Polymers, Metal Compounds and New Materials

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By

Vasile Gutsanu

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PREFACE

The monograph stands for an investigation of the interaction of strongly basic anion exchangers with some metal cations, a theoretically improbable process since such anionites have affinity towards anions. These polymers are produced at an industrial scale and are widely used in various chemical and technical operations, but most of all in the treatment of water at thermal and atomic power stations. Their interaction with metal cations, especially with iron, an unpredictable and uncontrollable process, leads to their intoxication and rapid exhaustion. However, if the interaction of these polymers with cations is controlled, then in the polymer phase, ultra-fine particles of the compounds are formed, that radically change their physical and chemical properties. These composites become selective sorbents and catalysts with good hydro and aerodynamic properties to conduct processes in flow, a key factor in technology. This is proven by patents on water purification from chromates, nitrate/nitrite, sulphides and air purification from iodine and hydrogen sulfide. These composites can be used to make anti-gas masks that would protect the personnel of atomic stations. The monograph shows for the first time that cations Fe^{3+}, Cr^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, lanthanide (III) in the phase of strongly basic anion exchangers form compounds of the jarosite mineral type. Bismuth (III) forms another type of compound. The compounds in the polymer phase, coordinating with polydentate ligands, allow the construction of various composite holding active multi-centres, which is very important, and not only for catalysis.

The jarosite is formed in the aqueous medium. That is why the discovery of the jarosite on Mars led to the discovery of water on the planet. Investigating the jarosite on Earth could give us much information about the evolution of the processes on some heavenly bodies. The catalytic properties of polymers modified with metallic compounds have not been practically studied. A wide field of activity opens up. The monograph shows that such composites can fix nitrogen from the air under normal conditions.

The monograph can be useful for chemists, technologists, environmentalists, specialists in the water treatment industry, chemical engineers, students and even mineralogists and others.

INTRODUCTION

What happens if a cross linked ionic polymer having strongly basic groups -$N(CH_3)_3Cl$ were to be placed in an electrolyte solution? Any chemist and not only chemists will say that there will be only a reversible and non-selective process of anion exchange: $R_4NCl + A^- \leftrightarrow R_4NA + Cl^-$. Due to this process such polymers are widely used in technologies of substances separation, concentration and water treatment. The positive aspect of these polymers is their ability to remove from solution all negatively charged particles regardless of their nature. This property, along with the property of the strongly acid cation exchangers to remove all particles with positive charges, is widely used to obtain deionized liquids, first of all water. The downside of the strongly basic polymers is that they are not selective. But the advanced technologies, especially in the chemical industry, medicine, analytical chemistry and environmental protection, need new adsorbents and catalysts with selective properties. The properties of polymers, containing strongly basic groups, would change essentially if they could be synthesized using metal compounds in their phase. However, their polymer matrix does not contain negatively charged or electron-donor atoms and, theoretically, they cannot interact with cations. Surprisingly, our investigation showed that under certain conditions these polymers can interact with metal cations from solutions such as Fe^{3+}, Cr^{3+}, Al^{3+} and others.

In this book the research findings of the interaction of cations containing Fe(III), Cr(III), Al(III), Ga(III), In(III) , Lanthanides (III) and BI(III) are discussed. In fact, hydroxocations, rather than hydrated metal cations, interact with functional groups of polymers. The processes, involving ionic cross-linked polymers containing strongly basic groups, were performed using the Mössbauer spectroscopy. In the second part of the book the results of applied research with the use of polymers containing metal compounds into their phase, using FTIR and EPR spectroscopy, SEM, powder X-ray diffraction and thermogravimetric analysis are presented. The book contains research findings of some unusual and incredible processes.

PART I.

METAL COMPOUNDS IN THE POLYMER PHASE

I.

IRON (III) COMPOUNDS IN THE POLYMERS PHASE

1.1. Historic

How did we get the idea to do such researches, the results of which are presented in this book? Was it mere chance or regularity? Firstly, we investigated the sorption of metal cations on different cross-linked ionic polymers [1-3]. We investigated the sorption of Zr(IV), Cr(III), Al(III), Fe(III), Fe(II), Co(II), Ni(II), and Cu(II) containing cations on different polymers (sulfocationites KU 1, KU 2, carboxylic cation exchangers KB-2, KB-4 , exchangers containing amino groups AV-16, EDE-10P, AN-2FN, AN-31 and strongly basic exchanger AV-17 [4]) in a wide range of pH of the solution with the use of so-called "nuclear filter" [5-7]. We have observed that the sorption, in the function of the pH, passes through maximum, which is usually in the range of pH in which existed hydroxide precipitate. Most of the research has been devoted to the complexation processes of metal cations with amine groups of the polymers. It was proved that sorption of Cu^{2+} ions from mixtures of metallic cations on the polymers that contain amine groups is contrary to the Langmuir sorption model. For example, the Cu^{2+} ions sorption by the polymer EDE-10P in solutions containing mixtures of $ZnSO_4$ and $CdSO_4$ is much higher than in their absence, although cations Zn^{2+} and Cd^{2+} also coordinates the amine groups [8-10]. It was shown that the nature and concentration of anions (SO_4^{2-}, NO_3^-, ClO_4^- F^-, Cl^-, Br^-) significantly influence the complexation of Cu^{2+} ions with the amine groups of the polymers [11-16]. Some anions influence positively and others negatively, the metallic cations sorption (complexation) on the polymers holding amine groups. Who could believe that anions can influence, especially negatively, complexation of the cations with amine groups of the polymers? Because of this, in many works the influence of the nature and concentration of the anions on the sorption of metal cations by amine polymers was neglected. Our research has shown that the influence of the nature and concentration of ions on the processes of complexing in the amine polymers phase is manifested in two ways. Anions influence the degree of protonation-deprotonating of amine groups and complexation can occur only with deprotonated groups [17, 18]. On the other hand, some anions coordinate the cations which are already linked to the amine groups. These processes correlate with each other. The investigation, conducted using EPR spectroscopy, showed that in the phase of amine polymers the anions SO_4^{2-}, F^-, Cl^- and cations Cu^{2+} form different isomeric complexes [18]. It also was seen that the nature and concentration of the anions affects differently the process of complexation of Al (III) and Fe (III) having cations with the carboxylic acid groups of the polymers [19-21].

Studying the influence of the anions on the complexation of metal cations with amine groups, we asked whether cations are retained in the polymer phase due to the formation of complexes with negative charges. To answer this question, we introduced a monofunctional cross-linked ionic polymer sample, which held groups of the type $-N(CH_3)_3Cl$ in a solution of $Fe_2(SO_4)_3$.

As known, strongly basic anion exchangers do not hold negatively charged or electron donor atoms in their matrix and, theoretically, they cannot interact with metal cations. They can retain only particles with negative charges. The decision to choose the electrolyte $Fe_2(SO_4)_3$ was determined by the fact that the sorption process can be investigated using Mössbauer spectroscopy that allows us to find whether the sorption occurs through anion exchange or by formation of coordinative bonds. The results of these tests will be depicted in the following paragraphs.

1.2. Iron compounds formed in phase of strongly basic anion exchanger

1.2.1. Transformations in Fe(III)-containing polymer on heating in air

Surprisingly, we have observed [21], that at room temperature cross linked ionic polymer AV-17(Cl) containing quaternary ammonium groups, can sorb Fe(III)-containing cations from sulfate solution, but not from chloride (in the absence of $[FeCl_4]^-$ in the solution) or nitrate solutions. The effects of Cl^-, SO_4^{2-} and other factors on Fe(III)-containing cations sorption by AV-17(Cl) [22-24] were evaluated by mathematical statistical techniques (the response surface methodology-the E.P.Box and K.B.Wilson method) [25]. The Student criterion of the coefficients significance in the regression equations (b_{sig}) was calculated at a level of significance of 5 % and number degree of freedom f =7. These effects are expressed by Equation (1-1), where Y is adsorbed iron (mg Fe/g):

$$Y = 3.074+1.566\,X_1-0.840\,X_2+0.969\,X_3-1.139\,X_4+0.790\,X_5,\quad B_{sig.}=t.s\{b_i\}=0.1759 \qquad (1\text{-}1)$$

The following notations are used with the variation intervals given in parentheses: X_1 = pH (1.6-2.0); X_2 = t (30-40°C); $X_3 = K_2SO_4$ (0.03-0.1 N); X_4= KCl (0.03-0.1N); X_5 = acetone (5-10 vol.%); X_6 = ethanol (5-10 vo.%) and X_7 = duration of polymer contact with solution (8-12 h).

An increase in the pH (X_1) and the concentration of SO_4^{2-} (X_3) and acetone (X_5) has a positive effect on Fe(III)-containing cations sorption by AV-17. On the other hand, an increase in the temperature (X_2) and the Cl^- concentration (X_4) has a negative effect on Fe(III)-containing cations sorption. The insignificance of the coefficient X_7 indicates that sorption equilibrium is almost set up after 10 h of polymer-solution contact. To elucidate the nature of the compounds that are formed in the polymer phase in contact with the solution of $Fe_2(SO_4)_3$, the following investigations were made. A commercial strongly basic anion exchanger [AV-17X8, holding $-N(CH_3)_3^+$ groups] in Cl form was used. The gel-type resin had a polystyrene – divinylbenzene matrix. Its full exchange capacity is 3.5– 4.0 mEq/g [4]. Dried polymer samples of 1 g were contacted with 500 mL of 0.01M $Fe_2(SO_4)_3$ solution for 24 h at room temperature, which was enough to set up equilibrium. The pH of the solution-sample systems was 2.0 ± 0.1. Following the contact with the solution, the samples were filtered, washed with distilled water, dried in air, and used for investigations. The Fe(III) content in the samples (12.5 mg/g ± 0.3 mg) was determined by the photo-colorimetry method [14] using 2,2-dipyridine after desorption with a solution of 1–1.5M HCl.

Samples of Fe(III)-containing polymer were heated in air at 100, 120, 140, 160, 180, and 200°C for 6–7 h. These samples were investigated by using Mössbauer, IR, and EPR spectroscopies. To modify the nature, content, and sizes of the Fe-containing particles of compounds in the polymer phase, several sorption– boiling in water cycles with samples of the exchanger were carried out. These samples were also investigated using Mössbauer spectroscopy. The EPR spectra were recorded at 300 K on a RE-1307 radio spectrometer with a 3-cm wavelength. The IR spectra were recorded at 300 K over the 400–4000 cm^{-1} interval on a SPECORD M-70 spectrometer. The Mössbauer spectra were obtained at 300 and 80 K.

NOTE: Here and further, the Mössbauer spectra were recorded on an ICA-70 spectrometer in the accelerated dynamic regime, and ^{57}Co in a Cr matrix was employed as the γ-ray source. In the case of spectra in the form of a doublet for determination of parameters such as isomeric shift (δ), quadrupole splitting (ΔE_Q), left line width (Γ_l), and right line width (Γ_r) of the doublet, sodium nitroprusside was used as the reference. In the case of spectra in the form of a sextet, metallic iron was used as a reference. The error of the intensity on the iron nuclei magnetic field ($H_{ef.}$) was ±5 kOe and for the other parameters was ±0.04 mm/s. All δ values are expressed relative to sodium nitroprusside.

Metallic compounds formed in the phase of strongly basic anion exchangers in contact with $Fe_2(SO_4)_3$ solutions are not $Fe(OH)_3$ or FeOOH. The Mössbauer spectra of the Fe(III)-containing strongly basic anion exchangers show large values of quadrupole splitting ($\Delta E_Q \sim 1$ mm/s) [26] whereas they are less for $Fe(OH)_3$ or FeOOH (about 0.7 mm/s). We suggest that the sorption of Fe(III)-containing ions from $Fe_2(SO_4)_3$ solutions on strongly basic anion exchangers takes place through formation in the polymer phase of $FeOHSO_4$ or jarosite mineral-type compounds $R_4N[Fe_3(OH)_6(SO_4)_3]$ and $H_3O[Fe_3(OH)_6(SO_4)_2]$ [27-29].

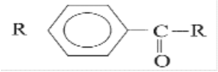
During thermal dehydration of $FeOHSO_4$, the ΔE_Q value increases from 0.97 to 1.5 mm/s at 298 K. Jarosite type compounds are stable to about 230 °C [30, 31]. One of the decay products at 230 °C is $FeOHSO_4$, which is stable up to 450–500 °C. However, when boiled in water, jarosite-type compounds of Fe(III) are transformed into highly dispersed particles of α-FeOOH [29] in the superparamagnetic state and the value of ΔE_Q decreases. Thus, the different behaviour of jarosite-type and $FeOHSO_4$ compounds on heating in air or boiling in water permit us to identify the nature of Fe(III) compounds in the polymer phase.

The Mössbauer spectra of the Fe(III)-containing samples of AV-17 heated at different temperatures present a doublet at 300 and 80 K [32]. Their parameters (Table 1-1) show that the Fe(III) states when heated to 160°C remain practically unchanged. Some changes observed in the spectral parameters of heated samples in the temperature interval from 120 to 160°C are conditioned by dehydration processes. In the heated samples transformations commenced at t >160°C, which resulted in partial reduction of Fe(III) to Fe(II) at 200 °C.

Table 1-1. Parameters of Mössbauer spectra of heated in air Fe(III)-containing AV-17 polymer

Temperature		Spectra parameters, mm/s			
Heating (^{0}C)	Spectrum recorder (K)	δ	ΔE_Q	Γ_l	Γ_r
120	300	0.62	0.88	0.59	0.56
	80	0.80	0.89	0.64	0.53
140	300	0.59	0.96	0.60	0.59
	80	0.74	0.94	0.55	0.56
160	300	0.51	0.99	0.74	0.63
	80	0.93	0.62	0.47	0.76
180	300	Unresolved spectrum			
	80	0.71	1.00	0.68	0.53
200	300	Unresolved spectrum			
	80	0.51	0.59	0.86	0.86
		1,35	2.72	0.53	0.53

Thus, the main conclusion of this part of the investigation is that the Fe(III) compound in the AV-17 phase is not $FeOHSO_4$, but it is probably a jarosite type compound. The reduction of Fe(III) to Fe(II) in the resin indicates mutual influences of Fe(III) compounds and the polymer on their thermal stability. Unresolved Mössbauer spectra of samples recorded at 300 K (Table 1-1) may be due to the breakimg of the polymer chain involving a large amplitude of the Fe(III)-containing particle vibrations. Supplementary information about changes taking place in the Fe(III)-containing polymer phase on heating in the air was obtained from EPR and IR spectra. In the EPR spectra of all heated samples, there are three spectral lines: one at $g = 4.3$ and two lines at $g = 2.003$. One of the lines at $g = 2.003$ is large, and another is narrow. The width of a large line is about 800 Oe for samples heated at $t \leq 140$ °C and decreases to 400 Oe for samples heated at $t > 140$ °C. The signals at $g = 4.3$ and 2.003 (wide line) are attributed to the Fe(III) ions in rhombic and octahedral surroundings, respectively [33]. As is known, jarosite-type compounds consist of octahedrons. The narrow signal at $g = 2.003$ is attributed to a stable radical, probably a semiquinone [34]. Its intensity increases with the increase of the heating temperature of the Fe(III)-containing polymer samples.

The IR spectra of the heated Fe(III)-containing samples of AV-17 (Fig.1-1), were interpreted according to Nakamoto [35] and Bellami [36]. In the IR spectrum of the sample heated at 120 °C a new absorption band at 1730 cm^{-1} appeared, and in the spectrum of the sample heated at 140 °C another band appeared at 1695 cm^{-1}. These bands were attributed to ν(C=O) of ketone groups. We suggest that the bands at 1730, 1105, 620, 550 and 420 cm^{-1} correspond to an aromatic ketone type: 

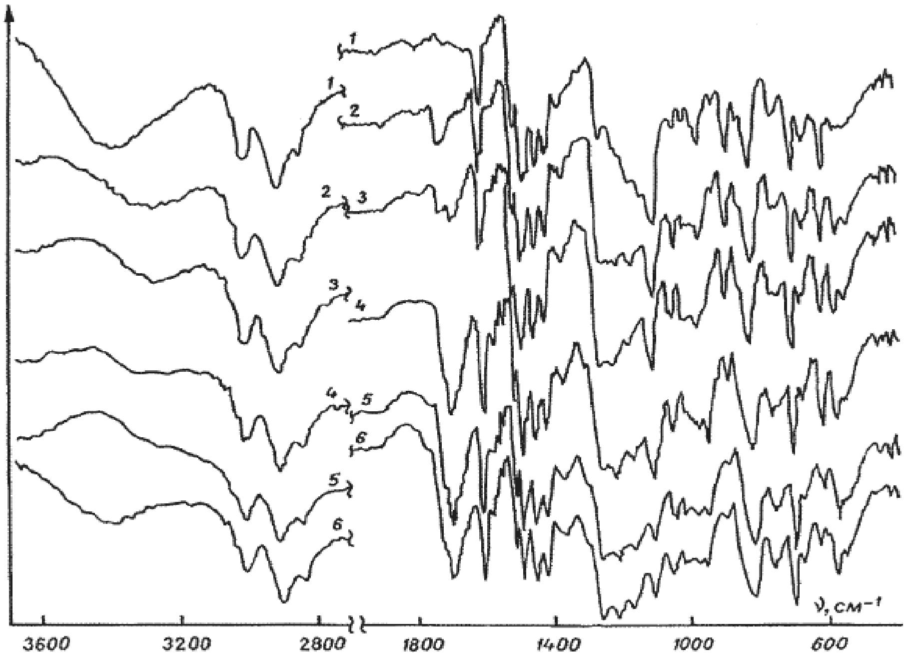


Figure 1-1. IR spectra of the Fe(III)-containing AV-17 after heating in air at 100 (spectrum 1), 120 (spectrum 2), 140 (spectrum 3), 160 (spectrum 4), 180 (spectrum 5), and 200°C (spectrum 6).

The absorption band at 1695 cm^{-1} corresponds to C=O groups in an aromatic nucleus, that is, to a quinone-type ketone. If this is true, the frequency of the valence vibrations of atoms in the C=C and C–H groups of the aromatic nucleus must be changed. Upon increasing the temperature of the heated samples, ν (C = C) moves from 2990 to 3010 cm^{-1}; ν(C–H) moves from 1610 to 1595 cm^{-1}; and band widening at 820, 970 and 1045 cm^{-1} takes place. In the IR spectrum of the sample heated at 200°C, a large absorption band of valence vibrations of an OH group appeared at 3500–3300 cm^{-1} and a band of ν(C=O) of a carboxylic group appeared at 1715 cm^{-1}. This fact and the growing intensity band at 1260 cm^{-1} [ν(C–O) of a carboxylic group] that increases with temperature permit us to suggest that carboxylic groups are formed on heating in the Fe(III)-containing polymer. It is also confirmed by the appearance in the IR spectra of an intensive band at 945 cm^{-1} (OH group), which increases with temperature at $t \geq 140°C$. The essential decreasing of the intensity of the band at 890 cm^{-1} in the IR spectra of the samples heated at $t \geq 160°C$ shows that the $-N(CH_3)_3^+$ groups undergo changes [37]. According to Karrer [38] on heating in the air the tetraalkylammonium bases are transformed into methanol and tertiary amines. The bands in the IR spectra at 1050 and 1160 cm^{-1} can be attributed to alcohol OH groups and at 1040 and 1680 cm^{-1} to aldehyde groups (Fig.1-1). The absorption bands at 1100 and 615 cm^{-1} show that the Fe(III)-containing polymer samples also contain a considerable amount of SO_4^{2-} anions.

It is reasonable to compare the obtained results with those studying the thermal behaviour of an AV-17 exchanger in the absence of Fe(III) compounds in its phase. The results of these investigations are reported by Tulupov and Grebeni [39] and Ugleanskaya et al. [40]. According to Tulupov and Grebeni [39] on heating an AV-17(Cl) exchanger in air, the following processes are carried out:

$$2RCH_2N(CH_3)_3Cl + H_2O \rightarrow RCH_2NH(CH_3)_2Cl + (CH_3)_4NCl + RCH_2OH \qquad (1\text{-}2)$$

$$RCH_2N(CH_3)_3Cl + RCH_2NH(CH_3)_2Cl + HOH \rightarrow RCH_2NH_2CH_3Cl +$$

$$+ (CH_3)_4NCl + RCH_2OH. \qquad (1\text{-}3)$$

As shown in [39], processes (1-2) and (1-3) take place in the polymer phase on heating at $t \geq 150$ °C. Ugleanskaya et al. [40], mention that air dried AV-17 is stable up to 200 °C, and degradation begins at 230 [AV-17(Cl)] or 220 °C [AV-17(OH)]. The results of our investigations show that the existence of Fe(III) compounds in the phase of a strongly basic anion exchanger influences not only the thermal stability of the polymer but also the mechanism of thermochemical processes.

1.2.2. Transformations in Fe(III)-containing polymer on boiling in water

When boiled in water, jarosite compounds are known [29] to be converted to highly dispersed particles of FeOOH in a superparamagnetic state. The Mössbauer spectra of β-, γ-, and α-FeOOH in the superparamagnetic state show only one doublet and each modification of FeOOH cannot be identified. However, when several cycles of sorption– boiling in water are carried out, large FeOOH particles in the polymer phase are obtained. The large FeOOH particles become magnetically ordered, which allows identification of their modification using Mössbauer spectroscopy.

The Mössbauer spectra of the AV-17 sample after one cycle of sorption– boiling in water are a doublet at 300 and 80 K (Fig.1-2).

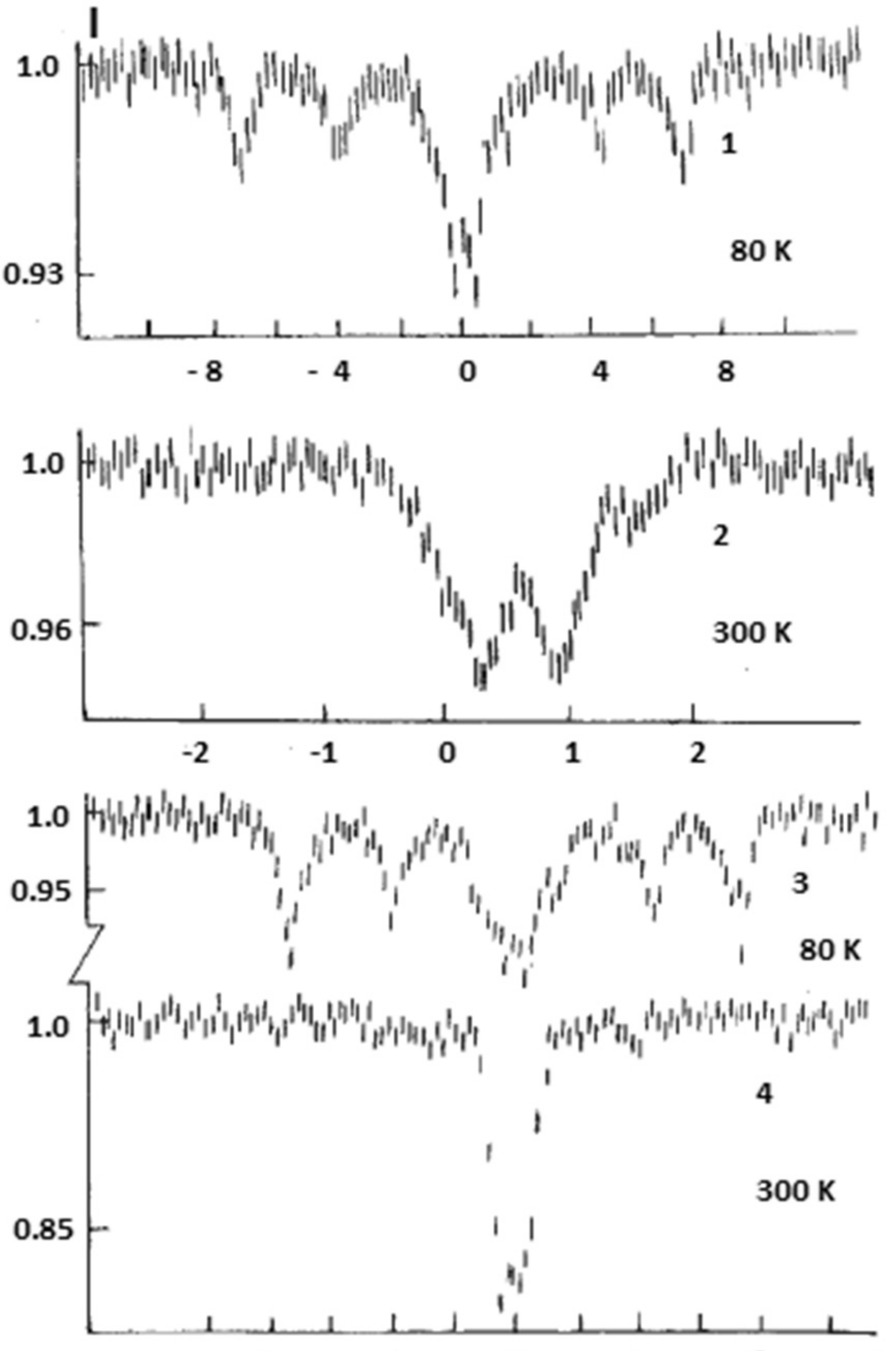


Figure 1-2. Mössbauer spectra of the Fe(III)-containing AV-17 after 3 (spectra 1 and 2) and 6 (spectra 3 and 4) sorption-boiling in water cycles

Mössbauer spectra of samples after two or more cycles of sorption– boiling in water present a doublet at 300 K and a sextet with a doublet in the centre of the spectrum at 80 K. The appearance of a sextet in the Mössbauer spectrum indicates the existence in the polymer phase of relatively massive and magnetically ordered Fe(III)-containing particles. The parameters of the sextet (Tab.1-2) correspond to β-FeOOH particles with varied sizes [42-43]. The massive particles of β-FeOOH are paramagnetic at room temperature and antiferromagnetic at T< 283 K [44]. The structure of the particles depends on the nature of anions presented in the medium of β-FeOOH formation [45-47].

Table 1-2. Parameters of Mössbauer spectra of AV-17 exchanger after different numbers of sorption-boiling in water cycles

No. cycles	Temp. (K)	Spectrum shape	Mössbauer parameters (mm/s)				H_{ef} (kOe)	Fe content (mg Fe/g sempe)
			δ	ΔE_Q	Γ_l	Γr		
1	300	Doublet	0.58	0.72	0.56	0.49	0	12.5
	80	Doublet	0.72	0.79	0.58	0.68	0	
2	300	Doublet	0.65	0.72	0.52	0.62	-	20,07
	80	Doublet	0.80	0.94	0.84	0.84	-	
		Sextet	0.80	o.18	-	-	462	
3	300	Doublet	0.61	0.72	0.57	0.42	0	25.8
	80	Doublet	0.66	0.76	0.61	0.61	0	
		Sextet	0.74	-0.23	-	-	479	
4	300	Doublet	0.59	0.69	0.55	0.55	0	45,6
	80	Doublet	0.69	0.77	0.77	0.77	0	
		Sextet	0.66	-0.19	-	-	456	
5	300	Doublet	0.63	0.72	0.43	0.51	0	57.8
	80	Doublet	0.82	0.87	0.77	0.77	0	
		Sextet	0.68	-0.14	-	-	454	
6	300	Doublet	0.61	0.71	0.51	0.48	0	65.2
	80	Doublet	0.68	0.70	0.70	0.77	0	
		Sextet	0.66	-0.18	-		450	

The doublet in the centre of the sextet is attributed to highly dispersed β-FeOOH in the superparamagnetic state, which stays in the narrow pores of the exchanger. With an increasing number of sorption– boiling in water cycles, the amount of massive β-FeOOH particles in the polymer phase grows. Jarosite-type compounds boiled in water are converted into α-FeOOH [29], but in the investigated polymer they are converted into β-FeOOH. The AV-17 exchanger was in Cl^- form and the formation of β-FeOOH may be conditioned by Cl^- anions still being in the polymer phase. According to several studies [45-49], β-FeOOH is formed in the presence of Cl^- or F^- anions in solution. The Cl^- anions are contained in the β-FeOOH structure and may participate in the anion exchange process [50]. The exchange capacity of the β-FeOOH depends on the concentration of anions and the pH of the solutions, being 1 mmol Cl^-/g at pH 3.0 [51]. However, Goncharov et al. [43], reported that β-FeOOH may be obtained in the absence of Cl^- or F^- anions. It is possible that the formation of FeOOH modifications depends on the size of the particles, which is analogous to the suggestion of α-, γ-Fe_2O_3 formation [52]. According to this suggestion, the Fe_2O_3 modifications depend on the critical diameter (d_{cr}) of the particles. Paramagnetic x-Fe_2O_3 exists when $d_{cr} = 8 \pm 2$ nm, ferromagnetic γ-Fe_2O_3 exists when $d_{cr} = 8–30$ nm, and antiferromagnetic α-Fe_2O_3 exists when $d_{cr} > 30$ nm. When d becomes more than d_{cr}, paramagnetic x-Fe_2O_3 particles spontaneously become magnetically ordered [54].

Thus, the transformations of the Fe(III)-containing compounds in the AV-17 phase when boiled in an aqueous medium permit us to suggest that the sorption of metallic cations from $Fe_2(SO_4)_3$ solutions on strongly basic anion exchangers takes place through formation of the jarosite-type compounds $R_4N[Fe_3(OH)_6(SO_4)_2]$ and $H_3O[Fe_3(OH)_6(SO_4)_2]$.

1.2.3. Chemisorption of Fe(III)- containing cations on strongly basic cross-linked polymers

The retaining of Fe(III)-containing cations from sulfate solutions takes place not only on AV-17(Cl) but on any polymer containing strongly basic groups. To confirm this, the sorption of Fe (III) containing cations from sulfate solution was performed not only on AV-17(Cl), containing - $N(CH_3)_3Cl$, but also on the commercial polymer Varion-AD, containing functional groups - $[N(CH_3)_2CH_2CH_2OH]Cl$ [53]. The full exchange capacity of the Varion-AD is 4.0 mEq/g [4].

Dried samples (0.2 g) of the polymers were placed in contact with 200 ml of $Fe_2(SO_4)_3$ solution for 24 h. The pH of the solution-sample systems was kept at 2.0±0.1 by using either H_2SO_4 or KOH solution. The temperature dependence of the sorption of Fe(III) containing ions in $2x10^{-2}$ M $Fe_2(SO_4)_3$ solutions was investigated over the temperature range of 20–70°C. The system temperature was kept at a constant with an error of ±1°C. There was no evidence of the resins degrading at these temperatures.

As is shown in Figure 1-3, the sorption of Fe(III) containing ions from the $Fe_2(SO_4)_3$ solution on strongly anion exchangers AV-17 and Varion-AD depending on temperature passes through a maximum at about 50°C.

The first important conclusion from the temperature dependence of the Fe(III) containing - ions retaining on polymers is that the sorption is not a physical but a chemical process. This fact excludes ion exchange as a possible process for the sorption of Fe(III) containing ions. It also excludes sorption due to the formation of an Fe(OH) precipitate in the polymer phase. As it is known [54], the degree of hydrolysis of ions in the exchange phase differs from that in solution. We suggest that the retention of the Fe(III) containing ions on the strongly basic anion exchangers is due to the formation of jarosite type compounds in the polymer phase.

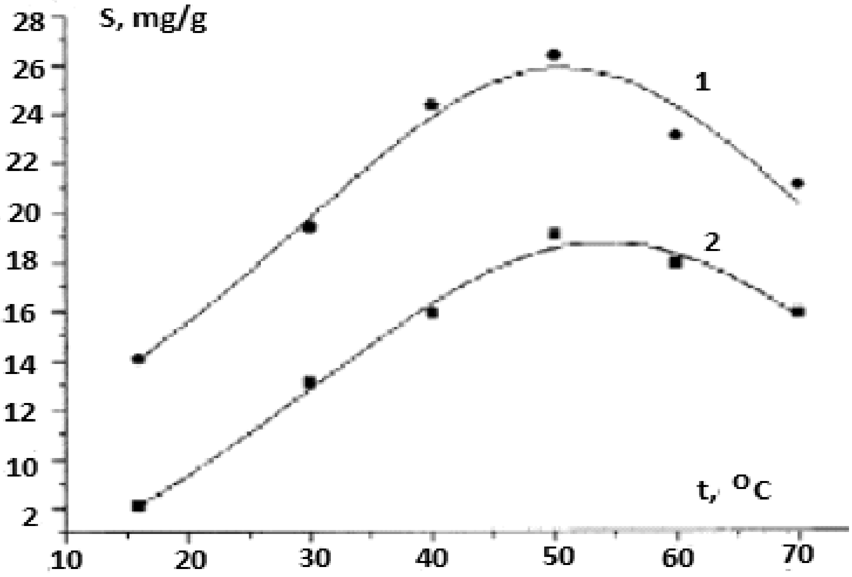


Figure 1-3. Temperature dependence of the Fe(III) containing ions' sorption on anion exchangers Varion-AD (1) and AV-17 (2).

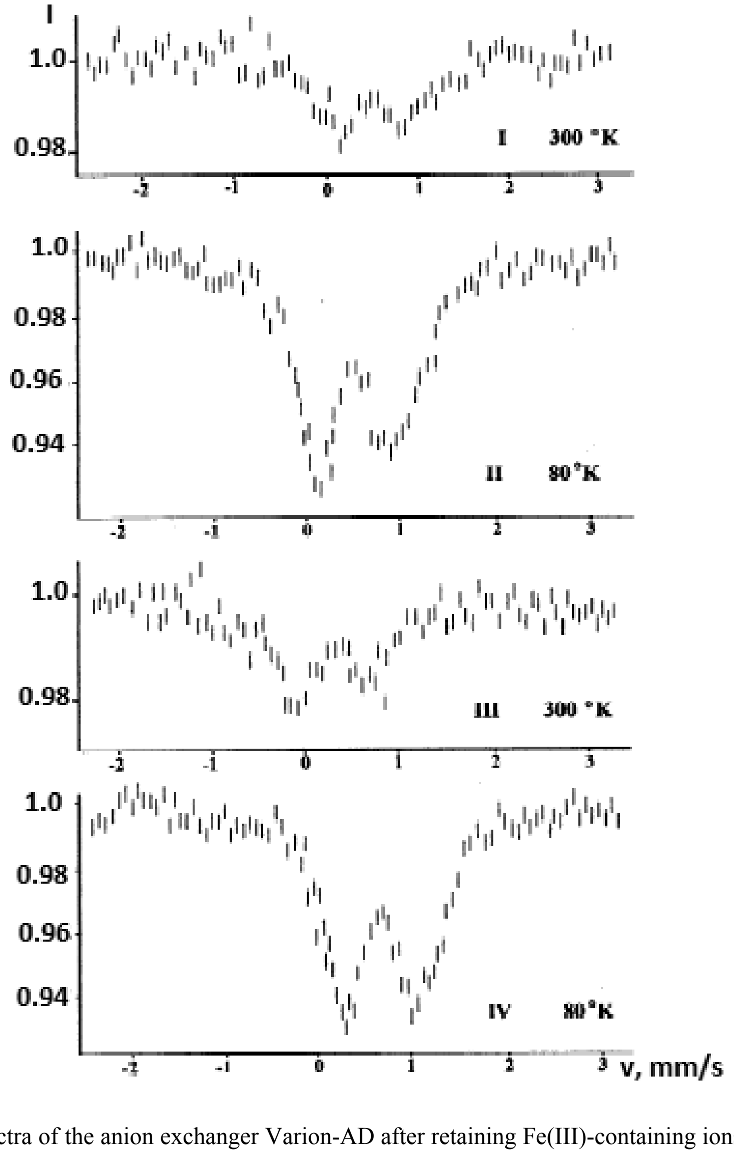


Figure 1-4. Mössbauer spectra of the anion exchanger Varion-AD after retaining Fe(III)-containing ions from $Fe_2(SO_4)_3$ solution at 30 (I, II) and 50^0C (III, IV).

The appearance of a maximum on the temperature dependence of sorption shows that in the polymer–$Fe_2(SO_4)_3$ solution system processes occur with opposing influences on sorption. These processes could take place in the polymer phase or in solution. To detect the existence of different Fe(III) compounds in the polymer phase we investigated Fe(III) containing samples of Varion-AD obtained at 30 and 50°C using Mössbauer spectroscopy. The resulting Mössbauer spectra are presented in Figure 1-4 and their parameters are listed in Table 1-3.

Table 1-3. Parameters of the Mössbauer spectra of anion-exchanger Varion-AD retaining Fe(III) containing ions from $Fe_2(SO_4)_3$ solutions at different temperatures

T, K	δ, mm/s	ΔE_Q, mm/s	Γ_l, mm/s	Γr, mm/s
				Samples obtained at 30°C
300	0.56	0.71	0.62	0.69
80	0.66	0.86	0.60	0.70
				Samples obtained at 50°C
300	0.65	0.77	0.68	0.64
80	0.54	0.79	0.63	0.70

They show that in the polymer phase there are only Fe(III) ions in the high spin state. A visible amount of Fe(II) ions is not detected, which indicates the absence of reducing centres in the polymers. The electronic state of Fe(III) ions in Varion-AD is almost the same as in AV-17 [26]. Perhaps some of the OH groups of Varion-AD coordinate with Fe(III) ions affect the symmetry of the compound. The shape of the spectra is important along with their characteristic values, showing that in the polymer phase there is only one type of Fe(III) compound. So, the Fe(III) containing ions sorption temperature dependence maximum (Fig. 1-3) is probably a result of the change which takes place in the $Fe_2(SO_4)_3$ solution on heating. It is known that in aqueous solutions Fe^{3+} ions hydrolyse.

The presence of some compounds such as Fe^{3+}, $FeOH^{2+}$, $Fe_2(OH)_2^{4+}$, $Fe_3(OH)_4^{5+}$, $Fe(OH)_2^{+}$, $Fe(OH)_3$ and $Fe(OH)_4^{-}$ will affect the influence of the concentration of the iron salt, pH, temperature and ionic strength of the solution on the sorption properties. The relative content of Fe(III)-containing ions in the solution we used, according to Refs. [55, 56] may be estimated as about 25% $[Fe(H_2O)_6]^{3+}$, 50% $[FeOH(H_2O)_5]^{2+}$ and 25% $[Fe_2(OH)_2(H_2O)_8]^{4+}$. Not all of these cations are able to participate in the formation of the Fe(III) compounds in the exchanger phase. While the pH increases, the concentration of $[Fe(H_2O)_6]^{3+}$ cations in solution decreases, but sorption of the Fe(III) ions on polymers containing R_4N^+ grows [57]. From solutions of $pH \leq 1.5$, the sorption of Fe(III) ions is absent. So, $[Fe(H_2O)_6]^{3+}$ cations do not take part in the formation of Fe(III) compounds in the polymer phase. While the temperature equilibrium (1-4) shifts to the right and in the absence of precipitate formation the concentration of $[Fe_2(OH)_2(H_2O)_8]^{4+}$ cations in solution increases [56]. But as is seen in Figure 3, at t >50°C sorption of Fe(III)-containing ions on the polymers decreases. Therefore the participation of the $[Fe_2(OH)_2(H_2O)_8]^{4+}$ cations in the Fe(III) compounds formation in the polymer phase is unlikely. On heating, the $[Fe_2(OH)_2(H_2O)_8]^{4+}$ cations are transformed into $[(H_2O)_5Fe–O–Fe(H_2O)_5]^{4+}$ ions. These dimer cations cannot easily be restructured to form new units [58], and they have not been detected in the polymer phase by Mössbauer spectroscopy. During the formation process of the Fe(III) compounds in the polymer phase, it is probable that the $[FeOH(H_2O)_5]^{2+}$ cations participate. When studying the effect of pH, the concentration of $[FeOH\ (H_2O)_5]^{2+}$ ions in the solution passed through a maximum [55]. The position and value of the maximum depends also on the concentration of iron ions, ionic strength and temperature. The degree of hydrolysis of Fe^{3+} ions in the polymer phase differs from the one in solution. The hydrolysis processes taking place in the resin may result in local changes in the $[H^+]:[OH^-]$ ratio, creating conditions for compounds to be formed according to Equation (1-5):

$$2[Fe(H_2O)_6]^{3+} \leftrightarrow 2[FeOH(H_2O)_5]^{2+} + 2H^+ \leftrightarrow [FeOH(H_2O)_8]^{4+} + 2H^+ + 2H_2O \quad (1\text{-}4)$$

$$3[FeOH(H_2O)_5]^{2+} + 3OH^- + 2SO_4^{2-} \leftrightarrow [Fe_3(OH)_6(SO_4]^- + 15H_2O \quad (1\text{-}5)$$

The complex anions polymerize themselves to form a solid-phase [59]. Equilibrium (1-5), and therefore the formation of jarosite type compounds, does not take place in the liquid phase of the systems we were using. The conditions of the formation of jarosite-type compounds in solution are described in Refs. [59, 60]. The experimentally obtained isotherms of Fe(III) ions sorption on anion exchangers AV-17 and Varion-AD were analysed using the Freund lich, Temkin and Langmuir sorption models.

Freundlich Sorption Model. The Freundlich nonlinear isotherm [61] is described by Equation (1-6) and the linear isotherm is described by Equation (1-7):

$$\boldsymbol{S_F = K_F * C^{1/n}}, \quad (1\text{-}6),$$

$$\boldsymbol{lnS_F = lnK_F + 1/n * lnC} \quad (1\text{-}7)$$

where: S_F is the sorption value at equilibrium (mg Fe/g), K_F is the Freundlich isotherm constant, C is the concentration of Fe(III) ions in solution at equilibrium (mg Fe/mL). The a and n are constants the physical and chemical nature of which was not identified. The *1/n* is a measure of the nature and strength of the adsorption process and of the distribution of active sites. If $1/n > 1$, bond energies increase with the surface density; if $1/n < 1$, bond energies decrease with the surface density; and when $1/n = 1$, all surface sites are equivalent.

Temkin Sorption Model. Ignoring very low and very large values of concentration, the Temkin equation is shown as Equation (1-8) [62, 63]:

$$S_T = a + b \ln C, \tag{1-8}$$

where a and b are constants, the nature of which is not defined, and S_T is the sorption value at equilibrium (mg Fe/g) and C is as in Equation (1-6).

Langmuir Sorption Model. The Langmuir nonlinear isotherm [64] is described by Equation (1-9) and the linear isotherm is described by Equation (1-10):

$$S = S_L K_L C/(1 + K_L C) \qquad (1\text{-}9),$$

$$1/S = 1/S_L K_L + C/S_L \tag{1-10}$$

where: S is as S_F the same as in Equation (1-6), S_L is the monolayer capacity of the sorbent (mg Fe/g); K_L is the Langmuir isotherm constant (mL/mg), and C is the Fe^{3+} concentration at sorption equilibrium (mg Fe/mL).

The application of the Langmuir equation suggests that the sorption energy is constant and does not depend on the degree of occupation of the active centres of a sorbent. For sorption on the sorbents having two energetically distinct kinds of sorption centres, Langmuir proposed the following Equation (1-11) of the isotherm:

$$S = S'_L K_L' C/(1 + K'_L C) + S''_L K_L'' C/(1 + K_L'') \tag{1-11}$$

where the constants K_L' and K_L'' characterize the centres with more and less affinity, respectively.

Under finite conditions the sorption may take place only on centres with low affinity, the high-affinity centres being completed. In this case the Langmuir Equation (1-12) is applied:

$$S = S'''_L + S''_L K_L'' C/(1 + K_L'' C) \tag{1-12}$$

There are some methods to resolve Equations (1-8) to (1-12). Most efficient is the method of non-linear regressions [16–18]. The isotherms obtained experimentally and calculated are shown in Figures 1-5 and 1-6, and their parameters are shown in Table 1-4.

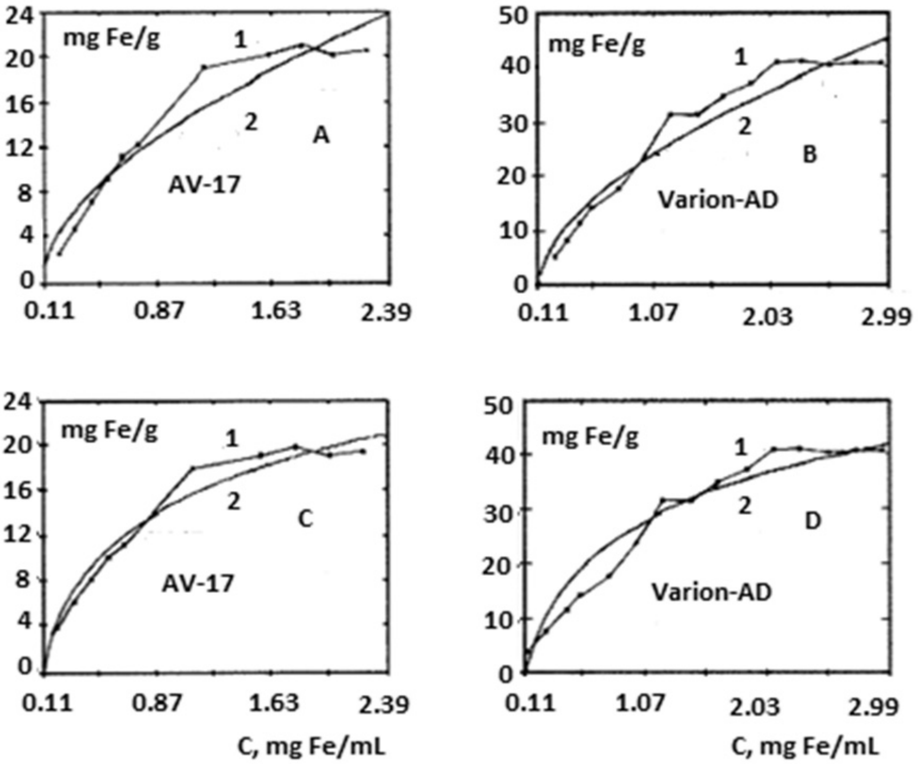


Figure 1-5. Experimental (1) and calculated (2) isotherms of Fe(III) containing cations' sorption on polymer AV-17 and Varion-AD using Freundlich (A, B) and Temkin (C, D) equations.

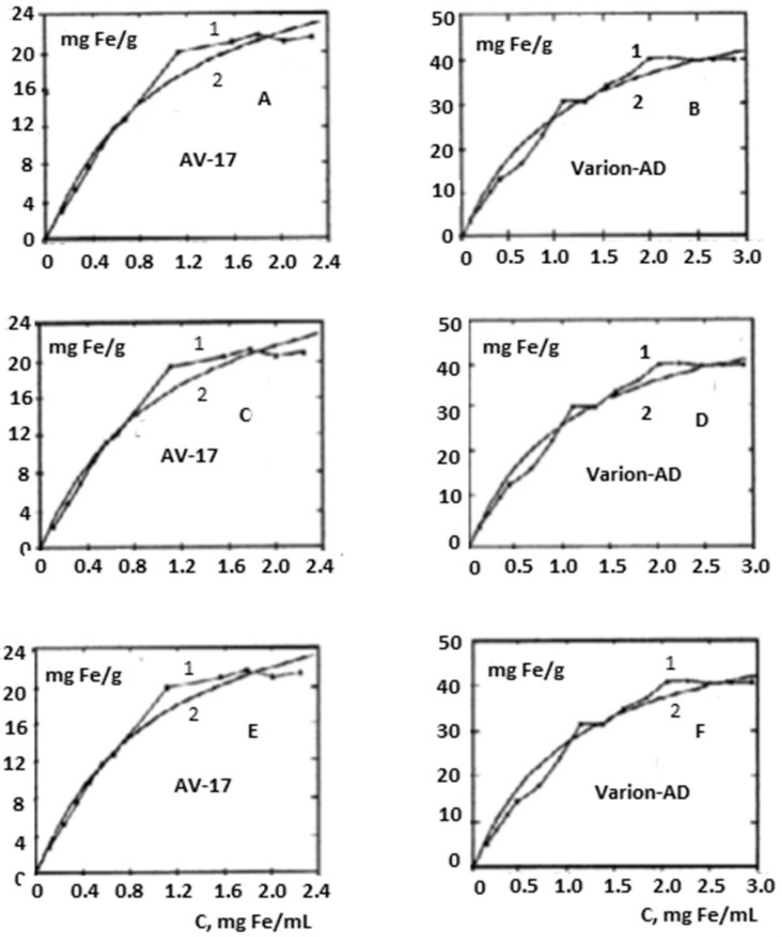


Figure 1-6. Experimental (1) and calculated (2) isotherms of Fe(III) containing cations' sorption on anion exchangers AV-17 and Varion-AD using Langmuir Eq. (1-9) (A, B), Eq. (1-11) (C, D), and Eq. (1-12) (E, F).

Statistical analysis and approximation of the experimental and calculated isotherms show that the Langmuir equations describe the Fe(III) ions sorption isotherms on the AV-17 and Varion-AD polymers more adequately than the Freundlich or Temkin equations. Equations (1-9), (1-11) and (1-12) show the same affinity of the less active sorption centres. These equations also describe identically the sorption capacities of polymers which are determined by the low-affinity sorption centres. The higher affinity sorption centres constitute only about 0.04–0.09% according to Eq.(1-12) or 0.03–0.04% according to Equation (1-11). This means that all active centres of polymers AV-17 and Varion-AD are energetically the same. These active centres of the polymers cannot be other than R_4N^+. So, R_4N^+ groups take part in the formation of metallic compounds in the polymer phase.

Table 1-4. Parameters of Freundlich, Temkin and Langmuir equations for Fe(III) containing ions' sorption isotherms on polymers AV-17 and Varion-AD

AV-17	Varion-AD
Freundlich. Eq. 1-6.	
K_F =14.72, n =1.788	K_F =24.06, n =1.731
Temkin. Eq. 1-8.	
α =16.09, b =7.11	α =27.14, b = 13.05
Langmuir. Eq. 1-9.	
K_L = 0.926 ml/mg, S_L = 32.91 mg/g	K_L = 0.907 ml/mg, S_L = 56.24 mg/g
Langmuir. Eq. 1-11.	
K'_L = 9.010 ml/mg, S'_L = 0.013 mg/g K''_L = 0931 ml/mg, S''_L = 32.970 mg/g	K'_L = 9.030 ml/mg, S'_L = 0.018 mg/g K''_L = 0.901 ml/mg, S''_L = 56.520 mg/g
Langmuir. Eq. 1-12.	
K''_L=0.924 ml/mg, S''_L=32.92 mg/g, S'''_L=0.015 mg/g	K''_L=0.902 ml/mg, S''_L= 56.34 mg/g, S'''_L=0.051 mg/g

1.2.4. Iron compounds in the polymer phase as precursors for the obtaining of sorbents and catalysts

The sorption of Fe(III) containing cations from sulfate solutions takes place through the formation in the polymer phase of the jarosite mineral type compounds: $R_4N[Fe_3(OH)_6(SO_4)_2]$ and some $H_3O[Fe_3(OH)_6(SO_4)_2$, where R_4N^+ is a functional group of the polymer. The jarosite mineral type compounds are formed as layers of 3 or 6 octahedral cycles [58]. The OH^- groups are in the equatorial plane, forming a bridge between metal ions, and SO_4^{2-} groups are in axial position, each coordinate 3 metal ions of 3 octahedra. Between the jarosite polymer layers there are mobile R_4N^+, H_3O^+ and other cations retained by Coulomb's electrostatic interactions. The jarosite mineral type compounds in the polymers phase change significantly their physical-chemical properties. In the previous investigation [33], the Fe(III)-containing cations sorption on AV-17(Cl) took place at the room temperature and iron content in the polymer phase has constituted only about 12 mg Fe/g. For obtaining effective and selective sorbents and catalysts the polymers must have a more consistent number of metallic compounds in their phase. It is also necessary to know and have a possibility to change the morphology and composition of structural units of ultrafine particles, their distribution on the surface and in the volume of polymer granule, a method to change particles sizes. In the investigation [64], the samples of the AV-17 polymer had a much higher amount of Fe (Tabs.1-5 and 1-6). The Mössbauer spectra of the AV-17 polymer samples after contacting with $Fe_2(SO_4)_3$ solution are doublets both at 300 and 80 K. The isomeric shift of these spectra is 0.70 and 0.83 mm/s and quadrupole splitting is 0.79 and 0.88 mm/s, respectively at 300 and 80 K (Tab.1-6, cycle 0). The values of the quadrupole splitting are smaller than in Ref. [33]. As it is seen in Figure 1-7, the Mössbauer spectra of the Fe(III) compounds in the AV-17 polymer phase after 2 h of heating in the water in a boiling water bath are doublets at 300 and 80 K. The ΔE_Q values of these doublets are much smaller (Tab.1-5), in comparison with that of the jarosite type compounds (Tab.1-6, cycle 0). It means that after 2 h of heating in the water, the jarosite type compounds in the polymer phase are transformed into FeOOH ultrafine particles in the superparamagnetic state. We cannot conclude what modification of FeOOH is formed in the polymer phase after 2 h of heating in the water of the jarosite-containing AV-17. The Mössbauer spectra of α-, β-, γ- or δ-FeOOH in the superparamagnetic state (nanoparticles), are doublets both at 300 and 80 K [65].

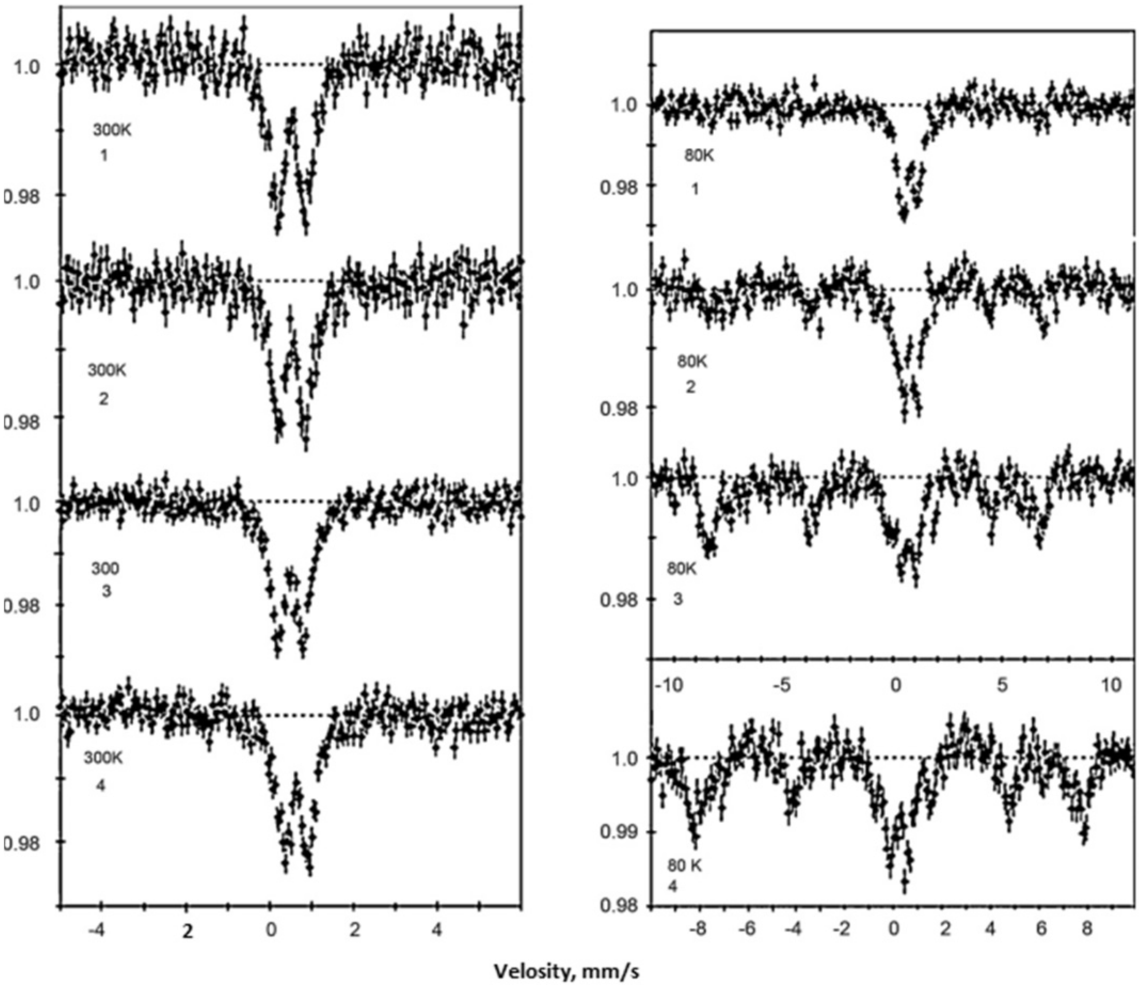


Figure 1-7. Mössbauer spectra recorded at 300 and 80 K of the Fe(III)-containing AV-17 after 2 (1), 4 (2), 6 (3) and 8 h (4) of heating in the water in a boiling water bath.

Table 1-5. Parameters of the Mössbauer spectra of the Fe(III) containing AV-17 after heating in water

Heating duration, h	T, K	Spectrum shape	Mössbauer parameters, mm/s				H_{eff}, kOe	Fe content, mg/g
			δ	ΔE_Q	Γ_l	Γ_r		
2	300	Doublet	0.76	0.57	0.57	0.48	0	39.7
	80	Doublet	0.62	0.66	0.40	0.40	0	
4	300	Doublet	0.60	0.63	0.42	0.38	0	31.6
	80	Doublet	0.76	0.57	0.57	0.48	0	
		Sextet	0.36	-	-	-	450	
6	300	Doublet	0.60	0.61	0.42	0.42	0	31.9
	80	Doublet	0.71	0.66	0.28	0.38	0	
		Sextet	o.33	-	-	-	450	
8	300	Doublet	0.63	0.55	0.41	0.43	0	31.3
	80	Doublet	0.70	0.73	0.32	0.24	0	
		Sextet	0.74	-	-	-	460	

Table 1-6. Parameters of the Mössbauer spectra of the Fe(III) containing AV-17 after some "Fe(III) – sorption – heating in water" cycles

No. cycles	T, K	Spectrum shape	Mössbauer parameters, mm/s				H_{eff}, kOe	Fe content, mg/g
			δ	ΔE_Q	Γ_l	Γ_r		
0^*	300	Doublet	0.70	0.70	0.49	0.32	0	24.9
	80	Doublet	0.83	0.88	0.57	0.51	0	
1	300	Doublet (a)	0.68	0.91	0.23	0.23	0	24.5
		Doublet (b)	0.67	0.42	0.19	0.19	0	
	80	Doublet (a)	0.77	1.27	0.33	0.33	0	
		Doublet (b)	0.88	0.55	0.28	0.28	0	
2	300	Doublet	0.78	0.53	0.48	0.44	0	45.4
	80	Doublet	0.70	0.74	0.63	0.63	0	
		Sextet	o.36	-	-	-	480	

To find the modification of the FeOOH using Mössbauer spectroscopy it is necessary to have massive particles of the compound. The Mössbauer spectrum of the Fe(III)-containing compounds in the polymer phase after 4 h of heating in the water medium is a doublet at 300 K and a sextet with a doublet in the centre of the spectrum at 80 K (Fig.1-7). The appearance of a sextet in the Mössbauer spectrum indicates the existence in the polymer phase of relatively massive and magnetically ordered particles of Fe(III)-containing compounds. The parameters of the sextet (Tab.1-5) correspond to β-FeOOH particles [42-44]. The massive particles of β-FeOOH are paramagnetic at $T > 283$ K (a doublet in the Mössbauer spectrum) and antiferromagnetic at $T < 283$ K (a sextet) [45]. So, we conclude that after 2 h of heating in water jarosite type compounds in the polymer phase are converted into highly dispersed particles of β-FeOOH in a superparamagnetic state.

As it is seen in Figure 1-7, with the increasing of the duration ($\tau > 2$ h) of heating in water of the polymer containing the jarosite, the spectral lines of the sextet in the Mössbauer spectra become more pronounced. It means that with the increasing duration of heating in water of the jarosite-containing polymer, more β-FeOOH particles become massive and the magnetically ordered. The doublet in the centre of the sextet in the spectra recorded at 80 K belongs to highly dispersed β-FeOOH particles in the superparamagnetic state which remain in the narrow pores of the polymer. Under heating of the jarosite-containing polymer in water medium in the water boiling bath the processes (1-13) and (1-14) take place:

$$2R_4N[Fe_3(OH)_6(SO_4)_2] \rightarrow 6(\beta\text{-}FeOOH) + (R_4N)_2SO_4 + 3H_2SO_4 \quad (1\text{-}13)$$

$$H_3O[Fe_3(OH)_6(SO_4)_2] \rightarrow 3(\beta\text{-}FeOOH) + 2H_2SO_4 + H_2O \quad (1\text{-}14)$$

The analysis of the experimental data shows a correlation between the amount of the Fe(III) in the polymer phase and samples heating in water duration to appear the β-FeOOH particles in a magnetically ordered state. So, when in the polymer phase is about 40 mg Fe/g, relatively massive magnetically ordered β-FeOOH particles appear after 4 h of heating in water medium in a boiling water bath (Fig.1-7, Tab.1-5). If the polymer has 25 mg Fe/g, magnetically ordered particles of β-FeOOH do not appear after 4 h of heating in water (Fig.1-8, Tab.1-6, cycle 1). In this case, after 4 h of heating in water of the jarosite-containing polymer, two doublets appear in the Mössbauer spectra (Fig.1-8).

The doublet (a) with a larger quadrupole splitting belongs to jarosite-type compounds particles and another doublet (b) belongs to β-FeOOH ultrafine particles in the superparamagnetic state. The Mössbauer spectra parameters (Tab.1-6, cycle 1) show that when heating in water of AV-17, ΔE_Q of jarosite type compounds in the polymer phase increases significantly from 0.79 and 0.88 to 0.91 and 1.27 mm/s (that is characteristic for jarosite) correspondingly at 300 and 80 K. This fact shows that during heating in water a part of the jarosite type compounds is converted into β-FeOOH in the superparamagnetic state and another part of jarosite becomes more structured. Unstructured jarosite type compounds in the polymer phase may be the explanation of the observed low values of the quadrupole splitting in some studies [53, 66].

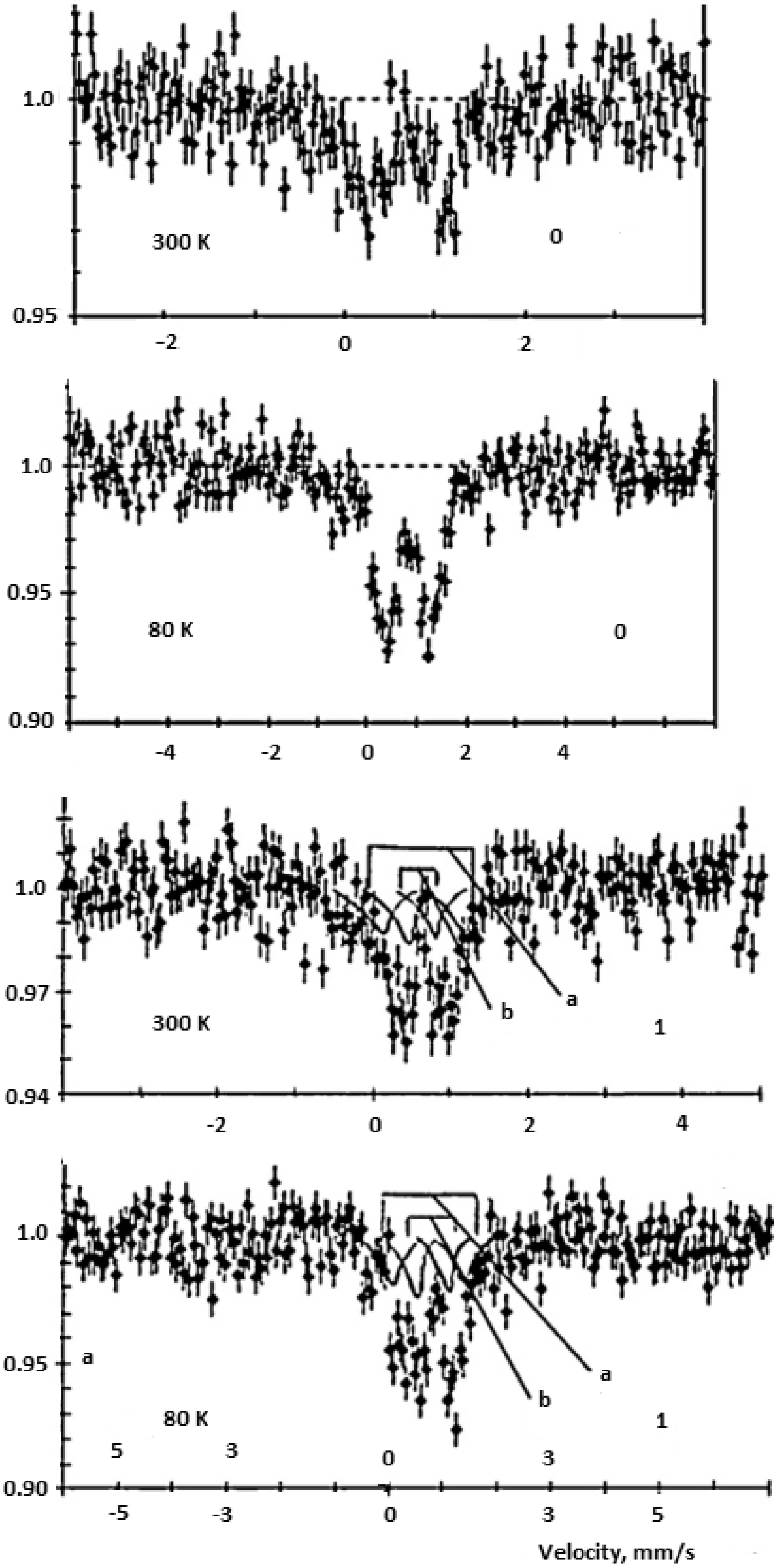


Figure 1-8. Mössbauer spectra of the jarosite containing AV-17 before (0) and after 4 h heating in water (1).

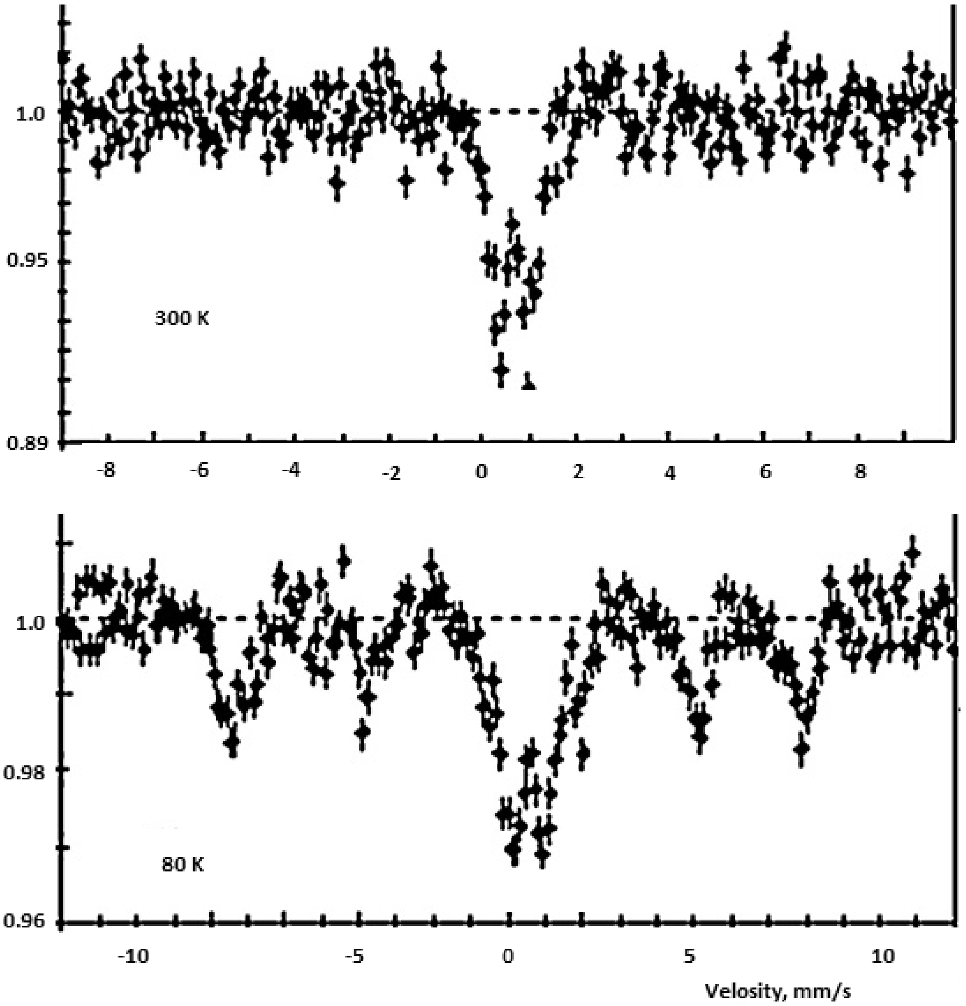


Figure 1-9. Mössbauer spectra of the Fe(III)-containing AV-17 after 2 cycles of "Fe(III) sorption – 4 h heating in the water".

When the polymer contains more Fe^{3+} (45.4 mg Fe/g), that was achieved after 2 cycles "Fe(III) sorption – heating in water for 4 h", jarosite type compounds in the polymer phase are completely transformed into β-FeOOH both relatively massive, magnetically ordered and in the superparamagnetic state particles (Fig.1-9; Tab.1-6, cycle 2).

The ideas mentioned above about jarosite transformation on boiling in water of the Fe(III)-containing AV-17 are confirmed by SEM investigation. The SEM images on the surface and in the volume of the jarosite-containing AV-17 polymer granule (cycle 0) are presented in Figure 1-10. These images confirm that jarosite type compounds in the polymer phase are in the form of ultra-dispersed particles.

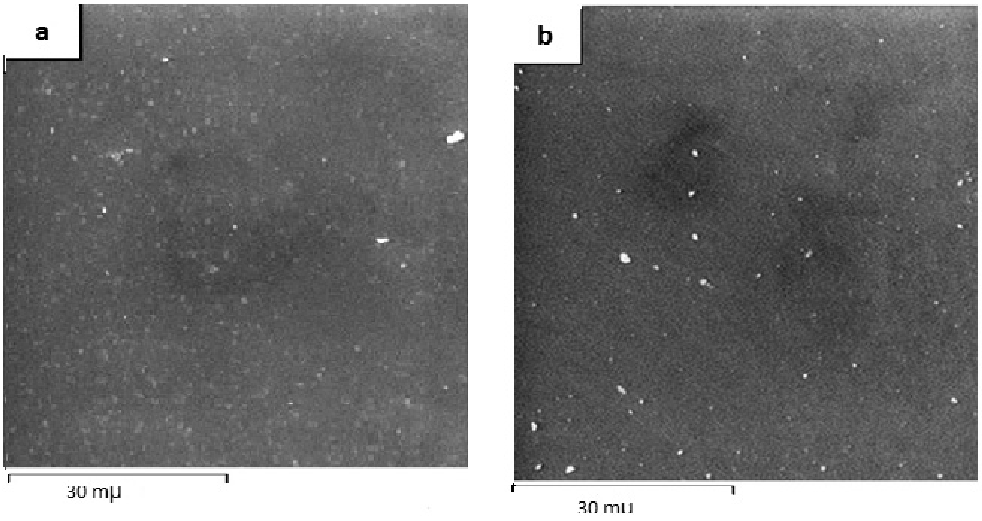


Figure 1-10. SEM images of the jarosite particles on the surface (a) and in the volume (b) of an AV-17 polymer granule.

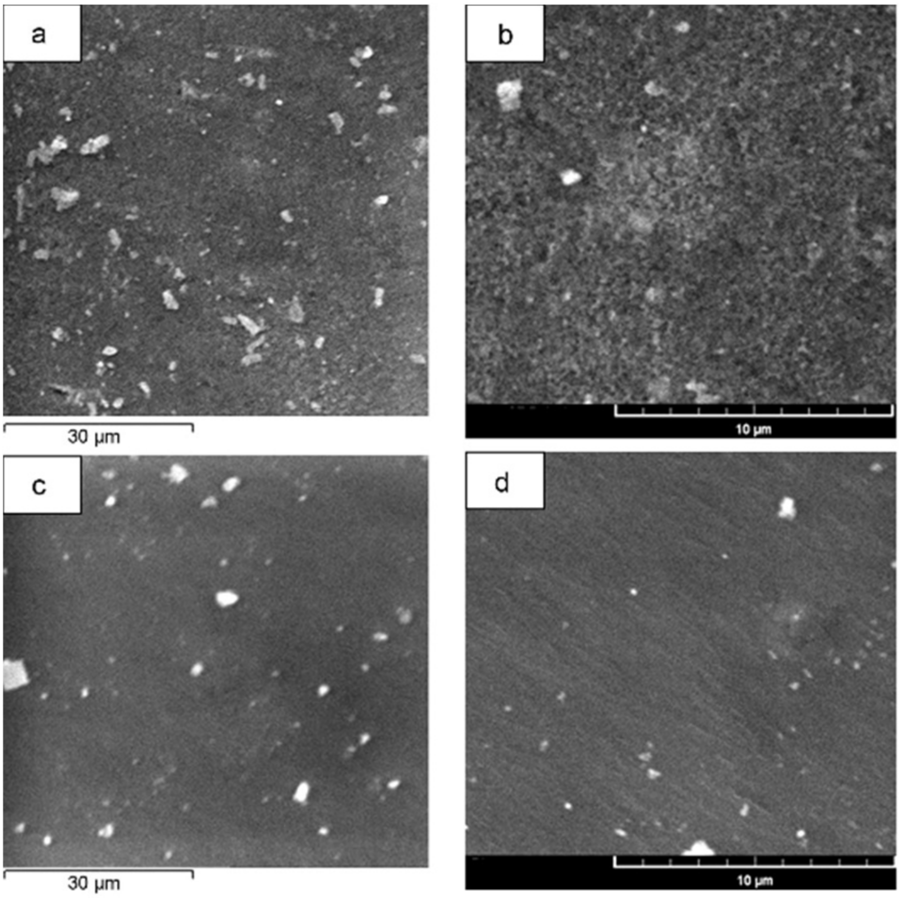


Figure 1-11. SEM images of the Fe(III)-containing compound particles on the surface (a, b) and in the volume of a polymer granule (c, d) after 2 h heating in water of jarosite containing AV-17.

The elemental composition of the Fe(III)-containing structural units were obtained by SEM –EDX investigation. Using the elemental composition of the Fe(III)-containing structural units, the brut formulas of the Fe(III)-containing structural units were calculated and constituted as $Fe_1O_{18.3}Cl_{1.8}S_{3.56}C_{88.0}$ (on the granule surface) and $Fe_1O_{18.1}Cl_{2.1}S_{3.5}C_{103.5}$ (in the volume of the polymer granule). These formulas show that composition of the Fe(III)-containing structural units on the surface and in the volume of the polymer granule is practically identical. Taking into consideration that the content of O and S atoms in the jarosite type compounds is less than in the Fe(III)-containing structural units in the polymer phase and that jarosite does not contain Cl and C atoms we suggest that jarosite particles in the polymer phase are situated on $[–N(CH_3)_3]_2SO_4$ and $–N(CH_3)_3Cl$ groups. As it is seen in Figure 1-11, after 2 h of heating in the water in the boiling water bath of jarosite- containing AV-17, highly dispersed particles of the Fe(III) compounds are observed both on the surface and in the polymer granule volume.

In the volume of the polymer granule, particles of the Fe(III)-containing compounds are fewer but larger than on the surface. It means that on heating in water a part of the Fe(III)-containing particles migrate up to the surface of the polymer granule. This is confirmed by the elemental composition data of the Fe(III)-containing structural unit. The brut formula of an Fe(III)-containing structural unit on the surface of the polymer granule is $Fe_1O_{8.2}Cl_{0.17}S_{0.86}C_{10.6}$ and in the volume $–Fe_1O_{11.1}Cl_{0.38}S_{1.21}C_{57.9}$. The elemental composition of the Fe(III)-containing structural unit is approximate because its composition includes a part of the polymer chain and atoms of functional groups. On the other hand, these structural units are statistically equally distributed both on the surface and in the volume of the polymer granule. It is known from Mössbauer spectroscopy data that the polymer phase comprised β-FeOOH compounds. Furthermore, SEM images confirmed the existence of β-FeOOH particles in a highly dispersed form. The existence of $Cl^–$ ions in the β-FeOOH structure has also been confirmed. Some of the $Cl^–$ ions could belong to R_4NCl groups because of the equilibrium (1-15), when the polymer contacts with $Fe_2(SO_4)_3$ solution:

$$2R_4NCl + SO_4^{2-} \leftrightarrow (R_4N)_2SO_4 + 2Cl^- \qquad (1\text{-}15)$$

The content of oxygen atoms in the brut formulas is much higher than corresponding to FeOOH. Taking into consideration that the AV-17 polymer matrix does not contain O and S atoms in its composition, it may be concluded that β-FeOOH particles are situated on $[–N(CH_3)_3]_2SO_4$ groups. A part of atoms of these groups is included in the composition of Fe(III)-containing structural units.

After 6 h of heating in water of the jarosite-containing polymer, both highly dispersed and massive particles of β-FeOOH are formed on the polymer granule surface [(Fig.1-12 (a)]. In the volume of the polymer granule

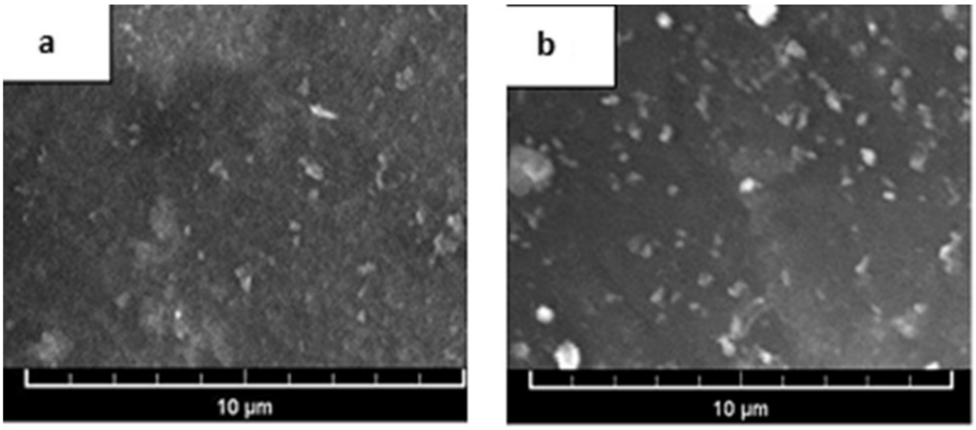


Figure 1-12. SEM images of the Fe(III)-containing compound particles on the surface (a) and in the volume of a polymer granule (b) after 6 h heating in water of jarosite containing AV-17.

there are only highly dispersed β-FeOOH particles [(Fig.1-12 (b)]. The brut formula of the Fe(III)-containing structural units on the polymer granule surface is $Fe_1O_{16.8}Cl_{0.25}S_{2.12}C_{68.3}$ and in the granule volume – $Fe_1O_{44.7}Cl_{0.36}S_{3.17}C_{206.6}$. The high content of O, C and S atoms in the brut formula confirms that β-FeOOH particles are situated on the $–N(CH_3)_3Cl$ and $[–N(CH_3)_3]_2SO_4$ groups, and on the $–CH_2$- polymer chain. When the jarosite-containing polymer has been heated in water for 8 h, almost all Fe(III)-containing compounds were situated on the polymer granule surface (Fig.1-13).

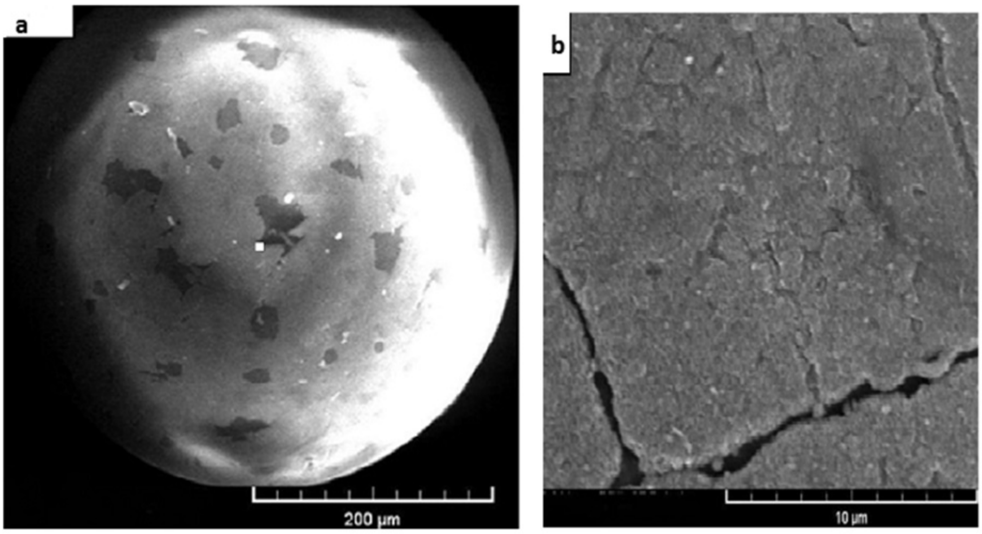


Figure 1-13. SEM images of the Fe(III)-containing compound particles on the surface (a, b) after 8 h heating in water of jarosite containing AV-17

There are many more relatively massive pieces of β-FeOOH on the polymer granule surface than in the case of 6 h of heating in water of jarosite-containing AV-17. This may create kinetic problems when using this sample of the Fe(III)-containing polymer as a sorbent or catalyst. The elemental composition of the Fe(III)-containing structural units on the surface and into the polymer granule of the jarosite containing AV-17 after 8 h of heating in water permits us to calculate the brut formula of the structural units. The brut formula of the Fe(III)- containing structural unit on the surface is $Fe_1O_{11}Cl_{0.12}S_{0.83}C_{15.4}$ and in the volume of the polymer granule – $Fe_1O_{111}Cl_{0.76}S_{6.38}C_{357}$. As in the cases described above, the particles of β-FeOOH are situated on the polymer's functional groups. Usually β-FeOOH and natural or synthetic jarosite are in the crystalline state, but there are jarosite compounds in an amorphous state as well [58]. Powder X-ray diffraction testing showed that both jarosite type compounds and β-FeOOH in the investigated polymer samples are in an amorphous state. In Ref. [67] it is shown that β-FeOOH and sulfated β-FeOOH particles have different morphologies. Obviously high SO_4^{2-} and Cl^- anion concentration in the polymer phase influences the morphology and crystallinity of jarosite and β-FeOOH particles.

To apply the Fe(III)-containing polymer as a sorbent or catalyst it is necessary to know its behaviour in different media. For that purpose, there was an investigation of thermal behaviour in the nitrogen medium of the Fe(III)-containing AV-17 and for comparison, thermal behaviour in the same conditions of the AV-17 in the form of SO_4^{2-} (AV-17(SO_4)).

From the literature [58], it is known that on heating in air in the range 220–450 °C synthetic jarosite loses water from its structure. The initial temperature of endothermic effects for $NH_4[Fe_3(OH)_6(SO_4)_2]$ is observed at 230, 350, 480, 515, 630°C [68] and for $H_3O[Fe_3(OH)_6(SO_4)_2]$ – at 230, 405, 515, 620, 660°C [69] or at 290, 370 and 510°C [58]. The thermogravimetric investigation of $NH_4[Fe_3(OH)_6(SO_4)_2]$ jarosite showed five mass loss steps at 120, 260, 389, 510 and 541°C [70].

The thermal treatment in air of β-FeOOH showed endothermic peaks at 230, 260 (a shoulder) and 275 °C, and an exothermic peak (small intensity) at 455°C. Endothermic effects correspond to dihydroxylation of β-FeOOH and the exothermic effect to the recrystallization of α-Fe_2O_3 [51]. The DTA curve of sulfated β-FeOOH showed two endothermic peaks at 275 and 350°C and an exothermic peak at 550°C. The jarosite and β-FeOOH compounds in the polymer phase were formed in conditions of high concentrations of SO_4^{2-} and Cl^- ions and their thermal behaviour is expected to differ from the thermal behaviour of $NH_4[Fe_3(OH)_6(SO_4)_2]$ and $H_3O[Fe_3(OH)_6(SO_4)_2]$. It was shown [33] that the polymer matrix influenced the thermal behaviour in the air of the Fe(III)-containing compounds, and metallic compounds influenced the thermal behaviour of the polymer.

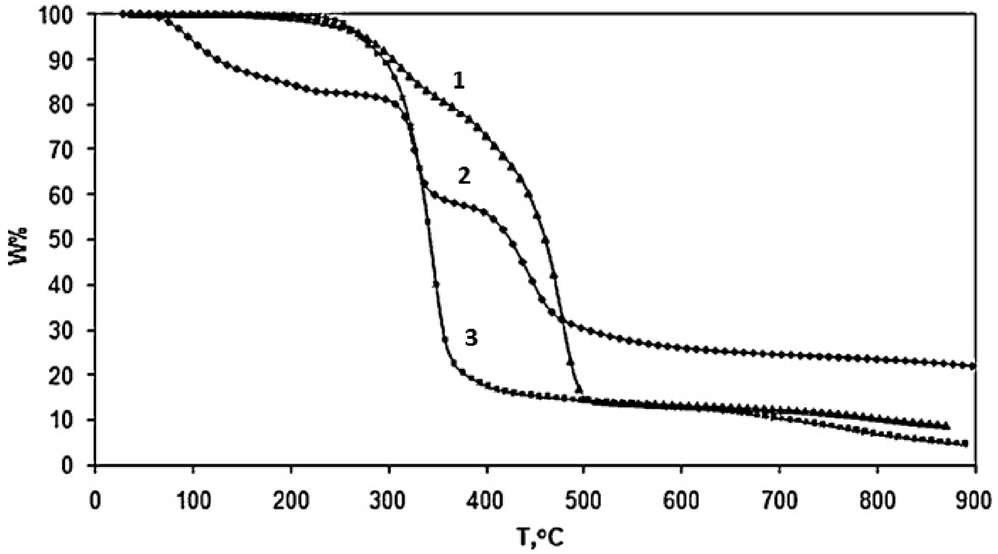


Figure 1-14. TG curves of the samples AV-17(Fe) (1), AV-17(SO_4) (2) and AV-17(FeOOH) (3).

The thermal stability of the compounds was evaluated by dynamic TGA in a nitrogen atmosphere. The TG curves of the samples are presented in Figure 1-14. According to the thermograms the thermal degradation runs in two, three or four stages, being accompanied by endothermic effects. Hence, the TG, DTG and DTA curves of the polymer samples, under an inert atmosphere, indicate a complex degradation pathway of these novel materials. The TGA data for AV-17 in SO_4^{2-} form – AV(SO_4) sample, the jarosite containing polymer – AV(Fe) sample and the heated in water jarosite containing polymer – AV(FeOOH) sample, included T_{onset} – the initial temperatures of thermal degradation, T_{peak} – the temperature corresponding to the maximum degradation rate, T_{endset} – the final temperature at which the degradation process for each stage ends and mass loss (wt.%) for nitrogen atmosphere, which are listed in Table 1-7.

The surveys were extended with the kinetic processing of thermogravimetric data. The Freemann–Caroll [71] method application is based on Equation (1-16) and considers incremental differences in (dα/dT), (1−α) and (1/T):

$$\frac{\Delta\ln(\frac{d\alpha}{dT})}{\Delta\ln(1-\alpha)} = n - \frac{E_\alpha}{R} \times \frac{\Delta(\frac{1}{T})}{\Delta\ln(1-\alpha)} \qquad (1\text{-}16)$$

where, α is a normalized fractional conversion defined as (1-17):

$$\alpha = \frac{m_i - m(t)}{m_i - m_f} \qquad (1\text{-}17)$$

m(t) is the mass at any time *t*, and m_i and m_f, respectively, are the initial and final sample mass; *Ea* is activation energy; *n* is the reaction order; *R* is the universal constant of gases and *T* is the absolute temperature in *K*. By plotting the graph of Δln(dα/dT)/Δln(1-α) dependent on Δ(1/T)/Δln((1-α) from the line slope we can compute the activation energy *Ea* and from origin of interception, we get the reaction order *n*. The pre-exponential factor is computed by Equation (1-18):

$$\frac{d\alpha}{dT} = \frac{1}{\alpha} A exp(\frac{-E\alpha}{RT}) f(\alpha) \qquad (1\text{-}18)$$

Table 1-7. Thermogravimetric and kinetic data of the samples AV(SO_4), AV(Fe) and AV(FeOOH)

Sample	Stage	$T_{onset,,}$ °C	$T_{peac,}$ °C	$T_{endset,}$ °C	W, %	Rezidue, %	Ea , kJ/ mol	n	Ln A
AV(SO_4)	I	70	91	133	13.98	19.09	54.35±0.98	1.87±0.003	13.23±0.34
	II	161	210	274	3.74		-	-	-
	III	315	326	339	25.53		555.8±6.97	2.80±0.003	108.94±1.43
	IV	409	440	539	37.66		209.9±2.07	1.62±0.001	31.18±0.36
AV(Fe)	I	256	311	339	19.33	7.58	95.90±0.86	1.48±0.001	14.54±0.19
	II	389	398	444	19.07		82.94±2.38	0.43±0.002	9.09±0.44
	III	444	476	498	54.02		185.4±8.24	0.52±0.004	24.63±1.37
AV (FeOOH)	I	251	263	299	8.26	3.71	98.85±5.29	0.70±0.006	16.46±1.21
	II	298	343	372	88.26		155.3±0.89	0.75±0.008	25.33±0.18

Table 1-7 reveals the kinetic characteristics data such as: *Ea* – the apparent activation energy, *n* – the reaction order and *lnA* –the pre-exponential factor corresponding to each stage. The first step (70–133°C) for the AV(SO_4) sample, is assigned to the water loss from their structures. The temperature corresponding to the maximum degradation rate in the next stages for this sample is seen at 210, 326 and 440°C, respectively. The thermal degradation of the jarosite-containing polymer – AV(Fe) sample, takes place in three stages, with different mass loss percentages. For this compound, the most important mass loss has been recorded in the last stage of the thermal degradation, at onset temperatures over 444°C. The thermal degradation in nitrogen atmosphere of AV(FeOOH) indicated two endothermic peaks at 263 and 344°C. For this sample, the degradation processes are almost complete, a small residue being left (3.71 wt.%). From the data of the thermal analysis we can conclude that the sorbent (catalyst) obtained by forming the Fe-jarosite compounds of the strongly basic polymers is stable up to about 250°C. It is also stable up to about 250°C and the adsorbent (catalyst) is made up of polymer and β-FeOOH.

As a result of the research, the sorbent (catalyst) AV-17 (Fe-jarosite) was obtained [72, 73] which is selective for the removal of CN^-, NCS^-, NCO^- ions from the solutions [74].

1.2.5. Iron compounds in the phase of polyfunctional polymers

1.2.5.1. Iron compounds in polymers also containing groups that can participate in anion exchange processes

In the earlier paragraphs, we discussed the processes for the formation of iron compounds in the phase of monofunctional polymers containing ammonium quaternary nitrogen. In such polymers, Fe^{3+} cations form jarosite-type compounds under certain conditions. Can jarosite type compounds be formed in polymers containing ammonium quaternary nitrogen and electron donor atoms? To answer this question, polymers with various functional groups were obtained (Cornelia Luca PhD and Violeta Neagu PhD,” Petru Poni” Institute of Macromolecular Chemistry, Iassy, Romania) and investigated [75, 76]. 4-vinylpyridine: divinylbenzene copolymer (4-VP: DVB) was investigated with a different cross-linking degree (for comparison) and a chemically modified copolymer. The preparation of the copolymer samples is described in detail in [75].

The interaction of 4-VP: DVB copolymers with the aqueous solution of $Fe_2(S0_4)_3$ was performed. Copolymer samples of 0.2 g were contacted with a 200 mL solution of 0.01M $Fe_2(SO_4)_3$ for 7 days. The pH of the sample-solution system was kept at 2.0 by use of a solution of either H_2S0_4 or KOH.

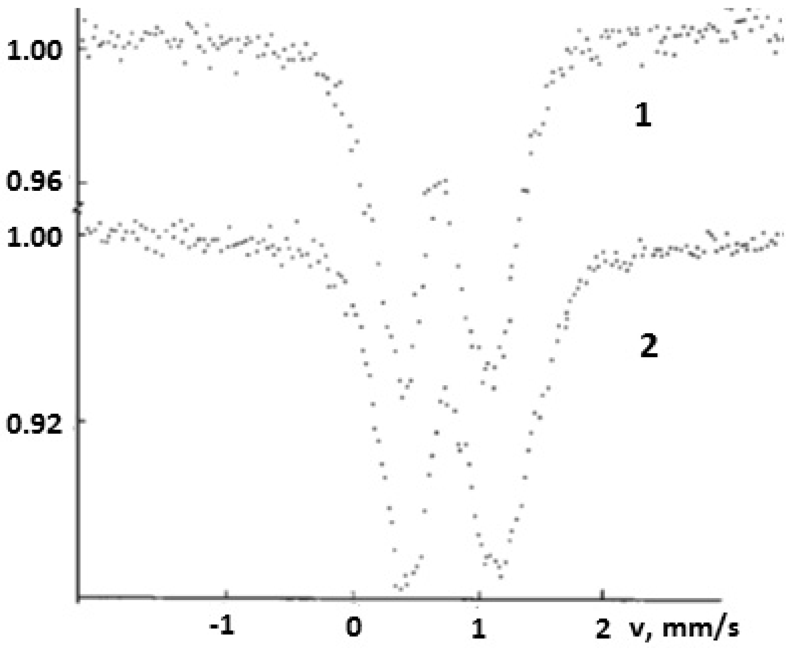


Figure 1-15. Mössbauer spectra of 4-VP: 10% DVB gel-type copolymer-Fe(III) complexes obtained at 300 (1) and 80 K (2).

Figures 1-15 and 1-16 present some typical Mössbauer spectra appearing as doublets. The parameters of the Mössbauer spectra, along with the retained amounts of Fe(III), are listed in Table 1-8. It can be noticed that the form of the spectra together with their characteristics values indicates the presence of Fe^{3+} ions in the high spin state and the octahedral configuration, as well as the absence of Fe^{2+} ions, i.e. the absence of a reducing agent in the copolymers.

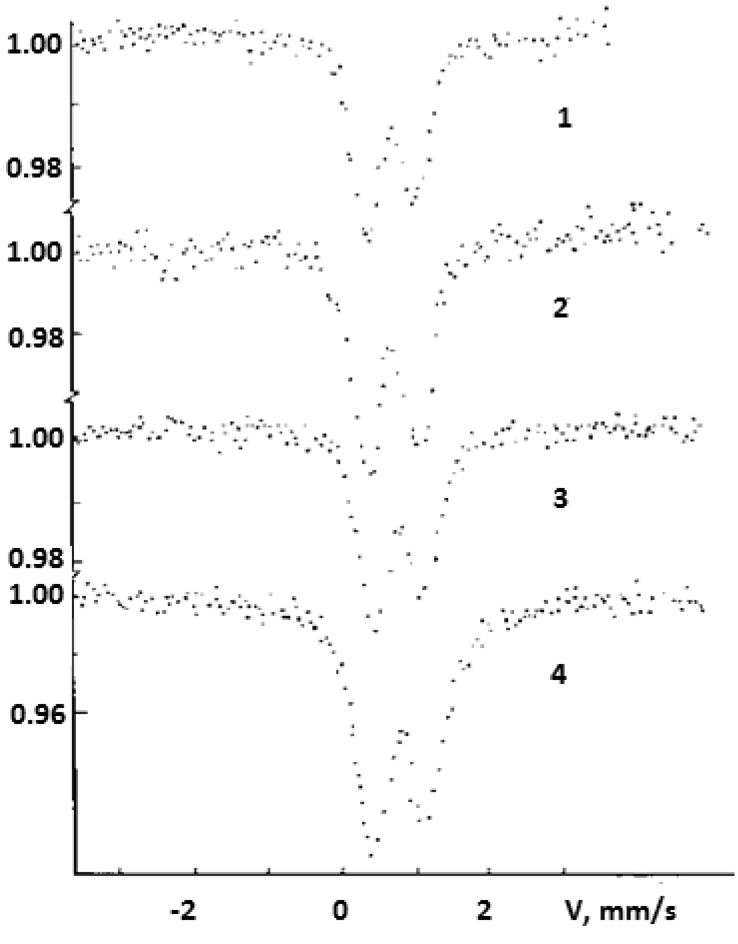


Figure 1-16. Mössbauer spectra of 4-VP: 2% DVB-Fe(III) complexes at 300 (1) and 80 K (2) and of 4-VP: 15% DVB toluene-modified copolymer-Fe(III) complexes at 300 (3) and 80 K (4).

Also, Table 1-8 shows that the determination of the spectra at 80 K induces a slight increase of the quadrupole splitting, with the increase of the cross-linking degree, meaning that the electronic state of Fe^{3+} in the copolymer hardly depends on the DVB content. The tendency of increasing the isomeric shifting with the increase of the crosslinking degree may also be observed, indicating a decrease of the covalent linking of the metal to the ligand. The line width in the studied spectra is higher as compared to that of crystalline structures; yet lower than that of ion exchangers retaining either iron cations or iron complex anions as a result of electrostatic interaction [77, 78]. The **Γ** values change with temperature, similar to those of the Fe^{3+} ions coordinated with the amine groups in weak basic anion exchangers [79]. For the samples containing 2 and 6% DVB, respectively, the width of the spectral lines does not depend on temperature. However, for the copolymers with ≥ 10% DVB, a certain dependence of **Γ** on temperature may be noticed, as a result of the spin-network type relaxation processes. The value of the probability (f ') of the Mössbauer Effect provides information on the oscillation of the coordinating centre of the macromolecular chain. As one can see from Table 1-8, the values of the f'_{300}/f'_{80} ratios (where f'_{300} *and* f'_{80} represent the probability of the Mössbauer Effect at 300 and 80 K**,** respectively) for the gel-type copolymers with 6 and 10% DVB and also for the copolymers synthesized in the presence of toluene, with 10% DVB, indicate a slight dependence of the Mössbauer Effect on temperature. The parameters of the Mössbauer spectra and their dependence on temperature support the conclusion that sorption of the Fe^{3+} ions on the 4-VP: DVB copolymer is conditioned, as expected, by the coordination process of cations with pyridinic nitrogen, the electronic state of Fe^{3+} ions in the copolymer depending, nevertheless, only slightly on their crosslinking degree. It has been also observed that in the complexed copolymers no complex ions of the $[Fe(H_2O)_6]^{3+}$, $[Fe_2(OH)_2(H_2O)_6]^{4+}$ and $[Fe(OH)(H_2O)_5]^{2+}$ types are formed. Consequently, as a result of the Fe(III) complexation with pyridinic nitrogen, destruction of the aqua-hydroxylic and dimeric complexes of Fe^{3+} occurs. From a quantitative point of view, Fe(III) is retained in the same order of magnitude by all 4-VP : DVB copolymers; the Fe(III) retention is significant, although sorption has been performed from an aqueous solution of $Fe_2(SO_4)_3$ and water is a poor solvent for the polyvinylpyridine chains.

The complexation of Fe^{3+} ions with the pyridinic groups of the 4-VP:DVB copolymers was confirmed by the IR spectra (Fig.1-17***)***. As known, complexation of polyvinylpyridine with ions of transitional metals is accompanied by an increase of the frequency of the C = N bond. The IR spectra (Fig.1-17***)*** evidence, besides the absorption band at 1600 cm^{-1}, attributed to the noncomplexed pyridinic rings, an intense band at about 1635 cm^{-1}, due to the nitrogen-metal bond; the analysis of some previous data shows that this absorption band is also present in quaternary ammonium containing polymers based on poly(4-vinylpyridine), i.e., compounds in which the pair of nitrogen-free electrons is occupied [80].

Table 1-8. Influence of the structure of 4-VP: DVB networks on quantitative and qualitative Fe(III) retaining complexes

Copolymer	Nitrogen, %	Fe, mg/g	T, K	Mössbauer parameters, mm/s				**f_{300}/f_{80}**
				δ	**ΔE_Q**	**Γ_l**	**Γ_r**	
4-VP: 2% DVB, gel type	10.80	16.24	300 80	0.62 0.73	0.70 0.68	0.47 0.47	0.47 0.47	0.37
4-VP: 6% DVB, gel type	10.25	20.71	300 80	0.70 0.75	0.70 0.73	0.57 0.52	0.57 0.57	0.67
4-VP: 10% DVB, gel type	10.30	19.94	300 80	0.68 0.77	0.72 0.77	0.44 0.49	0.52 0.64	0.66
4-VP: 10% DVB, toluene modified, $f_v = 0.7$	9.30	19.66	300 80	0.70 0.75	0.75 0.75	0.55 0.57	0.55 0.57	0.49
4-VP: 15% DVB, toluene modified, $f_v = 0.045$	9.35	19.14	300 80	0.62 0.65	0.68 0.73	0.49 0.62	0.55 0.62	0.22

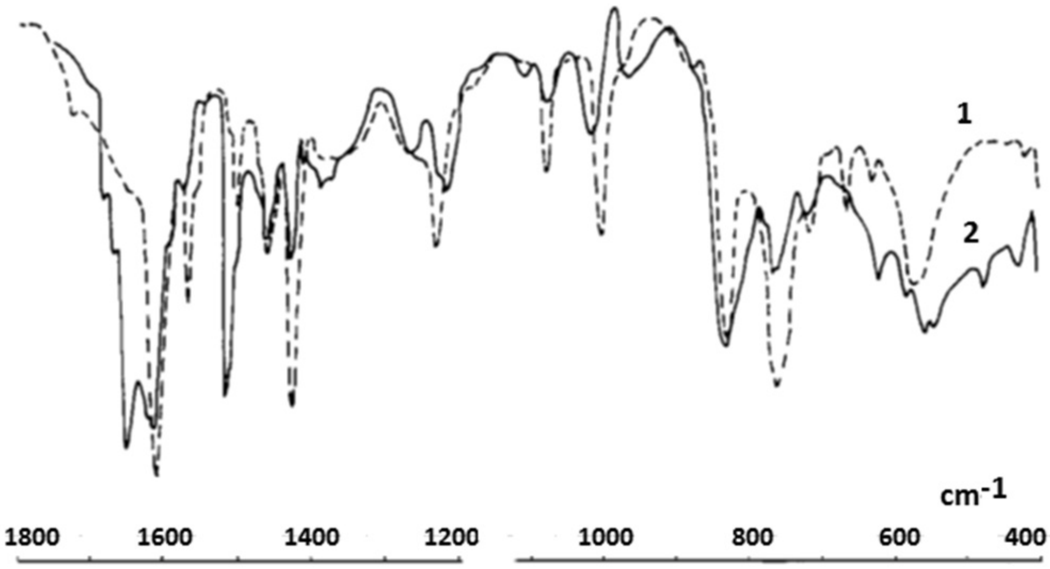


Figure 1-17. IR spectra 4-VP-8% DVB gel type copolymer (1) and 4-VP: 8% DVB gel-type copolymer – Fe(III) complex (2).

To obtain bifunctional polymers, the chemical modification of 4-VP: 8% DVB copolymers was carried out by the addition reaction of the copolymer to the carbon-carbon double bond of some electrophilic ethylenic compounds, such as acrylamide (AM), acrylonitrile (AN), and methyl vinyl ketone (MVK). The capacity of anion exchange (Cl^-↔SO_4^{2-}) and the sorption capacity (S) of cations (Fe^{3+}) from $Fe_2(SO_4)_3$ solution with pH 2.0 of modified copolymers were determined (Tab.1-9)

The 4-VP: DVB copolymers significantly change their nature upon modification. Consequently, the electron-donor pyridinic nitrogen is transformed into ammonium quaternary nitrogen, unable of forming donor-acceptor bonds. Also, in the chemically modified products appear functional groups having nitrogen and/or oxygen atoms, able of forming donor-acceptor bonds. It is assumed that such modifications essentially change the properties and, especially, the sorption mechanism of the Fe^{3+} cations. Table 1-9 shows some data on the chemically modified copolymer as compared to the precursor copolymer. The values presented in this table evidence distinct aspects: 1. The addition reaction of the 4-VP: DVB copolymer to ethylenic electrophilic compounds leads to unconventional strongly basic anion exchanger structures having exchange capacities with values close to those of common strong basic anion exchangers and - 2. The new crosslinked ionic structures retain Fe^{3+} cations in amounts close to the parent copolymer but much higher than the three-dimensional structures with benzyltrimethylammonium chloride or benzyldimethyl-2-hydroxyammonium chloride groups corresponding to strongly basic anion exchangers of types I or II**,** respectively.

Table 1-9. . Mössbauer parameters of synthesized ionic polymers-Fe(III) complexes

Code	Temperature, K	Mössbauer parameters, mm/s			
		δ	**ΔE_Q**	**Γ_l**	**Γ_r**
4-VP: 8% DVB + AN	300	0.79	0.94	0.37	0.57
	80	0.87	0.90	0.46	0.75
4-VP: 8% DVB + AM	300	0.74	0.92	0.49	0.77
4-VP: 8% DVB + MVK	300	0.73	0.84	0.50	0.61

Figure 1-18 plots the Mössbauer spectra of the ionic polymer-Fe(III) complexes; the Mössbauer spectra appear as a doublet. From the values of the Mössbauer spectra (Tab.1-10), one can observe that the state of the Fe^{3+} cations in ionic polymers is different from that in the 4-VP: DVB copolymers, namely, that the values of quadrupole splitting corresponding to the state of Fe^{3+} cations in jarosite-type compounds, formed in strongly basic anion exchangers.