Rate Constants and Rheological Properties of the Ultrasonic Degradation of Carboxymethyl Cellulose

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A R T I C L E   I N F O

A B S T R A C T

To degrade the polysaccharide with high molecular weight the effectiveness of ultrasound for carboxymethyl cellulose (CMC) in aqueous solution has been studied at a time of 60 min and temperature of 25 ℃ and for polymer solution with concentration up 0.1 g/L. The Huggins equation was appropriate to apply to the intrinsic viscosity of CMC before sonication to understand the influence of salt on degradation, CMC solution was premixed with 0.1 M NaCl, before ultrasonication. Developed a kinetic model, successfully implement to predict and quantify rates of degradation and efficiency. The values of reaction rate constants and reaction orders were found related to the salt and the concentration used, suggesting that, the presence and absence of salts could increase or decrease the degradation by ultrasonic radiation through   adjusting the molecular conformation of CMC

1   Introduction

The natural polymers (polysaccharides and proteins), and their degradation methods are of great interest to researchers. The degradation of polysaccharides give oligosaccharides, which are used for many industries and are considred of great importance in the food industry. Cellulose is a polysaccharide with a diverse range of applications that are built up as a linear homopolymer from 1,4-β-glycosidically linked glucose. Figure 1 shows the structural formula of native cellulose (Clasen and Kulick 2001). Carboxymethyl cellulose(CMC) is a cellulose derivative with carboxymethyl groups bound to the hydroxyl groups of the glucose unit (Guo et al 1998; Pourjavadi et al. 2006; Lakshmi et al.

2017).Chemical modified CMC withimproved properties is gaining increasing in many fields, not only because it is low in cost, but also mainly the polysaccharide portions of the products are biocompatible and biodegradable(Sakairi et al. 1998). CMC is an industrially relevant cellulose derivative, which has multiple uses for pharmicutical, food, and cosmetic industries as a thickener and binder (Kokol 2002; Lund et al. 1990; Capitani 2000). In recent years, CMC evoked considerable interest as a Texturing additive for foodstuffs (Samant et al.1993; Ganz 1974) and preparation of hydrogels from graft copolymerization of the hydrophilic monomers onto CMC (Bajpai and Giri 2003; Zaleska et al. 2001; Zaleska et al. 2001). Also, CMC was used in the oil industry as lubricant for drilling, and in the cosmetic industry as a stabilizer and a binder
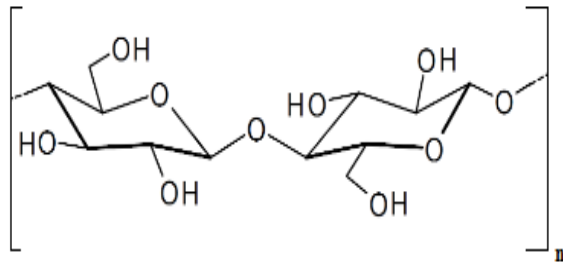
Fig. 1 Structure of water-soluble cellulose derivatives (carboxymethyl cellulose; R^1= CH$_2$ COONa).

Because of its no toxicity, biodegradability, and biocompatibility, CMC solution has also been widely used as a carrier for a bone graft (Santa-Comba et al. 2001). It is reported that CMC can improve the clinical Properties of calcium sulfate when used as a binder for particulate bone grafts (Reynolds et al. 2007).

In recent decades, many technique for degradation have been applied to polysaccharides, especially CMC, including biodegradation (Ahlgren 1993; Muchova et al 2009), thermal degradation (Soares et al 2005; Srivastava, et al. 2012), chemical degradation (Christensen et al 1993), and ultrasonic degradation (Milas et al. 1986). The advantage of degradation by ultrasonic technique compared to other types of degradation techniques, is one of the best ways to control the molecular weight of degradation products. Furthermore, the degradation polymers by ultrasonic technique don't change their basic chemical structure, as their parent molucule, and this feature cannot be obtained when using other (Basedow and Ebert 1977). Various physicochemical effects, such as radiation pressure, streaming, cavitations, and interface instabilities, that result from high-intensity ultrasound radiations (Mulet et al. 2002).

Cavitations are broadly accepted as the mechanism of ultrasonic degradation of polymers (Basedow and Ebert 1977). Recently, Gogate (Mohod and Gogate 2011) was investigated on some conditions and parameters, in the presence of additives, which affected the ultrasonic degradation of CMC and poly (vinyl alcohol)(PVA). Also, Anti teal (Antti and pntti 2008). Previously worked on ultrasonic degradation of CMC and studied the effect of different molecular mass and concentrations dynamic viscosity measurements. Because the enviromental conditions have a significant effect on the degradation efficiency within the solution, they have been studied to reduce it. In this research paper, we study the effect of salt on the degradation of CMC by ultrasonic radiation in aqueous solution. specifically study the influence of salt on the ultrasonic degradation of CMC in aqueous solution, which provides a possible way to a chive degradation beyond the limits seen in other degradation studied and with a faster degradation rate.

NaCl salt was used over a range of concentration, through the changes in the intrinsic viscosity of the solutions were used to follow the effectiveness of ultrasonic degradation . Also, the degradation kinetics model has been developed and used to quantify and compare degradation rates and rate constants at different environmental conditions.

1.1 Intrinsic viscosity Determination

The objective of rheological measurements of the solutions is to determine the intrinsic viscosity [η] as a function of ultrasonication for quantify the degradation process. The intrinsic viscosity is a measure of individual polymer molecule contribution to the viscosity of the solution. As shown in Eqs (1-3), to obtain the intrinsic viscosity value, solution –viscosity measurements are extrapolated to zero shear – rate (q→0) and infinite dilution (C→0) in order to eliminate the interaction effects between the polymer molecules. Where, η_{sp} is the specific viscosity, η_{rel} is the relative viscosity, η_s is the viscosity of the solvent, and η is the viscosity of the solution. The intrinsic viscosity is determined by measuring the specific viscosities of a solution at its initial polymer concentration, then diluting it several times by the solvent and measuring and calculating the specific viscosity of the polymer.

$$[\eta] = \lim_{\substack{q \to 0 \\ C \to 0}} \frac{\eta_{sp}}{C} \tag{1}$$

$$[\eta] = \eta_{rel} - 1 = \frac{\eta - \eta_s}{\eta_s} \tag{2}$$

$$\eta_{rel} = \frac{\eta}{\eta_s} \tag{3}$$

The relationship between concentration and viscosity of dilute polymer solution can be described by many empirical forms, the most common of which is the Huggins equation (Mohod and Gogate 2011), as shown in Eq.(4), where k is Huggins constant.

$$\frac{\eta_{sp}}{C} = [\eta] + k[\eta]^2 C \tag{4}$$

The Huggen equation can be simplified For applied to very dilute solutions, by removing the second-order term, and, thus, the intrinsic viscosity can be determined from the slope of a plot polymer concentration an against relative viscosity (Antti and pntti 2008).

$$\eta_{rel} = 1 + [\eta]C \tag{5}$$

1.2. Ultrasonic Degradation Kinetics

Generally, the degradation rate can be considred as an order reaction based on the total molar concentration of the polymer, as is shown in Eq.(6).

$$\frac{d[M]_t}{dt} = k[M]_t^n \qquad (6)$$

Where [M] is the total concentration of polymer molecules (and fragments) at time t, k is the degradation rate constant, and n is the order of reaction (Taghizadeh, and Mehrdad 2003).

Note that, the value of n is expected to be negative, because the ultrasonic degradation is a mechanical process. By integrating and applying the initial condition at Eq. (6) that, at t=0, $[M]_t = [M]_0$, where $[M]_0$ is the initial total molar concentration of polymer and t is Sonication time, Eq. (7) is obtained:

$$[M]_t^{1-n} - [M]_0^{1-n} = (1-n)kt \qquad (7)$$

The total molar concentration of polymer, which increases as degradation occurs, is related to the number-average molecular weight and polymer concentration in solution, as shown in Eq. (8). The viscosity average molecular weight, M_v is related to intrinsic viscosity through Mark–Houwink equation (White and Kim 2008), Eq. (9), and the number average molecular weight through Eq. (10).

$$[M] = \frac{C}{M_n} \qquad (8)$$

$$[\eta] = K M_v^\alpha \qquad (9)$$

$$M_n = [(1+\alpha)\Gamma[(1+\alpha)]^{\frac{1}{\alpha}} M_v \qquad (10)$$

Where α and K are the Mark-Houwink constant, and Γ is the standard gamma function. Furthermore, the values of $\Delta\eta$ determined from Eq.(12) (Taghizadeh, and Abdullahi 2011).

$$M = \left(\frac{KC^{\alpha+1}}{\sqrt{2}(1+\alpha)\Gamma(1+\alpha)}\right)^{\frac{1}{\alpha}} \Delta\eta \qquad (11)$$

Where, $\Gamma(1+\alpha) = \int_0^\infty e^{-t} t^\alpha$, and

$$\Delta\eta = \left(\frac{1}{\eta_{sp} - ln\eta_{rel}}\right)^{1/(2\alpha)}$$

By substituting Eq. (11) in (7) yields Eq (12)

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = (1-n) \times$$

$$\left(\frac{\sqrt{2}(1+\alpha)\Gamma(1+\alpha)}{KC^{\alpha+1}}\right)^{\frac{(1-n)}{\alpha}} kt \qquad (12)$$

or

$$\Delta\eta^{1-n} - \Delta\eta_0^{1-n} = kt \qquad (13)$$

2. Materials and Methods

2.1 Material and Solution Preparation

The Powder material Supplied by local Libyan Company (Jowfe) and used without Further Purification. Sodium chloride (NaCl) was purchased from Fluke (Sigma-Aldrich, Germany). Mother Solution of 1g/L concentration was prepared by adding a known weight of the Polymer to a fixed volume of double distilled water and dissolving with magnetic stirring, giving a clear solution. Some extra double distilled water was then added up to the required volume. A centrifuge was used at 2200rpm for 20 min to remove air bubbles from the solutions. After centrifuging, the solutions were ready for ultrasonic processing.

2.2 Density Measurement

By filtering Small samples of the centrifuged carboxymethyl cellulose solutions, the dissolved amount of CMC was measured. The evaporate solvent and dissolved material were determined gravimetrically, by adding aliquots to small flasks and heated overnight at 80ºC. All the measurements were performed in triplicate.

2.3 Sonication Treatment and Viscosity Measurement

The carboxymethyl cellulose solutions (25ml, 0.1g/L) were transferred into a cooling cell, and Sonicated by using a BANDELIN electronic, Heinrichstrabe 3-4 D-12207 Berline, Ger ate- type UW 2200, Pro-Nr. GB599.00003718.001. The amplifier frequency was fixed at 20 KHz, and the amplitude was fixed at 40%, which corresponds to approximately 95W of power. The temperature of the solutions in the cell was controlled by replacing the water in the water ice Path. After Sonication process, all solution were prepared at concentration of 0.1M of salt by adding necessary amount of salt, in order to make sure that all viscosity measurements were taken at the same ionic strength. Each sample was diluted by using the corresponding salt solutions with the concentration 0.1M, to produce concentrations of CMC in the range of 0.10-0.02g/L. The viscosity of the solution was determined by Ostwald glass capillary Viscometer (NO

11:75-1005, Nach Ostwald 486510, made by brand at W-Germany), thermostated with an accuracy of ± 0.015%, as well as to obtain linear and nonlinear regression line with corresponding equations and correction coefficients' (R^2) in order to assess the best model.

3. Results

The values of intrinsic viscosity of CMC solutions, which correspond to no sonication, 0.5 min, 5 min, 10 min, 30 min, or 60 min sonication treatments were calculated by appling Eqs. (4), (5) for estimation of intrinsic viscosities of CMC before and after sonication treatment. Which, (Fig. 2) represented the reducing viscosity Vs. CMC concentration: CMC solution (0.1 g/L) were premixed with 0.1 M NaCl, and then sonicated for the given time and (Fig. 3) represented the relative viscosity Vs. CMC concentration: CMC solutions (0.1 g/L) were premixed with 0.1 M NaCl, and then sonicated for the given time.

However, the results of our research showed an excellent fit to the model with correlation factor (R2=0.96) for the case of unsolicited solutions of CMC concentration ranging down to 0.02 g/L with 0.1M NaCl (Table 1). With sonication treatment, the intrinsic viscosities obtained by using the Huggins equation also show the reasonable correlation coefficient (R2 range from 0.72 to 0.97), which suggests that the Huggins equation is appropriate for determination of intrinsic viscosities of CMC solutions with polymer concentration higher than 0.02 g/L.
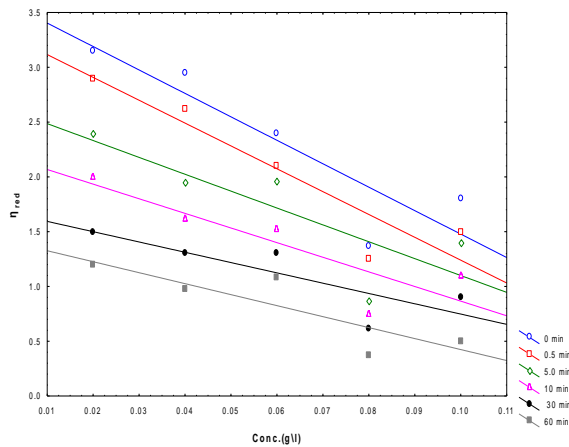

Fig. 2 CMC concentration Vs. reducing viscosity: CMC solutions (0.1 g/L) were premixed with 0.1 M NaCl, and then sonicated for the given time. After sonication, the sonication-treated solution was diluted with 0.1 M NaCl solution to produce polymer concentrations ranging from 0.10 to 0.02 g/L.

Fig. 3 CMC concentration Vs. relative viscosity: CMC solutions (0.1 g/L) were premixed with 0.1 M NaCl, and then sonicated for the given time. After sonication, the sonication-treated solution was diluted with 0.1 M NaCl solution to produce polymer concentrations ranging from 0.10 to 0.02 g/L.
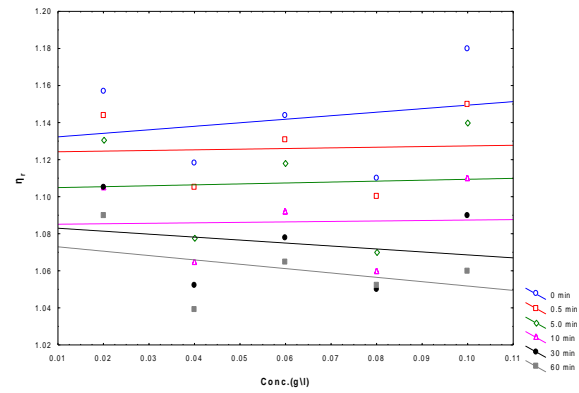
As a result, to maintain the comparison properly, we use Eq. (4) as the best model for intrinsic viscosity determination because of its acceptable linear fit to data obtained from both sonicated and non-sonicated CMC solutions.

Table 1. Intrinsic viscosity and correlation coefficients obtained from the Huggins equation

Sonication time (min)	$[\eta]$ (L/g)	R^2
0	3.618	0.96
0.5	3.325	0.97
5	2.64	0.94
10	2.201	0.95
30	1.688	0.89
60	1.4265	0.72

Some different rate models have been proposed for the degradation of polymers, but in this study, a simple model was employed via viscometry. The data consists of Eq. (13) by considering that order reaction molar concentration is approximately -1, thus Eq. (14)

$$\Delta\eta^2 - \Delta\eta_0^2 = kt \qquad (14)$$

The plot of $(\Delta\eta^2 - \Delta\eta_0^2)$ versus sonication time for different CMC concentrations presented in figure 4. The apparent degradation rate constant defined in Eq. (14) can be estimated from the slops of the plots in figure 4 and shown in table 2. Based on that, rate constants were calculated. The calculated rate constants, k, are correlated in terms of revers solution concentration (Fig.5).
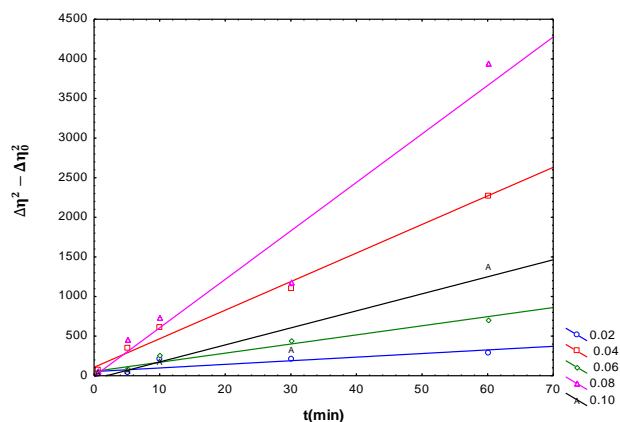
Fig. 4 The plot of $((\Delta\eta^2 - \Delta\eta_0^2)$) versus sonication time for different concentrations of CMC in 0.1 M NaCl solution at 25^0C.
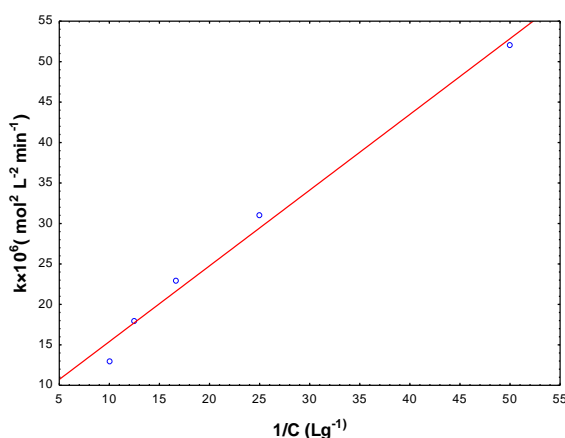

Fig. 5 The relationship between the calculated rate constants and reverse concentration of CMC in 0.1 M NaCl solution.

Table 2. Rate Constant and CMC Concentrations in 0.1 M NaCl Solution

$K \times 10^6$ $(mol^2L^{-2}min^{-1})$	52.0	31.0	23.30	18.10	13.20
Concentration (gL^{-1})	0.02	0.04	0.06	0.08	0.1

4. Discussion

When a plot a relative viscosity against concentration which is applied of the simplified Huggins equation (Eq. (5)) in which intermolecular interactions are not considered, the fitting linear plot could not be obtained by using this second model also this model has poor correlation coefficient values (0.15-0.440), with or without sonicated treatment. These results suggest that when molecular chains are long and tend to form entangled structures. The molecular interaction is essential and should not be neglected. On the contrary, since the molecular chains become shorter and stiffer,

due to sonication treatment, the influence of molecular interaction on intrinsic viscosity becomes smaller and less critical.

The data in table 2 indicate that the rate constant of ultrasonic degradation decreases with increasing solution concentration.

The interpretation of these observations is that there is less overlap between polymer chains at low concentrations. Therefore, they are more susceptible to the hydrodynamic forces generated around cavitation bubbles.

5. Conclusions

In this work, the ultrasonic degradation of CMC in salt solutions was systematically studied. The rate and extent of degradation of polymer decrease with increasing solution concentration. With increasing solution concentration, their viscosities increase, and it reduces the shear gradients around the collapsing bubbles. Therefore, degradation rate decreases too. A simple kinetic model using viscosity data was used for studying the kinetics of degradation. This model optimally interpreted the experimental findings and thus, viscometry is a practical approach for monitoring the degradation of polymers in a solution.

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