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Study of the stoichiometric polyelectrolyte complex between chitosan and carboxymethyl cellulose

W. Argüelles-Monal[1], M. Gárciga[2], and C. Peniche-Covas[3]

[1]IMRE, University of Havana, 10400, Cuba
[2]Pharmaceutical Enterprise, Havana, Cuba
[3]Faculty of Chemistry, University of Havana, 10400, Cuba

SUMMARY

The polyelectrolyte complex (PEC) between chitosan and carboxymethyl cellulose was studied. Turbidimetric measurements revealed that the amount of stoichiometric PEC increased gradually as the solution of one polyelectrolyte was added to the other; the turbidity of the solution reached a maximum for the stoichiometric ratio of the reacting polyelectrolytes in the mixture. At pH 4,0 the composition of the complex is very near to equimolarity. IR spectra and thermal analysis of the PEC exhibited significant differences from those of the 1:1 mixture of the starting polyelectrolytes.

INTRODUCTION

The study of the formation and properties of polyelectrolyte complexes (PEC) has increased notably in the last years, not only due to the synthesis of new polyelectrolytes, but also due to the increasing interest on macromolecular electrolytes of natural origin. Chitosan (CHI), an amino polysaccharide derived from chitin, has not been an exception.

The first works devoted to the investigation of PECs using CHI as the polycation can be found in the last decade (1,2,3). In particular, the PEC formed between CHI and carboxymethyl cellulose (CMC) has been studied by Fukuda et al. (4,5) from the point of view of some formation conditions as well as the characteristics of the complex. The CHI-polyacrylic acid PEC has also been investigated (6,7).

In a recent paper (8) we have reported the study of the formation reaction of the stoichiometric complex CHI-CMC, where it was shown that the formation of the PEC starts at a pH value near 2,6 (θ=0,10) and that the reaction proceeds cooperatively.

In the present work the conditions for the formation of this complex were further investigated and the characterization of the PEC was attempted.

EXPERIMENTAL

Chitosan (CHI; $\bar{M}v=2,4\cdot10^5$, deacetilation degree 72%) was obtained from shells of lobsters (*Panulirus argus*) and purified as described elsewhere (8). Sodium carboxymethyl cellulose (CMC; BDH reagent, $\bar{M}v=7,7\cdot10^4$, substitution degree 0,7) was used without further purification.

Turbidimetric titrations were carried out at 25°C in a SPEKOL 11 equipment with the corresponding accessory at $\lambda=540$ nm. Potentiometric measurements were performed at the same temperature in a digital pH-meter with an error of 0,02 pH units. IR spectra were recorded in a SPECORD M-80 spectrophotometer using KBr pellets; thermal analysis were performed on a Labor MOM derivatograph model 1000 TIR (Labor MOM, Hungary). Curves were recorded on photo-sensitive paper and a heating rate of 10°C·min^{-1} in air. Elemental analysis of samples were kindly performed at the Institute of Polymer Chemistry of the GDR's Academy of Sciences.

RESULTS AND DISCUSSION

A stoichiometric polyelectrolyte complex (S-PEC) can be formed by mixing solutions of chitosan hydrochloride and CMC. In the present study CHI acts as a lyophilizing or host polyelectrolyte (HPE, $\bar{P}_{HPE}\simeq1000$) and CMC as the supporting or guest polyelectrolyte (GPE, $\bar{P}_{GPE}\simeq250$) (9).

Due to the insolubility of the S-PEC, its accumulation can be followed using turbidimetric methods. Fig. 1 shows the addition of a solution of the GPE (CMC) to that of the HPE (chitosan hydrochloride). It can be observed that in this case the stoichiometry of the PEC depends on the pH of the reacting medium. At pH 3,6 the PEC is rich in the polyacid, while at pH 4,8 the excess component is CHI. The non stoichiometry of the insoluble PEC is known to occur when one or both of the reacting components is a weak polyelectrolyte (10). An insoluble non-stoichiometric PEC (N-PEC) has already been reported for the CHI-polyacrylic acid system (6,7).

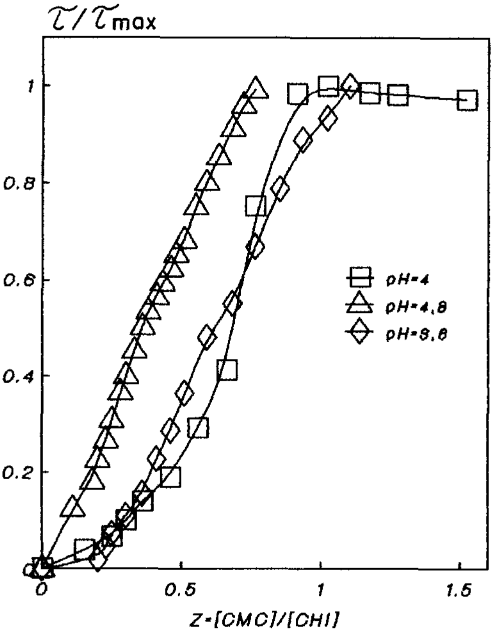


Fig. 1 Turbidimetric titrations curves of aqueous CMC solutions with CHI.

At pH ≅ 4 the turbidity increases with Z until it reaches a maximum at Z=1, (Z is the ratio between the molar concentration of the component present in deficient amount and the molar concentration of the component present in excess, that is Z= [CMC]/[CHI]) and remains constant for Z>1, where the precipitate of S-PEC coexists with a solution of the excess GPE, as represented in *Scheme 1*.

Scheme 1:

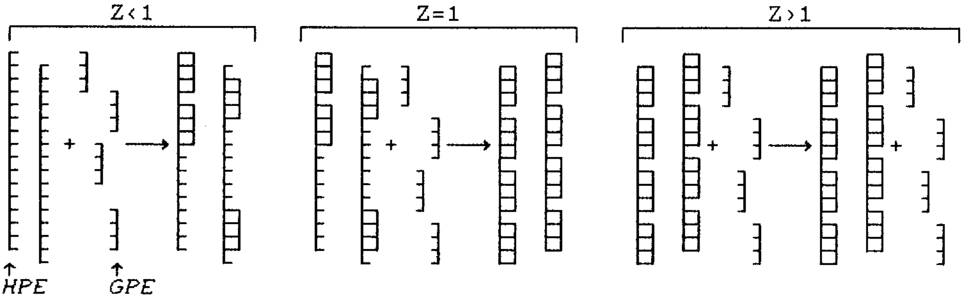


Fig. 2 shows the reverse effect, that is, the increase in the turbidity of the solution with the gradual addition of a solution of the HPE to the solution of the GPE at pH ≅ 4. The maximum turbidity also corresponds to an equivalent ratio of the polyelectrolytes in the system, Z=1 (now Z = [CHI]/[CMC]). Beyond this point, for Z>1, the turbidity is usually expected to decrease gradually with a further addition of the HPE, due to the formation of a soluble N-PEC as depicted in *Scheme 2*. Nevertheless it remained constant due to the insolubility of the N-PEC under these experimental conditions.

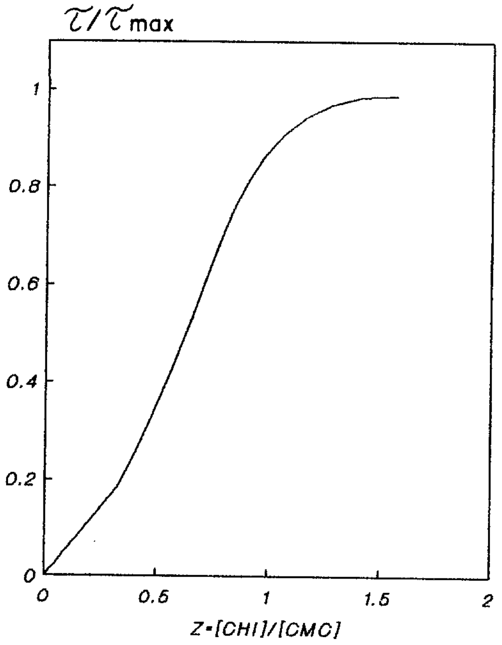
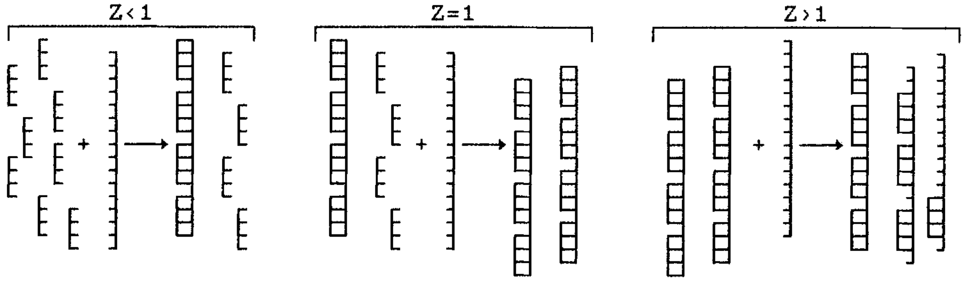


Fig. 2 Turbidimetric titration curve of aqueous CHI solutions with CMC.

In previous reports on the preparation and characterization of the PEC of CHI and CMC (4,5) no information is supplied on some relevant parameters, such as the molecular weight of the reacting polyelectrolytes and the deacetylation degree of CHI, and it is difficult to find a regularity as to the variation of the yield of PEC with the change on the precipitation conditions.

Scheme 2:



In view of the turbidimetric results just discussed we attempted to study the quantitative yield and characteristics of this PEC. To this end, CMC was dissolved in an aqueous solution of 0,1 mol·dm^{-3} NaCl, and CHI was dissolved in 0,1 mol·dm^{-3} HCl in the presence of the same concentration of NaCl. The polyelectrolyte concentration of the solutions was 4,0 g·dm^{-3}. pH was adjusted to 4,0 in both solutions which is a value in between those of 2,5 and 5,0 used by Fukuda et al. (4,5). In all experiments CMC solution was added dropwise to CHI solution in a similar way as in (4), but the PECs were washed only with deionized water.

Figure 3 (curve 1) shows the yields obtained in four different runs. It can be seen that for Z<1 the yield of PEC increase with the addition of CMC in the same way as did the turbidity of the medium during the turbidimetric measurements (Fig. 1), which is to be expected since they constitute equivalent experiments. It is worth noting the reproducibility obtained, as well as their correspondence with the theoretical

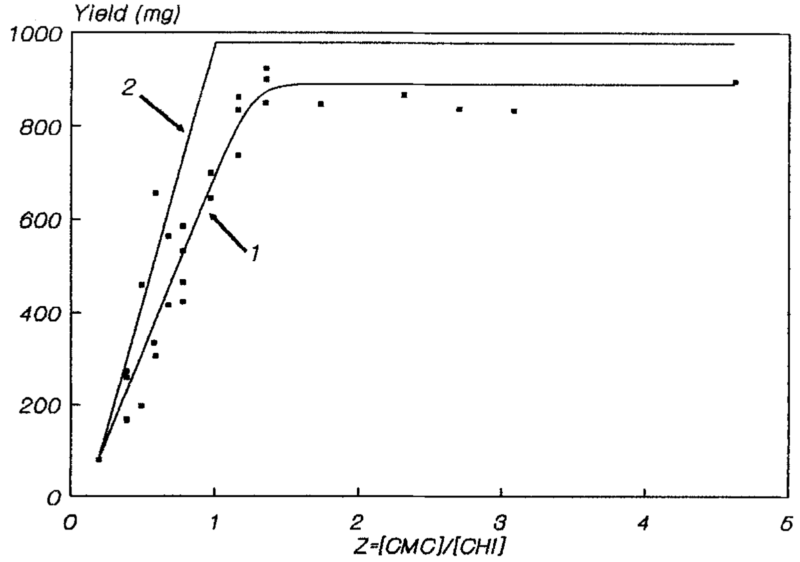


Fig. 3 Effect of the mixing ratio on the yield of insoluble PEC. 1-experimental; 2-theoretical.

yields calculated from the amount of equivalents reacted at each point (curve 2, Fig. 3). These yields are much higher than those previously reported (4,5). This could be due to partial solubilization of the PEC in the 0,01 mol·dm^{-3} HCl solutions used by these authors for washing, which would also explain the lack of regularity in their yields.

The composition of the PECs were determined by elemental analysis for $Z>1$, but for $Z<1$ they were obtained by potentiometric titration of the supernatant liquids after separation of the solids by centrifugation.

As it can be observed in Fig. 4 (curves 1, 2, and 3), there is a decrease in the concentration of CHI in the supernatant solution with the increase in the amount of CMC added for $Z<1$. Beyond the stoichiometric ratio, the excess of CMC added remains in the supernatant solution (Fig. 4, curve 4). As it was previously pointed out, this CMC (the guest polyelectrolyte) in excess cannot form a soluble N-PEC because of entropic reasons (9), and therefore it remains in solution.

The composition of the PECs obtained confirms in all cases the stoichiometry of the complex as revealed by the ratio N/COO$^-$ in Table 1. The formation of the PEC was accompanied by a decrease in the pH of the medium (Table 1), which is due to the participation of the undissociated carboxyl groups in the interpolyelectrolyte reaction:

$$\vdash\!NH_3^+\ Cl^- \ + \ HOOC\!\dashv \ \xrightarrow{\qquad\qquad} \ \vdash\!NH_3^+\ {}^-OOC\!\dashv \ + \ Cl^- \ + \ H^+ \qquad (1)$$

A consequence of reaction (1) is the linear dependence found for the increment of liberated protons on the increase in composition of the reacting system, Z, for $Z<1$ (Fig.5 curve 1). Conversely, a linear decrement on the amount of free protons is observed for $Z>1$, since the presence in solution of an excess

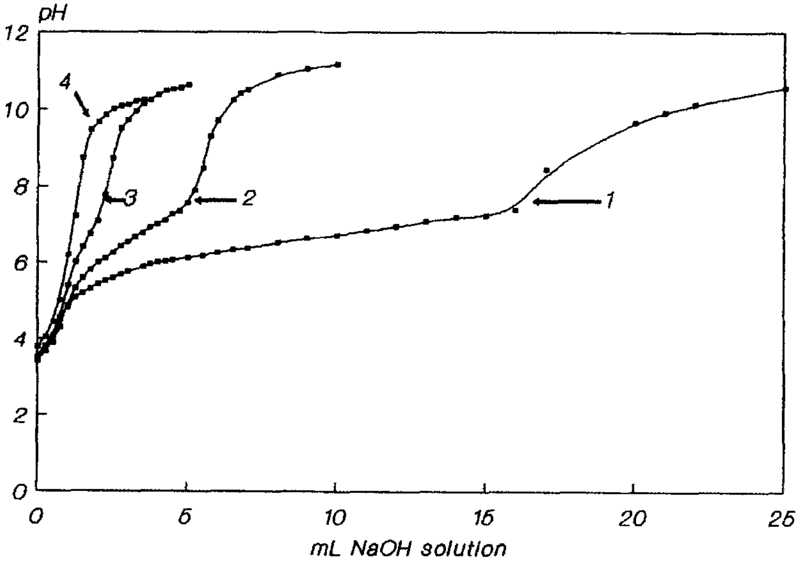


Fig. 4 Potentiometric titrations of the supernatant solutions (Vo=25 ml) with 0,01 mol·dm^{-3} NaOH.

Table 1 Yield and composition of the PEC obtained at different Z values and pH of the solution after the reaction (see the text for experimental conditions)

Z [CMC]/[CHI]	pH	Yield (mg)	Carbon in %	Nitrogen in %	N/COO$^-$
0.19	3.64	80	-	-	-
0.38	3.57	164	-	-	-
0.57	3.53	335	-	-	1.10
0.77	3.55	465	-	-	1.06
1.16	3.73	736	-	-	1.02
1.35	3.60	849	35.03	2.34	0.95
1.73	3.73	847	36.70	2.41	0.97
2.31	3.80	867	33.33	2.35	1.03
2.69	3.85	838	35.90	2.15	0.80
3.08	3.88	832	34.60	2.18	0.88

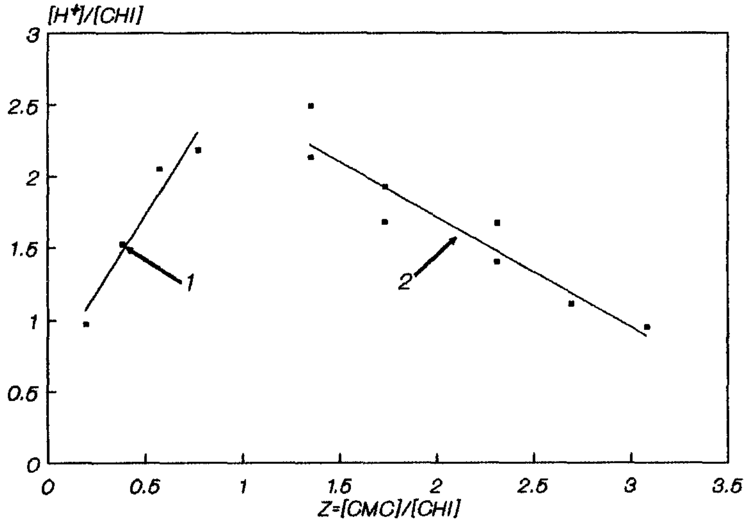


Fig. 5 Dependence of the amount of liberated protons on the composition of the reacting system.

of the supporting polyelectrolyte makes the equilibrium

$$\vdash COO^- + H^+ \longrightarrow \vdash COOH \tag{2}$$

shift to the right (Fig.5, curve 2). A similar effect, due to this buffering capacity of the polyelectrolyte in excess in solution, has also been observed for the system CHI-polyacrylic acid (7).

The IR spectrum of the PEC (Fig. 6) exhibits absorption bands around 1600 and 1410 cm^{-1}, attributed to the COO$^-$ groups, as well as other band at 1520 cm^{-1} characteristic of the protonated amino groups, which are all more intense than in the spectrum of the 1:1 physical mixture of the starting components. This, as it has been previously pointed out (4,7), is an evidence of the presence of interchain salt bonds in the PEC.

In Fig. 7 it can be seen that the thermal behaviour of the PEC differs from the one of the 1:1 physical mixture of the starting polyelectrolytes. The 1:1 mixture decomposes in four distinct stages, with a maximum rate of weight loss at 280°C; while the PEC is thermally less stable, with a maximum rate of weight loss at approximately 240°C, exhibiting at the most three distinct decomposition stages.

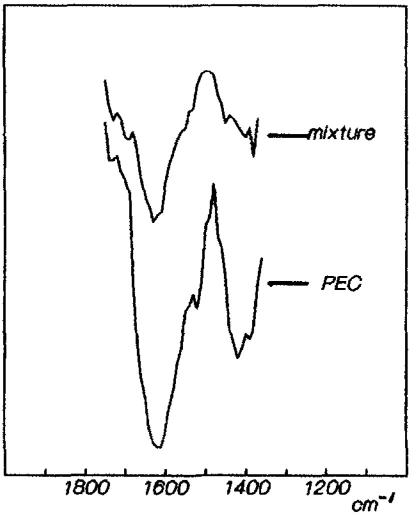


Fig. 6 IR spectra of the PEC and the 1:1 physical mixture of the starting polyelectrolytes.

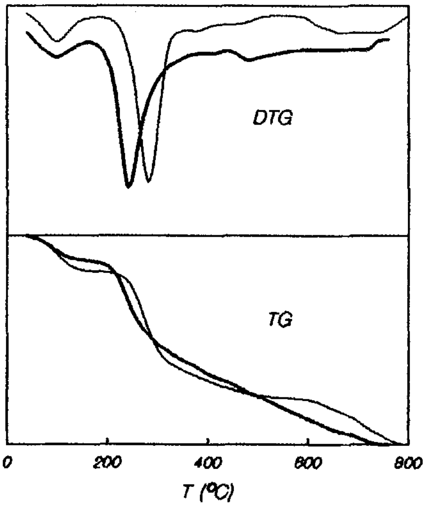


Fig. 7 Thermogravimetric and differential thermogravimetric curves of the PEC (▬) and the 1:1 physical mixture of the starting polyelectrolytes (—).

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