

# Metal Ion Binding Properties of Poly(*N*-vinylimidazole) Hydrogels

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**ABSTRACT:** The ability of poly(*N*-vinylimidazole) hydrogels to bind Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), Hg(II), Na(I) and Ca(II) cations, as well as uranyl, vanadium, rhenium, and molybdenum complexes, was studied by a batch equilibrium procedure using atomic absorption spectroscopy and UV-Vis spectrophotometry. The optimum pH for ion adsorption was determined in any case. The influence of the cross-linking degree of the hydrogel on the sorption kinetics and the sorption capacity at equilibrium were also studied. Sorption from the binary mixture Cu(II) + U(VI) was also analyzed at the optimum pH. Elution of the ions adsorbed from single and binary solutions was achieved in all cases. A selective desorption of loaded hydrogels with two types of ions was attained. The general conclusion is that poly(*N*-vinylimidazole) hydrogels are excellent materials for retention of all the ions studied here [except for Pb(II), Na(I), and Ca(II)]. The elution, which can be selective, allows regeneration of the hydrogel. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1109–1118, 1998

**Key words:** hydrogels; poly(*N*-vinylimidazole); metal ions; retention properties

## INTRODUCTION

Several decades ago, it was found<sup>1–3</sup> that binding sites for combination of some proteins with metals were the imidazole groups of histidine. This discovery was the driving force for further studies on the ion binding capacity of imidazole<sup>4</sup> (Im) and soluble poly(*N*-vinylimidazole) (sPVI).

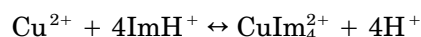
Continuous variation analysis of the complex sPVI-Cu(II) showed<sup>5</sup> a preferred coordination number (*N*) of four. Ion binding equilibrium constants ( $K_4$ ) for the reaction



were found to be in the range  $10^{11}$ – $10^{15}$  mol<sup>-4</sup> L<sup>4</sup>, depending on the ionic strength and polymer concentration. Some smaller  $K_N$  values were observed for other complexes: for Im-Ag,<sup>6</sup>  $K_2 = 10^7$  mol<sup>-2</sup> L<sup>2</sup>; for sPVI-Ag,<sup>7</sup>  $K_2 = 10^8$  mol<sup>-2</sup> L<sup>2</sup>; for Im-Zn,<sup>8</sup>  $K_4 = 10^2$  mol<sup>-4</sup> L<sup>4</sup>; and for sPVI-Zn,<sup>8</sup>  $K_4 = 10^3$  mol<sup>-4</sup> L<sup>4</sup>.

sPVI and Im show the same coordination number with several ions: *N* = 4 with Cu(II) and Zn(II),<sup>5</sup> *N* = 6 with Cd(II)<sup>3</sup> and *N* = 2 with Ag(I).<sup>6</sup> Some other *N* values<sup>7</sup> have been proposed for Im with the same or similar ions, depending on the counterions.

Equilibrium constants ( $B_4$ ) for the displacement reaction



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were found to be<sup>4</sup> larger for sPVI ( $10^{-7}$ ) than for the monomeric analog Im ( $10^{-16}$ ) and, as expected, much smaller than  $K_4$  in both cases (see above). For the complex sPVI–Ag,  $B_2$  is  $\sim 10^{-2}$  whereas it is  $\sim 10^{-7}$  for Im–Ag.<sup>6</sup>

Recently, considerable interest in studying polymer–metal ion complexes was generated, regarding the potential for using polymer systems as a method of treating metal-polluted surface waters. Most of the systems employed<sup>9–21</sup> are resins, i.e., crosslinked polymers with swelling degrees around (or less than) 1 gram of water per gram of dry resin. Hydrogels<sup>22,23</sup> are less known materials, qualitatively the same than resins (crosslinked polymers) but having larger swelling degrees, typically  $\sim 10$  grams of water per gram of dry gel.

The goal of this article is to analyze the applicability of poly(*N*-vinylimidazole) hydrogels (hPVI) to metal cation binding from aqueous solutions and to study the possibility of regenerating the hydrogel by cation elution.

## EXPERIMENTAL

### Preparation of Hydrogels

hPVI were synthesized by radical crosslinking polymerization of *N*-vinylimidazole (VIm) and *N,N'*-methylenebisacrylamide (BA) in aqueous solution, with AIBN ( $6 \times 10^{-3} M$ ) as initiator.<sup>24</sup>

VIm (purchased from Aldrich, Milwaukee, WI), was distilled under reduced pressure at 55°C just prior use. Water was distilled and purified by a Milli-Q system from Millipore. BA (from Aldrich) and AIBN (from Fluka) were high quality products, used as received.

The aqueous solution of VIm, BA, and AIBN was sonicated at 60°C during 10 min and then it was immersed in a bath at 90°C for 2 h. The hydrogels were taken out of molds and they were cut in pellets of the desired shape and size, or they were crushed in small particles of polydisperse size distribution. The hydrogel was then washed repeatedly with Milli-Q water for  $\sim 1$  week; water was spectrophotometrically analyzed to detect the end of the extraction of soluble material, in particular, of residual VIm. Clean hydrogels were dried in oven at 80°C for 24 h. The crushed portion was ground and the fractions of 180 to 250  $\mu m$  and 1.25 to 1.00 mm size were selected for this work; the first one was employed

**Table I Characteristics of the Hydrogels Employed**

Sample	$T_g$ (°C)	$S$ (g/g)	$F_N$ (%)
G40 (2)	186.6	4.32	0.15
G40 (4)	—	3.26	0.40
G40 (15)	185.9	1.76	3.04

Glass transition temperature ( $T_g$ ), swelling ability in grams of water per gram of dry gel ( $S$ ), and molar fraction of crosslinks ( $F_N$ ) determined in the final hydrogel by swelling measurements in methanol.

in most cases and the second one only when indicated.

The total monomer concentration  $C_T$  (in g/100 mL) and the crosslinking ratio  $C$  (in w/w % of BA) in the monomer feeding mixture determine the optical, thermal, and swelling properties of the final hydrogel. In the following, any sample will be denoted by the symbol  $GC_T(C)$ : for example, G40(2) represents a hydrogel obtained with a feeding mixture composition of 40 g/100 mL total monomer concentration and 2% w/w BA in the mixture of BA and VIm.

### Characterization of Hydrogels

Characterization of hydrogels was performed by DSC, TGA, SEM, FTIR, turbidimetric, and swelling measurements.<sup>25</sup> Table I shows the glass transition temperature,  $T_g$ , the swelling degree,  $S$ , in pure water, and the molar fraction of BA incorporated to the hydrogel in effective knots,  $F_N$ , determined through swelling measurements in methanol.

Swelling measurements were performed with cylindrical hydrogel pellets 1 mm thick and with a 10-mm diameter. Dry pellets were immersed into the swelling solvent (water or methanol) for  $\sim 1$  week. Once they have reached a constant weight, ( $m_h$ ),  $S$  is calculated as

$$S = \frac{m_h - m_o}{m_o}$$

where  $m_o$  is the weight of the dry pellet.

$S$  values determined in methanol, together with the interaction parameter PVI-methanol at 20°C,  $\chi = 0.472$  (calculated from data in ref. 26), allow calculation of the molecular weight between knots of the network ( $M_c$ ).<sup>27</sup>  $F_N$  is then calculated as

$$F_N = \frac{1}{2(M_c/M_0) + 1}$$

where  $M_0$  represents the molecular weight of VIm.

Gel effective concentration ( $C_{\text{eff}}$ ) was determined as the number of hPVI base-mol divided by the volume of the solution in which they were immersed.

### Sorption and Elution of Single-Metal Ions

Several magnitudes have been employed to characterize the adsorption of ions by polymers. Here we will employ two, the distribution coefficient ( $K_d$ )

$$K_d = \frac{\text{amount of metal ion in the hydrogel}}{\text{amount of metal ion in solution}} \times \frac{\text{volume of solution (mL)}}{\text{weight of dry hydrogel (g)}}$$

and the retention capacity ( $q$ )

$$q = \frac{\text{amount of metal ion in the hydrogel (meq)}}{\text{weight of dry hydrogel (g)}}$$

They depend on the nature of the ion, on the pH of the ion solution, on the contact polymer-solution time, and on the ion concentration. In the following, several experiments will be described. Each one intends to analyze the dependence of  $K_d$  and  $q$  on those variables.

### Retention Capacity in Two Hours ( $q_{2h}$ )

A batch-type equilibrium procedure was used to determine the metal ions adsorbed from solution by the hydrogel at different pH. Metal uptake was determined by shaking 0.1 g of dry gel with 10 mL of an aqueous solution containing 1 g/L (1000 ppm) of the metal ion, for 2 h at room temperature. The metal ions [Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), Ca(II), or Hg(II)] concentration was analyzed in the supernatant solution by atomic absorption spectrophotometry; Na(I) was analyzed by atomic emission spectrophotometry and Re(VII), Mo(VI), U(VI), and V(V) by colorimetry.

### Retention Capacity [ $q(c)$ ]

The retention capacity, in equilibrium with a metal ion concentration  $c$ , was determined at pH

= 2 but with 1 g dry gel and 50 mL metal ion solution. Shaking was maintained for 2 h. This process was repeated three times with renewed metal ion solutions of the same concentration and using the same hydrogel. The supernatants were collected together. In the first step, the metal concentration in the supernatant is much smaller than the initial concentration  $c$ , but in the third step, the concentration of the metal ion solution in equilibrium with the loaded hydrogel is about equal to  $c$ . The initial concentration  $c$  was 1000 ppm, and since this concentration is very large,  $q(c)$  reaches values close to the retention capacity at saturation ( $q_S$ ).

### Retention Capacity at Saturation ( $q_S$ )

0.1 g of dry hydrogel was contacted with 10 mL of an aqueous solution of Hg(II), Cd(II), Pb(II), Cu(II), or U(VI) at pH = 2. Five initial metal ion concentrations were used: 0.5, 1, 2, 3, and 4 g/L. Three samples of each metal ion concentration (and for each metal ion) were prepared and each of them was placed in a thermostatically controlled bath at 20, 40, or 60°C for 72 h. The metal ion concentration at equilibrium,  $c_e$ , was determined in the supernatants. Hg(II) concentrations  $c_e$  were so small (<10 ppm) that a hydride generator was necessary to analyze it. The retention capacity  $q(c_e)$  was determined by comparing  $c$  and  $c_e$  and  $q_S$  with the Langmuir's adsorption isotherm model.

### Elution Assays

Elution assays were carried out with the hydrogels loaded at equilibrium with 1000 ppm metal ion concentration. 0.1 g of dry gel loaded with any of the different metals was contacted with 10 mL of acid or sodium carbonate solutions at different concentrations. The mixture was stirred for 1 h. The hydrogel was separated by filtration and the metals were analyzed in the filtrate solution as in the previous section. The percentage of the metal eluted was calculated by comparing the amount of metal initially loading the gel and the amount of metal in the final supernatant.

### Sorption and Desorption Behavior from Cu(II) – U(VI) Binary Ion Mixture

10 mL of an aqueous solution containing 0.5 g/L of each metal ion at pH = 2 were contacted for 2

**Table II** Retention of Several Cations,  $q_{2h}$ , (mEq g<sup>-1</sup>) as a Function of pH

Cation	Counterion	Initial pH								
		0	1	2	3	4	5	6	8	10
Cu(II)	Cl <sup>-</sup>	—	0.44	2.27	2.23	2.27	2.86			
Co(II)	Cl <sup>-</sup>	—	0.33	1.98	0.58	0.61	0.41			
Ni(II)	Cl <sup>-</sup>	—	0.60	2.11	0.61	0.60	0.82			
Cd(II)	Cl <sup>-</sup>	0.16	0.12	1.49	0.98	0.93	1.05			
Zn(II)	Cl <sup>-</sup>	0.12	1.84	1.65	0.52	0.76	0.49			
Pb(II)	CH <sub>3</sub> —COO <sup>-</sup>	0.04	0.05	0.14	0.10	0.14	0.18			
Hg(II)	Cl <sup>-</sup>	0.65	0.84	0.80	0.91					
Re(VII)	ReO <sub>4</sub> <sup>-</sup> NH <sub>4</sub> <sup>+</sup>	0.90	1.35	2.63	0.90	0.94		0.45	0.71	0.49
Mo(VI)	HMoO <sub>4</sub> <sup>-</sup> Na <sup>+</sup>	4.25	6.82	5.69	3.50	2.56	2.25	3.69	3.31	2.75
U(VI)	SO <sub>4</sub> <sup>2-</sup> UO <sub>2</sub> <sup>2+</sup>	0.96	2.36	2.52	2.47	2.49	2.57	2.57	1.30	0.73
V(V)	SO <sub>4</sub> <sup>2-</sup> VO <sub>2</sub> <sup>2+</sup>	2.33	4.18	8.85	7.68	7.09	6.64	5.73	6.51	2.33
Na(I)	Cl <sup>-</sup>	—	—	0	0	0	0			
Ca(II)	Cl <sup>-</sup>	—	—	0	0	0	0			

Gel effective concentration,  $C_{eff}$ , = 0.1M. Size of dry gel particles  $0.250 > x > 0.180$  mm. Metal ion concentration in the feeding solution: 1000 ppm.

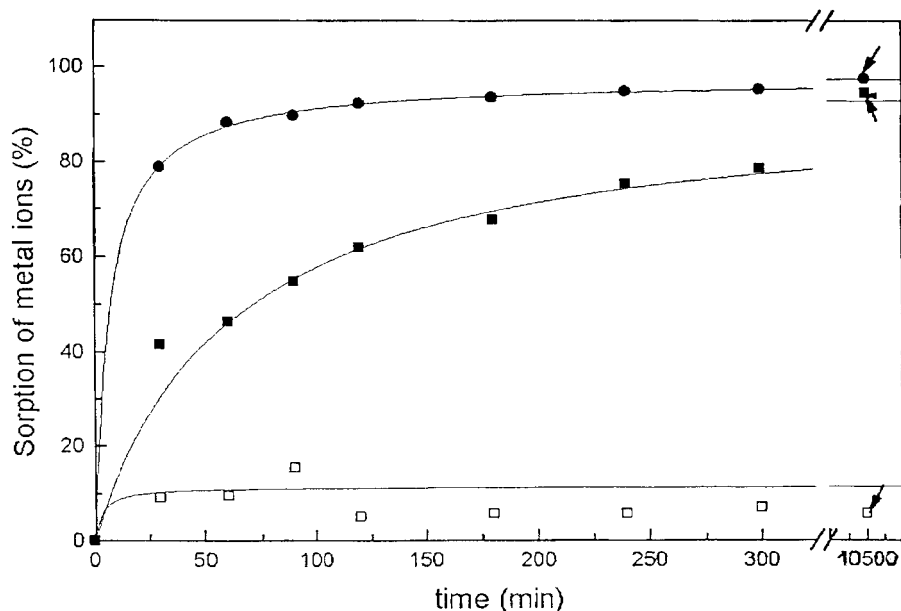
h with 0.5 g of dry hydrogel. Both metal ions were analyzed in the filtrates and  $q_{2h}$  was calculated.

The hydrogel loaded with two metal ions was dried in a stove at 70°C for three days. The ions were eluted by shaking a 0.1 g sample with 10 mL of H<sub>2</sub>SO<sub>4</sub> 0.1M or 10 mL of Na<sub>2</sub>CO<sub>3</sub> 1M. The hydrogel was separated by filtration and copper

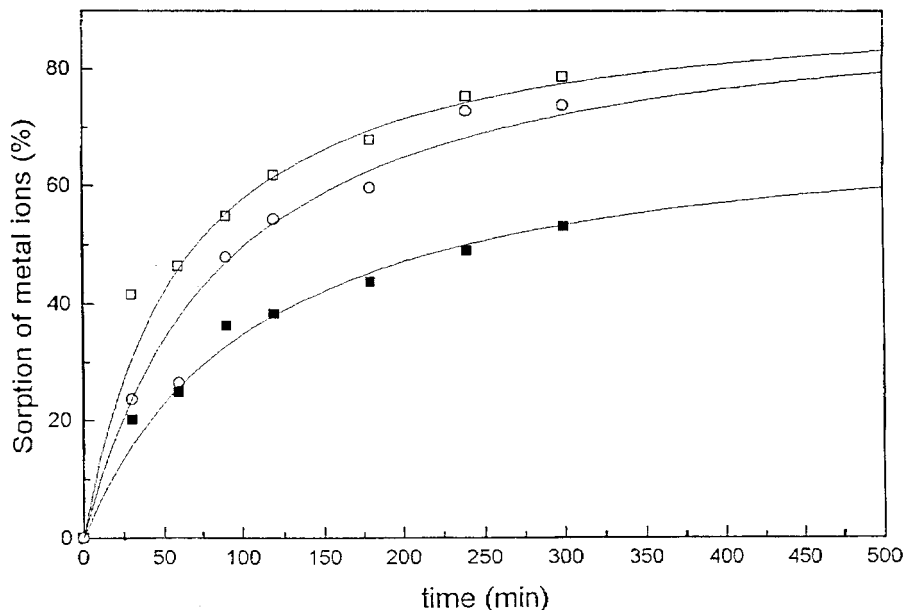
and uranium were analyzed in the supernatants by atomic absorption spectrophotometry and colorimetry, respectively.

#### Sorption Kinetics

Three hydrogels with different crosslinking degrees, G40(2), G40(4), and G40(15) were used.



**Figure 1** Binding of Cd(II) (—●—), Cu(II) (—■—), and Pb(II) (—□—) by G40(2) as a function of time. The arrows indicate the retention after 1 week. Gel effective concentration: 0.1M. Temperature ~ 20°C and pH = 2. Cation concentrations: 1050, 950, and 800 ppm, respectively.



**Figure 2** Kinetics of Cu(II) binding by the hydrogels (hPVI) G40(2) (— □ —), G40(4) (— ○ —), and G40(15) (— ■ —). Experimental conditions: Gel effective concentration 0.1M, temperature  $\sim 20^{\circ}\text{C}$ , pH = 2, and cation concentration 950 ppm.

1 g of dry hydrogel was stirred with 100 mL of 1 g/L metal ion solution. During the first 2 h, an aliquot of the supernatant was taken out every 30 min; after this time, the aliquots were taken each hour. The supernatant was analyzed after two days to complete the kinetics. In these experiments,  $c$  is constant and  $q(t)$  is therefore calculated.

### Instruments

Three different atomic absorption spectrophotometers were used in determining cation concentrations: Perkin–Elmer 306, Termo Jarrell Ash

Video 11E, and 2380 Perkin–Elmer connected with a hydride generator system.

The content of U(VI), Re(VII), Mo(VI), and V(V) was spectrophotometrically determined on CADAS 100 or Shimadzu UV-2101PC UV-V spectrophotometers.

The thermal behavior was studied with a Mettler DSC 30 at  $10\text{ K min}^{-1}$  heating rate in nitrogen atmosphere.

**Table III** Diffusional Exponent  $n$  and Diffusional Constant  $k$  for Cu(II) in Poly(*N*-vinylimidazole) Hydrogels of Three Different Crosslinking Degrees at  $20^{\circ}\text{C}$

Gel	Cation	$n$	$k$	$r^2$
G40(2)	Cu(II)	0.30	0.16	0.99
G40(4)	Cu(II)	0.55	0.040	0.96
G40(15)	Cu(II)	0.43	0.055	0.98
G40(2)	Cd(II)	0.078	0.64	0.98
G40(4)	Cd(II)	0.16	0.40	0.95
G40(15)	Cd(II)	0.25	0.21	0.96

Particle size was  $0.250 > x > 0.160$  mm.

## RESULTS AND DISCUSSION

The adsorption of cations by resins is strongly dependent on pH<sup>12,13</sup> and that is also the case for PVI hydrogels. Table II summarizes the results on metal ion binding by hPVI at different pH values. The optimum pH is 2, since the maximum cation retention in 2 h corresponds to about that pH value in almost any case. Metal ions such as Hg(II), Zn(II), and Mo(VI) present larger retentions at other pH values but the difference with the retention at pH = 2 is small, about equal to the experimental error. In order to use the same pH value in any experiment, pH = 2 will also be employed in any case. The optimum pH depends on the hydrogel and in general, also on the cation; some of the cations here studied have different optimum pH values in other polymer systems.<sup>10,21,28,29</sup>

**Table IV Retention Capacity,  $q(c)$ , of Several Metal Ions by Three Types of Gel**

Cation	Counterion	Gel	$q(c)$ (mEq g <sup>-1</sup> )	$K_d$ (10 <sup>2</sup> mL g <sup>-1</sup> )
Cu(II)	SO <sub>4</sub> <sup>2-</sup>	G40(2)	3.43	5.2
	Cl <sup>-</sup>	G40(2)	3.37	3.6
	Cl <sup>-</sup>	G40(4)	3.76	5.5
	Cl <sup>-</sup>	G40(15)	1.86	1.0
Ni(II)	Cl <sup>-</sup>	G40(2)	2.75	1.8
Co(II)	Cl <sup>-</sup>	G40(2)	3.16	2.1
Cd(II)	Cl <sup>-</sup>	G40(2)	2.45	10.6
	Cl <sup>-</sup>	G40(4)	2.54	15.0
	Cl <sup>-</sup>	G40(15)	1.98	3.6
Zn(II)	Cl <sup>-</sup>	G40(2)	3.33	7.8
Hg(II)	Cl <sup>-</sup>	G40(2)	1.38	33
Pb(II)	CH <sub>3</sub> —COO <sup>-</sup>	G40(2)	0.20	0.37
	CH <sub>3</sub> —COO <sup>-</sup>	G40(4)	0.28	0.47
	CH <sub>3</sub> —COO <sup>-</sup>	G40(15)	0.19	0.29
V(V)	SO <sub>4</sub> <sup>2-</sup> VO <sub>2</sub> <sup>2+</sup>	G40(2)	13.3	337
Mo(VI)	MoO <sub>4</sub> <sup>-</sup> Na <sup>+</sup>	G40(2)	9.75	13.6
U(VI)	SO <sub>4</sub> <sup>2-</sup> UO <sub>2</sub> <sup>2+</sup>	G40(2)	3.23	7.1
Re(VII)	ReO <sub>4</sub> <sup>-</sup> NH <sub>4</sub> <sup>+</sup>	G40(2)	3.36	3.8

Values taken after 6 h, at room temperature, pH = 2, in mEq/g of dry gel, and distribution coefficient ( $K_d$ ) in mL/g of dry gel. Gel effective concentration: 0.2M.

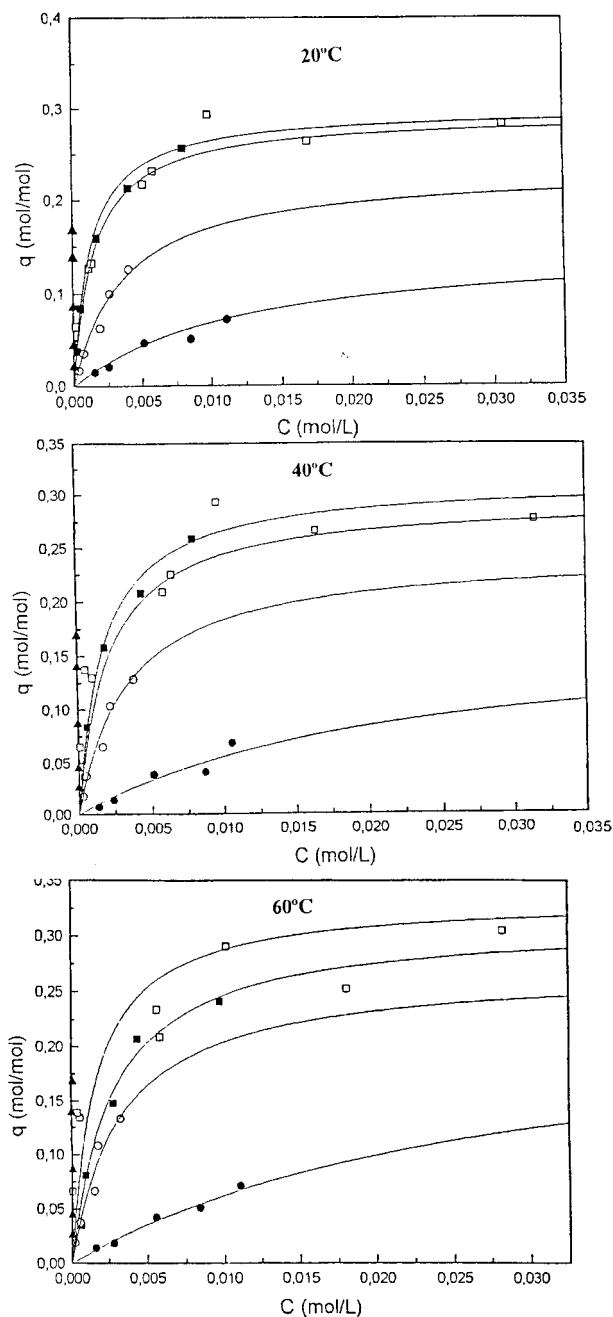
The interaction between the hydrogel and the different metal ions occurs basically through the nitrogen atoms coming from the different polymer chains.<sup>9,10</sup> It would be favored by the crosslinked nature of the PVI hydrogel.

In the experimental conditions regarding Table II, there are six ions which are retained up to 80%: Cu(II), Cd(II), Hg(II), Mo(VI), U(VI), and V(V). Only Pb(II) is retained below 50% and Na(I) as well as Ca(II) are not taken up in many

**Table V**

Cation	$T$ (°C)	$K/10^{-3}$ Lmol <sup>-1</sup>	$q_s/\text{mol mol}^{-1}$	$\Delta H/\text{kJ mol}^{-1}$
Cd(II)	20	0.51	0.36	-43.6
	40	0.21	0.54	
	60	0.06	0.99	
Cu(II)	20	2.18	0.23	28.8
	40	3.54	0.23	
	60	8.71	0.22	
Pb(II)	20	0.07	0.15	-7.3
	40	0.06	0.16	
	60	0.05	0.17	
U(VI)	20	0.19	0.29	-20.9
	40	0.18	0.35	
	60	0.51	0.18	

Binding constant ( $K$ ), binding enthalpy ( $\Delta H$ ), and maximum binding capacity ( $q$  in mole of bonded cation per base mol of dry gel) of G40(2) with an effective concentration 0.1M, for several cations and at different temperatures. Equilibration time was achieved after one week. Counterions were acetate for Pb(II) and chloride for the others, pH = 2 in any case. Particle size 0.25 >  $x$  > 0.16 mm.



**Figure 3** Adsorption isotherms of Pb(II) (—●—), Cu(II) (—□—), Cd(II) (—■—), U(VI) (—○—), and Hg(II) (—▲—) by the hydrogel G40(2) at pH = 2 and at 20, 40, and 60°C. The curve represents the best fit to the Langmuir equation. Gel effective concentration: 0.1M. Bars represent the 9% estimated error.

different conditions. Nevertheless, although  $q_{2h}$  is largest for V(V), it cannot be concluded that it is the metal better adsorbed by the hydrogel, since  $q_{2h}$  depends on the diffusion coefficients through the hydrogel and also on the retention capacity at

equilibrium for the given metal ion concentration 1000 ppm (see Table II).

The metal ion adsorption capacity  $q(c, t)$  increases with the time ( $t$ ) during the first 2 or 3 h and then levels off toward the equilibrium adsorption capacity  $q(c_e)$  (see Fig. 1). In Figure 2 the metal ion binding in three hydrogels with different crosslinking degrees is plotted using the following equation<sup>30</sup>

$$\frac{q(c, t)}{q(c_e)} = kt^n$$

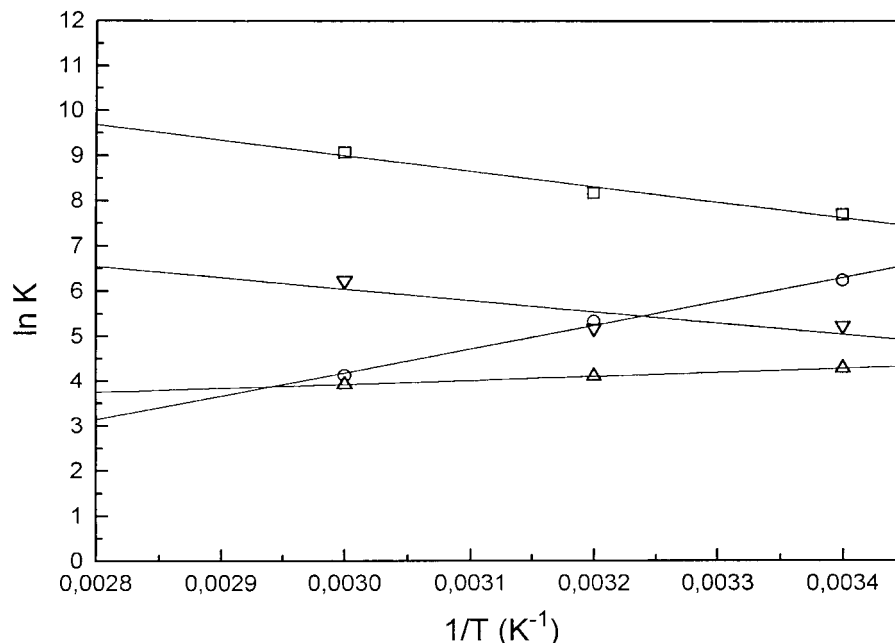
where  $k$  and  $n$  are constants. The values of the diffusional exponent  $n$  is equal to 0.5 for Fickian diffusion mechanism, while  $n = 1$  indicates a case II diffusional mechanism. For  $0.5 < n < 1.0$ , the diffusional mechanism is non-Fickian, and both diffusion and polymer relaxation control the metal ion uptake.<sup>30</sup> Table III summarizes the  $n$  and  $k$  values calculated for Cu(II) and Cd(II) with the three hydrogels, together with lineal correlation parameters ( $r^2$ ) for Figure 2-type plots. It is noteworthy that  $n$  is smaller than 0.5, in particular for the hydrogels with the smaller crosslinking ratio.

Cation binding is so fast that the measurements made a few minutes after putting in contact the hydrogel with the cationic solution are already close to saturation, and therefore time dependence is very low, close to zero. For example, Cd(II) binding, which is 0.078 and lower than the other metal ions.

As expected, for a given cation, i.e., Cu(II), the diffusion is faster for the gel with smaller  $F_N$  but comparing the size of the three cations considered in Figure 1, it is clear that the adsorption is not a diffusion-controlled process since the diffusion seems to be faster for Cd(II) than for Cu(II), being the second one lighter and smaller. The diffusion of Pb(II) is much slower for two reasons: it is a heavy cation of large size and its binding constant is lower than those for Cd(II) and Cu(II).

Table IV summarizes the retention capacity at equilibrium with 1000 ppm metal ion concentration at pH = 2 as a function of the gel crosslinking degree. The large values of the distribution coefficient,  $K_d$ , must be noticed. On the other hand, the concentration of Hg(II) inside the gel may be even 3300-fold the concentration in the supernatant in equilibrium with loaded hydrogel.

Langmuir's adsorption isotherm model was



**Figure 4** Temperature dependence of the binding constant by the hydrogel G40(2). Cu(II) (— □ —), Cd(II) (— ○ —), Pb(II) (— ● —), and U(VI) (— ▽ —). Gel effective concentration: 0.1M and pH = 2.

used to analyze concentration dependence of the metal ion retention.<sup>11,31,32</sup> The Langmuir equation

$$\frac{1}{q(c)} = \frac{1}{Kq_s C} + \frac{1}{q_s}$$

allows determination of two parameters which represent a measurement of the gel binding capacity for a given cation ( $K$ , the equilibrium binding constant), and the cation adsorption at saturation of the binding sites in the hydrogel ( $q_s$ ). The  $K$  and  $q_s$  values obtained for Cu(II), Cd(II), Pb(II), and U(VI) are shown in Table V and have been calculated from the slope and intercept of a lineal plot of  $q(c)^{-1}$  versus  $C^{-1}$ , the metal concentration in dissolution at equilibrium. The values for Hg(II) are not represented because the metal ion sorption at any concentration and temperature was close to 100%.

Binding constants  $K$  are in the same range as synthetic resins<sup>8</sup> or naturally occurring systems.<sup>31,32</sup>

Temperature does also influence the adsorption of cations, as shown in Figure 3 and Table V. From Figure 4 type plots it is possible to determine the binding enthalpy change,  $\Delta H$ , which is the energy balance of changes in imidazole solvation by water and cation uptake, calculated by using the Clapeyron equation.

In order to recover the hydrogel depending on the cations of sulfuric acid, hydrochloric acid, nitric acid, perchloric acid, and sodium carbonate at different concentrations were added to the cation-loaded gel. Table VI compiles these results.

In general, increasing the concentration of eluent increased the recovery of the hydrogel.  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$  are better eluted in acid medium than basic, but not uranium, which in  $\text{Na}_2\text{CO}_3$  solution probably a  $[\text{UO}_2(\text{CO}_3)_3]$  complex is formed.

Sorption study of uranium from U(VI)–Cu(II) cation mixture was carried out by determining the concentrations of the two cations in the aqueous phase (see Table VII). Both cations are sorbed but it is possible to get a selective elution varying the medium, as U(VI) forms a more stable complex with  $\text{Na}_2\text{CO}_3$  than Cu(II).

## CONCLUSIONS

The binding ability of the hydrogels depends on the crosslinking degree, i.e., Cu(II) was adsorbed faster for the G40(2) than that G40(15). The sorption process is not a diffusion-controlled process because the diffusion for Cd(II) is faster than that of Cu(II), being the last cation smaller and



**Table VI Recovery of Metal Ions From G40(2) Samples**

Cation	Eluent					
	H <sub>2</sub> SO <sub>4</sub>			Na <sub>2</sub> CO <sub>3</sub>		
	0.01M	0.1M	1M	0.25M	0.5M	1M
Cu(II)	4.5	71.6	76.1	0.1	0.2	0.6
U(VI)	13.3	4.8	21.9	15.6	81.3	80.5
Cation	HCl			Na <sub>2</sub> CO <sub>3</sub>		
	0.01M	0.1M	1M	0.25M	0.5M	1M
	Cd(II)	7.9	70.9	85.1	0.0	0.03
Zn(II)	10.8	72.5	81.7	0.3	0.6	3.3
Ni(II)	1.1	63.0	74.1	0.1	0.1	0.1
Co(II)	29.5	65.6	69.9	0.1	0.1	0.2
Cation	H <sub>2</sub> SO <sub>4</sub>			HClO <sub>4</sub>		
	0.01M	0.1M	1M	0.01M	0.1M	1M
	Mo(VI)	0.9	2.3	31.4	0.0	4.3
V(V)	7.3	7.3	8.9	0.0	0.0	20.7
Re(VII)	9.4	60.6	76.8	14.4	35.7	83.3
Cation	HCl			HNO <sub>3</sub>		
	0.1M	1M	4M	0.5M	1M	4M
	Hg(II)	3.6	5.0	21.4	64.3	81.6

Samples were loaded with 1000 ppm cation solutions to their maximum capacity, expressed as w/w %, with different eluents at different concentrations. Gel effective concentration: 0.1M. Temperature ~20°C.

lighter than Cd(II). The adsorption of cations depended on the solution pH and concentration of the cation as well as the time of the cation-hydrogel equilibrium.

Almost of the cations were best eluted in acid medium except uranium, which forms a more stable complex with sodium carbonate.

**Table VII Sorption Ability ( $q_{2h}$ ) and Recovery of the Hydrogel**

Cation	Cu(II)	U(VI)
Cu(II) + U(VI)	96.8	98.1
Cation	Eluent	
	H <sub>2</sub> SO <sub>4</sub> 0.1M	Na <sub>2</sub> CO <sub>3</sub> 1M
	Cu(II)	69.0
U(VI)	9.8	88.2

Performed with 0.1M H<sub>2</sub>SO<sub>4</sub> and 1M Na<sub>2</sub>SO<sub>4</sub>, of Cu(II) and U(VI) considering single and binary solutions, expressed in w/w %. Concentration of each metal: 500 ppm.

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