sorbents. This considerably extends the possibilities for producing specific sorbents with a diversity of functional groups on their surfaces.

We have considered chemically modified polymeric sorbents based on 2-methyl-5-vinylpyridine and divinylbenzene copolymers. The content of monomers in the copolymer was 85 and 15% (w/w). The copolymer was obtained by suspension polymerization in the presence of *n*-heptene as diluent (50%). To obtain a sorbent containing carboxyl groups and pyridine rings, the modification was performed by two methods: by oxymethylation (specimen 1) followed by oxidation of the product with nitric acid (specimen 2) and by N-oxidation of an initial sorbent (specimen 3) followed by acetylation with acetic anhydride (specimen 4). Table IV gives the retention indices for some polar compounds on the initial sorbent, intermediate copolymers (specimens 1, 3) and on sorbents obtained by chemical modification (specimens 2, 4) (Fig. 1).

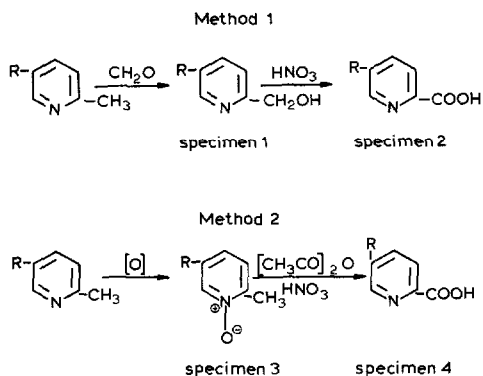


Fig. 1. Reactions employed for chemical modification of 2-methyl-5-vinylpyridine and divinylbenzene copolymers.

The retention indices of sorbates on the modified specimens 2 and 4 are considerably larger than on the initial sorbent, *i.e.*, the polymer-analogous reactions, while changing the chemical nature of the sorbent surface, also considerably change the GC properties. The retention induces on the oximethylated copolymer (specimen 1) are similar to those on the initial copolymer. Specimen 3, which contains N-oxypyridine groups, possesses considerably higher specificity and selectivity towards compounds of various classes, *e.g.*, alcohols, nitriles, ketones and aromatic hydrocarbons, compared to the initial sorbent.

TABLE IV

RETENTION INDICES FOR COMPOUNDS OF VARIOUS CLASSES ON 2-METHYL-5-VINYLPYRIDINE AND DIVINYLBENZENE COPOLYMERS AND ON MODIFIED SORBENTS BASED ON THESE COPOLYMERS

Column temperature: 150°C

<i>Sorbate</i>	<i>Initial copolymer</i>	<i>Modified sorbent</i>			
		<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
Methanol	765	821	1094	1272	1282
Ethanol	797	850	1075	1210	1285
Propanol	900	979	1162	1396	1183
Acetone	688	760	1080	1115	1122
Methyl ethyl ketone	730	841	1098	1185	918
Methyl propyl ketone	891	935	1191	1234	912
Acetonitrile	811	868	1118	1239	1285
Propionitrile	867	931	1169	1289	1284
Butyronitrile	976	1020	1252	1350	1089
Nitromethane	900	983	1186	1378	1390
Nitropropane	1073	1099	1263	1495	1284
Benzene	835	868	999	1198	723
Toluene	951	983	1145	1252	851
Ethylbenzene	1085	1072	1220	1337	900
Hexene-1	621	615	660	664	662
Heptene-1	730	732	748	761	765
Ethyl acetate	733	704	1005	1066	800
Diethyl ether	556	575	788	968	630
Tetrahydrofuran	811	900	1078	1095	781
Water	800	908	1073	1316	1285
Pyridine	1261	1292	1314	1398	1405
Thiophene	858	904	1112	1211	877

Chemically modified sorbents 2 and 4, which contain carboxyl groups and pyridine rings, are very selective towards polar compounds, especially alcohols, ketones, nitriles, water and amines. The data presented also indicate that the specific properties of the modified sorbents are strongly influenced by the method of modification employed. The retention of compounds is different on specimens 2 and 4 having the same functional groups; this may be related to different concentrations of carboxyl groups on the sorbent surface and, hence, to the different degree of oxidation of copolymer methyl groups compared with carboxyl ones and their different accessibility for sorbate molecules.

Thus, the ability of porous polymeric sorbents to undergo chemical transformations made it possible to vary the GC properties of initial specimens within wide ranges and to obtain a diversity of new types of sorbents based on known ones, thus allowing the resolution of new analytical problems. For example, polysorb, a universal non-polar sorbent may be used for separating all classes of organic compounds; nitropolysorb-1 is suitable for separating polar and non-polar compounds capable of donor-acceptor interactions, in particular, nitric compounds including nitric oxides; aminopolysorb-2 is useful for determining mixtures of non-polar compounds in organic solvents and acids as well as for separating compounds having

similar physical and chemical properties; the sulphopolysorbs are suitable for group separations of polar and non-polar compounds and for selective retention (removal) of highly polar compounds from complex mixtures of organic substances.

The results presented show that the chemical modification of known porous polymeric sorbents is important for producing sorbents with various selectivities in gas chromatography.

REFERENCES

- 1 K. I. Sakodynskii, G. P. Terekhova and L. I. Panina, *J. Chromatogr.*, 292 (1984) 227.
- 2 A. V. Kiselev and Ya. I. Yashin, *Gas-Adsorption Chromatography*, in Russian, Nauka Moscow, 1967.