Adsorption of water vapor on modified methacrylate polymeric sorbents

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Adsorption of water vapor on methacrylate copolymers and terpolymers was studied. An increase in the content of the cross-linking agent gives rise to increase in the limiting adsorption of water vapor at the saturation pressure (a_s) and to decrease in the concentration of primary adsorption centers. Modification of the initial copolymer containing 60 % of 2,3-epoxypropyl methacrylate (EPMA) monomer and 40 % of cross-linking agent, ethylene dimethacrylate, with diethylenetriamine (DETA) results in an increase in the a_s value, while modification with C_{12} and C_{18} alkyl, benzyl, and phenyl groups gives rise to decrease in the a_s values for the copolymeric sorbents. The concentration of primary adsorption centers (a_m) increases considerably on modification of the copolymer with DETA and C_{12} groups and decreases markedly on modification with benzyl and phenyl groups. For terpolymers, containing EPMA and styrene, an increase in the styrene/EPMA ratio reduces the a_s and a_m values. The copolymer modified with DETA groups possesses the most hydrophilic properties, while the copolymer modified with benzyl group exhibits the most hydrophobic properties. The mechanism of adsorption of water molecules on the polymers is discussed.

Key words: polymeric adsorbents, methacrylate copolymers, terpolymers, water vapor adsorption, primary adsorption centers, gas-chromatographic Kováts index.

Porous polymers are widely used sorbents in gas, liquid, and ion-exchange chromatography as well as selective adsorbents for ecologically damaged impurities. Modifying the conditions of synthesis of porous polymers allows one to regulate the spatial structure of the three-dimensional net of a polymer and to obtain adsorbents with various degrees of porosity. A change in the chemical properties of the surface of polymers during synthesis and modification of the porous framework already formed allows one to obtain adsorbents with various functional groups and thus to regulate their adsorption capacity and selectivity.[1—3]

Adsorption is one of the most common methods for analysis of porous structure and chemical state of the surface of adsorbents. In particular, the adsorption of a water molecule is very sensitive to both chemical state of the surface and fine details of porous structure of carbon adsorbents.[4—7]

The studies of the mechanism of adsorption of water vapors on non-porous carbon adsorbents[7—9] and active carbons with various parameters of porous structure and chemical state of the surface[4—6,9,10] have shown that the adsorption of water vapor in the range of small coverages was due to the interaction between water molecules and primary adsorption centers (PAC), which are usually the surface oxygen-containing functional groups.

Analysis of a shape of adsorption isotherms of water vapor with the use of a comparative method[6] allows one not only to estimate the content of PAC, the surface area of non-porous adsorbents,[7] mesopore surface,[11] and the average size of micropores in active carbons,[4,6] but also to study the nature of the interaction between water molecules and adsorbents.

The aim of this work is to study the structure and sorption properties of mesoporous polymeric modified adsorbents, obtained by the method of suspension radical copolymerization of EPMA and ethylene dimethacrylate (EDMA), by means of analysis of adsorption isotherms of water vapor.

Experimental

The subjects of the study were methacrylate polymers with similar structures containing 40 % of EDMA as cross-linking agent and 60 % of EPMA monomer (G-60) with different chemical states of the surface: EPMA/EDMA copolymers modified with diethylenetriamine (DETA) (G-60-DETA), with aliphatic C_{12} and C_{18} groups (G-60-C12 and G-60-C18, respectively),[12] with phenyl and benzyl groups (G-60-Ph and G-60-Bz),[13] as well as terpolymers with the following ratios of monomers EPMA/styrene (St): 50:10, 30:30, 10:50 (GSt-519, GSt-517 and GSt-520, respectively).[14] For comparison, copolymers containing 80 and 97.5 % EPMA (G-80 and G-97.5, respectively) were also studied. Table 1 presents the values of the specific surface areas of the polymers studied, which were determined by thermal desorption of nitrogen. Table 1 contains also the limiting values of the adsorption of water vapor

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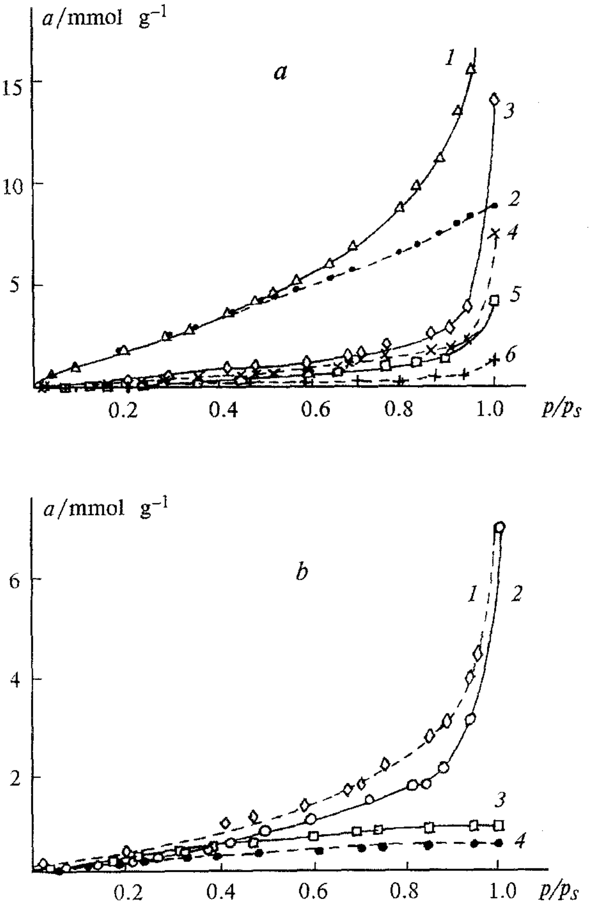

Fig. 1. Adsorption isotherms of water vapor at 20 °C on methacrylate copolymers (*a*) and terpolymers (*b*). *a*: G-60-DETA (*1*), G-60-C12 (*2*), G-60 (*3*), G-60-Ph (*4*), G-60-C18 (*5*), G-60-Bz (*6*). *b*: G-60 (*1*), GSt-519 (*2*), GSt-517 (*3*), GSt-520 (*4*).

at 20 °C and the saturation pressure (a_s) as well as the concentration of PAC (a_m) estimated on the basis of comparative plots of adsorption isotherms of water vapor on polymer sorbents and graphitized thermal carbon black.

Adsorption isotherms of water vapor at 20 °C were measured in a vacuum adsorption setup with quartz spring balance of 10^{-5} g sensitivity on the samples which were previously evacuated at 170 °C until retain a constant weight. Adsorption isotherms of water vapor on the initial and modified copolymers G-60 and sample G-80 are shown in Fig. 1, *a*, and adsorption isotherms on methacrylate terpolymers in Fig. 1, *b*. The adsorption isotherm for sample G-60 is also given there for comparison.

Results and Discussion

Comparative methods,[15] based on comparison of adsorption data for the studied and reference samples of an adsorbent, are commonly employed for characterization of the porous structure of sorbents. In this work, adsorption on polymer adsorbents was compared with that on Vulkan 7H graphitized carbon black.[6] Fig. 2 presents comparative plots for four copolymers and terpolymers. Experimental values for the adsorption of water vapor on these adsorbents (mmole/g) and graphitized carbon black (molecules/center) are determined at the same pressures and plotted on ordinate and abscissa axes, respectively. As seen from the figure, the initial regions of the comparative plots are well described by straight lines that pass through the origin. The concentrations of PAC, a_m, were obtained from the slope of the linear regions (Table 1).

Table 1. Adsorption characteristics of methacrylate copolymers and terpolymers

Polymer	$S(N_2)$ / m^2/g	$a_s(H_2O)$ / mmole/g	a_m / mmole/g
G-60	51	14.2	0.32
G-60-DETA	67	27.9	1.30
G-60-C12	60	9.10	1.30
G-60-C18	23	3.24	0.21
G-60-Ph	60	7.74	0.65
G-60-Bz	60	1.61	0.10
G-80	18	4.4	0.15
G-97.5		1.9	0.15
GSt-519	53	7.0	0.20
GSt-517	51	1.1	0.19
GSt-520	50	0.64	0.16

For all the polymers except G-60-C12, GSt-517, and Gst-520 the isotherms have a shape typical of porous glass-like polymers.[16] Apparently, the differences in a shape of isotherms are due to different mechanisms of sorption of water molecules by these polymers in the regions of medium and high coverages.

With increasing content of the cross-linking agent, both the limiting value of adsorption of water vapor in copolymers and the concentration of PAC increase. For modified copolymers, concentrations of PAC and limit-

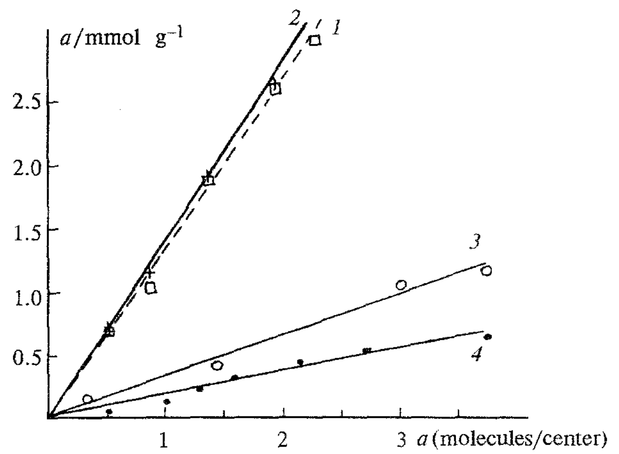

Fig. 2. Comparative plots of adsorption isotherms of water vapor on polymeric adsorbents G-60-DETA (*1*), G-60-C12 (*2*), G-60 (*3*), GSt-517 (*4*). Adsorption isotherm on graphitized thermal carbon black is taken as the isotherm for comparison.

ing values of adsorption of water vapor differ substantially from those for the initial sample G-60 (Table 1).

The concentrations of PAC, a_m, change in the following order: G-60-C12 = G-60-DETA > G-60 > G-60-Ph > G-60-C18 > G-60-Bz. The same concentrations of PAC were obtained for samples G-60-DETA and G-60-C12, although the concentrations of modifying groups (1.8 mmole/g for DETA and 0.1 mmole/g for C_{12}) strongly differed. Possibly, sharp increase in PAC for these samples is not connected directly with the nature of modifying groups but is due to modification of the structure of a monomeric part of a copolymer.

Modification of G-60 by C_{18} hydrocarbon groups, as well as phenyl and benzyl groups, significantly reduces the limiting value of the adsorption of water vapor and somewhat lowers the concentration of PAC. The G-60-Bz sample proved to be the most hydrophobic of all the copolymers studied, and G-60-DETA to be the most hydrophilic. An increase in the styrene/EPMA ratio slightly reduces the concentration of PAC in terpolymers and substantially decreases the limiting value of adsorption of water vapor. No correlation between the limiting value of the adsorption of water vapor and the specific surface area of the adsorbents determined by adsorption of nitrogen was found for the polymers studied. If one recalculates the a_s value with respect to the amount of dense monolayers on the surface of polymers, taking into account their specific surface area determined by adsorption of nitrogen, it can be shown that the number of layers changes from 0.2 to 30. Apparently, adsorption of water vapor proceeds *via* a mechanism that differs from that for adsorption of nitrogen.

Comparative methods allow one not only to estimate the parameters of porous structure of adsorbents[6,15] and the concentration of PAC[6], but also to analyze the mechanism of adsorption.[4,6–9] It is known that on carbon and some other adsorbents (*e.g.*, on silica and silica gel[9]) in the range of small coverages, the adsorption of water molecules involves the interaction between adsorbed molecules and PAC which results in the formation of hydrogen bonds.[4,9,17] These PAC are, as a rule, the surface oxygen-containing functional groups.[18,19] In the range of small pressures, comparative plots are the straight lines passing through the origin with a slope which is proportional to the concentration of PAC.[6] For all samples studied, the initial regions of comparative plots are linear, and they, in fact, pass through the origin as is seen in Fig. 2. This allows one to determine concentrations of PAC and conclude that adsorption on polymeric adsorbents at coverages below 3—4 molecules per center proceeds in the same manner as that on graphitized thermal carbon black. Here we deal with physical adsorption resulting in the formation of independent microclusters of associated water molecules.

When analyzing porous structure and chemical state of the surface of carbon adsorbents, deviations in comparative plots from linear dependence are usually explained by the formation of two-dimensional film or bridging bonds and three-dimensional net in micropores.[6] In general case, the deviation from linear dependence means that the mechanism of adsorption on the adsorbent studied differs from that on a reference sample.

For all polymeric adsorbents studied, in the range of coverages above 4—5 molecules per center, the deviation "down" from a straight line is observed. This means that adsorption proceeds less effectively than that on independent clusters at the surface of graphitized carbon black. As follows from the results of numerical simulation,[20] the nature of interaction of adsorbed water molecules with the carbon surface and that between molecules should lead to the situation, in which the shape of a cluster approaches to a semisphere when the number of molecules in the cluster increases. One can suppose that the differences in the configurations of clusters, which are formed on the surfaces of polymers and carbon, are the reason for the nonlinearity of comparative plots in the range of coverages of more than 4—5 water molecules per PAC.

For more detailed analysis of the effect of modification on the mechanism of adsorption of water molecules on polymeric adsorbents, it is expedient to take the adsorption isotherm on the initial copolymer G-60 as the isotherm of comparison. In this case, the isotherm for sample G-60 normalized to the concentration of PAC on the surface of this sample (0.32 mmole/g) is taken. As is seen in Fig. 3, *a*, for samples G-80, G-97.5, G-60-DETA, GSt-519 (and also for samples G-60-Bz and G-60-C18), comparative plots are linear in a wide range of coverages, and only at the values of adsorption of 12—14 molecules per center (p/p_s > 0.9) deviations from a straight line are observed. For samples of terpolymers GSt-517 and GSt-520, as well as for copolymers G-60-C12 and G-60-Ph, such deviations are observed already at the values of adsorption of 5—6 molecules per center (Fig. 3, *b*).

The results obtained give evidence that the mechanisms of adsorption of water molecules on samples G-60, G-80, G-97.5, GSt-519, G-60-DETA, G-60-Bz, and G-60-C18 are similar. The adsorption on these samples proceeds *via* another mechanism than that on graphitized thermal carbon black, because the linearity of comparative plots was not retained at coverages above 3—5 molecules per center when using the adsorption isotherm for the surface of carbon as the isotherm for comparison. Samples of G-80 and GSt-519 are the closest in their composition and structure to G-60 and differ from it in either the content of the cross-linking agent (G-80) or the relatively small amount of styrene in the terpolymer GSt-519.

Therefore, the mechanisms of adsorption of water molecules are close as is seen from the linearity of comparative plots nearly in all range of coverages. Modification of sample G-60 by DETA groups makes this sample the most hydrophilic among all adsorbents studied. At the same time, modification of G-60 with benzyl

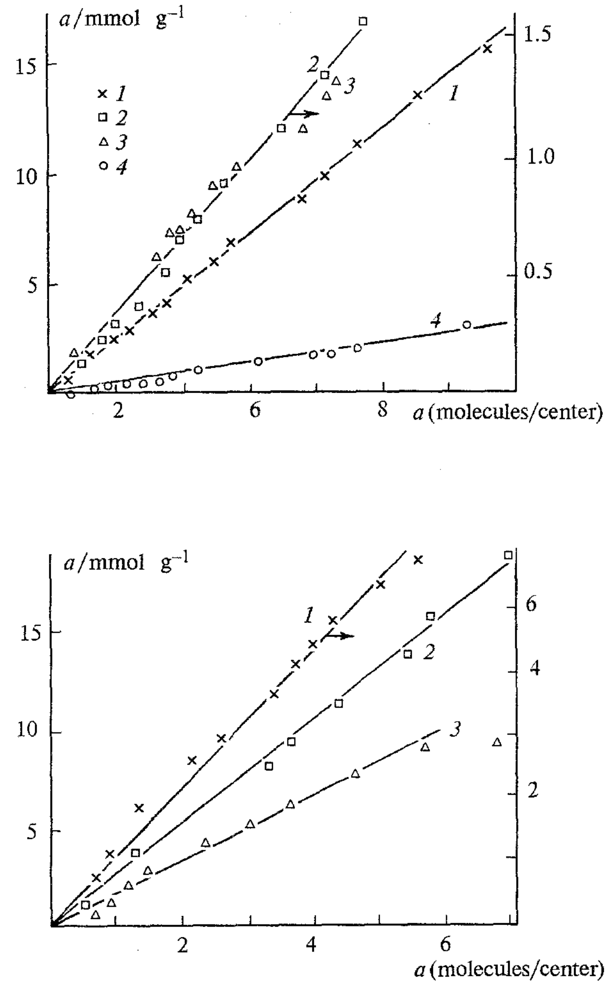

Fig. 3. Comparative plots of adsorption isotherms of water vapor on modified methacrylate copolymers and terpolymers. Adsorption isotherm on copolymer G-60 is taken as the isotherm for comparison. *a*: G-60-DETA (*1*), G-80 (*2*), G-97.5 (*3*), G-519 (*4*). *b*: G-60-C12 (*1*), G-60-Ph (*2*), GSt-517 (*3*).

Table 2. Coefficients of the equation of linear expansion of gas-chromatographic parameters

Sample	k_1	k_2	k_3	k_4
G-60	136	44	37	32
G-60-DETA	121	46	54	66
G-60-C12	119	32	41	56
G-60-C18	125	42	44	30
G-60-Ph	135	51	48	31
G-60-Bz	136	49	45	18
GSt-519	127	44	41	27
GSt-517	131	43	40	23
GSt-520	142	39	36	19

Note: k_1 characterizes dispersion, k_2 orientational, k_3 electron-releasing, and k_4 electron-withdrawing interactions.

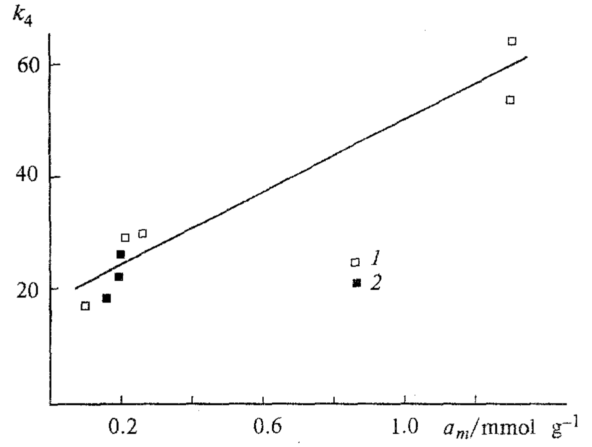

Fig. 4. Correlation between the content of primary adsorption centers (a_m) and coefficient k_4 of the equation of linear expansion of gas-chromatographic Kovat's indices for copolymers (*1*) and terpolymers (*2*).

groups results in an increase in its hydrophobicity, although the mechanisms of adsorption on samples G-60-DETA and G-60-Bz are close to that on the initial sample G-60.

Among the samples studied, two terpolymers, GSt-520 and GSt-517, and the copolymer G-60-C12 are characterized by a special shape of adsorption isotherm. On these adsorbents, the linearity of comparative plots is observed in a relatively narrow range of coverages (below 5—6 molecules per center). Adsorption on these samples, apparently, proceeds *via* the same mechanism as on other polymers studied only in the range of small coverages. Adsorption isotherms on terpolymers GSt-517 and GSt-520 are close in a shape to those on ultramicroporous carbon adsorbents[21] or hydrated silicas and silica gels.[15] Such a shape of isotherms, unlike those of types III and V isotherms[15] typical of relatively hydrophobic adsorbents, can testify that the growth of microclusters or filling of a pore volume in the range of comparatively high relative pressures are limited to space hindrances. One can suggest that on these polymers, the adsorption of water molecules proceeds through the filling of a limited volume of hydrophilic regions (peculiar micropores), which are formed on modification of the initial copolymer.

Thus, one can conditionally separate the adsorption isotherms of water vapor on polymeric sorbents studied into three regions. The first region reflects the adsorption of water molecules proceeding with the formation of independent microclusters of associated water molecules around primary adsorption centers. Water adsorption on graphitized carbon surface occurs in a similar way. This region includes the range of coverages of 3—4 molecules per center which corresponds to p/p_s = 0.4—0.5 range. The presence of a break between the first and second regions on comparative plots indicates a change in the mechanism of adsorption. A new mechanism, which is the same for all copolymers and terpolymers studied, assumes the formation of microclusters that differ in shape from hemispherical clusters on the carbon surface. For some samples, the second region includes the values of adsorption up to 10—14 water molecules per one PAC; this corresponds to the range of relative pressures from 0.4—0.5 to 0.90—0.95, *i.e.*, to virtually the whole range of medium and high relative pressures. For these samples, the third region is observed in a very narrow p/p_s range, if exists at all. At the same time, for terpolymers with a relatively high content of styrene and for the copolymer G-60-C12 (and to a lesser extent for G-60-Ph), the second region is limited to the values of adsorption of 5—6 molecules per center (p/p_s < 0.6). For these samples, one can separate the third region, which corresponds to the special mechanism of adsorption connected possibly with the presence in the adsorbent of strongly linked (quazi-microporous) regions with a limited adsorption volume.

The concentration of PAC characterizes the capacity of surface functional groups of adsorbents to interact with water molecules forming hydrogen bonds. It can be compared with the coefficients of the equation of linear expansion of gas-chromatographic Kováts indices. These coefficients characterize the capacity of the surface of sorbents for intermolecular interactions of various types[12,22] (Table 2). Figure 4 shows a correlation between the a_m value and the coefficient k_4, which is a measure of the electron-acceptor capacity of the surface of the initial and modified G-60 copolymers and terpolymers. As seen in the figure, a significant rise in the content of the primary adsorption centers in samples G-60-C12 and G-60-DETA corresponds to a significant increase in the coefficient k_4.

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