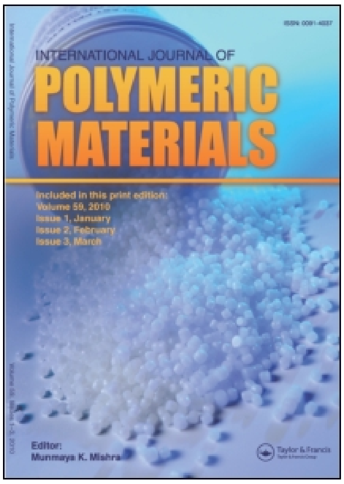

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SORPTION OF IONS OF HEAVY METALS BY NEUTRAL HYPERCROSSLINKED POLYSTYRENE

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Sorption of acetates and nitrates of mercury, lead, silver and bismuth from acetate buffers or nitric acid solutions by three types of neutral hypercrosslinked polystyrene materials has been studied. The sorbents were prepared by crosslinking either linear polystyrene or a styrene-0.7% DVB copolymer with monochlorodimethyl ether or p-xylylene dichloride, the degree of crosslinking amounting to 100% and more. The commercial hypercrosslinked sorbent, Macronet Hypersol MN-200 (Purolite), was used in the study, as well. The sorption of the above salts appears to be caused by the formation of π-complexes between the metal cations and two (or more) benzene rings of the hypercrosslinked polystyrene. The formation of the complexes was found to proceed slowly at room temperature with the rate depending on the network mobility and "pore" size. The sorption isotherms for mercury proved to be characterized by strong hysteresis, but, the mercury absorbed can be easily removed by washing the sorbent with HC1 or EDTA solutions. At a concentration of less than 20 mg/ml, MN-200 exhibits the largest capacity for mercury ions, up to 200 mg/g. At higher concentrations, the sorption capacity of the polymer based on styrene-DVB copolymer rises to 400 mg (or 2 mmol Hg) per 1 g of the polymer. The sorption of the other aforementioned ions is markedly lower and reversible.

Keywords: hypercrosslinked polystyrene sorbents, absorption, complexes, transition metal ions

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1. INTRODUCTION

Two sorption mechanisms of metal ions from aqueous solutions onto styrene-divinylbenzene (DVB)-based adsorbents are well documented in the literature, with sorption proceeding either by ion exchange or the formation of complexes. In the latter case, chelating functional groups, for example, imino diacetate, have to be introduced into the copolymer. It has been unexpectedly found however, that neutral hydrophobic hypercrosslinked polystyrene containing no polar functional groups at all, can also bind ions of heavy metals [1], first of all, the ions of Hg^{2+}. The quantity of mercury absorbed can reach a very high value, 400 mg/g. Undoubtedly, this non-trivial fact deserves a more detailed investigation. This paper describes basic regularities of the sorption of Hg^{2+}, Ag^{+}, Pb^{2+} and Bi^{3+} on three types of the hypercrosslinked polystyrene materials that differ in structure, pore size and network mobility.

2. EXPERIMENTAL

2.1. Synthesis

The hypercrosslinked polystyrene samples used in this study, were prepared as follows.

Sorbent l-XDC. 10.4 g (0.1 mole) of linear polystyrene of a molecular weight of *circa* 300.000 Da and 8.75 g (0.05 mole) of p-xylylene dichloride were dissolved in 150 ml ethylene dichloride. The solution was cooled to 0 to $-10^{\circ}C$ and 26.0 g (0.1 mole) of $SnCl_4$ were added. The mixture was agitated quickly and thoroughly and afterwards heated at 80°C for 10 h. The dark gel formed in this crosslinking reaction was desintegrated and washed with acetone, 0.5 N HCl solution and water till the complete absence of chloride ions in the water (test with $AgNO_3$). With the mole ratio of styrene repeating units to the bifunctional crosslinking reagent being 1:0.5, the formal crosslinking degree of the gel thus formed amounted to 100% [2]. The apparent inner surface area, S, of the polymer was found to be 1000 m^2/g, the pore volume was 0.6 cm^3/g, pore diameter was approximately 2–3 nm. The above values of S were measured by the low temperature sorption of argon (single-point BET-method) and the pore volume was calculated from the data on determining the true and apparent densities.

Sorbent 2-MCDE. Spherical gel-type copolymer of styrene with 0.7% divinylbenzene was obtained by conventional suspension polymerization. 10.4 g (0.1 mole) of the copolymer were swollen at room temperature in a solution of 8.05 g (0.1 mole) of monochlorodimethyl ether (MCDE) in 80 ml ethylene dichloride for 1 h and then supplied, under an extensive agitation, with 26.0 g (0.1 mole) of $SnCl_4$. The mixture was gently agitated for 10 h at 80°C. The final dark beads were filtered and carefully washed as described above. The crosslinking degree of the material thus synthesized significantly exceeded 100% [3]. Two additional sorbents, 3-MCDE and 4-MCDE, were prepared in a similar manner, but with the use of 0.5 moles of MCDE, to arrive at the formal degree of crosslinking of 100%. For the above set of polymers, the S-values were found to be 1500, 1000 and, unexpectedly, 400 m^2/g, respectively. The pore volume was 0.2–0.3 cm^3/g for samples 2-MCDE and 3-MCDE. The former sorbent exhibited pores of 2 to 3 nm in diameter, the latter had pores of slightly smaller sizes.

The commercial hypercrosslinked sorbent Macronet Hypersol MN-200 produced by Purolite International Ltd. (Great Britain) was also examined. According to the manufacturer's data, S amounted to 800–1000 m^2/g, pore volume was 1.1 cm^3/g. MN-200 had two types of pores, namely, micropores of 1.5 nm in diameter and large transport pores of 80–100 nm [4].

Prior to the sorption, all polymer samples were washed with acetone and then with a large amount of doubly distilled water. The excess of the latter was removed by centrifugation at 4000 rpm for 15 min.

The sorption of $Hg(CH_3COO)_2$ and $Pb(CH_3COO)_2$ occurred from acetate buffers with pH 4 and 5, while sorption of $Hg(NO_3)_2$, $AgNO_3$ and $Bi(NO_3)_3$ was carried out from aqueous nitric acid solutions with pH 3–4. Equal weighted amounts of polymers swollen with water, typically 0,4 to 0,8 g, were shaken with 10 ml of the above salt solutions of different concentrations for several days. The concentration of mercury ions in the final equilibrium solution was then determined either by titration with potassium rhodanide in the presence of ammonium iron alum or by using the spectrocolorimetric method based on the formation of a colored complex between mercury and dithizone [5]. The amount of mercury sorbed was also determined by the element analysis of isolated and dried polymer samples. The latter method was also used for the quantitative determination of sorbed lead, silver and bismuth ions. Prior to the analysis, the sorbents were filtered from the equilibrium solutions and dried at 80°C.

The thermodilatometric measurements were performed using UIP-70 equipment (Russia) on individual polymer beads with a diameter of between 650 and 700 microns. The experiments were repeated on 3 beads for each polymer. The relative change in the bead diameter, Δh, was calculated as $\Delta h = [D - D_o)/D_o] \times 100\%$, where D and D_o are the current and the starting diameter of the bead.

3. RESULTS AND DISCUSSION

The sorption of mercuric salts by neutral polystyrene-type materials proceeds very slowly. When examining the sorbent on the base of styrene-0,7% DVB copolymer, 3-MCDE, the adsorption capacity does not exceed 20 mg/g within the first 24 hours (Fig. 1). However, the amount of mercury absorbed increases to 180 mg/g in a week. Final equilibrium is established not earlier that within 8 days, leading to the incorporation of 200 mg of mercury per one gram of the final polymer. The equilibrium of sorption on MN-200 is reached even slower. No less then 300 hours are needed to introduce the above amount of mercury into the polymer.

Of course, the slow approach to the sorption equilibrium cannot result from a slow diffusion of the small ions into sufficiently large pores of the polymers. Neither can ineffective stirring and, as a consequence, a considerable thickness of the stationary film around the polymeric beads, explain satisfactorily the slow establishment of the equilibrium. Interestingly, the process of sorption was found to markedly accelerate at elevated temperatures (Fig. 2). If at room temperature it has been possible to introduce 50, 110 and 200 mg/g of mercury into 3-MCDE within 30, 70 and 140 hours, respectively, the sorption capacity of the sorbent at 55°C rose to 360 mg/g in 20 hours and 420 mg/g within 60 hours. This intensive increase in the sorption rate and capacity suggests that the uptake of Hg^{2+} ions represents a process differing from a trivial adsorption. In order to understand

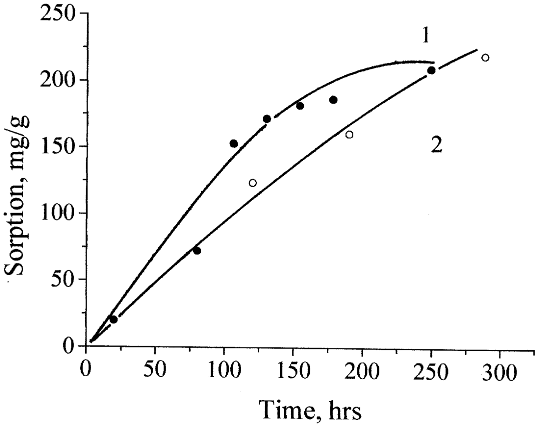

FIGURE 1 The sorption of mercury nitrate from diluted nitric acid on 3-MCDE (1) and MN-200 (2) at the initial concentration of the salt 31.2 (1) and 17.05 mg/ml (2) *versus* time.

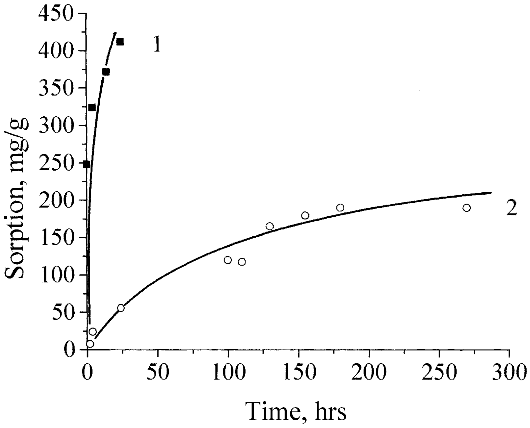

FIGURE 2 Sorption of mercury nitrate on 3-MCDE at 55°C (1) and 20°C (2) *versus* time.

whether or not the sorption is accompanied by a chemical reaction, the following experiments were performed.

Sorbents 2-MCDE, 4-MCDE and MN-200 were mercurated under standard conditions [6] by treating the polymers with an excess of mercury acetate in glacial acetic acid in the presence of $HClO_4$. Table 1 shows that all the polymers incorporate 30% of mercury. However, in another mercuration experiment, it proved to be possible to introduce as much as 55% of the metal into polymer 3-MCDE. This amount corresponds to 1.2 g of mercury per one gram of the initial polymer or one Hg atom per two phenyl rings. When using nitrobenzene as the solvent for the mercuration, the degree of substitution on benzene rings of the latter polymer decreases a little, but the polymer still

TABLE 1 The Content of Chemically Bonded Mercury in the Hypercrosslinked Polystyrene Samples before and after Washing

			Mercury content, %, after washing with	
Sorbent	S_{app} m^2/g	Initial content of Hg, %	1 M HCl	0.2 M EDTA
2-MCDE	1500	34.4	29.8	28.0
MN-200	1000	28.3	28.0	24.5
4-MCDE	400	27.1	ND*	26.0

*ND-not determined.

takes up 47% of the metal. It should be emphasized that, under the same conditions, only 8% of mercury can be introduced into a gel-type styrene-2% DVB copolymer highly swollen with nitrobenzene, and about 30% of the metal into a macroporous polystyrene sorbent Amberlite XAD-2 [7]. Undoubtedly, porous sorbents with a very high content of chemically bonded mercury are of particular interest for the selective absorption of halogen ions or S-containing organic substances, for example, S-containing peptides. For these purposes as well as for the present study it is very important to note that neither 1 M solution of hydrogen chloride, nor 0.2 M solution of ethylenediamine tetraacetic acid (EDTA) can break the chemical covalent CHg bond, and the above reagents do not elute mercury from the mercurated polystyrene (Tab. 1).

Mercury ions absorbed by the polymer are also strongly retained by the material. Even the exposure of the sorbent to a fresh portion of the acetate buffer for a period of two weeks, results in an insignificant removal of mercury ions, only (Tab. 2). The removed portion mainly belongs to the equilibrium solution which fills the pores of the material. The metal sorption isotherms are thus characterized by a very strong sorption hysteresis. However, a complete and fast desorption of the retained mercury ions occurs easily at treating the sorbents with solutions of either hydrogen chloride or EDTA. Consequently, the absorption of mercury into the hypercrosslinked polystyrene was not accompanied by the formation of chemical covalent C–Hg bonds.

Figure 3 compares the sorption isotherms for mercury acetate from the buffer solution onto the hypercrosslinked sorbents which have different structures. One can see that the sample based on styrene-0.7% DVB co-polymer and exhibiting the smallest apparent inner surface area of 400 m^2/g, absorbs the smallest amount of the mercuric salt, no more than 100 mg/g. As compared to this sample, 2-MCDE

TABLE 2 Removal of Mercury Absorbed by the Hypercrosslinked Polystyrene Samples

			Mercury content, % after washing with		
Sorbent	S_{app} m^2/g	Initial content of Hg, %	Acetate buffer	1 M HCl	0.2 M EDTA
2-MCDE	1500	21.0	18.9	2.02	2.8
MN-200	1000	17.6	13.3	0.02	1.4
4-MCDC	400	10.2	6.8	0	0

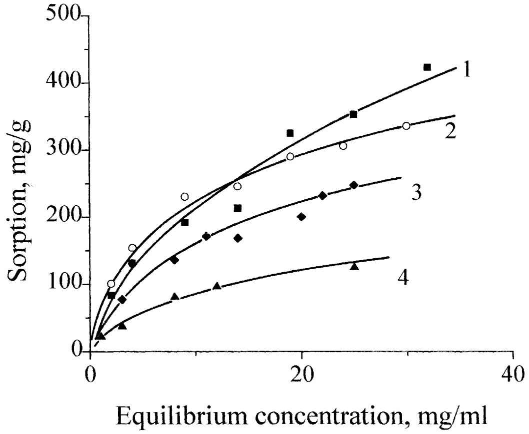

FIGURE 3 Sorption isotherms for mercury acetate from acetate buffer on 2-MCDE (1), MN-200 (2), 1-XDC (3) and 4-MCDE (4).

having surface area of 1500 m^2/g, is capable of absorbing significantly larger amounts of the salt, up to 420 mg/g. The sorption isotherm on sample l-XDC based on the linear polystyrene, locates between the above two isotherms belonging to 2-MCDE and 4-MCDE. MN-200 exhibits the highest sorption capacity if the equilibrium concentration of the solution is less than 20 mg/ml, however, this sorbent takes smaller amounts of mercury from more concentrated solutions than 2-MCDE does.

The type of the anion of the metal salt does not affect noticeably the sorption capacity of the samples based on the styrene-DVB copolymer, while the hypercrosslinked sorbent on the base of linear polystyrene better absorbs the mercury acetate (Fig. 4).

The aforementioned experimental results allow us to conclude that the acetate and nitrate salts of the bivalent mercury form complexes, most probably, the charge transfer or π complexes with solvent-exposed phenyl rings of polystyrene chains. For this reason we prefer to use the term absorption, rather than adsorption, to denote the process of incorporating heavy transition metal ions into the polymeric phase of the hypercrosslinked polystyrene material.

The hypercrosslinked sorbents on the base of both linear polystyrene and styrene-DVB copolymers are homogeneous one-phase polymers. Their structure represents the ensemble of mutually condensed and interpenetrating meshes formed by polystyrene chains and cross-bridges between the latter [8]. The identical structure is also characteristic of the polymeric microphase in the biporous MN-200. In

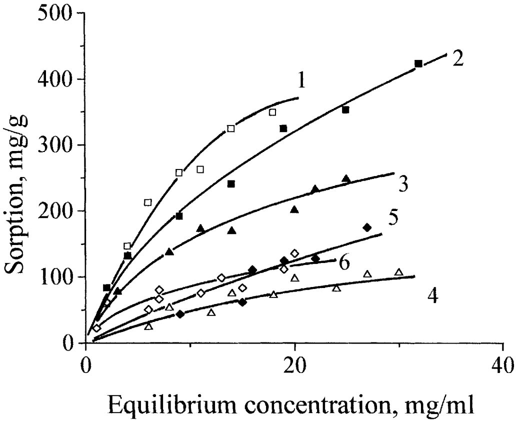

FIGURE 4 Sorption isotherms for mercury nitrate (1, 3, 5) from diluted nitric acid and mercury acetate (2, 4, 6) from acetate buffer onto 3-MCDE (1, 2), 1-XDC (3, 4) and 1-MCDE (5, 6).

such an open-work and permeable structure, most phenyls should be accessible for the interaction with the metal ions that display an affinity to aromatic systems. Obviously, at least two phenyl groups participate in the formation of the complex with one ion of mercury. If the coordination stoichiometry were 1 to 1, the complex formation would proceed much quicker, because no significant sterical obstacles exist for the diffusion of small inorganic ions into relatively large meshes of the hypercrosslinked network. On the contrary, the formation of a 2 : 1 complex has to proceed slowly, because it needs time for two phenyl rings to fit into the metal ion coordination sphere, which, in its turn, requires a cooperative conformational rearrangement of the rigid network. The slow approach to the metal coordination equilibrium thus reflects the slow shift of the whole system towards the global minimum of energy of two coupled processes, the formation of coordination bonds and conformational rearrangement of the highly crosslinked polymeric ligand. This situation differs fundamentally from generally very fast adsorption processes of organic compounds on the hypercrosslinked polystyrene adsorbing materials.

In a rigid hypercrosslinked network, polymeric chains and cross-bridges are located at a certain distance from each other. Unfortunately, the dimensions of the free space inside the meshes (so-called "pores") are not yet precisely known. It is quite evident, however, that the size of the opening depends on the starting concentration of polystyrene chains in the initial system that is subjected to cross linking. At the same crosslinking degree of the final network, the higher the concentration of the initial polymeric solution, the larger the number of polystyrene chains that is embraced by each mesh and the smaller the free space inside the mesh. This increase in the interpenetration of network meshes not only hinders the diffusion of free molecules but also restricts significantly the mobility of the hypercrosslinked network. In accordance with these suppositions, the polymer based on linear polystyrene should exhibit both the largest "pores" and the largest conformational mobility, while the smallest ones should be characteristic of MN-200. There exists some indirect evidence which supports the above suggestion. For example, the swelling of sorbents with water decreases in the sequence 1-XDC $>$ 3-MCDE $>$ microphase of MN-200, it being 0.85, 0.50 and 0.20 ml/g, respectively. Smaller dimensions of micropores in MN-200 in comparison to those in the 3-MCDE-type hypercrosslinked material were also found by gas chromatographic technique [9].

Relatively large dimensions of "pores" in 1-XDC appear to hinder the effective complexation of metal ions. That is why the sorption capacity of this sorbent is smaller than that of 2-MCDE. In the structure of MN-200, the spatial arrangement of aromatic rings seems to favor the formation of complexes. As a result, this sorbent, at low and moderate salt concentrations, takes up mercury better than the other sorbents. However, this polymer, being the most rigid and inflexible, acts slowly and yields in its final sorption capacity to sample 2-MCDE at higher salt concentrations (Fig. 3).

The formation of complexes which involve two (or more) aromatic rings should additionally diminish the mobility of the hypercross linked network, because the complexes act as additional crosslinks. The restriction in the network mobility can indeed be revealed by comparing the thermodilatometric behavior of the analogue of 3-MCDE (obtained on the base of styrene-0.3% DVB copolymer and having S of 950 m^2/g) before and after the sorption of mercury ions (Fig. 5). All sample beads exhibit expansion on heating to $200-250°C$. Although the differences are not very large, the samples coordinated to mercury demonstrate a noticeably smaller volume expansion. Breakdown and destruction of the hypercrosslinked network at higher temperatures is not discussed here.

The accessibility of aromatic rings of polystyrene chains for the coordination interaction with mercury, which is characteristic of the hypercross-linked polymers studied, was also found to characterize the macroporous polystyrene sorbent Amberlite XAD-4. Albright *et al.* [10] considered 42.3% of phenyl groups in this copolymer to be located on the walls of pores. Accordingly, XAD-4 also absorbs up to 300 mg/g of mercury. In this case, too, the equilibrium is established slowly. The

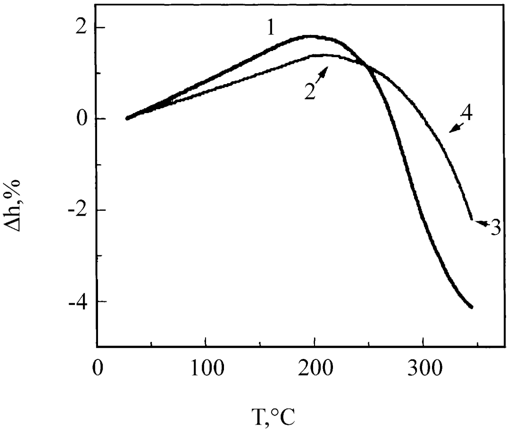

FIGURE 5 The thermodilatometric curves for the hypercrosslinked sorbents before (1) and after the sorption of 7.6 (2), 11.2 (3) and 16.5% (4) of mercury (mercury acetate from acetate buffer).

metal ions coordinated are then firmly retained and they cannot be removed by simple washing with a fresh portion of the buffer.

Beside mercury, some other transition metal ions were found to bind to hypercrosslinked polystyrene sorbents, though less effectively. One gram of the polymer 2-MCDE takes up approximately 170 mg of silver from a dilute nitric acid solution and about 80 mg of lead from a solution of lead acetate in an acetate buffer (Fig. 6). Bismuth ions are sorbed to somewhat smaller extent. Yet, according to the data of element analysis, the polymer retains 6% Bi^{3+}. Contrary to the mercury ions, the sorption of silver, lead and bismuth ions is reversible, the above ions being easily removed from the polymer by washing the latter with a fresh portion of buffer or a solution of nitric acid.

No noticeable sorption of Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} and Fe^{3+} was found to occur from solutions of corresponding nitrates in diluted nitric acid at room temperature. These metal ions definitely have higher affinity to water molecules than to π electrons of the aromatic rings. This finding does not contradict, however, the observation by Sutton *et al.* [11] that a chromatographic column with a microparticulate unmodified MN-200 quantitatively separates mixtures of ions of Bi^{3+} and Pb^{2+}, as well as mixtures of Zn^{2+} and Cd^{2+}. Chromatography is exceptionally sensitive in detecting weak interactions between the ions and the column packing material. Whereas these findings can open new possibilities for the ion chromatographic analysis of metal ions, the results of the above static sorption

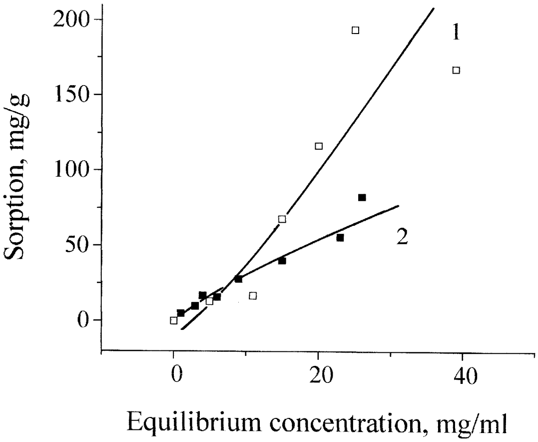

FIGURE 6 Sorption isotherms for silver nitrate (1) from diluted nitric acid and lead acetate (2) from acetic buffer onto 2-MCDE.

experiments may prove of great interest for practical removal of traces of heavy metal ions from potable or waste water streams.

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