

Ionic Polymers. III. Sorption of Fe(III) Ions on New Crosslinked Ionic Polymers Based on 4-Vinylpyridine: Divinylbenzene Copolymers

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SYNOPSIS

Copolymers of 4-vinylpyridine : divinylbenzene with various degrees of crosslinking have been obtained as precursors for ionic polymers. To this end, addition reactions of the 4-vinylpyridine : 8% divinylbenzene copolymer to electrophilic ethylenic compounds, such as acrylamide, acrylonitrile, and methyl vinyl ketone in the presence of HCl have been performed; the resulting ionic polymers contain, besides ammonium quaternary groups, other functional groups such as amide, nitrile, and ketone. The quantitative iron retention from aqueous $\text{Fe}_2(\text{SO}_4)_3$ solutions was determined photocolometrically for both 4-vinylpyridine : divinylbenzene copolymers and the synthesized ionic polymers. IR and Mössbauer spectroscopy were used to determine the state of the Fe(III) ions in the tridimensional networks. As expected, in 4-vinylpyridine : divinylbenzene copolymers, Fe(III) ions are retained by nitrogen atoms–Fe(III) complexes. The electronic state of metal ions hardly depends on the crosslinking degree. In the ionic polymers, the Fe(III) ions are retained through ionic exchange as the $\text{R}_4\text{N}^+[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]^-$ complex anion. The functional amide, nitrile, and ketone groups, although containing atoms able to form donor–acceptor bonds, do not take part in the complexation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The ability of certain polymers to form polymer–metal complexes may be applied in several domains such as hydrometallurgy, where the formation of complexes takes part in the recovery of different metals, or biochemistry, where iron–various ligands complexes lead to synthetic oxygen carriers like hemoglobin.^{1–5} At the same time, polymer–metal complexes are employed as catalysts in hydrogenation, oxidation, polymerization, or isomerization reactions.⁶

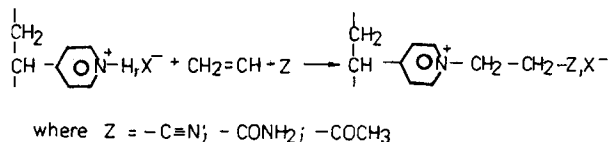
The chemical nature of the functional groups containing atoms able to form donor–acceptor bonds representing the basis of the polymer–metal complexes is very different and, generally, complicated.

The primary, secondary, and tertiary amine groups are probably the simplest.

The complex-formation ability of pyridine structural units of linear poly(2-methyl-5-vinylpyridine), poly(2-vinylpyridine), and poly(4-vinylpyridine) and transitional-metal ions as Fe(III), Co(II), Ni(II), Ru, Rh, and Pd is well known.^{7–10} In a previous study,¹¹ it was reported that polymers containing quaternary nitrogen atoms in benzyltrimethylammonium chloride or benzyl-*N,N*-dimethyl-2-hydroxyethyl-ammonium chloride groups, i.e., strongly basic anion exchangers of types I and II, respectively, retain Fe(III) ions from an aqueous $\text{Fe}_2(\text{SO}_4)_3$ solution in amounts of 7–14 mg Fe/g anion exchanger, in the form of $\text{R}_4\text{N}^+[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]^-$, like jarosite mineral. All polymers including such a compound are selective for NCS^- , CN^- , and NCO^- anions.¹¹

The present article deals with the study of Fe(III) sorption by chemically modified copolymers having

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Scheme 1

as a precursor the 4-vinylpyridine (4-VP) : 8% divinylbenzene (DVB) gel-type copolymer. The chemically modified copolymers contain, besides quaternary ammonium groups, other functional groups with electron-donor atoms such as nitrogen and/or oxygen, namely, amide, nitrile, and ketone groups.

Comparatively, similar studies have been performed on some 4-VP : DVB gels and diluent-modified copolymers. Toluene was used as a diluent.

The main objective of our study was to establish the influence of the morphology of 4-VP : DVB networks as well as of the chemical nature of the synthesized ionic polymers on quantitative and qualitative sorption of Fe(III) ions from aqueous Fe₂(SO₄)₃ solution. The state of the Fe(III) ions in the compounds considered in the present study was determined by IR and Mössbauer spectroscopy.

EXPERIMENTAL

Synthesis and Chemical Modification of 4-VP : DVB Copolymers

All monomers were purified by distillation prior to use. The GC analysis of DVB gave the following result: 57.45 wt % DVB and 38.97 wt % ethylstyrene. 4VP : DVB copolymers were obtained by suspension copolymerization of 4-VP with DVB using 1.5 wt % of benzoyl peroxide as an initiator. The aqueous phase consisted of 3 wt % NaCl, 0.12 wt % gelatine, and 0.5 wt % ammonium salt of poly(styrene-co-maleic anhydride).

The organic : aqueous phase ratio was 1 : 5 v/v for all copolymerization processes. The reaction was allowed to proceed for 10 h at 80°C and 2 h at 90°C. Following polymerization, the copolymer beads were washed with warm water and then extracted with methanol in a Soxhlet apparatus to remove traces of residual monomers, linear oligomers, and diluent, then vacuum dried at 50°C for 48 h.

The content of DVB units in the copolymers was assumed to be the same as in the monomer content in feed. The samples (0.3–0.8 mm diameter) were characterized by their nitrogen content, determined by elemental analysis.

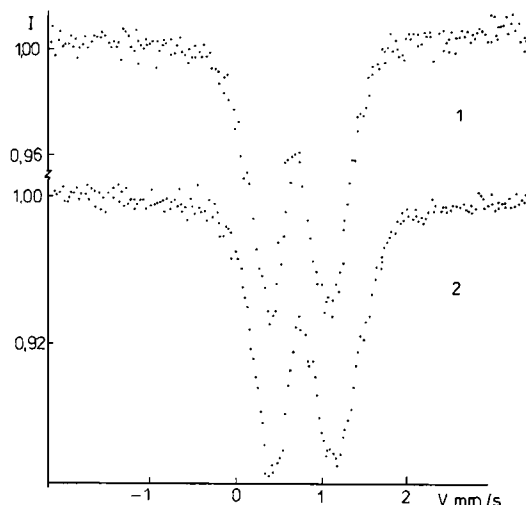


Figure 1 Mössbauer spectra of 4-VP : 10% DVB gel-type copolymer — Fe(III) complexes at (1) 300 K and (2) 80 K.

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

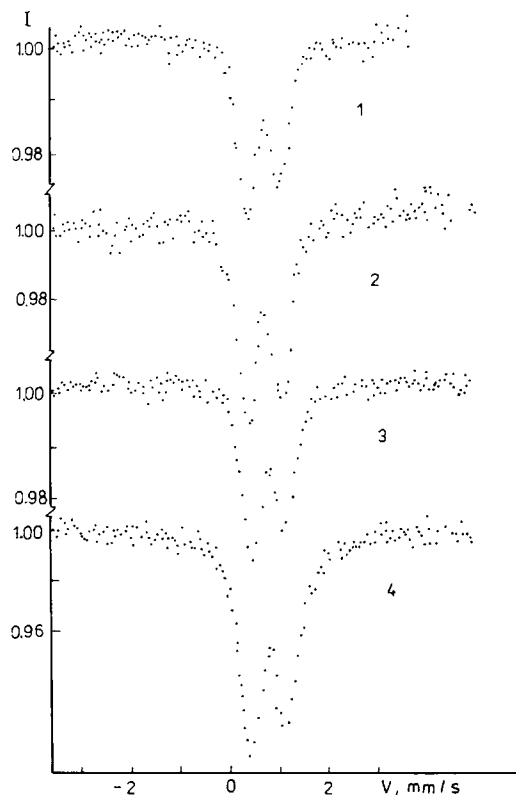


Figure 2 Mössbauer spectra of 4-VP : 2% DVB — Fe(III) complexes at (1) 300 K and (2) 80 K and of 4-VP : 15% DVB toluene-modified copolymer — Fe(III) complexes at (3) 300 K and (4) 80 K.

Table I Influence of the Structure of 4-VP : DVB Networks on Quantitative and Qualitative Fe Retaining

Copolymer	Nitrogen Content (%)	Fe Content (mgFe/g sample)	Temperature (K)	Mössbauer Parameters (mm s ⁻¹)				
				ΔE_I	δE_Q	Γ_l	Γ_r	f'_{300}/f'_{80}
4-VP : 2% DVB gel type	10.80	16.24	300	0.62	0.70	0.47	0.47	0.37
			80	0.73	0.68	0.47	0.47	
4-VP : 6% DVB gel type	10.25	20.71	300	0.70	0.70	0.57	0.57	0.67
			80	0.75	0.73	0.52	0.57	
4-VP : 10% DVB gel type	10.30	19.94	300	0.68	0.72	0.44	0.52	0.66
			80	0.77	0.77	0.49	0.64	
4-VP : 10% toluene-modified $f_V = 0.7$	9.30	19.66	300	0.70	0.75	0.55	0.55	0.49
			80	0.75	0.75	0.57	0.57	
4-VP : 15% toluene-modified $f_V = 0.45$	9.35	19.14	300	0.62	0.68	0.49	0.55	0.22
			80	0.65	0.73	0.62	0.62	

f_V = volume of monomers/volume of monomers + volume of diluent.

of some ethylenic electrophilic compounds, such as acrylamide (AM), acrylonitrile (AN), and methyl vinyl ketone (MVK), according to Scheme 1.

The addition reactions were performed at 50°C in a glass round-bottomed flask equipped with a stirrer, reflux condenser, and thermometer. The following method was used: The copolymer was poured into the flask, then methanol, 1N aqueous HCl solution, and the ethylenic compound were added. A nitrogen : HCl : ethylenic compound molar ratio of 1 : 1.2 : 1.2 was used. After stirring 24 h at 50°C, beads were isolated by filtration, followed by extraction with water, dimethylformamide, or acetone to remove AM, AN, or MVK, respectively. The samples were then washed with methanol and vacuum-dried at 50°C for 48 h.

The chemically modified copolymers were characterized by strongly basic anion-exchange capacities and IR spectroscopy. The exchange capacity was determined by $\text{Cl}^- \rightarrow \text{SO}_4^{2-}$ ion exchange.¹²

Sorption and Fe(III) State into the Polymer Networks

The Fe(III) ion-sorption capacity was determined as follows: Copolymer samples of 0.2 g—prepared as described—were contacted with a 200 mL solution of 0.01M $\text{Fe}_2(\text{SO}_4)_3$ for 7 days. The pH of the sample-solution system was maintained at 2.0 by use of a solution of either H_2SO_4 or KOH. Following the contact, the samples were filtered, washed with dis-

tilled water, and air-dried. The Fe(III) content of the samples was determined photocolometrically by use of α, α' -dipyridine, after desorption of this ion with a solution of 1–1.5M HCl. Several desorptions were performed, until no traces of Fe(III) were found in the eluent.

The polymers with and/or without Fe(III) ions were studied by IR spectroscopy at room temperature. IR spectra were recorded over the 400–4000 cm^{-1} interval on a Specord TM-80 spectrometer. The samples were tabletted with KBr (composition 1 : 200).

The Fe(III)-containing products were analyzed by Mössbauer spectroscopy, at 300 and 80 K. The Mössbauer spectra were obtained on an ICA-70 spectrometer, in an accelerated dynamic regime, Co^{57} in a Cr matrix being employed as a γ -ray source. In the case of spectra in the form of doublets, for determination of parameters such as isomeric shift (ΔE_I), quadrupole splitting (δE_Q), left line width (Γ_l), and, respectively, right line width (Γ_r) of the doublet sodium nitroprussiate was used as a reference substance. The error of the experimental determinations was ± 0.04 .

RESULTS AND DISCUSSION

Sorption of Fe(III) by 4-VP : DVB Copolymers

The interaction of 4-VP : DVB copolymers with the aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ was performed, the

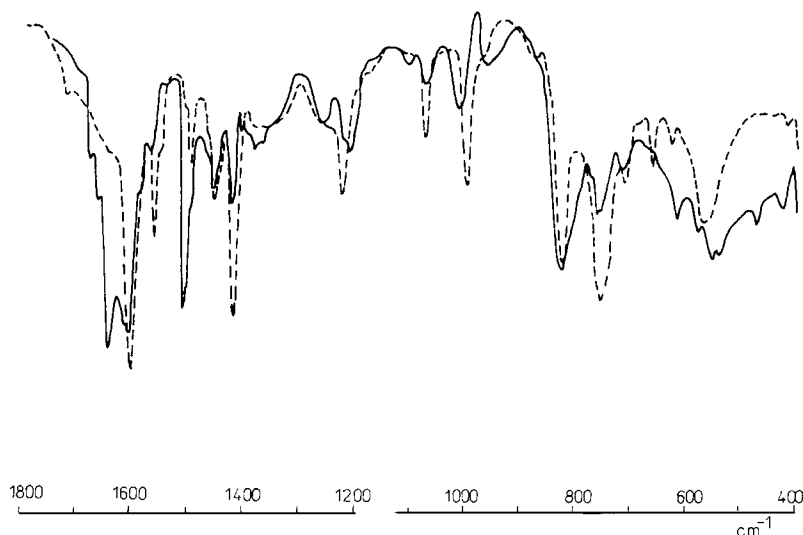


Figure 3 IR spectra of (---) 4-VP : 8% DVB gel-type copolymer and (—) 4-VP : 8% DVB gel-type copolymer — Fe(III) complex.

resulting products being analyzed by Mössbauer spectroscopy. Figures 1 and 2 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 I. One can see that the shape of the spectra along with their characteristic values indicate the presence of only Fe(III) ions in the state of high spin with octahedral surrounding the copolymers as well as the absence of the Fe(II) ions, i.e., the absence of a reductive agent in the copolymers.

Also, Table I shows that the determination of the spectra at 80 K induces a slight increase of the quadrupolar splitting, with increase of the crosslinking degree, meaning that the electronic state of Fe(III) in the copolymer hardly depends on the DVB content. The tendency of increasing the isomeric shifting with 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

Table II Some Characteristics of 4-VP : 8% DVB Chemically Modified Copolymers as Well as of the Parent Copolymer

Code	Structural Ionic Unit	Strongly Basic Exchange Capacity		S^* (mg Fe/g sample)
		meq/g	meq/mL	
4-VP : 8% DVB	$\begin{array}{c} \parallel \\ \text{N} \\ / \end{array}$	—	—	25.0
4-VP : 8% DVB + AN	$\begin{array}{c} \parallel \\ \text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{CN}, \text{Cl}^- \\ / \end{array}$	4.00	1.80	40.58
4-VP : 8% DVB + AM	$\begin{array}{c} \parallel \\ \text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{CONH}_2, \text{Cl}^- \\ / \end{array}$	2.20	1.34	57.15
4-VP : 8% DVB + MVK	$\begin{array}{c} \parallel \\ \text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{CH}_3, \text{Cl}^- \\ / \end{array}$	2.23	1.30	63.76

S^* = sorption capacity of Fe(III) ions from $\text{Fe}_2(\text{SO}_4)_3$ aqueous solution (pH 2.0).

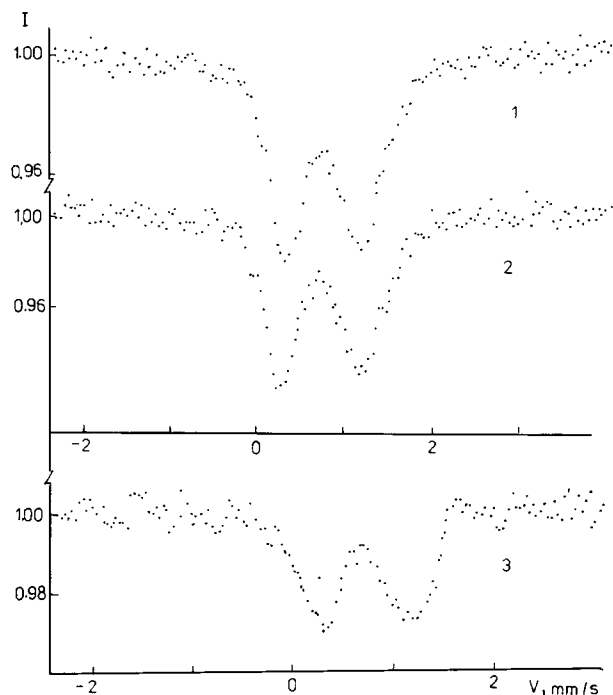


Figure 4 Mössbauer spectra of complexes of Fe(III)-4-VP-8% DVB chemically modified copolymer with (1) AN, (2) AM, and (3) MVK. All spectra were registered at 300 K.

than that of ion exchangers retaining either Fe cations or Fe complex anions as a result of electrostatic interactions.^{13,14} The Γ values change with temperature, similarly to those of the Fe(III) ions coordinated with the aminic groups in weak basic anion exchangers.¹⁵

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 $\geq 10\%$ 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 center of the macromolecular chain.

As one can see from Table I, 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(III) 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(III) 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 $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}_2(\text{OH})_2(\text{H}_2\text{O})_6]^{4+}$, and $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ 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(III) 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 $\text{Fe}_2(\text{SO}_4)_3$ and water is a poor solvent for the polyvinylpyridinic chains.

The complexation of Fe(III) ions with the pyridinic groups of the 4-VP : DVB copolymers was confirmed by the IR spectra (Fig. 3). 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. 3) 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.¹⁶

Table III Mössbauer Parameters of Synthesized Ionic Polymers-Fe(III) Complexes

Code	Temperature (K)	Mössbauer Parameters (mm s^{-1})			
		ΔE_T	δE_Q	Γ_i	Γ_r
4-VP : 8% DVB + AN	300	0.79	0.94	0.37	0.57
	80	0.87	0.90	0.45	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

Sorption of Fe(III) Ions by Chemically Modified 4-VP : DVB Copolymers

The 4-VP : DVB copolymers change essentially 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 containing 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(III) ions.

Table II shows some data on the chemically modified copolymer as compared to the precursor copolymer. The values presented in this table evidence different aspects:

- 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.
- The new crosslinked ionic structures retain Fe(III) ions in amounts close to the parent copolymer but much higher than do 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.

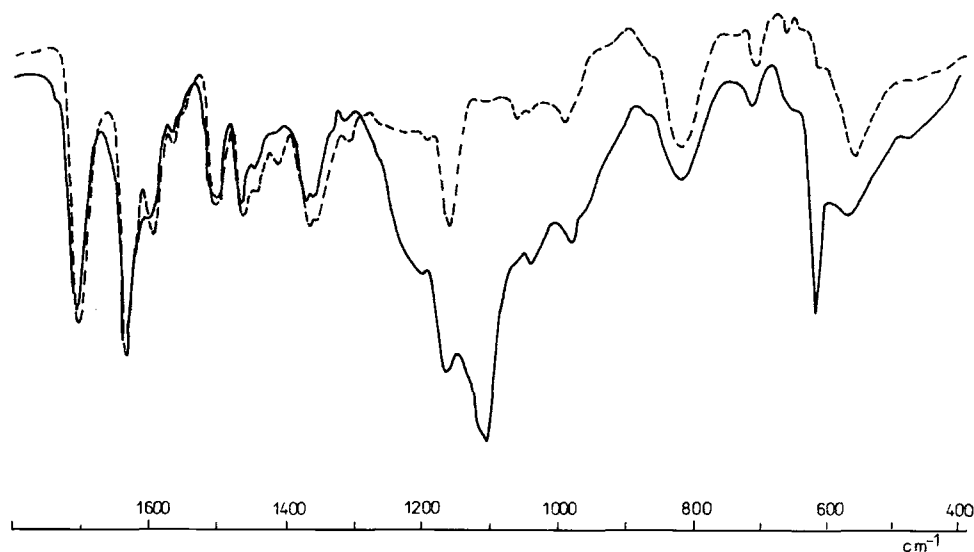


Figure 5 IR spectra of (---) 4-VP : 8% DVB + MVK sample and (—) 4-VP : 8% DVB + MVK-Fe(III) complex.

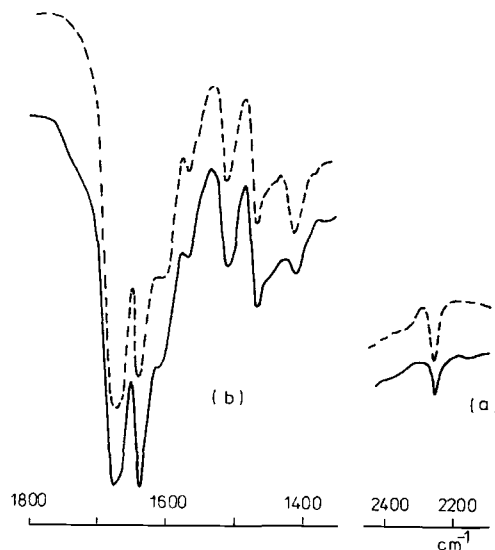


Figure 6 Characteristic absorption bands of IR spectra for (a) 4-VP : 8% DVB + AN sample and its Fe(III) complex and (b) 4-VP : 8% DVB + AM sample and its Fe(III) complex. Broken lines represent the initial samples while the complexes are represented by full lines.

Figure 4 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 (Table III), one can observe that the state of the Fe(III) ions in ionic polymers is different from that in the 4-VP : DVB copolymers, namely, that the values of quadrupole splitting are higher in the ionic polymers as compared to those corresponding to the state of Fe(III) ions in jarosite-type

compounds, formed in strongly basic ion exchangers. At the same time, the Mössbauer spectra show that in the synthesized ionic polymers the Fe(III) ions appear in a single electronic state, i.e., they form a single type of compounds. Consequently, the amidic, ketonic, and nitrilic functional groups do not participate through their nitrogen and/or oxygen atoms to complexation with Fe(III) ions.

Additional proof of such an assertion is provided as well by IR spectroscopy (Figs. 5 and 6). The IR spectra of the chemically modified copolymers containing Fe(III) ions evidence absorption bands at 1100, 870, and 620 cm^{-1} , belonging to the free SO_4^{2-} ions. The absorption bands at 1200 and 1300–1130 cm^{-1} belong to SO_4^{2-} coordinated with three metallic ions while the absorption band at about 480 cm^{-1} is assigned to the $\nu(\text{M}-\text{O})$ metal–oxygen bond from SO_4^{2-} , OH^- , and H_2O .¹⁷

Another aspect of the IR spectra of the ionic polymer—Fe(III) complexes is worth mentioning here. The bands characteristic to the amidic, ketonic, and nitrilic functional groups are not subjected to any shift. They may be found at the following values: $\nu(\text{CN}) = 2250 \text{ cm}^{-1}$, $\nu(\text{CO}) = 1710 \text{ cm}^{-1}$, and $\nu(\text{CONH}_2) = 1670 \text{ cm}^{-1}$, similarly to the situation in ionic polymers without Fe(III).

All these observations lead to the conclusion that the Fe(III) ions are retained by the synthesized ionic polymers only through ionic exchange, due to the quaternary nitrogen atoms, retention occurring in the form of a jarosite-type compound. It was also observed that, although containing atoms able to form donor–acceptor bonds, the functional groups do not participate to complexation.

Probably, the presence of the nitrogen quaternary atom with an inductive effect ($-I$) reduces the electron density from the donor atoms of the functional groups, preventing their complexation with metallic ions. Additional evidence supporting the retention of the Fe(III) ions by the synthesized ionic structures by ionic exchange consists in the fact that they do not retain the metal from FeCl_3 , but only from $\text{Fe}_2(\text{SO}_4)_3$.

CONCLUSIONS

The retention of Fe(III) ions by 4-VP : DVB copolymers depends only slightly on their crosslinking degree. The ionic polymers obtained through the addition, in the presence of HCl, of the 4-VP : DVB copolymers to electrophilic ethylenic compounds (acrylamide, acrylonitrile, MVK) contain quater-

nary ammonium groups which determine a strong basic exchange capacity, as well as amide, nitrile, and ketone functional groups, as evidenced by IR spectroscopy.

Fe(III) ions from the aqueous solution of $\text{Fe}_2(\text{SO}_4)_3$ are retained by the synthesized ionic polymers only through ionic exchange, in the form of the $[\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6]^-$ complex anion, as demonstrated by both Mössbauer and IR spectroscopy. Quantitative sorption of iron on such ionic cross-linked structures is higher than on ionic structures with groups of benzyltrimethylammonium chloride and benzyl-*N,N*-dimethyl-2-hydroxyethylammonium chloride which represent classical structures for strong basic anion exchangers of types I and II, respectively.

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