

Effect of surface area chemistry on gas-chromatographic properties of polymeric sorbents

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Abstract - A comparative study on chromatographic properties of a number of porous polymeric sorbents with various functional groups has been made. Wide possibilities for regulating the specificity and selectivity of porous polymeric sorbents and for creating the sorbents with required gas-chromatographic properties by changing the chemical nature of their surface have been shown.

The interrelation between the surface area chemical nature and gas-chromatographic properties of sorbents determining the gas-chromatographic retention of the components is convincingly exemplified by the study of the properties of porous polymeric sorbents (Ref. 1-3). In-depth studies were performed to investigate the chromatographic properties of the sorbents based on the copolymers of styrene or ethylstyrene and divinylbenzene of porous structure. The retention values given in Table 1 and in all the other tables were determined on a gas chromatograph equipped with a detector of thermoconductivity and a flame-ionization detector at 150°C with helium as the carrier gas at a flow-rate of 30 ml/min. The analyses were carried out in columns 1 m X 3 mm I.D.

Incorporation of the monomers containing different functional groups into the polymerization mixture changes the chemical nature of the surface of the sorbents obtained and affects the character of intermolecular interactions of the sorbents with the components being separated. This fact is reflected by the changes in the characteristics of the sorbents and, first of all, in the changes of the relative retention times of the compounds with respect to hydrocarbons and the values of retention indices values.

The effect of the chemical nature of the surface on the gas-chromatographic properties of porous polymeric sorbents can be observed in the process of comparing the relative retention times of some polar compounds on porous polymeric sorbents with ether, nitrile, hydroxyl, amide, phosphinate functional groups, on the sorbents based on the vinyl derivatives of pyridine. These

Table 1. Relative retention times of polar molecules on the sorbents based on the copolymers of styrene and divinylbenzene

Sorbate	$\alpha, \text{Å}^3$	t'R / t'R of n-pentane					
		μ, D	Poly-sorb-1	Pora-pak Q	Pora-pak QS	Chromo-sorb 102	10% squalane on poly-chrom-1
Water	1.49	1.84	0.12	0.17	0.08	0.15	0.33
Methanol	3.23	1.67	0.19	0.25	0.14	0.25	0.16
Ethanol	5.06	1.70	0.40	0.51	0.34	0.50	0.33
Acetonitrile	6.11	3.94	0.60	0.66	0.45	0.63	0.37
Acetone	6.32	2.73	0.69	0.83	0.58	0.81	0.56
Diethyl ether	9.02	1.17	0.87	0.93	0.89	0.94	0.80
n-pentane	9.95	0	1.0	1.0	1.0	1.0	1.0

data are given in Table 2 (see Note a). It can be seen that a change in the chemical nature and concentration of functional groups of the polymeric sorbents surface area results in a change of the values of relative retention times of the sorbates and their elution sequence.

The application of the method of polymer-analogous transformations also allows the incorporation of various functional groups into the polymeric matrix of the original sorbents and, as a result, the regulation of the porous polymeric sorbents specificity. Polymer-analogous reactions of chloromethylation, nitration, amination, sulfurization, phosphorylation, oximethylation and others are often used to perform the chemical modification of polymers. We have studied, in particular, the retention characteristics of a number of sorbates on the polymeric sorbent polysorb-1 and polysorb-2 containing nitro- and amino groups chemically grafted to benzene rings of the polymeric matrix of the sorbents (Table 3).

The data cited in Table 3 show that grafting the nitro groups capable of the donor-acceptor interaction to the surface of styrene and divinylbenzene copolymers substantially increases its specificity, selectivity towards acids, nitriles, alcohols, amines, nitrocompounds. The employment of the copolymers which contain less amount of the cross-linking agent (20% DVB instead of 40%) for chemical transformations of polymers makes it possible to obtain the sorbents of a higher chromatographic specificity. This assumption is supported by the retention indices of a number of organic substances on nitropolysorb-2 and aminopolysorb-2 whose polymeric matrix is a copolymer of 20% divinylbenzene and 80% styrene. These sorbents considerably surpass nitropolysorb-1 and aminopolysorb-1 (their polymeric matrix is a copolymer of 40% DVB

Table 2. Relative retention times of polar molecules on polymeric sorbents containing various functional groups

Sorbate	t'R / t'R of n-pentane						
	Poly-sorb-ate-1	Poly-sorb-ate-2	Poly-sorb-ol	Polysor-bonit-riple	Poly-sorb-amide	Poly-sorb-P	Polysorb N(30)
Water	0.5	3.5	0.7	1.8	1.7	4.9	1.4
Methanol	0.6	2.7	0.8	1.5	1.5	3.8	1.4
Ethanol	1.0	3.8	1.4	2.7	3.5	5.8	1.8
Acetonit-riple	1.5	7.4	1.6	6.2	1.8	5.5	2.2
Acetone	1.3	3.7	1.9	3.7	3.3	3.7	1.6
Diethyl ether	1.2	1.7	1.1	1.3	1.9	1.7	1.1
n-pentane	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Table 3. Retention indices of a number of organic compounds on the polymeric sorbents containing nitro- and aminogroups

Sorbate	Poly-sorb-1	Nitropolysorb		Aminopolysorb	
		-1	-2	-1	-2
Ethanol	405	580	995	555	1180
Benzene	660	735	1140	645	1250
Nitromethane	540	780	1325	635	1300
Pirydine	735	930	1460	855	1485
Acetonitrile	475	745	1210	575	1295
Ethylacetate	615	750	1005	680	1265
Acetic acid	515	825	1310	775	1540

Note a. Polysorbate-1 is the copolymer of 60% methylmethacrylate and 40% divinylbenzene, Polysorbate-2 is the copolymer of 80% methacrylate and 20% divinylbenzene, polysorb-ol is the copolymer of 40% allyl alcohol and 60% DVB, polysorbonitrile is the copolymer of 60% acrylonitrile and 40% DVB, polysorbamide is the copolymer of 60% acrylamide and 40% DVB, polysorb P is the copolymer of 70% methyl ether of styrenephosphorus acid and 30% DVB, and polysorb N(30) is the copolymer of 70% 2-methyl-5-vinylpyridine and 30% divinylbenzene.

and 60% styrene) in terms of specificity of their molecular interaction. This can be due to the fact that a greater amount of functional groups can be involved in a less cross-linked matrix of the styrene and divinylbenzene copolymers. Thus, the content of elemental nitrogen in nitropolysorb-2 and nitropolysorb-1 is equal to 7.3% and 5.3%, respectively, whilst it is 9.1 and 5.8% in aminopolysorb-2 and aminopolysorb-1, respectively.

To estimate the contribution of the specific interaction energy into the total energy of the organic substances sorption we determined the values of the free sorption energy changes $\Delta (-\Delta G)$ of a number of molecules with respect to n-butane on the tested sorbents using the chromatographic method. The biggest values of $\Delta (-\Delta G)$ for the given sorbates with CO-, OH-, CN- and COOH-functional groups were found on aminopolysorb-2, which indicates the highest specificity of the latter.

Table 4. The increment values of the sorption free energy of some substances with respect to n-butane at 150°C

Sorbate	$\Delta (-\Delta G)$, kJ/mole				
	Polysorb-1	Nitropolysorb-1	Nitropolysorb-2	Aminopolysorb-1	Aminopolysorb-2
Methylethylketone	4.67	8.69	11.56	8.23	11.83
Butanol	6.38	9.84	12.45	11.20	15.25
Butyronitrile	6.80	10.77	14.40	11.37	18.54
Butyric acid	9.55	12.76	15.45	16.55	21.44

Table 5. Relative retention times of sorbates on sorbent with phosphorus-containing functional groups (tR'/tR' of n-pentane)

Copolymer of Styrene 70% Divinylbenzene 30% with functional groups of	Ethanol	Methylethylketone	Benzene	Acetonitrile	Nitromethane
phosphonous acid	15.8	15.3	7.0	5.8	12.6
phosphonic acid	33.2	16.0	4.3	20.1	17.1
propylphosphonic acid	4.2	4.0	4.1	3.5	5.5
Original polymer	0.8	2.1	3.9	1.4	2.1

Porous polymeric sorbents exhibit highly specific properties when they have phosphorus-containing functional groups like the groups of phosphonous acid, phosphonic acid, and propylphosphonic acid. The data given in Table 5 show that these sorbents exhibit much higher relative retention times of all classes of polar sorbates as compared with the original sorbents. High specificity of the molecular interaction typical for the sorbents concerned is due to strong proton-donor properties of phosphorus-containing functional groups. The most distinctly pronounced specificity is exhibited by the sorbents with the functional groups of phosphonous and phosphonic acids. When transition from the sorbent with phosphonic groups to the sorbent with propylphosphonic groups takes place, the specificity of the sorbent abruptly decreases, which is due to a weakening of the proton-donor properties of the functional groups resulting from the inductive effect of the C_3H_7 radical.

The studied made have shown that the highest values of relative retention times and retention indices of polar compounds with respect to n-hydrocarbons are exhibited by the sorbents with the ionogenic SO_3H -groups grafted to their surface and carrying strongly protonated hydrogen atoms (Table 6). Thus, sulfopolysorb-1 is highly selective towards the compounds capable of donor-acceptor interactions, in particular, towards water, carboxyl- and carbonyl-containing compounds, amines, nitriles, nitrocompounds, aromatic hydrocarbons. In terms of A.V. Kiselev's classification sulfopolysorbs should be classed with the Type II sorbents which are of great interest for researchers (Ref. 5).

Table 6. Retention indices of organic substances on sulfopolysorb-1

Sorbate	Polysorb-1	Sulfopolysorb-1
Benzene	660	1145
Methylethylketone	590	1480
Nitromethane	540	1420
Water	269	1335
Acetonitrile	475	1295
Diethyl ether	495	1220
Ethylacetate	615	1395
Formaldehyde	295	1705
Pyridine	734	1800
Acetic acid	515	1610

Table 7. Increments of a change in the sorption free energy of n-butane derivatives on polysorb-1 and sulfopolysorb-1

Sorbate	$\Delta (-\Delta G)$ kJ/mole	
	Polysorb-1	Sulfopolysorb-1
Pentane	2.61	1.81
Ethylacetate	5.80	19.14
Diethyl ether	2.51	15.74
Butyronitrile	6.80	19.54
Methylethylketone	4.96	20.72
Butyric acid	9.55	26.35

Table 8. Retention indices of organic compounds on metal-containing polymeric sorbents

Sorbate	Sulfocation exchangers in the form of				Polycomplexonate Cu ¹¹
	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	
Ethanol	1485	1505	1405	1500	935
Water	1560	1585	1680	1605	1060
Methylethylketone	1310	1095	1030	1245	930
Nitromethane	1265	1250	1180	1185	1065
Acetonitrile	1470	1485	1540	1440	1040
Ethylacetate	1035	1010	910	955	825

The difference in the values of retention indices of the group D molecules (acid, amine, water) on sulfopolysorb-1 and the original sorbent, polysorb-1, is equal to more than 1000 units and for the B group molecules it is equal to 500-900 units. This is confirmed by the high increment values of the sorption free energy changes (Table 7).

A new qualitative leap in the change of chromatographic properties of porous polymeric sorbents resulting from a change in the character of intermolecular interactions in the sorbate-sorbent system can be seen upon the transition to metal-containing polymeric sorbents, for example, to cation exchangers of macroporous structure. For sulfocation exchangers in Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺-forms, it is characteristic to exhibit irreversible retention of ammonium, amines, a very strong retention of water, alcohols, nitriles, ketones, as compared with paraffins (Table 8).

The gas-chromatographic properties of metal-containing sorbents substantially depend on how the metal is bonded with the polymeric matrix. The data given in Table 8 show that the sulfocation exchanger in the Cu⁻ form exhibits a higher chromatographic specificity.

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