

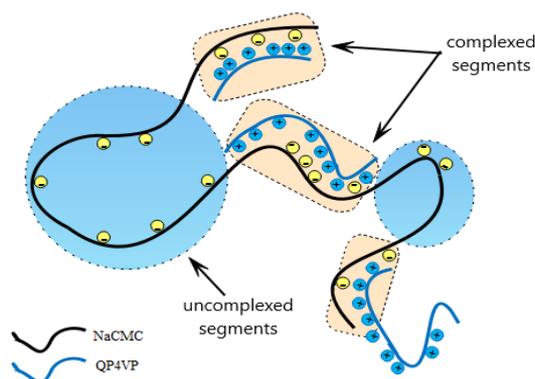
POLYELECTROLYTE COMPLEXES FORMATION BASED ON CARBOXYMETHYLCELLULOSE SODIUM SALT (NACMC) AND QUATERNIZED POLY(4-VINYLPYRIDINE) (QP4VP)

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Combining solutions of oppositely charged polyelectrolytes can lead to formation of polyelectrolyte complexes (PECs). PECs are a topic of considerable interest; we use them for a number of applications. We discuss here the formation and the rheological behavior of the polyanion-polycation system. It consists of a long chain carboxymethylcellulose sodium salt (NaCMC) and a short chain charged poly(4-vinylpyridine) (QP4VP). The rheological properties of this system were improved by studying some effects on complex behavior, such as polycation concentration, salt concentration and temperature variation. PEC exhibited a shear thinning behavior at low shear rate, then it became newtonian at higher shear rate. The increase in QP4VP concentration led to a remarkable rise in viscosity of the complex. After that, we remarked a loss in viscosity caused by a total complexation of NaCMC. As a consequence, the complex changed its conformation.



INTRODUCTION

Polyelectrolytes (PEs) have the tendency to form complexes with one or more oppositely charged ions forming polyelectrolyte complexes (PECs). A PEC is formed through cooperative electrostatic interactions, which are predominative, between polycations and polyanions upon mixing of aqueous solutions of oppositely charged PEs leading to the formation of a dense phase that is separated from the solvent.¹ PECs have already been studied in literature,^{2–8} they are found in many fields such as biomedical applications,^{9–11} flocculation,^{12,13} tissue engineering,¹⁴ paper making¹⁵ and many other applications.^{16,17}

Gardlund *et al.* described the most common method for complex formation which is the simple titration of polyelectrolytes,¹⁸ also called the drop-by-drop method. Its principle is to add slowly a polyelectrolyte solution (titrant) to another oppositely charged PE solution under stirring.

There are many studies on the rheological behavior of polyelectrolyte complexes carried out in our laboratory. Tennouga *et al.*^{19,20} studied the rheological behavior of hydrolyzed polyacrylamide-poly(4-vinylpyridine) (AD37-P4VP) polyelectrolyte complex with cationic surfactant dodecylpyridinium chloride (DPC) and with sodium dodecylsulfate (SDS) interactions in aqueous solution. Their results showed that complex interaction is favored

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in the presence of the DPC where electrostatic interactions were dominant. Three rheological behaviors were determined for (AD37-P4VP-DPC) system: shear thinning, shear thickening and Newtonian. For (AD37-P4VP-SDS) system, two characters were determined (Newtonian, and shear thinning).

Travan *et al.*²¹ studied the rheology of mixed alginate-hyaluronan (Alg/HA) aqueous solutions. The rheological study in their work encompassed steady flow and mechanical spectra for Alg/HA systems at different weight fractions with hyaluronan at different molecular weights. According to these extensive analyses, they can propose a model for the molecular arrangement in solution that envisages a mutual exclusion between the two polysaccharides even though a clear phase separation does not occur.

The study of rheological behavior for polyelectrolyte complexes was also investigated by Shuwei *et al.*²² between partially hydrolyzed polyacrylamide (HPAM) and xanthan (XG) in saline solutions. In their work, the results indicated that the calculation of relaxation time for the mixed solutions also demonstrated an interaction between the HPAM and xanthan in aqueous solutions.

Polyelectrolyte complexes based on carboxymethylcellulose sodium salt (NaCMC) polyanion have been studied in several previous studies.²³⁻³⁰ As for the poly(4-vinylpyridine) (P4VP), it is found in many works which described the complexation process.³¹⁻³³ On the other hand, few researches described the complexation process between NaCMC and QP4VP. H. Jin *et al.*³⁴ worked on the preparation of membranes based on NaCMC/QP4VP PECs used in the pervaporation dehydration of ethanol, which showed a high performance.

The main purpose of this work is to understand the interactions between NaCMC and QP4VP, also to study the effect of some parameters on rheological behavior of this system. For this fact, several experimental techniques such as conductivity, potentiometry and viscometry as well as other techniques have been used.

RESULTS AND DISCUSSION

FTIR analysis

The structures of polyions used in this work were confirmed by the presence of characteristic bands in the FTIR spectra shown in Fig.1, using a Fourier

Transform Infrared Spectral data (SHIMADZU 8400-FTIR).

FTIR spectrum of pure NaCMC showed a very strong absorbance at 3313 cm^{-1} , ascribed to the vibrations of intramolecular hydrogen bond. The shoulder at 2910 cm^{-1} was assigned to stretching vibrations of the C-H bond, strong peak at 1589 cm^{-1} and a very weak peak at 1267 cm^{-1} belonged to the stretching and bending vibrations in the carboxylate group and hydroxyl group, respectively. A medium peak at 1327 cm^{-1} was assigned to the stretching vibrations of C-O bond. Absorption band at 1058 and 1014 cm^{-1} reflected the bending vibrations of the ether, which represented the glycosidic linkage.

For QP4VP sample, bands at 1595 , 1556 , 1493 and 1414 cm^{-1} corresponding to C=N and C=C stretching in pyridine ring. Peaks at around 2800 - 3300 cm^{-1} were due to the aromatic and aliphatic C-H stretching.

The formation of PEC was confirmed by the presence of characteristic bands of the two polyelectrolytes QP4VP and NaCMC in the FTIR spectra of QP4VP/NaCMC complex. The C=N band in QP4VP is shifted from 1595 to 1636 cm^{-1} in the complex, this groups can form hydrogen bonding with carboxylic groups of NaCMC. This suggestion is confirmed also by the decrease of the intensity of C=O peaks, and it's shifting from 1589 to 1602 cm^{-1} . In addition, the strong reduction in intensity and displacement of hydroxyl groups from 3313 to 3344 cm^{-1} evidenced the formation of strong polyelectrolyte complexes. These results revealed that hydrogen bond forms between the pyridine group in QP4VP and OH groups in NaCMC (Fig. 2).

Complexation process followed by conductimetric and potentiometric titration

Figure 3 shows conductivity variation of NaCMC as a function of the added volume of QP4VP solution ($\alpha=0.6$). During titration process conductivity decreased, this can be explained by a charge screening (Fig. 4), linked to the combination of carboxylate groups (COO^-) and pyridinium groups (HN^+) during their random collisions in aqueous solution. Therefore, NaCMC/QP4VP complex was formed through the electrostatic interaction.

A proposed mechanism shown in Fig. 5 for PEC formation provided by electrostatic interactions can explain the experimental results that are presented in Fig. 3.

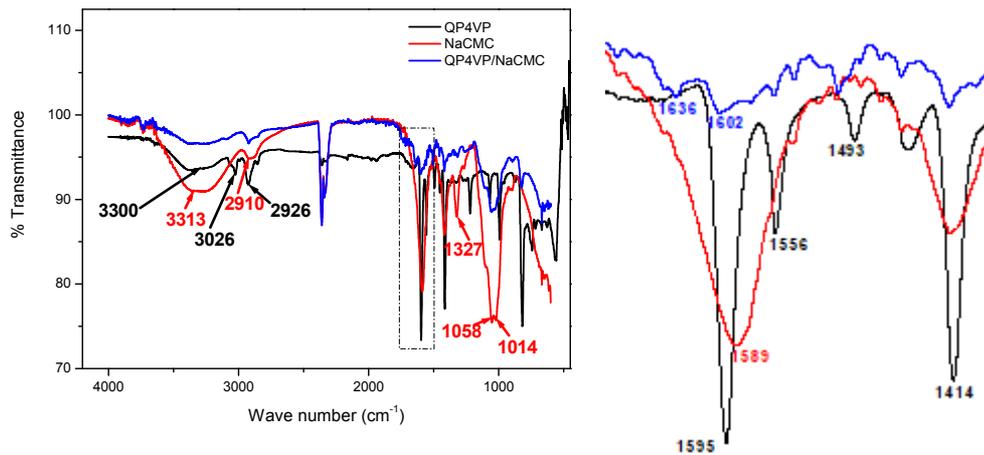


Fig. 1 – FTIR spectra of NaCMC, QP4VP and the polyelectrolyte complex.

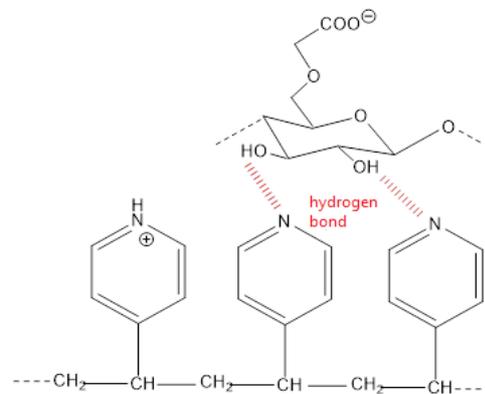


Fig. 2 – Proposed mechanism of hydrogen bonds formed during complexation process.

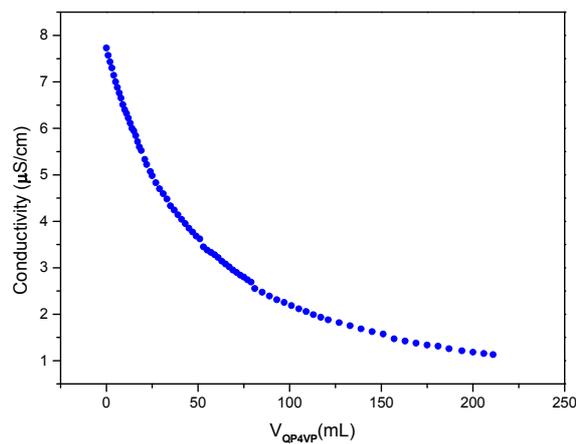


Fig. 3 – Conductivity variation of NaCMC as a function of the added volume of QP4VP, at 25 ± 0,1°C.

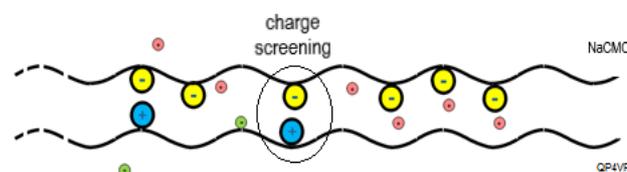


Fig. 4 – Proposed schema of charge screening phenomenon between the two polyelectrolytes.

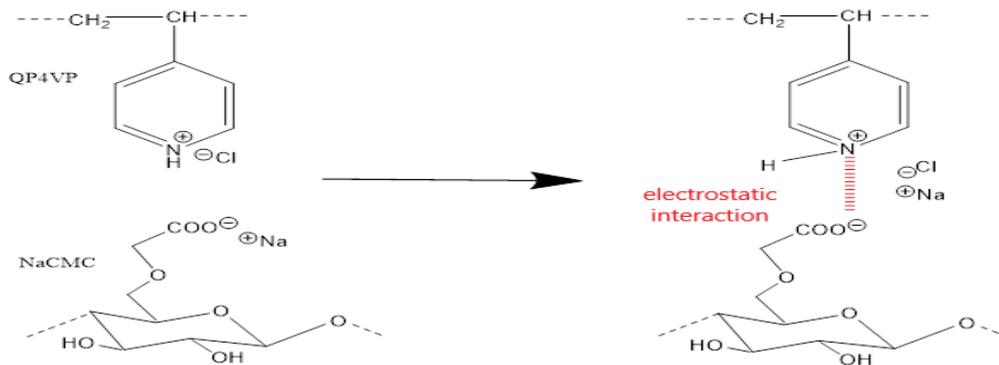


Fig. 5 – Proposed mechanism of electrostatic interactions between NaCMC and QP4VP.

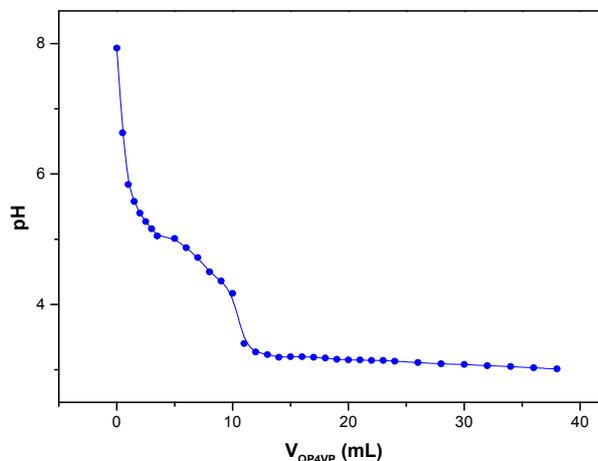


Fig. 6 – pH variation of NaCMC as a function of the added volume of QP4VP at 25± 0,1°C.

The pH changes when NaCMC solution is titrated by QP4VP solution are shown in Fig. 6. The decrease in pH at the beginning of titration followed by a stabilization, gives another explanation about complexation process between the two oppositely charged polyelectrolytes. The formation of complex is ensured by acid-base interaction between carboxylate function (COO⁻) of the polysaccharide and (HNCl⁺) function of the pyridine ring (Fig. 7). Consequently, the formation of hydrogen bonds between the two polyelectrolytes.

Rheological measurements

Rheological behavior of each polyelectrolyte sample

To evaluate the polymer concentration effect on rheological properties of each polyelectrolyte, flow behavior has been studied at different polymer concentrations, as shown in Fig. 8.

In Figure 8 (a), the increase of NaCMC concentration led to an increase in dynamic viscosity, which is absolutely logical. However, by increasing

the shear rate, polymer molecules are elongated in the shear direction which consequently reduces the viscosity of NaCMC. Moreover, when the polymer concentration is below the coil overlap concentration, a newtonian behavior is observed. On the other hand, the solutions exhibit a shear-thinning behavior when the polymer concentration is higher than $C^*=2.10^{-3}$ g/mL.

Dynamic viscosity change of QP4VP with different concentrations as a function of shear rate is illustrated in Figure 8 (b). It is observed that variation of polymer viscosity was not important in the case of all concentrations of QP4VP which have been chosen for this fact. Thus, this behavior is considered newtonian.

Rheological behavior of NaCMC/QP4VP complex

Effect of QP4VP concentration on rheological behavior of complex

The rheological method is one of the most widely used techniques for the determination of dynamic viscosity of polyelectrolyte complexes

(PECs) and to examining the polymer-polymer interaction. Since NaCMC-QP4VP interaction causes structural changes in the solution, it can be assumed that they will be sensitive to shear rate influence during rheological measurements.

The influence of QP4VP concentration on rheological characteristics of this system was investigated at fixed NaCMC concentration equal to $5 \cdot 10^{-3}$ g/mL, and at QP4VP concentrations ranging from 10^{-6} g/mL to $2,5 \cdot 10^{-4}$ g/mL.

The variation of dynamic viscosity of PECs as a function of shear rate at $25 \pm 0.1^\circ\text{C}$ is presented in Figure 9. A shear thinning behavior is observed for NaCMC/QP4VP complex. From this figure, we observed that the increase in QP4VP concentration led to an increase in the complex viscosity, which can be explained by complexation provided by the interactions formed (Figure 10), until a QP4VP

concentration g/mL. Above this value the viscosity dropped from 340 to 222 mPa.s and remained almost constant afterward. This can be explained by the passage of complex chains from one conformation to another i.e. the complexation reaches the end point and the chains of the PEC shrink and take the form of coil structure.

Effect of salt on rheological behavior of complex

The ionic strength is an important parameter in complex coacervation. Above a certain salt concentration, no complexation will occur as all charges are screened. We examined the effect of increasing concentrations of monovalent salt (NaCl) on complex viscosity as a function of shear rate at $25 \pm 0.1^\circ\text{C}$ (Fig. 11).

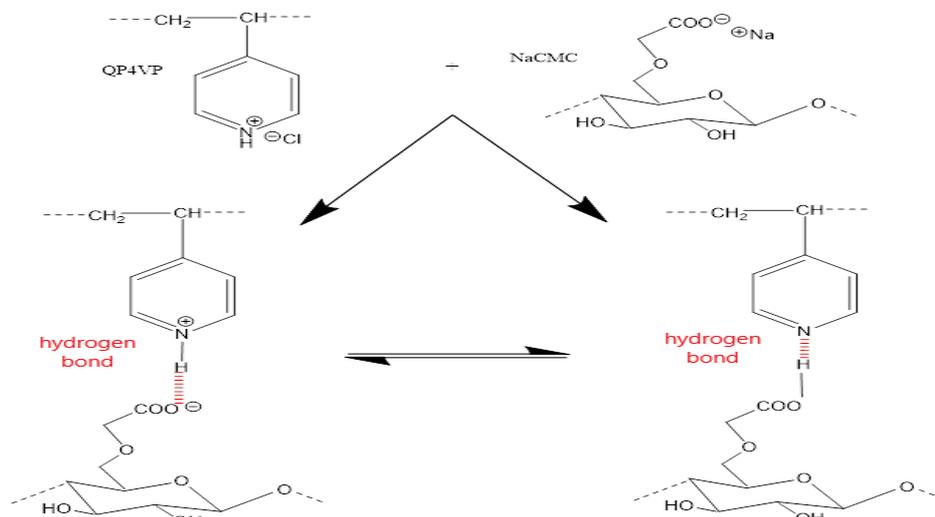


Fig. 7 – Proposed mechanism for the formation of hydrogen bonds between NaCMC and QP4VP.

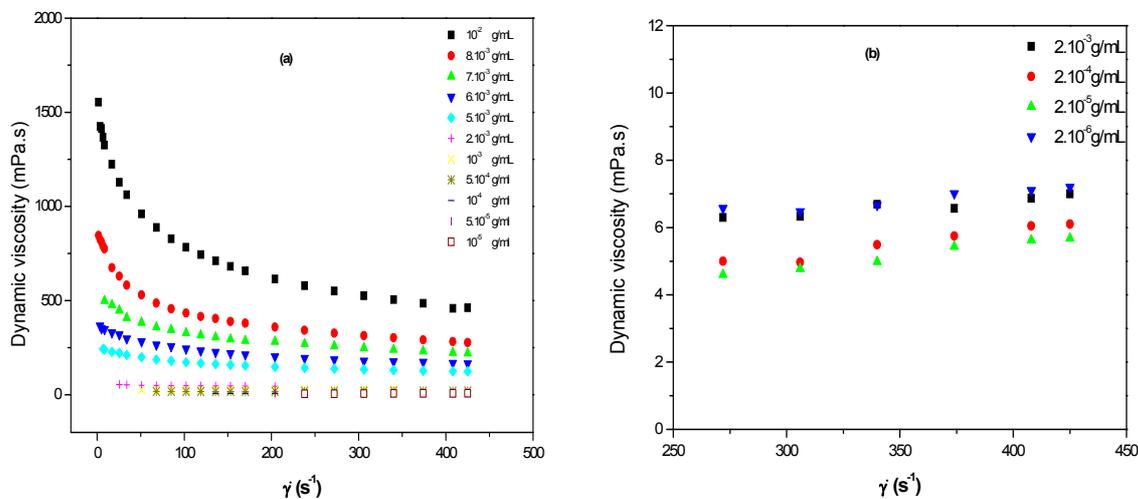


Fig. 8 – Dynamic viscosity change of NaCMC (a) and QP4VP (b) at different concentrations as a function of shear rate, at $25 \pm 0.1^\circ\text{C}$.

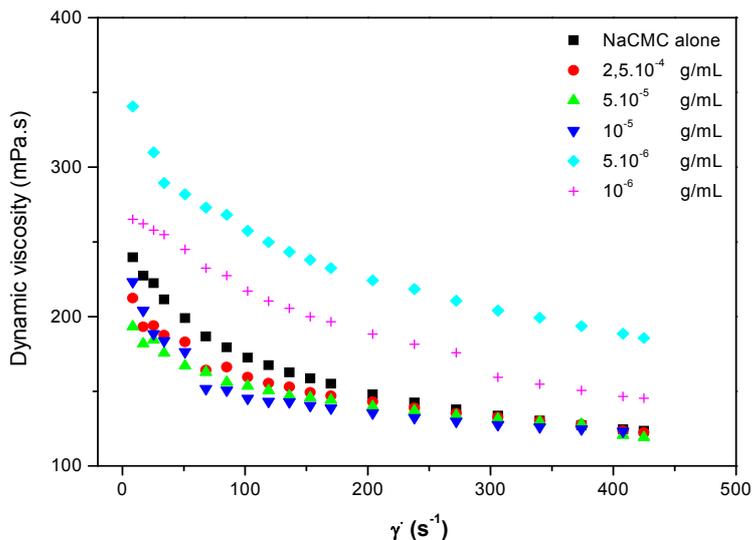


Fig. 9 – Dynamic viscosity variation of the polyelectrolyte complex versus shear rate at fixed concentration of $C_{NaCMC}=5.10^{-3}$ g/mL and for different concentrations of C_{QP4VP} 10^{-6} , 5.10^{-6} , 10^{-5} , 5.10^{-5} and $2,5.10^{-4}$ g/mL at $25 \pm 0,1^{\circ}C$.

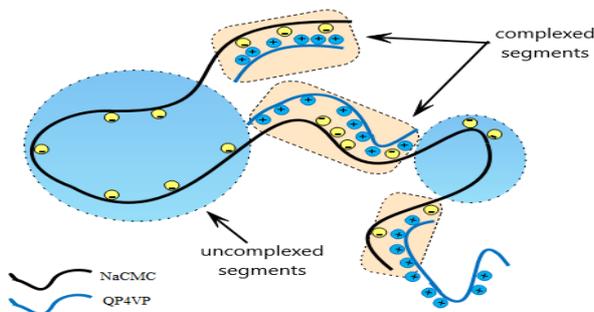


Fig. 10 – Proposed scheme represents the interactions responsible for the complexation between NaCMC and QP4VP.

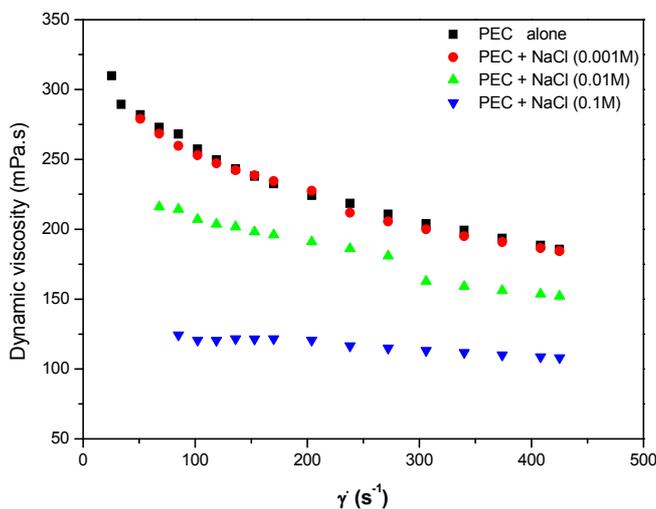


Fig. 11 – Dynamic viscosity variation of the complex NaCMC/QP4VP= $5.10^{-3} /5.10^{-6}$ g/mL alone and at different salt concentrations C_{NaCl} (0.001; 0.01 and 0.1M) at $25 \pm 0,1^{\circ}C$.

The non-Newtonian behavior of the complex is related to the non-Newtonian behavior (shear thinning) of the polysaccharide derivative (NaCMC), and this is due to the electrostatic interactions which

result in the loss of flexibility and mobility of the polymer. However, the reaction is favored by the gain in enthalpy and entropy due to the release of counterions and water molecules.^{35,36}

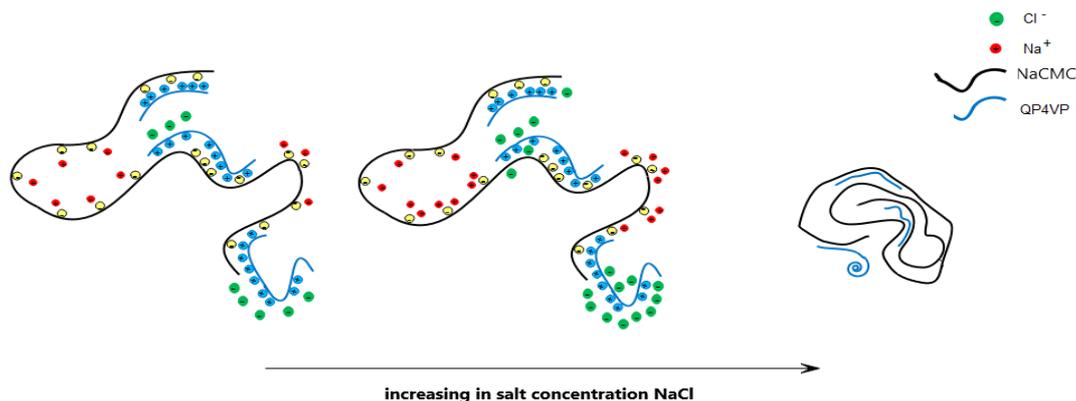


Fig. 12 – Proposed scheme explains the effect of salt.

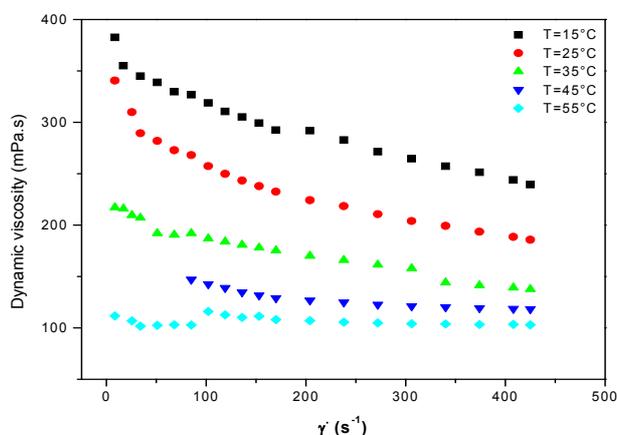


Fig. 13 – Dynamic viscosity variation of the complex NaCMC/QP4VP=5.10⁻³ / 5.10⁻⁶g/mL as a function of shear rate at different temperatures (T= 15°, 25°, 35°, 45° & 55°C).

The viscosity of PEC solution containing a small amount of salt was low compared to that in absence of NaCl. The addition of a larger amount of salt (0.01M) produced a higher decrease than the first one. It is noted that in the presence of an enough amount of salt (0.1M), the polyelectrolyte complex loses its charge by electrostatic screening, and its behavior consequently became Newtonian. Therefore, when we added the salt which has a destabilizing effect, the complex loses its viscosity because it changed its conformation to a coil structure (Fig. 12) and its behavior became Newtonian. The electrostatic interactions between NaCMC and QP4VP were not strong enough to compensate for the destabilizing effect of the salt.

Effect of temperature on rheological behavior of complex

Figure 13 shows the variation of dynamic viscosity of PEC as a function of shear rate at different temperatures values.

Temperature influences the PECs behavior by favoring the hydrophobic and covalent interactions

at high temperatures and the hydrogen bonding at low temperatures.³⁷ From Figure 13, we noticed that the viscosity of complex gradually decreased during heating between 15 and 55 °C, and its shear-thinning behavior disappeared at high temperature, because the thermal stirring favors the sliding of the chains relative to each other and the viscosity decreases until reaching a threshold value at which the behavior will change from shear thinning to Newtonian.

MATERIALS AND METHODS

Materials

Carboxymethylcellulose Sodium salt (NaCMC) (from PROLABO) was designated by the degree of carboxymethylation (DS) values included between [0.82-0.95] given by PROLABO. Its average molecular weight was made by viscometry technique. 4-vinylpyridine (4VP, 95%) was distilled under reduced pressure, hydrochloric acid (HCl, 35-38%),

toluene, methanol, ethyl ether and benzoyl peroxide, were obtained from Sigma-Aldrich. Sodium hydroxide and sodium chloride were supplied by Riedel de Haën and Cheminova respectively.

Poly(4-vinylpyridine) synthesis

Poly(4-vinylpyridine) (P4VP) was prepared by radical polymerization of 4-vinylpyridine in chloroform, using azobis(isobutyronitrile) (AIBN) as initiator, as described elsewhere⁷. Its molecular weights ($M_n=22633$, $M_w=43258$ and $M_v=68383$ g/mol) were determined by Steric Exclusion Chromatography (SEC) using Alliance 2690 (USA) with PSS columns, combined with multiangle light scattering (MALS) detectors from Wyatt technology corps, USA (University of PAU and Pays de L'Adour, France). P4VP solutions were injected at a concentration of about 5 mg/mL. Samples were prepared by dissolution of the polymers in DMF 0.5g/L Toluene 0.1g/L LiCl solutions and filtered on 0.45 μm filter (Millipore). The data were collected and analyzed by using the ASTRA SEC software (version 4.90, Wyatt Technology Corp, USA). The calculations of molar mass were carried out according to the Zimm fit method.

Preparation of quaternized poly(4-vinylpyridine)

A volume of methanol 12.5 mL was added to an amount of pure P4VP introduced into a graduated flask of 25 mL under stirring. A quantity of HCl was added in order to adjust the neutralization degree ($\alpha=0.25$ and 0.6). After that, the volume was adjusted with distilled water to 25 mL and stirred during 3 days at room temperature.

Preparation of polyanion (NaCMC) solutions

The aqueous solutions of NaCMC were prepared by dissolving a known amount of polymer in distilled water under constant stirring until complete hydration of the polymer. The other concentrations were prepared by diluting the stock solution for about 25–30 min under stirring.

A standard Ubbelohde capillary viscometer, with a thermostated bath at $25.0 \pm 0.1^\circ\text{C}$ was used to determine its molecular weight using Mark-Houwink law³⁸.

The determined intrinsic viscosity was of the order of 556.10 mL/g. Using this value, we calculated

the viscometric molecular weight of NaCMC which was of the order of 316405 g/mol according to Mark-Houwink law (eq. 1) and we deduced also the coil overlap concentration (C^*) by Frish's and Simba's relation³⁹ (eq. 2) which was of the order of 2.10^{-3} g/mL.

$$[\eta] = 5,37.10^{-4} . M_v^{0,73} \quad (1)$$

$$C^* = \frac{1}{[\eta]} \quad (2)$$

Methods

In this study, we adopted two methods to prepare the polyelectrolyte complexes (PECs). The first one consisted in adding the polycation QP4VP to the NaCMC polyanion solution by “drop-by-drop” addition. We used both potentiometric and conductimetric titrations to study the complexation process of PECs prepared by this procedure.

The second method consisted in preparing the reaction mixture by “one shot” addition under stirring at 300 rpm for 1h. The resulting complexes were characterized by Fourier Transform Infrared Spectral data. The rheological properties were done by a rheometer Brookfield model DV-III+.

Conductimetric and potentiometric measurements

Conductimetric and potentiometric titrations were carried out in a glass cell at $25 \pm 0.1^\circ\text{C}$. For that purpose, a CDM 210 conductimeter (Radiometer, Meter Lab) and a potentiometer Denver instrument model 225 (pH +ISE meter) were employed. The variation of conductivity and pH of NaCMC solutions as a function of QP4VP solutions were obtained under stirring at 300 rpm.

Rheological measurements

All reaction mixtures were prepared at ambient temperature. The rheological measurements were performed using a rheometer Brookfield DV-III+ type. QP4VP concentration effect on the rheological properties of this system was investigated at fixed NaCMC concentration ($C_{\text{NaCMC}}=10^{-2}$ g/mL), and for various concentrations (C_{QP4VP} ranging from 10^{-6} g/mL to $2,5.10^{-2}$ g/mL), at $25.0 \pm 0.1^\circ\text{C}$. The effects of salt and temperature on the rheological behavior of complex mixtures were quantified.

CONCLUSIONS

The complexation between Carboxymethylcellulose Sodium salt (NaCMC) and quaternized poly (4-vinylpyridine) (QP4VP) occurred upon mixing of solutions. Conductivity and potentiometric titration of NaCMC by QP4VP with different concentration ratios and with a degree of neutralization equal to 0.6 showed that the formation of complex ensured by electrostatic interactions between negative charges of carboxylate function (COO^-) and positively charged nitrogen atom of the pyridinium ring (HN^+), as well as hydrogen bonding. Characterization by infrared spectroscopy also shows the existence of electrostatic interactions and hydrogen bonds.

We also showed by the rheological study of our system the influence of some parameters on behavior of complexes formed. The behavior of NaCMC/QP4VP complex as a function of shear rate exhibited a shear thinning character. More the concentration of polycation increases more the viscosity increases, which indicates that the complexation is ensured by electrostatic interactions up to a threshold concentration of QP4VP at which the viscosity of the complex drops, this is the end point. Reaching this stage indicates that the majority of the charges are complexed, and the complex takes the form of a coil structure. The addition of salt, which has a destabilizing effect, reduces the viscosity of the complex by electrostatic screening. The increase in temperature facilitates the sliding of the complex chains relative to each other which reduces the viscosity and the behavior becomes Newtonian.

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