

# Cationic Water-Soluble Polymers with the Ability To Remove Arsenate Through an Ultrafiltration Technique

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**ABSTRACT:** Different cationic water-soluble polymers with  $(R)_4N^+X^-$  groups and pyridinium groups were prepared, and their arsenate retention performance was investigated with the liquid-phase polymer-based retention technique. Poly[3-(methacryloylamino)propyl]trimethylammonium chloride, poly[2-(acryloyloxy)ethyl]trimethylammonium chloride, poly(*ar*-vinylbenzyl)trimethylammonium chloride, poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate, poly(4-vinyl-1-methyl pyridinium)bromide, and poly[3-(methacryloylamino)propyl]dimethyl(3-sulfo-propyl)ammonium hydroxide were prepared. The synthesis of the polymers by solution radical polymerization produced a yield higher than 77%. Structural analyses were performed with Fourier transform infrared and  $^1H$ -NMR spectroscopy and thermogravimetry/differential scanning calorimetry. Commercial poly(4-vinyl-1-methyl

pyridinium)bromide and poly(*ar*-vinylbenzyl)trimethylammonium chloride were also used. The liquid-phase polymer-based retention technique was employed to study the retention of arsenate species. The polymer structure and exchange groups, such as methyl sulfate, chloride, bromide, and hydroxide, presented different properties for removing arsenate anions from aqueous solutions. The type of voluminous quaternary ammonium group present influenced arsenic retention. All the polymers could bind  $HAsO_4^{2-}$  species from an aqueous solution more selectively at pHs 8 and 6 than at pH 4. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 89–94, 2007

**Key words:** hydrophilic polymers; ion exchangers; membranes

## INTRODUCTION

The presence of arsenic in water in amounts exceeding the permitted level (0.05 ppm according to the World Health Organization) is detrimental to living organisms.<sup>1</sup> It is known that the coexistence of inorganic arsenite and arsenate anions is controlled by factors such as the medium's pH, redox potential, and solubility. It has been reported that the As(III) form is difficult to separate from water and that this should be possible only after the oxidation step.<sup>2</sup> There are several methods for removing arsenic from aqueous solutions: precipitation/coagulation with inorganic oxides, adsorption, ion exchange, and reverse osmosis.<sup>2–4</sup> There are different natural and synthetic products that present ion-exchange properties, and organic resins are by far the most important ion exchangers.<sup>5,6</sup> Although many two-phase methods have been developed and successfully used, their applications can be related to problems of heterogeneous reactions and interphase transfer. On the other hand, membrane filtration methods are among the most promising technologies for the enrichment of several ions from solutions and their separation.<sup>7–10</sup>

Furthermore, water-soluble polymers are commercially available or can be synthesized by different routes and are easy to apply. One group of special polymers is the quaternary ammonium compounds, which have been very important and have been extensively used as cationic polyelectrolytes.<sup>11</sup>

This article concerns different cationic polymers with anion-exchange groups from quaternary ammonium groups and pyridinium groups in the polymer structure and their ability to remove As(V) from an aqueous solution. This removal capability is based on the possibility of exchanging the arsenate anions with the counterions of ammonium and pyridinium groups. The preparation and structural characterization were carried out with  $^1H$ -NMR and infrared spectroscopy, and the thermal behavior was determined with thermogravimetry/differential scanning calorimetry (TG-DSC). The performance of different water-soluble polymeric structures with the liquid-phase polymer-based retention technique was carried out through the washing method at a constant ionic strength and under various medium conditions at pHs 4, 6, and 8.

## EXPERIMENTAL

### Reagents

The following were used: a [3-(methacryloylamino)propyl]trimethylammonium chloride solution (50 wt %

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in water; Aldrich, St. Louis, MO), a [2-(acryloyloxy)ethyl]trimethylammonium chloride solution (80 wt % in water; Aldrich), (*ar*-vinylbenzyl)trimethylammonium chloride (99%), [2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate, poly(4-vinyl-1-methylpyridinium)bromide [P(BrVMP); 20 wt % solution in water, Polysciences, Inc., Warrington, PA], and [3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide (inner salt, 96 wt %; Aldrich). Ammonium persulfate (AP; Aldrich) was used as an initiator of polymerization. A 1000 ppm Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O solution (Merck, Stuttgart, Germany) was also used.

### Synthesis and characterization of the homopolymers

The different homopolymers were synthesized by radical polymerization. Five grams of each monomer and 1 mol % AP as the initiator were dissolved in 40 mL of water in an inert atmosphere. The reaction was kept at 70°C under N<sub>2</sub> for 24 h. The water-soluble products were then lyophilized. The polymerization yields were 99% for poly[3-(methacryloylamino)propyl]trimethylammonium chloride [P(CIMPTA)], poly[2-(acryloyloxy)ethyl]trimethylammonium chloride [P(CIAETA)], and poly(*ar*-vinylbenzyl)trimethylammonium chloride [P(CIVBTA)], 77% for poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulfate [P(SAETA)], and 83% for poly[3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide [P(HMPDSPA)] over a fraction greater than 100,000 D. The products were dissolved in water, purified with ultrafiltration membranes, 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 with Fourier transform infrared (FTIR), <sup>1</sup>H-NMR, and TG-DSC.

### Retention-of-arsenic procedure

Through a washing method, 0.2 mmol in polymer fractions greater than 100.00 g/mol was dissolved in twice distilled water, and a solution containing 0.01 mmol of arsenic was added to the cell solution. The solution was brought to a total volume of 20 mL, and the pH was adjusted by the addition of 0.1M NaOH or 0.1M HNO<sub>3</sub>. The washing water in the reservoir was at the cell solution's pH. Filtration runs were performed under a total pressure of 3.5 bar with 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 the metal-ion concentration was analyzed. One blank experiment, without a polymer, was also performed.

### Measurements

The arsenic concentration was measured in the filtrate by atomic absorption spectrometry with a Perkin-Elmer (Waltham, MA) 3100 spectrometer, and the quantity retained was determined from the difference with the initial concentration. The pH was controlled by a pH meter (H. Jürgen and Co., Germany).

The FTIR spectra were recorded with Nicolet (Madison, WI) Magna 550 and Nexus spectrometers. By quantitative analysis, 1 mg of the sample per 100 mg of KBr was employed. The NMR spectra were recorded with a Bruker (Billerica, MA) AC 250 multinuclear spectrometer at 250 MHz and room temperature with D<sub>2</sub>O as the solvent.

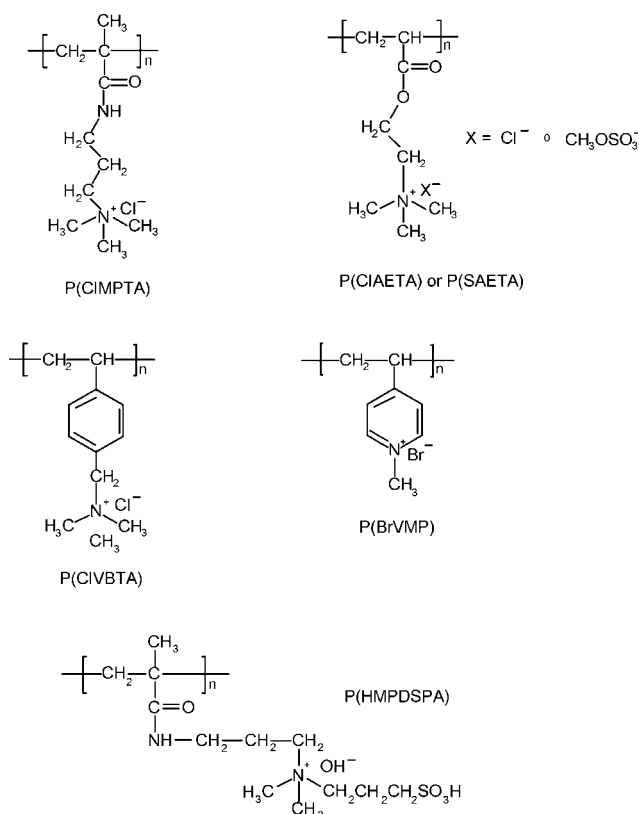
The thermal behavior under N<sub>2</sub> was studied with a TGA 625 thermogravimetric analyzer from Polymer Laboratories, U. K. The heating rate was 10°C/min. The weights of the samples were 0.5–3 mg.

## RESULTS AND DISCUSSION

### Synthesis and characterization of the homopolymers

The polymers were synthesized by radical polymerization. These polymers were completely soluble in water.

The polymer structures are shown in Scheme 1.



Scheme 1

TABLE I  
Characteristic Absorption Bands ( $\text{cm}^{-1}$ ) of the Different Polymers

Functional group	P(CIAETA)	P(SAETA)	P(CIMPTA)	P(HMPDSPA)	P(CIVBTA)	P(BrVMP)
$\nu(\text{N-H})$ or $\nu(\text{OH})$	3430	3442	3435	3449	3439	3430
$\nu(\text{C-H})$	3020	3015	2930	3043,2972	3022,2897	3030,2925
$\nu(\text{C=O})$	1732	1733	1640 (amide I)	1646 (amide I)	—	—
$\nu_{\text{asym}}(\text{COO}^-)$	1635	1636	—	—	—	—
$\nu(\text{C=C})$	—	—	—	—	1641–1408	1641–1470
$\delta(\text{N-H})$ (amide II band)	—	—	1534	1539	—	—
$\delta(\text{N-H})$ of $\text{RN}^+(\text{CH}_3)_3$	1483	1485	1482	1484	1484	—
$\nu_{\text{asym}}\text{SO}_2$	—	1253–1219	—	—	—	—
$\nu_{\text{sym}}\text{SO}_2$	—	1061–1018	—	—	—	—
$\delta(\text{C-H})$	—	—	—	—	900–675	900–675
$\nu(\text{S-N})$	—	760	—	—	—	—
$\nu(\text{C-S})$	—	—	—	605	—	—

The characteristic FTIR absorption bands were 1482 [ $\rho(-\text{N}^+\text{CH}_3)$ ], 1640 [ $\nu(\text{C=O})$ , amide group], 1733 [ $\nu(\text{C=O})$ , acryloxy group], and 1641–1408  $\text{cm}^{-1}$  [ $\nu(\text{C=C})$ , aromatic ring; see Table I].

The  $^1\text{H-NMR}$  spectra of the monomers and homopolymers were analyzed comparatively, and the absence of the signals at 5.44 and 5.68 ppm, corresponding to protons of the  $\text{C=C}$  double bond, indicated that vinyl monomer polymerization did occur.

The  $^1\text{H-NMR}$  assignments of the homopolymers were as follows:

P(CIMPTA) and P(HMPDSPA). Vinyl protons of the side chain:  $\delta = 2$  ppm (2H). Protons of side groups:  $\delta = 1$  ppm (3H) and  $\delta = 3.18$  ppm (9H) for the quaternary ammonium group; P(HMPDSPA),  $\delta = 3.16$  ppm (6H) for the quaternary ammonium group and  $\delta = 3.4$  ppm (2H) for the  $(\text{CH}_2)\text{SO}_3$  group.

P(CIAETA) and P(SAETA). Vinyl protons of the main chain:  $\delta = 2$  ppm (2H) and  $\delta = 2.5$  ppm (1H). Protons of the side groups:  $\delta = 3.75$  ppm (2 H),  $\delta = 4.5$  ppm (2H), and  $\delta = 3.18$  ppm (9H) for the quaternary ammonium group; P(SAETA),  $\delta = 3.69$  ppm (3H) for the  $\text{OSOCH}_3$  group.

P(CIVBTA). Vinyl protons of the main chain:  $\delta = 2$  ppm (2H) and  $\delta = 2.5$  ppm (1H). Protons

of the side groups:  $\delta = 4.35$  ppm (2H) and  $\delta = 7.4$  ppm (1H) for the aromatic ring.

P(BrVMP). Vinyl protons of the main chain:  $\delta = 2$  ppm (2H) and  $\delta = 2.5$  ppm (1H). Protons of the side groups:  $\delta = 4.27$  ppm (3H),  $\delta = 7$ – $7.6$  ppm (1H) for the *o*-position, and  $\delta = 8.5$  ppm (1 H) for the *p*-position of the aromatic ring.

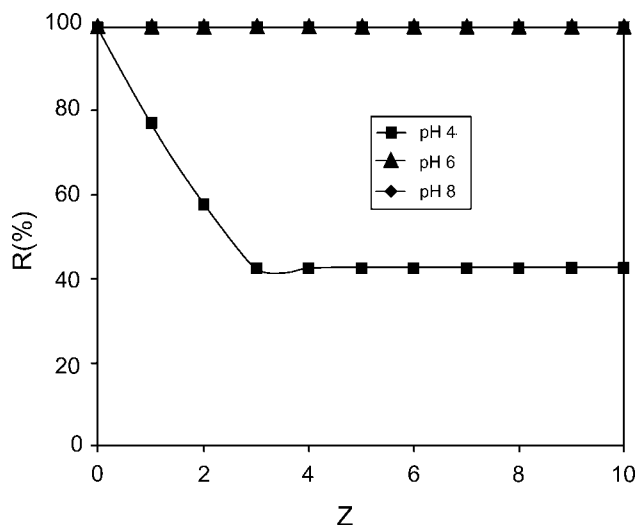
Table II shows the maximum decomposition temperature, weight-loss percentage, and enthalpy [decomposition heat (mcal/mg)] obtained by TG–DSC assays. The primary thermograms for all the polymers presented a typical sigmoid shape, indicating that the polycationic structures degraded in several steps. In DSC, the decomposition maximum temperature occurred in each step. For all cases, the total weight loss was around 89%.

#### Arsenic retention properties of the water-soluble polymers

Figures 1–6 present the As(V) retention profiles for the different cationic polymers as a function of the pH. These profiles show the retention factor ( $R$ ) versus the filtration factor ( $Z$ ).  $Z$  is defined as the ratio of the volume of the filtrate to the volume of the cell. In the literature, there are reports on the equilibrium diagram for As(V) species as a function of

TABLE II  
Thermal Properties of the Water-Soluble Polymers

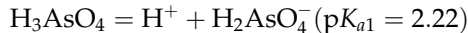
Polymer	Maximum decomposition temperature ( $^{\circ}\text{C}$ )	Decomposition heat (mcal/mg)	$\Delta m$ (wt %)	$\Delta T$ ( $^{\circ}\text{C}$ )
P(CIMPTA)	309, 415	106, –29.8	44, 23	112
P(CIAETA)	255	88	53	61
P(SAETA)	245, 332	126	12, 57	42, 86
P(CIVBTA)	278	105	41	100
P(BrVMP)	287, 339	20, 85	19, 67	33, 62
P(HMPDSPA)	297	52	45	90



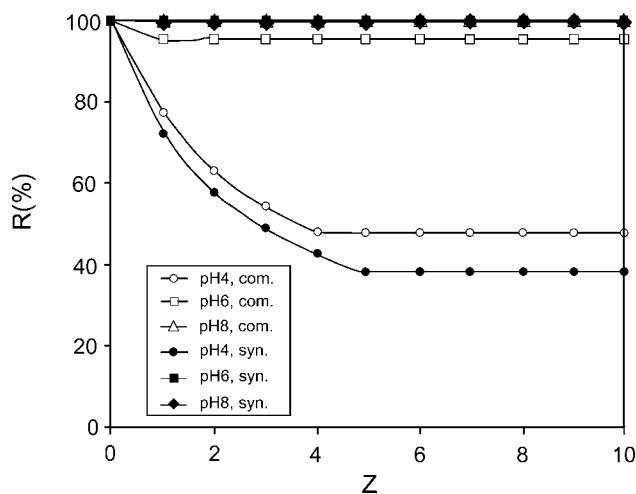
**Figure 1** Retention profiles for As(V) with P(CIMPTA) (absolute polymer amount = 0.2 mmol, absolute As(V) ion amount = 0.01 mmol).

the redox potential and pH in an aqueous system.<sup>1,11</sup>

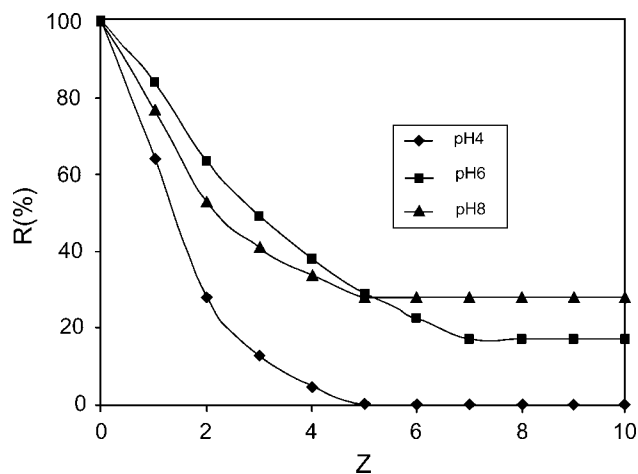
The equilibrium and dissociation constants of the As(V) species are as follows:



The divalent anionic species  $\text{HAsO}_4^{2-}$  predominates at higher pHs (7–12), whereas the monovalent anionic species  $\text{H}_2\text{AsO}_4^-$  predominates at lower pHs (2–7).



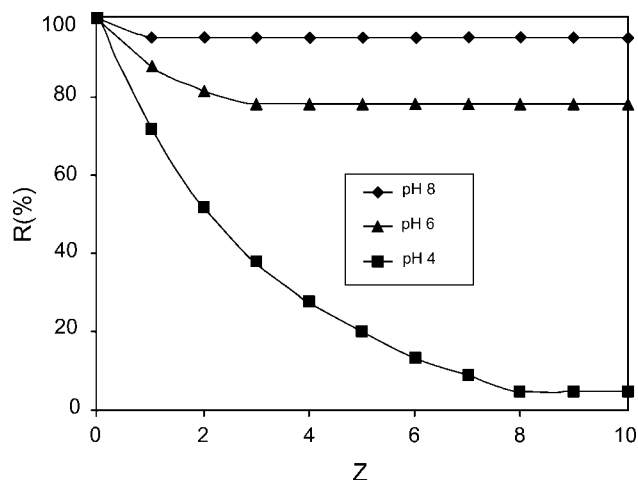
**Figure 2** Retention profiles for As(V) with P(CIVBTA) (absolute polymer amount = 0.2 mmol, absolute As(V) ion amount = 0.01 mmol): (○) the synthesized polymer and (●) the commercial polymer.



**Figure 3** Retention profiles for As(V) with P(HMPDSPA) (absolute polymer amount = 0.2 mmol, absolute As(V) ion amount = 0.01 mmol).

onic species  $\text{H}_2\text{AsO}_4^-$  predominates at lower pHs (2–7).

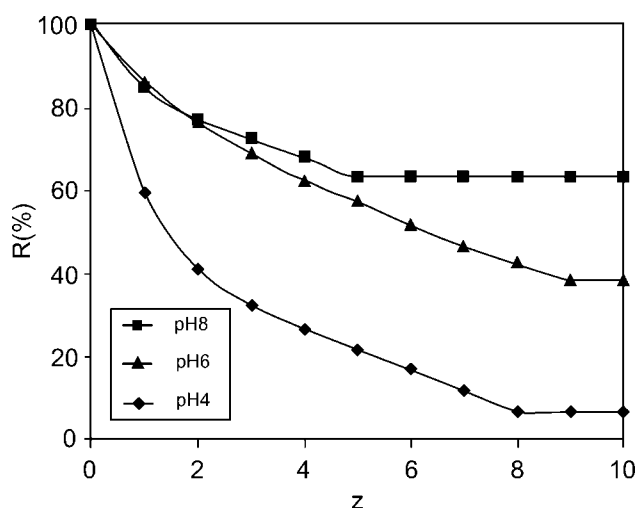
In general, As(V) is more easily retained at higher pHs (6 and 8) than at lower pHs. At pH = 4, at which the reactivity is lower or the number of effective active sites of the homopolymer is low, the predominating species in a solution are monovalent anions ( $\text{H}_2\text{AsO}_4^-$ ) in equilibrium with the nondissociated salt. It is assumed that the functional group's polarity should be one parameter controlling the exchange selectivity. At pH = 6, there is an equilibrium between monovalent ( $\text{H}_2\text{AsO}_4^-$ ) and divalent ( $\text{HAsO}_4^{2-}$ ) anions. It is suggested that the anionic exchanger prefers divalent anions over monovalent anions under the same medium conditions (acidic pH), and this can be corroborated by the polymers' higher retention ability at a basic pH, at which diva-



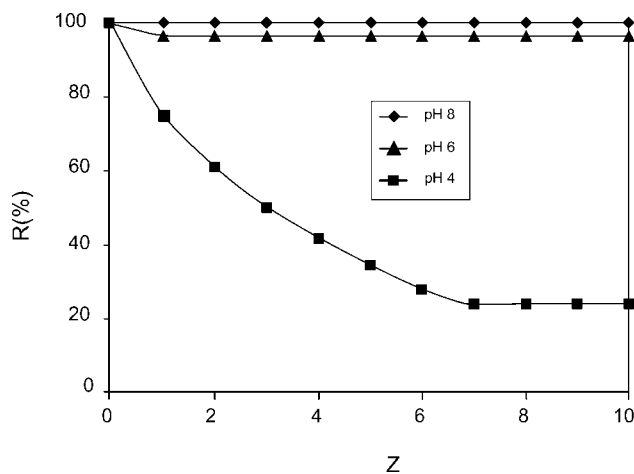
**Figure 4** Retention profiles of As(V) with P(BrVMP) (absolute polymer amount = 0.2 mmol, absolute As(V) ion amount = 0.01 mmol).

lent species predominate. A polymer's capacity to bind to arsenate anions is attributed to the anionic exchange between chloride anions and arsenate anions and the binding of these species with the ammonium quaternary cationic group. This bond is presumably through nitrogen of the ammonium group (positively charged) with oxygen of arsenate anions forming a dipole, as we previously described.<sup>12</sup>

The most remarkable selectivity has been found for those polyelectrolytes with exchanger chloride anions, such as P(CIMPTA), P(CIAETA), and P(CIVBTA), in comparison with P(BrVMP), P(SAETA), and P(HMPDSPA). The retention profile is similar to those for exchanger-chloride group polymers, the highest yield, 100%, being obtained at basic and neutral pHs for P(CIMPTA) and P(CIVBTA) (see Figs. 1 and 2). A comparative study of the synthesized polymers and commercial P(CIBVTA) (see Fig. 2) showed no differences in the retention ability. The polymers' binding capacity could be attributed to the anionic exchange between the polymers' anionic groups and arsenate anions and the binding of the later with the ammonium quaternary cationic group. This is attributed to the quaternary ammonium group's easier release of  $\text{Cl}^-$  anions with respect to  $\text{OH}^-$  or  $\text{CH}_3\text{OSO}_3^-$  in solution. The larger, more polarizable ion produces a greater disruption in the local water structure, and it associates more easily with the quaternary ammonium ions.<sup>13</sup> Specifically, polarizable monovalent ions will be more retained in comparison with chloride because of the greater hydrophobicity of the anion-exchange site with a higher capacity at a given hydrophobicity.<sup>14</sup> On the other hand, it has been reported for halogens that when the electronegativity decreases in the



**Figure 5** Retention profiles for As(V) with P(SAETA) (absolute polymer amount = 0.2 mmol, absolute As(V) ion amount = 0.01 mmol).



**Figure 6** Retention profiles of As(V) with P(CIAETA) (absolute polymer amount = 0.2 mmol, absolute As(V) ion amount = 0.01 mmol).

order of  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ , the exchange capacity increases for the P(CIVBTA) resin.<sup>15</sup> The higher selectivity presented for P(BrVMP), nearly 95% at a basic pH, could be attributed to the aryl ammonium quaternary ion's effect on the structure and the role of the bromide ion (see Fig. 4). It is known that the alkyl ion is a stronger base than the pyridinium ion, and its conjugate, the quaternary ammonium ion, is a weaker acid. On the other hand, as the quaternary ammonium ion becomes larger, it more easily forms a water-structure-induced ion pair with hydroxide, and in this form, the polymer's retention capacity for arsenate anions will be diminished (see Fig. 3). A highly remarkable difference in the selectivity is presented by the same structures and different quaternary ammonium groups and anionic exchanger groups, as is the case for P(CIMPTA) and P(HMPDSPA) (see Figs. 1 and 3). At a basic pH, the highest yield of P(CIMPTA) drops to nearly 30% for P(HMPDSPA).

Figures 5 and 6 present the results for P(SAETA). This polymer has methyl sulfate groups as ion-exchange groups, and this is a structural difference with respect to P(CIAETA). The retention results can be explained by the increased difficulty in exchanging the voluminous  $(\text{OSO}_3\text{CH}_3)^-$  groups, which are less polarizable than the single  $\text{Cl}^-$ , resulting in diminished arsenate retention (40–60%).

## CONCLUSIONS

The cationic polymers, synthesized by radical polymerization and containing different anions as ion-exchange groups, present different arsenate retention properties. The quaternary ammonium water-soluble polymers containing chloride exchange groups show

the greatest ability for removing arsenate ions (100%) at higher pHs.

The characteristics of the voluminous quaternary ammonium group, especially its hydrophobicity, influence the retention capacity, which diminishes as the hydrophobicity of the quaternary ammonium group increases.

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