

Nature of Compounds Formed in Phase of Strongly Basic Anion Exchanger in Contact with Fe₂(SO₄)₃ Solutions

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ABSTRACT: The thermochemical changes taking place in the phase of a Fe(III)-containing strongly basic anion exchanger (AV-17) are investigated by using Mössbauer, IR, and EPR spectroscopy. During the heating of Fe(III)-containing resin in air up to 200°C, redox processes in the polymer phase take place. On boiling in water, the jarosite-type compounds in the polymer are converted into higher dispersed β -FeOOH particles. After sorption-boiling in water cycles in the polymer phase, relatively massive and magnetically ordered β -FeOOH particles are formed. A portion of the

β -FeOOH particles remains in the highly dispersed superparamagnetic state distributed in the narrow pores of the exchanger. It is suggested that the Fe(III) ion sorption from Fe₂(SO₄)₃ solutions by an exchanger takes place through the formation in the polymer phase of solid ultrafine particles of jarosite mineral-type compounds. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 59–64, 2006

Key words: ion exchangers; transition metal chemistry; supports; IR spectroscopy

INTRODUCTION

It is well known that crosslinked ionic polymers containing R₄N⁺ groups are used in water purification and other branches of industry and science. Usually, these polymers are employed as strongly basic anion exchangers:



where R₄N⁺ are polymer groups and A⁻ and B⁻ are anions.

However, in our previous studies^{1–3} we reported that strongly basic anion exchangers are able to retain Fe(III)-containing cations from aqueous solutions of Fe₂(SO₄)₃, but not from Fe(NO₃)₃ or FeCl₃ solutions. Often the retention of Fe(III)-containing ions is an uncontrollable process that contaminates anion exchange materials. In contrast, the synthesis and transformation of metallic compounds in the polymer phase could expand the use of ion exchange materials, particularly in obtaining selective sorbents,⁴ catalysis,⁵ and modeling of biochemical processes.⁶

The strongly anion exchangers containing Fe(III) compounds are selective for NCS⁻, CN⁻, and NCO⁻ anion sorption.⁷ To understand processes taking place on polymers modified with metallic compounds, we must know the nature of these compounds.

The retaining of Fe(III)-containing ions from Fe₂(SO₄)₃ solutions on strongly basic anion exchangers through anion exchange processes is unlikely. In a 10⁻² M Fe₂(SO₄)₃ solution at pH 2.0, there are species of ions such as [Fe(H₂O)₆]³⁺, [FeOH(H₂O)₅]²⁺, and [Fe₂(OH)₂(H₂O)₈]⁴⁺.⁸ In contrast, the desorption of Fe(III)-containing ions exchange processes [according to eq. (1)] do not take place. The observed strong temperature dependence of the Fe(III)-containing ion sorption (through the maximum) on such polymers⁹ is not typical for ion exchange.

Metallic compounds formed in the phase of strongly basic anion exchangers in contact with Fe₂(SO₄)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 ($\Delta E_Q \approx 1$ mm/s),² whereas they are less for Fe(OH)₃ or FeOOH (about 0.7 mm/s).

The main objective of these investigations is to identify the nature of the Fe(III)-containing compounds formed in the polymer phase when a strongly basic anion exchanger is in contact with an Fe₂(SO₄)₃ solution.

We suggest that the sorption of Fe(III)-containing ions from Fe₂(SO₄)₃ solutions on strongly basic anion exchangers takes place through formation in the polymer phase of FeOHSO₄ or jarosite mineral-type compounds R₄N[Fe₃(OH)₆(SO₄)₃] and H₃O[Fe₃(OH)₆(SO₄)₂].^{10–12}

During thermal dehydration of FeOHSO₄, 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.^{13,14} One of the decay products at 230°C is

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TABLE I
Parameters of Mössbauer Spectra of Heated in Air Fe(III)-Containing AV-17 Exchanger

Temperature (°C)		Mössbauer parameters (mm/s)			
Heating	Spectrum recorder	δ	ΔE_Q	Γ_L	Γ_R
120	300	0.62	0.88	0.59	0.56
	80	0.8	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	0.76	0.93	0.62	0.47
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

FeOH₂SO₄, which is stable to 450–500°C. However, when boiled in water, jarosite-type compounds of Fe(III) are transformed into highly dispersed particles of α -FeOOH¹² in the superparamagnetic state and the value of ΔE_Q decreases. Thus, the different behavior of jarosite-type and FeOH₂SO₄ compounds on heating in air or boiling in water permit us to identify the nature of Fe(III) compounds in the polymer phase.

EXPERIMENTAL

A commercial strongly basic anion exchanger [AV-17X8, containing N⁺(CH₃)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 mequiv/g.¹⁵

Dried 1-g polymer samples were contacted with 500 mL of 0.01M Fe₂(SO₄)₃ solution for 24 h at room temperature, which was enough to establish 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 photocolometrically by 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 radiospectrometer 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 samples were tableted with KBr (1 : 200 composition). The Mössbauer spectra were recorded at 300 and 80 K on an ICA-70 spectrometer in the accelerated dynamic regime, and ⁵⁷Co 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 (ΓE_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.

RESULTS AND DISCUSSION

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

The Mössbauer spectra of the Fe(III)-containing samples of AV-17 heated at different temperatures present a doublet at 300 and 80 K. Their parameters (Table I) show that the Fe(III) states when heated to 160°C remain practically unchanged. Some observed changes 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 >160°C, which resulted in partial reduction of Fe(III) to Fe(II) at 200°C.

Thus, the main conclusion of this part of the investigation is that the Fe(III) compound in the AV-17 phase is not FeOH₂SO₄, 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 I)

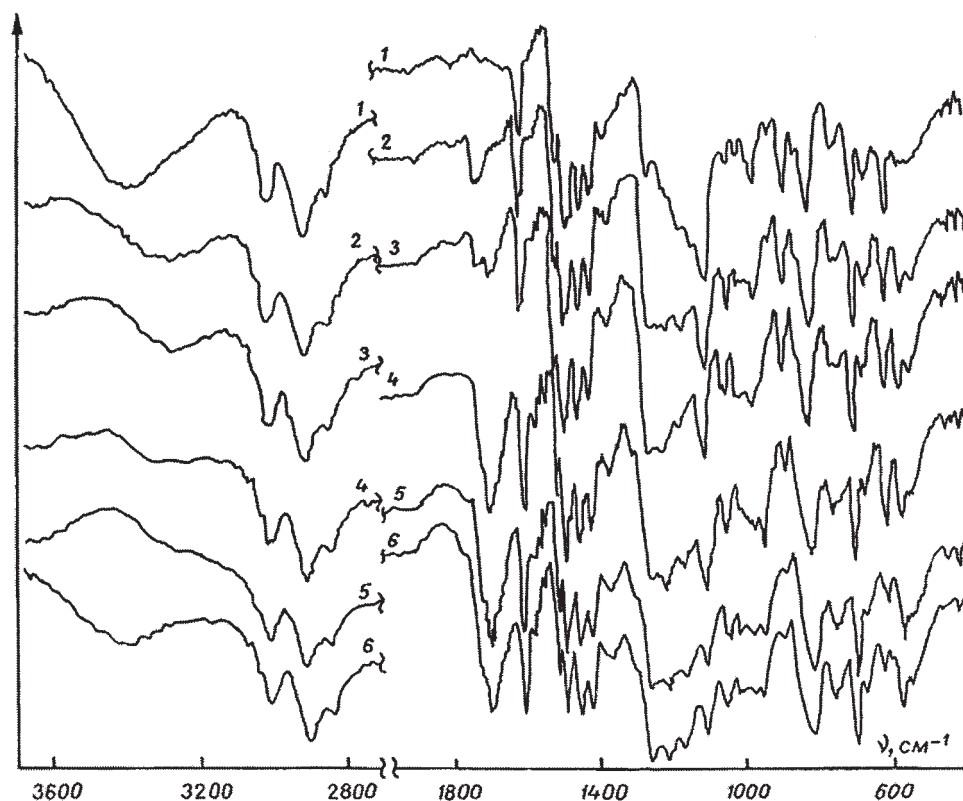
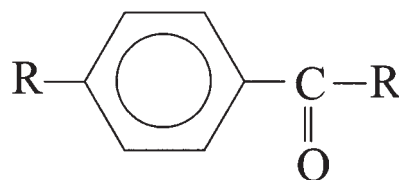


Figure 1 IR spectra of the Fe(III)-containing AV-17 after heating in air at 100 (spectrum 1), 120 (spectrum 2), 140 (spectrum 3), 160 (spectrum 4), 180 (spectrum 5), and 200°C (spectrum 6).

may be due to the break 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 air were obtained from EPR and IR spectra. In the PR 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 $\leq 140^\circ\text{C}$ and decreases to 400 Oe for samples heated at $> 140^\circ\text{C}$. The signals at $g = 4.3$ and 2.003 (wide line) are attributed to the Fe(III) ions in rhombic and octahedral surroundings, respectively.¹⁶ 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.¹⁷ Its intensity increases with the increase of the heating temperature of the Fe(III)-containing polymer samples.

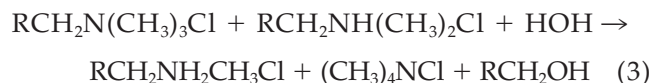
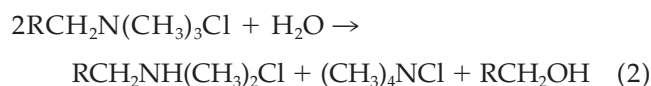
The IR spectra of the heated Fe(III)-containing samples of AV-17 (Fig. 1) are according to Nakamoto¹⁸ and Bellami.¹⁹ In the IR spectrum of the sample heated at 120°C a new absorption band at 1730 cm^{-1} appeared, and in the spectrum of the sample heated at 140°C another band appeared at 1695 cm^{-1} . These bands were attributed to $\nu(\text{C}=\text{O})$ of ketone groups. We suggest that the bands at 1730, 1105, 620, 550, and 420 cm^{-1} correspond to an aromatic ketone type:



The absorption band at 1695 cm^{-1} corresponds to $\text{C}=\text{O}$ groups in an aromatic nucleus, that is, to quinone-type ketone. If this is true, the frequency of the valence vibrations of atoms in the $\text{C}=\text{C}$ and $\text{C}-\text{H}$ groups of the aromatic nucleus must be modified. When increasing the temperature of the heated samples, $\nu(\text{C}=\text{C})$ shifting from 2990 to 3010 cm^{-1} ; $\nu(\text{C}=\text{H})$ shifting from 1610 to 1595 cm^{-1} ; and band widening at 820, 970, and 1045 cm^{-1} take 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 $\nu(\text{C}=\text{O})$ of a carboxylic group appeared at 1715 cm^{-1} . This fact and the growing intensity band at 1260 cm^{-1} [$\nu(\text{C}-\text{O})$ of a carboxylic group] that increases with temperature permit us to suggest that carboxylic groups are formed on heating in Fe(III)-containing polymer. It is also confirmed by the appearance in the IR spectra of a band at 945 cm^{-1} (OH group) intensity, which increases with temperature at $\geq 140^\circ\text{C}$. The essential decreasing of intensity of the band at 890 cm^{-1} in the

IR spectra of the samples heated at $\geq 160^\circ\text{C}$ shows that the $-\text{N}(\text{CH}_3)_3$ groups undergo changes.²⁰ According to Karrer,²¹ on heating in 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). 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 behavior of an AV-17 exchanger in the absence of Fe(III) compounds in its phase. The results of such investigations are reported in Tulupov and Grebeni²² and Ugleanskaya et al.²³ According to Tulupov and Grebeni,²² on heating an AV-17 (Cl) exchanger in air, the following processes are carried out:



As shown in Tulupov and Grebeni,²² processes (2) and (3) take place in the polymer phase on heating at $\geq 150^\circ\text{C}$. Ugleanskaya et al.²³ 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.

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

When boiled in water, jarosite compounds are known¹² to be converted to highly dispersed particles of FeOOH in a superparamagnetic state. The Mössbauer spectra of α -, β -, γ -, and δ -FeOOH in the superparamagnetic state show only one doublet and each modification of FeOOH cannot be identified. However, when several sorption-boiling in water cycles are carried out, large FeOOH particles in the polymer phase are obtained. The large FeOOH particles become magnetically ordered, which permits identification of its modification using Mössbauer spectroscopy.

The Mössbauer spectra of the AV-17 sample after one sorption-boiling in water cycle are a doublet at 300 and 80 K (Fig. 2). The Mössbauer spectra of samples after two or more sorption-boiling in water cycles present a doublet at 300 K and a sextet with a doublet in the center of the spectrum at 80 K. The

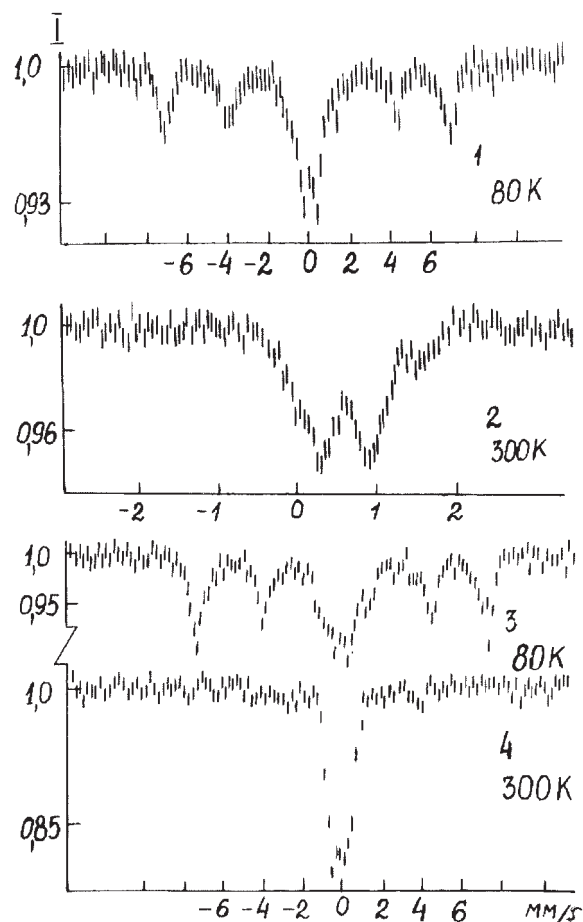


Figure 2 Mössbauer spectra of the Fe(III)-containing AV-17 after 3 (spectra 1 and 2) and 6 (spectra 3 and 4) sorption-boiling in water cycles.

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 (Table II) correspond to β -FeOOH particles with different sizes.²⁴⁻²⁶ The massive particles of β -FeOOH are paramagnetic at room temperature and antiferromagnetic at < 283 K.²⁷ The structure of the particles depends on the nature of anions presented in the medium of β -FeOOH formation.^{28,29}

The doublet in the center of the sextet is attributed to highly dispersed β -FeOOH in the superparamagnetic state, which remains 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,¹² 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 remaining in the polymer phase. According to several stud-

TABLE II
Parameters of Mössbauer Spectra of AV-17 Exchanger after Different Numbers of Sorbtion–Boiling in Water Cycles

No. cycles	Temp. (K)	Spectrum shape	Mössbauer parameters (mm/s)				H_{ef} (kOe)	Fe content (mgFe/g sample)
			δ	ΔE_Q	Γ_1	Γ_Γ		
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	0	20.07
	80	Doublet	0.80	0.94	0.84	0.84	0	
3	300	Sextet	0.80	0.18	—	—	462	25.8
		Doublet	0.61	0.72	0.57	0.42	0	
		Doublet	0.66	0.76	0.61	0.61	0	
4	300	Sextet	0.74	−0.23	—	—	479	45.6
		Doublet	0.59	0.69	0.55	0.55	0	
		Doublet	0.69	0.77	0.77	0.77	0	
5	300	Sextet	0.66	−0.19	—	—	456	57.8
		Doublet	0.63	0.72	0.43	0.51	0	
		Doublet	0.82	0.87	0.77	0.77	0	
6	300	Sextet	0.68	−0.14	—	—	454	65.2
		Doublet	0.61	0.71	0.51	0.48	0	
		Doublet	0.68	0.70	0.70	0.77	0	
	80	Doublet	0.66	−0.18	—	—	450	

ies,^{28–31} 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.³² 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 3.0.³³

However, Goncharov et al.²⁶ 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.⁶ According to this suggestion, the Fe_2O_3 modifications depend on the critical diameter (d_{cr}) of the particles.

Paramagnetic x - Fe_2O_3 exist when $d_{\text{cr}} = 8 \pm 2$ nm, ferromagnetic γ - Fe_2O_3 exists when $d_{\text{cr}} = 8$ –30 nm, and antiferromagnetic α - Fe_2O_3 exists when $d_{\text{cr}} > 30$ nm. When d becomes more than d_{cr} , paramagnetic x - Fe_2O_3 particles spontaneously become magnetically ordered.⁶

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 $\text{Fe}_2(\text{SO}_4)_3$ solutions on strongly basic anion exchangers takes place through formation of the jarosite-type compounds $\text{R}_4\text{N}[\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2]$ and $\text{H}_3\text{O}[\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2]$.

Unfortunately, the particles of the jarosite-type compounds in the polymer phase are too small to use the X-ray diffraction method for their identification.

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