Removal of Hg(II) from Acid Aqueous Solutions by Poly(*N*-Vinylimidazole) Hydrogel

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ABSTRACT: Caption of Hg(II) from acid aqueous solution by immersed poly(*N*-vinylimidazole) hydrogel particles was studied as a function of pH, counterion, and cation concentration. Fitting parameters to several sorption isotherms have been determined. Their values depend mostly on pH and less, on temperature and counterion, and suggest a large affinity of imidazole groups in the gel and mercury cations. Practically total removal (94.4%) of Hg(II) is achieved at pH = 2, with 10 g of dry gel per liter of solution, when cation concentration was as large as 15,000 ppm (0.075 *M*). Polymer protonation decreases about fourfold the cation affinity, supporting competitive protonation-complexation mechanisms. By its side, metal uptake decreases polymer protonation. Thermal stability of loaded gels decreases with respect to metal free hydrogels. Scanning electron micrographs reveal no changes in the gel morphology upon cation binding, but T_g increases significantly with the Hg(II) content of loaded gels and swelling decreases moderately, indicating the role of the cation as ionic crosslinker. Practically total elution of Hg(II) is achieved with 1 *M* HNO$_3$ in consecutive loading-elution cycles. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1467–1475, 2001

Key words: poly(vinylimidazole) hydrogel; sorption isotherms; mercury ions uptake

INTRODUCTION

The presence of heavy-metal ions in the environment is one of the major concerns due to their toxicity to many life forms. Numerous research efforts are being done to develop methods to remove heavy metal ions, particularly in waste waters streams of hydrometallurgy and related industries, and to subsequently reuse them. Most treatment methods to remove metal ions from waste waters include filtration, chemical precipitation, simple and chelating ion exchange, sorption, membrane systems, etc. The sorption of metal ions by certain naturally occurring biopolymers and synthetic polymers has recently gained much attention. In particular, the search for pairs metal ion-specific resin has increased notably. Polymer resins and hydrogels bearing electron donor groups have the ability to bind metal cations[1,2] from aqueous solutions by batch methods. This phenomenon has many important applications.[3]

Mercury is one of the most dangerous heavy metals,[4] and that is why the discharging limit of waste water streams has been fixed by law in very

small values. Different methods have been proposed to remove Hg(II): ion-exchange resins,[5] polymer-enhanced ultrafiltration,[6] and precipitation agents.[7] The goal is to achieve total removal of Hg(II) with minimum steps, fastest processes, and maximum retention capacity (minimum cost) of the removing material. Hydrogels have the additional value that transfer no substance to the aqueous solution, and that they can be easily cleaned up to be used indefinitely.

We are interested in removing metals from polluted waters, and with that concern we have previously studied the ability of poly(N-vinylimidazole) (PVI) hydrogels to retain several metal cations from aqueous solution.[1] The aim of this article is to study the ability of poly(vinylimidazole) hydrogel to bind mercury ions under different conditions as well as the recovery of the hydrogel by nitric acid.

EXPERIMENTAL

Materials

Mercury (II) chloride was purchased from Merck and used as received. Hydrochloric and sulfuric acids in normalized solutions were provided by Panreac.

Poly(N-vinylimidazole) hydrogel was synthesized by radical crosslinking polymerization of N-vinylimidazole (VI) and N,N'-methylen-bis-acrylamide (BA) in aqueous solution, as described in ref. 1. The total monomer concentration C_T and the crosslinking ratio C in the comonomers feeding mixture were 40 g/100 mL and 2% w/w BA, respectively. Hydrogel particles were exhaustively washed and dried in oven at 80°C for 2 days. Afterwards, they were sized by screening, and the fraction with mesh size in the range 0.16 to 0.125 mm was chosen.

Characterization of unloaded hydrogels was reported previously.[1] The average molecular weight between crosslinks of the sample employed in this work was 3.2 10[4], and its swelling ability in pure water was 4.32 g of water per gram of dry gel.

Measurements of Hg(II) sorption were performed in batch with hydrogel particles suspended in the aqueous solution. Loading experiments were made with an effective concentration of 10 g of dry polymer per liter of solution. The equilibration time was taken as 2 days at r.t. (20°C), although time-dependent retention measurements allow to conclude that 15 min are enough to reach equilibrium.

Apparatus and Methods

Glass transition temperatures were determined with a Mettler DSC 30, at 10 K min^{-1} heating rate in nitrogen atmosphere. Thermal stability was studied with a Perkin-Elmer Thermogravimetric Analyzer TGA7. SEM micrographs were taken with a microsope ETEC Autoscann U-1. The surface of the hydrogel was coated with gold (150 Å) with an Edwards Sputter Coater. The concentration of mercury ions was determined in a 2380 Perkin-Elmer atomic absorption spectrometer, connected with a hydride generator system. Potentiometric measurements (pHmeter from Metrohm model 654) were performed to determine the hydrogel degree of protonation α, by the expression:

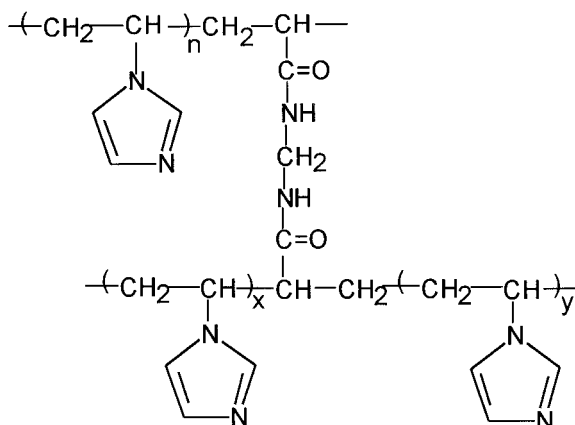$$\alpha = \frac{10^{-pH_i} - 10^{-pH_f}}{c_{ef}} \qquad (1)$$

where pH_i, pH_f represent the initial pH of the solution (without hydrogel) and the equilibrium pH of the solution reached after PVI immersion, respectively. The hydrogel effective concentration, c_{ef}, is the number of mol of imidazole immersed per liter of solution. In loading experiments, the hydrogel effective concentration was 10 g/L = 0.1 M.

RESULTS AND DISCUSSION

The poly(vinylimidazole) hydrogel synthesized by radical crosslinking polymerization has the following general structure (see Scheme 1):

Sorption Isotherms

The ability to bind mercury ions by batch equilibrium procedure depends mostly on pH and less, on temperature and counterion, and suggests a large affinity of imidazole groups in the gel and mercury cations. Table I shows several examples. Practically total removal (94.4%) of Hg(II) is achieved at pH = 2 with 10 g of dry gel per liter of solution, when cation concentration was 15.000 ppm ($7.5 \cdot 10^{-2} M$) and only small rests (<1 ppm) remain in solution when cation concentration is in the range of 500 ppm ($2.5 \cdot 10^{-3} M$), still a value

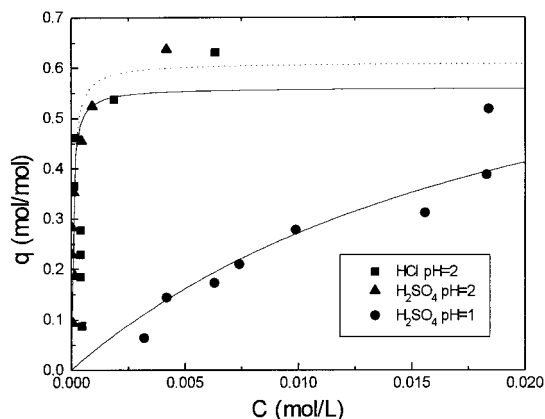**Scheme 1**   Structure of PVI hydrogels.

Figure 1   Sorption isotherms of Hg(II) by PVI hydrogel in different conditions. Polymer effective concentration 10 g/L. Lines correspond to the best fit to the Langmuir isotherm function.

much above the typical values of practical cases as mines and industrial wasting waters.

Figure 1 shows the sorption isotherms at 20°C, of Hg(II) by PVI hydrogel particles suspended in H_2SO_4 and HCl aqueous solutions with initial pH = 2 and 1.

Three isotherm models have been used:

$$q = K_F \cdot C^x \qquad (2)$$

$$q = \frac{q_s K_L C}{1 + K_L C} \qquad (3)$$

$$\frac{q}{C} = K_S(q_s - q) \qquad (4)$$

In these expressions, q represents the degree of binding, that is to say, the quantity of adsorbed metal per unit mass of polymer (mol/mol), q_s is the maximum value of q, corresponding to saturation of the hydrogel, K is the equilibrium sorption constant, and C (mol/L) is the concentration

Table I   Initial and Final Concentrations of Hg(II) in Acid Aqueous Solutions with PVI Effective Concentration 10 g/L at Two Different Initial pHs

Acid	pH_i	$[Hg(II)]_i$ (ppm)	$[Hg(II)]_f$ (ppm)
H_2SO_4	1	2 000	640
		15,000	3700
H_2SO_4	2	500	0.7
		2 000	1.3
		15,000	840

of free metal in the solution at the sorption equilibrium. Generally, the experimental capacity of a resin is smaller than the calculated maximum capacity, because part of the ligands is not accessible to the metallic ions.[8]

The Langmuir sorption [eq. (3)] model assumes that sorption takes place on the homogeneous surface of the substrate and that at saturation, a monolayer is formed. This model fits well the experimental results, except for low concentrations. This is due to the heterogeneity of the hydrogel internal surface: the first adsorbed ions bind on the most active (or accessible) imidazole groups, and those adsorbed later interact with the less active sites. In consequence, the heat of sorption depends on the binding site, and K_L is a function of the number of more active sites and therefore, of the hydrogel heterogeneity.

The isotherm of Freundlich [eq. (2)] fits quite well the experimental values that are not close to saturation, because expression (2) does not spread to a limit. For small values of q the agreement is good, especially for the cases of strong sorption, when the heterogeneity of the substrate is important.

The Scatchard isotherms [eq. (4)] represent intermediate situations, close to the Langmuir model (see Table II). Figure 2 shows the different types of fitting isotherms for the results obtained with pH = 2 and H_2SO_4, whereas in Figure 1 drawn lines correspond to the Langmuir isotherms of the experimental results obtained with different pHs and acids.

Langmuir treatment of Figure 1 plots yields (see Table II), for initial pH = 2, binding con-

Table II   Langmuir, Freundlich, and Scatchard Parameters Fitting the Experimental Results Obtained at 20°C

Acid	pH	K_L (L/mole)	q_s (L) (mole/mole)	K_F (L/mole)^x	x	K_S (L/mol)	q_s (S) (mole/mol)
H_2SO_4	2	1.58×10^4	0.56	1.86	0.19	1.38×10^4	0.59
HCl	2	1.33×10^4	0.61	1.14	0.12	1.20×10^4	0.62
HCl	2[a]	1.46×10^4	0.65	1.13	0.10	1.37×10^4	0.65
H_2SO_4	1	46	0.86	8.66	0.76	16	1.94
H_2SO_4	1[a]	64	1.16	10.5	0.69	35	1.76

[a] Corrected α.

stants of 10^4 L/mol and a binding degree, at saturation of the hydrogel, equal to 0.564 mol of Hg(II) (1.13 equivalents) per mol of imidazole group. This reflects the large affinity of imidazole groups and Hg(II), because Langmuir binding constants reported for similar polymer–cation systems[2,9,10] are in the range of 10^2 to 10^3.

For solutions with initial pH = 1, the Langmuir analysis yields parameters without physical meaning when the total effective concentration of PVI is taken as reference in determining q. Indeed, only nonprotonated imidazole groups are expected to be involved in Hg(II) complexation and, thus, q should be substituted by $q/(1-\alpha)$ in eqs. (2) to (4). The binding constants at initial pH = 1, obtained with this correction, decreases in almost fourfold with respect to those obtained with the same correction for the hydrogel protonated in less than 10% (see Table II, initial pH = 2).

Competitive Protonation and Hg(II) Complexation

For initial pH = 2, PVI effective concentration equal to 10 g/L and Hg(II) concentrations below 12,000 ppm (0.04 M), the equilibrium pH is around 4, and therefore, about 10% of imidazole rings are protonated, the same proportion that in absence of Hg(II) cations (see Fig. 3). Only for Hg(II) initial concentrations above 0.05 M, the degree of protonation decreases slightly upon increasing metal sorption (see Fig. 3), protons are slightly shifted by Hg(II).

The progressive substitution of protons by Hg(II) cations is much more clear for initial pH = 1, as shown in Figure 3: the degree of protonation of the hydrogel decreases from 90% in the absence of metal to about 40% for Hg(II) initial concentrations around 0.05 M (one-half of the proton concentration). It must, therefore, be concluded that protons and Hg(II) cations compete to be bonded by the imidazole groups, and the number of heterocycles joined to protons or to metal cations depend on the concentration of both and on their relative affinity, which is larger for imidazole-Hg(II) than for imidazole-H$^+$. This is a qualitative conclusion that may be quantified by comparing the equilibrium constants for PVI protonation and Hg(II) complexation.
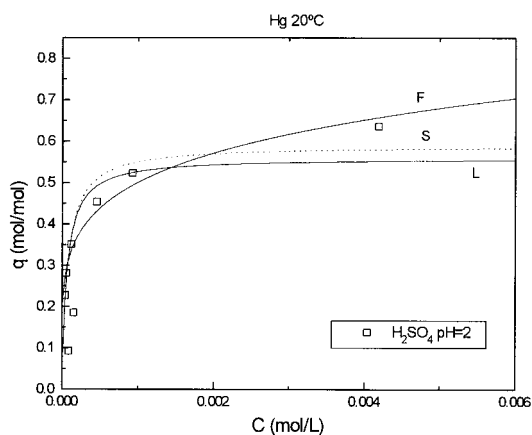

Figure 2   Langmuir, Freundlich, and Scatchard isotherms fitted to the experimental results obtained with initial pH = 2, effective concentration of PVI 10g/L and H_2SO_4.
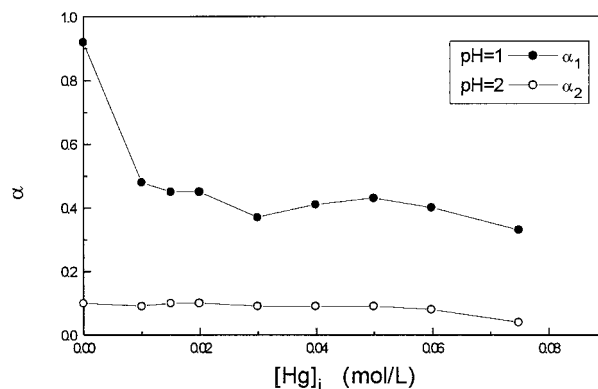

Figure 3   Protonation degree of PVI hydrogel at two different initial pH values, as a function of Hg(II) initial concentration.

The stability constant of the PVI-Hg(II) complexes, β_a, as much as the coordination index n or number of imidazole ligands surrounding a Hg(II) cation, were calculated as follows. In a system where a metallic ion, M, is coordinated with a ligand, L, several consecutive equilibrium reactions are needed to get the complex with the maximum number of ligands n. The product of the partial equilibrium constants gives an apparent constant of the formation of the complex.[11] The global process may be represented with the balance:

$$M + nL \rightleftarrows MLn$$

and the apparent constant of the complex formation is:

$$\beta_a = \frac{[ML_n]}{[M][L]^n} \qquad (5)$$

The coordination index of the complex may be calculated as a function of the initial metal concentration, $[M]_0$, the initial ligand concentration, $[L]_0$, the concentration of the bonded metal to the polymer to form the complex, $[M]_u$, and the concentration of ligand that is forming complex with the metal, $[L]_u$:

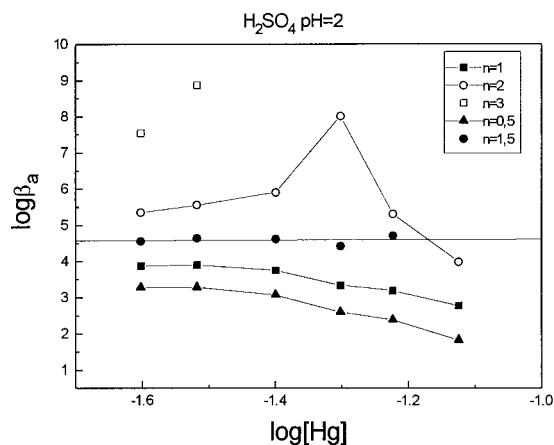$$n = \frac{[L]_u}{[M]_u} = \frac{[L]_0 - [L]}{[M]_0 - [M]} \qquad (6)$$

with:

Figure 4 Log plot of eq. (5) for different tentative n values.

Table III Apparent Stability Constant (β_a) and Coordination Index (n) for Hg(II)–PVI Complex Formed at 20°C and with Different Acids and Initial pHs

Acid	pH	n	β_a ($L^n \cdot mol^{-n}$)
HCl	2	1.57	7×10^4
HCl	2[a]	1.45	3.9×10^4
H_2SO_4	2	1.5	4.8×10^4
H_2SO_4	1	1	235
H_2SO_4	1[a]	1	105

[a] Initial concentration of ligand corrected with α.

$$[L] = [L]_0 - n([M]_0 - [M]) \qquad (7)$$

To calculate $[L]$ by means of the previous equation and, later on, β_a, it is necessary to know the value of n. To determine n, eq. (5) was used in logarithmic form. The concentration of free ligand was substituted by eq. (7) and $\log[M]$ was plotted vs. $\log \beta_a$ for several tentative values of n ($0 < n < 4$). The correct value of n is the one giving β_a values independent on concentration.

Imidazole groups are not in solution, and therefore, there is not a true ligand concentration but better an effective polymer concentration (10 g/L), which can be expressed in terms of effective molar concentration of ligands $[L]_0 = 0.1 \, M$ in all cases. Figure 4 shows an example of the log plot of eq. (5) with several tentative n values. Wrong n values give curves, and the straight line corresponds to the correct n value. Table III summarizes the values of n and β_a found by this method for the system PVI-Hg(II).

In the β_a calculation for initial pH = 1, gel protonation decreases the number of available places for metal binding. The correction carried out consisted in multiplying the concentration of initial ligand for the factor $(1 - \alpha)$. Corrected and uncorrected values of n and β_a are not very different, and appear summarized in Table III.

pK_a values determined by potentiometric titration of PVI particles immersed in the same experimental conditions employed in Hg(II) caption measurements[12] are 5.01 and 4.24 for α around 10% (pH = 2) and 4.63 and 3.42 for α around 40% (pH = 1.5), in H_2SO_4 and HCl solutions, respectively. Therefore, the effective equilibrium constant for gel protonation (K_a^{-1}) is in between 10^4 and 10^5, in the range of β_a values (10^2–10^5).
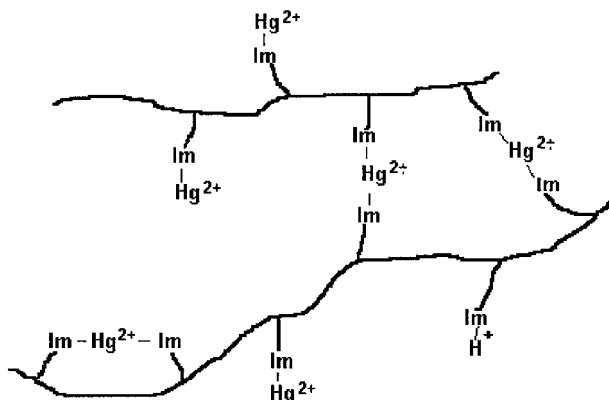
Scheme 2   Representation of PVI-Hg(II) interaction.

Figure 5   Occupancy number of imidazole groups by Hg(II) sorption or by protonation.

PVI–Hg(II) Complex

The coordination index in metal–polymer complex depends on the polymer nature, the metallic ion, and the reaction conditions. The values of n shown in Table III are average values. When the ligands are joined to a polymeric chain, some ions cannot be coordinated but they can be stuck to the surface of the polymer particles, increasing the value of n with regard to its real value. Steric effects can diminish the value of n.

β_a and n values have been reported[13] for a system similar to the one here studied, poly(4-vinylpyridine)–Cu(II), $n = 1.41$ and $\log \beta_a = 10.3$ ($\beta_a = 2 \cdot 10^{10}$). For the system PVI–Hg(II), the association constant is smaller ($\beta_a = 3.5 \cdot 10^4$), but the average number of ligands joined to a cation is slightly larger.

Scheme 2 represents a portion of PVI showing 10 ligands or groups of imidazole (Im). One of them is protonated (as for $\alpha = 10\%$), and there is total occupancy of ligands because the other nine Im groups are joined to six Hg(II) cations with an average coordination index 1.5 (see Table III). But the occupancy number may not be 100%; there may be a fraction of free Im groups.

Lets define the occupancy number as $nq + \alpha$, the molar fraction of bonded imidazole groups in PVI, either to Hg(II) or to protons. Figure 5 shows the occupancy number of PVI loaded at initial pH = 1 or 2, and with different degrees of binding to Hg(II). At pH = 1, the coordination index is $n = 1$, and because upon binding the firsts cations (q small) α decreases abruptly, the occupancy number decreases also. That is to say, the repulsive interactions of protons and cations bonded, induce the existence of unoccupied Im groups in an anticooperative-like mechanism. Both at initial
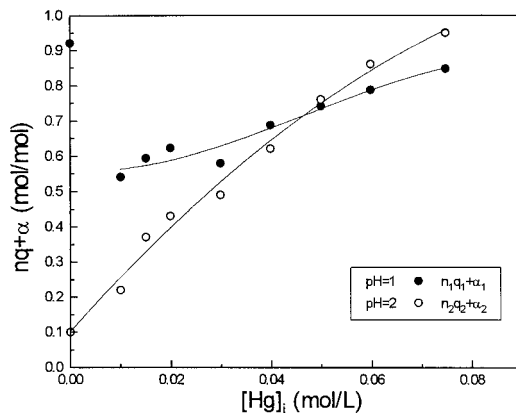
pH = 1 or 2, the occupancy number tends to 1 for large degrees of Hg(II) binding (Fig. 5). For example, when the initial pH is 2 and the initial concentration of mercury is 15,000 ppm, only 5% of the imidazole rings are free. For initial pH = 1, larger initial concentratios of Hg(II) are needed to reach occupancy numbers so close to 100%.

To analyze the mechanism of Hg(II) caption by PVI hydrogels, swelling capacity and T_g of loaded and clean hydrogel samples were compared. Table IV shows that the counterion effect on swelling is quite significant at initial pH = 2, both in loaded and unloaded gels. Swelling in acid solutions increases appreciably with respect to that in pure water, but the increment is smaller for sulfuric than for HCl solutions, and Hg(II) uptake decreases slightly swelling with respect to cation free acid solutions in both cases. PVI swells more in acid solutions than in pure water because of the repulsive interactions between neighbor protonated rings.[12] In acid solutions with sulfuric acid, swelling is smaller than for HCl because of

Table IV   Swelling Characteristics (S) of Clean and Loaded PVI Hydrogel as a Function of the Loading Conditions: Type of Acid and Initial pH and Initial Concentration of Hg(II)

Acid	pH_i	$[Hg(II)]_i$ (ppm)	S (g/g)
HCl	2	—	13.38
HCl	2	1000	12.68
H_2SO_4	2	—	9.70
H_2SO_4	2	1000	9.52
—	—	—	4.32[a]

[a] It was determined in distilled water.
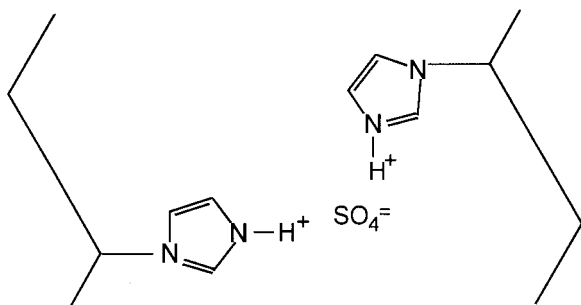
Scheme 3   Ionic interactions between neighbor protonated rings and sulfate counteranions.

the divalent character of sulfuric acid anions, which cause an apparent increase in the crosslinking degree of the hydrogel (Scheme 3). The effect of Hg(II) uptake is similar to that of sulfuric anions; being divalent, they increase the effective crosslinking degree (see Scheme 2) and decrease swelling.

Tanaka et al.[14] reported the collapse of poly-(acrylamide-*co*-acrylic acid) hydrogel by caption of Cu(II) in solution, whereas such effect is not observed for Ni(II). This decrease of the volume is explained by formation of stable complexes, which behave as ionic crosslinks. For PVI–Hg, there is neither a collapse nor a large decrease of swelling because the amount of uptaken mercury ions is small, and because the coordination index is smaller than 2, the efficiency in forming ionic crosslinks is small (see Scheme 2).

The T_g dependence on Hg(II) uptake supports the previous interpretation of bonded Hg(II) as ionic crosslinker. Figure 6 shows T_g of loaded PVI samples as a function of q. For $q > 0.1$, T_g increases, and therefore, the rigidity of the system
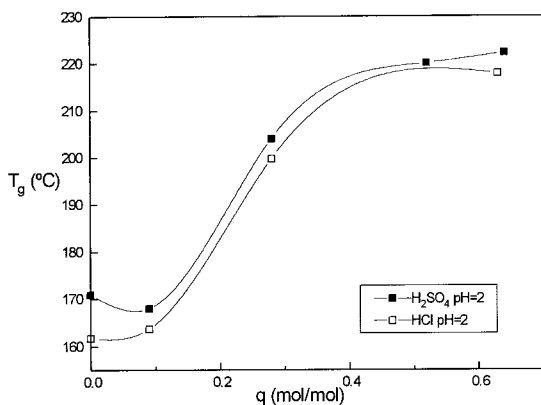

Figure 6   Glass transition temperatures of PVI as a function of the Hg(II) binding q.
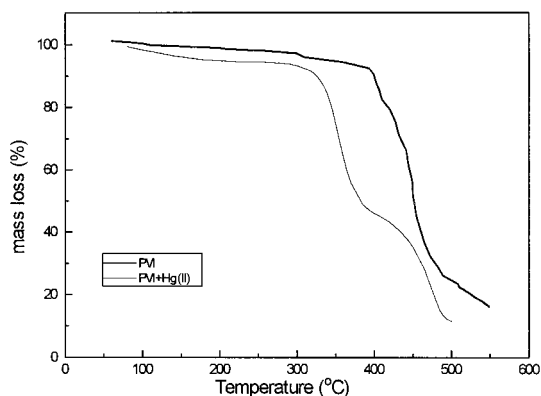

Figure 7   Thermogravimetric traces of clean PVI and Hg(II)-loaded PVI.

increases also. Sulfuric counterion has an additive effect shifting up the T_g vs. q curve with respect to HCl.

The T_g of PVI is 179.8°C. A slight decrease of T_g with respect to that value was observed for small amounts of bonded Hg(II) (0.09 mol of Hg(II)/mol of dry hydrogel). It is similar to that produced by small degrees of protonation and, therefore, it seems that the additional crosslinking by the incorporation of mercury ions is negligible. But, when the incorporation of Hg(II) is larger than 0.2 mol/mol dry hydrogel, T_g increases. This must be attributed to the role of Hg(II) bonded to two nonneighbor imidazole groups (see Scheme 2). Such complexes are ionic crosslinkers,[15] which increase the rigidity of the system.

FTIR spectra with and without loading are essentially the same, in particular in the region of $400–700 \text{ cm}^{-1}$. TGA analysis reveals the intimate imidazole-Hg(II) interaction (see Fig. 7), which causes the thermal instability of loaded gels with respect to clean PVI. Nevertheless, loading causes no important morphological changes as shown in scanning electron micrographs (see Fig. 8).

Recovering of PVI Hydrogels

Elution (82%) of Hg(II) from the bonded state in PVI hydrogel particles was achieved with 0.5–4 M HNO$_3$ aqueous solutions. With a hydrogel effective concentration equal to 0.1 g of dry gel per liter of solution and an acid concentration equal to 1 M, more than 80% of Hg(II) loading PVI was recovered. Figure 9 shows the retention–elution cycles. After four cycles, the retention of mercury ions decreases from 96.8 to 69.6%. In the first step
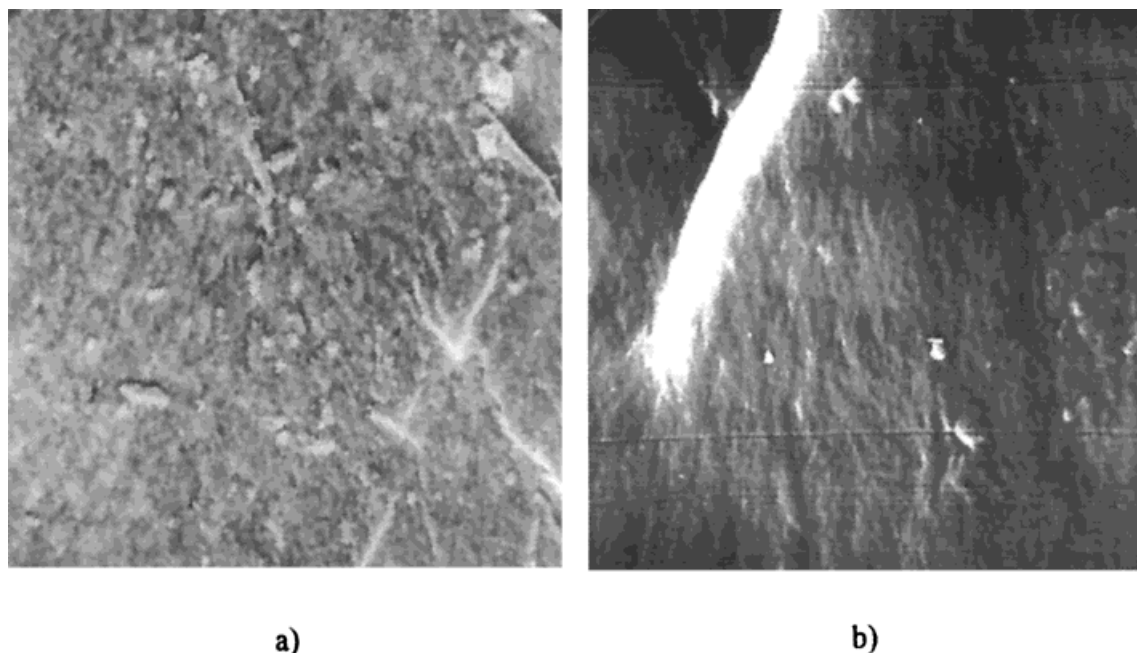
a)   b)

Figure 8   Scanning electron micrographs of (a) PVI hydrogel (400×) and (b) Hg(II) loaded PVI (400×).

of the first cycle the hydrogel is protonated; the pH increases from 2.0 to 2.3 ($\alpha = 0.04$), and in the elution the protons substitute completely to the Hg(II) yielding a protonation degree close to 1.0.

CONCLUSIONS

The vinyl imidazole groups showed a high affinity to mercury cations. At pH 2.0 practically total
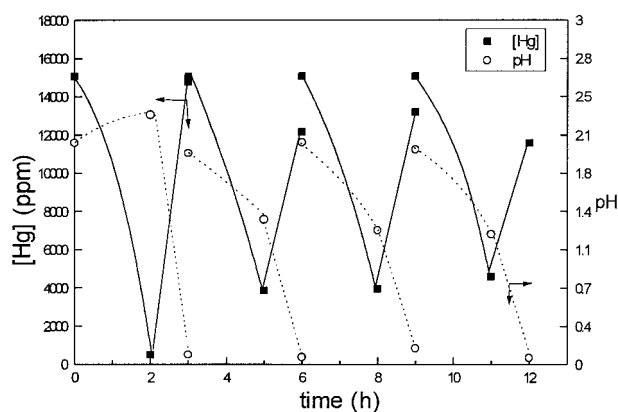

Figure 9   Loading–elution cycles of mercury ions on PVI hydrogel. Effective concentration of PVI 10 g/L, particle size: 0.125–0.100 mm; initial pH = 2; [Hg(II)] = 15 g/L; eluent: 1 M HNO$_3$; contact time: 1 h.

removal of Hg(II) was achieved. It was founded that for each three ligands there are two mercury cations. Therefore, if there are six cations there will be nine bonded ligands. An effect of the acid medium on the hydrogel swelling was also observed. In sulfuric acid, swelling was smaller than that HCl because the divalent character of sulfuric acid anions that causes an apparent increase in the crosslinking degree of the hydrogel. The effect of the Hg(II) uptake is similar to that of sulfuric anions.

It is possible elute (82%) the mercury ions from the hydrogel by 0.5–4.0 M HNO$_3$ aqueous solution . This behavior decreased after four cycles.

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