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Peculiarities of the kinetics of polyelectrolyte hydrogel collapse in solutions of copper sulfate

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The kinetics of polyelectrolyte hydrogel collapse in water solutions of $CuSO_4$ was studied. It was shown that the equilibrium degree of contraction essentially depends on the route by which the equilibrium is attained. The hydrogel kinetics of collapse in solutions of polyvalent metal salts is interpreted from the point of view of two different mechanisms of gel collapse. The transition from one mechanism to the other one is determined by the time of hydrogel interaction with the salt solution and by its concentration.

(Keywords: polyelectrolyte hydrogel; polyvalent metal salts; kinetics of collapse)

INTRODUCTION

Studies of the behaviour of strongly swelling polyelectrolyte hydrogels in water–salt solutions are of current interest both in their theoretical and technical aspects. Investigations of the regularities of gel contraction in salts of different valency form the basis for understanding many essential questions on the mechanism of polyelectrolyte hydrogel swelling[1–5]. In the realms of the analysis of inhomogeneous distribution of the ionogenic groups arising in this process, the premises for understanding and modelling the stages of prebiological evolution connected with the formation of proto cell membranes and capsules may appear. Also these studies may be considered as a basis for purification and enrichment technologies (including different stages of biotechnology). The hydrogels may be used in these processes as separating membranes or for ion exchange with high sorption rate in regions far from the equilibrium[6,7].

The kinetics of hydrogel contraction in low-molecular-weight salt solutions has still not been described in detail. Different approaches to the description of the kinetics of polymer gel swelling in pure water or in water solutions of different ionic strength were used in refs 8–12. In most of the articles the results of the interaction of hydrogels with different metal ions are interpreted from the point of view of attainment of thermodynamic equilibrium. However, as will be shown later, the characteristics of the sample in the equilibrium state noticeably depend on the route by which it was attained. In particular, in the communication by Hirotsu[13] it was shown that the equilibrium degree of swelling and the phase transition temperature essentially depend on the sample dimensions.

In addition one must keep in mind the possibility of the occurrence of sharp (and 'sudden') non-linear effects leading to a total loss of diffusion-controlled kinetics and, as a consequence, a drastic increase in the overall and partial rates of the particular molecular and electro-osmotic processes[14]. This problem has some additional and 'more prosaic' difficulties, which are connected, for example, with taking into account the diffusional flows of salt solutions inside and outside the hydrogel (because of the gel contraction the flow of water from the sample may lead to the appearance of a concentration gradient of salt solution). Besides, the problem becomes complicated because of the inhomogeneous chemical crosslinking of hydrogel ionogenic groups by polyvalent metal ions. Thus systematic studies of the hydrogel kinetics of collapse in polyvalent metal salt solutions are necessary.

In this paper experimental studies of the kinetics of contraction of strongly charged polyelectrolyte hydrogels in solutions of copper sulfate were carried out. The influence of the salt solution concentration on the rate of contraction and on the equilibrium value of the degree of contraction was investigated.

The aim of the work was to show that the kinetics of contraction and the degree of contraction in the equilibrium state also depend on the dimensions of the sample. A number of experimental studies of hydrogel contraction in water–salt solutions have been performed for thin cylindrical samples (with the cylinder diameter much lower than its height[1,9,15] or small round particles with a diameter near 1 mm[3,5,16]. Thus we have chosen large gel cubes (see the detailed description in Experimental) to ascertain new kinetic effects.

As mentioned above, studies of hydrogel contraction in polyvalent metal salt solutions were carried out in solutions of copper sulfate of different concentrations. We have chosen this salt solution because, on the one hand, the collapse in $CuSO_4$ solution of the same small gel particles has already been studied[5,16]. On the other hand, it was shown[5,16] that the hydrogel contractile behaviour in salt solutions of different polyvalent metal

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*To whom correspondence should be addressed salts ($CuSO_4$, $CoSO_4$, $NiSO_4$) does not depend on the identity of the metal ion. Thus copper sulfate solution was used as a typical one.

EXPERIMENTAL

Materials and methods

A strongly swelling polyelectrolyte hydrogel based on sodium polyacrylate was studied. The sample synthesis is described in detail in ref. 17. The hydrogel was synthesized by radical polymerization of acrylamide in aqueous solution (monomer concentration during polymerization was 20%). Water-soluble allylcarboxymethylcellulose (degree of substitution in respect to allyl groups was 0.4, its weight fraction in the reaction solution was 0.2%) was used as the crosslinking agent. After polymerization the samples were subjected to hydrolysis in a 0.1 M solution of NaOH. The degree of swelling of the gel in water in equilibrium was $3600\ g\ g^{-1}$.

The synthesized hydrogel has good elastic and mechanical properties[17] because the polymer chains of allylcarboxymethyl cellulose, the crosslinking agent used in this study, are stiff and play the role of 'rigid cross-bars'. The gel can sustain its own shape even at the largest degrees of swelling. Thus it was convenient to use these samples for the study of their contractile behaviour.

The samples were swelled-in-water hydrogel cubes in the equilibrium state of side 2 cm. They were placed in water solutions of $CuSO_4$ of different concentrations. To avoid the appearance of a salt solution concentration gradient during hydrogel contraction the solution was slowly stirred. In the fixed times t the sample weight $p(t)$ was rapidly measured and the degree of contraction α was determined: $\alpha = p(t)/p_0$, where p_0 is the initial weight of the swollen-in-water gel. Errors in α determination were less than 10%. The volume ratio of hydrogel to solution was constant and equal to 1:10. For convenient comparison the reduced salt concentration C_s/C_p will be used, C_s being the salt solution concentration and C_p the concentration of hydrogel ionogenic groups, both calculated in $mol\ l^{-1}$ for the total volume of hydrogel + solution. Errors in concentration determination were less than 3%.

It must be noted that for investigations of the kinetics of hydrogel contraction in copper sulfate solutions we have chosen a region of salt concentrations where it is known that the small hydrogel particles collapse almost to the 'dry' state[1,5,16]. In other words, it is the region of concentrations $C_s > C_p$, where the hydrogel contraction is caused not only by polyelectrolyte swelling suppression of sodium polyacrylate, but by a strong reduction of network swelling due to electrovalent bonding with copper ions.

RESULTS

In *Figure 1* the dependences of hydrogel degree of contraction on time for different $CuSO_4$ concentrations are given. For the first few hours the samples that were in more concentrated solutions contracted more quickly. This is quite expected and natural. However, in the equilibrium state (more than ~4 days) the samples that were in more dilute solutions became more collapsed. The hydrogel samples placed in copper sulfate solutions with Cu^{2+} concentration exceeding C_p by 1–2 orders of magnitude approach the equilibrium state more quickly, than under $C_s \sim C_p$, but the equilibrium value of their degree of contraction is two to three times higher. This is confirmed by kinetic curve intersections.

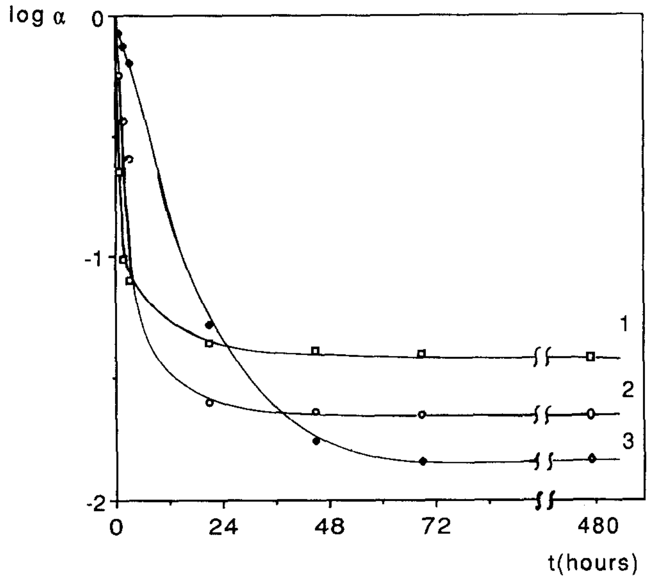

Figure 1 Kinetic dependences of hydrogel contraction for the cubic sample of side 2 cm in copper sulfate solutions of different concentrations: $\log(C_s/C_p) = 2.93$ (curve 1), 0.63 (curve 2) and −0.07 (curve 3)

Figure 1 shows that there are two main regions on the kinetic curves of contraction. The first is the region of short times, where the hydrogel contraction is fast. The second is the region of intermediate and large times where a slow approach to the equilibrium state takes place. The boundary of these regions, for example, for $\log(C_s/C_p) = 0.63$ is about 5 h (see curve 2 on *Figure 1*).

To clarify the situation an additional test experiment was performed. Three identical samples were placed in $CuSO_4$ solutions of the same concentration ($\log(C_s/C_p) = 0.63$). After four hours one of the samples was placed in an empty test vessel, the second one in water, and the third one was left in the initial solution. In the equilibrium state (in 3–4 days) all three samples attained the same degree of contraction.

Since relatively large hydrogel samples are under consideration, let us briefly discuss the influence of the dimension of the sample on the kinetics of its contraction in solutions of copper sulfate. In *Figure 2* the kinetic curves of hydrogel contraction for samples with a different size (edge dimension of the cubes 1.5 cm, curves 1′ and 2′) for salt solutions of different concentrations are given. It is clear that for the same salt concentration the contraction of the smaller hydrogel sample occurs more quickly (for example curves 1′ and 1 or 2′ and 2), but the patterns of the contraction connected with copper concentration influence are the same.

The results obtained, namely, the dependence of the kinetics of the hydrogel contraction on $CuSO_4$ concentration, may conveniently be analysed on a more detailed graph of log α *vs.* $\log(C_s/C_p)$ for the fixed times of observation. In *Figure 3* such dependences are given for hydrogel samples which were contracting for 45 min, 110 min, 21 h, 69 h and 20 days (curves 1, 2, 3, 4 and 5, respectively).

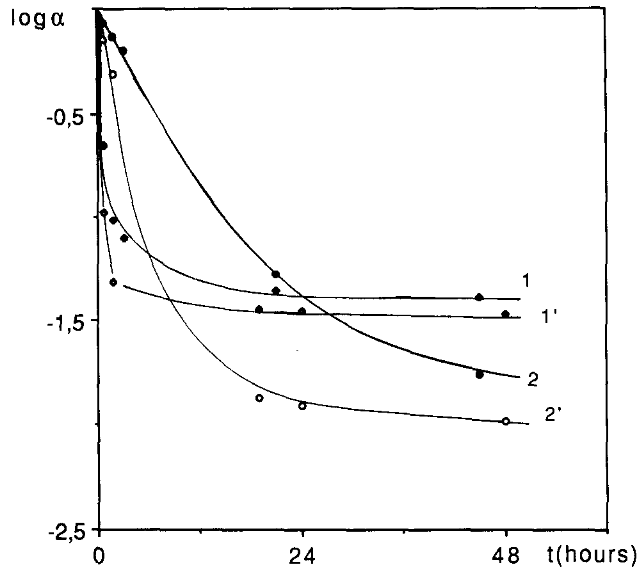

Figure 2 Kinetic curves of hydrogel contraction for cubic samples of side 2 cm (curves 1 and 2) and 1.5 cm (curves 1′ and 2′) in $CuSO_4$ solutions of concentrations $\log(C_s/C_p)=2.93$ (1, 1′) and -0.07 (2, 2′)

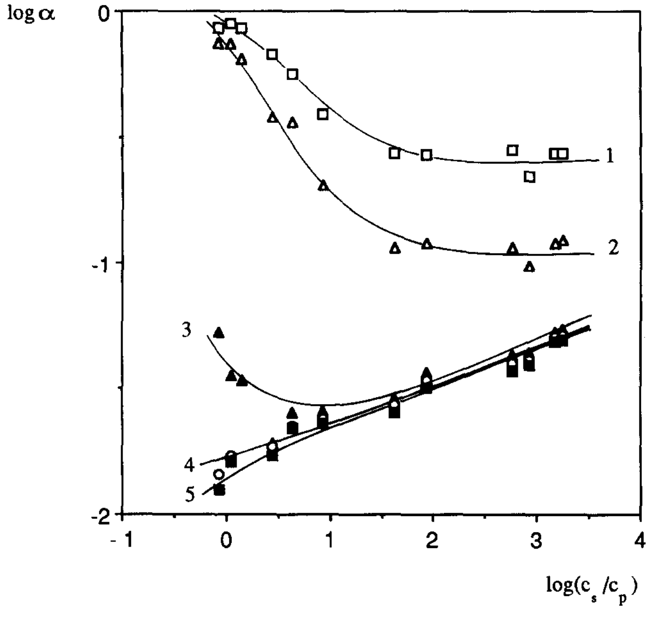

Figure 3 Dependences of hydrogel degree of contraction (for cubic sample of side 2 cm) on salt solution concentration in 45 min (□), 110 min (△), 21 h (▲), 69 h (○) and 20 days (■)

For small times of observation (1–2 h) the contraction of samples which are placed in a more concentrated solution is more pronounced. When the salt solution concentration is higher than the ionogenic group concentration by two or more orders the curves approach saturation, i.e. there is in fact no dependence of degree of contraction on copper concentration.

In 10–15 h the effects which lead to the abnormal dependence of equilibrium degree of contraction on C_s/C_p begin to show themselves (*Figure 3*, curve 3). This is expressed in the change of sign of the curves $\log \alpha$ *vs.* $\log(C_s/C_p)$ slope (the existence of a minimum on curve 3 reflects the change of slope of this curve).

Finally, in 3–4 days the system hydrogel–solution reaches the equilibrium state, which is characterized by more pronounced collapse under lower salt concentrations.

DISCUSSION

The results obtained allow us to analyse separately the hydrogel contraction for short, intermediate and large observation times. *Figure 3* shows that the boundary between these regions depends on salt concentration; however, all of them are present for any concentration. This allows us to assume that there are at least two different mechanisms of hydrogel contraction in polyvalent metal salt solution.

For small time periods the electrochemical crosslinking of the hydrogel by metal ions predominates. When the gel is placed in $CuSO_4$ solution a 'shell' on the surface of the sample starts to form due to the chemical reaction between COO^- and Cu^{2+}. This shell differs essentially in density from the hydrogel swelled in water. The rate of formation and thickness of this shell depend on salt solution concentration. In other words, on this linear part of the kinetic curve the hydrogel contraction is connected with the syneresis caused by the crosslinking reaction on the surface layer of the sample.

For intermediate lengths of time another mechanism of collapse begins to predominate. During the shell formation on the sample surface the electric double layer which was formed on the surface of hydrogel swollen in water (as a result of thermal counterion mobility)[5] is destroyed. The imbalance between the contributions of electrostatic forces and forces corresponding to a non-charged polymer network (elastic forces, etc.) leads to a change of the total hydrogel swelling. In this case the forces that make the gel collapse are determined by the fact of the existence of the shell and do not depend on further hydrogel interaction with polyvalent metal ions. This conclusion is confirmed by the results of the additional test experiment described above.

The results of our studies show (*Figure 1*) that reaching equilibrium is a slow process. The rate of this process is determined by the rate of water diffusion from the sample during contraction through the thick surface layer formed on the gel sample. The weaker collapse under high salt concentrations may be caused by purely kinetic factors: if there are 'a lot' of Cu^{2+} ions the process proceeds so quickly that inhomogeneously distributed areas with high density and toughness appear. They create obstacles to water flow and prevent the changes of hydrogel samples form and/or volume. In addition the diffusion of copper ions from the solution through this shell into the sample may also be impeded. As a result the samples placed in more concentrated solutions are more swollen in the equilibrium.

It is necessary to note that the experimental data obtained do not allow us to be sure if the observed equilibrium state is a genuine thermodynamic equilibrium or whether there may be a complicated set of metastable states. We have kept the term 'equilibrium state' because we did not obtain any other results during the observation period. It may be assumed that a subsequent transition to the real equilibrium state may occur: the copper ions will be homogeneously distributed over the sample without any dependence on its initial dimensions. In this case, there will be no more dependence of the degree of contraction on the salt concentration. However, in 'real' time (about a month) this state was not reached.

CONCLUSIONS

The studies performed on the kinetics of the contraction of large hydrogel samples in $CuSO_4$ water solutions show that:

- it is possible to distinguish two time regions which differ in the type of hydrogel collapse;
- the first time region is characterized by quick gel contraction as a result of direct hydrogel interaction with metal ions on the sample surface;
- the second region is typified by the fact that the rate of contraction is almost independent of the further penetration of metal ions into the sample. In this region the contraction is determined by the influence of the elastic properties of the network and the water diffusion through the thick boundary layer of the sample.

A quite explicit effect of sample size is observed, in total accord with the laws of thermodynamics of small systems. However, of more importance, though somewhat more implicit, is the conclusion that on attaining a certain size of hydrogel different non-linear effects are triggered which affect not only the rate but also the very nature of the kinetics observed, so that the whole situation should be reconsidered in terms of modern non-linear dynamics of polymers[18]. If this turns out to be true, then the value of the described experiments for biological modelling increases dramatically since non-linear dynamics opens many routes to avoid low-rate (e.g. diffusion-controlled, etc.) processes that contradict the very existence of living matter.

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