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ESR study of hypercrosslinked polystyrene carbonizate—organic solvent—oxygen systems

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Carbonizates of hypercrosslinked polystyrenes were studied by ESR spectroscopy. Conditions for preparation of paramagnetic carbon sorbents used as oxygen sensors were determined. These sorbents are characterized by an intense narrow ESR singlet for air desorption by pyridine, glycerol, ethanol, methanol, and water. For the carbonizates of nonionogenic biporous hypercrosslinked polystyrenes (**I**) or sulfonic cation-exchange resins based on biporous hypercrosslinked polystyrenes (**II**), the ESR line width decreases from 10 G in oxygen to 0.4—1.2 G (0.4 G for glycerol) upon solvent introduction, and the signal amplitude increases by two—three orders of magnitude. When solvents with the linear structure of molecules (alkanes, their mono- and dichlorosubstituted derivatives, alcohols) are introduced, the ESR line can decrease to 2.3±0.3 G. Carbonizates **I** and **II** obtained by pyrolysis at temperatures 580—620 °C possess a large internal surface (up to 680 $m^2\,g^{-1}$) and contain packets of condensed aromatic polycycles with delocalized π-electrons.

Key words: ESR spectroscopy, carbonizates of hypercrosslinked polystyrenes, polyconjugated systems, oxygen sensors.

Carbon semiconductors are promising materials widely used in various areas of energetics, radioelectronics, and chemical technology and in studies of chemical kinetics and catalysis.[1] In biology and medicine porous carbon materials have been used long ago as universal sorbents. In the recent time, carbon sorbents with paramagnetic properties have been proposed as oxygen sensors. This oxymetry method using NMR and ESR instruments was developed for monitoring oxygen *in vivo* in tissues and physiological fluids.[2] Carbonizates of tropical tree wood[3,4] and lithium phthalocyanines[5] recommended themselves as the best oxygen sensors. For instance, for lithium phthalocyanine in an oxygen atmosphere the line width is 1.6 G, whereas in the absence of oxygen it is only 0.05 G. At the same time, unstable properties and complicated technology for preparation of these oxygen sensors restrict their use, so that development of new routes for their preparation is an urgent task.

Some types of coals[6] and polyethylene carbonizates[7] are also characterized by intense and narrow ESR signals (line width 2—4 G) during prolong evacuation of samples, while in the presence of oxygen the signal is considerably broadened or disappears completely. It is assumed for another type of carbons, *viz.*, products of sugar pyrolysis, that paramagnetic centers are certain agglomerates of condensed aromatic cycles, which are strongly conjugated electronic systems. A similar conclusion follows from Refs 8 and 9: the narrow line with the Lorentzian shape and high intensity of the ESR signal indicates the presence of a polyconjugated system with a high concentration of delocalized π-electrons. Polyconjugated systems manifesting semiconducting properties were found in some pyrolysis products of phenolformaldehyde polymers, copolymers of styrene with diethynylbenzene,[10] poly(vinyl chloride) and poly(vinylidenechloride),[11] products of thermoradiation modification of polyethylene,[7] petroleum cokes,[12] and others. These carbon materials give a narrow singlet ESR signal (width of 0.5—4 G for evacuated samples), which changes sharply upon gas adsorption.[1,7]

The behavior in aqueous systems is important for oxygen sensors based on carbon sorbents with paramagnetic properties. The NMR studies of aqueous suspensions of carbon obtained by the pyrolysis of solid wood species showed[13] that water protons form oriented, relatively stable pairs with unpaired electrons.

For the purpose of searching for new carbon materials appropriate for use as oxygen sensors in biomedicine, in this work we studied by ESR the carbonizates of a series of hypercrosslinked polystyrenes[14] and revealed a strong influence of various organic solvents on the paramagnetic properties of a carbonizate—solvent system.

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Experimental

Carbon materials based on several types of polymers were prepared and studied. The initial polymers were polydivinylbenzene (PDVB); hypercrosslinked polystyrenes formed by crosslinking of the copolymer of styrene with divinylbenzene (0.3%) by monochlorodimethyl ether (1 mole per base-mole of polystyrene) (CPS(0.3)200E) or by crosslinking of linear polystyrene by *p*-xylylenedichloride (1 mole per base-mole of polystyrene) (LPS200X); sulfonic cation-exchange resin based on the gel-like phenol-aldehyde polymer Wofatit F (H^+ form) (earlier produced in German Democratic Republic); commercial hypercrosslinked polystyrene sorbents (Purolite Int. Co., UK): nonionogenic biporous sorbents MN-202 and MN-200 (micropores 2—3 nm and macropores 100—150 nm), MN-200-based sulfonic cation-exchange resin MN-500 (H^+ form, sulfur content 7.9%), and carboxylic cation-exchange resin MN-600 (H^+ form).

Polydivinylbenzene was prepared by suspension free-radical polymerization in the presence of the initiator 2,2´-azobisisobutyronitrile. Divinylbenzene and the initiator (Merck) were used without additional purification. Divinylbenzene contained 65 wt.% of the main substance (mixture of *m*- and *p*-isomers) and 33 wt.% of a mixture of *m*- and *p*-ethylvinylbenzene.

Carbonizates based on several hypercrosslinked polymers are good carbon sorbents with the developed internal surface (500—600 $m^2 g^{-1}$) and regular spherical shape of granules (0.5—0.8 mm).[14]

Hypercrosslinked polystyrenes CPS(0.3)200E and LPS200X were synthesized according to a known procedure.[15]

Carbon materials based on the above-listed polymeric networks containing many benzene rings were obtained by pyrolysis at 500 or 600 °C (1 h) in an argon flow (180 mL min^{-1}) in a Pt crucible in the cell of a Q-1500 derivatograph (MOM, Hungary). The yield of the coke residue was determined from the thermogravimetric curves recorded in the isothermal regime.

The contents of carbon and hydrogen in the prepared carbons were determined by pyrolytic burning in the presence of lead oxide (1 : 10) in an oxygen flow (30 L min^{-1}) at 900 °C (15 min).

Parameters of the porous structure of the carbon sorbents were determined from the nitrogen adsorption isotherms at 77 K, which were obtained by the gravimetric method on a Gravimat setup (Netzsch, Germany). Specific surface values S_{BET} were calculated by the Brunauer—Emmett—Teller (BET) method; the mesopore surface S_{me} was determined using a comparative method, and the averaged adsorption isotherm on samples of nonporous technical carbon (soot) was taken as reference.[16] The mean width of micropores $2\bar{x}$ for the slit-like model was determined by the generalized Stoeckli equation[17] that related the $2\bar{x}$ value to the characteristic energy of nitrogen adsorption E_0 through the empirical correlation $2\bar{x} = 10.8/(E_0 - 11.4)$. The characteristic adsorption energy E_0 and micropore half-width x_0 were determined according to the volume micropore filling theory for the slit-like model.[18]

The compression strength of granules based on 1 granule (F) was determined for uniaxial compression of single granules (diameter 1±0.1 mm) from the limiting load until their destruction (average value by results of 10—15 measurements).

The apparent density d_{app} was established with an accuracy of 5—7% from the ratio of the total volume to the weight of 70—100 defect-free granules of regular spherical shape. The granular volume was calculated by results of measuring the diameter of each granule with a microscope. The average density value was calculated for each sample from the data for three—four series of measurements.

The true density d_{tr} of granules was measured by the densimetric method in a helium medium on a Micromeritics Instrument Corporation apparatus.

Absorption of toluene and ethanol by the sorbents was studied under static conditions. The sample under study was kept for 24 h in toluene or ethanol; after the liquid was removed on a centrifuge (15 min, 3000 rpm), the sample was weighed, dried at 100 °C to constant weight (~24 h), and weighed again. Solvent absorption by the sorbents was determined from the difference between the weights of the sample before and after drying referred to the weight of the dry sample.

ESR spectra of the carbon materials in air were recorded on a Bruker ER-200D instrument at low power levels P without saturation (in the region of a linear dependence of the signal amplitude on $\sqrt{P}$); the modulation width was 0.1 G, and the frequency was 100 kHz. The carbon materials were used 2—4 days after pyrolysis of the polymers. Carbon samples (25—35 mg, ~0.1 mL) were placed in quartz ampules ~3.0—3.4 mm in diameter. For each measurement, the position of the ampule in the resonator was strictly the same, as well as the level of the SHF power (2.0—2.9 mW), and only the amplification value was changed. After measurements in air, dichloromethane (2—3-fold excess over the sample volume) was introduced into the ampules containing the samples, and then the ampules were sealed off. ESR spectra of a carbonizate—solvent system were recorded 2 days after introduction of the solvent and after its complete sorption and stabilization of the ESR signal. The relative amplitude of the signal I^* and the relative integral signal intensity S^* referred to the same amplification value and the line width ΔH_{max} were estimated. The S^* value was calculated by double integration of the ESR signal as the first derivative of the absorption curve using the Origin 4.0 computer program. The number of detected paramagnetic centers [PMC], which is proportional to S^*, was estimated using a benzene solution of the stable radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the reference.

The influence of the type of the absorbed sorbent on the parameters of ESR spectra of a sorbent—adsorbate system was studied for the carbonizates of hypercrosslinked polystyrenes MN-500 and MN-202 prepared by pyrolysis at 500 (HS5 and H5, respectively) and 600 °C (HS6 and H6). Carbonizates were used after long storage (4 years for HS5 and HS6 and 1 year for H5 and H6) in a desiccator above $CaCl_2$ in air. To examine the influence of the solvent type on the parameters of the ESR spectra, spectral data were used for sorbent—adsorbate systems stored for 4—6 days after the introduction of an adsorbate when the signal amplitude and the line width stopped changing. For systems of the carbonizates with glycerol, methanol, and water, ampules 2 mm in diameter were used. An ESR signal for the liquid layer above the sorbent was found to be absent when any solvent was used. Samples filled with oxygen were prepared by multiple cycles of evacuation of ampules, introduction of oxygen, and subsequent sealing of the ampules.

Results and Discussion

The temperature of pyrolysis of polymer is the main factor determining the properties of final carbon materials. Therefore, the products obtained by the pyrolysis of the hypercrosslinked polystyrene sulfonic cation-exchange resin MN-500 were studied at several different temperatures by various methods, first of all, ESR. Analysis of the parameters of the ESR spectra (Fig. 1) allows us to distinguish the temperature region of pyrolysis in which the line width and the signal amplitude for the same sample differ sharply in air and in dichloromethane. The maximum amplitude of the ESR signal is characteristic of the pyrolysis products obtained at ~500 °C, if the spectra are recorded in air and the minimum of the signal amplitude falls on the products prepared at 600 °C. On the contrary, for carbonizate—dichloromethane systems, the sharp increase in the signal amplitude (by 60 times) falls on the samples prepared at 600 °C. The ESR line width for the samples pyrolized in a temperature interval of 400—500 °C in both air and dichloromethane changes slightly (Fig. 1, *b*). At pyrolysis temperatures ~600 °C, the ESR line width for the samples in air increases twofold, whereas it decreases threefold for the samples filled with the solvent. It is known[7] that for the products of thermo-radiation treatment of polyethylene at temperatures above 600 °C the ESR line with a width of 7.5 G is transformed for the maximum desorption of atmospheric oxygen by evacuation into a new line with a width of 0.5 G, *i.e.*, a particular spin packet is isolated. This effect is determined by the interaction of delocalized electrons of the carbonizates with unpaired electrons of oxygen.[19] A similar effect seems to take place in the carbonizates of hypercrosslinked polystyrenes under study. However, it should be assumed that the pyrolysis at 500 or 600 °C produces carbon materials with different structures and different paramagnetic centers.

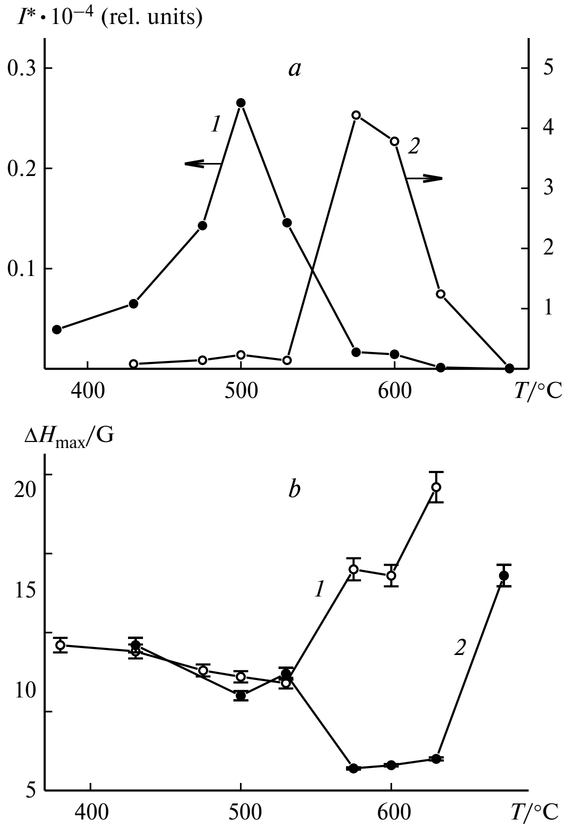

Fig. 1. Plots of the amplitude of the ESR signal (*a*) and the maximum in the ESR line width (*b*) of the carbon materials based on MN-500 in air (*1*) and dichloromethane (*2*) *vs.* pyrolysis temperature. Hereinafter, I^* is the relative signal amplitude referred to the same amplification value.

By analogy to petroleum cokes,[12] we believe that at temperatures <550 °C (see Fig. 1) paramagnetic centers insensitive to oxygen prevail in the carbonizates of hypercrosslinked polystyrenes. These centers represent localized uncompensated σ-electrons formed by the cleavage of the C—C bonds due to the thermal destruction of the polymeric network. It is known[20] that in the temperature region from 350 to 550 °C volatile pyrolysis products are removed and cyclic aromatic carbon structures only begin to form. It is most likely that pyrolysis at 500 °C generates a considerable amount of stable free radicals during the decomposition of the polymeric network and, therefore, the [PMC] value in the HS5 and H5 carbonizates is by 20 and 3 times, respectively, higher than that in HS6 and H6. Pyrolysis does not result yet in compacting of aromatic structures to form paramagnetic packets.

At higher pyrolysis temperatures, *viz.*, in a range of 550—650 °C, oxygen-sensitive paramagnetic centers already predominate. These centers are polycyclic radicals with delocalized uncompensated π-electrons. In this case, the carbonizates of hypercrosslinked polystyrenes obtained by pyrolysis at 600 °C (Table 1) and possessing a developed polyconjugated system should also exhibit the semiconducting properties. This assumption is confirmed by measurements of the specific resistance of sample **V** (see Table 1), whose value for the granular form of the sorbent was $1.4 \cdot 10^4$ Ohm cm.

At temperatures above 600 °C the radicals recombine to form new C—C bonds, decreasing sharply the amplitude of the ESR signal. As a result, multilayer three-dimensional polycyclic structures are formed, regularly decreasing in the specific electric resistance.[19] For the carbonizates under study obtained at temperatures above 700 °C, measurements of ESR signals become impossible because of a considerable decrease in the resistance: from $1.4 \cdot 10^4$ to $3.9 \cdot 10^2$ Ohm cm at 600 and 900 °C, respectively.

Thus, the samples obtained at 600 °C are of most interest. These are porous carbon sorbents with the highly developed internal surface (up to 600 m^2 g^{-1}) and,

Table 1. Properties of the carbonizates of different polymers prepared by pyrolysis at 600 °C

Sample	Initial polymer	C.r.[a] (%)	S_{BET} /m^2 g^{-1}	ΔH_{max}/G		[PMC] • 10^{-18}/spin g^{-1}		I/I_{air}[b]
				Air	Dichloromethane	Air	Dichloromethane	
I	PDVB	15.7	160	4.8	3.8	34.2	57.0	8
II	CPS(0.3)200E	44.6	35	14.4	1.2	40.0	37.4	320
III	LPS200X	41.7	60	~14.0	1.5	1.9	61.8	5380
IV	Wofatit F (H$^+$)	56.7	7	1.2	1.3	14.7	85.0	8
V	MN-500 (H$^+$)	53.4	500	~13.2	1.6	17.0	69.0	260
VI	MN-202	55.5	600	14.8	0.7	11.0	52.5	1700

[a] C.r. is coke residue (here and in Table 3).

[b] The amplitude of the ESR signal from the carbonizate referred to the signal amplitude in the air medium.

most likely, with the highly developed polyconjugated system formed by packets of polycyclic structures with delocalized π-electrons. Since oxygen sorption in these systems is accompanied by their transformation into non-paramagnetic complexes, the ESR spectra of the carbonizates in air is broadened to a diffuse singlet ~14 G in width with a small amplitude (Fig. 2, *a*). When dichloromethane is introduced into this sample, oxygen is desorbed, most likely, from the pore surface of the carbon sorbent and its paramagnetic centers are liberated. Therefore, the ESR signal from the sample in dichloromethane becomes narrow (1.4 G) and very intense in amplitude (Fig. 2, *b*).

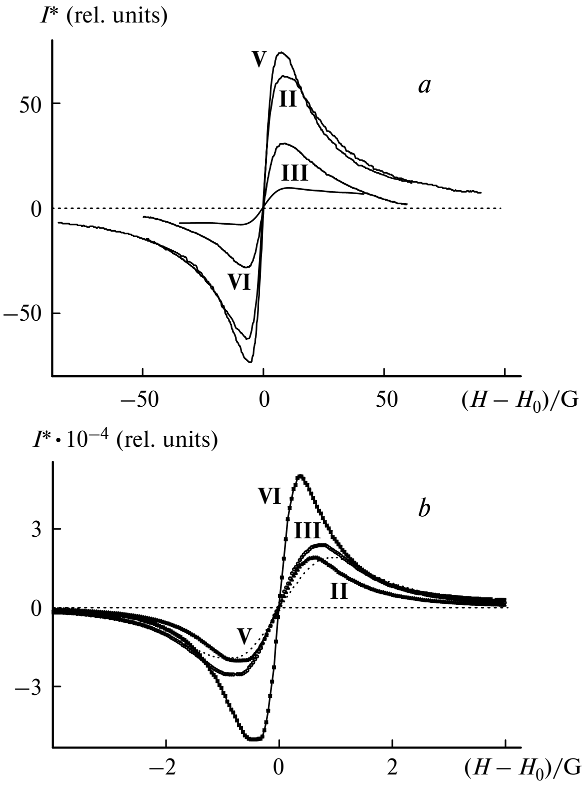

Fig. 2. ESR spectra of the carbonizates of hypercrosslinked polystyrenes **II**, **III**, **V**, and **VI** in air (*a*) and dichloromethane (*b*) (see Table 1); H_0 = 3494 G.

A similar effect of a sharp decrease in the ESR spectrum upon oxygen desorption by the solvent was also observed for the carbonizates (600 °C) of the nonionogenic polymeric materials: hypercrosslinked polystyrenes CPS(0.3)200E and LPS200X and the industrial sorbent MN-202 (see Table 1). The ESR spectra of these carbon materials in air are low-intensity broad lines 13—14 G in width (see Fig. 2, *a*). For the same samples, the introduction of dichloromethane increases the amplitude of the ESR signal by up to 5000 times, and the line width decreases by 10 times (see Fig. 2, *b*). The carbonizates based on other polymeric networks, *viz.*, polydivinylbenzene and sulfated phenol-aldehyde polymer, have a rather narrow ESR signal, whose line width changes slightly upon solvent introduction and the signal amplitude increases only by 8 times (see Table 1). It is most likely that no oxygen-sensitive polyconjugated system is formed in these carbon materials with a small number of pores (S_{BET} from 7 to 160 m^2 g^{-1}), and the paramagnetic centers, which are radicals formed by the C—C bond cleavage, are inaccessible to oxygen in such a dense matrix.

Thus, the carbon sorbents with the paramagnetic polyconjugated system can be identified and classified by their relation to oxygen and solvent. If the ESR spectrum of the porous sample filled with air becomes sharply narrower and the signal amplitude increases considerably when the solvent is introduced into the sample, then its paramagnetic centers are accessible to both oxygen and solvent, and the latter can desorb oxygen. The parameters of the ESR spectra in a sorbent—adsorbate system are determined by the type of the solvent introduced, namely, the structure and size of the molecule, on the one hand, and the structure of sorbent pores, on the other hand. Sorbent—adsorbate systems were studied for the carbonizates based on the industrial hypercrosslinked polystyrenes MN-500 and MN-202 prepared by pyrolysis at 500 °C (HS5, H5) and 600 °C (HS6, H6).

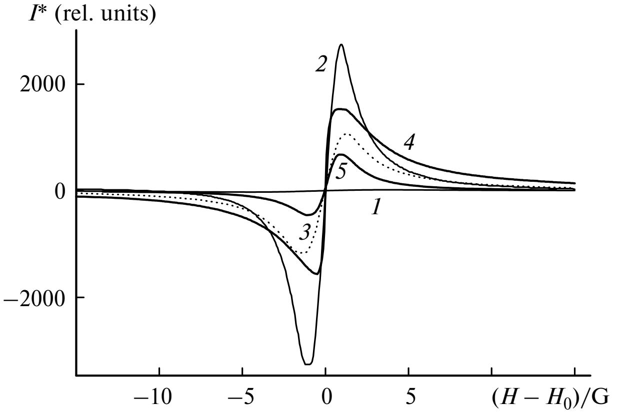

Fig. 3. ESR spectra of the H6 carbonizate in air (*1*), nitrobenzene (*2*), THF (*3*), and octane (*4*) and HS6 in acetonitrile (*5*); H_0 = 3494 G.

Analysis of the ESR spectra of the HS6 and H6 carbonizates filled with different solvents (Fig. 3, Table 2) showed that the parameters of the spectra changed mainly in a similar way compared to the spectra of these samples in air for the following order of organic compounds: hexane (or heptane, octane), tetradecane, benzene, dichloromethane, nitrobenzene, and tetrahydrofuran (only for HS6). The line width decreases from 7—9 to 2—2.6 G, and the integral intensity of the signal (and correspondingly, [PMC]) increases by 10—13 times for the HS6 carbonizate and by 2—5 times for the H6 carbonizate. The introduction of *tert*-butyl alcohol, carbon tetrachloride, cyclohexane, and chloroform (only for HS6) into the HS6 and H6 carbonizates results in a considerably lower change in the parameters of the ESR spectra. Probably, for molecules of these compounds, the micropores (Table 3) in HS6 and H6 remain inaccessible, especially for bulky molecules of *tert*-butyl alcohol. In fact, direct measurements of volumes of methanol and *tert*-butyl alcohol absorbed by these sorbents indicate that almost 30% of the porous space of the material are inaccessible for *tert*-butyl alcohol. At the same time, the removal of atmospheric oxygen by prolong helium purging through

Table 2. Parameters of the ESR spectra of the carbon sorbents in different media

Sorbent*	ΔH_{max} /G	$[PMC]\cdot10^{-18}$ /spin g^{-1}	ΔH_{max} /G	$[PMC]\cdot10^{-18}$ /spin g^{-1}	ΔH_{max} /G	$[PMC]\cdot10^{-18}$ /spin g^{-1}	ΔH_{max} /G	$[PMC]\cdot10^{-18}$ /spin g^{-1}
	Oxygen		Air		Pyridine		Dichloromethane	
HS5	10.0	5.2	7.6	22.1	5.8	9.3*	5.0	27.9
HS6	10.0	0.7	9.2	0.8	1.1	40.5	2.0	8.3
H5	10.0	11.0	7.6	23.1	7.2	22.2	7.2	27.0
H6	6.4	7.4	6.4	7.5	0.6	26.4	1.9	37.8
	Hexane		Tetradecane		Benzene		Benzyl alcohol	
HS5	4.4	34.7	4.4	32.3	4.0	26.5	6.0	23.3
HS6	2.8	7.5	2.4	8.1	2.5	10.5	2.4	2.9
H5	7.2	35.3	6.8	33.0	7.2	37.0	7.6	22.0
H6	2.0	35.0	2.4	19.0	2.0	38.2	2.4	18.6
	tert-Butyl alcohol		Benzyl alcohol		Ethanol		Glycerol	
HS6	4.0	1.2	—	—	2.0	13.6	0.8	22.5
H6	6.0	6.0	2.2	14.0	0.6	44.7	0.4	28.0
	Methanol		Acetone		Ethyl acetate		Cyclohexane	
HS6	1.5	9.1	2.0	0.7	—	—	3.6	4.6
H6	0.8	30.0	2.0	6.6	2.8	1.6	3.6	12.0
	Chlorobenzene		Chloroform		Carbon tetrachloride		Dichloroethane	
HS6	2.6	5.8	3.6	2.2	4.0	1.9	2.4	4.8
H6	2.2	2.4	2.9	18.2	5.2	15.5	2.0	23.4

* The HS5 sorbent contains the pyrolysis products extracted with pyridine (solution above the sample layer in the ampule gains dark blue color), and no changes in the solvent color were observed for other carbonizates.

Table 3. Physical characteristics and parameters of the porous structure of the carbonizates of hypercrosslinked polystyrenes MN-500 and MN-202

Sorbent	C.r. (%)	Content (%)		d_{tr}	d_{app}	F /kg	Absorption /mL g^{-1}		E_0 /kJ mol^{-1}	S_{BET}	S_{me}	$2\bar{x}$	$2x_0$
		C	H	g cm^{-3}			Ethanol	Toluene		m^2 g^{-1}		nm	
HS6	55.3	93.9	1.8	1.601	0.83	1.2	0.50	0.50	34.4	680	50	0.47	0.46
H6	55.0	92.7	2.5	—	1.03	1.0	0.29	0.22	25.1	670	20	0.79	0.78

the carbonizates filled with *tert*-butyl alcohol or chloroform results regularly in narrowing of the ESR line to 2.4 or 1.7 G, respectively, *i.e.*, to the same limits as the pore filling with solvents with small sizes of molecules. It is most likely that molecules of this group of solvents are not only too large (diameter of a CCl_4 molecule is 0.61 nm[21]) for the micropores of these carbonizates and also are structurally rigid, which does not allow them to penetrate into the micropores. Larger but flexible molecules of unbranched alkanes, such as hexane (diameter of a molecule is 0.67 nm[21]), octane, and even tetradecane, can enter into the micropores of the carbons under study and displace oxygen. Therefore, we can assume that the micropores are slit-like gaps between the planar structures of condensed polycyclic aggregates.

Acetone exerted an unexpected effect: the line width decreased to 2 G, but [PMC] for the HS6 and H6 carbonizates remained completely unchanged compared to the systems in air. Ethyl acetate and chlorobenzene have similar effects on the parameters of the ESR signal for the H6 carbonizate: the [PMC] and line width decreased by 5 and 2—3 times, respectively, for these solvents (Fig. 4). Perhaps, a size of 0.56 nm of a "crab-like" acetone molecule (the more so, of ethyl acetate and chlorobenzene) exceeds the size of enters into the micropores or the size of the micropores themselves, if they are considered to be slit-like. Only mesopores are accessible for these molecules and, hence, the narrowing of the ESR line is caused by oxygen desorption only from the mesopores.

A particular group presented solvents, whose introduction into the HS6 and H6 sorbents results in the maximum narrowing of the ESR line, namely, to 1.5 and 0.5 G, respectively. These solvents are pyridine, methanol, glycerol, ethanol, and acetonitrile. In this case, the signal amplitude increases considerably (by two—three orders of magnitude). The [PMC] also increases: for the HS6 sorbent, by 30 and 50 times in glycerol and pyridine, respectively; for the H6 sorbent, by 6 times in ethanol. The maximum oxygen desorption even from micropores should be considered as the main reason for the sharp change in the parameters of the ESR spectra. This is favored by small sizes and polarity of methanol, ethanol, and acetonitrile molecules, the planar structure and high affinity of pyridine to aromatic systems, and flexibility of a glycerol molecule. The different changes in the parameters of the ESR signals for the HS6 and H6 carbonizates are caused, most likely, by their different abilities to absorb these adsorbates, because the micropore structures, their shape, and chemical structure of the surface in the HS6 and H6 carbonizates differ substantially. It can be assumed that not all pores of the HS6 sorbent are accessible for ethanol or pyridine molecules, and oxygen can remain in the micropores and result in a smaller narrowing of the ESR line than that for the H6 carbonizate (see Table 2). This fact agrees with calculations of the mean micropore width $2\bar{x}$ or $2x_0$ for the slit-like model when these two carbonizates were studied by the method of low-temperature nitrogen sorption (see Table 3). The micropores in the HS6 sample are by 1.7 times smaller than those in H6, although their number, judging from the $S_{BET} - S_{me}$ difference, is almost the same. The calculated value of the micropore width is 0.47 nm for HS6, which is possibly close to the real value if the pore sizes are estimated from the effect of narrowing of the ESR line due to oxygen desorption by small methanol and ethanol molecules with a diameter of 0.46—0.52 nm.

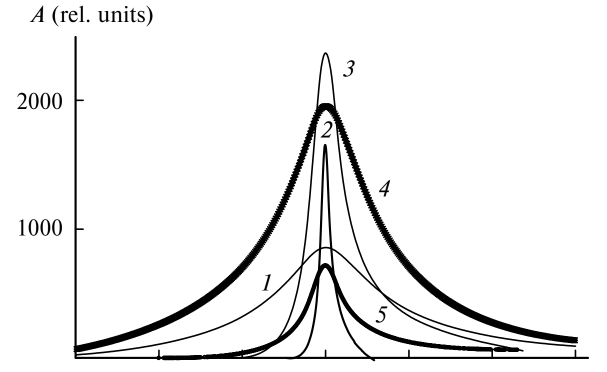

Fig. 4. ESR spectra in the integral form for the H6 carbonizate in air (*1*), ethyl acetate (*2*), acetone (*3*), carbon tetrachloride (*4*), and chlorobenzene (*5*); *A* is the relative absorption of electromagnetic radiation; H_0 = 3494 G.

If interlayer distances in carbons with the large internal surface are considered to be micropores, the sizes of such slit-like pores can be estimated from the true density of the material, using published data.[22] For the linear approximation of the dependence of the true density on the mean interlayer distance[22] for the HS6 sample under study (density 1.6 g cm^{-3}), the slit-like pores should be ~0.45 nm in size.

For the H6 sorbent, the calculated micropore width $2\bar{x}$ = 0.79 nm (see Table 3) is overestimated, because carbon tetrachloride and acetone, whose molecules are 0.61 and 0.56 nm in diameter,[21] do not enter, most likely, into its micropores, whereas ethanol easily displaces oxygen due to which the ESR line width decreases to 0.6 G. According to these data, it can be assumed that the micropore size of the H6 sorbent ranges from 0.52 to 0.56 nm.

The study of the porous structure of the sorbents by the method of low-temperature nitrogen sorption showed that the sorption isotherms of N_2 (Fig. 5) can be classified, according to their shape, as type I by the BET classification, which is characteristic of microporous materials with the molecular-sieve character of adsorption.[21] The mesopore surface S_{me} for both materials is insignificant compared to the total surface S_{BET} (see Table 3).

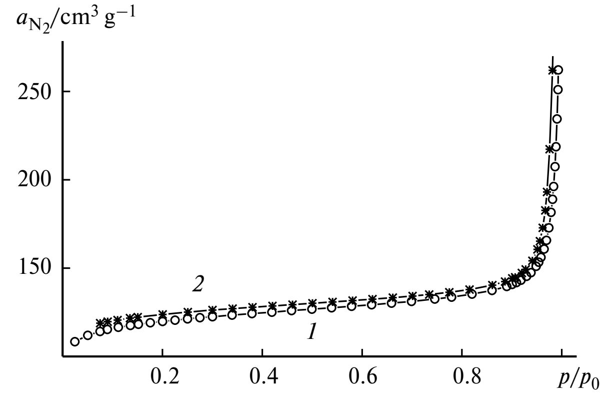

Fig. 5. Isotherms of nitrogen adsorption (*1*) and desorption (*2*) at 77 K on the HS6 sorbent.

At the same time, the sorbents contain both meso- and macropores that existed in the precursor hypercrosslinked sorbents. Their number in the HS6 sorbent is somewhat greater than that in H6 and, therefore, the first sorbent sorbs the 1.6-fold greater amount of low-molecular-weight solvents (toluene and ethanol) than the second material (see Table 3).

The systems of the H6 and HS6 carbonizates with alcohols are characterized by the regular decrease in the line width with a decrease in the molecular size, which is caused by the greater amount of O_2 desorbed from the micropores (see Table 2).

Unlike the carbon sorbents obtained at 600 °C, for the carbon materials, being products of pyrolysis at 500 °C, the introduction of various solvents, as well as dichloromethane, exerts virtually no effect on the parameters of the ESR spectrum.

Among all the studied carbon materials, the use of only two microporous carbon sorbents HS6 and H6 seem to be promising as oxygen sensors. Since the biomedicine oxygen sensors are used in aqueous media, it is important that an aqueous suspension of the sorbent containing no oxygen should give an intense and narrow ESR signal.[13] Indeed, after air was removed from the HS6 carbon sorbent with methanol, thorough washing of the sample with water, and subsequent purging of helium, the ESR spectrum of the sorbent with water was an intense and narrow singlet. As it is well seen from the data in Fig. 6, the ESR line width for an HS6—water system is by 10 times smaller and the signal amplitude is by 30 times higher than those for the same sorbent filled with oxygen. The creation of a sufficiently sensitive oxygen sensor on the basis of this range of changes in the ESR spectrum of the HS6 material seems quite possible.

Thus, the ESR study of the carbonizates of hypercrosslinked polystyrenes showed that pyrolysis at 500 °C generates the products with a high concentration of oxygen-insensitive radical paramagnetic centers. The microporous carbon materials were prepared by pyrolysis at 600 °C. Atmospheric oxygen is well sorbed by these carbonizates and desorbed when they are introduced in media of various solvents, resulting in a change in the parameters of the ESR spectrum. The ability to displace oxygen is determined, first of all, by the size and geometry of adsorbate molecules and the porous structure of the carbon sorbent. Pyridine, methanol, and ethanol penetrate maximally into the micropores and displace oxygen, whereas glycerol does it on heating. The micropores are inaccessible for *tert*-butyl alcohol and CCl_4. The micropores are probably slit-like gaps between the planar structures of condensed polycyclic aggregates. Analysis of the ESR spectra of the carbon sorbents contacting with various solvents can be a method for estimation of the micropore size. The carbonizates of the sulfonic cation-exchange resins MN-500 and nonionogenic hypercrosslinked polystyrenes MN-202 are characterized by penetration into the micropores of sorbates with molecular sizes of 0.46—0.52 and 0.52—0.56 nm, respectively.

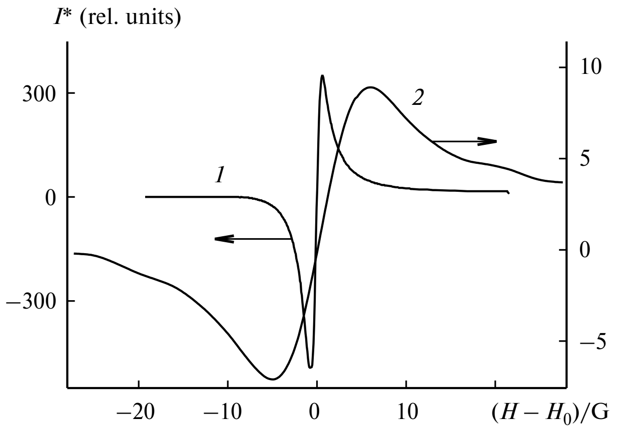

Fig. 6. ESR spectra of the HS6 carbonizate in water (*1*) and oxygen (*2*); H_0 = 3494 G.

The carbonizates of the sulfonic cation-exchange resins and nonionogenic hypercrosslinked polystyrenes prepared by pyrolysis at temperatures 580—620 °C possess the large internal surface (up to 680 m^2 g^{-1}) and a developed polyconjugated system formed by packets of condensed aromatic polycycles with delocalized π-electrons. For these carbon sorbents, the ESR line width is determined by the oxygen content and changes from 6.4—10 G at the 100% oxygen content in the gas phase to 0.4—0.8 or 1.2 G for traces of oxygen in systems of the carbonizate with glycerol or water. These carbon sorbents can find use for the creation of oxygen sensors to determine its concentration by the ESR method in tissues of living organisms.

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