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Study of the Structure of Chelate Fibrous Ionites by IR Spectroscopy

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Abstract—Structure of fibrous chelate ion exchangers FIBAN X-1 and FIBAN X-2 prepared by a two-step synthesis was studied by IR Fourier spectroscopy. The first step of the ion exchanger preparation consists in the production of an aminated fiber (AF). The process can be carried out in different phases: either vapor, or aqueous. It is found that conditions of the synthesis of AF affect differently the ion exchanger structure. For the ion exchanger FIBAN X-1 it does not a matter in which phase is AF synthesized, and the FIBAN X-1 sorbent has amidoamine structure. The structure of chelate ion exchanger FIBAN X-2 depends on the conditions of the synthesis of AF. When the process is carried out in aqueous medium the FIBAN X-2 has amidoamine structure, while amination in the vapor phase leads to formation of the FIBAN X-2 ion exchanger mainly containing in its structure imidazoline rings.

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Increasing technogenic influence on the environment affects negatively the drinking water quality, both underground water near the water intakes and the water in open basins, the latter even to a greater extent. It has been revealed that drinking water is contaminated with heavy and transition metals. The problem of purification of drinking water from the bivalent iron and manganese ions and other cations of heavy and transition metals was solved in the Institute of Physical Organic Chemistry, National Academy of Sciences of Republic Belarus, where a new fibrous chelate ion exchange material FIBAN was synthesized [1–4]. The advantage of the chelate ion exchangers over common ion exchangers in the process of water purification from the ions of the complex forming metals is well known [5, 6]. The chelate fibrous sorbents differ from the sorbents of other types by the presence of the functional groups capable of interaction with the metal ions in water with the formation of chelate complexes. These groups were introduced into a polymer matrix consisting of "Nitron" PAN fiber produced by Novopolotsk united plant "Polymer" by a two-stage synthesis. The first step of the process is amination of the PAN fiber with polyethylenepolyamines: ethylenediamine (EDA) and diethylenetriamine (DETA). The fiber amination can be carried out either in aqueous solution (water phase) or in the amine vapor (vapor phase). The second step of the process is alkylating the aminated fiber with monochloroacetic acid or its sodium salt. Study of sorption properties of fibrous sorbents FIBAN X-1 (aminated with EDA) and FIBAN X-2 (aminated with DETA) showed that the ion exchangers FIBAN X-2 prepared in the first step in vapor phase adsorbs manganese ions from water 2–3-fold better than the ion exchanger prepared in water phase [7, 8].

In this work the structure of chelate fibrous ion exchangers was studied by the method of IR Fourier spectroscopy in relation to the conditions of the amination reaction of PAN fiber.

We chose as objects 8 samples, of them four samples of intermediate aminated fibers obtained by amination of PAN-fiber with EDA in water (AFEW) and in vapor (AFEV) phases, the samples obtained by amination of PAN-fiber with DETA in water (AFDW) and vapor (AFDV) phases, and chelate ion exchangers: FIBAN X-1(W), obtained by alkylation of AFEW, ion exchanger FIBAN X-1(V) from AFEV, ion exchanger FIBAN X-2 (W) synthesized by alkylation of AFDW and FIBAN X-2 (V) prepared from AFDV.

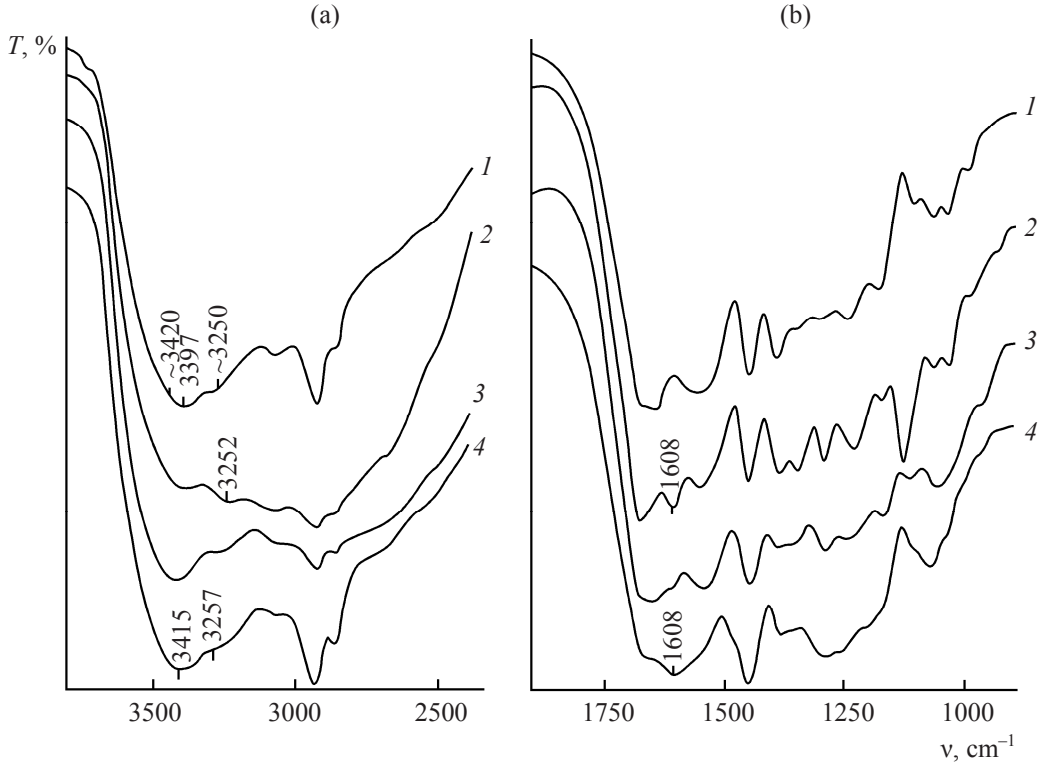


Fig. 1. IR spectra of PAN-fiber aminated with EDA in (*1*) water and (*2*) vapor phases, with DETA in (*3*) water and (*4*) vapor phases.

In Fig. 1 are presented the general IR spectra of the samples AFEW, AFEV (spectra *1*, *2*) and AFDW, AFDV (spectra *3*, *4*). The spectra in the region of 1700–1500 cm^{-1} used for the identification of samples consist of a series of broad asymmetric and poorly resolved absorption bands, therefore we used instead the derivatives of the spectra, namely, selfdeconvolution spectra where the half-width of the individual bands in a complex spectrum were considerably diminished while simple bell-like form of the resulting contour remained [9]. The results of investigation are shown in Fig. 2. As seen from the image, the derivatives spectra reveal the number of overlapping absorption bands and allow the determination with better precision of their maxima positions. In the IR spectra of AFEW (Figs. 1, 2, *1*) there are absorption bands at 1681, 1642, 1560, and ~3250 cm^{-1} characteristic of the vibrations of C=O and N–H bonds of the secondary amide. Besides, on the high-frequency slope of the broad absorption band at 3500–3330 cm^{-1} in the general spectrum (Fig. 1a, *1*) and on the low-frequency slope of the absorption band at 1681 cm^{-1} in the derivative spectrum (Fig. 2, *1*) weakly expressed inflections can be seen at ~3420 and ~1665 cm^{-1}, respectively, that characterize stretching and bending

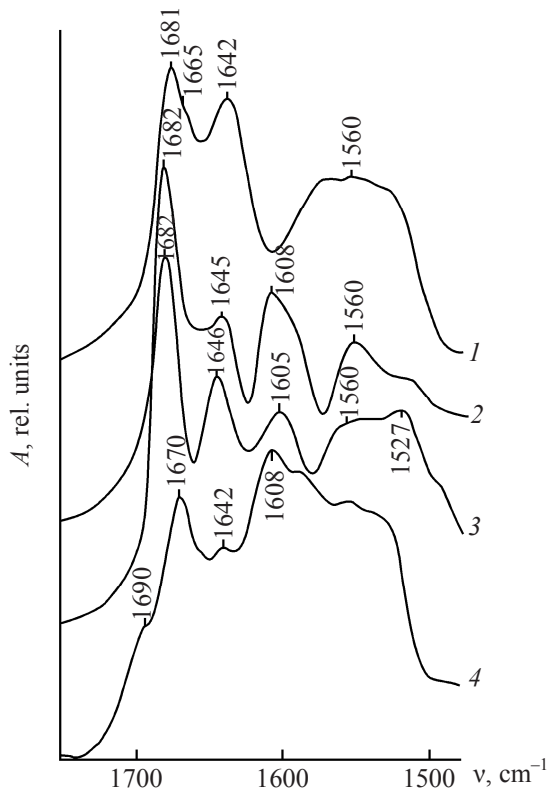
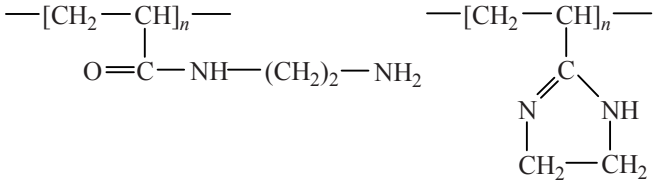


Fig. 2. Derivative IR spectra of PAN-fiber aminated with EDA in (*1*) water and (*2*) vapor phases, with DETA in (*3*) water and (*4*) vapor phases.

vibrations of the primary amino group. In the IR spectra of AFEV an absorption in the region of 1608 cm^{-1} (Fig. 1, *2*) appears that is not observed in the case of the samples of AFEW (*1*). According to [10] the absorption at 1610–1607 cm^{-1} is characteristic of the systems containing in their structure imidazoline ring, and it corresponds to the vibration of C=N bond. Besides, in the IR spectra of AFEV there are absorption bands of low intensity at 1682, 1645, 1560, 3252 cm^{-1}, characterizing the presence of some amount of secondary amide.

According to these spectral data the structure of AFEW obtained by amination of PAN-fiber in water phase can be represented as a completely amidoamine structure **I**, while the structure of AFEV obtained by amination of PAN-fiber in vapor phase can be regarded as consisting mainly of imidazoline structure (**II**) and partially containing a fraction of aminated fiber with linear amidoamine structure **I**.



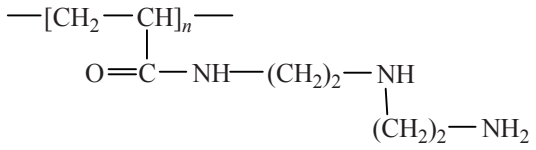
I

II

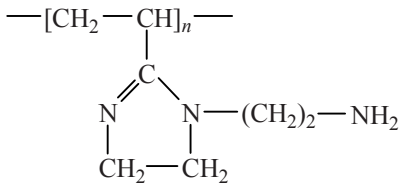
Analysis of the IR spectra of fibers AFDV and AFDW obtained by amination with DETA also showed difference in the spectra of the samples aminated in the alternative phases. From the derivative spectrum of the sample AFDW (Fig. 2, *3*) follows that in the spectra the absorption bands at 1682, 1646, 1560 cm^{-1} appeared owing to the secondary amide groups. In the spectrum a band is clearly seen belonging to the bending vibrations of secondary amino group at 1527 cm^{-1}. In addition, in the general IR spectra absorption band at 3257 cm^{-1} was observed that also characterizes stretching vibrations of secondary amino group [11]. A band at 3415 cm^{-1} (Fig. 1a, *3*) corresponds to the stretching vibrations of primary amino group. In the spectrum of AFDW a weak absorption band at 1605 cm^{-1} is present related to the vibrations of the imidazoline ring C=N bond.

In the derivative IR spectrum of AFDV (Fig. 2, *4*) there is an absorption band at 1608 cm^{-1} that corresponds to vibrations of C=N bond in the ring. There is also an absorption band at 1670 cm^{-1} typical of primary amino groups. Besides, there are a shoulder at ~1690 cm^{-1} and absorption bands of low intensity at 1642 and ~1560 cm^{-1} that suggest the presence of a small amount of secondary amide.

As a result of this investigation of structure of the fiber obtained by DETA amination in water phase we propose linear amidoamine structure (**III**) with a small fraction of imidazoline structure (**IV**), and for the fiber aminated in vapor phase the imidazoline structure **IV** with a small fraction of amidoamine structure **III**.



III



IV

The chelate sorbents FIBAN X-1 and FIBAN X-2 are formed by alkylation of the aminated PAN-fiber with monochloroacetic acid or its sodium salt. The IR spectra of these ion exchangers are shown in Figs. 3, 4. According to the IR spectra (Figs. 3, 4, *1* and *2*) of the sorbent FIBAN X-1 obtained in the first step either in vapor or in water phase are identical. In the derivative spectra of FIBAN X-1 there are absorption bands at 1680, 1629, 1563 cm^{-1}, characterizing the presence of amide structure. The absence of a band in the region of 1670–1660 cm^{-1} that would belong to a primary amino group shows that alkylation reaction has occurred. Therewith appeared absorption bands at 1731 cm^{-1} and a broad band at 2700–2500 cm^{-1} related to the vibrations of C=O and O−H bonds in COOH group respectively. From the IR spectra of FIBAN X-1 follows that in the process of alkylation of the aminated fiber in water alkaline solution a cleavage occurs of the imodazoline ring in AFEV, and the alkylation proceeds at the primary amino group of the amidoamine. The same opening of imidazoline ring in alkaline medium has been observed by Kasperchik et al. [12]. The results obtained showed that at the synthesis of the sorbent FIBAN X-1 the medium where was performed the amination did not matter. The final chelate ion exchanger FIBAN X-1 contains only linear amido-amine structures. The addition of monochloroacetic acid occurs at the primary amino group to form the chelate structure.

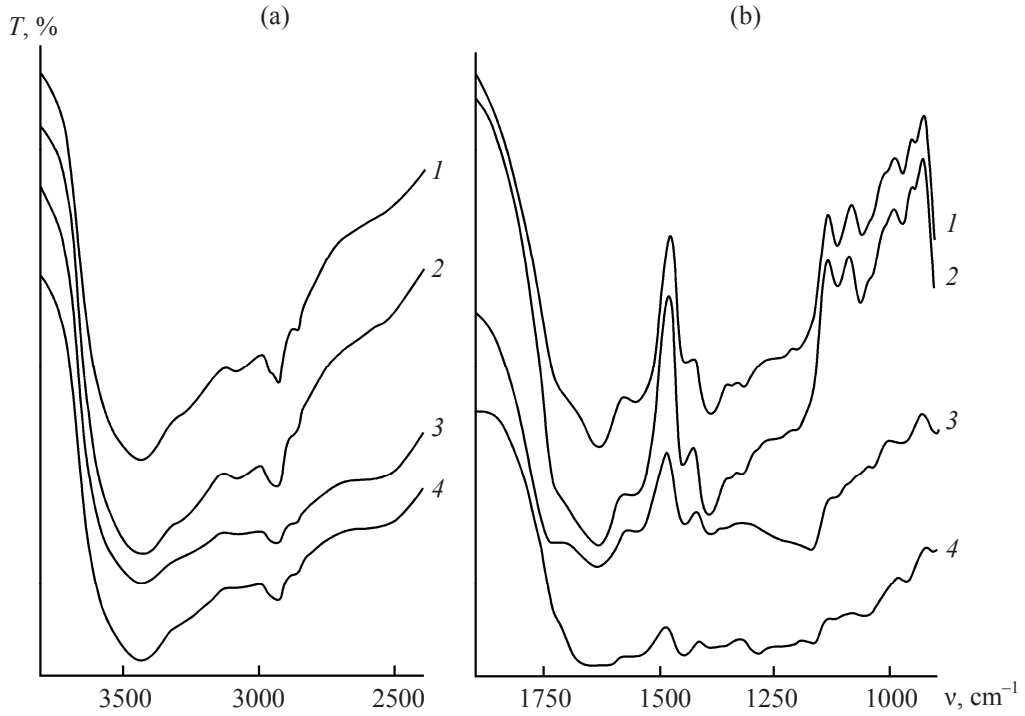
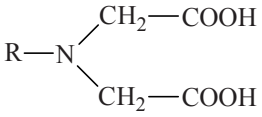


Fig. 3. IR spectra of chelate sorbents FIBAN X-1 obtained in (*1*) water and (*2*) vapor phases and FIBAN X-2 obtained in (*3*) water and (*4*) vapor phases.



Analysis of the spectra of chelate sorbent FIBAN X-2 that is obtained by alkylation of the PAN-fiber aminated with DETA shows a difference in the IR spectra of chelate depending on the medium used in the first step. In the IR spectrum of FIBAN X-2(V) the strong absorption band at 1608 cm^{-1} (Fig. 4, *4*) that corresponds to C=N bond in the imidazoline ring is retained. In the spectra the absorption band at 1670–1660 cm^{-1} characterizing the primary amino group is lacking but appears absorption band at 1720 cm^{-1} that corresponds to C=O of iminodiacetate groups indicating the occurrence of the alkylation. The intensities of absorption bands at 1680, 1650, 1570 cm^{-1} belonging to the bonds of secondary amide group slightly increase as compared with the case of AFDV that indicates a partial opening of imidazoline rings at the alkylation and an increase in the fraction of amidoamine structure in the FIBAN X-2(V) ion exchanger.

The derivative IR spectrum of the ion exchanger FIBAN X-2(W) (Fig. 4, *3*) is rather complex as com-

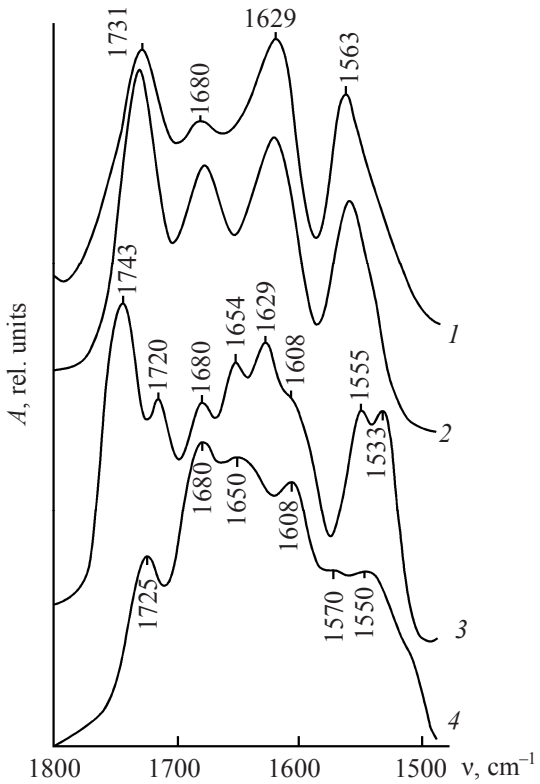
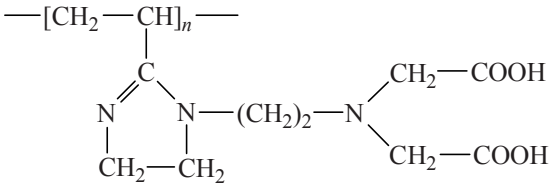


Fig. 4. Derivative IR spectra of chelate sorbents FIBAN X-1 obtained in (*1*) water and (*2*) vapor phases, and FIBAN X-2 obtained in (*3*) water and (*4*) vapor phases.

pared with the spectrum of FIBAN X-2(V). In the IR spectrum absorption bands at 1680, 1654, 1629 cm^{-1} are observed belonging to secondary amide and bands in the region of 1740–1720 and 2700–2500 cm^{-1} characteristic of the presence of COOH groups in the system. However, in the region of absorption of C=O bond appear two bands, at 1743 and 1720 cm^{-1}, instead of one at 1725 cm^{-1} as in the case of the sample of FIBAN X-2(V) that indicates that the formed COOH groups are not all alike. It can be assumed that the absorption band at 1720 cm^{-1} belongs to chelate C=O groups formed at the addition of monochloroacetic acid to the primary amino group while the band at 1743 cm^{-1} characterizes the C=O group of the monochloroacetic acid added to the secondary amino group of amidoamine. The shoulder at 1608 cm^{-1} shows the presence of some amount of the structure containing imidazoline ring in the ion exchanger.

Thus the synthesis of the fibrous chelate ion exchanger FIBAN X-2(W) leads to formation of the sorbent containing basically amidoamine structure **III**. The synthesis of the sorbent FIBAN X-2 performed in vapor phase in the first step leads to the chelate fiber that predominantly has structure with imidazoline ring **IV** while the ion exchanger with amidoamine structure is formed in a minor amount.

On the basis of the obtained results it is possible to explain (1) equal and not very high sorption of manganese from drinking water by the chelate sorbent F**I**BAN X-1 obtained at the carrying out first step either in water, or in vapor phase and (2) difference in sorption activity of the sorbent FIBAN X-2 depending on the conditions of the first step, namely, much higher sorption efficiency of the sorbent obtained in vapor phase. Probably the prevailing structure of the chelate sorbent FIBAN X-2(V) is much more appropriate for the formation of complex compounds with manganese ion and hence for better sorption of manganese.



The results obtained in this work allowed us to elucidate the structure of chelate fibrous sorbents FIBAN X-1 and FIBAN X-2 and to show that the conditions of the sorbent preparation not equally affect the structures of the two ion exchangers. The fibrous chelate ion exchanger FIBAN X-1 has amidoamine structure regardless the phase used in the first step of the process at the fiber amination: despite the fact that the structures of aminated fibers are different at the synthesis in vapor or in water phase, at the alkylation the imidazoline ring of the fiber aminated in vapor phase undergoes cleavage and the amidoamine structure is solely formed. The structure of the fibrous chelate ion exchanger FIBAN X-2 depends on the phase used for in first step of the process. At the amination of PAN-fiber in water phase the aminated fiber and the final ion exchanger FIBAN X-2 have amidoamine structure, while amination of PAN fiber in vapor phase leads to the structure containing mainly imidazoline rings in the aminated fiber and the final ion exchanger FIBAN X-2.

EXPERIMENTAL

The samples for recording IR spectra were prepared by ordinary procedure of pressing finely cut fibers with carefully dried powdered potassium bromide. The fiber concentration in the mixture was 1.5%. The spectra were registered on a Nicolet Protege 460 IR-Fourier spectrometer. Resolution 4 cm^{-1}, number of scans 256 for each spectrum. The mathematic treatment of both general and derived spectra was carried out with the service program package OMNIC, version 3.1a. For each fiber sample were measured the IR spectra from 3 separately prepared tablets.

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