

Ultrafine Particles of Bismuth(III) Compounds in the Phase of Crosslinked Polymers: Precursors for New Sorbents and Catalysts

V. Gutsanu,¹ L. Cojocaru,¹ G. Lisa,² G. F. Volodina³

¹Moldova State University, 60 A. Mateevici str., Chisinau, MD 2009, Moldova

²Department of Chemical Engineering, Gheorghe Asachi Technical University, 700050 Iassy, Romania

³Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academiei str. Chisinau, Moldova 2028, Moldova

Received 15 September 2009; accepted 12 April 2010

DOI 10.1002/app.32615

Published online 29 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, we show that strongly basic anion exchangers (AV-17 and Purolite A-400) are able to retain Bi(III)-containing cations from Bi(NO₃)₃ solutions. The sorption isotherms of the cations at 30 and 50°C were obtained. The sorption increased with increasing temperature. Scanning electron microscopy showed that in the polymer phase, ultrafine particles of Bi(III)-containing compounds were formed. On heating (87°C) in water and in an Na₂SO₄ solution, Bi(III)-containing ultrafine particles became relatively massive. Powder X-ray diffraction showed the existence of the crystalline phase of BiOCl and Bi₂O₃ on the surface and in the volume of the polymer granules. The behavior of the Bi(III)-containing poly-

mer in the HCl, HNO₃, and H₂SO₄ solutions (pH 0–2.5) was investigated. The Bi(III)-containing compounds in the polymer phase were stable at pH > 2. The desorption degree of Bi³⁺ in the HNO₃ solution was much greater than in the HCl or H₂SO₄ solutions. Thermogravimetric investigation (in an N₂ atmosphere) in the range 25–1000°C of the Bi(III)-containing polymer was also carried out. The Bi(III)-containing polymer was stable up to 120°C. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2674–2681, 2010

Key words: adsorption; electron microscopy; ion exchangers; thermal properties; X-ray

INTRODUCTION

Crosslinked ionic polymers containing R₄N⁺ functional groups are largely used in water purification and other branches of industry and science. These polymers are used as strongly basic anion exchangers:



where A⁻ and B⁻ are different anions.

Strongly basic anion exchangers theoretically cannot retain metallic cations from solutions because they do not contain negatively charged or electron donors atoms in their matrix.

However, in previous works,^{1–4} it has been reported that in certain conditions, strongly basic anion exchangers were able to retain M(III)-containing cations (hydroxocomplex cations) from solutions of M₂(SO₄)₃, where M is Fe³⁺, Cr³⁺, or Al³⁺. However, cation retention from M(NO₃)₃ or MCl₃ solutions did not take place.

We suggest that the retention of Fe(III)-, Cr(III)-, and Al(III)-containing cations by strongly basic anion exchangers takes place through the formation in the polymer phase of ultrafine particles of jarosite (alunite) mineral type compounds: R₄N[M₃(OH)₆(SO₄)₂] and H₃O[M₃(OH)₆(SO₄)₂].⁵ It is known^{6–8} that jarosite-type compounds can be formed in the presence of SO₄²⁻ anions only. On boiling in water, Fe-jarosite-type compounds in the polymer phase are converted into more highly dispersed β-FeOOH particles.⁵

The synthesis and transformation of metallic compounds in the polymer phase expands the use of ion-exchange materials, particularly, in obtaining selective sorbents,^{9,10} in catalysis, and in the modeling of biochemical substance transfer processes.¹¹

It is well known that the anion exchange of inorganic anions on a strongly basic exchanger is not a selective process because it is conditioned by Coulomb's interactions. Being modified with metallic compounds, strongly basic anion exchangers become selective sorbents for some kind of anions and molecules.¹⁰

Recently,¹² we found that strongly basic anion exchangers are able to retain Bi(III)-containing cations from Bi(NO₃)₃ solutions. It is clear that Bi(III) compounds in the phase of strongly basic anion

Correspondence to: V. Gutsanu (gutsanu@gmail.com).

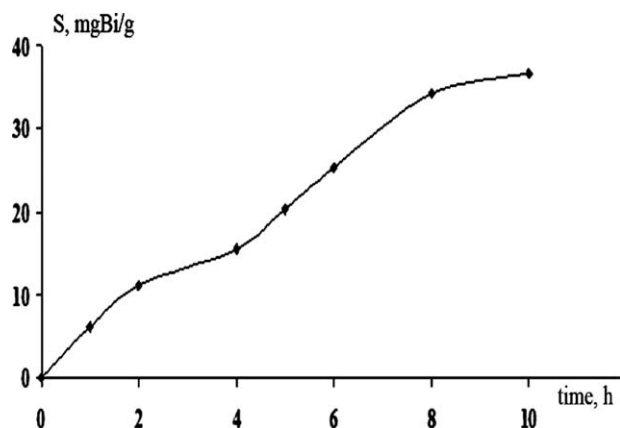


Figure 1 Kinetic curve of the Bi(III)-containing cation sorption at 55°C on the AV-17 polymer. S, sorption; E, concentration.

exchangers are not jarosite mineral types. Modified with Bi(III)-containing compounds, strongly basic anion exchangers become selective sorbents for some kind of anions.¹²

To apply Bi(III)-containing polymers in different processes, it is necessary to elucidate the interaction processes of the polymers with $\text{Bi}(\text{NO}_3)_3$ solutions and the behavior of Bi(III)-polymer systems in various media.

EXPERIMENTAL

The commercial strongly basic anion exchangers AV-17 and Purolite A-400 in Cl^- form were used. Both exchangers were gel-type crosslinked polystyrene-divinylbenzene polymers containing $-\text{N}^+(\text{CH}_3)_3$ functional groups and 8% divinylbenzene. Their full anion-exchange capacities were 3.8–4.5 mg of equiv/g (AV-17) and 4.0 mg of equiv/g (Purolite A-400).¹³

The sorption of Bi(III)-containing cations took place upon the contact of 0.2 g of dried polymer samples with 100 mL of $\text{Bi}(\text{NO}_3)_3$ solution at pH of about 0.25. We prepared the $\text{Bi}(\text{NO}_3)_3$ solutions by dissolving metallic Bi in an HNO_3 solution. The temperature of the polymer-solution systems was maintained constant with an error of $\pm 1^\circ\text{C}$. The Bi^{3+} content in the polymer was determined photocolometrically with thiourea¹⁴ after desorption.¹²

The Bi^{3+} desorption degree (D_s) from the polymer phase was determined upon the contact of 0.2 g of the Bi(III)-containing polymer sample with 50 mL of HCl, HNO_3 , or H_2SO_4 solution with different concentrations at 20 or 50°C.

Scanning electron microscopy (SEM) images were obtained with an SEM-energy-dispersive X-ray spectroscopy microscope (England-Germany).

For the SEM investigation, AV-17 polymer granules containing 65.3 mg of Bi/g were used. We prepared the Bi(III)-containing polymer sample as follows. A 12.5-g sample of the strongly basic anion

exchanger AV-17(Cl) was put in contact with 500 mL of a 0.015M $\text{Bi}(\text{NO}_3)_3$ solution at 50°C for 6 h. Then, the sample was filtered, washed with distilled water, and dried at 60°C for 3 h.

Powder X-ray diffraction investigation was used with a DRON-UM 1 diffractometer (Saint-Petersburg, Russia) (Cu $K\alpha$ radiation, Ni filtered, $\theta/2\theta$ method).

To investigate the Bi(III)-containing polymer behavior in the HCl, HNO_3 , and H_2SO_4 solutions, we put 0.1 g of polymer sample in contact with 50 mL of acid solution for 10 h. After the contact time expired, Bi^{3+} ions in the liquid phase were quantitatively determined.

The thermal behavior of the Bi(III)-containing AV-17 and AV-17(Cl) in the range 25–1000°C was investigated under an N_2 atmosphere with a Mettler Toledo TGA-SDTA 851 derivatograph. The N_2 gas flow rate was 20 mL/min, and the heating rate was 20°C/min.

RESULTS AND DISCUSSION

Sorption of the Bi(III)-containing cations

As shown in Figure 1, the sorption equilibrium of the Bi(III)-containing cations on the strongly basic anion exchanger AV-17 was established at about 10 h of polymer contact with a 0.015M $\text{Bi}(\text{NO}_3)_3$ solution at 55°C. In a previous study, it was shown¹² that the sorption of Bi(III)-containing cations on strongly basic anion exchangers depended on the temperature. The low rate of sorption and its strong dependence on the temperature showed that the retention of Bi(III)-containing cations by anion exchangers is a chemical process. The S-form of Bi(III) sorption isotherms at different temperatures (Fig. 2) confirmed the chemical nature of the sorption process. We suggest that when the strongly basic anion exchanger was in contact with the

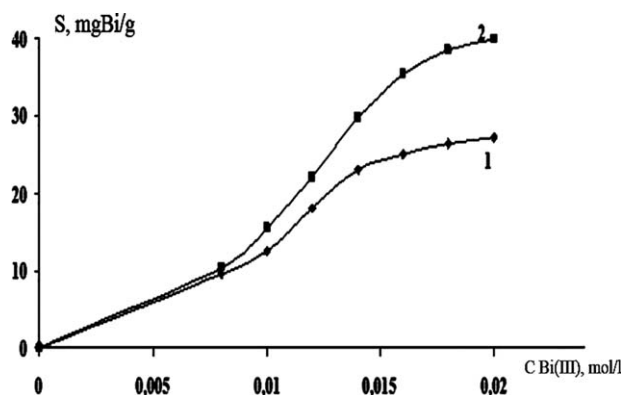


Figure 2 Sorption isotherms of the Bi(III)-containing cations on AV-17 at (1) 30 and (2) 50°C. S, sorption; E, concentration.

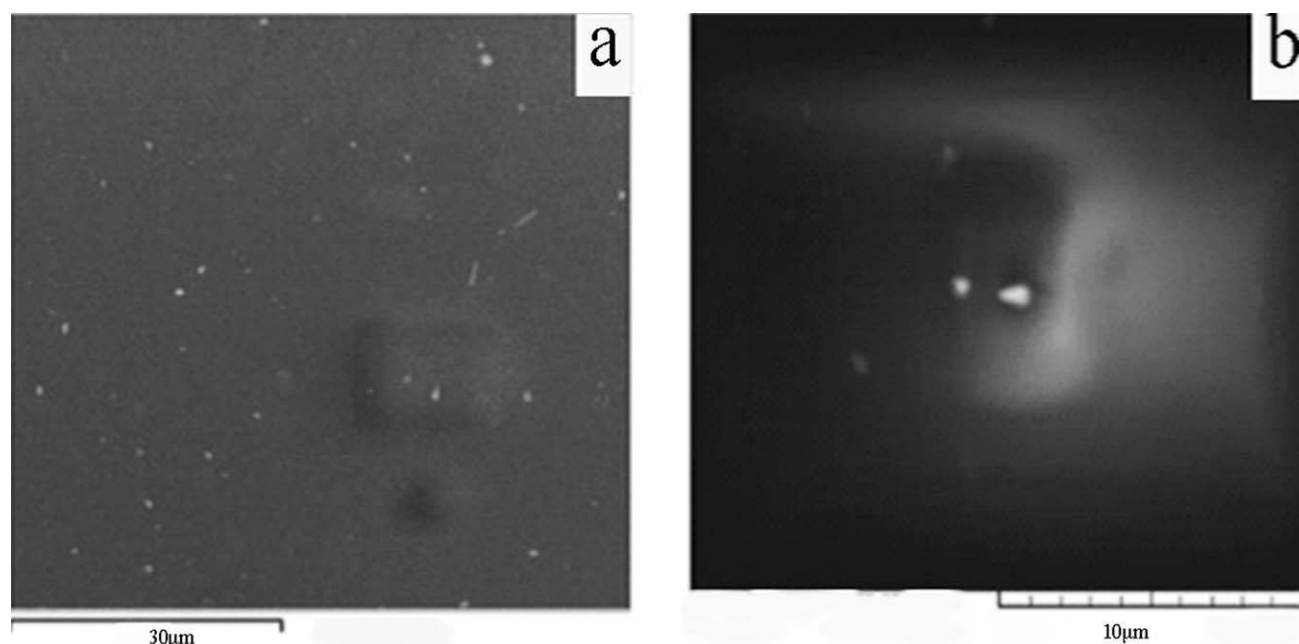


Figure 3 SEM images of the (a) surface and (b) volume of the Bi(III)-containing AV-17 granule.

Bi(NO₃)₃ solutions, the formation of Bi(III) compound particles in the polymer phase took place.

SEM investigation

The existence of solid particles of the Bi(III) compounds on the surface and in the volume of the polymer granules was confirmed by the SEM investigation. The obtained SEM images are presented in Figure 3. Concomitantly, the elemental composition of the Bi(III)-containing structures on the surface and in the polymer granule was determined (Tab. 1).

As shown in Figure 3, on the surface and in the polymer granule, there were ultrafine particles of Bi(III) compounds with particle diameter (d) < 1 μm. with the data from Table I, the brute formulas of a Bi(III)-containing structural unit were computed and were Bi₁O_{31.6}Cl_{3.1}N_{24.1}C₂₁₀ on the polymer granule surface and Bi₁O_{29.2}Cl_{3.0}N_{24.3}C₂₂₈ in the granule.

We suggest that on the surface and in the polymer granule, really there were BiOCl and BiONO₃ particles, and C atoms belonged to the polymer. These particles were situated on the —CH₂N(CH₃)₃Cl and —CH₂N(CH₃)₃NO₃ polymer groups.

We also suggest that part of the BiOCl and BiONO₃ compounds was in the molecular form. To confirm this, we heated at 87°C the Bi(III)-containing polymer sample in acidulated (with HNO₃ solution) distilled water (pH 3.4) for 3 h. It is known⁵ that upon on heating in water in the polymer phase, the fusion of molecular compounds takes place.

The Bi(III)-containing polymer sample obtained after heating in water was investigated with SEM.

As shown in Figure 4, the fusion of small Bi(III)-containing particles in the polymer phase really took place. On heating in water, the surface of the polymer granule was covered with particles of Bi(III)-containing compounds [Fig. 4(a,b)]. On heating in

TABLE I
Elemental Composition of the Bi(III)-Containing Structural Units on the Surface and in the Volume of the AV-17 Granule

Element	On the surface of the granule (atom %)			In the volume of the granule (atom %)			
	Initial AV-17(Bi)	AV-17(Bi) heated in water	AV-17(Bi) heated in an Na ₂ SO ₄ solution	Initial AV-17(Bi)	AV-17(Bi) heated in water		AV-17(Bi) heated in an Na ₂ SO ₄ solution
					Small particle	Large particle	
C	77.88	82.29	57.71	79.84	87.41	83.90	77.58
N	8.92	—	—	8.52	—	—	—
O	11.69	13.60	32.15	10.22	11.45	9.34	18.80
Cl	1.16	2.47	—	1.06	0.80	3.48	—
Bi	0.37	1.65	10.14	0.35	0.35	3.28	3.62

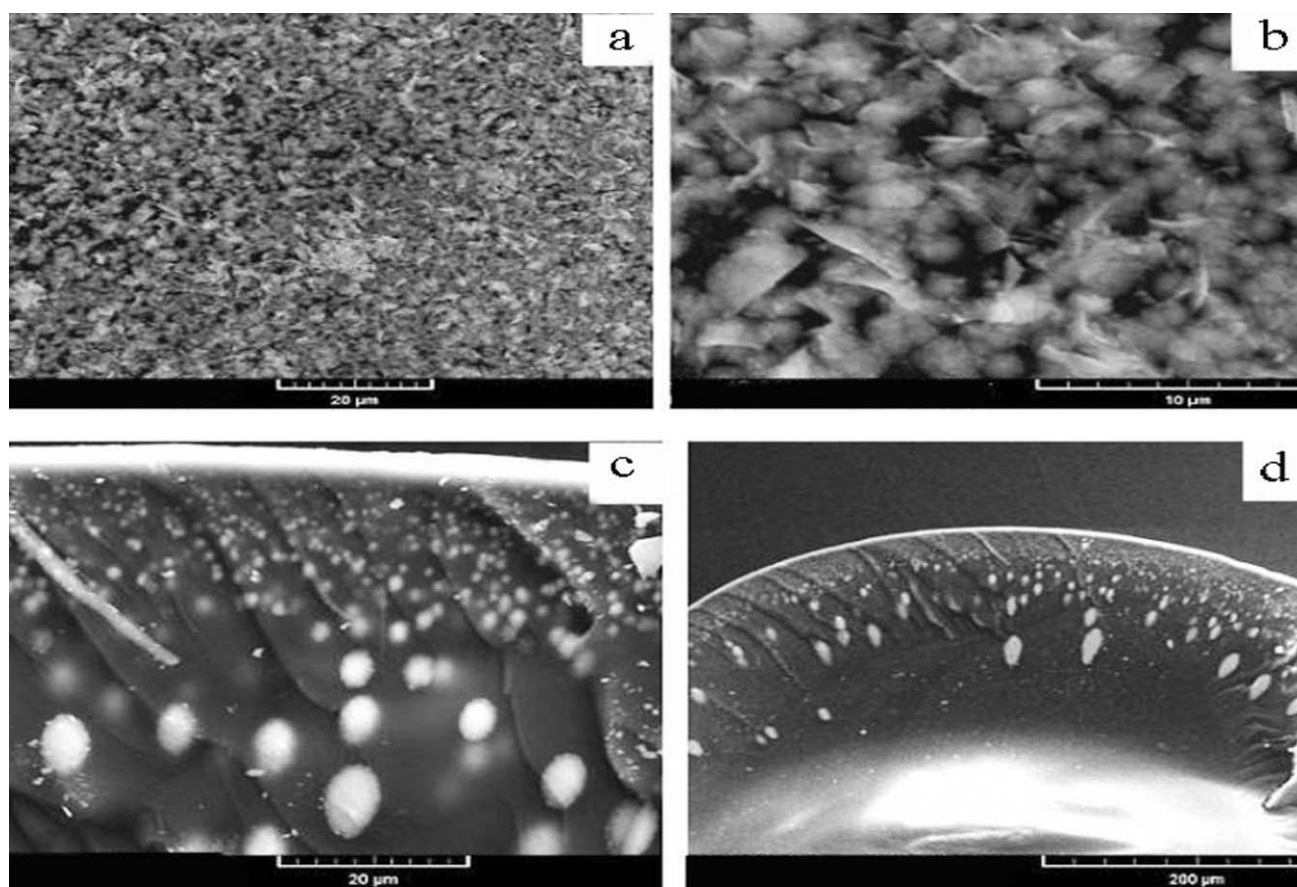


Figure 4 SEM images of the (a,b) surface and (c,d) volume of the Bi(III)-containing AV-17 granule after heating in water.

water in the polymer phase, two processes took place: Bi(III)-containing particles became larger, and compounds migrated to the granule surface [Fig. 4(c,d)]. Up to the polymer granule surface, Bi(III)-containing particles were greater in number but smaller.

The elemental composition of the Bi(III)-containing structures on the surface and of larger and smaller particles in the polymer granule is presented in Table I. The brute formulas of the Bi(III)-containing structural units on the polymer granule surface and the large and small particles in the polymer granule were $\text{Bi}_1\text{O}_{8.2}\text{Cl}_{1.5}\text{C}_{49.9}$, $\text{Bi}_1\text{O}_{2.8}\text{Cl}_{1.1}\text{C}_{25.6}$, and $\text{BiO}_{32.7}\text{Cl}_{2.3}\text{C}_{250}$, respectively.

By comparing the data of Table I, we determined that after heating in water, N atoms in the Bi(III)-containing structures in the polymer phase were absent. Also, the larger the Bi(III)-containing structures were, the lower were the O, Cl, and C atom contents (Table I). We suggest that on the surface and in the polymer granules heated in water, there were, particularly, BiOCl particles and a small amount of Bi_2O_3 compound. These particles were situated on the $-\text{CH}_2-$ and $-\text{CH}_3$ groups and O atoms of the $-\text{CH}_2\text{N}(\text{CH}_3)_3\text{NO}_3$ polymers groups, and N atoms were not detected. A number of par-

ticles containing BiOCl and Bi_2O_3 were situated on the $-\text{CH}_2\text{N}(\text{CH}_3)_3\text{Cl}$ groups.

Interesting results were obtained on investigation of the Bi(III)-containing AV-17 after heating in the 0.1M Na_2SO_4 solution (pH 3.4) at 87°C at 3 h (Fig. 5).

First, we observed that Bi(III)-containing particles were concentrated on the polymer granule surface. Also, the Bi(III)-containing particles were much larger than before they were heating in the Na_2SO_4 solution. The elemental composition of the Bi(III)-containing structures was different, too (Table I). The Bi(III)-containing structures in the polymer phase after heating in the Na_2SO_4 solution contained only Bi, O, and C atoms and did not contain N and Cl atoms. The brute formula of the Bi(III)-containing structure on the polymer granule surface was $\text{Bi}_1\text{O}_{3.2}\text{C}_{5.7}$, and that in the polymer granule was $\text{Bi}_1\text{O}_{5.2}\text{C}_{21.4}$. The composition of the Bi(III)-containing structures permitted us to conclude that on the surface and in the polymer granule, there were $\text{Bi}(\text{OH})_3$ and Bi_2O_3 particles. These particles were situated on $-\text{CH}_2-$, $-\text{CH}_3$, and O atoms of $-\text{[CH}_2\text{N}(\text{CH}_3)_3\text{]}_2\text{SO}_4$ groups. The elemental analysis was focused on Bi_2O_3 particles, but in the polymer phase, there were BiOCl particles, too.

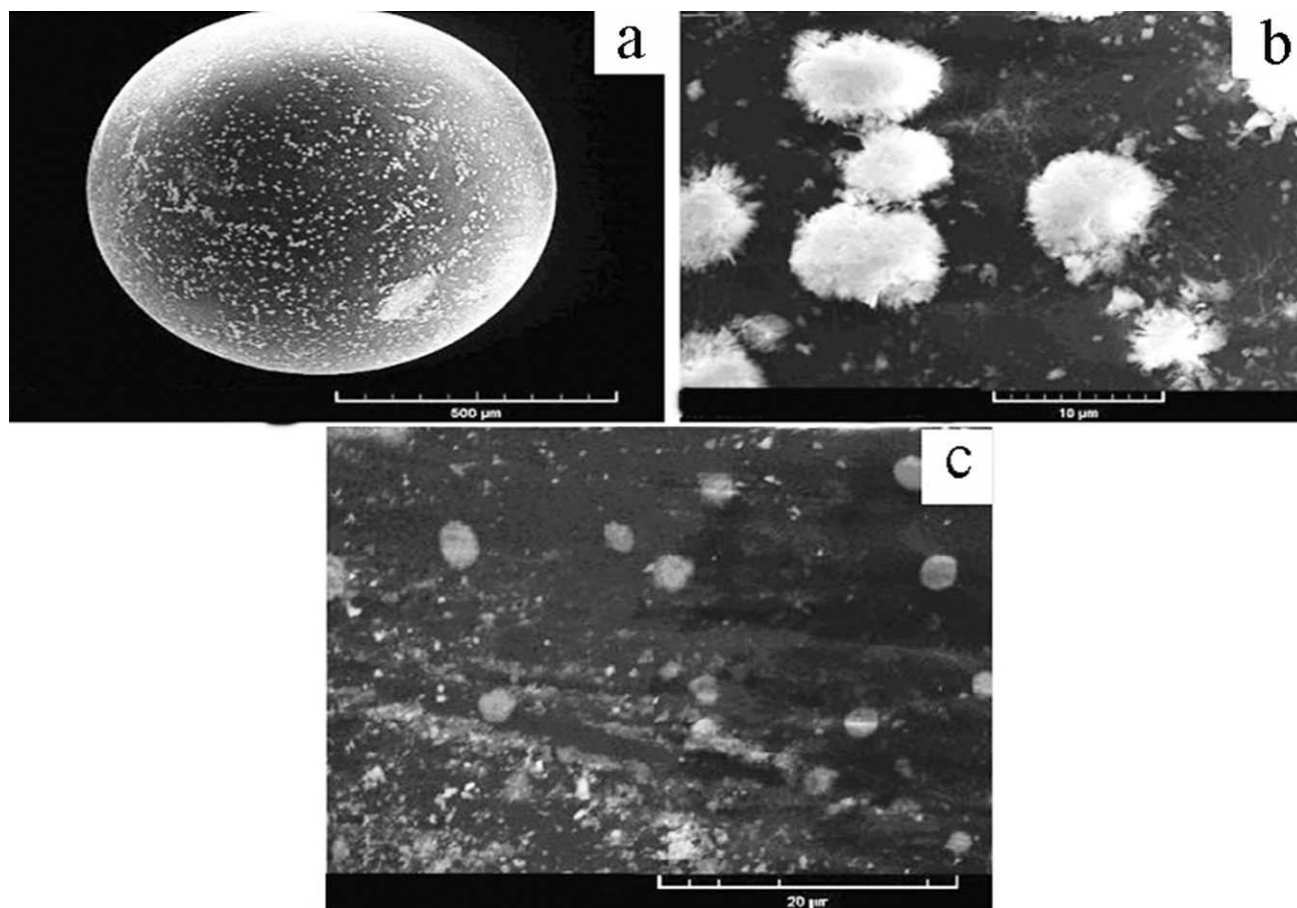


Figure 5 SEM images of the (a,b) surface and (c) volume of the Bi(III)-containing AV-17 granule after heating in an Na_2SO_4 solution.

This fact was confirmed by powder X-ray diffraction investigation. The X-ray diffractogram (Fig. 6) of the Bi(III)-containing AV-17 was a typical spectrum of an amorphous polymer with the large broadening of diffraction peaks corresponding to interplanar distances (d 's) of 4.7 and 2.5 Å. This spectrum did not show any characteristic peaks for bismuth compounds. After the Bi(III)-containing polymer was heated in water at 87°C, the crystallized BiOCl appeared, and its sharp diffraction peaks were located on the polymer matrix curve [Fig. 6(b)]. When the Bi(III)-containing polymer in the Na_2SO_4 solution was heated, the polycrystals of BiOCl were formed but in smaller quantities (the BiOCl spectrum peaks decreased). In this diffractogram appeared a new peak ($d = 3.2$ Å), which was attributed to the Bi_2O_3 phase [Fig. 6(c)].

Behavior of the Bi(III)-containing polymers in an acid medium

To apply Bi(III)-containing polymers to liquid purification, it is necessary to determine their behavior in different media. In this study, the Bi(III) compounds'

destruction in the polymer phase during contact with HCl , HNO_3 , and H_2SO_4 solutions of different concentrations (equivalent with solution pH) were studied.

The strongly basic anion exchanger Purolite A-400, containing 65.7 mg of Bi/g was used. The Bi(III)-

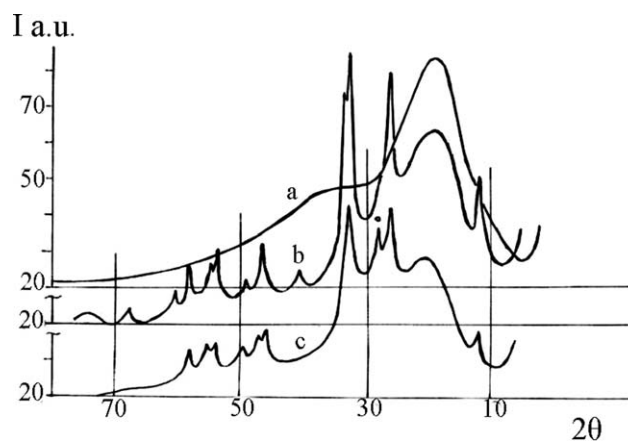


Figure 6 X-ray diffraction spectra of the (a) Bi(III)-containing AV-17 and the Bi(III)-containing polymer after heating in (b) water and (c) a 0.1M Na_2SO_4 solution. I, signal intensity, arbitrary units.

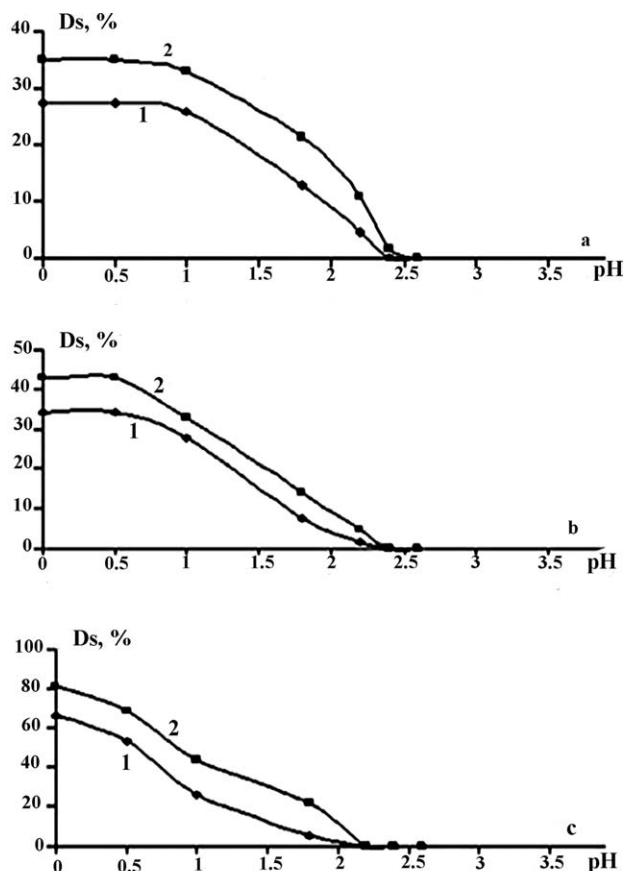


Figure 7 Bi^{3+} ion D_s from Purolite A-400 at (1) 20 and (2) 50°C as a function of pH in (a) HCl, (b) H_2SO_4 , and (c) HNO_3 solutions.

containing polymer was prepared according to ref. 12. The Bi(III) compounds in the Purolite A-400 phase were the same as in the AV-17 polymer. The behavior of the Bi(III) compounds in the Purolite A-400 phase in different acid solutions through the Bi^{3+} D_s , performed at 20 and 50°C, was investigated.

As shown in Figure 7, the Bi(III)-containing compounds in the polymer phase were stable at pH > 2.4 in H_2SO_4 and HCl acid solutions and at pH > 2.2 in HNO_3 acid solution at 20 and 50°C. The pH dependence of the Bi^{3+} D_s in HNO_3 and H_2SO_4 acid solutions showed that in the polymer phase, there were two kinds of Bi(III) compounds with different solubilities. Probably, in the HCl acid solution, all of the Bi(III) compounds were in the form of more stable BiOCl .

D_s of the Bi^{3+} cations from Purolite A-400 in the 1M HNO_3 solution was much greater than in the 1M HCl or 0.5M H_2SO_4 solutions (Fig. 7). D_s of the Bi^{3+} cations also increased with increasing temperature.

The temperature and acid nature influenced the Bi^{3+} ions desorption kinetics (Fig. 8). The Bi^{3+} ion desorption rate in the 1M HNO_3 acid solution was much greater than in the 1M HCl or 0.5M H_2SO_4 solution. After 10.5 h of contact of the Bi(III)-containing polymer with 0.5M H_2SO_4 and 1M HNO_3 acid

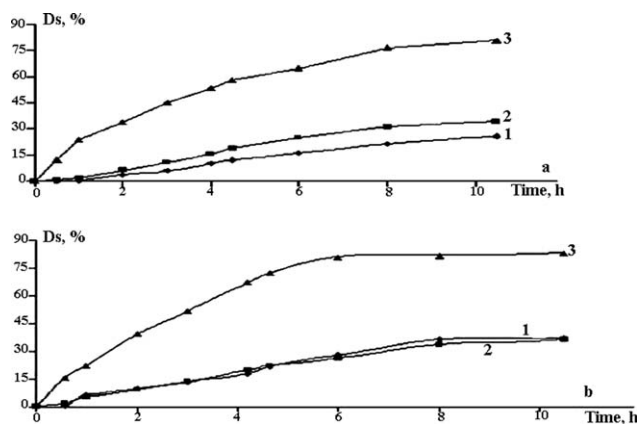


Figure 8 Kinetic curves of the Bi^{3+} ion desorption from Purolite A-400 in (1) 1M HCl, (2) 0.5M H_2SO_4 , and (3) 1M HNO_3 solutions at (a) 20 and (b) 50°C.

solutions, the D_s values were about 34 and 36%, respectively, at 20°C. At 50°C, the D_s values were 80.5 and 83%, respectively.

Thermal behavior of the Bi(III)-containing AV-17

To apply a Bi(III)-containing polymer as a sorbent or a catalyst in processes with gases, it is necessary to determine their thermal behavior.

There was an investigation of the thermal behavior in an N_2 medium of the Bi(III)-containing AV-17 and, for comparison, that of the AV-17(Cl) under the same conditions.

As shown in Figure 9, in the thermogravimetry (TG), differential thermogravimetry (DTG), and

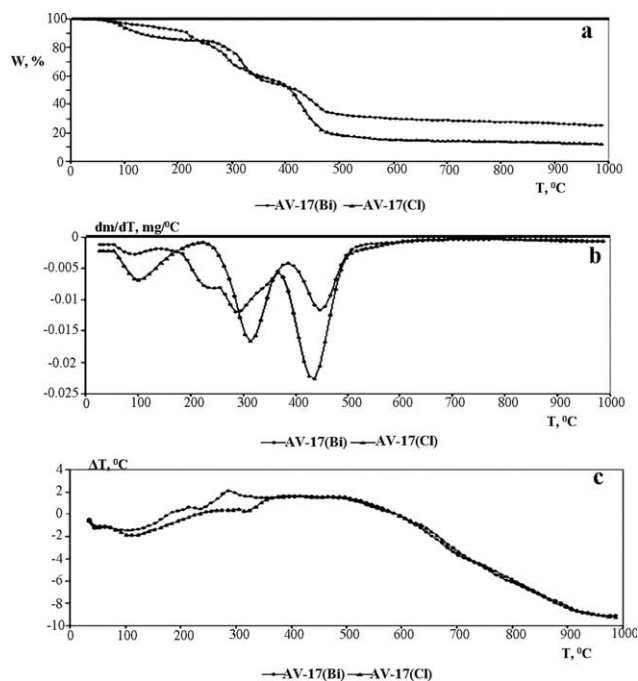
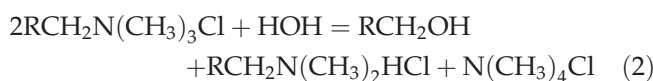


Figure 9 (a) TG, (b) DTG, and (c) DTA curves of the AV-17(Cl) and initial AV-17(Bi).

TABLE II
TG and Kinetic Data Obtained in the Investigation of the Bi(III)-Containing AV-17(Bi) and AV-17(Cl) Samples

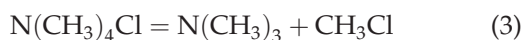
Sample	Stage	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)	Residue (%)	E_a (kJ/mol)	n	$\ln A$
AV-17(Bi)	I	64	86	131	6.63	24.37	33.74 ± 1.07	0.91 ± 0.002	6.63 ± 0.38
	II	215	267	243	11.12		54.28 ± 3.22	0.12 ± 0.003	6.78 ± 0.72
	III	281	333	355	28.83		—	—	—
	IV	417	451	476	29.05		239.90 ± 1.65	1.42 ± 0.001	35.87 ± 0.28
AV-17(Cl)	I	68	99	165	14.47	11.53	56.00 ± 0.47	2.44 ± 0.001	13.68 ± 0.16
	II	267	316	337	29.14		120.88 ± 3.66	0.98 ± 0.005	20.11 ± 0.79
	III	393	433	470	44.86		194.02 ± 3.11	1.67 ± 0.002	28.78 ± 0.55

differential thermal analysis (DTA) curves of the AV-17(Cl), three stages were distinguished. The summary of the important TG characteristics obtained from the thermograms included the initial temperature of thermal degradation (T_{onset}), the temperature corresponding to the maximum degradation rate (T_{peak}), the final temperature at which the degradation process for each stage ended (T_{endset}), mass loss (W ; %), and residual weight loss after the end of the decomposition process; these are listed in Table II. In stage I, two processes took place: elimination from the polymer phase of hydration and free water and, partially, the following process:¹⁶



The process in eq. (2) continued at temperatures greater than 265°C.

In stage II, the processes of $\text{N}(\text{CH}_3)_4\text{Cl}$ decomposition took place according to eq. (3) with the elimination of $\text{N}(\text{CH}_3)_3$ and CH_3Cl :



In stage III, the complete decomposition of the polymer residue took place.

The TG, DTG, and DTA curves of the Bi(III)-containing AV-17 (Fig. 9) differed from those of AV-17(Cl). Examination of the TG and DTG curves in Figure 9 also reveal the existence of a thermal stability domain in the 120–160°C temperature interval for the AV-17(Bi) sample. The temperature in the beginning of the second degradation stage was about 215°C. In the stages II and III, there was a superposition of some thermal processes. On heating of the Bi(III)-containing AV-17, in addition to the processes in eqs. (2) and (3) and water elimination, the decomposition of the Bi(III) compounds took place. More important was that the Bi(III)-containing polymer could be used as a catalyst or as a sorbent without an irreversible state up to 120–160°C.

The surveys were extended with the kinetic processing of the TG data. The Freeman–Carroll¹⁶ method is based on eq. (4) and considers incremen-

tal differences in $d\alpha/dT$, $1 - \alpha$ (where α is the normalized fractional conversion), and $1/T$:

$$\frac{\Delta \ln \frac{d\alpha}{dT}}{\Delta \ln(1 - \alpha)} = n - \frac{E_a}{R} \times \frac{\Delta \left(\frac{1}{T} \right)}{\Delta \ln(1 - \alpha)} \quad (4)$$

where α is defined as follows:

$$\alpha = \frac{m_i - m(t)}{m_i - m_f} \quad (5)$$

where $m(t)$ is the mass at any time t ; m_i and m_f are the initial and the final sample masses, respectively; E_a is the activation energy; n is the reaction order; R is the universal gas constant; and T is absolute temperature (K).

The kinetic characteristics are reported in Table II.

By plotting the graph of $\Delta \ln(d\alpha/dT)/\Delta \ln(1 - \alpha)$ dependent on $\Delta(1/T)/\Delta \ln(1 - \alpha)$ from the line slope, we computed E_a , and from the origin interception, we got n . The pre-exponential factor was computed by the following equation:

$$\frac{d\alpha}{dT} = \frac{1}{a} A \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \quad (6)$$

The n and E_a values (Table II) indicated that the thermal decomposition of the Bi(III)-containing polymer and AV-17(Cl) was a complicated process. The kinetic parameter value determination for each thermal decomposition stage provided information on the degradation mechanism. The thermal degradation process consisted of successive reactions, and higher E_a values occurred in the last stage at temperatures exceeding 400°C. This stage corresponded to thermal polymer degradation. The almost similar E_a values occurring in the last stage suggested similar degradation mechanisms.

CONCLUSIONS

Crosslinked ionic polymers with strongly basic groups were able to retain Bi(III)-containing cations (hydroxocations) from $\text{Bi}(\text{NO}_3)_3$ solutions. The Bi(III) sorption isotherms had an S-form. With increasing temperature, Bi(III)-containing cation sorption increased; this indicated the chemical nature of the

sorption. The sorption of Bi(III)-containing cations took place through the formation on the surface and in the polymer granule volume of ultrafine particles of solid compounds.

The powder X-ray diffraction did not detect a crystalline phase of the Bi(III)-containing compounds in the polymer phase. On heating in water at pH 3.4 and 87°C, the fusion of molecular sizes of the particles took place. SEM images showed that particles were concentrated up to and on the polymer granule surface. X-ray diffraction showed that in the polymer phase, there existed a crystalline form of BiOCl. Some Bi₂O₃ was also formed. On heating in a 0.1M Na₂SO₄ solution at pH 3.4 and 87°C, the Bi(III) compounds in the polymer phase were in the form of Bi₂O₃ and BiOCl particles. The Bi(III)-containing compounds in the polymer phase were stable at pH > 2 in H₂SO₄ and HNO₃ acid solution and at pH > 2.4 in HCl acid solutions at 20 and 50°C. With increasing acid concentration (up to pH 0) and temperature, Bi³⁺ *D_s* increased, too. *D_s* in the HNO₃ acid solution was much greater than in the HCl or H₂SO₄ solutions. The TG data indicated that the Bi(III)-containing polymer was stable on heating under an N₂ atmosphere up to 120–160°C.

The authors thank I. Tighineanu and E. Monayco for their assistance in the SEM investigation.

References

1. Gutsanu, V. L.; Gafiichuk, V. A.; Turta, C. I.; Shofransky, V. N. *Zh Fiz Khim* 1988, 62, 2415.
2. Gutsanu, V.; Drutsa, R.; Rusu, V. *React Funct Polym* 2001, 46, 203.
3. Drutsa, R.; Gutsanu, V.; Rusu, V. *J Appl Polym Sci* 2006, 102, 3978.
4. Gutsanu, V.; Drutsa, R. BOPI 2003, 8, 25; Pat. MD 2241, Republic of Moldova, 2003.
5. Gutsanu, V.; Gafiichuk, V.; Turta, C.; Shofransky, V. *J Appl Polym Sci* 2006, 99, 59.
6. Arkhipenco, D. K.; Devyatkina, E. T.; Palcik, N. A. *Cristalochemical Particularities of Synthetic Jarosites*; Nauka: Novosibirsk, Russia 1987 (in Russian).
7. Hrynkiwicz, A. Z.; Kubisz, I.; Kulgawczuk, D. S. *J Inorg Nucl Chem* 1965, 27, 2513.
8. Ohyabu, M.; Ujihira, Y. *J Inorg Nucl Chem* 1981, 43, 1948.
9. Gutsanu, V.; Drutsa, R. BOPI 1997, 8, 24; Pat. 810 MD, Republic of Moldova, 1997.
10. Gutsanu, V.; Rosca, I. BOPI 2005, 4, 33; Pat. 2746 MD, Republic of Moldova, 2005.
11. Suzdalev, I. P. *Gamma Resonance Spectroscopy of Proteins and Model Compounds*; Nauka: Moscow, 1987.
12. Gutsanu, V.; Cojocar, L. BOPI 2007, 3, 42; Pat. MD 3295, Republic of Moldova, 2007.
13. Lurie, A. A. *Sorbents and Chromatographic Carriers*; Nauka: Moscow, 1972.
14. Marcenko, Z. *Photometrical Determination of Elements*; Mir: Moscow, 1971.
15. Tulupov, P. E. *Stable of Ion Exchange Materials*; Khimia: Moscow, 1984.
16. Freeman, E. S.; Carroll, B. *J Phys Chem* 1958, 62, 314.