Swelling of membranes from the polyelectrolyte complex between chitosan and carboxymethyl cellulose

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SUMMARY

The swelling of membranes of polyelectrolyte complexes formed from chitosan and carboxymethyl cellulose is reported. These membranes adsorb water until a maximum swelling is achieved after which they slowly shrink to an equilibrium value. The maximum swelling value and the time at which it is attained increases as the pH of formation of the complex increases from 4.0 to 5.8. Shrinkage observed at longer times is the result of the segmental mobility of the polyelectrolyte chains in the swollen state which allows the completion of the interpolyelectrolyte reaction. The water uptake up to maximum swelling obeys second order kinetics.

INTRODUCTION

Polyelectrolyte complexes (**PEC**) are formed when dissolutions of macromolecules carrying opposite charges are mixed. Essentially, this is the result of electrostatic interactions between both polymers. Depending on a variety of conditions, it may provoke the complex to separate into a concentrated coacervate phase, or in a more or less compact hydrogel or precipitate.

The best known application of polyelectrolyte complexes, as an end product, is in the preparation of membranes. These membranes can find application in controlled-release devices for drugs and agricultural pesticides based on swellable polymer matrices.

Due to its unique cationic character, chitosan ($(1\rightarrow4)$-2-amino-2-deoxy-β-D-glucan) has found increasing attention as a polymer component in a variety of such complexes (1-5). Among them, the stoichiometric polyelectrolyte complex formed with carboxymethyl cellulose was formerly studied by Fukuda (6,7), and later in our laboratory (8,9). However, no information has been provided as to the swelling behaviour of membranes prepared from this **PEC**.

In the present paper the preparation of membranes from the interpolymer complex between chitosan and carboxymethyl cellulose, as well as the evaluation of their swelling behaviour, has been considered.

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EXPERIMENTAL

Materials

Crab chitosan from *Protan* ($\overline{M}v$ = 6.9·10⁵) with an 82% deacetylation degree was employed. Carboxymethyl cellulose (**CMC**; $\overline{M}v$ = 7.7·10⁴, substitution degree 0.7) was purchased from *BDH*. The molecular weight of chitosan was determined viscometrically at 25 ± 0.01°C in the solvent proposed by Roberts (10), and the degree of deacetylation was measured by the UV-first derivative method (11).

Deionized water was employed in all experiments. All other reagents were analytical grade.

Complex preparation

1 g of chitosan was dispersed in 25 ml of water and dissolved by adding 5 ml glacial acetic acid. **CMC** (1.7 g) was dissolved in 25 ml of water. Both polyelectrolyte solutions were allowed to stand overnight.

The solutions were mixed, and 1.5 ml hydrochloric acid were added. Then the pH of the solution was adjusted to the desired value by dropwise addition of 10% (w/v) NaOH under vigorous agitation. The fine dispersed hydrogel formed was poured into a plane sintered glass filter (ϕ = 8.5 cm), and allowed to decant and dry for a few days. A transparent, rigid and brittle membrane was obtained.

Swelling measurements

Dried and previously weighted membranes were immersed in an excess of water at pH = 5.5 (approximately 1 liter). The solvent was regularly changed in order to eliminate the low molecular weight electrolytes diffused out of the membrane, which was monitored by conductimetric measurements. During the experiment the temperature was kept at 25°C. The weight of the membrane was measured periodically after carefully removing the excess of solvent from its surface.

The swelling degree, M, was estimated as

$$M = \frac{P-P_o}{P_o} = \frac{P}{P_o} - 1 \qquad [1]$$

where P_o is the weight of the dry membrane, and P is the weight of the swelled membrane. Experiments were carried out using three replicates, and the swelling degrees reported are average values.

Cupric ion retention measurements

A strip of a swelled membrane was weighted (approximately 1 g) and stirred during 3 hours in 0.05 mol/l CuCl₂ aqueous solution at 25°C. After this, the membrane was once washed with water and left to dry.

A portion of this membrane was weighted, digested with nitric acid and the copper content was measured in a Philips SP-9 atomic absorption spectrophotometer at λ = 238.4 nm with air/acetylene flame. The copper uptake was then reported as grams of Cu²⁺ per gram of dry membrane.

RESULTS AND DISCUSSION

The properties of **PEC** membranes are strongly dependent on the preparation conditions -pH, ionic strength, temperature, concentration and molar ratio of reacting polyelectrolytes, among others- and therefore it was a premise of this work that the membranes prepared should exhibit a reproducible behaviour.

This was accomplished by mixing equivalent amounts of chitosan and **CMC** solutions and lowering the pH of the mixture below 2. At this pH value the solution remains homogeneous, since the complex is not formed (8). The solution pH was then adjusted to the desired value by addition of dilute NaOH solution and the polyelectrolyte complex precipitated as small hydrogel particles. The mixture was then poured into a sintered glass filter in order to eliminate the supernatant solution and the solid was allowed to dry as a membrane when left at room temperature in a dry place for a few days. Following carefully this procedure it was possible to reproducibly obtain **PEC** membranes.
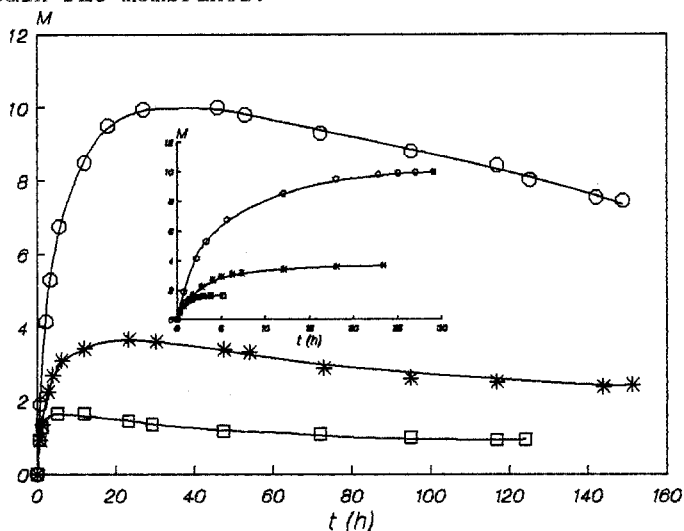

Figure 1 *Swelling curves of* **PEC** *membranes prepared at different pH values: pH = 4.2 (□); pH = 5.0 (*); pH = 5.7 (o)*

These membranes, though transparent and brittle in the dry state, became opaque and flexible when left for some time in a humid place, since because of their high hydrophilicity they easily adsorb water from the surrounding medium. This results in a lowering of Tg of the **PEC** due to the plasticizing effect of the adsorbed water.

The swelling behaviour of the membranes prepared at different pH values when immersed in water at 25°C is shown in Figure 1. The curves exhibit a characteristic pattern invariably found in these experiments: the membranes adsorb water at a considerable rate until a maximum swelling is achieved, but

for prolonged immersion times they steadily loose weight until a final equilibrium value is reached. The maximum swelling value, and the time at which it is attained, increases as the pH of formation of the **PEC** increases. This kind of dependence, of the swelling degree of the **PEC** with the pH value at which it was formed, has been reported before for **PECs** prepared from other weak polyelectrolytes (12).

During the first part of the swelling process -which is shown enhanced inside Figure 1- the maximum swelling is attained as a result of the equilibration between the osmotic force causing the penetration of water inside the membrane and the opposing elastic force of the stressed ionic network of the **PEC**.

It must be recalled that the **PEC** has been obtained by reacting equimolar quantities of **CMC** and chitosan hydrochloride according to Scheme 1.

Scheme 1:
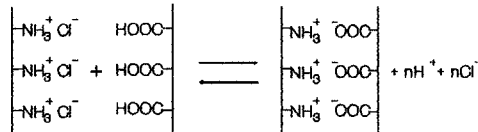
The degree of conversion, θ, -defined as the ratio of concentration of interchain salt bonds formed to the initial concentration of functional groups of any of the polyelectrolytes- , is strongly dependent on the pH of formation of the **PEC** (8, 13). It is evident that as θ increases the amount of free ionic groups in the **PEC** decreases and the complex becomes less hydrophilic.

The higher swelling capacity of membranes formed at pH 5.7 indicates that this **PEC** has more free ionic groups than the ones formed at pH 5 and 4.2. In other words, the degree of conversion, θ, of the **PECs** decreases as the pH of formation increases from 4 to 5.8. The high slope of the curve obtained when plotting the maximum swelling value, M_{max}, as

Figure 2 Dependence of (*) maximum swelling, M_{max}, and (□) equilibrium swelling, M_{eq}, on the pH of formation of the **PEC**

a function of the pH of formation of the **PEC** (Figure 2, curve 1) is a direct consequence of the strong dependence of θ on pH, typical of cooperative transitions.
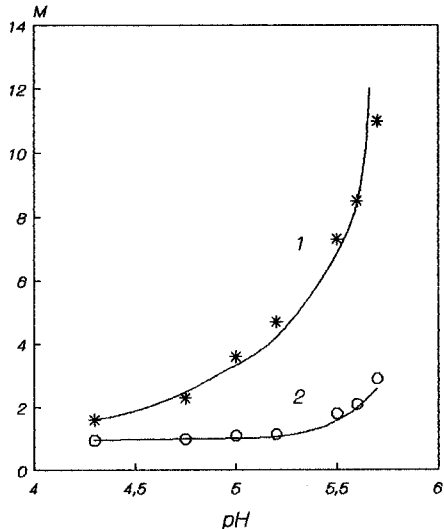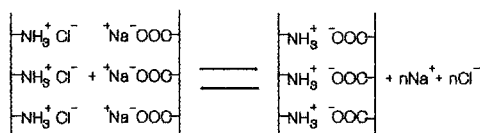
The steady shrinkage observed for these highly swelled

membranes when maintained immersed in water for a prolonged
period of time can be accounted for if one considers that at
the pH value at which swelling experiments were carried out
(pH = 5.5), the free carboxylic groups of **CMC** in the **PEC** are
present as sodium carboxylate and the free amino groups of
chitosan are protonated, so that new interpolyelectrolyte
saline bonds can be formed through the reaction depicted in
Scheme 2.

Scheme 2:

$$\begin{array}{ll} -NH_3^+ Cl^- & {}^+Na^- OOO- \\ -NH_3^+ Cl^- + {}^+Na^- OOO- \\ -NH_3^+ Cl^- & {}^+Na^- OOO- \end{array} \quad \rightleftharpoons \quad \begin{array}{l} -NH_3^+ {}^- OOO- \\ -NH_3^+ {}^- OOO- \\ -NH_3^+ {}^- OOO- \end{array} + nNa^+ + nCl^-$$

   This reaction is favoured by the migration of Na$^+$ and Cl$^-$
ions outside the membrane. The segmental mobility of the poly-
electrolyte chains in the swollen state should be sufficient
to allow the adequate spatial arrangements of the reacting
groups for this reaction to proceed. As a result of this, θ
increases, thus producing the observed steady shrinkage until
an equilibrium value, M_{eq}, is attained. It can be seen in
Figure 2 (curve 2) that M_{eq} tends, in all cases, to a similar
value, very close to M_{max} at pH 4.

   In order to verify this explanation the swelling of **PEC** membranes was studied in media with different ionic strength. Swelling experiments were carried out as before, but NaCl solutions were used as well as water. To this end, portions of the same membrane were subjected to different 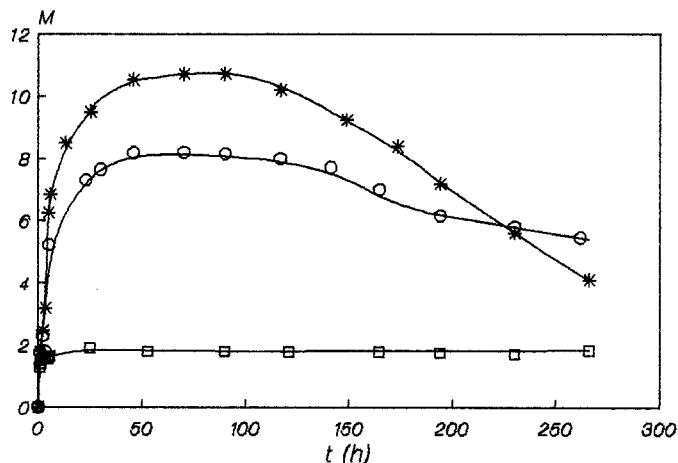saline concentrations and the results are shown in Figure 3. As in all other cases the points represent the average of three experiments.

Figure 3 *Swelling curves of* **PEC** *membranes formed at pH = 5.7 in solutions with different ionic strength: water (***); 0.001 mol/l NaCl (o); 1 mol/1 NaCl (□)*

   Two facts are manifested in this Figure: the lower value
of M_{max} in 10^{-3} mol/l NaCl solution as compared to M_{max} in wa-
ter, and the smaller fall in the degree of swelling with time

in the saline solution after the maximum swelling had been reached.

Under the above considerations this is to be expected, since in the presence of a 10^{-3} mol/l NaCl solution, the osmotic pressure inducing the penetration of water inside the membrane decreases, consequently, decreasing M_{max}. On the other side, the migration of Na$^+$ and Cl$^-$ ions out of the swelled membrane occurs in a minor extent when swelling is carried out in 10^{-3} mol/l NaCl solution due to the smaller concentration gradient of the solution inside and outside the membrane, thus producing a lower shrinkage. In the solution of much higher ionic strength (1 mol/l NaCl) there is a drastic decrease in M_{max}, and no further change in the swelling degree is observed.

The adsorption capacity for Cu^{2+} ions of the **PEC** membrane at different stages of the swelling process gives a further confirmation of the mechanism proposed. Since under the conditions selected for the experiments (pH = 5.5) the free amino groups are protonated, and the carboxylic groups are as carboxylate, the interaction of Cu^{2+} is expected to occur with the latter (14). As it can be seen in Figure 4, the higher retention capacity for Cu^{2+} ions is achieved when the membrane is at the maximum swelling state. It is smaller before reaching M_{max} because the -COO$^-$ groups are less accessible at lower swelling, and diminishes as time increases after reaching M_{max} because of the progressive decrease in free -COO$^-$ groups as the result of the reaction represented in Scheme 2.
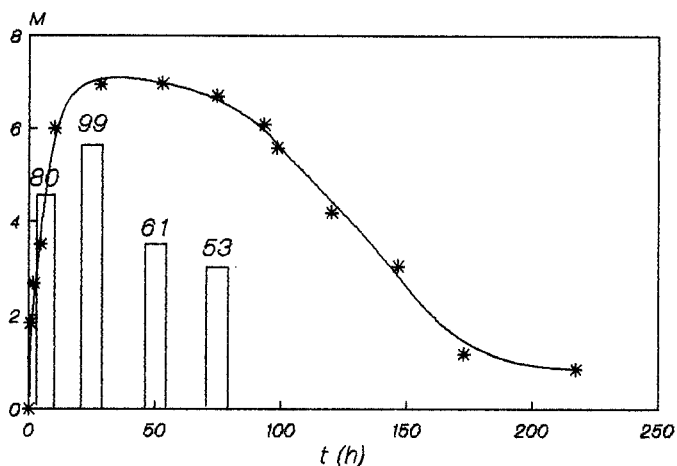

Figure 4 *Cupric ion retention at different stages of the swelling curve. The value at the top of each bar is the uptake in gr Cu per gr of membrane (**PEC** prepared at pH = 5.5)*

The diffusion-controlled uptake of polymer films and membranes can be expressed by (15):

$$\frac{M}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{-\pi^2 D(2n+1)^2 t}{4H^2}\right] \qquad [2]$$

where M_∞ is the maximum equilibrium uptake by the polymer film, M is the uptake at time t, D is the diffusion coefficient of the penetrating solvent, H is the thickness of the film and n is an integer. For long swelling times equation [2] can be approximated to

$$\ln\frac{M_\infty}{M_\infty-M}-\frac{\pi^2 Dt}{H^2} \qquad [3]$$

Equation [3] reproduces a first order rate equation as far as D and H are constant. However, Schott (16) has pointed out that for extensive swelling neither H nor D remain constant, and under these circumstances a first order kinetics does not apply. In his study of the swelling behaviour of gelatin and cellulose films he was able to fit the data to the empirical equation

$$\frac{t}{M}-A+Bt \qquad [4]$$

which he demonstrated that corresponds to a second order swelling kinetics. In this equation $B-\frac{1}{M_\infty}$, the reciprocal of maximum swelling and A is the reciprocal of the initial rate of swelling, since for short swelling times $A >> Bt$, and in the limit equation [4] becomes

$$\lim_{t\to 0}(\frac{dM}{dt})-\frac{1}{A} \qquad [5]$$

Figure 5 shows the straight lines obtained by applying equation [4] to the initial part -up to the maximum swollen state- of the swelling curves of PEC membranes represented in Figure 1. The excellent fits obtained at the three pH values studied indicate that this PEC membranes obey a second order swelling kinetics.

The values of M_∞ calculated with equation [4] were in good agreement with those obtained experimentally.

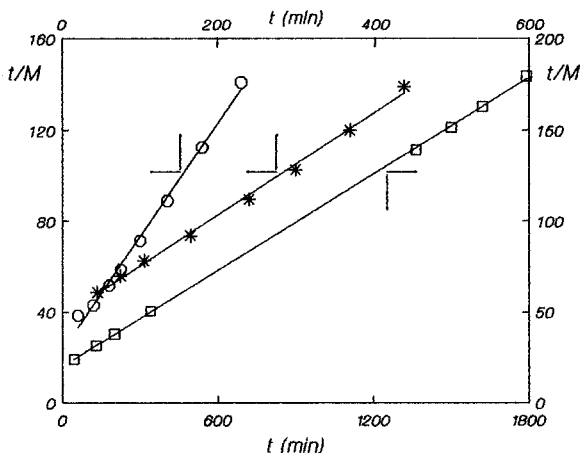Figure 5 Plots according to eq. [4] of the first period of PEC swelling curves shown in Fig. 1: pH = 4.2 (o); pH = 5.0 (*); pH = 5.7 (▯

Furthermore, the specific rate constants evaluated from the

aforementioned kinetic model increase as the pH of formation decreases, in concordance with the longer times required to attain the maximum swelling state at higher pH values.

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