

Retention Properties of Arsenate Anions of Water-Soluble Polymers by a Liquid-Phase Polymer-Based Retention Technique

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ABSTRACT: The retention properties of arsenic ions from an aqueous solution by water-soluble cationic polymers and cationic–anionic copolymers were investigated. Poly[(3-methacryloylamine)propyl]trimethylammonium chloride [P(CIMPTA)] and poly[(3-methacryloylamine)propyl]trimethylammonium chloride–*co*-acrylic acid [P(CIMPTA-*co*-AA)] were synthesized by radical polymerization. The copolymers were prepared with feed mole ratios of CIMPTA to AA of 1 : 1, 1 : 2, and 2 : 1. The copolymer compositions were evaluated by FTIR spectroscopy, TG-DSC, and elemental analysis. The liquid-phase polymer-based retention (LPR) technique was used. This technique consists of retention of arsenate anions by the quaternary ammonium salt of a water-soluble polymer in a filtration membrane cell. It was shown that the polymers could bind H_2AsO_4^- species from an aqueous solution more selectively at pHs of 6 and 8, than at a pH of 4. An

increase in the polymer concentration was associated with increased retention capacity but not linearly. At the highest concentration the influence of pH was better observed. Investigation of copolymers showed the concerted action of polycations and polyanions on the ability to retain arsenic. At the lowest pH, the role of ionic strength of the media had a remarkable effect on the retention ability, independently of copolymer composition. At a pH of 6 a copolymer polycation/polyanion composition of 2 : 1 had the highest selective effect. At a pH of 8, a nonequimolar copolymer composition showed the same efficiency for the retention of arsenate species. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2677–2684, 2006

Key words: radical polymerization; water-soluble polymers; ion exchanger

INTRODUCTION

The development of polymers as anionic exchangers has been very important in the treatment of water as a method that protects the environment. Conventional methods include the use of water-insoluble polymers.^{1–5} On the other hand, it is well known that arsenic is highly toxic in water, at a concentration of around of 0.05 ppm.⁶ Arsenic is a widely distributed element in the earth's crust. Arsenic is toxic to all living organisms, and its presence thus creates serious environmental concerns. It exists naturally in the earth's crust, rock, soil, water, air, plants, and animals. Arsenic is found in natural surface water and groundwater because of the release of arsenic compounds from minerals. Arsenic occurs in a variety of forms and oxidation states. The main arsenic species in natural waters are arsenate (oxidation state V) and arsenite (oxidation state III) ions. Exposure to arsenic increases the risk of skin, lung, and kidney cancer. Con-

ventional elimination techniques of arsenic of waters involve ion exchange, precipitation, adsorption, reverse osmosis, and complexation.⁶ It is known that the coexistence of As ions is controlled by factors such as pH, redox potential, and solubility of media. The arsenic(III) species changed according to thermodynamic predictions. It was reported that the As(III) form is difficult to separate from water, and at the lowest levels this separation should only be possible after an oxidation step.⁷ The application of glycolmethacrylate with thiol ligands resin in the recovery of As(III) at a pH of less than 0 was also reported.⁸ The separation of As(V) and As(III) has been studied by anionic resin exchanger,^{9,10} including modifications with metals.¹¹ One complete study¹² of exchange species with As(III), As(V), arsenic monoethyl acid, (MMA), and dimethyl arsenic acid (DMA) was performed with anionic-cationic ion-exchange columns.

Although many of the two-phase methods mentioned have been developed and successfully used, their application have problems with heterogeneous reactions and interphase transfer.

A membrane filtration method is among the most promising methods for enriching and separating several ions from solution.^{13,14} This method is known as the liquid-phase polymer-based retention (LPR)

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technique.^{15,16} Water-soluble polymers are commercially available or can be synthesized by different routes.¹⁷ Membrane filtration easily allows the separation of metal ions bound to water-soluble polymers from unbound metal ions.¹⁸ Applications of water-soluble polymers to the homogeneous enrichment or selective separation of various metal ions from dilute solutions have been reported. Ultrafiltration has been found to be the most suitable technique for LPR studies, and many studies using this technique have been published.^{19–25}

The aim of the present study was to obtain water-soluble polymers with a quaternary ammonium group and ion-exchange properties for arsenate anions at different pHs. The preparation of poly[(3-methacryloylamine)propyl]trimethylammonium chloride (CIMPTA) and copolymers with an acrylic acid, poly{[(3-methacryloylamine)propyl]trimethylammonium chloride-co-acrylic acid} [P(CIMPTA-co-AA)], at different feed mole ratios by radical polymerization was carried out.

EXPERIMENTAL

Reagents

[(3-Methacryloylamine)propyl]trimethylammonium chloride (CIMPTA; Aldrich, Milwaukee, Wisconsin) and acrylic acid (AA; Aldrich, Milwaukee, Wisconsin) were purified by distillation. Ammonium persulfate (AP; Aldrich, Milwaukee, Wisconsin) was used as the initiator of polymerization (1000 ppm and 4 mM Na₂HAsO₄ × 7H₂O solution; Merck, Stuttgart, Germany).

Synthesis of homopolymers

Poly[(3-methacryloylamine)propyl]trimethylammonium chloride [P(CIMPTA)] was synthesized by radical polymerization as previously described.²⁶ Then 0.027 mmol of monomer (CIMPTA) and 1.4 mmol of AP were dissolved in 40 mL of water in an inert atmosphere. The reaction was kept at 70°C under nitrogen for 24 h. The products were soluble in water and were lyophilized. The polymerization yield was 97.2%. The product was dissolved in water, purified by an ultrafiltration membrane, and fractionated by ultrafiltration membranes with different molecular-weight exclusion limits (10,000, 30,000, 50,000, and 100,000 g/mol). The different fractions were characterized by FTIR spectroscopy, ¹H-NMR spectroscopy, and TG-DSC. The ¹H-NMR spectra of the monomer (CIMPTA) and the homopolymer P(CIMPTA) were compared. The ¹H-NMR spectra of P(CIMPTA) indicated that the polymerization of CIMPTA monomer occurred because of the absence of the signals at 5.44 and 5.68 δ (ppm), corresponding to the ¹H of the double bond.

Poly(acrylic acid) was synthesized by radical polymerization. First, 0.069 mmol of the AA monomer and

1 mol % of AP were dissolved in 50 mL of water. The reaction was maintained at 70°C for 24 h. The products were soluble in water and were lyophilized. The polymerization yield was 96%. The product was dissolved in water, purified by an ultrafiltration membrane, and fractionated by ultrafiltration membranes with different molecular-weight exclusion limits (10,000, 30,000, 50,000, and 100,000 g/mol), which were characterized by FTIR spectroscopy, ¹H-NMR spectroscopy, and TG-DSC.

Copolymer preparation

P(CIMPTA-co-AA) was prepared by radical polymerization at feed mole ratios of 1 : 1, 1 : 2, and 2 : 1 using ammonium persulfate as the initiator. The reaction was maintained at 70°C for 24 h. The products were soluble in water and were lyophilized. The polymerization yield was 99%. Then the copolymers were purified and fractionated by ultrafiltration membranes as described above.

The ¹H-NMR spectra of the P(CIMPTA) homopolymer showed the signal to be close to 1 ppm, attributed to the CH₃ group. The signal at 2 ppm corresponded to the ¹H of CH₂ groups. The signal at 3.14 ppm corresponded to the ¹H of the CH₃ of the quaternary ammonium. The ¹H-NMR spectrum of P(AA) showed the following signals: 1.756–1.921 δ (ppm) corresponding to the ¹H of the CH₂ group; 2.379 δ (ppm), corresponding to the ¹H of the CH group; and a high field at 7.0 ppm, corresponding to the ¹H of the OH group. The signal at 4.9 ppm corresponded to the protons of the water. As both homopolymers had the same type of proton absorbed in a similar region, it was not possible to determine copolymer composition from the spectra by comparison of the proton integration areas. Therefore, alternative methods were used.

Procedure

Using the washing method, 0.2 mmol in the range of more than 100,000 g/mol polymer fractions was dissolved in twice-distilled water, and a solution containing 0.01 mmol arsenic was added to the cell solution. Enough solution was added to make a total volume of 20 mL, and the pH was adjusted by adding 0.1M NaOH or 0.1M HNO₃. The washing water in the reservoir was at the same pH as that of the cells. Filtration runs were performed under a total pressure of 3.5 bar by using an ultrafiltration membrane with an exclusion rating of 10,000 g/mol. The total volume in the cell was kept constant. Fractions of 20 mL were collected by filtration, and metal ion concentration was analyzed. The enrichment method by maximum capacity measurements, was also applied. A 4 mM solution of Na₂HAsO₄, with 0.8 mmol of P(CIMPTA) in 20 mL of cells at 300 mL of total filtrate volume were

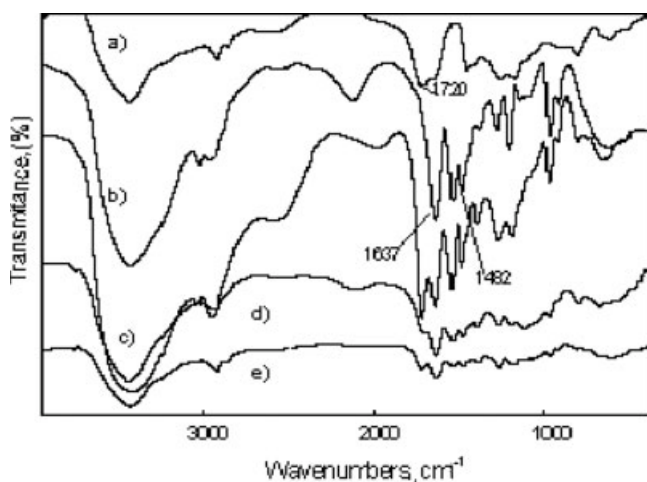


Figure 1 FTIR spectra (KBr) of (a) poly(acrylic acid) [P(AA)], (b) poly[(3-methacryloylamine)propyl]trimethylammonium chloride (CIMPTA), (c) 1 : 2 poly[(3-methacryloylamine)propyl] trimethylammonium chloride-co-acrylic acid [P(CIMPTA-co-AA)], (d) 2 : 1 P(CIMPTA-co-AA), (e) 1 : 1 P(CIMPTA-co-AA).

the experimental conditions used. One blank experiment, without polymer, was also performed.

Measurements

Arsenic concentration was measured in the filtrate by atomic absorption spectrometry with a Perkin Elmer 3100 spectrometer. The quantity retained was determined by the difference with the initial concentration. The pH was controlled by a pH meter (H. Jurgen and Co.).

Fourier transformed infrared spectroscopy was performed with a Magna Nicolet 550 and Nexus Nicolet spectrometers. For quantitative analysis, 1 mg of the sample per 100 mg of KBr is employed. The NMR spectra were recorded with a multinuclear Bruker AC 250 spectrometer at 250 MHz at room temperature using D₂O as the solvent.

Thermal behavior under N₂ was studied by a thermogravimetric analyzer using a TGA 625 from Polymer Laboratories. The heating rate was 10°C/min. The samples weighed 0.5–3 mg.

The Kjeldahl method for organic nitrogen was carried out by vapor stream in sulfuric acid with a reduction in the nitrogen of the polymer, producing NH₃ free, which was then evaluated with 1N HCl.

RESULTS AND DISCUSSION

Synthesis and characterization of water-soluble polymers

The FTIR studies of P(CIMPTA) were carried out in the range of 400–4000 cm⁻¹. The most characteristic absorption bands (in cm⁻¹) observed were 3437 ν (N–H), 1637 ν (C=O), 1482 δ [–N⁺(CH₃)], 1532 coupling of ν (C–N), and δ (N–H) [see Fig. 1(a)]. The spectrum of P(AA) showed characteristic absorption bands (in cm⁻¹) at 3438 ν (OH), 2926 ν (C–H) of the CH₂ group, 1709 ν (C=O), 1413 δ (C–O–H), and 1252 ν (C–O).

The FTIR spectra of the copolymers were basically the same and showed the most important absorption bands at 3437 ν (N–H), 1708 ν (C=O) of the acid group, 1637 ν (C=O) of the amide group, 1482 δ [–N⁺(CH₃)], and so on [see Fig. 1(c–e)].

Quantitative determination of copolymer composition was done by comparison of the integration area of the absorption bands of ν (C=O) coming from the amide and acid groups. In all cases, 1 mg of sample was used for quantitative determination. Using method A, the internal standard, the mole ratio was calculated directly on the basis of the area of C=O bands of the amide and acid groups of each copolymer. Using method B, the ratio of the integration area of C=O groups of the pure homopolymer was used as a standard factor of the intensity. The calculated values are shown in Table I.

TG-DSC was another method used for qualitative and quantitative evaluation of copolymer composition and was useful for structural analysis. The primary thermograms of all polymers showed a typical sigmoid shape. P(AA) and P(CIMPTA) degraded in several steps. On DSC it was observed that the decomposition maximum temperature occurred in each step. The analysis of the homo- and copolymers is shown in Table II. The mole ratios of monomers in the

TABLE I
Mole Composition of Copolymers P(CIMPTA-co-AA) by FTIR Spectroscopy

Polymer	Feed monomer ratio	Copolymer composition		
		Method A	Method B	
			Mole ratio	Area ratio P(CIMPTA)/P(AA)
P(CIMPTA)/P(AA)	—	—	0.26	
P(CIMPTA-co-AA)	1 : 1	1.06 : 1	3.4	1.0 : 1.13
P(CIMPTA-co-AA)	1 : 2	1 : 2.3	1.81	1.0 : 2.12
P(CIMPTA-co-AA)	2 : 1	2.5 : 1	7.34	1.9 : 1.0

TABLE II
Mole Composition of P(CIMPTA-co-AA) Copolymers by TG-DSC

Polymer	Feed monomer ratio	Weight loss at different temperatures (°C)					Method C	Method D
		60	241	308	424	>550		
P(CIMPTA)		23	—	44	24	—		
P(AA)		15	—	—	—	80		
P(CIMPTA-co-AA)	1 : 1	8	19	29	21		1.02 : 1	1 : 1
P(CIMPTA-co-AA)	1 : 2	4	38	22	24		1 : 2.3	1 : 1.8
P(CIMPTA-co-AA)	2 : 1	11	8	36	21		2.6 : 1	2.28 : 1

copolymer structure were evaluated from the thermograms, according to two methods, method C, which evaluated the total weight loss of each monomer in the copolymer, and method D, which only evaluated the weight loss of one peak, (maximum at 415°C), which had resulted from the decomposition of one functional group of one monomeric unity. The results are summarized in Table II.

Elemental analysis of total N₂ (Kjeldahl method) was another method used for determining copolymer composition. The results are included in Table III. It must be taken into account that only 84.22% of total nitrogen in P(CIMPTA) was reduced.

Arsenic retention properties of water-soluble polymers

Figure 2 shows the retention profile of As(V) as a function of pH by P(CIMPTA). This profile shows a retention factor, *R*, versus a filtration factor, *Z*. *Z* was defined as the ratio volume of the filtrate (*V_f*) versus volume of the cell (*V₀*). In general, As (V) was more easily retained at a higher pH (pH 6 and 8) than at a lower pH. At a pH of 4, where reactivity was lower or the number of effective active sites of the homopolymer was low, the predominating species in solution were monovalent (H₂AsO₄⁻) anions in equilibrium with the nondissociated salt. It was hypothesized that the polarity of the functional group would be one controlling parameter of exchange selectivity. At a pH of 6, in solution there was equilibrium between monovalent (H₂AsO₄⁻) and divalent (HAsO₄²⁻) anions. It was suggested that the anionic exchanger would prefer divalent anions for the monovalent anions in medium in the same conditions (acidic pH). This could be cor-

roborated by the greater retention ability of the polymers at a basic pH, where divalent species predominated. The binding capacity of the polymer was attributed to the anionic exchange between chloride anions and arsenate anions, and the binding of these with the ammonium quaternary cationic group. This bond presumably occurred through the nitrogen of the ammonium group (positively charged) with the oxygen of the arsenate anions, forming a dipole, according to the structure shown in the Scheme 1.

The interaction apparently was not purely electrostatic, presumably because of the formation of ion pairs between a covalent bond between a partially movable functional group on the polymeric network and one on the oppositely charged anion. This pairing may be explained by the water structure induced by ion pairing,²⁷ where the larger and more polarizable ions disrupt the local water structure and associate more easily with a given quaternary ammonium ion.

The FTIR spectra of P(CIMPTA) before and after the exchange reaction with As(V) are shown in Figure 3(a-c). In the high region of the spectra, only the vibrations of a functional group corresponding to P(CIMPTA) could be identified. At 1700–1300 cm⁻¹ some modifications were observed for the pure spectra. The band of ν(C=O) at 1637 cm⁻¹ was considered the base; it was marked by a decrease in the intensity of the bands at 1534 cm⁻¹ [coupling of ν(C–N) and δ(N–H)] and 1482 cm⁻¹ by δ(–N⁺(CH₃)). There was a new band at 1380 cm⁻¹ from arsenate groups corresponding to ν(As=O).^{28,29} The intensity of this band

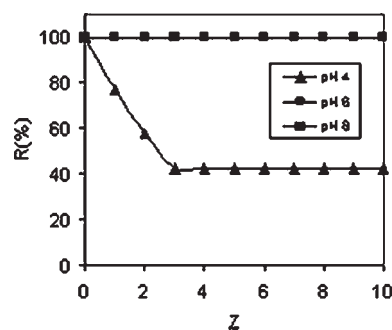
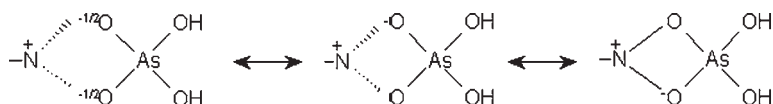


Figure 2 Retention profiles of As (V), using poly[(3-methacryloylamino)propyl]trimethylammonium chloride (CIMPTA), with 0.2 mmol absolute polymer to 0.01 mmol absolute As (V) ion.

TABLE III
Mole Composition of P(CIMPTA-co-AA) Copolymers by Elemental Analysis

P(CIMPTA-co-AA)	N ₂ (wt %)	Mole ratio
1 : 0	10.68*	—
1 : 1	8.05	1 : 1.38
1 : 2	6.59	1 : 2.5
2 : 1	8.69	1.2 : 1

* Theoretical value of N₂ was 12.68 wt %.



Scheme 1

was lower at a pH of 4 than at a basic pH, indicating weaker interaction with arsenate anions. That the intensity of the band at 1380 cm^{-1} was dependent on pH supports that there was an interaction zone. The band at 845 cm^{-1} was assigned to $\nu(\text{As}-\text{O})$. At lower frequencies, the region of $200\text{--}500\text{ cm}^{-1}$, deformation modes, showed one strong band at 369 cm^{-1} by $\delta(\text{As}-\text{O})$. Frequencies below 200 cm^{-1} , were assigned to the lattice modes of the crystal.

The effect of the concentration of the P(CIMPTA) polymer is shown in Figure 4. By increasing the polymer concentration from 0.2 to 2 mmol, retention increased. This increased concentration involved the number of functional groups in solution and increases in the polymer/As(V) ratios. However, an increase in the amount of polymer did not induce a proportional increase in retention. The profile exhibited a tendency similar to that described above. But there was a slight difference in the retention between pH 8 and 6 at a higher concentration of polymer. Studies with an excess of polycations in the copolymer composition were performed. An interesting behavior was shown by the copolymer with the 4 : 1 ratio, whose profile at a pH of 6 was the same as that of the pure P(CIMPTA) homopolymer.

The assays of P(CIMPTA) to determine, using the enrichment method, the maximum retention capacity for arsenic anions of an aqueous solution at a pH of 8 are shown in Figure 5.

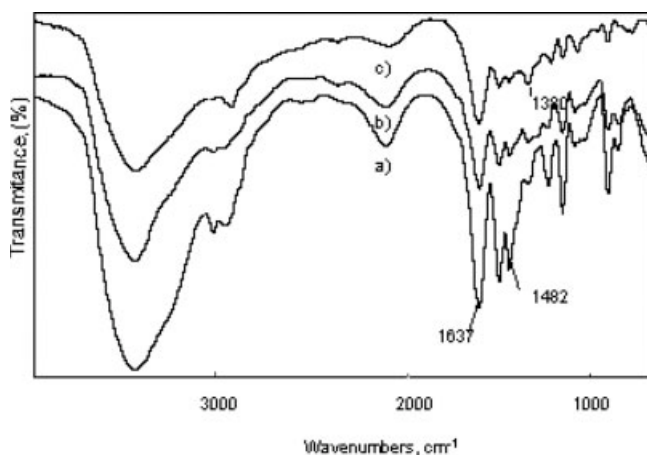


Figure 3 FTIR spectra (KBr) of (a) poly[(3-methacryloylamine)propyl]trimethylammonium chloride (CIMPTA), (b) poly[(3-methacryloylamine)propyl]trimethylammonium chloride, with arsenate at pH 4, (c) poly[(3-methacryloylamine)propyl]trimethylammonium chloride, with arsenate at pH 8.

Maximum retention capacity was defined as:

$$C = MV/P_m$$

where P_m is the amount of polymer (g), M is the initial concentration of As (V) (mg/L), V is the filtrate volume (defined volume) of membrane free of As (V), (mL), and C is 117 mg/g corresponding to a total filtrate volume of 300 mL.

Assuming a quantitative retention of As (V), the enrichment factor ($E = 3.5$) was determined according to the following relationship:

$$E = (PC)/M$$

where P is the concentration of polymer (g/L), C is the maximum capacity of the polymer (mg/g), and M is the initial concentration of the metal salt (mg/L).

Studies of the concerted action of water-soluble copolymers having anionic and cationic ion-exchange sites for the retention of As(V) from an aqueous medium are presented. These P(CIMPTA-co-AA) copolymers were synthesized at feed mole ratios of cation : anion of 1 : 2, 1 : 2, and 2 : 1. The action of the polycations and polyanions of the copolymer versus pH and its arsenic retention capacity are shown in Figures 6–8. At a feed mole ratio of 1 : 1 it can be seen that the copolymer lost its ability to bind anions independently of the pH. This can be explained by an interaction of the COO^- group of the P(AA) with the $-\text{N}^+(\text{R}_3)$ groups of P(CIMPTA) by charge transfer that should have blocked both functional groups.

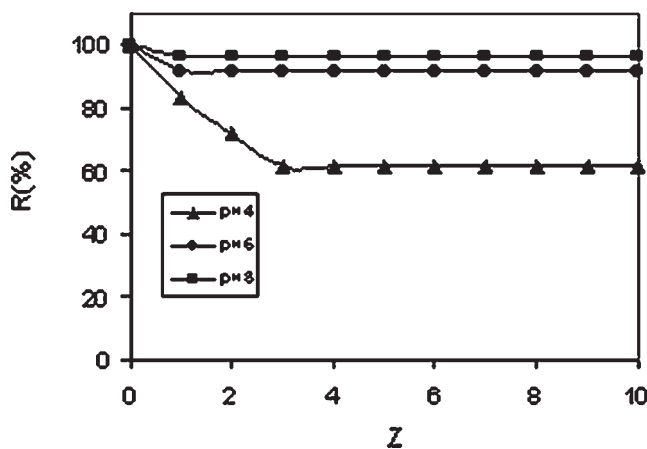


Figure 4 Retention profile of As(V), using poly[(3-methacryloylamine)propyl]trimethylammonium chloride (CIMPTA) with 2 mmol polymer to 0.1 mmol As(V) ion.

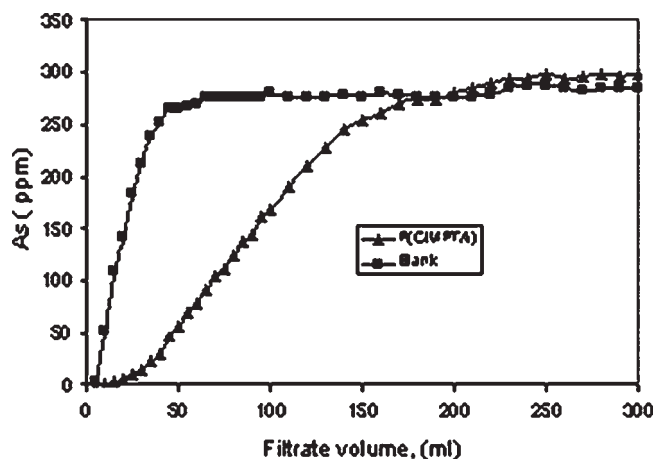


Figure 5 Arsenic(V) concentration versus filtrate volume of poly[(3-methacryloylamine)propyl]trimethylammonium chloride (CIMPTA) with 0.8 mmol polymer and a pattern solution of 4 mM As(V).

It is known that P(AA) is a proton-donating polymer, but complexation with a polycation of another polymer depends not only on the composition of each component of the copolymer, but also on the pH of the aqueous solution. The dissociation of P(AA) was increased in the presence of P(CIMPTA). At a pH lower than 4 (beyond $pK_a = 5.6$), the dissociation of P(AA) was suppressed. The crosslinking by both hydrogen and covalent bonds between polycations and polyanions inhibited the function of copolymers by the retention of anions, independently of whether the mole ratio was 1 : 2 or 2 : 1. It has been said that monomer units form "complexes," taking this form because the retention of arsenate is negligible. At a pH of 6, when most of the carboxylic acid groups of P(AA) were carboxylate anions groups and therefore

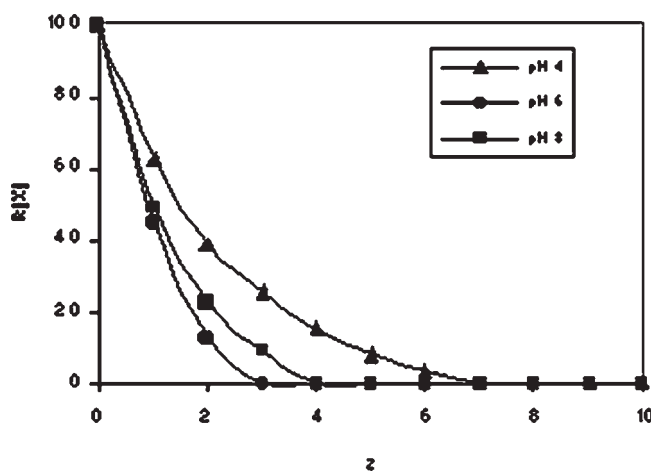


Figure 6 Retention profile of As(V) of poly[(3-methacryloylamine)propyl]trimethylammonium chloride-co-acrylic acid [P(CIMPTA-co-AA)] at a 1 : 1 ratio with 0.2 mmol polymer and 0.2 mmol absolute As(V) ion.

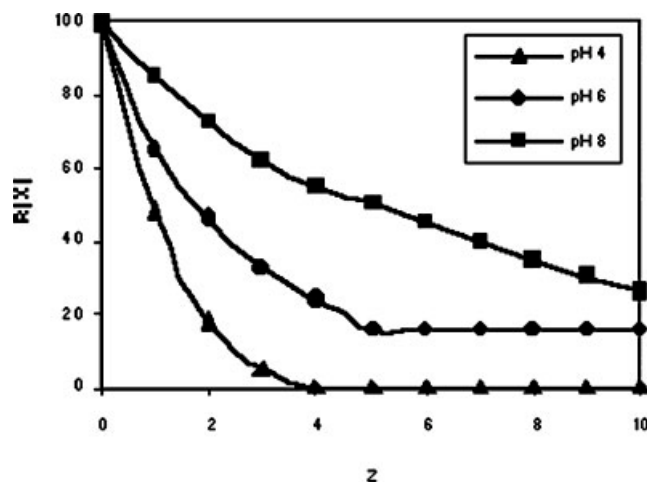


Figure 7 Retention profile of As(V) of poly[(3-methacryloylamine)propyl]trimethylammonium chloride-co-acrylic acid [P(CIMPTA-co-AA)] at a 1 : 2 ratio with 0.2 mmol polymer and 0.01 mmol absolute As(V) ion.

able to participate in the formation of complexes, such conditions could not be totally satisfied. It was suggested that some of the additional active sites were dissociated by the extraction of protons from the aqueous solution without being incorporated into the domain of the polymer chains. Therefore, a great part of quaternary ammonium groups were free and available to bind with the arsenate of the solution when the mole ratio of the copolymer composition was not equimolar. This effect was higher when the ratio of polycations to polyanions was greater than 1, when most of the $-N^+(CH_3)_3$ were free to interact with arsenate anions, increasing the retention ability, as can be seen in the profile in Figure 8. At a pH of 8 the retention of arsenate ions increased for both copoly-

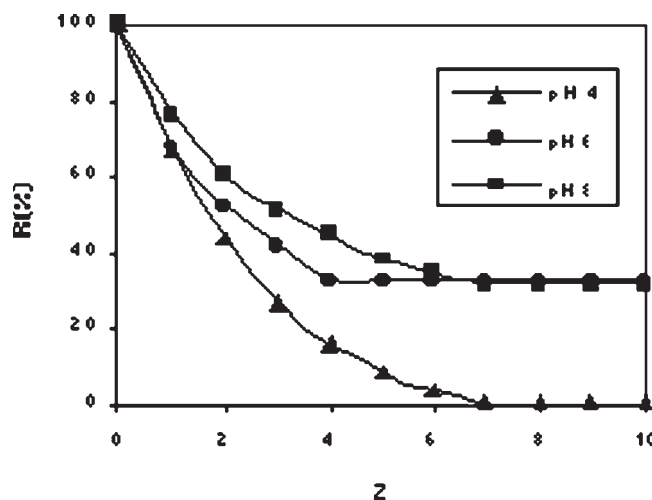


Figure 8 Retention profile of As(V) for poly[(3-methacryloylamine)propyl]trimethylammonium chloride-co-acrylic acid [P(CIMPTA-co-AA)] at a 2 : 1 ratio with 0.2 mmol polymer and 0.01 mmol As(V) ion.

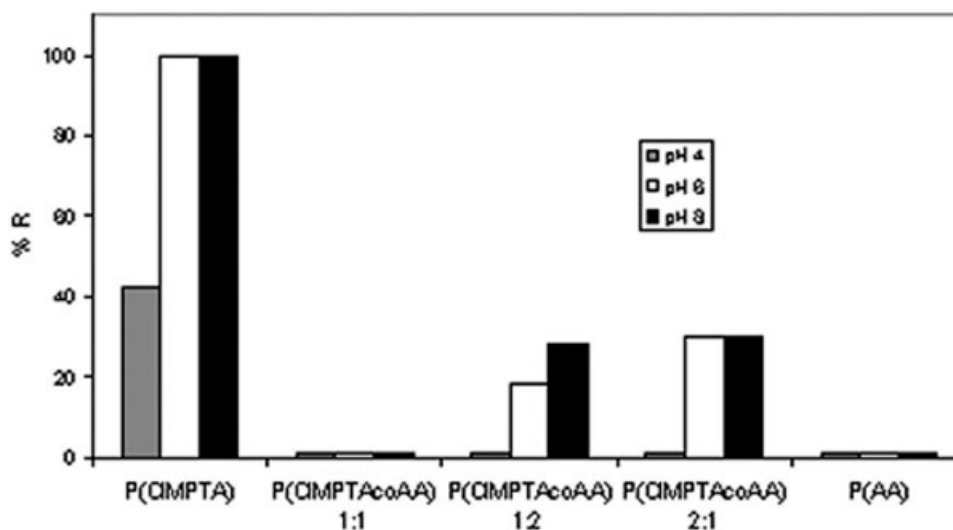


Figure 9 Retention values of As(V) by different polymers at several pHs and $Z = 10$.

mers without an equimolar ratio, to 30% at $Z = 10$. It was reported in the literature³⁰ that increasing ionic strength ($> \text{pH}$) produced a reduction in electrostatic interaction of the polymeric "complexes" because of the screening effect of microsals, or by accelerating dissociation of weak polyelectrolytes.^{30,31} It was suggested that this effect could improve the ability of the quaternary ammonium group in the copolymer.

The effects of the filtration factor and pH on As(V) binding ability are shown in Figure 9. It was shown that at $Z = 10$ the increasing of the number of quaternary ammonium groups in the copolymers enhanced retention capacity similarly at pHs of 6 and 8. P(AA) was found to have a negligible effect on the retention of arsenate anions, independently of the pH of the medium.

CONCLUSIONS

The liquid-phase polymer-based retention (LPR) technique was shown to be a convenient method for retaining anions from aqueous solution. The polymer with all the interacting groups as quaternary ammonium was shown to have an important ability to retain arsenate anions. The retention behavior of the arsenic anions depended on the pH, polymer concentration, and copolymer composition. It was shown that the quaternary ammonium salt polymers of P(CIMPTA) could bind HAsO_4^- species in an aqueous solution more selectively at pHs of 6 and 8 than at a pH of 4, with a yield of nearly 80%–100%. Above this, the maximum capacity of the sample at one defined volume was calculated as 117 mg/g. The retention behavior with copolymers showed that at a copolymer mole ratio of 1 : 1 no interaction as polycations and polyanions was possible because of blocking of active sites. The interaction rate increased with the pH for copoly-

mers with mole ratios of 1 : 2 and 2 : 1, the difference in activity of polycations being more remarkable at a pH of 6. The highest values were obtained at a pH of 8 with 1 : 2 and 2 : 1, which was attributed to the reduction in the number of electrostatic interactions of possible intra- or interpolymer chain complexes by screening the effect of neutral microsals or to a major degree dissociation of polyelectrolytes.

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