Revue Roumaine de Chimie, **2007**, *52*(12), 1145–1149

POLY(VINYL ALCOHOL) HYDROGELS INTERACTIONS WITH ELECTROLYTES IN AQUEOUS SOLUTION

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Received November 9, 2006

The interactions between hydrogels and electrolytes have been analyzed. In this paper the interaction between PVA hydrogels, obtained by freezing-thawing techniques, and different chlorides (NaCl, KCl) has been studied.
PVA hydrogels evidence a high capacity of water absorption. The hydrogels, that initially reached the swelling equilibrium, collapse while inserting them in electrolytes aqueous solutions, leading to the modification of their mass, volume and density due to the water elimination. The collapse degree and the kinetic of the hydrogel swelling-collapse processes depend on the type and the concentration of the electrolyte. The reversibility of swelling-collapse process has been also investigated. The differences between the initial swelling and re-swelling equilibrium are due to the interactions between the hydrogels and electrolytes.

INTRODUCTION

Hydrogels can be described as a three-dimensional network of hydrophilic polymers that can imbibe a large amount of water or biological fluids without dissolving. They maintain their solid state due to the presence of the crosslinks.[1,2] The hydrophilic polymer chains from the network can be connected through either chemical or physical bonds.[3] Depending on the crosslinking method used to design the hydrogels, these can be classified in two general classes: chemical and physical hydrogels. In the chemically crosslinked hydrogels, different polymers chains are linked by covalent bonds. In the physically crosslinked hydrogels the chains are connected by electrostatic forces, hydrogen bonds, hydrophobic interactions or chain entanglements.

Polymeric hydrogels have large applications in agriculture, cosmetics, food industry, photography, etc. In the last decade, due to their dynamic structural properties, the hydrogels have become important materials with biomedical applications. The hydrogels were intensely used in pharmaceutical and biomedical fields because they exhibit biocompatibility to the human body and own similar characteristics to the natural tissue.[4]

Poly (vinyl alcohol) [PVA] is a bio-degradable, biocompatible, non-toxic and non-cancerous polymer that leads to the hydrogels generation through different methods and techniques. The PVA hydrogels crosslinked by radical polymerization, irradiation or with bi-functional group containing chemical agents (*e.g.* glutaraldehyde,[5] acetalaldehyde,[6] formaldehyde[3]) suffer from several disadvantages. Therefore, the preparation of PVA hydrogels was focused onto an alternative method that does not use toxic additives, in order to avoid component leaching associated with the traditional chemical crosslinking techniques.[7] The physically crosslinked hydrogels based on PVA, prepared by repeated cycles of freezing-thawing[7-11] are stable hydrogels due to the presence of crystalline regions. In addition to their non-toxic characteristics, the freeze/thawed PVA hydrogels own enhanced mechanical properties that make them suitable to wide pharmaceutical and biomedical applications.

PVA hydrogels are stimulus-responsive or smart hydrogels because they undergo strong conformational changes (*e.g.* swelling or shrinking) upon very small changes of the environment. The environment factors that actuate the hydrogels are: temperature, pH, electric or magnetic fields, ions, solvents, pressure, etc.[11-15]

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RESULTS AND DISCUSSION

In this paper the behaviour of the PVA hydrogels, prepared by successive cycles of freezing-thawing, in the presence of aqueous solutions of electrolytes (NaCl and KCl) has been investigated.

The water desorption from the PVA hydrogels was quantified in terms of normalized water mass kept into the hydrogel, m_{H_2O} / m_x , at a pre-determined time *t* (min.) after the immersion of the samples into the electrolyte solutions.

The immersing of the PVA hydrogel samples into the aqueous solutions of NaCl and KCl, with concentrations of 1M, 2M and respectively 3M, determined the modification of the hydrogel mass as it is depicted into Fig. 1.

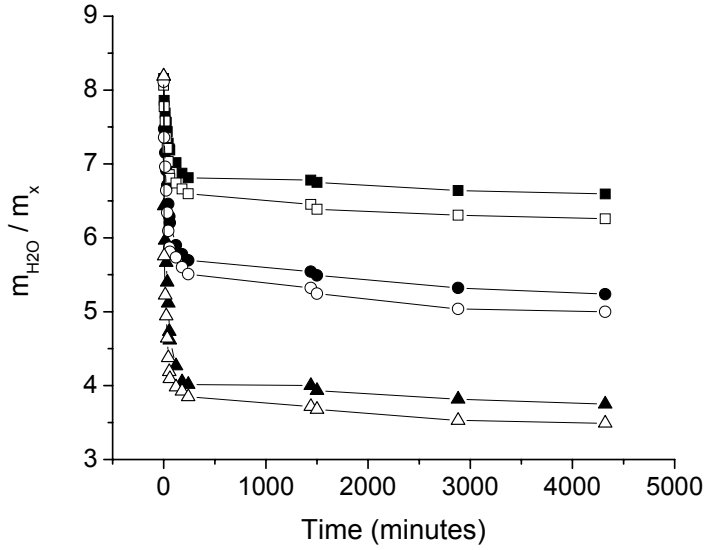

Fig. 1 – Normalized water mass kept into the hydrogel, m_{H_2O} / m_x variation versus time, in the presence of NaCl and KCl electrolyte solutions: (■)NaCl 1.0M; (●)NaCl 2.0M; (▲)NaCl 3.0M; (□)KCl 1.0M; (○)KCl 2.0M and (△)KCl 3.0M.

The presence of aqueous electrolyte solutions, either NaCl or KCl, leads to the collapse of the PVA hydrogel samples because of the elimination of a certain amount of water. In the first interval of analysis (between 0 and 500 minutes) the quantity of water eliminated from the hydrogel samples is significant; after 500 minutes the amount of water delivered is reducing, reaching the equilibrium state at approximately 1500 minutes.

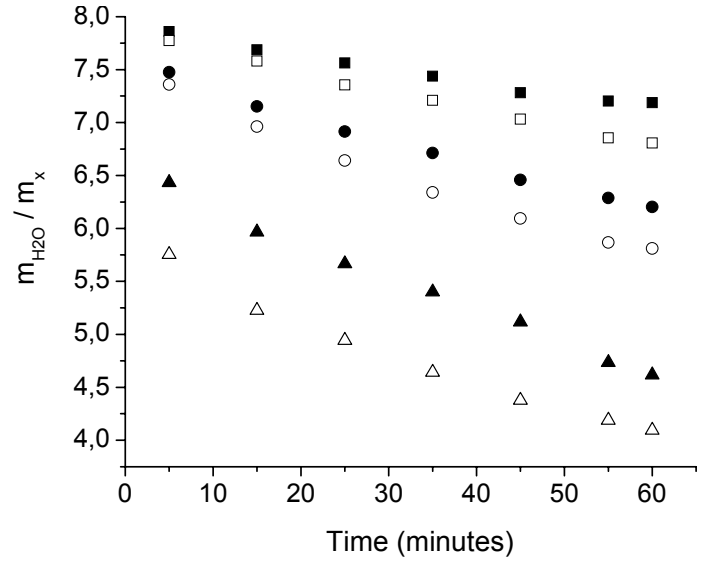

Fig. 2 – The kinetic of water desorption from the PVA hydrogels
(■)NaCl 1.0M; (●)NaCl 2.0M; (▲)NaCl 3.0M; (□)KCl 1.0M; (○)KCl 2.0M and (△)KCl 3.0M.

The mass of the water removed from the PVA hydrogel samples varies depending on the concentration and the type of the electrolyte solutions, as it is illustrated in Fig.2.

The concentration of the electrolyte solutions influences the mass modification of the PVA hydrogels in the following manner: the higher the concentration of the electrolyte solution is, the bigger the water mass elimination is.

The graphical representation of the normalized kept water mass versus the concentration of the aqueous electrolyte solutions (Fig.3), after 1500 minutes of incubation, illustrates that the quantity of the water removed from the sample immersed into the KCl solution is higher than the quantity of water eliminated from the samples inset into the NaCl solution.

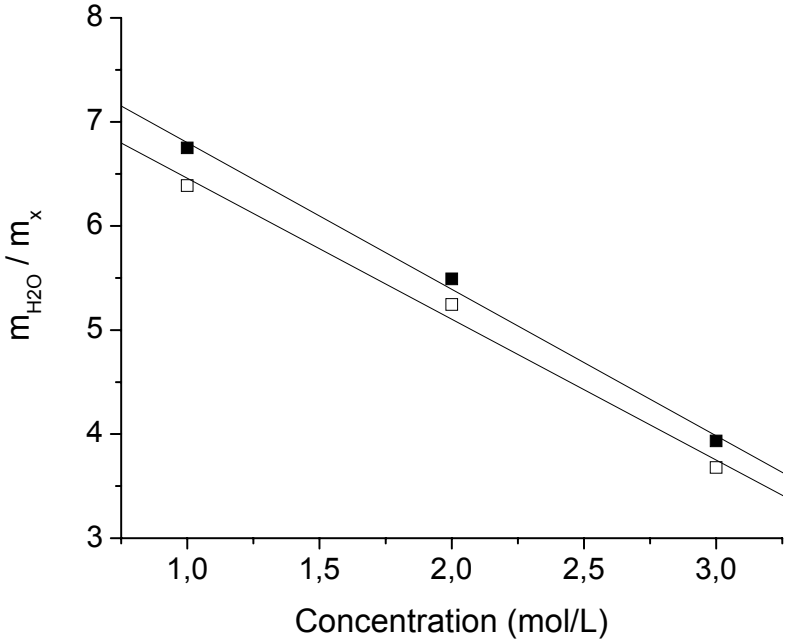

Fig. 3 – The normalized water mass retained by the PVA hydrogel as function of the electrolyte solution concentration: (■)NaCl and (□)KCl.

The higher amount of water eliminated from the samples immersed into the KCl solution is due to the capacity of the K^+ ions from the KCl electrolyte solution to break down the hydrogen bonds existing between the components of the polymeric system.[16] The breaking down of the hydrogen bonds existing between the H_2O molecules and the polymer macromolecules produces a powerful interaction between the K^+ ions and the PVA macromolecules, and therefore determines a higher collapse degree of the PVA hydrogels.

To evidence the re-swelling capacity of the PVA hydrogels, samples initially contracted as result of the insertion into the electrolytes solution (*e.g.* NaCl) were immersed into distilled water and weighted at pre-determined period of time.

Normalized kept water amount was monitored in function of time. The results are shown in the Fig. 4.

The graphical representation (Fig. 4.) illustrates that the samples of PVA hydrogel reabsorb significant quantity of water, once they are immersed into distilled water, and therefore their mass is increasing. The hydrogels mass increases until the swelling equilibrium is reached, irrespectively of the concentration of the electrolyte solutions where the samples were initially immersed.

In Fig. 4 it is shown that the PVA hydrogels re-swelling depends on the concentration of the electrolyte solution used to contract the samples.

The experiment results obtained show that the PVA hydrogels are able to absorb water and re-swell, exhibiting a mechanical active property when the environment conditions are changed.

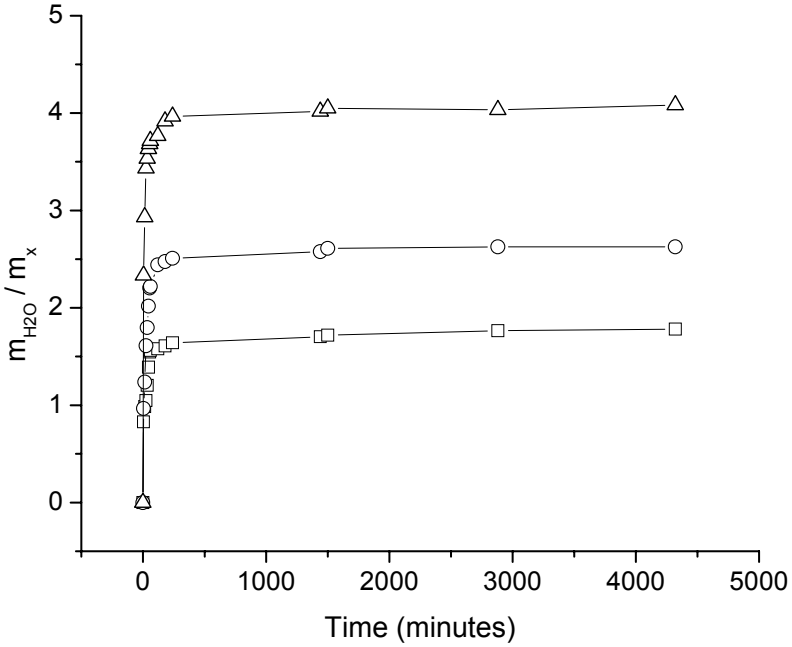

Fig. 4 – Hydrogels re-swelling in water as function of time: (□)NaCl 1.0M; (○)NaCl 2.0M and (△)NaCl 3.0M.

EXPERIMENTAL

Materials

Poly (vinyl alcohol) – PVA 90-98 (degree of polymerization 900 and degree of hydrolyze 98) having industrial grades was purchased from The Chemical Plant Râşnov and used without being submitted to further purifications to prepare PVA hydrogels. Sodium chloride and kalium chloride with analytical reagent grade and distilled water were used to prepare 1M, 2M and respectively 3M aqueous solutions of electrolytes.

Methods

Preparation of PVA hydrogel

PVA hydrogel was prepared by using the technique of successive freezing-thawing cycles. 30g of PVA powder were solved in 250mL of distilled water under magnetically stirring at 80°C for 3 hours. The obtained PVA solution, cooled at room temperature, was inset into poly(vinyl chloride) containers with diameter of 1.80cm and kept for 12 hours at -20°C. The frozen gel was then thawed for 12 hours at the room temperature (22°C), and again kept at -20°C for 12 hours. This freezing-thawing cycle repeated by three times leads to the converting of PVA solution into an opaque white hydrogel mass with good mechanical resistance and heterogeneous structure. The obtained PVA hydrogel has the concentration in the solid matter CS = 10.98%. The hydrogel so prepared was immersed in distilled water until the swelling equilibrium was reached.

Determination of concentration in solid matter

Samples of PVA hydrogels weighting approximately 1g were introduced into weighting phials and kept for 10 hours at 110°C into the stove. The PVA hydrogels samples took out from the stove were introduced into the exsiccator, cooled at the room temperature and then weighted in order to determine the mass of the xerogel. The formula:

$$CS \quad (\%) = \frac{m_x}{m_{we}} \cdot 100 \tag{1}$$

was used in order to determine the concentration in solid matter for the PVA hydrogel prepared; m_{we} represents the equilibrium mass of the swollen hydrogel in water and m_x represents the mass of the xerogel.

Study of the collapse process

Samples weighting 4-6 $\cdot 10^{-2}$g were cut from the swollen PVA hydrogel bone and inset in 20mL of aqueous solutions of electrolytes with concentrations of 1M, 2M and respectively 3M, in order to study the phenomena of water desorption in the presence of electrolytes. The hydrogel samples were taken out from the electrolytes solutions at pre-established intervals of time and weighted after the excess of the electrolyte solutions was removed by gently pressing the sample between two filter papers. An analytical balance (Kern ABS/ABJ, Germany) with a precision of 10^{-4}g was used in order to weight the samples of PVA hydrogels.

Study of the re-swelling process

PVA hydrogel samples, initially immersed into NaCl aqueous solutions, are immersed in 20mL distilled water. At the pre-established time intervals the samples are taken out, gently pressed between two filter papers to remove the water excess and finally weighted by the analytical balance.

CONCLUSIONS

In this paper the desorption of water from the PVA hydrogels, obtained by freezing/thawing

techniques, in the presence of NaCl and KCl aqueous solutions with different concentrations has been studied.

The PVA hydrogels exhibit an active mechanical behavior illustrated by the shrinking in the presence of electrolyte solution and the swelling in the presence of water evidence that.

The experimental results show that a higher amount of water is eliminated from the hydrogel in the presence of KCl electrolyte, due to the fact that the K^+_{ions} stronger interacts with the PVA hydrogel, comparing with the Na^+ ions. It has also been evidenced that the collapse degree of the hydrogel increases with the increasing of the immersion time and the concentration of the electrolyte solutions.

The hydrogel re-swelling study has illustrated that the contracted samples are able to absorb significant amount of water, but the coming back to the initial balance of swelling is not total.

The study of PVA hydrogels behavior in electrolyte solutions is very important due to their applicability into pharmaceutical (*e.g.* controlled drug delivery) and sensors (hydrogel capacity to load with different salts) domains.

Acknowledgements: This study has been funded by The National University Council (CNCSIS), through the national grants CEEX10/2005 and CEEX18/2005.

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