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Rheological and electrokinetic properties of carboxymethylcellulose-water dispersions in the presence of salts

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The purpose of this work is to investigate the effect of the addition of salts in the form of calcium chloride, sodium chloride and potassium chloride on the rheological and electrokinetic properties of diluted sodium carboxymethylcellulose (Na-CMC) dispersions (0.50%). The rheological data of a water-CMC-salt system were obtained using coaxial cylinder viscometer covering a wide range of shear rate (0 to 600 s^{-1}). Ostwald–de Waele power law was used for fitting flow curves of various samples. The presence of salts in CMC aqueous solutions leads to the reduction of the consistency index and the increase of flow index as salinity increases. When the concentration of salts is greater than 3%, the rheological parameters of CMC solutions in saline medium are quasi stable. The electrokinetic measurements show an increase of the zeta potential of CMC dispersions when the concentration of salts in solution increases. Calcium chloride caused the greatest increase in zeta potential. Excluding the monovalent cations, the divalent cation is able to reverse the sign of the zeta potential from negative to positive.

Key words: Rheology, zeta potential, salt, carboxymethylcellulose sodium (CMC).

INTRODUCTION

Polymers, such as cellulose derivatives (Kok and Alikaya, 2005; Benyounes et al., 2007, 2010; Hughes et al., 1993), biopolymers (Xie and Lecourtier, 1992; Navarrete et al., 2001) and guar gum (Sharma and Mahto, 2006) were introduced in the water based drilling fluids for their rheological performance and for ecological considerations. In comparison with other natural polymers, the cellulose derivative is the most used because it is biodegradable and compatible with other materials. Carboxymethylcellulose (CMC) is produced by reacting cellulose obtained from wood pulp or cotton fibers with chloroacetic acid and NaOH. The presence of polar carboxyl groups makes the cellulose soluble, chemically reactive and strongly hydrophilic (Wang et al., 2011). CMC is a white to almost white powder, non-toxic and biodegradable, odorless and does not ferment under normal conditions of use. It is also a low-cost commercial soluble and it can be dissolved in hot or cold water. It is largely used in industry, due to its exceptional rheological properties in aqueous solutions. It is also employed as an additive in food industry (Gómez-Díaz and Navaza, 2002, 2003; Yasar et al., 2007) and pharmaceuticals (Kamel et al., 2008). The rheological properties of CMC depends of the concentration in polymer and the degree of substitution which varies from 0.5 to 1.2 (deButts et al., 1957; Barba et al., 2002). Aqueous solutions of CMC are stable at pH 2 to 10. Precipitation can occur below pH 2, and solution viscosity decreases rapidly above pH 10. Generally, solutions exhibit maximum viscosity and stability at pH 7 to 9 (Rowe et al., 2006). CMC is regarded as a polyelectrolyte, once it is dissolved in water, the Na-CMC molecule is separated into sodium cations and into anionic polymer. Ghannam and Esmail (1997) have shown that the CMC dispersions exhibited

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thixotropic and viscoelastic behavior at high CMC concentrations. Kulicke et al. (1996) found out that the rheological behavior of CMC solution is dominated mainly by the molar mass and the concentration of polymer. Edali et al. (2001) have studied the rheological properties of CMC solutions at high concentrations by using rheometer, they concluded that the solutions showed rheopexy behavior for very small shear rates and they have not detected the yield stress. Yang et al. (2007) investigated the influences of several salt ions, glycerin, konjac glucomannan (KGM) on the viscosity of CMC at higher concentrations; they reported that the increase of molar concentration of aluminium salt leads to the increase of the viscosity of CMC solution. Sharma et al. (2010) measured the intrinsic viscosities of sodium carboxymethylcellulose (Na-CMC) in water and ethylene glycol-water mixed solvent media, they revealed that for a given salt concentration, the values of intrinsic viscosities of CMC decrease as the solution becomes richer in ethylene glycol. Several papers were published regarding the influence of CMC on the rheological properties of clay dispersions (Hughes et al., 1993; Amorim et al., 2007; Benchabane and Bekkour, 2006; Benyounes et al., 2010; Benyounes et al., 2010a; Kelessidis et al., 2011). However, little published information is available on rheological behavior and electrokinetic of CMC in the presence of electrolyte (Matsumoto and Mashiko, 1988; Yang and Zhu, 2007; Sharma et al., 2010). The aim of this work is to study the effect of salts, such as NaCl, KCl and CaCl$_2$ on the rheological parameters and zeta potential of CMC solutions. For this reason, the rheological and electrokinetic properties of CMC solutions at different salt concentrations (0.05 to 6.00%) are studied.

MATERIALS AND METHODS

Solutions preparation

The Na-CMC used in this work wassupplied from Sigma-Aldrich. Its molar mass is 700,000 g/mol, with the degree of substitution in the range of 0.65 and 0.85. The complete dissolution of the polymer in the water requires a lot of time, depending on temperature, concentration polymer and ionic strength. Therefore, aqueous solutions of CMC in absence of salt were prepared by dissolving the appropriate amount of CMC in distilled water at room temperature. All samples were stirred magnetically for 24 h at low speed, in order to avoid the formation of air bubbles and promote good hydration of the polymer.

The preparation of CMC solutions in the presence of salts is made by the addition of the desired quantity of electrolyte in aqueous solution of CMC aged of 24 h. The obtained mixture is stirred for about 12 h.

Rheological measurement

The rheological measurements were carried out on a VT550 rotational viscometer. This apparatus was equipped with concentric

cylinder geometry of outer radius of 21 mm and gap width of 1.64 mm. The shear rates were in the range 0 to 600 s^{-1}. For all measurements, the temperature was kept constant at 20°C, and it was controlled using a circulating wash bath. After filling the cup, the sample was presheared during 1 min at shear rate of 100 s^{-1} followed of 1 min of rest.

Electrokinetical measurement

The electrokinetic tests of CMC in various electrolyte solutions were measured with an automated electrophoresis instrument (Zetasizer 2000, Malvern Instruments Ltd., Malvern, UK) equipped with a microprocessor unit. The unit calculates the electrophoretic mobility of the particles and converts it to the zeta potential using the Smoluchowski equation (Hunter, 1981) as follows:

$$\zeta = \frac{4\pi V_t}{D_t} xEM \qquad (1)$$

where EM is electrophoretic mobility at given temperature, V_t is viscosity of the aqueous medium, D_t is dielectric constant, π is constant and ζ is the zeta potential.

Each zeta potential value is the average of five data, using standard deviation as experimental error of measurements.

RESULTS AND DISCUSSION

In this study, we carried out a series of rheological tests in steady state flow on CMC solutions in the presence of several salts (NaCl, KCl and CaCl$_2$). The concentration of each type of salts varies between 0.05 and 6%, while the concentration of CMC is set at 0.50%. Benchabane and Bekkour (2008) and Clasen and Kulicke (2001) conducted some rheological tests on the solutions of CMC to search the critical concentration which marks the limit between the dilute and semi-dilute regime. They found out that the critical concentration of CMC solution was 1%. The CMC solution at 0.5% is clearly below the critical concentration. In this case, chains polymer are remote and isolated the ones as compared to others, and interactions between the polymer and solvent are dominant. The interactions between the polymer chains are limited and the macromolecule stretches at maximum (Figure 1a). The variation of the shear stress as a function of shear rate of systems CMC/KCl, CMC/NaCl and CMC/CaCl$_2$ at different concentrations of salts are as shown in Figures 2, 3 and 4. For the three type of salts, one can notice that the shear stress increases when the shear rate increases. A pseudoplastic flow (a nonlinear relationship between shear stress and shear rate) was observed for all the samples (Figures 2 to 4). Many authors reported that the rheological behaviour of CMC solutions at various concentrations and molecular weights are non-Newtonian pseudoplastic (Benchabane and Bekkour, 2008; Benyounes et al., 2007; Edali et al., 2001; Ghannam and Esmail, 1997; Gómez-Díaz and Navaza, 2002; Yang and Zhu 2007). In the absence of salts, the different rheogramms show the absence of
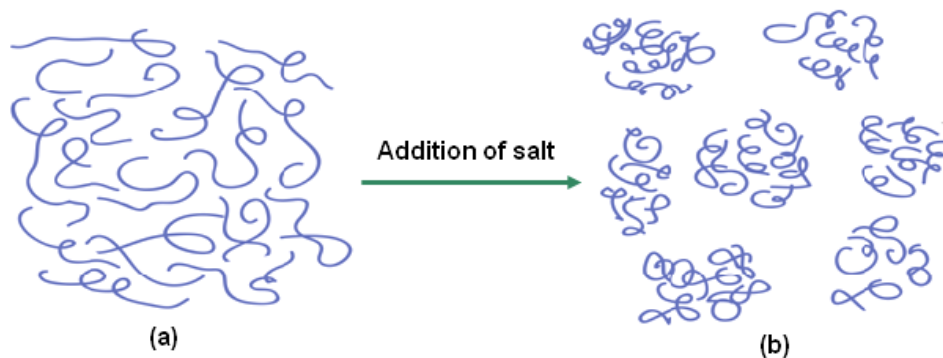
Figure 1. Structure of CMC chains: (a) in the absence of salts and (b) in the presence of salts.
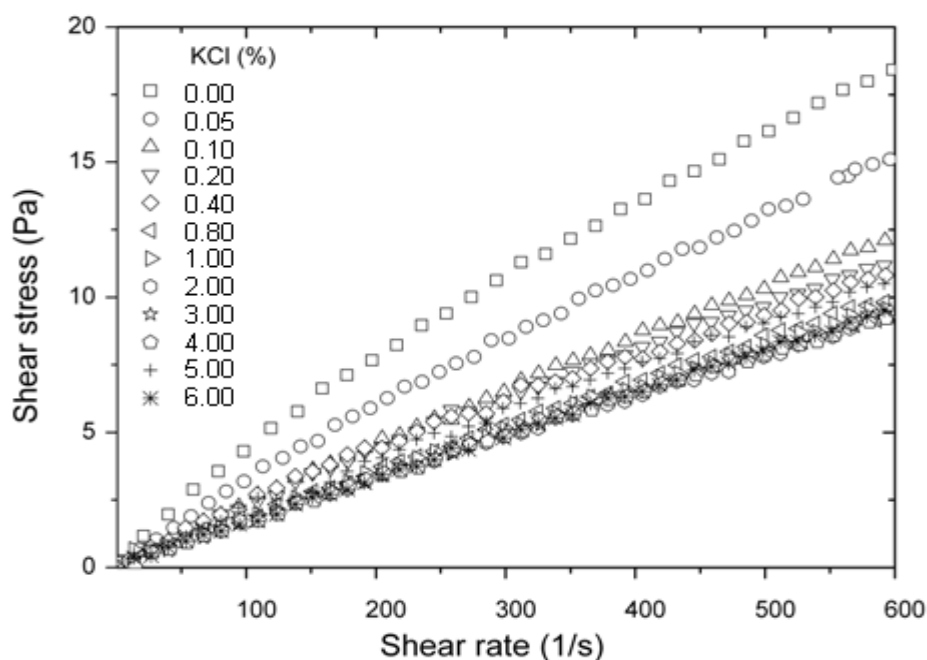
Figure 2. Flow curves of CMC dispersion at different concentrations of KCl.

yield stress. This can be attributed to the disentanglements of polymer chains, on account of dilute regime of polymer solution and also of the flexible character of the polymer. Benyounes (2010b) carried out the dynamic test on the CMC solution in the absence of salt. The results obtained show that the CMC solution has a viscous nature for a polymer concentration less than 1% and confirm well the absence of yield stress for CMC solution at 0.5%. It can be clearly seen that the addition of salts in polymer solutions does not lead to the appearance of yield stress.

The flow curves for all CMC solutions containing the electrolytes were situated below the curve of the salt-free CMC solution, and therefore, the apparent viscosity of these dispersions are lower. We remark also that, at constant shear rate, increase of salt concentration was conducted to the decrease of the shear stress.

As the flow curves are nonlinear and the yield stress does not appear in the rheogramms, it is obvious that the Ostwald-de Waele rheological model can be utilized to fit flow curves of CMC solutions due its simplicity, which is defined as follows:

$$\tau = k.\dot{\gamma}^n$$

(2)

where τ is the shear stress, k is the consistency index, $\dot{\gamma}$ is the shear rate and n represents the flow index that characterizes a material. If n=1, the fluids is Newtonian; if
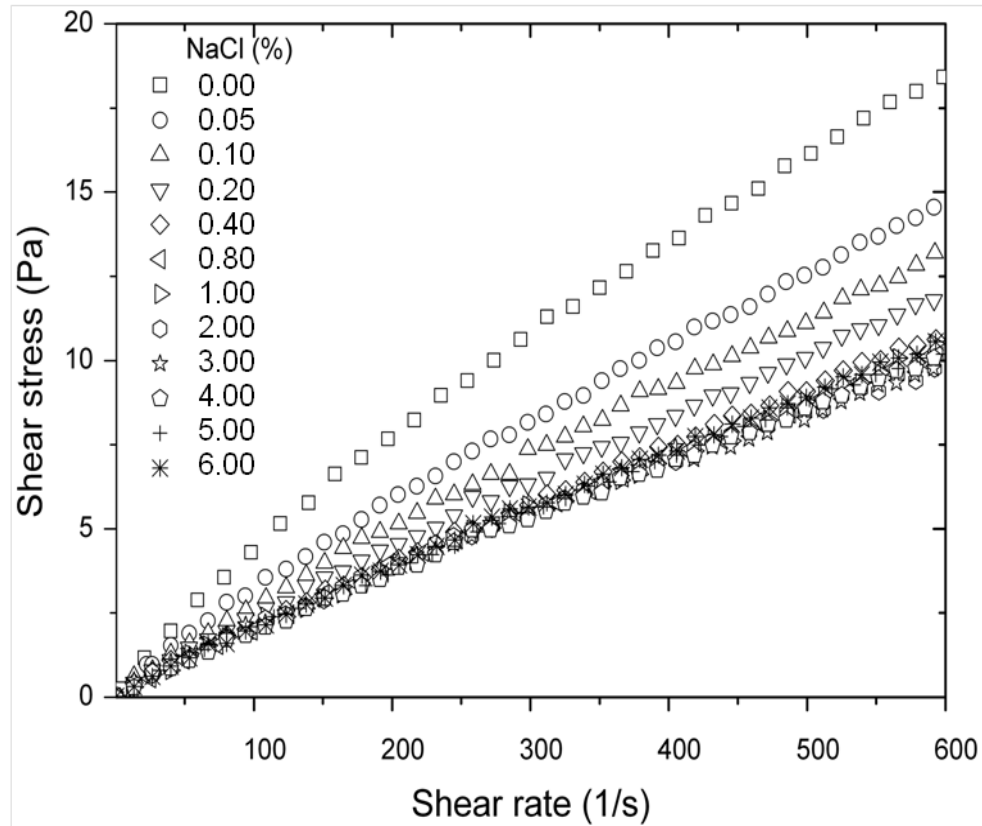
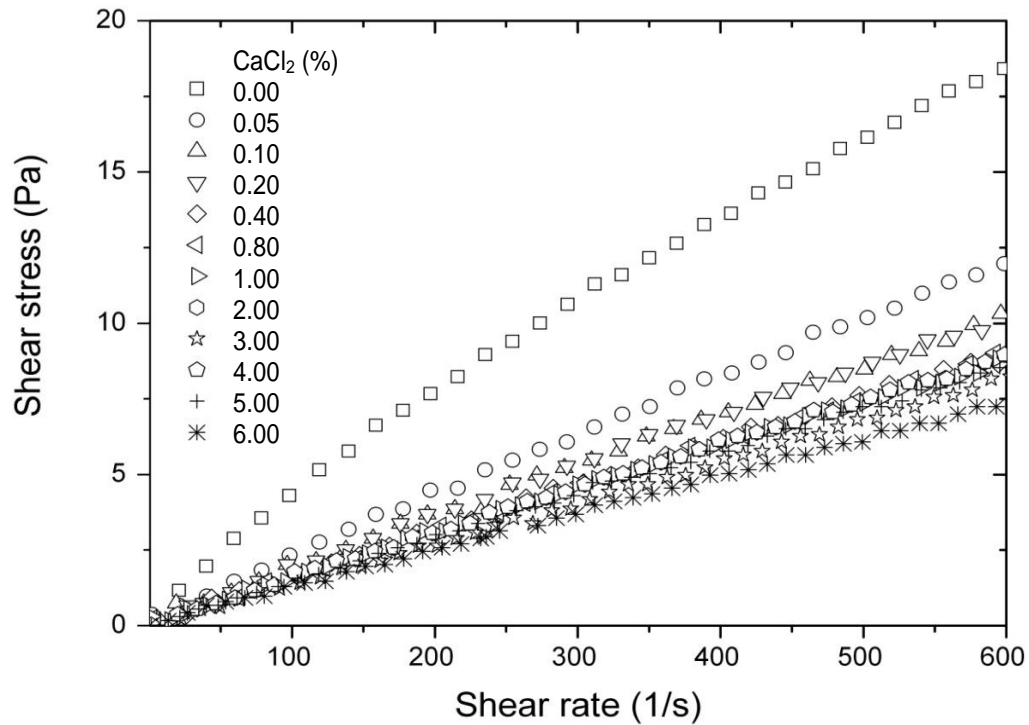**Figure 3.** Flow curves of CMC dispersion at different concentrations of NaCl.

Figure 4. Flow curves of CMC dispersion at different concentrations of CaCl$_2$.
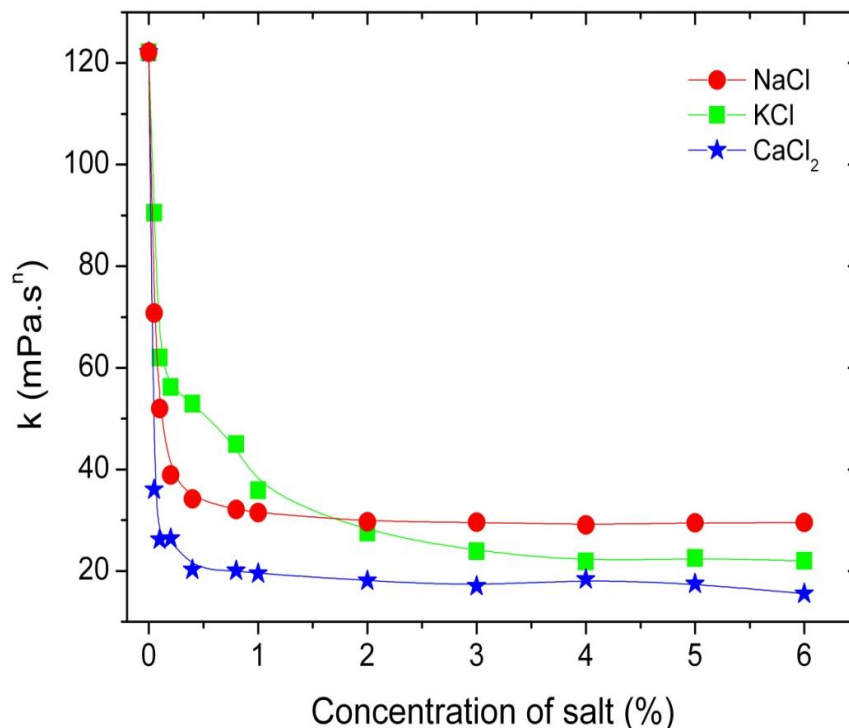
Figure 5. Consistency index as a function of salt concentration.

N<1, pseudoplastic; and if n>1, dilatants.

Many authors (Ghannam and Esmail, 1997; Edali et al., 2001; Cancela et al., 2005; Fellouah et al., 2010; Kelessidis et al., 2011) found out that the rheological law of CMC dispersions in water at different concentrations of polymer can be well described by the Ostwald-de Waele rheological model. To show the change of rheological properties of CMC solutions in presence of electrolytes, we adjusted the flow curves using the rheological model of Oswald for estimating the two rheological parameters (n, k). The fitting of the experimental data was done based on the value of the correlation coefficient from the linear form, given by the following equation:

$$\ln(\tau) = \ln(k) + n.\ln(\gamma) \qquad (3)$$

Flow curves was adjusted with a correlation coefficient $R^2 > 0.95$. The values of consistency index (k) and flow index were obtained from the regression analyses. Figure 5 shows the evolution of the consistency index as a function of salts concentration. For all salts, one can notice that the consistency index tends to decrease sharply with increasing electrolyte concentration until a certain concentration of salt, and then it remains almost constant. The decrease of the consistency index is due to the shielding of ionized COO^- groups by the presence of low molecular weight ions (Na^+, K^+ and Ca^{++}) resulting in less expanded structure (Yang and Zhu, 2007). This will promote the aggregation of CMC chains. The salts concentrations that correspond to the constancy of consistency index values for NaCl, KCl and $CaCl_2$ are of 1%, 3% and 1%, respectively. The addition of salts in CMC solutions at concentrations > 3.5% did not show any significant changes of consistency index values. The flow index increases when the concentration of salts increases, then its value becomes constant (Figure 6). Whatever the type and the concentration of salts, the value of flow index is between 0.79 and 0.97. When the salt concentration increases, the values of the flow index tend to one, the shear thinning nature of solutions becomes less pronounced. For salt concentration of 4% (NaCl, KCl and $CaCl_2$), the flow index values do not change. The most probable reason of the stability of the consistency and the flow indices values is that majority of anionic sites of CMC are absorbed by the cations. The further addition of salt will not change the rheological characteristics. At high concentrations of salt, the CMC chains lose their flexibility, the hydrodynamic size of the molecule diminishes, producing an agglomeration of polymer chains (Figure 1b), resulting in the decrease of the consistency index and the increase of the flow index. Whatever the salt concentration, the results show that the value of consistency index is greater for the polymer solutions containing NaCl or KCl than those containing $CaCl_2$. This can be explained by the fact that sodium and potassium ions are hydrated by water, and consequently
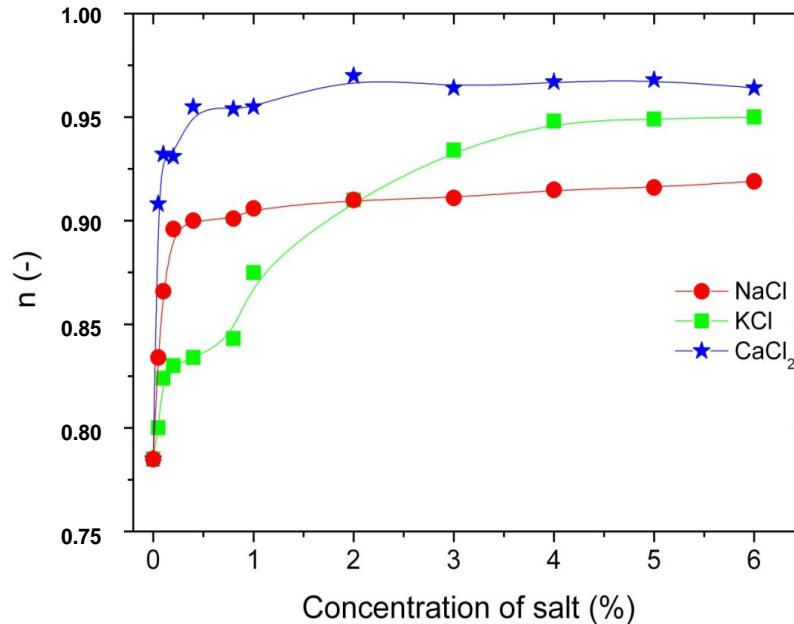
Figure 6. Flow index as a function of salt concentration.

water availability is limited. Calcium ion is even more hydrated by water than the sodium and potassium ions. This prevents the full hydration of the polymer in their presence. The two rheological parameters (n, k) of the Ostwald–de Waele model have been fitted by the power law (Figure 7). The presence of salts in CMC solution leads to deterioration of rheological parameters. Kulicke et al. (1996) showed that for low concentrations of CMC, the addition of NaCl at various concentrations reduces the viscosity of the CMC solution. By cons, at high concentrations of CMC, the increase of NaCl concentration does not affect the viscosity of the CMC solution. Atomic force microscopy (AFM) is a new technique to examine the chain conformation of macromolecules (Decho, 1999). Recently, Ueno et al. (2007) studied conformational changes in CMC chains at different salt concentrations deposited on a highly oriented pyrolytic graphite (HOPG) surface by AFM. The results of this study revealed that the increase of the concentration of salt produces conformational changes from aligned single chains to globular aggregates. Studies conducted on the anionic polysaccharides (Balnois et al., 2000; Camesano and Wilkinson, 2001) showed that the polymer undergoes morphology changes in presence of salts in solution. The results of this study confirmed that the rheological behavior of CMC solution is affected by the nature and the concentration of salts.

The dispersion of CMC solution has high zeta potential value of -80 mV in the absence of electrolytes in the aqueous phase, this proves that CMC solution are very stable (Riddick, 1968). The negative charge of CMC is generally believed to be due to the dissociation of Na^+ from carboxylic groups. Figure 8 shows the relationship between the zeta potential and the salt concentration for CMC in NaCl, KCl and $CaCl_2$ solutions, It is interesting to note that in presence of gradually increasing concentrations of chlorides of sodium, potassium and calcium, the zeta potential of the CMC solution goes on decreasing. The CMC/NaCl and CMC/KCl solutions have a negative zeta potential for a wide range of salt concentrations (0 to 6%), whereas the zeta potential of the CMC/$CaCl_2$ solution varies between -80 to 0 mV for a $CaCl_2$ concentration less than 4%. Beyond this concentration, the zeta potential of this solution becomes positive. This can be explained by the fact that the COO^- groups have a higher affinity for Ca^{2+} than Na^+ and K^+. The zero zeta potential value displayed by CMC in the presence of $CaCl_2$ is probably due to the preferential binding of Ca^{2+} to functional groups of the chains polymer and subsequent charge neutralization.

The decrease of zeta potential of saline solutions can likewise be explained by screening of negative charges on the chains of polymers by salts, leading to a decrease in electrostatic interactions between polymeric chains. According to Riddick (1968), the values of zeta potential for a stable solution are between -30 and -40 mV. The results of zeta potentials showed that the solutions of systems (CMC-NaCl and CMC-KCl) are stable for concentrations in salts<1%.By cons, the CMC-$CaCl_2$ solutions present a stability for concentrations in salts less than 0.03%. The curves of zeta potential as a function of the concentration of various salts have been fitted with linear and nonlinear regressions. The regression models with their correlation coefficients are
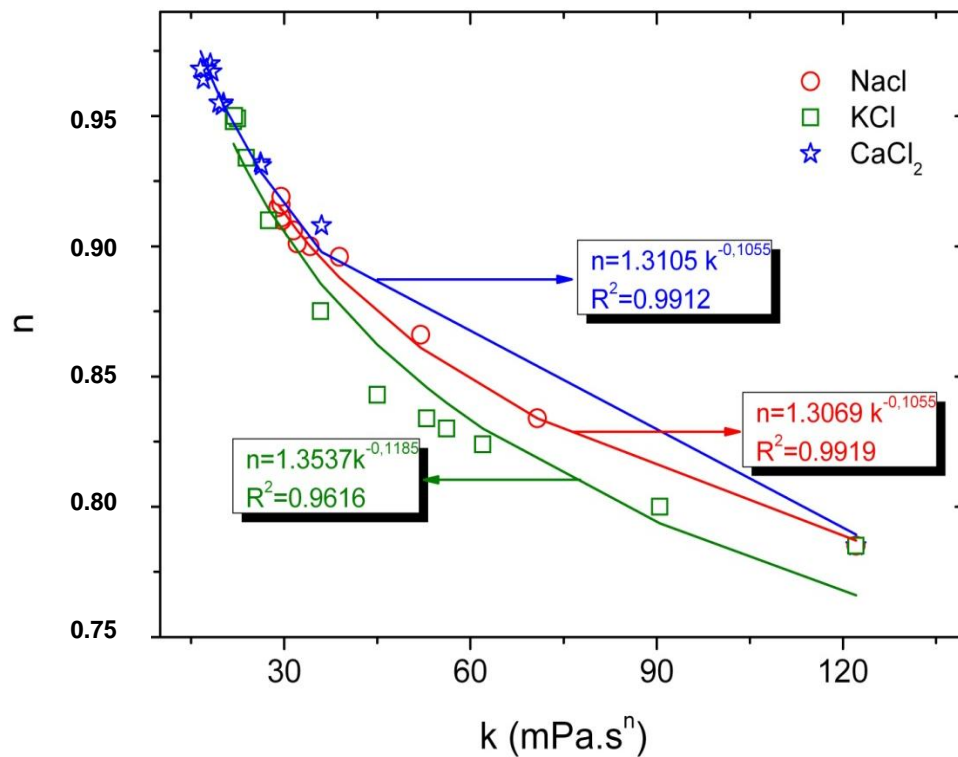
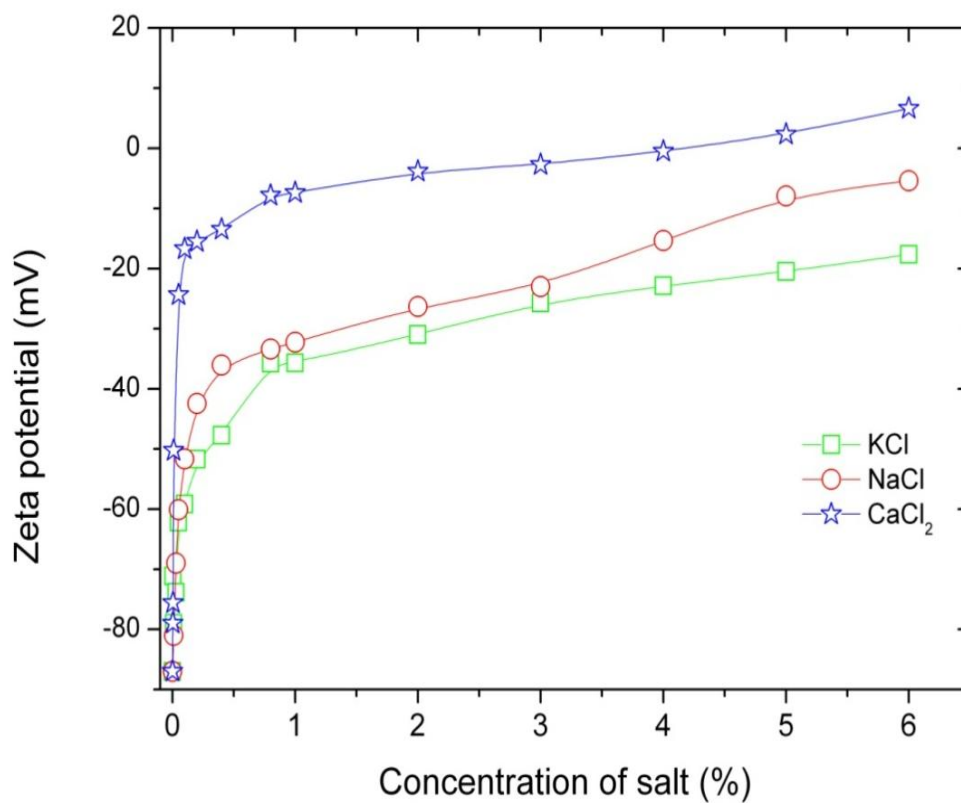**Figure 7.** Flow index as a function of consistency index concentration.

Figure 8. Zeta potential of CMC as a function of salt concentration.

Table 1. Linear and logarithmic regression of zeta potential for CMC dispersion with different salts.

Solution	Equation	R^2
CMC/CaCl$_2$	$\xi=8.5097.c-34.319$	0.4006
	$\xi=10.065.\ln(c)-8.2496$	0.9003
CMC/NaCl	$\xi=9.369.c-53.502$	0.7219
	$\xi=10.799.\ln(c)-29.264$	0.9775
CMC/KCl	$\xi=8.6267.c-59.199$	0.7111
	$\xi=8.6695.\ln(c)-35.998$	0.9574

indicated in Table 1. Based on the values of correlation coefficients, one can notice that the experimental curves were best fitted by the logarithmic regression.

Conclusion

In the present work, rheological and electrokinetic measurements have been used to characterize the carboxymethylcellulose-water-salt system. CMC dispersions in the absence and in presence of salts exhibit non-linear curves flow. The rheogramms are well described by the Ostwald-de Waele model. The addition of electrolyte CaCl$_2$, NaCl and KCl modified the rheological parameters of CMC solutions. When the salinity of CMC solution increases, the consistency index decreases and the flow index increases. At high salt concentrations (>3%), the flow index and the consistency index remain practically constant. The divalent cation salt produced more reduction in the consistency index than the monovalent cations. The zeta potential values of CMC solutions diminish in absolute values with increase in salts amounts. The reversal of sign of the charge of CMC from negative to positive was observed by increasing CaCl$_2$ concentration. Thus, the electrical repulsion between polymeric chains diminishes due to the screening effects of negative charges on the polymer.

ACKNOWLEDGEMENT

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