Polymer 51 (2010) 383–389

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Design and development of ion-selective polymer-supported reagents: The immobilization of heptamolybdate anions for the complexation of silicate through Keggin structure formation

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A R T I C L E I N F O

Article history:
Received 7 September 2009
Received in revised form
7 November 2009
Accepted 18 November 2009
Available online 3 December 2009

Keywords:
Polymer-supported reagents
Separations
Water treatment

A B S T R A C T

A silicate-selective polymer-supported reagent has been developed that utilizes the reactivity of silicate to generate polyanionic Keggin structures. Heptamolybdate and heptatungstate anions are immobilized onto trimethylammonium ligands bound to microporous poly(vinylbenzyl chloride) beads. The heptamolybdate complexes >90% of the silicate from a 20 ppm solution at pH 7; the heptatungstate has a lower affinity, complexing 40% of the silicate. Complexation by the heptamolybdate remains high throughout the pH range 3.8–10.7. Sorption is unaffected by the presence of chloride, sulfate, and nitrate ions. The apparent rate of reaction is maximized by immobilizing the ligand on an expanded gel support: whereas the microporous polymer requires 24 h to complex all of the silicate from a 100 ppm solution, the expanded gel attains that level in 4 h. The rate-limiting step is thus identified as accessibility of the silicate to the heptamolybdate rather than the rate of reaction to form the silicomolybdate. FTIR spectra confirm silicomolybdate formation: The heptamolybdate polymer has four characteristic bands at 715, 845, 912 and 945 cm^{-1} and these bands get weaker as silicate reacts with the heptamolybdate; at complete reaction, the band at 845 cm^{-1} disappears. The spectrum of the silica-saturated polymer has strong bands at 900–904 cm^{-1} and 790–800 cm^{-1}, consistent with the spectrum of tert-butylammonium silicododecamolybdate.

1. Introduction

Silica is one of the most abundant elements on Earth. All natural water contains dissolved silica at levels of 1–30 ppm [1] with some water, such as that in New Mexico, having levels higher than 50 ppm [2]. The solubility of silica in water is 120–140 ppm [3]. Silica is a major concern for power plants, desalination units and the microelectronics industries. It deposits on the surface of boilers, cooling systems, and reverse osmosis (RO) membranes causing energy losses and increased maintenance costs. Scaling problems are obviated when the silica level is <10 ppm in RO feed water at a water recovery rate of >98% [4]. The silica concentration in water to high pressure boilers should be <8 ppm to prevent scale formation [5].

Silica is present in water in three principal forms: suspended solids (which is not problematic in water purification), colloidal silica (which can be efficiently removed by filtration and RO), and reactive silica (the major component of which is silicic acid in equilibrium with SiO_2) [6]. Silicic acid is a weak acid, with pK_a values of 9.5 and 13.5 [7]. It is less than 1% ionized at pH values below 7.5 and so cannot be selectively removed by ion exchange resins from natural water. It can be removed with type 1 and type 2 strong base anion exchange resins in the hydroxide form [8] but they are not selective (*vide infra*) and raise the pH of the effluent water (which is unacceptable in most applications).

The objective of this research was to design and prepare a reactive polymer for the selective removal of silicate from water. The main prerequisite was identifying a species that could react with silicate and be immobilized onto a polymer. Keggin anions are one class of polyanions having the general formula $[XM_{12}O_{40}]^{n-}$, where *M* is either Mo or W, and *X* is one of a number of atoms, including Si and P [9]. The heptamolybdate ion is able to complex reactive silica to form the silicomolybdate [10] and the heptatungstate ion forms the silicotungstate [11]. Since ionically bound species retain their reactivity within a polymer support [12], crosslinked poly(vinylbenzyl chloride) beads were thus prepared, functionalized with trimethylamine, and modified with heptamolybdate and

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doi:10.1016/j.polymer.2009.11.040

heptatungstate anions by ion exchange. The sorption affinities were then quantified and the selectivity for silicate evaluated.

2. Experimental section

Copolymer beads of vinylbenzyl chloride (VBC) and 2 wt% divinylbenzene (DVB) were prepared by suspension polymerization with 0.5% benzoyl peroxide as initiator [13]. Gel and expanded gel beads were prepared in the same manner except that toluene was added in an equal weight to the monomer when preparing the latter. The toluene was removed after polymerization by washing the beads with methanol. The beads were sieved and a particle size of 250–425 μm was used. Silica solution was prepared from a 1000 ppm silica standard (LabChem). Phosphate solution was prepared from a 1000 ppm phosphate standard (LabChem). Molybdate solution was prepared from ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) (Fisher Scientific). VBC, DVB, Na_2SO_4, NaCl, KNO_3, Dowex®1_2 ion exchange resin, sodium tungstate, and aqueous trimethylamine were purchased from either Sigma–Aldrich or Acros. Ionic concentrations were determined by ICP-AES (Spectroflame M120E).

2.1. Synthesis of trimethylammonium chloride resin

PolyVBC beads (10 g) were placed in a 1 L round bottom flask equipped with a condenser and overhead stirrer, 400 mL of 20% aqueous trimethylamine was added, and the mixture was refluxed for 17 h to give the trimethylammonium resin. After washing, the beads were conditioned with 1 L each of water, 1 M HCl, and water.

2.2. Preparation of trimethylammonium heptamolybdate resin (TMAMo)

The chloride-form resin (5 g wet wt.) was eluted with 1 L of 0.5 N ammonium molybdate solution (pH 5.3) and washed with 4 L of water.

2.3. Preparation of trimethylammonium monomolybdate resin

The chloride-form resin (5 g wet wt.) was eluted with 1 L of 0.5 N ammonium molybdate solution (pH adjusted to 7.3 with 1 M NaOH) and washed with 4 L of water.

2.4. Preparation of trimethylammonium monotungstate resin

The chloride-form resin (5 g wet wt.) was eluted with 1 L of 0.5 N sodium tungstate solution (pH 9) and washed with 4 L of water.

2.5. Preparation of trimethylammonium heptatungstate resin (TMAW)

The chloride-form resin (5 g wet wt.) was eluted with 1 L of 0.5 N sodium tungstate solution (pH adjusted to pH 5.5 with 1 M HCl) and washed with 4 L of water.

2.6. Elemental analyses

The nitrogen elemental analysis was done by digesting 0.200 g of dry resin in 0.25 g of $CuSO_4 \cdot 5H_2O$, 10 g of K_2SO_4, and 25 mL of concentrated H_2SO_4 in a 500 mL three-neck round bottomed flask. After digestion, 100 mL of distilled water was added and the flask equipped with a 150 mL addition funnel and distillation apparatus connected to a funnel via Tygon tubing in a 600 mL beaker containing 50 mL of a standardized 0.100 M HCl solution. NaOH (150 mL of 6 M solution) was added to the flask from the addition funnel. The resulting amine was distilled into the beaker until the condensate was neutral. The HCl solution was transferred to a 250 mL volumetric flask and diluted to the mark with distilled water. Fifty milliliter aliquots of the HCl solution were titrated with standardized 0.100 M NaOH. The molybdenum elemental analysis was done similarly in that 0.100 g of dry resin was digested with 0.125 g of $CuSO_4 \cdot 5H_2O$, 5 g of K_2SO_4 and 12.5 mL of concentrated H_2SO_4 in a 100 mL three-neck round bottomed flask. The solution was quantitatively transferred to a 250 mL volumetric flask and diluted to the mark with distilled water. The molybdenum concentration was determined by ICP-AES.

2.7. Determination of silica affinity

Experiments were done in 20 mL plastic vials. Silica solutions were prepared from a standard 1000 ppm silica solution with the pH adjusted by adding HCl solution. The contact time was 17 h unless otherwise noted.

To compare silica affinities, enough of each resin (monomolybdate, heptamolybdate, monotungstate, heptatungstate, or chloride, or Dowex® 1×2 in the hydroxide form) to give 0.10 mmol ammonium groups was contacted with 10 mL of 20 ppm silica solution at pH 7.

To determine the effect of pH, 118 mg of dry TMAMo resin was contacted with 10 mL of 100 ppm silica solutions with the pH adjusted to 3.8, 5.2, 6.7, 9.1 and 10.7. The sorption isotherm was determined by adding 10 mL of 100 ppm silica solution at pH 7 to nine vials containing 12.0 mg, 26.5 mg, 53.0 mg, 82.0 mg, 102.2 mg, 128.1 mg, 190.6 mg, 255.0 mg and 378.7 mg of dry TMAMo resin. A three-day contact time ensured equilibrium.

The rate of complexation by the Dowex (R) 1 × 2 (OH) or TMAMo resin was determined by contacting enough of each resin to give 0.167 mmol nitrogen with 5 mL 100 ppm silica solution at pH 7 for 1 h, 2 h, 4 h, 8 h and 24 h. Selectivity was determined by contacting enough of Dowex (R) 1 × 2 (OH), TMAMo, or TMAW to give 0.10 mmol nitrogen with a solution of 1 mM $CaCl_2$/0.5 mM $MgCl_2$/0.5 mM Na_2SO_4/0.5 mM KNO_3 and 20 ppm silica. In studying the effect of phosphate on silica sorption by TMAMo, 61.3 mg of dry resin was contacted with either 10 mL of 50 ppm silica or 10 mL of 50 ppm silica and 50 ppm phosphate, each at pH 7.7.

3. Results

The hydrophilicity (as measured by the percent solids), nitrogen capacity, and molybdenum capacity of the trimethylammonium gel resins are given in Table 1. A comparison of the calculated and experimental nitrogen capacities shows that full functionalization has been achieved. The chloride-form resin retains a large amount of water due to the ionicity of the ligand–substrate interaction. The hydrophilicities of the heptamolybdate and heptatungstate form of the resins are significantly less while the monomolybdate and monotungstate are intermediate between the two. The monomolybdate resin has an N/Mo ratio of 2, as expected from the charges on the cation and anion. The heptamolybdate Mo capacity of 3.39 mmol/g equates to 0.48 mmol $Mo_7O_{24}^{6-}$/g and a ligand to anion ratio of 4.8:1.

Table 1
Percent solids and capacities of the quaternary amine gel resins.

Counterion	% Solids	N content (expt), mmol/g	N content (calc), mmol/g	Mo capacity, mmol/g
Cl^-	22.9	4.30	4.60	–
MoO_4^{2-}	33.8	3.44	3.82	1.64
$Mo_7O_{24}^{6-}$	61.3	2.32	2.79	3.39
WO_4^{2-}	36.2	3.00	3.27	–
$W_7O_{24}^{6-}$	71.7	2.29	2.17	–

Table 2
Silica sorption by the trimethylammonium gel resins from solutions initially at pH 7.

Counterion	%Si sorbed	Final pH
Cl^-	1.2	5.6
MoO_4^{2-}	4.5	5.6
$Mo_7O_{24}^{6-}$	94.8	4.8
WO_4^{2-}	1.4	7.1
$W_7O_{24}^{6-}$	40.5	5.1
Dowex (OH^-)	96.8	10.8

The extent of silica sorption by the resins is given in Table 2. The chloride, monomolybdate and monotungstate resins complex little silica, the heptatungstate has an intermediate affinity, and the heptamolybdate has a high affinity. The Dowex resin in the hydroxide form has a high affinity for silica through ion exchange but at a substantial increase in the final pH of the solution.

The TMAMo gel resin effectively removes silica from solution over a wide pH range (Fig. 1). There is a low level of Mo leakage in solutions of pH 7 and below; this leakage is <1% of the total since, if all of the Mo on the resin were to enter the solution, the amount would be 3950 ppm. The amount in solution becomes significant as the pH exceeds 9. The TMAW gel resin has a significantly lower affinity for silica, complexing 42% at pH 4 and 48% at pH 10. Leakage of heptatungstate is comparable to that of heptamolybdate.

Silica sorption by the TMAMo and TMAW resins in the presence of other ions was investigated in order to assess their selectivity. Resins were contacted with synthetic groundwater solution containing 1 mM $CaCl_2$, 0.5 mM $MgCl_2$, 0.5 mM Na_2SO_4, 0.5 mM KNO_3, and 20 ppm silica; the Dowex (OH^-) resin was also contacted. It was thus determined that silica sorption by the TMAMo and TMAW resins are unaffected by the presence of other ions and have negligible affinity for other ions (Fig. 2). The Dowex resin has a higher affinity for both chloride and sulfate than for silica. Given the higher silica affinity of the TMAMo resin, the remaining studies were done with it alone.

Since phosphate reacts with molybdate to form phosphomolybdates [14], the phosphate ion was tested as a potential interferant in the sorption of silica by TMAMo. The resin was contacted with 10 mL of a solution at pH 7.7 containing 50 ppm silica and 50 ppm phosphate and found to sorb 24.6% of the silica in contrast to 91.2% sorption in the absence of phosphate.

The sorption capacity of the TMAMo resin was calculated through its isotherm by contacting 100 ppm silica solutions at pH 7 with increasing amounts of resin (Fig. 3). The capacity was calculated to be 0.23 mmol silica/g resin.

The rate of silica sorption onto the TMAMo gel and Dowex resins was determined (Fig. 4). The Dowex operates through ion exchange, which is rapid in a hydrophilic resin. The TMAMo gel resin takes longer to reach equilibrium; this could be due to either the slow rate of the chemical reaction forming the Keggin structure or to slow accessibility of the silicate into the less hydrophilic polymer matrix. In order to explore whether accessibility is the rate-determining step, the polymer was modified by preparing it as an expanded gel.

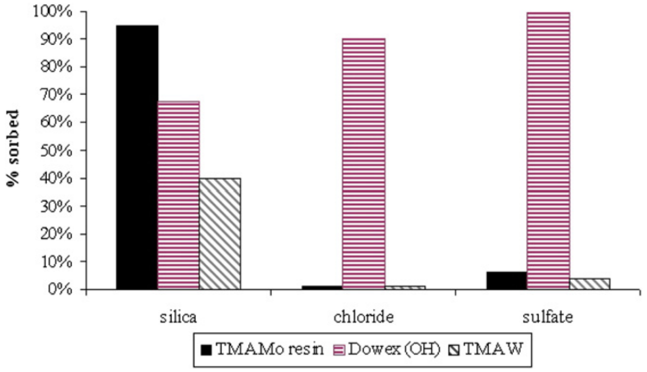

Fig. 2. Selectivity of the resins for silica in the presence of chloride, sulfate and nitrate ions.

Expanded gel resins have a more open structure than gel resins [15]. An expanded gel trimethylammonium resin was thus prepared which, in the chloride form, had 10.7% solids and a capacity of 4.20 mmol/g, indicating the same (complete) level of functionalization as the gel resin yet at a solids that was half its value due to its ability to accommodate more waters of hydration within its open structure. Converting to the molybdate form gave a resin with 49.0% solids (decreasing from 61.3% in the gel resin) while the nitrogen and molybdate capacities remained, within experimental error, the same as found with the gel resin.

The results in Fig. 4 thus show that a resin with an expanded gel matrix has a greater rate of complexation.

4. Discussion

Functionalization of the polyVBC beads with trimethylamine leads to the quaternary ammonium resin which, in the chloride form, has a low solids level (Table 1). This is due to the inherent hydrophilicity of the ionic ligand within a polymer network that is lightly crosslinked. Molybdate exists in solution as different oxomolybdenum species depending on the Mo concentration and the pH of the solution [16]. In alkaline and neutral solutions, molybdates are present as the monomeric $[MoO_4]^{2-}$ ion. At Mo concentrations above 10^{-3} M and pH 5–6, the heptamolybdate ion becomes the predominant species. Accordingly, the heptamolybdate and monomolybdate

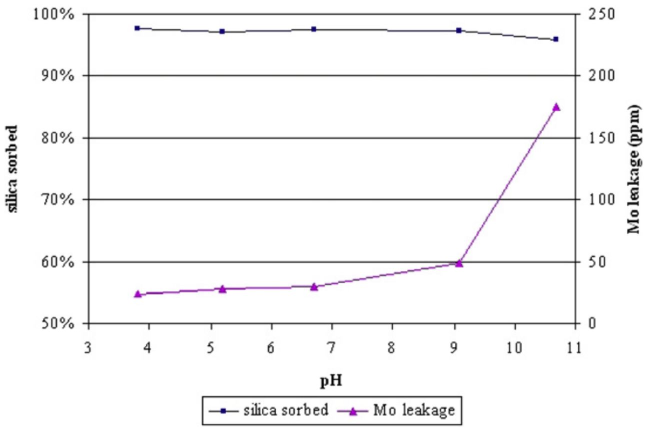

Fig. 1. Silica sorption and Mo leakage by the TMAMo resin as a function of pH.

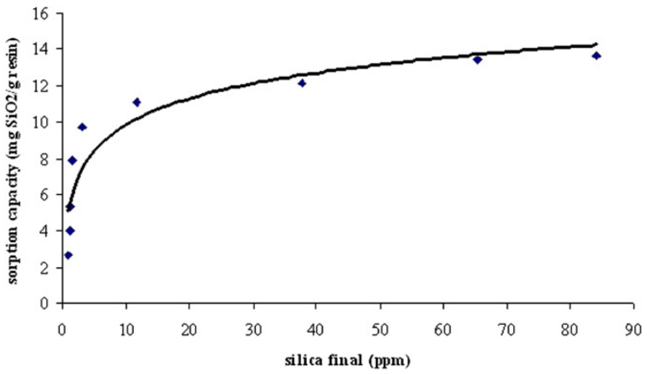

Fig. 3. Sorption isotherm of silica onto the TMAMo resin.

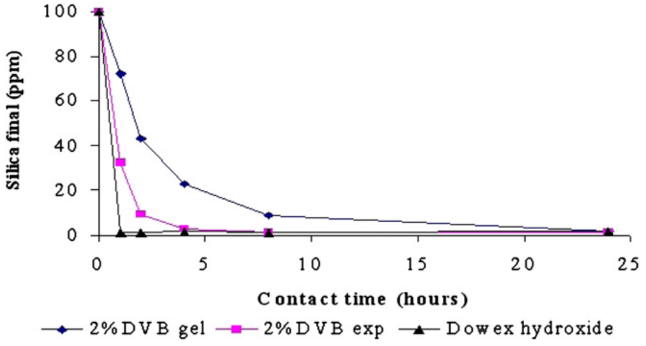

Fig. 4. Rate of silica sorption onto the TMAMo and Dowex resins.

resins were prepared from pH 5.3 and pH 7.3 molybdate solutions, respectively.

The FTIR spectra of the two resins are different in the fingerprint region below 1000 cm^{-1} (Fig. 5). The solids level increases after exchanging the chloride ion for the monomolybdate because the divalent ion brings the ligands closer for charge neutralization, leaving less free volume for the water molecules to occupy. The biggest change in solids is evident when the heptamolybdate is bound to the ligands since it brings a number of ammonium ligands closer together, effectively increasing the apparent cross-linking of the network and further decreasing the free volume. The network must be sufficiently flexible to permit rearrangement of the polymer chains for charge neutralization of the Mo$_7$O$_{24}^{6-}$. Elemental analyses show that there are 0.48 mmol heptamolybdate ions per 2.32 mmol ammonium ligands or a molar ratio of 1:4.8. The anion thus has ~5 proximate ammonium ligands and

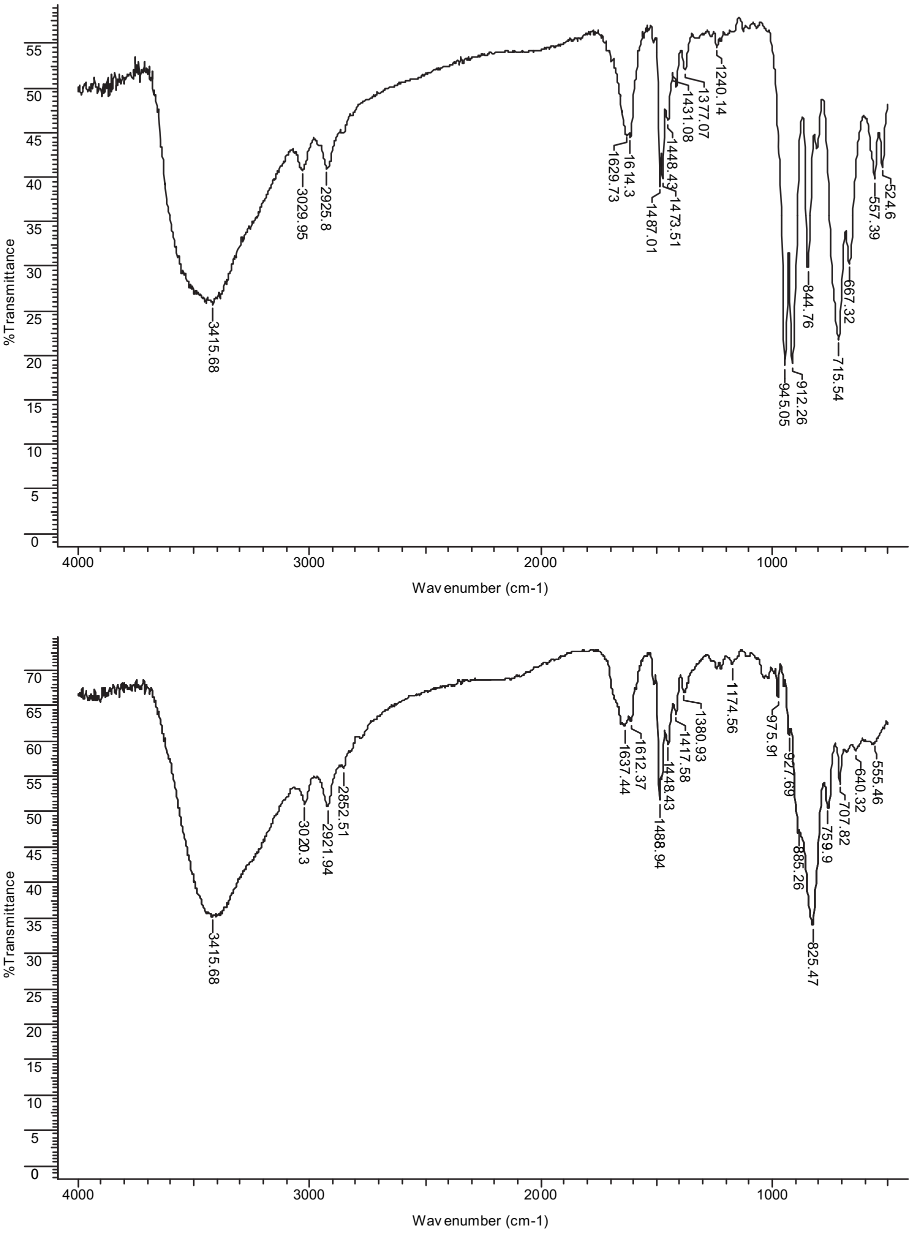

Fig. 5. FTIR spectra of the TMAMo (top) and monomolybdate (bottom) resins.

a proton must remain bound from solution to complete neutralization of the charge.

The results in Table 2 show that the heptamolybdate resin has a high affinity for silica whereas the monomolybdate resin has no affinity. Contact with the silica-containing solution by the Dowex resin also shows a high affinity but leads to an increase in pH, as expected if ion exchange were occurring, while the TMAMo resin shows a slight decrease in pH. The TMAMo resin retains its high affinity for silica over the entire pH range studied (Fig. 1). However, the sorption mechanism does not remain the same across the pH range (see below). The silica remains unionized below pH 9 and the small amount of heptamolybdate which enters the solution below pH 7 may be due to interstitial ion since the amount lost is the same as that when the resin contacts deionized water. Ion exchange with OH^- is responsible for the loss of $Mo_7O_{24}^{6-}$ in solutions above pH 9. Silica sorption by the heptamolybdate resin differs from that of the strong base anion exchange resin in that the latter prefers chloride and sulfate anions relative to silica while the TMAMo resin is highly selective for silica and unaffected by the presence of SO_4^{2-}, NO_3^- or Cl^- ions (Fig. 2). The results thus suggest that in neutral and acidic solution, TMAMo sorbs silica by a complexation mechanism.

The heptatungstate resin has 71.7% solids, indicating that it is less hydrophilic than the heptamolybdate resin, and a nitrogen capacity of 2.29 mmol/g. It, however, has a lower affinity for silica, complexing 40.5% of the silica from solution under conditions where the TMAMo resin complexes 94.8%. The lower affinity may be due to its lower hydrophilicity. The monotungstate resin has no affinity for silica, as found with monomolybdate. Both heptatungstate and heptamolybdate have an affinity for silica that is independent of pH and both have an affinity only for silica in the presence of chloride and sulfate ions. The FTIR spectra for the TMAW and monotungstate resins are given in Fig. 6 for comparison to the Mo analogues. While the region between 1700 and 1000 cm^{-1} is similar among all four resins, and the region below 1000 cm^{-1} is similar between the monomolybdate and monotungstate resins, that region is different for the heptamolybdate and heptatungstate resins.

The reaction of silicic acid with the heptamolybdate anion in solution results in the formation of the silicomolybdate Keggin heteropolyanion [17] and this can be the mechanism within the polymer. In acidic solution, the reaction occurs according to the equation below:

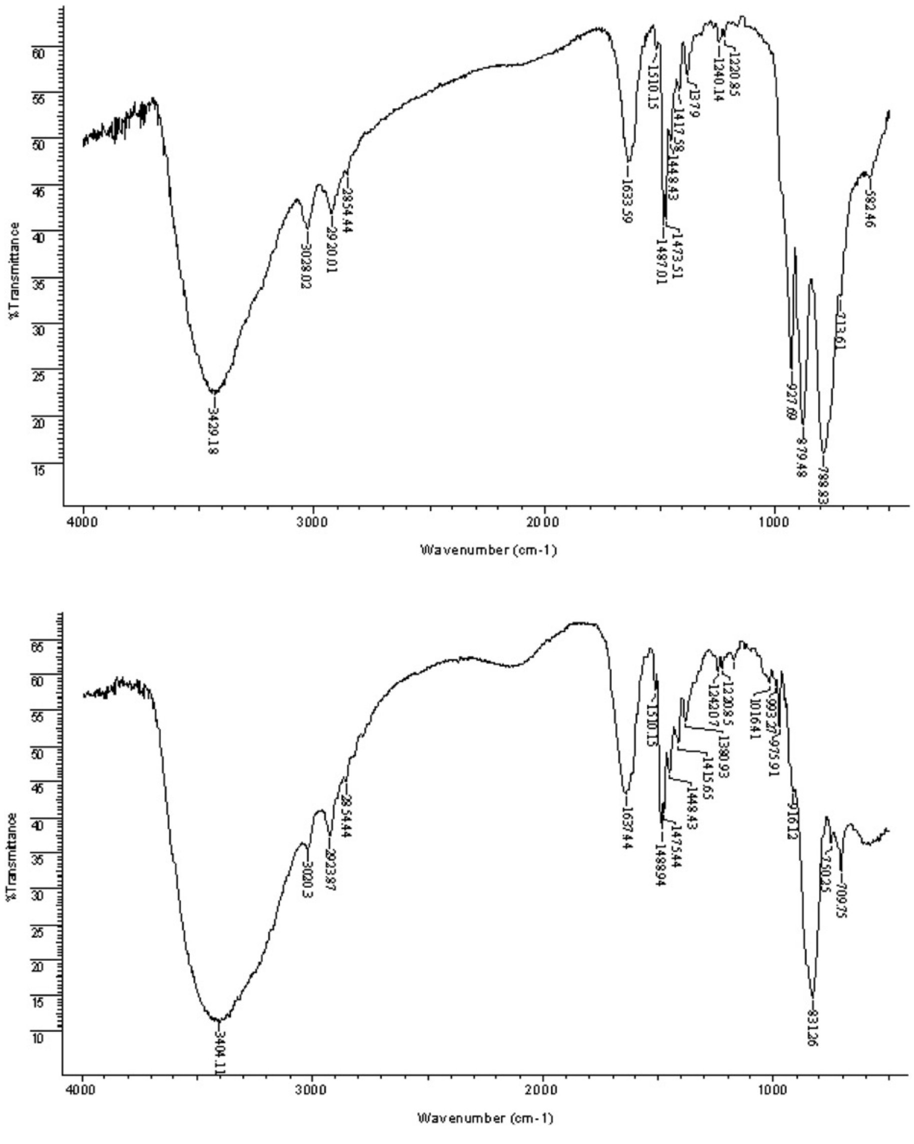

Fig. 6. FTIR spectra of the TMAW (top) and monotungstate (bottom) resins.

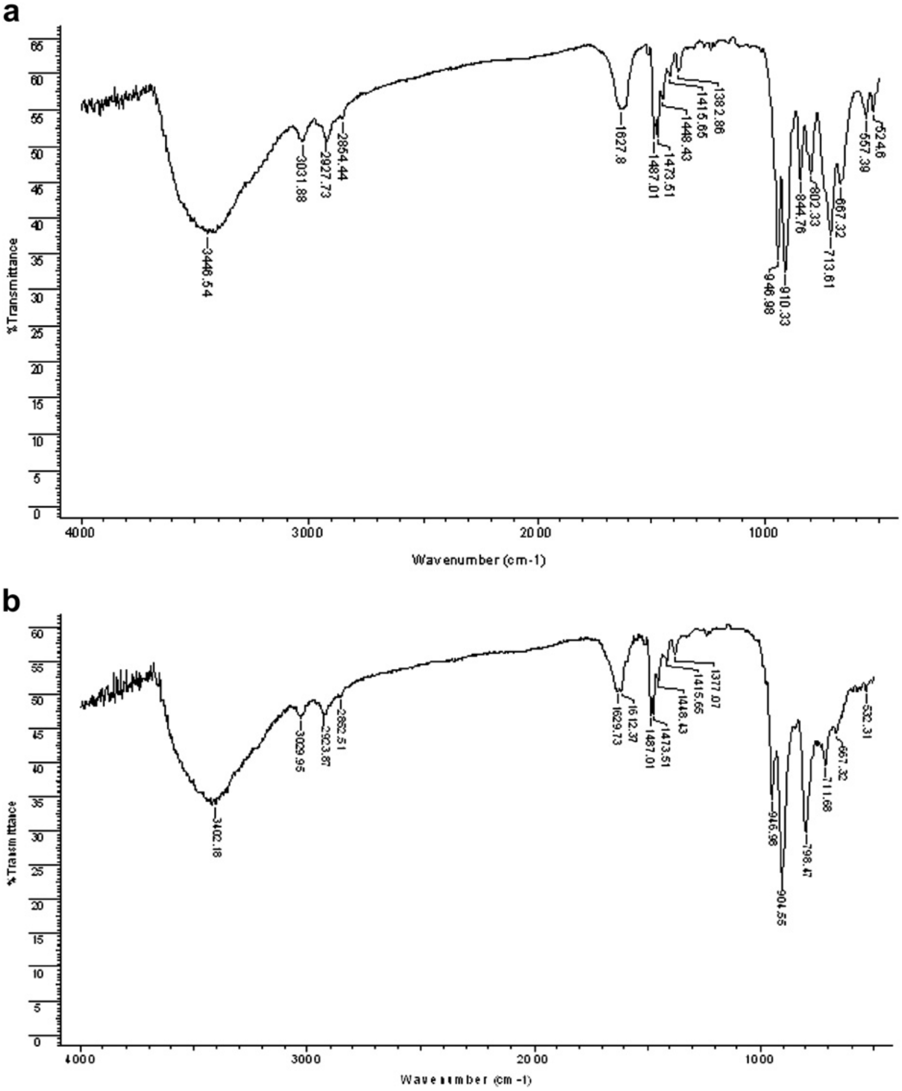

Fig. 7. (a) FTIR spectrum of the heptamolybdate resin partially saturated with silica. (b) FTIR spectrum of the silicomolybdate resin.

$$7Si(OH)_4+12Mo_7O_{24}^{6-}+44H^+\rightarrow 7SiMo_{12}O_{40}^{4-}+36H_2O$$

Based on this reaction and the Mo capacity of the TMAMo resin, a theoretical capacity of 0.28 mmol silica/g_{resin} can be calculated which is similar to that from the isotherm (0.23 mmol silica/g_{resin}; Fig. 3). The FTIR spectrum of the silicomolybdate resin (Fig. 7) supports the mechanism. There are four characteristic $Mo_7O_{24}^{6-}$ bands at 715, 845, 912 and 945 cm^{-1}. As silica is complexed by the heptamolybdate resin, these bands get weaker (Fig. 7a). Once the resin approaches complete reaction, the band at 845 cm^{-1} completely disappears (Fig. 7b). The IR spectrum of the silica-saturated resin is consistent with that of silicomolybdate compounds with strong bands at 900–904 cm^{-1} and 790–800 cm^{-1} [18]. FTIR analysis of a soluble tert-butylammonium silicododecamolybdate [19] shows important similarities to Fig. 7b and allows the assignment of 946 cm^{-1} to $\nu_{as}(Mo–O_t)$, 904 cm^{-1} to symmetric coupling between the $\nu_{as}(Mo–O)$ and $\nu_{as}(Si–O)$, and 798 cm^{-1} to the asymmetric stretch of Mo–O–Mo.

Based on Fig. 1, it is reasonable to expect that the mechanism on the resin follows the equation above up to about pH 6.6. In solutions with pH $\geq$ 9, Mo leakage is significant and the high affinity for silica shown by the resin is due to ion exchange and not the equation giving the formation of $SiMo_{12}O_{40}^{4-}$. The pH region between 6.6 and 9 is transitional, as the extent of Mo leakage, and thus ion exchange, becomes of increasing importance.

The heptamolybdate anion complexes phosphate to give the phosphomolybdate anion [20] $[PMo_{12}O_{40}]^{3-}$. It is therefore consistent that phosphate affects the sorption of silica by the TMAMo resin since both anions compete for the heptamolybdate on the resin. In any application, this would be dealt with by removing the phosphate first by any of a number of techniques, including the use of zeolites [21], hydrotalcites [22], or precipitation [23].

The TMAMo gel resin displays relatively slow sorption compared to the strong base ion exchange resin (Fig. 4). While it is reasonable to ascribe this to the fact that a chemical reaction, rather than simple ion exchange, is occurring, the results with the expanded gel resin emphasize the importance of investigating the role of accessibility in results with polymer-supported reagents. The more hydrophilic structure permits greater accessibility of the silicate ion onto the ligand bearing the molybdate and hence a rapid approach to equilibrium.

5. Conclusion

Immobilization of a molybdate ion within a crosslinked polymer does not hinder its reaction with silica to form a Keggin ion despite the large size of that ion. The large size of the anion limits the overall capacity of the polymer for Si on a millimolar basis, even at full functionalization of the polymer. Access of the silica into the polymer is hindered if the matrix does not have a high water content, but increasing the resin hydrophilicity increases the apparent rate of reaction. The most important influence of the polymer support microstructure is its effect on the water content of the matrix which permits a greater level of accessibility of the reactant to the immobilized ion. Current research centers on X-ray diffraction studies to confirm the formation of $SiMo_{12}O_{40}^{4-}$ within the polymer. Solid state Si and Mo NMR studies are also planned.

Acknowledgment

We gratefully acknowledge support from the New York State Energy Research and Development Authority, the Pall Corporation, and the Department of Energy, Office of Basic Energy Sciences through Grant No. DE-FG02-ER15287.

References

[1] Al-Rehaili AM. Comparative chemical clarification for silica removal from RO groundwater feed. Desalin 2003;159:21–31.
[2] Wohlberg C, Buchholz JR. Silica in water in relation to cooling tower operation. Avail. Natl. Assoc. Corros. Eng., Publ. Dept., Houston, Tex. Report. Los Alamos Sci. Lab.; 1975 (CONF-750401-20), 31 pp.
[3] Siever R. Silica solubility, 0-200_ and the diagenesis of siliceous sediments. J Geol 1962;70:127–50.
[4] Potts DE, Ahlert RC, Wand SS. A critical review of fouling of reverse osmosis membranes. Desalin 1981;36:235–64.
[5] Kemmer FN, editor. The Nalco water handbook. New York: Nalco Chemical Company, McGraw-Hill; 1979.
[6] Mabic S. Water purification technologies and silica breakthrough. Am Lab 2002;34:18–20.
[7] Sjoeberg S. Silica in aqueous environments. J Non-Cryst Solids 1996;196:51–7.
[8] Ali MBS, Hamrouni B, Bouguecha S, Dhahbi M. Silica removal using ion-exchange resins. Desalin 2004;167:273–9;
McGarvey J, McGarvey FX. Silica removal by ion exchange. Power 1950;94:93–5.
[9] Jeannin YP. The nomenclature of polyoxometalates: how to connect a name and a structure. Chem Rev 1998;98:55–69.
[10] Strickland JDH. The preparation and properties of silicomolybdic acid III: the combination of silicate and molybdate. J Am Chem Soc 1952;74:872–6.
[11] Teze A, Herve G. α-, β-, and γ-Dodecatungstosilicic acids: isomers and related lacunary compounds. Inorg Synth 1990;27:85–96.
[12] Sherrington DC. Polymer-supported metal complex oxidation catalysts. Pure Appl Chem 1988;60:401–14.
[13] Alexandratos SD, Strand MA, Quillen DR, Walder AJ. Synthesis and characterization of bifunctional phosphinic acid resins. Macromolecules 1985;18: 829–35.
[14] Beckwith PM, Scheeline A, Crouch SR. Kinetics of the formation of 12-molybdo-phosphate in perchloric, sulfuric, and nitric acid solutions. Anal Chem 1975;47:1930–6.
[15] Wei R, Chen J, Chen L, Fei Z, Li A, Zhang Q. Study of adsorption of lipoic acid on three types of resin. React Funct Polym 2004;59:243–52.
[16] Aveston J, Anacker EW, Johnson JS. Inorg Chem 1964;3:735–46;
Mitchell PCH. Chemistry of molybdenum. In: Ullmann's encyclopedia of industrial chemistry. 5th ed. International Molybdenum Association, http://www.hse.imoa.info/Default.asp?Page=113; 1990. A16, Chapter 7, pp. 675–682 and references therein.
[17] Coradin T, Eglin D, Livage J. The silicomolybdic acid spectrophotometric method and its application to silicate/biopolymer interaction studies. Spectrosc 2004;18:567–76.
[18] Rocchiccioli-Deltcheff C, Fournier M, Franck R, Thouvenot R. Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum(VI) and tungsten(VI) compounds related to the Keggin structure. Inorg Chem 1983;22:207–16.
[19] Wery ASJ, Gutierrez-Zorrilla JM, Luque A, Vitoria P, Roman P, Martinez-Ripoll M. tert-Butylammonium silicododecamolybdate. Synthesis, vibrational study, crystal structure, thermal behavior and electrochemical properties. Polyhedron 1998;17:1247–55.
[20] Herve C, Teze A, Contant R. General principles of the synthesis of polyoxometalates in aqueous solution. In: Borras-Almenar JJ, Coronado E, Muller A, Pope M, editors. Polyoxometalate molecular science. Dordrecht: Kluwer Academic Publishers; 2001.
[21] Onyango MS, Kuchar D, Kubota M, Matsuda H. Adsorptive removal of phosphate ions from aqueous solution using synthetic zeolite. Ind Eng Chem Res 2007;46:894–900.
[22] Miyata S. Dephosphorizing agent for stripping dissolved phosphates from polluted water and its regeneration method. Japan Kokai Tokkyo Koho 2000;5. JP 2000024658.
[23] Grohmann A, Althoff HW, Koerfer P. Kinetics of phosphate precipitation with iron(III) salts and the effect of calcium ions. Vom Wasser 1984;62: 171–89.