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Surface chemistry of methacrylate polymeric sorbents: chromatography and adsorption

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Abstract - The specificity and selectivity of polymeric methacrylate sorbents is comparatively readily regulated by changing the chemical nature of the surface in the process of synthesis and modification. Porous copolymers obtained by copolymerization of 2,3-epoxypropylmethacrylate with the resulting modification by various amines and amino alcohols have been investigated. The geometric structure of the sorbent has been studied by using various methods, the dependences of the structure parameters on different factors being established. The thermodynamic characteristics for the adsorption of organic substances which are used to test for various types of intermolecular interactions were determined by the method of gas-chromatography. The thermodynamic characteristics of adsorption of benzene derivatives from non-polar and polar eluents on the polymers containing different functional groups were determined by the method of HPLC. The method of frontal chromatography and the static vacuum method were used to study the range of the average covering of the surface. The regularities in the effect of the quantity and the nature of the functional groups on the adsorption of sulfur and carbon dioxides have been found.

INTRODUCTION

Development of chromatographic and adsorption methods is closely connected with the production of new sorbents responsive to much higher requirements. Thus they are supposed to be spheres (granules of a narrow fractional composition of various size), to be stable in various media, thermally stable and selective towards certain compounds. Polymeric sorbents fully comply with these requirements. A choice of monomers allows the regulation of their thermostability and resistance to the effect of acids and alkalis. Since the chemical nature of the polymer surface can be readily varied by bonding various functional groups, it is possible to obtain the sorbents which selectively adsorb the required component of the mixture to be analyzed. Moreover, the copolymerization reaction carried out in the medium of inert solvents and containing different amounts of cross-linking agent makes it possible to change and adjust the spatial structure of the resulting three-dimensional network of the polymer and to obtain sorbents of various porosity.
Methacrylate-based copolymers containing reactive epoxy groups readily undergo chemical modifications. Therefore they are found to be very promising for their application in chromatography and adsorption requiring regulation and adjustment of their adsorption and selectivity properties.

I. SYNTHESIS OF METHACRYLATE COPOLYMERS AND THEIR MODIFICATIONS

For the synthesis of chemically active polymers were used macroporous copolymers of 2,3-epoxypropylmethacrylate (EPMA) or 2,3-epithiopropylmethacrylate (ETPMA) with ethylenedimethacrylate (EDMA) obtained in the process of suspension radical polymerization with various amount of monovinyl monomer and various ratio between the solvent and the precipitator in the inert phase (of cyclohexanol and dodecanol) (ref.1). The following abbreviation was used to designate the geometric modifications of methacrylate porous

Table 1. Modification of the copolymer EPMA-EDMA with amines. Reaction conditions: copolymer 10 g, amine 30 ml, temperature 80°C, time 6 hours

II	R'	R	Reagent I
a	-H	-H	ammonium
b	-H	$-(CH_2)_2NH_2$	ethylenediamine
c	-H	$-(CH_2)_2NH(CH_2)_2NH_2$	diethylenetriamine
d	-H	$-(CH_2)_2OH$	2-hydroxyethylamine
e	$-CH_3$	$-CH_3$	dimethylamine
f	$-(CH_2)_2OH$	$-(CH_2)_2OH$	di-2-hydroxyethyl-amine

copolymers EPMA-EDMA: the part of EPMA in a mixture with EDMA-the ratio cyclohexanol/dodecanol. For example, porous polymer 40-91/9 was obtained with 40% EPMA with the ratio of cyclohexanol/dodecanol equal to 91/9. Copolymers contain reactive $-CH\overset{O}{\diagdown}CH_2$ groups which react with amines and amino alcohols according to the scheme:

I II a - f

II. CHARACTERISTICS OF THE GEOMETRIC STRUCTURE AND ITS DEPENDENCE ON VARIOUS FACTORS

Application of various methods for characterizing the porous structure. The properties of polymeric sorbents are determined by both chemical properties of their surface and the geometric structure. The possibility of application of adsorption methods and the method of mercury porosimetry for studying the porosity of such "non-rigid" structures as porous polymers including polymers of methacrylate type has been studied (ref.2). Specific surface areas of the samples were measured using the dynamic method of thermal nitrogen desorption. Mercury porograms were obtained in the range of pressures from 0.2 to 10^5 kPa, which made it possible to determine the pores of 8 nm and higher in diameter (ref.2). The isotherms of the vapour adsorption were measured with the use of the Mac-Ben-Bakr vacuum balance on the sample predominantly pumped out at 70°C to 10^{-3} kPa. Perfluoro-n-octane ($n\text{-}C_8F_{18}$) in which polymeric sorbents practically do not swell was used as adsorbate (Fig.1) (ref.3). The same polymeric samples were used to measure the sorption isotherms of cyclohexane vapour in which polymers partilly swell (irreversibility of the isotherm at low p/p_0). The pore volume was also determined by weighing the centrifuged sample of the polymer after filling the pores with liquid cyclohexane. The investigations (ref.2) have shown that the values of the specific surface area $S_{C_8F_{18}}$ are near the values of S_{N_2}, though the former are considered as evaluating ones since the energy constant of the equation BET in this case is small (refs.2,3). The fact that the surfaces of the adsorption film $S'_{C_8F_{18}}$ formed at the beginning of the capillary condensation (ref.4) and $S_{C_8F_{18}}$ practically coincide as well as the fact that the S values measured with respect to the adsorption of a small nitrogen molecule and rather a large C_8F_{18} molecule are also close to each other indicate that micropores are absent in the samples. The S_{Hg} value in some cases exceeds the S value taken from adsorption data. There is a probability that these samples contain a sufficient amount of pores with narrowing (broadening).

A comparison of the pore volumes measured according to the amount of mercury impressions and the amount of $n\text{-}C_8F_{18}$ and $cyclo\text{-}C_6H_{12}$ vapours adsorbed by the polymers at $p/p_0=1$ shows that, firstly the values of $V_{C_8F_{18}}$ and $V_{C_6H_{12}}$ practically coincide despite certain swelling of the polymers in the cyclohexane vapours (Fig.1) and, secondly, $V_{Hg} \geqslant V$, though this difference does not exceed 0.1 cm^3/g. The latter fact shows that the sorbents under study do not contain any significant amount of pores with $d > 200$ nm.

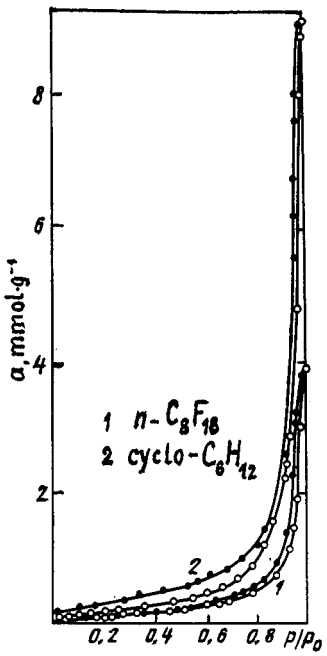

Fig.1. Isotherms of the adsorption of n-C_8F_{18} (I) and cyclo-C_6H_{12}(2) at 25°C on the EPMA-EDMA copolymer (60-91/9) modified by diethylenetriamine (IIc). Solid dots designate desorption.

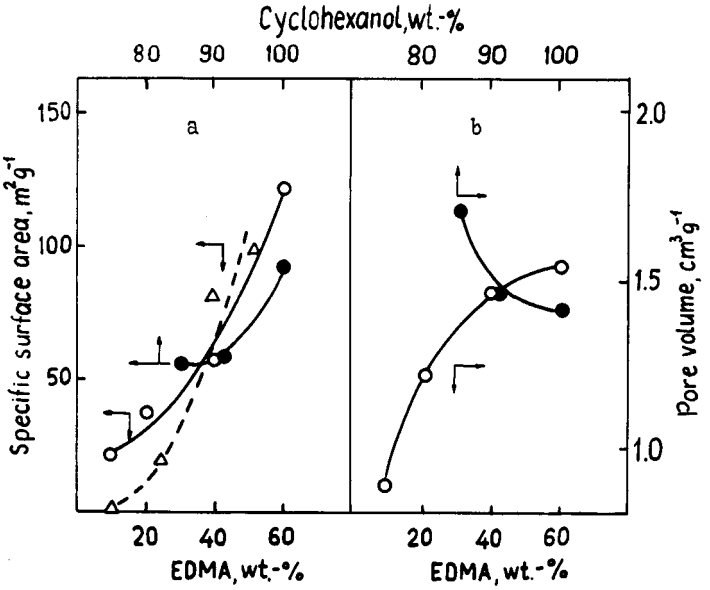

Fig. 2. The dependence of the specific surface area (a) and the pore volume (b) on the content of the cross-linking agent (●) and cyclohexanol (○) for the EPMA-EDMA copolymer (○,●) and the HEMA-EDMA copolymer (△).

Thus it follows that the adsorption method (using adsorbates in which polymers practically do not swell) and the mercury porosimetry method for the determination of the pores size and volumes produce compatible results for the polymers containing the pores with d up to 200 nm. In (refs. 5,6), to characterize the porous structure of EPMA-EDMA copolymers the gel permeation chromatography (GPC) was employed along with the electron microscopy, mercury porosimetry and nitrogen sorption. It has been shown that the characteristics of the porous structure differs in the dry state and in the swollen state: the average pore diameter measured according to mercury porosimetry is greater than that determined by GPC. The investigation of the morphology of EPMA-EDMA copolymers by the method of scanning electron microscopy (ref.7) has shown that the copolymers consist of two types of spheric micro particles, namely, the primary particles, nodules 10 nm in size (which explains the large S of copolymers), which form aggregates to yield the secondary particles, globules. The character of aggregation of micro particles on the surface substantially differs from that inside the globules. The micro particles on the surface and in the globule volume are of the same size, however, they form more compact aggregations on the surface. The pore size in the surface layer (approximately 0.1 mkm) is much smaller than the pore size in the volume. According to the authors (refs. 8,9) the surface layer of the globules consists of mobile polymeric chains.

Regulation of the porous structure. The dependences of S_{N_2} and V on the amount of the cross-linking agent EDMA and cyclohexanol are given in Fig.2 for the EPMA-EDMA copolymers (ref.10) and the copolymers of 2-hydroxyethylmethacrylate HEMA-EDMA (ref.11). The figure shows that the majority of the copolymers under study exhibit developed porosity. The specific surface area of the polymers increase with an increase of the amount of the cross-linking agent. The pore volume of EPMA-EDMA copolymers increases with an increase of the EDMA part from 10 to 20%, but with a further increase of the EDMA part up to 60% changes negligibly. The same dependences of the specific surface area and the pore volume on the content of the cross-linking agent and on the composition of the inert mixture were established for copolymers of methylmethacrylate (MMA) with EDMA, MMA and HEMA with EDMA,

akrylonitrile (AN), HEMA with EDMA (refs.11,12), ETPMA with EDMA (refs.13, 14), copolymers of styrene and divinylbenzene (ref.15), vinylpyridine and divinylbenzene (ref.15), which indicates that these regularities are common for all types of macroporous polymers. The introduction of ionogenic groups into monomers substantially affects their ability to be solvated by certain solvent, the rigidity of the polymer network and, consequently, the polymer porosity. The more polar the comonomer, i.e. in the series MMA < HEMA < AN (ref.12), the more pronounced is a decrease of S and V of methacrylate terpolymers with an increase of the comonomer content. In other words, the more polar the monomer, the less is the porosity of the resulting copolymer, which is due to the differences in the copolymerization rates affecting the composition and the texture of copolymers. The effect of the changes in the copolymers structure after involvement of various functional groups was studied for the EPMA-EDMA copolymers. Amination with ammonium leads to a growth of S, while amination with amines, on the contrary, results in a decrease of S of the polymer as compared with S of the non-modified copolymer, however, in the case of high crosslinked polymers this decrease is negligible (ref.10). Amination of the copolymer results in a growing globule size, especially in the case of large molecules of the aminating agent, which manifests itself in a decrease of S and V. When the EPMA-EDMA copolymers are sulfurized the polymeric structure changes markedly. S and V decrease, this effect being especially pronounced in the case of high crosslinked polymers (refs. 15,16). Consequently, the polymer-analogous conversions lead to noticeable changes in the porous structure of copolymers. These changes depend on the basicity of the ionogenic groups being introduced and the porosity of the original copolymer.

III. INVESTIGATION OF THE CHEMICAL PROPERTIES OF THE POLYMER SURFACE BY CHROMATOGRAPHIC METHODS (the range of initial surface covering)

The application of chromatographic methods with the use of high-sensitive detectors for studying the surface chemistry of sorbents and the interaction of the latter with the adsorbed molecules allows one to carry out the investigation of the conditions at which the concentration of the adsorbate molecules in the volume phase and on the surface area is so small that the adsorbate-adsorbate interaction can be possibly neglected. As adsorbates it is feasible to choose the molecules capable of various intermolecular interactions, such as, dispersion, orientational ones, and also capable of forming π-complexes, hydrogen bonds.

Thermodynamic characteristics of organic substances adsorption. Gas-adsorption chromatography. The pioneer investigations concerned EPMA-EDMA copolymers with various amounts of EDMA (ref.17). The polymers under study had S from 44 to 434 m^2/g, their thermal stability slightly changed with an increasing content of EDMA and was equal to 207-223°C. The dependence of the retention volumes (relative to pentane) of various compounds from S (refs. 7,17) shows that in the range up to 200 m^2/g the retention of non-specifically adsorbed substances increases, while the retention of specifically adsorbed substances decreases with the increase of S. Analogous dependences were obtained for ETPMA-EDMA and EPMA-EDMA copolymers (ref.14). Fig.3 shows the dependences of $\ln K_I$ ($K_1 = V_s = V_{g/S}$ -Henry constant) of various substances on S polymers. As in the case given in (refs. 7,17), with an increase of S the retention of n-hydrocarbons increases sharply with increasing of the molecule length. The retention of specifically adsorbed molecules decreases with an increase of S. The following interpretation of the observed dependences was proposed: when the molecule lengthens in the order of one or a few CH_2-groups, the contribution of non-specific interactions with the surface increases, and, consequently, the retention of n-hydrocarbons increases with an increase of S. A decrease in the retention of specifically adsorbed molecules indicates a decreasing amount of polar groups of adsorbents. The dependence of the Rohrschneider constants on S shows that with an increase of the polymers S their polarity decreases in accordance with the decreasing amount of the functional (epoxy- or epithio-) groups.

The chromatographic properties of methacrylate polymers are greatly affected by the conditions of predominant thermal treatment (ref.18). Thermal treatment of polymers results in a shorter time for analysis and a change in the selectivity of the separation of certain mixtures, which is explained by conformational changes in the polymeric chains.

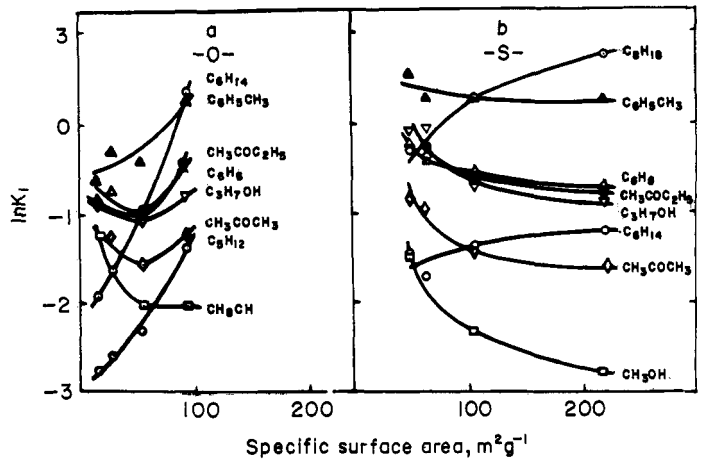

Fig. 3. The dependence of $\ln K_1$ of various substances on the specific surface area value of the EPMA-EDMA copolymers (a) and ETPMA-EDMA copolymers (b).

A promising direction in the regulation of selectivity and polarity of polymeric sorbents is found to be their modification which can be attained by using various monomers or by conducting chemical reactions with copolymers. In (refs.12,19) there were studied chromatographic properties of the sorbents obtained by copolymerization of various monomers, namely, MMA-EDMA, MMA-GMA-EDMA, AN-GMA-EDMA. The least polar copolymer was found to be MMA-EDMA, the most polar was AN-GMA-EDMA, the polarity of the latter increases with a decrease of the content of the crosslinking agent. Comparison of the gas-chromatographic properties of copolymers EPMA-EDMA and ETPMA-EDMA of close geometric structure has shown that the adsorptive capacity of the sulfur-containing polymer with regard to the studied substances of different nature is higher than that of oxygen-containing polymer, which is due to higher polarizability of the sulfur atom (ref.14). The retention of specifically adsorbed substances on the ETPMA copolymer decreases with an increase of S, while on the EPMA copolymers with large S the retention is increasing due to an increasing contribution of dispersion interactions (Fig. 3). The effect of the hydrocarbon part of the molecules on their retention is more pronounced in the case of oxygen-containing polymers. Therefore, the specific interaction on the polymers containing sulfur plays a more important role than on the polymers containing oxygen in the functional group. The presence of the reactive epoxy group in the copolymers EPMA-EDMA allows a comparatively ready performance of their chemical modifications and production of sorbents of various polarity. The polymers containing butyl, dodecyl, hexadecyl, nitrile and amino groups were also investigated (ref.20) The least contribution of dispersion interactions upon adsorption of all the substances under investigation is observed for the polymer containing hexadecyl groups. The greatest contribution of specific interactions was observed for a sample containing amino groups. For all the polymers considered, the Rohrschneider constants (ref.20) were maximal for nitromethane, that is, in all the cases the predominant interaction was found to be orientational one. All the sorbents studied, with the only exception of the copolymers with MMA, to a great extent are able to form hydrogen bonds, which is manifested by high values of the constants for ethanol. The copolymer MMA-EDMA is the least polar, the copolymers GMA-AN-EDMA and EPMA-EDMA with NH_2 groups are the most polar.

Thermodynamic characteristics of organic substances adsorption. Liquid chromatography. As adsorbents, the porous polymers are of particular interest also in liquid chromatography since they can be employed both with non-polar and polar eluents. For LC, the porous polymers based on GMA, styrene, akrylonitrile and divinylbenzene, 2-hydroxyethylmethacrylate(spherones) are used (refs. 21,22).

The copolymer EPMA-EDMA contains the epoxy groups and is classed with slightly specific adsorbents of type III (according to classification given in Ref. 23), for the negative charges are locally concentrated on its surface. A macroporous sample 60-91/9 (S = 55 m^2/g, V = 1.5 cm^3/g, $\bar{d}$ = 106 nm) (ref.21) was employed in LC. The capacity factors k_i and relative

(towards benzene) changes of adsorption free energy $\Delta(\Delta F) = -RT\ln(k_i/k_{C_6H_6})$ of benzene derivatives were measured. The dependences of $\lg k_i$ and $\Delta(\Delta F)$ on the number of carbon atoms in the polymethylbenzene molecules (PMB) and monoalkylbenzene molecules (MAB) (eluent-n-hexane) show that the retention of MAB decreases, the retention of PMB whilst with an increase of the electron density on the benzene ring at first decreases from benzene to mesitylene and only at n>9 the retention is observed to increase. Such a behaviour is due to the relationship between non-specific intermolecular interaction with the eluent and the weak specific and non-specific interaction with the adsorbent.

The order of retention of the benzene derivatives having polar substituents on EPMA-EDMA is drastically different from the retention on silica gel with hydroxylated surface (eluent-n-hexane) (ref.21). A linear dependence of retention on the dipole moment value μ of the adsorbate molecule is observed on the polymer (Fig.4), which indicate a substantial contribution of the electrostatic orientational interaction of the benzene derivatives with the oxygen groups on the polymer surface with the exception of aniline, phenol and benzyl alcohol, that is, the substances able to form hydrogen bonds.

Also are studied in LC the copolymers EPMA-EDMA modified by dimethylamine (IIe), di-2-hydroxyethylamine (IIf), diethylenetriamine (IIc) (Table 1) (ref.24). Upon elution with n-hexane, the relative retention of polar aromatic derivatives on the polymers studied increases from anisole to benzonitrile and aniline, which is due to an increasing contribution of the specific interaction of polar adsorbates with the polymer functional groups to the total energy of interaction. When the water-isopropanol mixture is used as eluent, the relative retention of the polar derivatives increases in the order from aniline to toluene. Thus, the polymers containing amino and hydroxyl groups exhibit unusual and interesting regularities of retention of the polar derivatives of benzene (both with non-polar and polar eluents), which makes a complicated separation of complex mixtures quite possible.

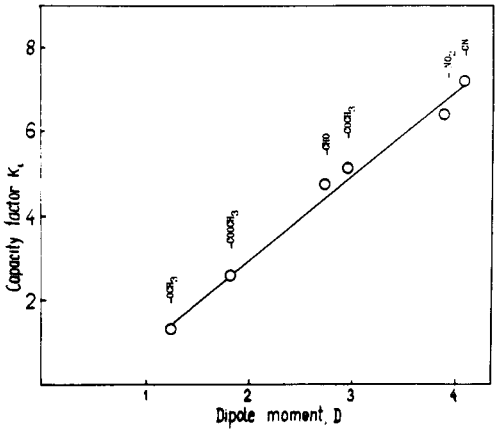

Fig.4. The dependence of the capacity factor of the benzene polar derivatives on the dipole moments (μ) of these molecules on the EPMA-EDMA copolymer (60-91/9). The column: 25x0.6 cm, the particle size: 7-13 mkm; eluent: n.hexane, eluent rate: 2.3 cm^3/min, 26°C.

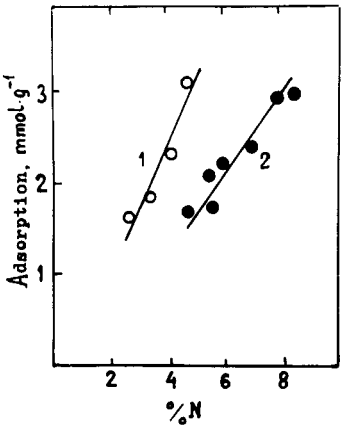

Fig. 5. The dependence of the adsorption value of SO_2 (at p=2kPa) on the nitrogen content in the polymers containing one nitrogen atom (1) and several nitrogen atoms (2) in sorption active functional group.

IV. INVESTIGATION OF THE CHEMICAL PROPERTIES OF THE POLYMER SURFACE BY ADSORPTION METHODS (the range of average surface covering)

The previous chapter was devoted to the consideration of the range of a small (practically zero) covering of the surface when the intermolecular interactions can be neglected. As to the range of large surface covering, the interaction substantially affects the adsorption characteristics. Acid gases, such as, dioxides of carbon and sulfur, are found to be convenient adsorbates for studying the chemical properties of the polymer surface.

The adsorption in the range of average surface covering was investigated by using the static volume method and the method of frontal chromatography (ref.15). According to the first procedure, the adsorbent was pumped out prior to measuring under 10^{-3} kPa at 70-100°C, and in the second case it was heated in the inert gas flow (nitrogen or helium) at 70-100°C.

The effect of the functional groups nature on the adsorption of gases. The adsorption of carbon and sulfur dioxides by the EPMA-EDMA copolymers modified by various amines and amino alcohols has been studied (refs.10,25). The polymers containing one or several ternary groups as well as the polymers containing one amino group with ethanol substitutes practically do not adsorbed CO_2. Involvement of primary or secondary amino groups in the polymer results in a marked increase of the CO_2 adsorption. The greatest values of the CO_2 adsorption are exhibited by the polymers containing a combination of several primary and secondary amino groups. On the contrary, in the case of SO_2, all the polymers adsorb SO_2 in considerable amounts, the polymer containing one ternary nitrogen atom in the functional group exhibits the maximal capacity with respect to SO_2. The capacity of this polymer exceeds that of the polymer containing several nitrogen atoms in the functional group (Fig.5).

The effect of the amount of functional groups on the adsorption of gases. The amount of functional groups is regulated by changing the monomer-crosslinking agent ratio. Therefore, modified EPMA-EDMA copolymers (IIa,b,c,d,f) of different geometric structure have been studied (Fig. 6). It was only

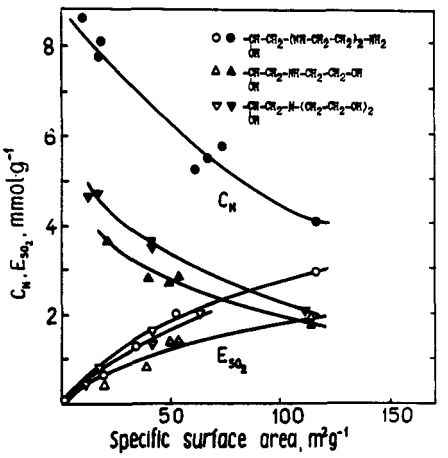

Fig. 6. The dependences of the sorption capacity towards SO_2 (at p= 2 kPa) (○, △, ▽) and the content of amino groups (●, ▲, ▼) in the polymers IIc (○, ●), II d (△, ▲), IIf (▽, ▼) on the specific surface area.

natural to expect that, similar to the gas adsorption by styrene-divinylbenzene anionites containing analogous functional groups and exhibiting analogous adsorption of organic substances (chapter III), the CO_2 and SO_2 adsorption values would grow with an increase of the amount of functional groups in the polymer. However, the values of SO_2 adsorption by methacrylate polymers increase with an increasing amount of the crosslinking agent (an increase of S), in other words, with a decreasing amount of functional groups. The dependence found can be resulting from the fact that in the case of weakly crosslinked polymers the pore volume is small and, consequently, the majority of functional groups is not accessible for the adsorbing SO_2 molecules. When the amount of the crosslinking agent increases (S increases), the number of functional groups decreases but their accessibility increases due to an increase in the volume and size of the pores. In other words, the dependence obtained show that with an increase of S the concentration of the accessible surface functional groups increases. The ability of polymers to regeneration is an important factor for the discussion of the gas adsorption mechanism. The work (ref.25) has shown that all the polymers investigated are completely regained from CO_2 by

evacuation at 70-90°C. The CO_2 adsorption mechanism resulting in the formation of carbamate complex is suggested following the analogy with the styrene-divinylbenzene anionites (ref.15). The study of the polymer regeneration from SO_2 has shown that in the case of the polymers modified by ethylenediamine and diethylenetriamine probably there formed a sufficiently stable adsorption complex of the SO_2 molecule with two amino groups similar to the carbamate compound (ref.25). Introduction of hydroxyl groups decreases the basicity of the amino groups situated nearby, the SO_2 interaction with the functional groups weakens, which results in a much easier regeneration of the polymers.

V. CONCLUSION

The investigation of the porous structure of the polymeric methacrylate sorbents by various methods has shown that these sorbents have high porosity. The porous structure is readily varied by a change in the content of the crosslinking agent and the composition of porogenic mixture. The macroporous structure practically remains intact in the process of modification by various organic compounds, while the polarity of the sorbents changes. The investigation of the surface chemistry of the polymers containing epoxy and epithio groups has shown that the retention of non-specific adsorbing organic substances increases with an increase of the specific surface area. In this case, the retention of specifically adsorbed substances decreases indicating the decreasing amount of polar groups. In the case of adsorption of polar molecules, the orientational interaction as well as the formation of hydrogen bonds contribute greatly to the process. The effect of the nature and the amount of functional groups on the adsorption of acid gases was established. The promising future for the application of polymers in the adsorption and chromatography has been demonstrated.

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