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Regulation of the adsorption and chromatographic properties of polymeric adsorbents by varying their porous structure

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ABSTRACT. The review surveys the results of studies (using various physicochemical methods) of the geometrical structures of 2,3-epoxypropyl methacrylate–ethylene dimethacrylate and styrene–divinylbenzene copolymers as well as ultracross-linked polystyrenes ("Styrosorbs")—both the initial structures and those modified by amines and aminoalcohols. The influence of the porous structure of the aminated polymers on the adsorption and chromatographic properties was examined mainly in relation to the absorption of carbon and sulphur dioxides. The importance of the optimisation of the structures of the polymeric adsorbents in their practical application is demonstrated.

The bibliography includes 132 references.

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I. Introduction

Studies of the chemistry of the surfaces of solids, adsorption, and chromatography have developed appreciably in recent times. This was promoted by the creation of new adsorbents—in particular porous polymers. Polymeric adsorbents are widely used as sorbents in gas, liquid, ion-exchange, and ion chromatography, sieve (exclusion) chromatography of oligomers and polymers, biospecific (affinity) chromatography, and the ligand exchange chromatography of optical isomers and also as catalysts and selective absorbers of substances polluting the atmosphere.[1–3] Furthermore, the creation of polymeric adsorbents promotes the development of the molecular theory of adsorption on inhomogeneous surfaces.

Porous polymers have many important advantages over traditional adsorbents such as silicas, zeolites, and charcoals. They can be obtained not only as spherical grains corresponding to a narrow fraction comprising different sizes but also in the form of fabrics, films, and membranes.[4–7] The selection of monomers in the synthesis of porous polymers makes it possible to regulate their thermal stability and resistance to acids and alkalis. Porous polymers are highly permeable. They actively adsorb substances from both dry and moist atmospheres and from solutions. Finally, porous polymers can be readily regenerated by heating or by washing with acids and alkalis, which is important in their practical application.

In order to employ porous polymers in chromatography and also for the adsorption of gases and vapours, it is essential to be able to regulate their adsorption and selective properties. By varying the conditions in the synthesis of porous polymers, namely by carrying out the copolymerisation reactions of the monomers in inert solvents of different nature and composition and using different amounts of the cross-linking agent, it is possible to regulate the steric structure of the resulting three-dimensional polymer network and to obtain adsorbents with different porosities, i.e. their adsorption properties can be varied. By changing the chemistry of the surfaces of polymers during synthesis (by using monomers with specific functional groups) and by modifying the porous framework already formed (by carrying out polymer-analogue reactions), one can obtain adsorbents with a great variety of narrowly specific functional groups, i.e. one can regulate within wide limits their adsorption capacity and selectivity in relation to a wide variety of compounds.[1,8]

There have been so far no reviews of this problem, although extensive data have accumulated. In this review an attempt is made to survey studies on the geometrical structures of various porous polymers and its influence on the adsorption and chromatography of molecules of different natures. The elucidation of this problem is associated with the development of a specific synthesis of porous polymers with the optimum structure, which is imnportant in their practical application.

II. Classification of polymeric adsorbents in terms of their geometrical structures

Porous polymers are usually obtained by copolymerising mono- and di-vinyl monomers in the presence of inert solvents (pore-forming agents), which effectively dissolve the mixture of monomers and precipitate the polymer formed but do not participate in the copolymerisation reaction.[9–29] In the synthesis of porous polymers, a mixture of a solvent and a precipitant is sometimes used.[30] Low-molecular-weight and high-molecular-weight compounds of the solvating and non-solvating type are used most often as pore-forming agents.[9–29] After the removal of the solvent occupying the interstructural spaces, cavities or pores remain in the copolymer.

Since the porous structures of the majority of organic polymers of the polymerisation type as well as inorganic xerogels are formed on drying the gel, pore structures of the same type are therefore observed for them. Inorganic xerogels—silica gels and alumina gels—have corpuscular and especially globular structures (see the list of references in Kiselev and Yashin's book[31]). Electron microscope

studies on a series of organic porous polymers showed that their structures are also globular.[32–40,54] The suspension copolymerisation process consists in the construction of gel microparticles and their agglomeration into globules. The pores consist of the channels between the globules.

Table 1 presents a classification of the polymeric sorbents in terms of the nature of their geometrical structures on the basis of ideas developed for traditional adsorbents: the structure is believed to be macroporous if the pore diameter (d) is greater than 200 nm, mesoporous if $d = 3-200$ nm, and microporous if d is less than 3 nm.[41] Pore diameters $d > 100$ nm, $d = 4-100$ nm, and $d < 4$ nm respectively have been adopted by Gregg and Sing.[42] Copolymers of the methacrylate type are mesoporous adsorbents, but, under certain conditions of synthesis, macroporous specimens can also be obtained. Styrene–divinylbenzene copolymers have a mesoporous structure, but they contain as a rule a small number of micropores as a result of the parallel divinylbenzene–divinylbenzene copolymerisation.[105] Cross-linked macronetwork isoporous polystyrene copolymers (Styrosorbs) can have mesoporous and microporous structures and the mesoporous specimens can also contain micropores, i.e. can have a biporous structure. The polymers obtained on polycondensation of *m*-aminophenol with formaldehyde have only a macroporous structure, while phenol–formaldehyde resins have a mesoporous structure.[106,107] Thus polymeric adsorbents of different structural types have now been synthesised.

Table 1. Classification of the polymeric adsorbents investigated in terms of the nature of their porosity.

Type	Polymer chain	Designation or brand of the initial and modified polymers	$d>200$ nm (macropores)	$d=3$ to 200 nm (mesopores)	$d<3$ nm (micropores)	Refs.
I	2,3-Epoxypropyl methacrylate (glycidyl methacrylate)–ethylene dimethacrylate	EPMA–EDMA, GMA–EDMA, EPMA–EDMA–modifying agent (60 wt.% EPMA), G-60–modifying agent	+	+	–	[30, 37–40, 43–57]
II	Styrene–divinylbenzene	ST–DVB, CMC (chloromethylated copolymer), anion exchangers: AN-201, AN-211, AN-221, AN-511, AN-521, AN-531, AN-541	–	+	–	[9–24, 26–28, 32 58–74]
III	Polystyrene–xylylene dichloride	PS–XDC, PS–XDC–modifying agent	–	+	+	[75–93]
	Polystyrene–chloromethyl methyl ether	PS–CMME, PS–CMME–modifying agent, Styrosorb, Styrosorb-modifying agent				
IV	Vinylpyridine (vinyl pyridine derivatives)–divinylbenzene	VP–DVB, VP–DVP, anion exchangers: AN-231, AN-251, AN-401, AN-431, AN-441, AN-451	–	+	–	[1–30, 94–104]
	Vinylpyridine–divinylpyridine					

III. The study of the porous structures of polymeric adsorbents of different types

Polymeric adsorbents swell appreciably in many solvents. In gas-chromatographic studies and also in the study of the adsorption of gases and vapours, where the adsorbates have a comparatively low vapour pressure, kinetic measurements have shown that mainly adsorption processes take place. However, in certain cases absorption, the extent of which is determined by the nature of the polymer and of the adsorbed molecule as well as by the nature and regularity of the cross-linking of the polymeric skeleton, may occur. Fairly complete and reliable information about the nature of the porous structure of such "non-rigid" adsorbents can therefore be obtained by employing a set of different techniques.

1. Methods for the measurement of the parameters of the porous structures of polymers

In the analysis of the porous structures of polymers, we shall consider the adsorption method using adsorbates of different nature—nitrogen, cyclohexane (in the vapour of which partial swelling of the polymers takes place), and perfluoro-n-octane (in the vapour of which polymers hardly swell). The use as the adsorbate in the adsorption method of perfluoro-n-octane, which is adsorbed as a result of weak non-specific interactions with the polymer surface, makes it possible to investigate the porous structures of both initial (as a rule non-polar) matrices and the anion-exchange resins obtained from them.[73,108] This review considers also the mercury porometric method[108] whose application to polymers is complicated by the possibility that the skeleton may be compressible.[23]

The isotherms for the adsorption of nitrogen by porous polymers presented in this review were measured by the vacuum volumetric method at –195 °C. The specific surfaces of the specimens S_{N_2} were then calculated from them by the Brunauer–Emmett–Teller (BET) method. The specific surfaces were also measured by the dynamic method involving the thermal desorption of nitrogen or argon (S_{N_2}, S_{Ar})[109] on the Quantosorb apparatus (USA) or on the Sorbtometr apparatus (USSR). The calculation was carried out by the BET method on the basis of three adsorption points or using as the standard a polymer specimen with a known value of S calculated by the BET method from the nitrogen adsorption isotherm at –195 °C. In calculating S for the polymers, use was made of the surface area per nitrogen molecule in a dense monolayer $\omega_m = 0.162$ nm^2. This value is usually employed for adsorbents such as carbon blacks and silica gels.[110] However, one should bear in mind that ω_m for nitrogen depends on the chemical nature of the adsorbent. The influence of the chemical state of the surface on the packing density of the nitrogen adsorption layers has been studied.[111] Loose layers are formed on non-polar and polar organic surfaces with $\omega_m^{N_2} = 0.20$ nm^2. The value $\omega_m = 0.22-0.28$ nm^2 has been obtained by a comparative method[112] for organic polymeric sorbents. The values of S calculated using such values of ω_m are greater, but the observed features are not altered.

This review presents and analyses the adsorption isotherms for nitrogen vapour on polymers measured at –195 °C with the temperature of the specimen raised to 30 °C.[73] One measures initially the degree of adsorption at –195 °C by the generally accepted method and the specific surface S_{N_2} is then calculated from this isotherm by the BET method. Subsequently the experiment is carried out as follows: the adsorption isotherm is measured at –195 °C up to a certain point (for example, up to the equilibrium pressure $p = 8$ mmHg) and the specimen, contained in a small closed volume, is then heated to 30 °C. As a result of desorption, the nitrogen pressure over the specimen increases under these conditions. After this, the adsorbent is again cooled to –195 °C and is maintained at this temperature until the attainment of equilibrium. For certain polymers, the equilibrium pressure does not change under these conditions, while for others the equilibrium pressure

diminishes, the decrease being appreciable in certain cases—for example from 8 to 0.5 mmHg. In the latter case, the degree of adsorption of nitrogen is measured at −195 °C, the heating−cooling operation described above being repeated, and a second isotherm is obtained. It lies above the first. The specific surface S_2 is calculated from this isotherm using the BET equation. Comparison of S_{N_2} and S_2 permits certain conclusions about the structures of the porous polymers.

The adsorption isotherms for the vapours of organic substances quoted in this review were measured at 25 °C with the aid of a McBain−Baker vacuum balance (with quartz springs) on specimens evacuated beforehand to 10^{-4} kPa at 70−80 °C.[109] S was estimated from the degree of sorption of n-C_8F_{18} vapour using the area ω_m = 1.06 nm^2. The specific surface $S'_{C_8F_{18}}$ of the adsorption film formed on the sorbent at the beginning of the capillary condensation was also calculated from the n-C_8F_{18} vapour sorption isotherm.[109,113] For polymers containing mesopores and micropores, S_{meso} was determined by a comparative method,[114,115] using the sorption isotherm for the n-C_8F_{18} vapour on a coarsely porous styrene copolymer with 12% of divinylbenzene as the reference standard.[73]

The volume of the pores was calculated from the degree of sorption of the n-C_8F_{18} ($V_{C_8F_{18}}$) and cyclohexane ($V_{C_6H_{12}}$) vapours at p/p_0 = 1. For polymers containing mesopores and micropores, the volume of the micropores V_{micro} was initially determined by the comparative method and then the volume of the mesopores V_{meso} was calculated. For comparison, the limiting volume of the absorbed liquid sorbate was determined from the degree of swelling of the polymer in the latter (in the case of cyclohexane, this will be designated by $V^L_{C_6H_{12}}$).[116] The pore volume can also be calculated from mercury porograms in terms of the amount of mercury forced into the specimen (designated by V_{Hg}). The overall volume of the cavities in the initial sorbents was calculated from the true and apparent densities of the polymer (the designation V^p is introduced in this case) or was estimated from its bulk density ($V^{b.d}$).[117]

The effective pore diameters at the maxima on the pore volume distribution curves were calculated from the mercury porograms (d_{Hg}) and from the desorption branches of the n-C_8F_{18} isotherms using the Thompson−Kelvin equation ($d_{C_8F_{18}}$).[118] The average pore diameter was calculated from the formula $\bar{d} = 4V/S$.[37]

2. The porous structure of polymers of the methacrylate type

Methacrylate polymers were obtained by the suspension radical copolymerisation of epoxypropyl methacrylate with different amounts of ethylene dimethacrylate as the cross-linking agent and different proportions of solvent (cyclohexanol) and precipitant (dodecanol) in the inert phase.[43–57] Depending on these factors, specimens with different structures can be obtained. Electron microscope studies[38,39,48] showed that the structure of the methacrylate polymers is globular: the porous structure is formed as a result of the formation of gel microparticles and their agglomeration into globules. The porosity of the polymers is determined by the size of the globules and the distance between neighbouring globules, which depends on their packing.[37] The nature of the aggregation of the microparticles on the surface and in the bulk of the globules is significantly different. The microparticles on the surface and in the bulk of the globules have the same sizes, but on the surface they aggregate in a more compact manner. The pore size in the surface layer is smaller than in the bulk phase. It is believed[55,57] that the surface layer of the globules consists of relatively mobile poly(glycidyl methacrylate) chains. In the case of highly cross-linked methacrylate copolymers, the large values of S can be explained by the presence of very fine microspheres—nodules (whose size is about 10 nm), from which the globules are formed. Using gel permeation chromatography (GPC),[54,56] it has been shown that the characteristics of the porous structures of copolymers in the dry and swollen states are different: the average pore diameter, determined by mercury porometry, is greater for the dry copolymers than the value determined for the swollen copolymers by gel permeation chromatography.

In order to be able to distinguish the geometrical modifications of the copolymers, the following notation has been introduced: the fraction of one of the monomers and the solvent/precipitant ratio are quoted. Thus the EPMA-EDMA-40-91/9 (G-40-91/9) copolymer is obtained by the copolymerisation of 2,3-epoxypropyl methacrylate (2,3-EPMA) (40 wt.%) and ethylene dimethacrylate (EDMA) (60 wt.%) with a cyclohexanol/dodecanol ratio of 91/9. Table 2 presents certain characteristics of such copolymers. The study of the porous structure of EPMA−EDMA by mercury porometry and on the basis of the sorption of nitrogen vapour[30,40,51] showed that, for highly cross-linked copolymers, the pores with d = 3−60 nm (which some authors refer to as micropores) make a large contribution to the value of S. In the presence of a small amount of the cross-linking agent, pores with d < 20 nm are absent. The pore volume determined by mercury porometry is much lower than the pore volume determined from the swelling of the polymers in cyclohexane. This is evidently associated with the partial swelling of the specimens.

Table 2. Characteristics of the porous structures of methacrylate copolymers with different degrees of cross-linking.[30,40,51]

Designation	EDMA content, wt.%	S, m^2 g^{-1}	$V^L_{C_6H_{12}}$, cm^3 g^{-1}	$V_{Hg,\ cm^3}$ g^{-1}	d**, nm
G-5-91/9	95	434	–	1.07	30
G-30-91/9	70	197	–	1.00	40
G-40-91/9	60	120	1.51	–	(50)
G-45-91/9	55	130	–	1.01	40
G-60-91/9	40	69	1.47	1.03	60
G-75-91/9	25	44	–	0.99	80
G-80-91/9	20	36	1.20	–	(132)
G-90-91/9	10	22	0.88	–	(134)
G-60-85/15	40	57	1.71	–	(120)
G-60-100/0	40	94	1.43	1.00	–
G-80-100/0	20	20	0.62	–	(126)

*G denotes the EPMA−EDMA copolymer (see Table 1).
**Here and henceforth the average value of $\bar{d}$ is given in brackets, while the figure without brackets denotes the effective value.

The structure of certain aminated EPMA−EDMA specimens has been investigated by various methods (Table 3).[30,40,51,108] The isotherms of the adsorption of cyclohexane vapour, in which the polymers partly swell (for low values of p/p_0 the isotherms are irreversible), were measured on these specimens (Fig. 1). The n-C_8F_{18} adsorption isotherms on the modified specimens are reversible in the initial region of relative pressures and have a distinct and narrow capillary-condensation hysteresis loop of the H1

type, which is characteristic of sorbents with cylindrical pores. The structural parameters of polymers were estimated from such isotherms (Table 3). Table 3 shows that the specific surfaces of the adsorption film $S'_{C_8F_{18}}$ and $S_{C_8F_{18}}$ virtually coincide and the values of S determined from the adsorption of the small nitrogen molecule and the fairly large n-C_8F_{18} molecule are also similar. This indicates the absence of micropores in the test specimens. The values of S_{Hg} exceed in certain cases those of S obtained from adsorption data, sometimes by a factor of two. In all probability, such specimens contain an appreciable number of pores with constrictions (or widened regions), since it is in fact in such cases that $S_{BET} < S_{Hg}$.[118]

Table 3. Characteristics of the porous structures of modified methacrylate copolymers.[30,40,51,108]

Designation	Aminating agent	S, $m^2 g^{-1}$				V, $cm^3 g^{-1}$				d, nm	
		S_{N_2}	$S_{C_8F_{18}}$	$S'_{C_8F_{18}}$	S_{Hg}	$V_{C_8F_{18}}$	V_{Hg}	$V_{C_6H_{12}}$	$V^L_{C_6H_{12}}$	$d_{C_8F_{18}}$	d_{Hg}
G-60-91/9		63	–	–	–	–	1.03	–	1.47	–	60
G-60-91/9	A	100	106	100	108	1.08	1.13	–	1.28	70	70
G-60-91/9	DETA	69	69	70	54	1.03	0.97	–	1.03	66	80
G-60-91/9	DETA	67	74	–	74	1.02	1.01	1.00	–	70	70
G-60-91/9	DETA(alk)	50	58	41	61	0.88	0.92	0.90	1.31	65	100
G-60-91/9	MEA	60	–	–	–	–	0.93	–	–	–	60
G-60-91/9	EDA	70	–	–	–	–	1.00	–	–	–	60
G-80-91/9	—	36	–	–	–	–	–	–	1.20	–	(132)
G-80-91/9	A	48	35	24	102	0.71	0.99	0.72	1.15	80	100

The low-temperature adsorption of nitrogen on specimens of methacrylate polymers with the specimens heated in a closed space have been investigated.[73] For all the specimens, $S_{N_2} = S_2$, i.e. the polymers have a very regular structure. This can be explained by the following causes. Polymers containing in their chains an appreciable number of polar groups are fairly rigid structures. Furthermore, in the synthesis of these polymers it is possible to obtain a uniformly cross-linked framework, which does not contain highly cross-linked microporous sections.

Determination of the pore volume from the adsorption of C_8F_{18} and C_6H_{12} vapours showed that the values of $V_{C_8F_{18}}$ and $V_{C_6H_{12}}$ are virtually identical (Table 3) despite some swelling of the polymers in cyclohexane vapour (Fig. 1). For the highly cross-linked specimen (40% EDMA), $V_{Hg} \simeq V_{ads}$. This shows that either the framework does not change at elevated pressures and the specimen does not contain an appreciable number of macropores with $d > 200$ nm or the framework is compressed but the specimen contains pores with $d > 200$ nm, the effects cancelling out. The first hypothesis appears more probable. For the weakly cross-linked specimen, $V_{Hg} > V_{ads}$ ($d_{Hg} > d_{ads}$). Possibly the specimen becomes more coarsely porous under the conditions of mercury porometry.

The method of determining the pore volume from the adsorption of liquid, for example, cyclohexane,[117] yields unduly high results owing to the more extensive swelling of the polymers in liquids than in vapours. However, formal calculation of the average pore diameter $\bar{d}$ using $V^L_{C_6H_{12}}$ and S_{N_2} yields values close to d_{Hg}.

Table 3 shows that the parameters of the porous structure of the polymers (S, V, d) hardly change on modification with amines and aminoalcohols. Only on amination with ammonia does S increase for all degrees of cross-linking of the copolymer, possibly owing to the additional cross-linking of the framework. It has been shown[51] that, when copolymers are aminated by amines and aminoalcohols, the volumes of small (8–50 nm) and very large ($d > 100$ nm) pores diminish and the number of pores with $d = 60–80$ nm increases sharply, so that the overall pore volume hardly changes and remains ~ 1 $cm^3 g^{-1}$.

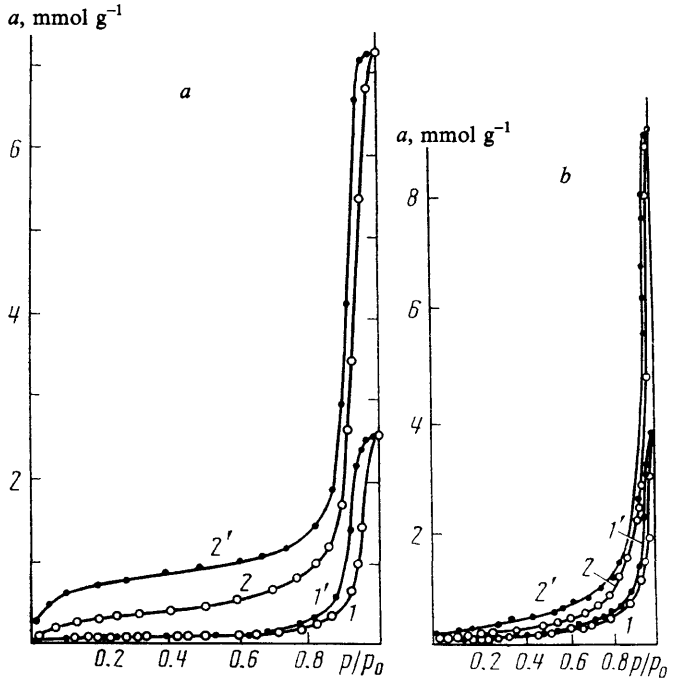


Figure 1. Adsorption (curves *1* and *2*) and desorption (curves *1'* and *2'*) isotherms for n-C_8F_{18} (curves *1* and *1'*) and cyclo-C_6H_{12} (curves *2* and *2'*) vapours at 25 °C: (*a*), on the styrene–divinylbenzene (8%) copolymer modified with diethylenetriamine (AN-511 anion exchanger) obtained in n-decane (100%) as the pore-forming agent; (*b*) on the 2,3-epoxypropyl methacrylate–ethylene dimethacrylate copolymer (60% of 2,3-epoxypropyl methacrylate) modified with diethylenetriamine.

Table 2 and Fig. 2 show that the values of S for the methacrylate polymers increase with increase in the amount of ethylene dimethacrylate and depend on the solvent/precipitant ratio. With increase in the fraction of ethylene dimethacrylate to 40%, the pore volume also increases, but, on still further increase in the fraction of ethylene dimethacrylate (to 60%), it changes little. With increase in the amount of the pore-forming agent (cyclohexanol) in the mixture with the precipitant (dodecanol), S_{N_2} increases, while $V_{C_6H_{12}}$ diminishes, i.e. the specimen acquires a more finely porous structure.

The porous structures of methacrylate copolymers obtained by cross-linking monomers of different polarity with ethylene dimethacrylate have been investigated.[44,49] It was found that the specific surface and the pore volume diminish with increase in the content of the polar monomer: $S_{MMA} > S_{HEMA} > S_{AN}$ (MMA = methyl methacrylate, HEMA = hydroxyethyl methacrylate, AN = acrylonitrile). The polymers contain no pores with $d > 100$ nm and the preferred pore size is $d = 40-80$ nm. The pore structure of sulphur-containing methacrylate copolymers is also regulated by varying the content of ethylene dimethacrylate and the solvent/precipitant ratio. With increase in the amount of ethylene dimethacrylate in the copolymers, S and V increase, while the content of epithio-groups falls.[119,120]

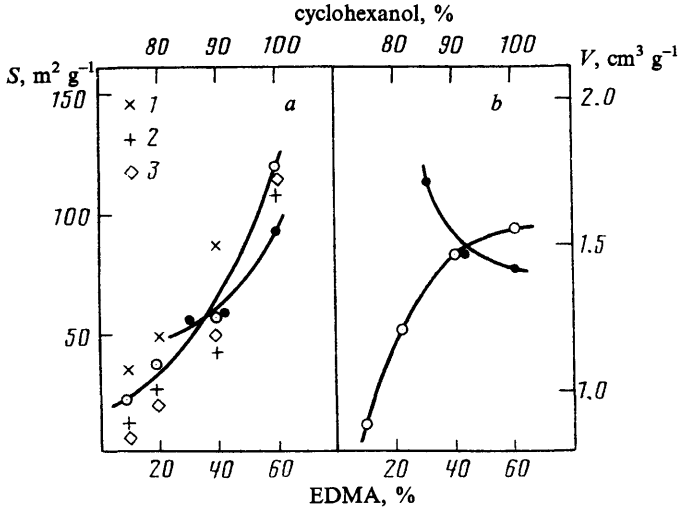


Figure 2. Dependence of the specific surface S (*a*) and pore volume V (*b*) on the content of the cross-linking agent (open symbols) and the solvent (cyclohexanol) (filled symbols) for the epoxypropyl methacrylate–ethylene dimethacrylate copolymers. Fig. 2*a* also presents the values of S for polymers with different degrees of cross-linking modified by ammonia (*1*), ethylenediamine (*2*), and diethylenetriamine (*3*).

Thus methacrylate polymers have an extensive porosity. These are mainly mesoporous adsorbents. The pore structure of the polymers is regulated by varying the amount of the cross-linking agent (ethylene dimethacrylate) and the solvent/precipitant ratio and by introducing a polar monomer. On modification of these copolymers, the parameters of the porous structure do not change greatly.

3. The porous structure of polymers of the styrene – divinylbenzene type

Porous styrene–divinylbenzene copolymers are obtained by the suspension copolymerisation of styrene with divinylbenzene. The principal factors influencing the porosity of these copolymers are the degree of cross-linking of the three-dimensional copolymer framework, which is determined by the amount of the cross-linking agent (divinylbenzene) and by the nature of the pore-forming agent and its concentration in the mixture of the polymerising monomers. The structure of the styrene–divinylbenzene copolymers has been investigated by the adsorption method (from the adsorption isotherms of water vapour and methanol) and by mercury porometry (see the literature references in Table 1). The present review deals primarily with the porous structures of anion exchangers obtained from styrene–divinylbenzene copolymers. The study of the adsorption and desorption isotherms of methanol, n-hexane, perfluorobenzene, and perfluoro-n-octane on the AN-221 anion exchanger containing ethylenediamine groups showed that, as for the epoxypropyl methacrylate–ethylene dimethacrylate copolymers, the anion exchanger does not swell only in the vapour of the fully fluorinated saturated hydrocarbon, the interaction of the molecules of which with the surface of the polymer are not only non-specific but also weak (Fig. 1). The isotherm is fully reversible. At high values of p/p_0, a distinct capillary-condensation hysteresis is observed, as for inorganic adsorbents with a rigid skeleton.

In order to be able to distinguish the geometrical modifications of the styrene–divinylbenzene copolymers, the following notation has been introduced: the ratio of the amounts of the cross-linking agent and the pore-forming agent is stated and then the pore-forming agent is indicated. Thus the 12/80, BR-1 copolymer is obtained by copolymerising 88% of styrene with 12% of divinylbenzene in the presence of 80% of petrol of type BR-1 as the pore forming agent.

The porous structure of a number of anion exchangers has been investigated by various methods (Table 4). The surface area S of the test specimens varies in the range from 11 to 130 m^2g^{-1}, V varies from 0.05 to 1.29 cm^3g^{-1}, and d varies from 24 to 100 nm, which is associated mainly with the nature and amount of the cross-linking and pore-forming agents. The ranges of variation of S, V, and d obtained for 8 specimens of AN-221 (12/80, BR-1) have been published:[26] $S = 75-120$ m^2g^{-1}, $V = 0.4-0.8$ cm^3g^{-1}, and $d = 20-100$ nm; similar data have been published for 12 specimens of AN-511 (8/100, n-decane): $S = 25-40$ m^2g^{-1}, $V = 1.0-1.3$ cm^3g^{-1}, and $d = 100-200$ nm. This indicates some non-reproducibility of the conditions in the synthesis of the given polymers.

Table 4 shows that the specific surfaces of the film S' and S, determined from the adsorption of C_8F_{18}, are virtually identical. Furthermore, the values of S determined from the adsorption of the small nitrogen molecule and the fairly large C_8F_{18} molecule are also similar. This indicates the absence of an appreciable number of micropores in the test specimens.

Comparison of the pore volumes determined by mercury porometry and from the adsorption of vapours shows that, within the limits of the reproducibility of the measurements, $V_{Hg} \simeq V_{ads}$. This indicates the absence of an appreciable number of macropores with $d > 200$ nm in the test specimens. The above conclusion is confirmed also by the pore volume distribution curves. Thus both adsorption methods using adsorbates in which the polymers hardly swell and mercury porometry are applicable to the study of the structures of the test polymers.

In order to elucidate the influence of the polymer-analogue reactions on the structural characteristics of the polymers, measurements were made of the adsorption isotherms of C_8F_{18} on the initial styrene–divinylbenzene copolymer (8/100, n-nonane), the chloromethylated copolymer (CMC) and the anion exchangers AN-221, AN-511, and AN-541 (specimens *1–5* in Table 4). A narrow pore distribution is observed for these substances and virtually all the specimens have $d_{eff} \simeq 60$ nm. Changes in the structure occur mainly in the chloromethylation stage, whereupon V

Table 4. Characteristics of the porous structures of the styrene–divinylbenzene anion exchangers.[73,108]

Specimen	Brand or dessignation	Pore-forming agent	DVB/pore-forming agent	S, $m^2 g^{-1}$				V, $cm^3 g^{-1}$		d, nm	
				S_{N_2}	$S_{C_8F_{18}}$	$S'_{C_8F_{18}}$	S_{Hg}	$V_{C_8F_{18}}$	V_{Hg}	$d_{C_8F_{18}}$	d_{Hg}
1	ST–DVB	n-Nonane	8/100	60	–	62	–	0.84	–	49	–
2	CMC	»	8/100	–	46	50	–	0.73	–	57	–
3	AN-221*	»	8/100	53	55	53	63	0.74	0.79	57	60
4	AN-511*	»	8/100	49	50	55	95	0.79	0.89	57	55
5	AN-541*	»	8/100	–	58	53	–	0.77	–	57	–
6	AN-221	BR-1	8/100	11	–	14	–	0.05	–	24	–
7	AN-221	»	12/80	60	64	54	98	0.56	0.66	30	30
8	AN-221	»	15/100	61	66	61	121	0.60	0.71	40	35
9	AN-221	»	20/80	69	67	61	–	0.68	–	45	–
10	AN-221	»	30/100	130	95	72	–	1.29	–	100	–
11	AN-221	Isooctane	12/80	60	66	59	75	0.61	0.64	40	40
12	AN-511	n-Decane	8/100	31	32	42	–	0.75	–	100	–
13	AN-511	»	8/100	32	27	42	64	0.63	0.70	60	60
14	AN-221	PS	10/10	–	–	7	–	0.13	–	55	–

*The AN-221, AN-511, and AN-541 anion exchangers contain EDA, DETA, and MEA groups respectively.

falls somewhat as a result of the removal of pores with sizes ranging from 20 to 30 nm. On subsequent amination, these parameters hardly change. After the introduction of highly basic groups, the parameters of the porous structure change more appreciably.

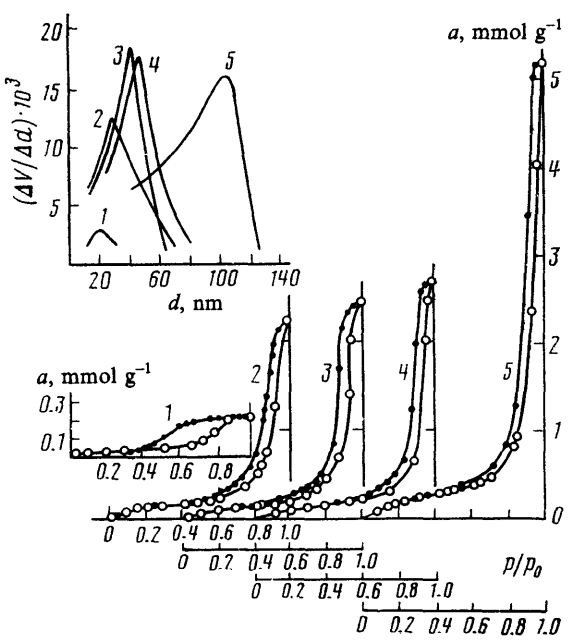


Figure 3. Isotherms for the adsorption (open circles) and desorption (filled circles) of n-C_8F_{18} vapour on the AN-221 anion exchanger (BR-1 pore forming agent, specimens *6–10* in Table 4) at 25 °C. The inset shows the corresponding curves for the distribution of pore volumes with respect to the effective diameters. Amount of divinylbenzene (%): (*1*) 8; (*2*) 12; (*3*) 15; (*4*) 20; (*5*) 30.

The influence of the amount of the cross-linking agent on the structure of the AN-221 anion exchangers has been investigated. Fig. 3 presents the adsorption and desorption isotherms for C_8F_{18} vapour on the anion exchangers with different degrees of cross-linking. The parameters of the porous structure listed in Table 4 were calculated from the isotherms. With increase in the amount of divinylbenzene in the anion exchanger matrix from 8 to 30%, S, V, and the pore size increase. Similar relations have been observed for styrene–divinylbenzene copolymers. With increase in the amount of the cross-linking agent, the polymer framework becomes more rigid and its contraction after the removal of the solvent during synthesis diminishes, which leads to an increase in the size and volume of the pores. The highly cross-linked specimen (30% DVB) contains a larger number of fine pores, which explains its higher value of S.

The dependence of the structure of the AN-221 and AN-511 anion exchangers on the molecular size of an inert solvent (hydrocarbon) has also been investigated. The largest pores ($\geqslant$100 nm) are present in anion exchangers whose matrix has been obtained in the presence of a solvent such as n-decane.[26,73] The porosity of the styrene–divinylbenzene copolymer in the dry state is greater the lower the degree of solvation of the copolymer by the solvent.[64] With increase in the molecular size of the solvent in the series petrol < isooctane < n-nonane < n-decane, the solvating power of the solvent diminishes, as a result of which the contraction of the copolymer on removal of the solvent during synthesis diminishes and the fraction of large pores in the adsorbent increases.

The porous structure of the anion exchangers has also been investigated by the static nitrogen adsorption method at −195 °C with the specimen being warmed during the measurement of the adsorption isotherm. S_{N_2} and S_2 were determined in this way.[73] In contrast to methacrylate polymers, $S_2 > S_{N_2}$ for the styrene–divinylbenzene copolymers and anion exchangers. Thus an appreciable increase (up to 200%) in S after the specimen heating–cooling cycle has been observed for styrene–divinylbenzene copolymers. Apparently, when the specimen is heated, as a result of the increase in the pressure of nitrogen its molecules can

permeate into pores with constrictions or micropores which are inaccessible to the adsorbate under the usual experimental conditions. This phenomenon is analogous to the effect of activated breakthrough, i.e. to the increase in the degree of adsorption with increase in temperature which is characteristic of microporous adsorbents.[118] There is then a possibility of the enforced elastic deformation of the polymer pore walls[121] which persists on subsequent cooling to a greater extent the more elastic the polymer and the smaller its rigidity. In the chloromethylation of the copolymer, a polar group ($-CH_2Cl$) is introduced into the polymer, which leads to the additional cross-linking of the polymer chains[122] and to an increase in the rigidity of the polymer and hence to a decrease in the difference between S_{N_2} and S_2. The introduction of amino-groups into the polymer makes it still more rigid and the enforced elastic deformation on desorption of nitrogen during heating diminishes. With increase in the amount of the cross-linking agent in the anion exchanger matrix, the difference between S_{N_2} and S_2 increases owing to the dominant influence of the factor associated with the increase in the amount of highly cross-linked sections containing micropores in the anion exchangers. The values of S measured by the nitrogen thermal desorption method agree with those of S_{N_2} (with the exception of highly cross-linked specimens).

Thus the application of various methods to the study of the porous structure of polymers permits a more detailed characterisation of the structures of these complex objects. The porous structure is readily regulated by the introduction of different amounts of the cross-linking agent (in the given instance divinylbenzene), by the alteration of the divinylbenzene/pore-forming agent ratio, and by the nature of the pore-forming agent.

4. The porous structure of copolymers of vinylpyridine derivatives and divinylbenzene

Porapak S as well as Polysorb N, which are vinylpyridine–divinylbenzene copolymers, are widely used in chromatography. Porous copolymers of this class are obtained by the suspension copolymerisation of the initial monomers—vinylpyridine derivatives containing ionogenic groups, with divinylbenzene or divinylpyridine. Porous copolymers of 4-vinylpyridine with ethylene dimethacrylate and 2,5-divinylpyridine having specific surfaces up to 400 m^2g^{-1} have also been synthesised and investigated.[103,104] The synthesis of such ion exchangers consists of a single stage and their structure is formed in the copolymerisation stage and does not undergo further changes. The porous structure of such copolymers has been investigated by the adsorption method (in relation to nitrogen and methanol) and by mercury porometry (see the literature references in Table 1). The structure of the vinylpyridine–divinylbenzene anion exchangers has been investigated[73] by the nitrogen thermal desorption method and by the low-temperature adsorption of nitrogen with warming of the specimen in a closed volume. For these copolymers, $S_2 > S_{N_2}$. As for the styrene–divinylbenzene copolymers, the heating of the vinylpyridine–divinylbenzene specimens can entail, as a result of the increased pressure of nitrogen, the penetration of its molecules into the pores with constrictions or micropores which are inaccessible to the sorbate under the usual conditions. The difference between S_{N_2} and S_2 for AN-251, cross-linked by divinylpyridine, is smaller than for AN-251 cross-linked by divinylbenzene, which can be explained by the increased rigidity of the polymer framework when divinylpyridine is used as the cross-linking agent. The introduction of polar groups into the polymer chains increases their rigidity to a greater extent the more polar the group and the greater their number introduced into the chain. On passing from AN-251, containing pyridine nitrogen, to AN-451, containing also tertiary nitrogen, the difference between S_{N_2} and S_2 therefore diminishes.[73] The quantity S, determined by the nitrogen thermal desorption method, corresponds to S_2 and not to S_{N_2}, as in the case of the styrene–divinylbenzene copolymers.

5. The porous structure of ultracross-linked polystyrenes (Styrosorbs)

The macronetwork isoporous polymers based on polystyrenes (see the literature references in Table 1) are porous in the dry state and have an extensive inner surface only in the presence of large amounts of the cross-linking agent (>30%). The Styrosorb (I) sorbents are obtained using a method involving the cross-linking of linear polystyrene (PS) chains dissolved in an organic solvent [in most cases dichloroethane (DCE)] by *p*-xylylene dichloride (XDC), 4,4′-bis(chloromethyl)biphenyl, chloromethyl methyl ether (CMME), or methylal in the presence of a Friedel–Crafts catalyst.

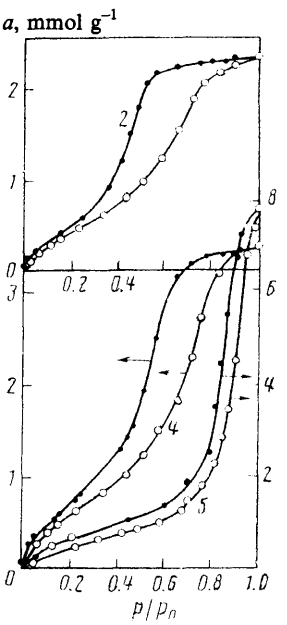


Figure 4. Isotherms for the adsorption (open circles) and desorption (filled circles) of n-C_8F_{18} vapour on Styrosorbs I (specimens *2*, *4*, and *5* in Table 5) at 25 °C.

The study of the structure of Styrosorbs obtained in dichloroethane by electron microscopy, small angle X-ray scattering, and gel permeation chromatography showed that they are microporous sorbents in which the main fraction of pores have diameters of the order of 1 nm.[83,89,90] The Styrosorbs (I) examined in this study were obtained by cross-linking linear polystyrene dissolved in cyclohexane (CH) with chloromethyl methyl ether. The molecular weight of the polymer varied from 13×10^3 to 3×10^6. A Styrosorb (II) specimen, synthesised by the cross-linking with chloromethyl methyl ether of a copolymer of styrene with 2% of divinylbenzene swollen in dichloroethane, was also investigated (Table 5).[90] All the polymers investigated had a degree of cross-linking of 100%. In the study of the porous structure of the Styrosorbs, n-C_8F_{18} was used as the sorbate. In its vapour the Styrosorbs swell to a lesser extent than in other organic solvents.

Table 5. Structural characteristics of Styrosorbs I (specimens *2*–*6*) and II (specimen *1* with 2% DVB).[92]

Specimen	Molecular weight of initial polystyrene $\times 10^{-3}$	Solvent	S, $m^2 g^{-1}$				V, $cm^3 g^{-1}$				d, nm	
			S_{Ar}	$S_{C_8F_{18}}$	$S'_{C_8F_{18}}$	S_{meso}	$V^{b.d.}$ (V^{ρ})	$V_{C_8F_{18}}$	V_{micro}	V_{meso}	d_{eff}	$\bar{d}$
1	300	DCE	1000	650	–	–	0.20	–	0.20	–	–	1
2	3000	CH	330	300	235	–	0.74	0.6	0.17	0.57	7	8
3	300	CH	545	400	280	280	0.78	0.4	0.42	0.36	4	4
							(0.70)	0.4	0.34	0.36	4	4
3a *	300	CH	–	510	–	–	–	0.6	–	–	4	4
4	80	CH	405	400	285	280	(0.90)	0.9	0.04	0.86	9	9
5	17	CH	430	250	–	240	1.94	1.9	0.03	1.91	30	30
6	13	CH	330	280	200	200	1.30	1.1	0.23	1.07	20	16

**3a* represents specimen *3* chloromethylated and aminated by DETA.

Fig. 4 presents the n-C_8F_{18} sorption isotherms on three specimens of Styrosorbs (specimens *2*, *4*, and *5*, Table 5) obtained in cyclohexane by cross-linking polystyrenes having different molecular weights. They differ in the position and form of the hysteresis loop, which can provide some idea about the size and shape of the pores present in the given sorbents. It is possible to distinguish two varieties of Styrosorbs I. The first includes polymers obtained by cross-linking polystyrene having a high molecular weight ($3 \times 10^6 - 8 \times 10^4$) dissolved in cyclohexanes. Such Styrosorbs have sorption isotherms with a hysteresis loop which belongs to the H2 type according to de Boer's classification. The second variety of Styrosorbs I is obtained by structure formation in polystyrene having a low molecular weight ($13-17 \times 10^3$). Their sorption isotherms exhibit a narrow capillary-condensation hysteresis of the H1 type. The comparatively large degrees of sorption of n-C_8F_{18} on Styrosorbs for low values of p/p_0 and the slight irreversibility of the isotherms in the initial region are striking. The latter feature may be associated both with the low degree of swelling of the polymers in the given sorbate and with the slow rate of sorption of n-C_8F_{18} in the micropores present in these specimens.

Analysis of the data in Table 5 permits the following conclusions. The cross-linking of polystyrene chains in dichloroethane, which is a thermodynamically effective solvent, leads to the formation of microporous sorbents with $d \simeq 1$ (specimen *1*). This is also indicated by the low value of $S_{C_8F_{18}}$ compared with S_{Ar}. It is noteworthy that solvents such as hexane and methanol, in which polystyrene does not dissolve, are capable of solvating vigorously the polymer chains of ultra-cross-linked polystyrene, as a result of which $V^L_{C_6H_{14}}$ and $V^L_{CH_3OH}$ reach 4 $cm^3 g^{-1}$.[83,89,90] The appearance of micropores in the given Styrosorbs is a consequence of the loose packing of the polymer chains in the single-phase network cross-linked by a large number of rigid bridges, which hinder the mutual approach of the polymer chains when the solvent is removed from the swollen polymer produced. The high strain in the structure of Styrosorbs in the dry state imparts to them a unique capacity to swell in any medium even in inert media such as perfluorooctane.[90]

When the thermodynamically effective solvent dichloroethane is replaced by cyclohexane (a solvent with a lower affinity for polystyrene), the structure of the sorbents changes. They contain not only micropores but also mesopores (specimens *2*–*6* in Table 5 and Fig. 4). Such Styrosorbs swell least in the n-C_8F_{18} vapour. The rigid n-C_5F_{12} fills the cavities in the polymer, whereupon the specimen hardly swells. The weak swelling of Styrosorbs I in fluorinated hydrocarbons is indicated primarily by the form of the isotherms and the closeness of the values of $V_{C_8F_{18}}$ to V^{ρ} or $V^{b.d.}$ (specimen *3* containing a large number of micropores is an exception). For specimens *2*–*4*, $V < 1$ $cm^3 g^{-1}$, while S_{meso} is the same as S' and less than $S_{C_8F_{18}}$, which indicates the presence in the specimen of fine pores ($d \simeq 3$ nm) accessible to C_8F_{18} molecules. Specimens *5* and *6* have $V > 1$ $cm^3 g^{-1}$. Their effective pore diameter is much greater than for specimens *2*–*4* and amounts to 20–30 nm. As in the case of specimens *2*–*4*, S_{meso} for specimens *5* and *6* is approximately equal to S' and is less than $S_{C_8F_{18}}$, while V_{micro} is not large.

Fig. 5 presents the dependence of the effective pore diameters of the Styrosorbs on the molecular weight of the initial polystyrene. A decrease in the polymer chain length leads to an increase in d. The high mobility of the low-molecular-weight polystyrene facilitates the phase decomposition of the solution. Pores whose size amounts to several tens of nanometers therefore arise in the final polymer. If the rate of the chemical reaction is sufficiently high while the mobility of the chains is, on the other hand, limited (a polystyrene with a fairly high molecular weight), then the chains are fixed in the three-dimensional structure very rapidly and in such a system there are no favourable conditions for microlayer formation. The mesopores in the given Styrosorbs consist of gaps between individual coils of polystyrene macromolecules (or their aggregates), which exist in the initial solution and are fixed by cross-links.[92,93]

Thus the nature of the porous structure of the Styrosorbs can vary within wide limits and depends both on the nature of the solvent and on the molecular weight of the polystyrene.

In the chloromethylation and amination of Styrosorb (I) by DETA, its structure (specimen *3a*, Table 5) changes, $S_{C_8F_{18}}$ and $V_{C_8F_{18}}$ increase, while d_{eff} remains unchanged. The polymer-

analogue reactions probably involve the formation of small ($d \simeq$ 3 nm) pores, which are nevertheless still accessible to C_8F_{18} molecules.

The anion exchanger obtained from Styrosorb I by chloromethylation and amination using ethylene and diamine and additionally ammonia has been investigated by the low-temperature nitrogen adsorption method with the specimen being warmed in a closed space. In this case, S increases by only 14%, i.e. the specimen has very regular cross-links, because the reactivity of all the polystyrene units is the same and the network polymer obtained has statistically distributed cross-links. Furthermore, the anion exchanger framework is cross-linked to the extent of 100%, i.e. it is rigid, and the enforced elastic deformation is small, which is manifested by the significant increase in S on heating the specimen.

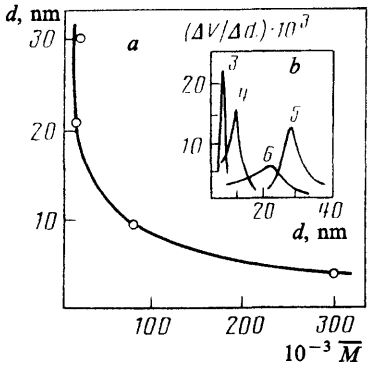


Figure 5. Dependence of the pore diameter for Styrosorbs I on the molecular weight of the initial polystyrene (*a*) [points corresponding to the maxima on the curves for the distribution of the pore volumes with respect to the diameters (*b*)].

When the Styrosorb is sulphonated, it becomes non-porous. This probably takes place as a result of the increase in the volume of the sulpho-groups caused by the binding of the water molecules and as a result of the high cohesion energy, which holds together the highly cross-linked but mobile polymer network.

IV. The influence of the porous structure of polymers on their adsorption and chromatographic properties

1. Characteristic features of the adsorption of organic vapours

The study of the influence of the porous structure of methacrylate polymers on their gas-chromatographic properties has shown that the less cross-linked polymers possess better chromatographic properties (more symmetrical peaks, lower retention times of all substances and lower heights equivalent to the theoretical plate) since they contain the smallest number of bottle-shaped pores and pores with $d < 5$ nm.[38,43–47,49–52,54] With increase in the specific surface of the methacrylate polymers, the specific retention volumes of all the substances also increase. The relative retention volumes of the non-specifically sorbed n-hydrocarbons increase with increase in the amount of the cross-linking agent (ethylene dimethacrylate) (owing to the increase in S and in the contribution of dispersion interactions), while those of specifically sorbed substances (for example, benzene, alcohols, ethyl methyl ketone, nitromethane, and pyridine) fall, which can be explained by the decrease, with increased S, in the concentration of surface functional groups responsible for the specific interactions with these molecules.[25,47,120,123]

The gas-chromatographic properties of vinylpyridine–divinylbenzene copolymers have been investigated in relation to the AN-251 anion exchangers obtained with the same amount of n-heptane as the pore-forming agent (80% of the total monomers) for different contents of divinylbenzene.[124] The retention volumes V_R of n-hydrocarbons increase on passing from the AN-251-15/80 specimen to the AN-25-30/80 specimen and diminish somewhat for the AN-251-40/80 specimen, while the specific surfaces of this series increase monotonically. The decrease in retention volumes for the AN-251-40/80 specimen can probably be accounted for by the decrease in the degree of swelling and in the overall pore volume of this highly cross-linked ion exchanger. The values of V_R for the specifically adsorbed molecules are appreciably higher than those for the non-specifically adsorbed molecules and, on passing to highly cross-linked specimens, they decrease owing to the decrease in the number of functional groups in the polymer.

The methacrylate and styrene–divinylbenzene polymers poorly sorb hydrocarbon vapours and undergo partial swelling in C_6H_{14} vapour; the C_6H_{14} adsorption isotherms on the initial (S = 25 m^2g^{-1}) and chloromethylated (S = 32 m^2g^{-1}) copolymers as well as the copolymer aminated by ethylenediamine (S = 31 m^2g^{-1}) are the same, i.e. the introduction of functional groups into the polymer does not alter the sorption of the n-alkane, since the sorption takes place as a result of a non-specific interaction. The same features have been observed for the sorption of CH_3OH, i.e. the contribution of specific interactions is in this case small.

Styrosorbs, which have a more extensive porous structure, effectively sorb hydrocarbon vapours.[84,90] In a study[125] of the kinetics of the sorption of n-heptane and n-hexane by Styrosorb, it has been shown that the process takes place in two stages: the first, rapid stage involves a rearrangement of the sorbent structure and the second, slow stage is associated with the permeation of the n-C_5H_{12} and n-C_6H_{14} molecules into the microcavities formed as a result of the segmental mobility of the polymer chain units. The degree of sorption of CH_3OH and H_2O vapours by Styrosorbs is not high. The CH_3OH vapour sorption isotherm on Styrosorb II (a microporous specimen) lies above that on Styrosorb I (a biporous specimen containing micropores and mesopores) and has a different form—it is linear up to $p/p_0 = 0.6$. On the other hand, on being immersed in CH_3OH or H_2O, these polymers absorb up to 6.0 and 4.0 cm^3g^{-1} of these liquids respectively.[92]

The cyclohexane sorption isotherms on the initial and DETA-modified polymers of this type are similar up to $p/p_0 \simeq 0.8$; for higher values of p/p_0, the sorption isotherm on the initial copolymer lies in a much higher position, evidently due to its greater swellability at high pressures. On sulphonation, the specimen becomes non-porous and the degree of sorption of n-C_6H_{14} and cyclo-C_6H_{12} diminishes almost to zero.[80]

Thus the study of the sorption of organic substances on the test specimens showed that their capacity is determined to a large extent by the geometrical structure of the sorbent. Styrosorbs exhibit a high capacity with respect to organic compounds.

2. Characteristic features of the absorption of carbon and sulphur dioxides

It was shown above that the geometrical structure of the polymeric sorbents is determined by the amount and nature of the components involved in their synthesis. The influence of these factors on the adsorption and chromatography of certain adsorbates,

in particular carbon and sulphur dioxides, has therefore been investigated. These gases were selected because they are, firstly, of interest from the practical point of view and, secondly, they are effectively adsorbed by polymers containing amino-groups.

(a) The influence of the amount and nature of the cross-linking agent

Anion exchangers based on styrene–divinylbenzene and vinylpyridine–divinylbenzene (divinylpyridine) copolymers and Styrosorbs.[1,80,126–130] Measurements were made of the CO_2 adsorption isotherms by the static volumetric method and of the output curves (frontal chromatograms) for CO_2 and SO_2 on AN-221 specimens with different degrees of cross-linking (Fig. 6). Table 6 presents the ratios of the amounts of divinylbenzene and of the pore-forming agent for the AN-221 anion exchanger containing ethylenediamine groups, the static exchange capacities (SEC) with respect to 0.1 M HCl, S_{N_2}, S_{CO_2}, as well as the capacities with respect to CO_2 and SO_2 before break-through (E_0); data for anion exchangers based on Styrosorbs are not included. For styrene–divinylbenzene copolymers not containing functional groups, an increase in capacity before the break-through of SO_2 is observed with increase in the amount of divinylbenzene (with increase in S), since the molecules are adsorbed mainly as a result of dispersion interactions. Figs. 6 and 7 show that the capacities of the AN-221 anion exchangers with respect to CO_2 and SO_2 diminish with increase in the amount of cross-linking agent in them and that the same behaviour is observed for the AN-251 exchangers (Fig. 8). With increase in the divinylbenzene content, S_{N_2} and the overall pore volume (V) of the anion exchangers increase. On the other hand, with increase in divinylbenzene content in the polymerising system, the number of monomer units carrying functional groups diminishes. In the styrene–divinylbenzene copolymers, these are styrene rings, which are subsequently chloromethylated and aminated, while in the vinylpyridine–divinylbenzene copolymers these are vinylpyridine rings. As a result, an increase in the divinylbenzene content in the anion exchangers entails a diminution of the overall number of functional groups (the SEC characterises the content of functional groups in the swollen ion exchanger, i.e. virtually the total number of functional groups). The decrease in the number of functional groups entails a decrease in the degree of adsorption of CO_2 and SO_2 adsorbed on anion exchangers as a result of dispersion interaction with the anion exchanger framework and specific interactions with the functional groups, i.e. the dominant factor is the interaction with functional groups. Therefore, a decrease in the SEC of the anion exchanger entails, despite the increase in S, a diminution in the degrees of adsorption of CO_2 and SO_2. Similar variations in the degrees of adsorption by the dry AN-221 anion exchangers have been obtained for SiF_4 [131] and the acrylonitrile–divinylbenzene copolymer (or acrylonitrile) in relation to phenol and aniline.[25] The weaker dependence of the capacity of the AN-251 anion exchanger before the break-through of SO_2 on the amount of divinylbenzene compared with the dependence of the total capacity shows that the capacity before break-through depends to a greater extent on S than the total capacity, which is mainly determined by the SEC of the anion exchangers (Fig. 8).

The absorption of SO_2 on the AN-251 anion exchangers cross-linked not by divinylbenzene but by divinylpyridine i.e. anion exchangers in which both the cross-linking agent and the monomer contain pyridine nitrogen, has also been investigated. For specimens with a similar structure, it has been shown that the time of the protecting action and hence also $E_0^{SO_2}$ for the AN-251-DVP,15/50 anion exchanger is greater than for AN-251-DVB,15/50, i.e. the use of divinylpyridine as the cross-linking agent increases the number of functional groups in the anion exchanger and its capacity with respect to SO_2.

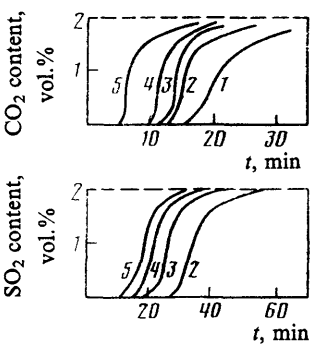


Figure 6. CO_2 and SO_2 output curves on the AN-221 anion exchanger (BR-1 pore-forming agent). Experimental conditions: carrier gas flow rate 250 cm^3 min^{-1}, CO_2 or SO_2 content in the carrier gas 2 vol.%, column diameter 15 mm, column length 50 mm for CO_2 and 25 mm for SO_2 and column temperature 20 °C. Amount of divinylbenzene (%): (*1*) 8; (*2*) 12; (*3*) 15; (*4*) 20; (*5*) 30.

Table 6. Characteristics of the AN-221 anion exchangers with different geometrical structures (specimens *1–8*) and anion exchangers based on Styrosorb I (specimens *9–11*) and their capacities with respect to CO_2 and SO_2.[80,126–130]

Specimen	Solvent	DVB/solvent	S_{N_2}, m^2 g^{-1}	S_{CO_2}, m^2 g^{-1}	SEC, mequiv. g^{-1}	$E_0^{CO_2*}$, mg g^{-1}	$E_0^{SO_2*}$, mg g^{-1}
1	BR-1	8/100	51	142	6.7	40	147
2	BR-1	12/80	65	124	6.4	30	173
3	n-Heptane	15/100	61	101	5.5	24	134
4	BR-1	15/100	75	–	5.3	–	–
5	BR-1	15/100	62	–	5.5	25	–
6	BR-1	20/80	90	92	4.1	18	126
7	BR-1	30/100	140	–	3.0	12	–
8	BR-1	30/100	150	64	3.4	20	92
9	DCE	MCDE/100-EDTA+NH_3	664	64	3.5	18	–
10	DCE	MCDE/100-EDA	–	64	3.0	16	–
11	DCE	XDC/100-EDA	710	64	3.0	18	–

For the highly cross-linked macronetwork polystyrene ion exchangers (Styrosorbs containing ethylene diamine groups—specimens *9–11* in Table 6), the values of $E_0^{CO_2}$ are close to those for highly cross-linked AN-221 anion exchangers.[80] The CO_2 adsorption isotherms on the macronetwork anion exchanger and on AN-221-30/100, having identical ethylenediamine groups and similar values of SEC (3.0–3.5 mequiv.g^{-1}), are identical despite the fact that the value of S for the macronetwork anion exchanger is almost 5 times greater than that for the AN-221 anion exchanger. The CO_2

adsorption isotherm on AN-221-15/100 (specimens 3), having a value of S smaller by a factor of 10 than the macronetwork specimen but a higher value of SEC, lies above the CO_2 adsorption isotherm on the macronetwork anion exchanger.

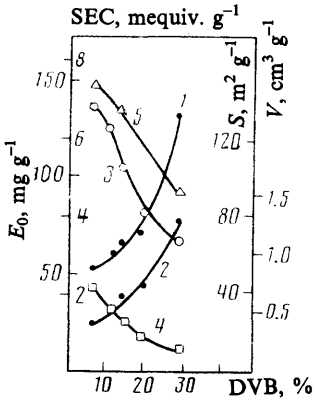


Figure 7. Dependence of the specific surface (curve *1*), pore volume (curve *2*), static exchange capacity (curve *3*), and capacities before the break-through of CO_2 (curve *4*) and SO_2 (curve *5*) on the divinylbenzene content in the AN-221 anion exchangers.

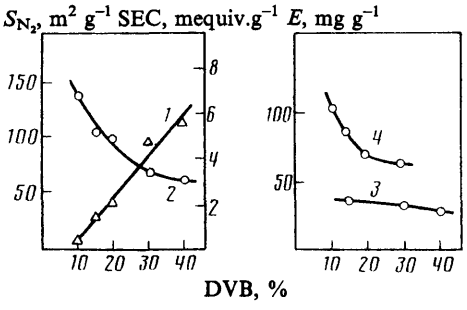


Figure 8. Dependence of the specific surface (curve *1*), static exchange capacity (curve *2*), the capacity before the break-through of SO_2($E_0^{SO_2}$) (curve *3*), and the total capacity (E^{SO_2}) (curve *4*) on the divinylbenzene content in the AN-251 anion exchangers.

The CO_2 and SO_2 adsorption isotherms on the anion exchangers investigated are described approximately by the Langmuir equation. The monolayer capacity a_m were determined from the slopes of the linear plots of p/a against p and S_{CO_2} and S_{SO_2} were calculated (the values of S_{CO_2} are listed in Table 6; the area per CO_2 molecule in the monolayer is 0.171 nm^2). In the case of the weakly cross-linked polymer (specimen *1*), S_{CO_2} exceeds S_{N_2} almost by a factor of three, while in the case of the highly cross-linked anion exchangers it is much lower. This indicates an appreciable local interaction of CO_2 molecules with the amino-groups of the anion exchangers and, in the case of the weakly cross-linked anion exchangers, the adsorbed molecules permeate into the matrix. Calculations showed that the fraction of the amino-groups participating in the adsorption of CO_2 on the least cross-linked specimen (8% DVP) is somewhat greater than on the remaining specimens and hardly changes with increase in the amount of divinylbenzene to 30%. The static exchange capacity is by no means fully utilised in the adsorption of CO_2—at best to the extent of 50%. In the case of SO_2, it is possible to attain 100% utilisation of the amino-groups of the anion exchangers, which can be accounted for by the stronger acid properties of the SO_2 molecule compared with CO_2.

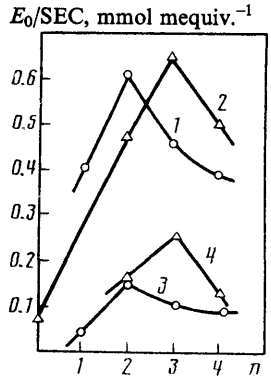


Figure 9. Dependence of the capacities of the anion exchangers before break-through (calculated per unit SEC) with respect to SO_2 (curves *1* and *2*) and CO_2 (curves *3* and *4*) on the number of amino-groups (n) in the aminating agent: (*1*) and (*3*) anion exchangers obtained from the styrene–divinylbenzene copolymer with d = 30 nm (12/80, isooctane); (*2*) and (*4*) ditto for the styrene–divinylbenzene copolymer with d = 60 nm (8/100, n-nonane).

(b) The influence of the amount and nature of the pore-forming agent

Anion exchangers based on styrene–divinylbenzene and vinylpyridine–divinylbenzene copolymers.[124,129,130,132] The change in the porous structure of the polymers induced by the change in the content and nature of the pore-forming agent influences appreciably their adsorption capacity. Firstly, the increase in the volume and size of the polymer pores with increase in the size of the hydrocarbon (pore-forming agent) molecule increases the accessibility of the functional groups to the molecules being adsorbed. Secondly, an increase in the size of the copolymer pores makes it possible to modify the copolymer by larger molecules containing several amino-groups. Fig. 9 presents the dependences of $E_0^{CO_2}$ and $E_0^{SO_2}$, referred to the SEC, on the number of amino-groups in the functional unit of the styrene–divinylbenzene anion exchangers having different pore sizes. An increased number of amino-groups in the molecule of the aminating agent increases the capacity of the anion exchanger, but the introduction of larger molecules (for example diethylenetriamine) into the copolymer with d = 30 nm is difficult. Furthermore, the configuration of the diethylenetriamine molecules in the pores is such that the amino-groups are inaccessible to the molecules being adsorbed. As a result, the capacity of the AN-511 anion exchanger with d = 30 nm diminishes. In the case of the more coarsely porous specimen with d = 60 nm, the configuration of the large molecule of the aminating agent (diethylenetriamine) in the copolymer pores is favourable for the molecules undergoing adsorption and the capacity of the anion exchanger increases.

The dynamics of the adsorption of CO_2 on different beds (ranging from 7 to 90 cm) of the AN-221 anion exchangers obtained in the presence of pore-forming agents of different natures (PR-1 petrol, n-heptane, isooctane, and n-decane) has been investigated. It has been shown that the anion exchanger whose matrix has been synthesised in n-decane (having the largest pores among the polymers investigated) exhibits the best dynamic characteristics together with a high capacity with respect to CO_2.

The influence of the nature and amount of the pore-forming agent on the absorption of SO_2 has been studied for anion exchangers of different types containing different amino-groups.[1,130] For the same divinylbenzene content (for the virtually identical value of SEC), the capacity of the anion exchangers before the breakthrough of SO_2 passes through a maximum as the amount of the solvent (pore-forming agent) increases. It is known that S also passes through a maximum under these conditions, while V and d increase. In the region of the SO_2 absorption maximum, the optimum ratios of the values of S, V, and d for the anion exchangers are apparently attained. The use of a solvent with a larger molecular size (white spirit instead of heptane) for AN-251 shifts the maximum towards lower concentrations of the pore-forming agent.

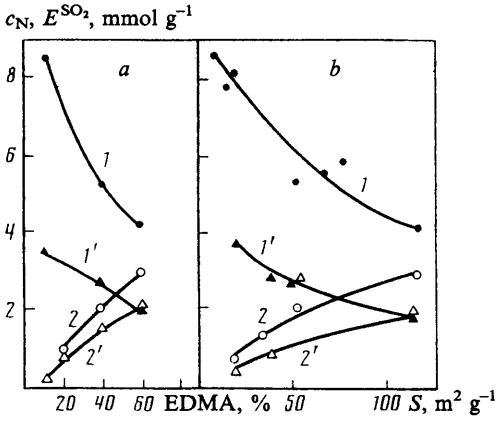


Figure 10. Dependence of the concentration of the amino-groups c_N (curves *1* and *1'*) and of the capacity with respect to SO_2 (E_0) (curves *2* and *2'*) on the amount of the cross-linking agent (*a*) and S (*b*) in the epoxypropyl methacrylate–ethylene dimethacrylate copolymers modified by dithylene triamine (curves *1* and *2*) and ethylmethylamine (curves *1'* and *2'*).

(c) The influence of the amount of the cross-linking agent and of the solvent/precipitant ratio

Methacrylate polymers.[40] Fig. 10 presents the dependences of $E_0^{SO_2}$ and of the concentration of amino-groups c_N on the percentage content of ethylene dimethacrylate and S. They differ from the similar dependences for the anion exchangers of the styrene–divinylbenzene series (Figs. 7 and 8). For the methacrylate polymers, an increase in the amount of the cross-linking agent (simultaneously with an increase in S and V and a decrease in c_N) in the polymers increases their capacity with respect to SO_2. The amount of SO_2 adsorbed by a weakly cross-linked polymer is much smaller than the amount of amino-groups, apparently because the values of S and V for such polymers are small and most of the amino-groups are not accessible to the SO_2 molecules undergoing adsorption. As a consequence of the increase in S and V, an increase in the amount of ethylene dimethacrylate entails an increase also in the content of the surface amino-groups and in their accessibility, so that the capacity with respect to SO_2 increases. This is confirmed by the fact that, with increase in the ethylene dimethacrylate content, the number of surface epoxy-groups rises.[30] It is important to note that, as the content of ethylene dimethacrylate increases, the ratio E_0/c_N tends to unity, i.e. the complete utilisation of the amino-groups is attained.

For the polymers differing in the cyclohexanol/dodecanol ratio, an increase in the adsorption capacity with respect to SO_2 with increase in S is also observed (Fig. 10*b*).

It is noteworthy that, despite the different forms of the dependences of E_0 on the amount of cross-linking agent for AN-221 and epoxypropyl methacrylate–ethylene dimethacrylate–ethylenediamine, containing identical functional groups, the optimum (as regards the absorption of CO_2 and SO_2) structure of the specimens is the same: $S \simeq 50$ m^{2}g^{-1} and $d \simeq 100$ nm, although in the former case the copolymer was obtained with 8% of the cross-linking agent (divinylbenzene), while in the latter case 40% of the cross-linking agent (ethylene dimethacrylate) was used. For such structural parameters, the maximum accessibility of the amino-groups to the molecule being adsorbed is apparently achieved regardless of the nature of the polymer matrix.

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Thus the study of the porous structures of polymeric sorbents of different structural types by a set of physicochemical methods and the determination of the dependences of the parameters of the porous structure on the conditions of synthesis (the amount and nature of the cross-linking agent, the amount and nature of the pore-forming agent, and the molecular weight of polystyrene) permits the specific synthesis of porous polymers with a particular structure. It has been shown that, with increase in the amount of the cross-linking agent in the anion exchanger matrix, the specific surface and the pore volume and size increase; an increase in the molecular size of the pore-forming hydrocarbons also entails an increase in the size of the anion exchanger pores. The nature of the porous structure of Styrosorbs depends likewise on the nature of the solvent in which the cross-linked copolymer is formed and on the molecular weight of the initial polystyrene. The polymer-analogue reactions of the mesoporous styrene–divinylbenzene and epoxypropyl methacrylate–ethylene dimethacrylate copolymers do not lead to significant changes in their porous structure. The relations established for the adsorption of carbon and sulphur dioxides by modified polymers of different structure make it possible to optimise their porosity, for which the maximum accessibility of the functional groups to the molecules undergoing adsorption is ensured.

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