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ABSORPTION OF METAL IONS AND SWELLING PROPERTIES OF POLY(ACRYLIC ACID-CO-ITACONIC ACID) HYDROGELS

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ABSTRACT

Hydrogels of acrylic acid and itaconic acid has been synthesized with different monomers ratios. The swelling process of the different xerogels immersed in water and salt solutions has been studied. The swelling of hydrogels loaded with metal cations (Cu^{2+} , Zn^{2+}) was also investigated. The swelling process was monitored by the increase in the weight of hydrogel as a function of time. The absorption properties of metal ions were studied by using the hydrogel, and different concentrations of copper and zinc solutions (prepared from sulphate salts). The influence of pH on the absorption process was studied. For the absorption of metal ions, the amount of ions absorbed within the hydrogel can be calculated from the initial and equilibrium concentrations of the metal ions in aqueous phase, the weight of the hydrogel, and the volume of solution used. Metal absorption increased when pH, salt concentration in external solution and itaconic acid content is levelled.

The swelling isotherms which consisted of an initial fast increase levelled off asymptotically to the equilibrium swelling limit. The experimental data clearly suggest that our hydrogels follow a second-order kinetics for both cases (unload and metal loaded). The kinetics rate constant and the equilibrium water content, K , have been calculated for every monomer ratio from the experimental data according to the kinetics equation. Both magnitudes decreased as the itaconic acid content decreases in the xerogels.

Key Words: Metal ions; Hydrogels; Swelling properties.

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INTRODUCTION

Polyelectrolyte hydrogels have been attracting much attention as functional polymers that possess properties of water absorption. At the same time, these hydrogels have been expected to find use as functional polymers.

When a polymeric network is immersed in an appropriate solvent, it swells. The hydration power or water absorption is one of the most important factors, which is determined by the functionality and quality of the hydrogel, moreover the majority of properties are directly influenced by this one. The behavior of highly swollen hydrogels is therefore a function of the network characteristics.

The polyelectrolyte hydrogels can be applied to the recovery of precious metal, removal of toxic or radioactive elements from various effluents, and to metal preconcentration for environmental sample analysis [1–5].

It has been shown that metal absorption is generally limited by metal diffusion inside the hydrogel and the hydrogel-water interfacial area [6]. Coordination resins have been used in metal extractions [7], but they present poor swelling in water, limiting the mobility of the ligands. If we considered this fact, hydrophilic polymeric networks (polyacrylamide, polymethacrylic and polyacrylic acids) will be very advantageous, as they can absorb an amount of water that can be a thousand times the mass of the original dry polymer. This water superabsorbent property has been widely used for pharmaceutical applications and agriculture materials [8–10].

Hydrogel collapse can be achieved in acidic medium allowing the hydrogel regeneration. Fundamental studies about the complexation of metal cations with polyelectrolyte hydrogels, have been carried out and used successfully in the recovery of metal ions [11–14]. Thus, the swelling of a polyelectrolyte network in metal aqueous solution, can be applied to the treatment of diluted aqueous effluents in environmental studies.

The present paper, which deals with the absorption of copper and zinc with a poly(acrylic acid-co-itaconic acid) hydrogel, illustrate this application. The aim of this paper has been the synthesis of several poly(acrylic acid-co-itaconic acid) hydrogels with different composition. Hydrogel composition influence on the swelling behavior has been studied. The swelling kinetics, kinetic order, and rate constants of the polyelectrolyte hydrogel have been determined. The amount of metal was determined in aliquots of metal ion solutions after hydrogel contact (at equilibrium) with the aqueous solutions.

EXPERIMENTAL

Material and Synthesis

Acrylic acid (Fluka) and itaconic acid (Merck), analytical pure grade, were used as monomers. N,N'-methylololacrylamide (Aldrich Chemical) was

employed as a crosslinking agent and 2,2'-azobis (2-amidinopropane) dihydrochloride (V50) (Wako Pure Chemical Industries) as initiator.

Aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ salts (Panreac), pure quality, were used as solvent in the absorption experiment. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is a colored solution which allows solvent penetration inside the hydrogel to be clearly seen. All products were used without further purification.

Preparation of Hydrogel

Hydrogels were prepared by radical copolymerization of acrylic acid (AA) and itaconic acid (IA), at 60°C , for 4 hours in a nitrogen atmosphere, in cylindrical glass tubes. Total monomer concentration in the reaction solution (water) was 25% (2.5 g) in weight. Acrylic acid/itaconic acid ratio in the copolymer hydrogels ranged from 100:0 to 80:20. The initiator and crosslinking agent concentrations were 0.1 and 1% in weight respectively, with respect to the monomers. All solutions were degassed prior to polymerization. The hydrogels were maintained in distilled water during 4 weeks to remove water-soluble material from the samples. FTIR analysis realized at all monomer compositions, indicated the presence of less of 0.2% of residual monomer.

The resultant hydrogels were cut into cylinders and washed in distilled water for removal of unreacted monomers. They were initially dried in air at room temperatures and then under vacuum, at 50°C , for 7 days until a constant weight was reached. The discs were polished to obtain uniform surfaces. The dimensions (9 mm diameter, 1 mm thick, approximately) were determined using a micrometer.

Xerogel samples were swollen to equilibrium, at room temperature, in distilled and deionized water, as well as in metal aqueous solutions to determine the hydration equilibrium degree, H_∞ .

Hydrogel Swelling

The swelling behavior of poly(acrylic acid-co-itaconic acid) hydrogels was followed gravimetrically. A dried disc were immersed in distilled and deionized water and aqueous solutions with varying concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, at 25°C . The discs were weighed before and after contact with aqueous solutions. Swollen hydrogels were removed from the bath at regular intervals, were quickly and carefully dried superficially with filter paper. Measurements were taken until equilibrium was reached. Swelling in salt solutions was performed in a thermostatic vessel, keeping constant stirring.

For the swelling of hydrogels loaded with metal ions (Cu^{2+} and Zn^{2+}) in water, about 0.1 g of hydrogel was introduced into 50 mL of $3.1 \cdot 10^{-2}$ M aqueous metal ion solutions until the equilibrium was reached. Samples were dried to constant weight and swelling in water was studied.

The percentage degree of hydration can be expressed as:

$$H = \left(\frac{m - m_0}{m} \right) \times 100 \quad (1)$$

where m is the mass of the wet sample at time t and m_0 is the weight of the dry sample. The maximum percentage degree of hydration, H_∞ , was considered as the equilibrium percentage degree of hydration.

The volume fraction of polymer within a hydrogel, ϕ_2 , at a particular temperature is:

$$\phi_2 = \left(\frac{D_0}{D} \right)^3 \quad (2)$$

where D_0 and D are the diameters of dry and equilibrium swollen discs, respectively.

Physical Characterization of the Hydrogels

Compression Measurements

A Perkin-Elmer DMA7 Dynamic Mechanical Analyzer with a parallel plate geometry was used for compression stress-strain tests. The hydrogel discs were immersed in deionized water during measurements to minimize water losses. Young's moduli, E , were obtained as the slopes of linear plots of stress τ as a function of strain $(\lambda-1)$. Also the compression modulus, G , and the values of the effective crosslinking density, ν_e , were derived from the slopes of linear plots of the stress, τ , as a function of $(\lambda-\lambda^{-2})$ according to Equation 3 [15] and then the use of Equation 4 [16].

$$\tau = G(\lambda - \lambda^{-2}) \quad (3)$$

$$G = RT\nu_e\phi_2^{-1/3} \quad (4)$$

Here, τ is the applied force per unit area of hydrogel and λ is the ratio of deformed length to undeformed length of hydrogel, RT has its usual meaning. Network parameters for the hydrogels, at 25°C, are presented in Table 1.

Metal Extraction and Analytical Procedure

Absorption experiments with the hydrogel were carried out by placing about 0.1 g of poly(acrylic acid-co-itaconic acid) (80:20) xerogels into 50 mL of different concentrations of metal salts solutions (copper and zinc sulphate, $C(M^{2+})$ from 10^{-5} to 10^{-1} M) and left stirring. After equilibrium was reached, metal inside the hydrogel was determined after back extraction in 0.1 M H_2SO_4 solutions. Aliquots

Table 1. Properties Obtained from Compression-Strain Measurements, at 25°C, for Poly(acrylic acid-co-itaconic acid) Hydrogels, at Different Compositions

Monomer Ratio AA:IA	E (Pa)	G (Pa)	$\phi_2 \cdot 10^2$	$v_e \cdot 10^3$ (mol·L ⁻¹)
100:0	19977	6493	9.08	5.83
95:5	17637	5727	8.14	5.33
90:10	13046	4289	7.46	4.11
85:15	10222	3338	6.90	3.28
80:20	8928	2756	4.85	3.05

of metal ions were withdrawn and analyzed after suitable dilution by atomic absorption using a Perkin Elmer (560) Spectrophotometer.

The dependence of metal uptake on pH and salt concentration of external solution was studied at pH 4.7, 6.0 and 9.0 using buffers solutions of HOAc/NaOAc (pH 4.7) and K₂HPO₄/KH₂PO₄ (pH 6.0). For experiments at pH 9.0 a commercial buffer (Prolabo) was used. Metal absorption was monitored with a digital pH meter using a glass reference electrode.

Uptakes of metal ions onto hydrogel systems can be calculated from the following relation:

$$\text{mg M}^{2+} / \text{g}_{\text{xerogel}} = \frac{C_i - C}{m} \cdot V_t \quad (5)$$

where C_i and C are the initial and the equilibrium concentrations of metal ions in mg·L⁻¹, V_t is the total volume of metal solutions in liters, and m is the mass of the dry polymer in grams.

RESULTS AND DISCUSSION

Hydrogel Swelling in Pure Water: Influence of the Hydrogel Composition

Figure 1 shows the variation of hydration degree as a function of swelling time for hydrogels prepared from copolymers with the composition indicated below.

As shown in Figure 1, the swelling time of treatment increases with an itaconic acid content in the hydrogels (from 0 to 20%). The hydration degree increases sharply at the beginning, reaching more than 400% in the first 100 minutes. At this time, water has already diffused through the whole discs which becomes soft and elastic. Later, swelling increases slowly to reach an asymptote at equilibrium, H_{∞} , (between 990 to 1800% for all compositions analyzed).

The equilibrium hydration degree increases as the content of itaconic acid increases, in agreement with the introduction of more hydrophilic groups. Itaconic Acid has twice the number of carboxyl groups per chain length than acrylic acid. Therefore, the observed behavior is a consequence of the higher number of ioniz-

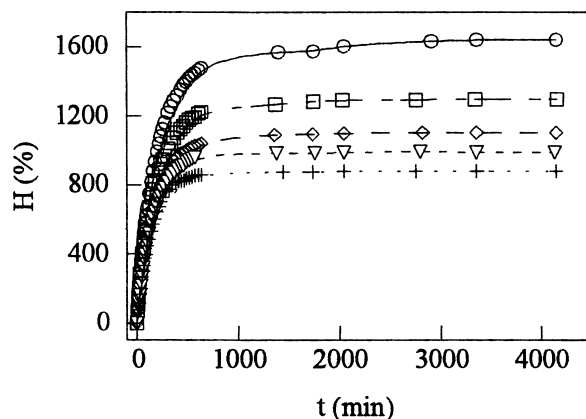


Figure 1. Swelling isotherms of hydrogels prepared from different acrylic acid-itaconic composition: (O) 80:20, (□) 85:15, (◇) 90:10, (▽) 95:5, (+) 100:0.

able groups on the polymer, which enhance repulsive forces of $-\text{COOH}$ groups with the neighboring chains. This electrostatic repulsion is responsible for the network swelling with the expected reduction of the hydrostatic pressure inside of the network. Additionally, as itaconic acid increases in the system, osmotic pressure inside the network is higher resulting in swelling of the hydrogels.

These acrylic acid and itaconic acid networks are held together by hydrogen bonding and other secondary valence forces between adjacent polymer chains. Water swells the polymer networks because it penetrates between the chains and breaks interchain secondary valence bonds by forming hydrogen bonding with carboxyl groups of acrylic acid and itaconic acid. This fact permits the polymer networks to expand in order to accommodate the influx of water through relaxation of the stresses produced by osmotic pressure.

Hydrogel Swelling in Copper Solutions

Hydrogels were repeatedly immersed for two days in fresh solutions with the given salt concentrations until the hydrogel mass ceased to change. Figure 2 shows the maximum and minimum percentage degrees of swelling in water and different concentrations of Cu^{2+} aqueous solution for the fixed composition studied.

Increasing the concentration of copper in the bath solution decreases the percentage degree of swelling. Maximum uptake of copper by the hydrogel is indicated by its intensive green color, which increases when the concentration of the external solution is also increased.

Water diffusion into the hydrogel (swelling), and copper binding to carboxylic groups, which decreases the ionic pressure inside the hydrogel (deswelling), are competitive.

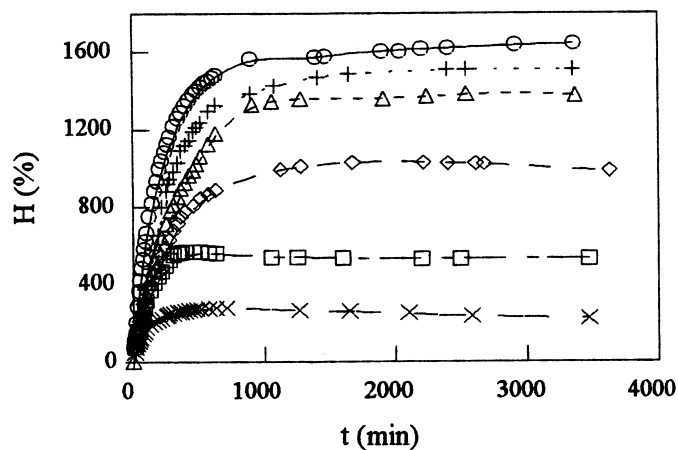


Figure 2. Swelling isotherms of poly(acrylic acid-co-itaconic acid) (80:20) hydrogels: (○) in water, (⊕) 10^{-5} M Cu^{2+} , (∇) 10^{-4} M Cu^{2+} , (◇) 10^{-3} M Cu^{2+} , (□) 10^{-2} M Cu^{2+} , (×) 10^{-1} M Cu^{2+} .

At low copper concentration ($\leq 10^{-4}$ M), the copper bounded to carboxylic groups is negligible, and swelling is produced by the difference between ionic pressures inside and outside the hydrogel. When the initial concentration of Cu^{2+} is increased, the appearance of complex between copper ions and carboxylic groups is more probable and a simultaneous pH decrease in the outer solution is observed. In accordance with complexation of carboxylate groups, the hydrogels deswell. Figure 3 show an example of swollen hydrogel collapse when is immersed in $(\text{Cu}^{2+})_i = 10^{-2}$ M solution.

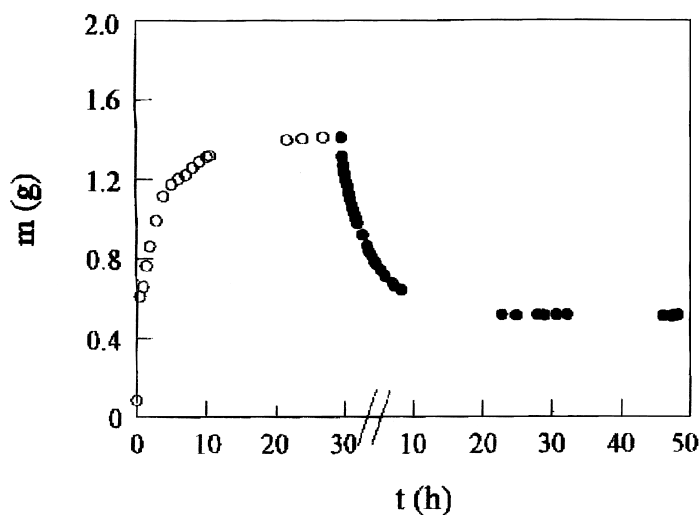


Figure 3. Variation of the mass hydrogel (acrylic acid-itaconic acid 80:20) correlated with the absorption of Cu^{2+} : (○) swelling in water, (●) deswelling in $\text{Cu}^{2+} 10^{-2}$ M solution.

When salt solutions are diluted down the swelling curve remains horizontal, while for concentrated solutions, the hydrogels present a deswelling phenomenon and their initial size is almost recovered. This phenomenon can be attributed to the electrostatic repulsion between charged groups on the network and to a concentration gradient of ions inside and outside the hydrogel governed by the Donnan potential. As salt concentration rises the ionic force decreases and the mobile ion concentration in the external solution will approach that inside the hydrogel.

In the previously proposed mechanism of ionic hydrogels, a barrier through which the dissociated ions cannot come out is assumed [17]. However, swelling mechanism can be explained also by considering that dissociated ions distribute themselves between the hydrogel and the solution according to the Donnan effect, which relates the balance between the diffusion force of the dissociated ions and the electrical attractive force by the charged network, and then an electrical potential distribution is generated due to the local imbalance of electrical charge [18]. In this swelling mechanism, collapse of the hydrogel is considered to result from a decrease on the degree of the dissociation of functional groups according to the degree of ion exchange and to the increase of hydrogen ion concentration in the solution.

Metal Ions Uptake

Itaconic acid in aqueous solution presents some characteristics such as: two-steps dissociation process of dicarboxyl groups, binding of counter ions, etc. These characteristics are attributed to the hydrophobic interaction of no polar side chains and the short-range electrostatic interaction of a carboxyl group pairs. The presence of these carboxyl groups is responsible for metal absorption from aqueous solutions.

Metal absorption is in agreement with the exchange between metal ion in the external solution and H^+ from the polar groups in the polymer chain, considering that carboxyl groups in the hydrogel bound with metal ion due to the electrical charge. Table 2 show this behavior for copper.

Table 2. Copper Absorption from Aqueous Solutions of Different Concentrations by Poly(acrylic acid-co-itaconic acid) 80:20 Hydrogels

$C(Cu^{2+})_i$ (M)	pH _{initial}	pH _{final}	mg Cu/g _{xerogel} (desorbed)
10^{-5}	5.2	4.2	0.5
10^{-4}	5.1	3.6	4.5
10^{-3}	5.0	3.1	18.0
10^{-2}	4.9	2.9	49.3
10^{-1}	4.7	2.8	99.0

As the initial pH of the solution was lowered, the amount of hydrogen ion released increases, and hydrogel volume normalized to the initial swollen volume, decreases. These results suggest that the $-\text{COOH}$ groups fixed on the network were partially changed. Even if the salt concentration is sufficiently high, a decrease of pH in the outer solution, which is associated with the ion exchange, must be taken into account.

The kinetics of metal ion uptake process is relatively slow, the diffusion of ion inside the hydrogel is likely the rate limiting factor. In metal ion solutions, the polymer network first swells but, because of the neutralization of electric charged by metal ion binding to the carboxylate anions, it quickly deswells.

Tanaka *et al.* [17] developed a theory for the elucidation of the swelling mechanism of ionic hydrogels. They identified three forces acting on the ionic hydrogels: the rubber elasticity, the interaction force between polymer strands and solvent, and the dissociated ion pressure. The latter has been recognized as the determining factor in the swelling degree of ionic hydrogels [19]. They called the sum of these forces the osmotic pressure of the hydrogel, and concluded that hydrogels adjust their volume so that the osmotic pressure becomes zero.

According to their interpretation, the decrease of water absorption capacity in electrolyte solutions is considered to be due to the decrease in osmotic pressure difference between the inside and the outside of the hydrogel. Poly(acrylic acid-co-itaconic acid) hydrogels have $-\text{COOH}$ groups fixed on the hydrogel network as functional groups, so they can be substantial like weak acid type cation exchange resin. When it is immersed in electrolyte solutions, ion exchange takes place during the swelling process having a considerable effect on the water absorption.

Effect of pH and Metal Concentration

Variations of copper and zinc absorption are shown in Table 3. Metal ion absorption is pH dependent in agreement with the carboxylic proton-metal ion exchange process. When the pH of salt solutions is increased, the ion swelling

Table 3. Absorption Metal Variation with pH and Metal Concentration Solution for Poly(acrylic acid-co-itaconic acid) 80/20 Hydrogels

C(M) ²⁺ (M)	mg M ²⁺ /g _{xerogel}					
	pH = 4.7		pH = 6.0		pH = 9.0	
	Cu	Zn	Cu	Zn	Cu	Zn
10 ⁻⁵	0.4	0.5	0.4	0.5	0.5	0.5
10 ⁻⁴	2.8	3.0	3.1	3.3	4.6	5.8
10 ⁻³	23.7	27.4	29.5	30.5	32.2	36.9
10 ⁻²	72.7	145.0	96.0	176.0	163.0	198.0
10 ⁻¹	96.4	303.8	147.0	328.0	320.0	343.2

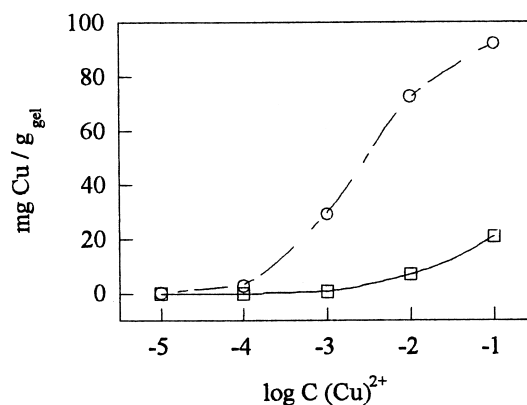


Figure 4. The isotherms absorption of copper from aqueous solution of copper sulphate onto poly(acrylic acid-co-itaconic acid) hydrogels, containing 20% itaconic acid at pH = 4.7. Copper absorption: (○) xerogel, (□) swollen hydrogel.

pressure will increase due to the increasing production of free counter ions by dissociation of -COOH groups in the hydrogel.

Experiments at pH 2.0 and 3.0 were carried out, but in this case metal absorption was not observed. At this pH the equilibrium with exchange ions yields low absorption of metals. Ionization degree is very low and the resulting hydrogels are uncharged (entirely protonated) and shrink. The swelling is affected above a pH of 4.0, which is related to the carboxylic acid dissociation. Increasing the pH increases the hydrogel ionization and upper values of metal absorption are reached. Uptakes of copper ions onto the swollen hydrogels were investigated. Absorption isotherms of the swollen and the initially dry hydrogels are given in Figure 4.

Figure 4 shows that the uptake of copper ions is higher in dry hydrogels compared with the swollen ones. This behaviour can be explained because in the dry hydrogels in addition to the diffusion phenomena, the solution absorption during the swelling has been taking place. In the swollen hydrogel carboxyl groups can interact with water and these groups can prevent the uptake of copper ions.

Influence of the Hydrogel Composition on the Absorption

The variation of the absorption of copper ions with the itaconic acid content in the hydrogels was investigated. The mass of absorbed copper per gram of the hydrogel versus the itaconic acid content of the hydrogel is plotted in Figure 5.

Uptakes of copper ions into poly(acrylic acid-co-itaconic acid) hydrogels increase with an increase of the itaconic acid content. Ionizable groups on the polymers were increased by adding itaconic acid to acrylic acid monomer, therefore these hydrogels have many carboxyl groups that can increase the electrostatic interaction between the cationic metal ions and the anionic groups of itaconic acid

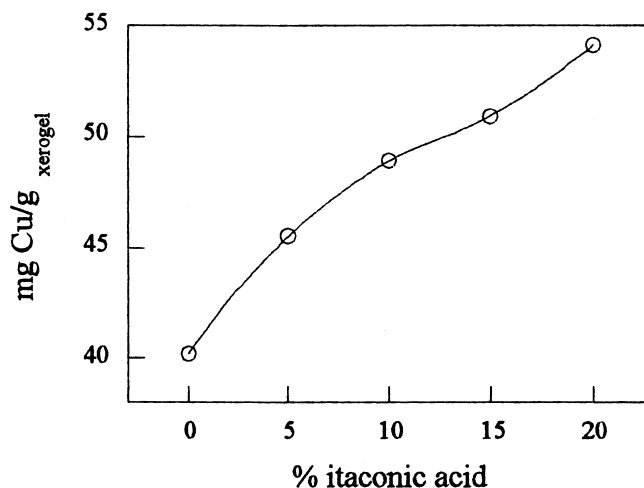


Figure 5. The variation of absorption of copper ions from aqueous solutions in initial concentration of $\text{Cu}^{2+} = 3.1 \cdot 10^{-2} \text{ M}$ into poly(acrylic acid-co-itaconic acid) hydrogels with itaconic acid content.

in the hydrogels. Hydrogels taken out of the metal solutions, and were allowed to stand for two days in H_2SO_4 0.1 M solution. The desorption of copper ions were shown by the return of hydrogels to their original color.

Presence of metal ions in polyelectrolyte hydrogels is reported in several theoretical and experimental studies [14, 19–21]. As we said before, these phenomena were described theoretically mainly from the point of view of the change of the osmotic pressure of mobile counter ions. The effect of counter ions binding to the polyions of the network is of great importance

Swelling of Metal Loaded Hydrogels

Swelling of metal loaded hydrogels was investigated. The xerogel were immersed in Cu^{2+} and Zn^{2+} ($3.1 \cdot 10^{-2} \text{ M}$) aqueous solutions. When the equilibrium was reached, the samples were dried and their swelling in water was studied. Figure 6 shows the plot of $H(\%)$ as a function of time for poly(acrylic acid-co-itaconic acid) 80:20 hydrogels loaded with metal cations.

Swelling Kinetic

The water uptakes of swollen hydrogels can be expressed as:

$$W = \frac{m - m_0}{m} \quad (6)$$

where m and m_0 are the weights of the hydrogels and xerogel respectively.

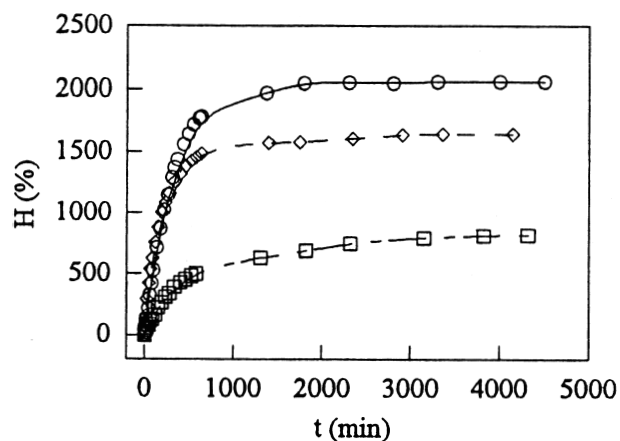


Figure 6. Swelling isotherms for poly(acrylic acid-co-itaconic acid) (80:20) hydrogels: (\diamond) unloaded hydrogels, (\square) loaded with copper, (\circ) loaded with Zn.

Combining Equations 1 and 2, we get:

$$W = \frac{H}{H+1} \quad (7)$$

The water sorption kinetics proposed by Schott [22] for the extensive swelling of polymer is given by:

$$\frac{t}{W} = A + Bt \quad (8)$$

where W is the swelling at time t , $B = 1/W_{\infty}$, the inverse of maximum swelling and $A = 1/(dW/dt)_0$, the reciprocal of the initial swelling rate.

Equation 1 implies second-order swelling kinetics expressed as:

$$\frac{dW}{dt} = K(W_{\infty} - W)^2 \quad (9)$$

upon integration between the limits t, W and $0, 0$, and after rearrangement, the following equation is obtained:

$$\frac{t}{W} = \frac{1}{KW_{\infty}^2} + \frac{1}{W_{\infty}} t \quad (10)$$

Substituting Equation 6 in 9 and rearranging, the above equation as function of hydration degree can be written as:

$$\frac{t(H+1)}{H} = \frac{(H_{\infty}+1)^2}{KH_{\infty}^2} + \frac{(H_{\infty}+1)}{H_{\infty}} t \quad (11)$$

According to this equation, the representation of $t(H+1)/H$ as a function of time for the experimental data must be a straight line with a slope of $(H_{\infty}+1)/H_{\infty}$ from

Table 4. Kinetics Parameter Obtained from a Second-Order Linear Regression for Every Studied Hydrogel Composition

Monomer Ratio AA-Ia	Cu		Zn	
	H (%)	K·10 ² (min ⁻¹)	H (%)	K·10 ² (min ⁻¹)
80:20	897	2.6	2392	10.6
85:15	666	2.4	1965	9.7
90:10	580	1.9	1835	8.4
95:5	501	1.4	1761	7.4
100:0	465	1.1	1683	4.5

which it is possible to calculate the equilibrium hydration degree. The increasing resistance of the polymer network progressively retards the limited swelling of polymer. At equilibrium or saturation, the swelling is approached asymptotically to the equilibrium value, and from the intercept of the straight line the value of K (swelling constant rate) is obtained for every studied hydrogel.

Water sorption kinetics satisfactorily fit the expression 11 over the entire range of values. These results suggest that swelling processes conform to a second-order kinetics. Values of the constants H and K obtained from the linear regression for load and unload hydrogels are summarized in Table 4. Figure 7 shows the representation of these values with the itaconic acid content

As observed from the previous figures, swelling in water is higher and faster when itaconic acid is increased according to the reasons explained before. Swelling of hydrogels loaded with zinc is higher and faster (higher kinetics constant) than those loaded with copper.

The minor swelling for hydrogels loaded with copper can be explained by the complexation of -COO- groups with Cu²⁺ forming neutral -COOCuOOC-group.

It is interesting to note that the swelling index of poly(acrylic acid-co-itaconic acid) hydrogels loaded with zinc is higher than that of the unloaded hydrogels. due to the possible formation of (-COO-)M⁺ ion pairs. If we assume that this type of complex is positively charged, water diffusion will occur inside the hydrogel. However, the rate of water diffusion through the hydrogel is slower than that of the unloaded one due to the superficial barrier formed by metal complexes.

In water, the polyelectrolyte hydrogel can be regarded as a weak acid where the ionizable groups are partially dissociated according to solution acid-base equilibrium, therefore swelling is limited by dissociation of (-COOH) inside the hydrogels.

The lowest value of swelling rate constant for samples loaded with copper can be explained if we take into account that copper binds to carboxyl groups. This makes water absorption slower due to a more difficult diffusion through polymer chains.

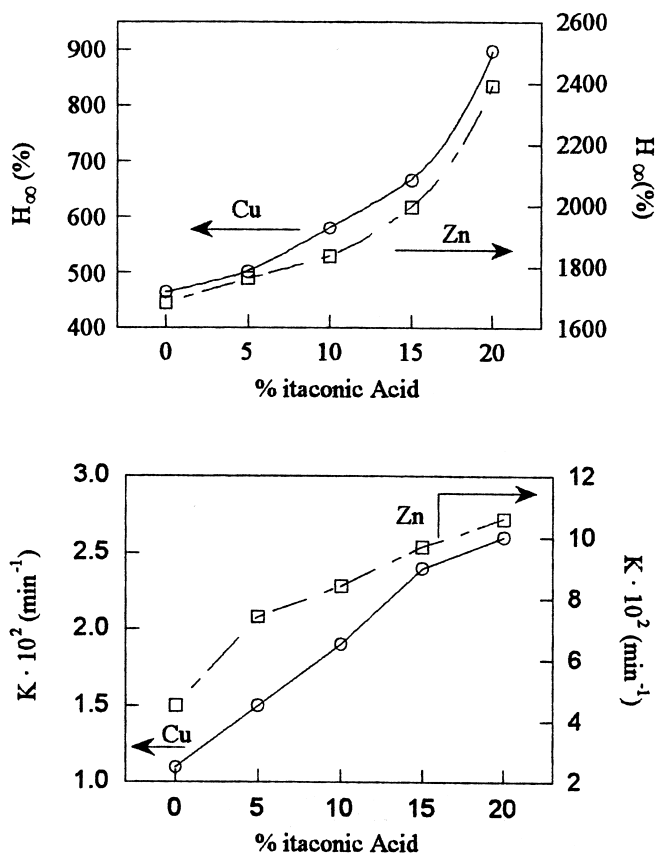


Figure 7. Variation of equilibrium hydration degree and the specific rate constant for the swelling in water with the itaconic acid content: (○) loaded with copper, (□) loaded with zinc.

Some authors have studied the collapse of polycarboxyl hydrogels by X-ray diffraction measurements and have shown that hydrogel collapse is due to the formation of copper concentrated nodules separated by stretched polymer chains [23]. In this type of hydrogels the formation of binuclear complexes is often observed, in which the carboxylate form bridges between the copper atoms [24]. In our study, paramagnetic electronic resonance measurements showed that copper-copper interactions may occur, but it is difficult to give a definitive description of the complex type or the molecular structure of metal complexes inside the hydrogel. We are not aware of the existence of a rigorous description of metal-network binding, so we restrict ourselves to a qualitative discussion.

CONCLUSION

Swelling properties of poly(acrylic acid-co-itaconic acid) hydrogels in water and salt solutions were studied. Hydrogel swelling decreases when concentration of metal ions increases and it increases with itaconic acid content.

Metal absorption increases as the pH of the external solution is increased. Variations in the pH observed in the outer solution shows that the extraction occurs by a cation exchange mechanism.

The effect of pH and salt concentration are correlated with the swelling behavior of the hydrogels, which is interpreted by the Donnan potential of the hydrogels, where the ionization of carboxyl groups plays the most important role. Metal stripping from loaded hydrogels is achieved in acid medium.

Swelling kinetics of unloaded and metal loaded hydrogels was studied. The experimental data indicate that swelling process follows a second-order kinetics. The specific rate constant and the equilibrium percentage degree of hydration depend on the monomer ratio of the hydrogel and increase as itaconic acid content increases.

It was shown that poly(acrylic acid-co-itaconic acid) hydrogels could be used as metal absorbents, applied to waste water and preconcentration of metal cations before analysis in environmental studies. These hydrogels are expected to be applicable to absorption of other ions.

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