



Activation functions of photodegraded carboxymethyl cellulose in solution: Viscosity measurements

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ABSTRACT

Carboxymethyl cellulose (CMC) is used in several applications exposed to light and radiation, such as food and medical products. The exposure to photons could affect the CMC properties and behaviour therefore the products. Our main objective is to investigate the relative viscosity/temperature relationships of CMC fragments in a NaCl solution. The method of photodegradation technology has been used, and the data were attained viscometrically. The decrease in macromolecular mass and concentration brought down the reduction in solution viscosity, while the temperature had the opposite effect. Eyring's parameters as functions of concentration and molar mass were then illustrated. The enthalpy and Arrhenius factor have increased with increasing concentration and molar mass, while the entropy has decreased. The polyelectrolytic CMC fractions in salt solutions behaved like polymers in neutral solutions. The photodegraded solution of CMC had better solvation quality than the native one.

الدوال التنشيطية لمحللول كربوكسي ميثيل سيليلوز المتحلل ضوئياً: قياسات اللزوجة

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الكلمات المفتاحية:

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محللول كربوكسي ميثيل السليلوز
معاملات التنشيط

الملخص

يستخدم كربوكسي ميثيل السليلوز (CMC) في العديد من التطبيقات المعرضة للضوء والإشعاع، مثل المنتجات الغذائية والطبية. يمكن أن يؤثر التعرض للضوء على خصائص CMC وسلوكها وبالتالي المنتجات. هدفنا الرئيسي هو دراسة علاقات اللزوجة النسبية/درجة الحرارة لـ CMC المتكسر في محلول ملحي. تم استخدام طريقة تقنية التحلل الضوئي، وتم الحصول على البيانات بقياسات اللزوجة. حيث أدى الانخفاض في الكتلة الجزيئية والتركيز إلى انخفاض في لزوجة المحلول، بينما كان لدرجة الحرارة تأثير معاكس. ثم تم توضيح معاملات إيرينج كدوال التركيز والكتلة المولية. زاد عامل المحتوى الحراري وعامل أرهينيوس مع زيادة التركيز والكتلة المولية، بينما الانتروبيا انخفضت. تصرف CMC متعدد الإلكتروليت في المحاليل الملحية مثل البوليمرات في المحاليل المحايدة. كان لمحللول CMC المتحلل ضوئياً جودة إذابة أفضل من المحلول الأصلي.

Introduction

The energetic behaviour of viscous flow is an essential parameter in nowadays applications, ranging from the rheological industrial to the biocompatible domain for polysaccharides in solution [1]. Eyring [2] has interpreted the viscous flow of polymers as an activated rate process according to the following equation:

$$\eta = A_{\eta} e^{-\Delta S_{\eta}/R} e^{\Delta H_{\eta}/RT} \quad 1$$

where η , ΔH_{η} , A_{η} , and ΔS_{η} are the solution viscosity, the appeared enthalpy of activation, the Arrhinus proportionality constant, and the entropy of activation, respectively. Thus for Equation 1 in the form of relative viscosity, one may write that

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$$\eta_r = A_{\eta,r} e^{\Delta H_{\eta,r}/RT} \quad 2$$

in which:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t_f \times \rho}{t_{f0} \times \rho_0} \cong \frac{t_f}{t_{f0}} \quad 3$$

$$A_{\eta,r} = \frac{N_A h}{V_{m,r}} e^{-\Delta S_{\eta,r}/R} \quad 4$$

$$V_{m,r} = \frac{V_m}{V_{m,0}} \sim 1 \quad 5$$

$$\Delta H_{\eta} = \Delta H_{\eta,r} + \Delta H_{\eta,0} \quad 6$$

$$A_{\eta} = A_{\eta,r} A_{\eta,0} \quad 7$$

$$\Delta S_{\eta} = \Delta S_{\eta,r} + \Delta S_{\eta,0} \quad 8$$

Here the subscripts r and 0 denote the words relative and initial, respectively; while V_m is molar volume and N_A , h and R are the Avogadro, Planck, and gas constants. Moreover, the respective values of $\Delta H_{\eta,0}$, $A_{\eta,0}$ and $\Delta S_{\eta,0}$ are $18.73 \text{ kJ mol}^{-1}$, $0.582 \text{ kg m}^{-1} \text{ s}^{-1}$ and $-83.46 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively [3].

Moore [4] has pointed out that the ΔS_{η} , of dilute solutions of flexible chain polymers, decreases with increasing the polymer concentration (C) and its molar mass (M_{η}). In contrast, ΔS_{η} for stiff and extended cellulose derivatives in dilute solutions generally increases with an increase in C and M_{η} .

Carboxymethyl cellulose (CMC) is a water-soluble polyelectrolyte, that belongs to the cellulose ethers family [5]. Although many studies of the thermal conductivity of CMC have been done [6] yet there is no published study on the thermodynamic conformational behaviour of CMC in semidilute solutions in the temperature range of $20\text{--}60 \text{ }^{\circ}\text{C}$. Our aim in this work is to use the Equations from 1 to 8 to investigate such behaviour.

2. Experimental

2.1 Material

The native CMC powder in Figure 1 was a gift from Jowfe Company, Benghazi, Libya, and was used as received.

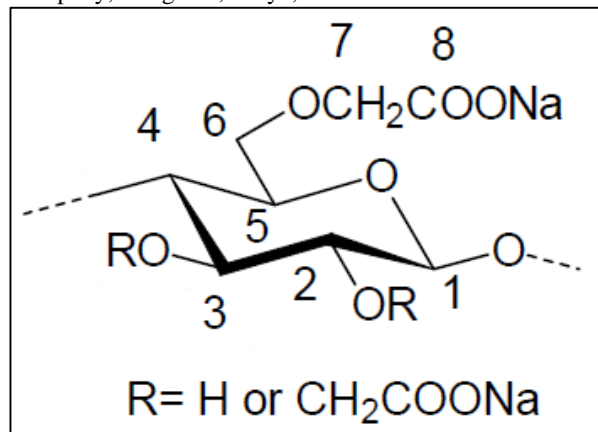


Figure 1. Monomer molecular structure of a CMC sodium salt [5]. Reproduced with permission of John Wiley and Sons.

2.2 Preparation and measuring methods

The native solution was photodegraded by ultraviolet (UV) irradiation at room temperature. The non-degraded (high M_{η}) and degraded (low M_{η}) CMC solutions were prepared with concentrations ranging from 0.5 to 1.00 mg cm^{-3} . The non-degraded solutions (highly viscous samples) were labeled as HV-CMC, while the degraded solutions (low viscous samples) were labeled as LV-CMC. Monitoring the change in each sample was done immediately after irradiation, and at intervals afterwards for each sample, by using the Ostwald-viscometric technique [7]. The viscosity measurements were taken at the temperature range of $20\text{--}60 \text{ }^{\circ}\text{C}$, ± 0.02 .

3. Results and discussion

The results are shown in the forthcoming Fig. 2 to Fig. 5. Fig. 2 illustrates the logarithmic form of Equation 1. Fig. 2a demonstrates a typical Huggins concentration dependence of viscosity for photodegraded CMC solution [8]. The deviation from the linearity, in Fig. 2b, can be attributed to the excluded volume effect, due to the higher M_{η} of CMC in the native solution [9, 10]

Fig. 3-5 show the activation functions of CMCs in NaCl solutions. Their activation parameters, like ΔH_{η} , A_{η} , and ΔS_{η} , were obtained by applying Eyring's viscosity theory on the plots of Fig. 2, via Equations 2-8 [2, 4]. All the functions, in Fig. 3-5, show typical plots of flexible chains in solution [4].

The increase in ΔH_{η} , with C and M_{η} , in Fig. 3, indicates that the CMC chains require more energy to change their equilibrium positions at higher concentration values. This would naturally lead to the formation of aggregated chains at such values [11].

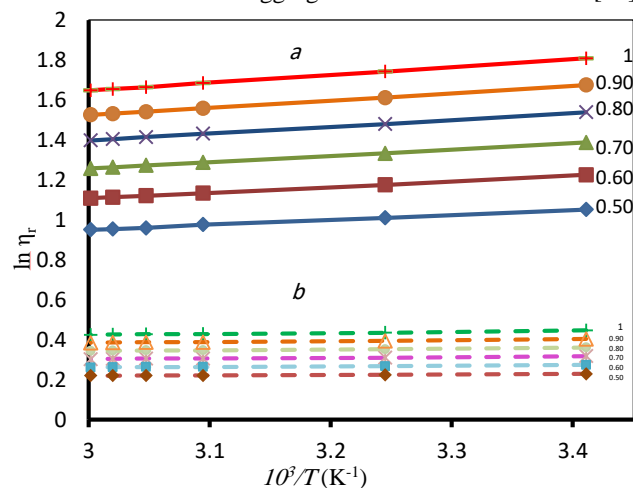


Fig. 2: $\ln \eta_r$ vs. T^{-1} at different concentrations ($0.50, 0.60, 0.70, 0.80, 0.90$ & 1.00 mg cm^{-3}), (a) is the HV-CMC and (b) is the LV-CMC.

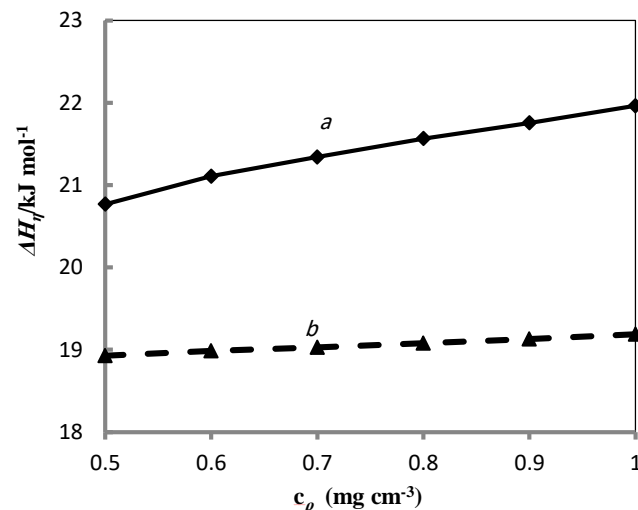


Fig. 3: CMC-Concentration dependence of ΔH_{η} , (a) is the HV-CMC and (b) is the LV-CMC

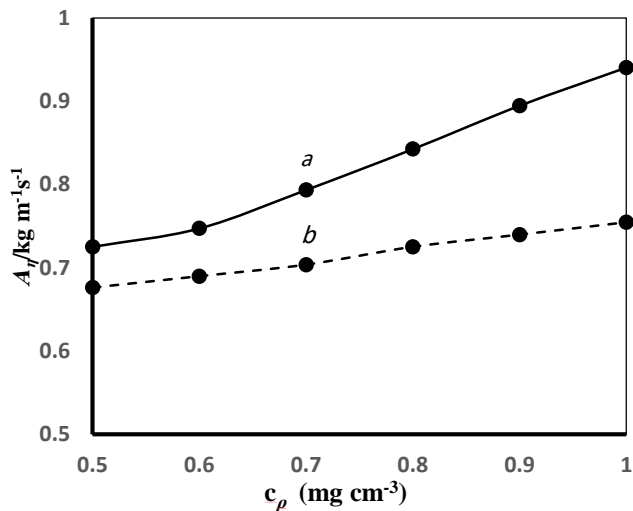


Fig. 4: CMC-Concentration dependence of A_η , (a) is the HV-CMC and (b) is the LV-CMC.

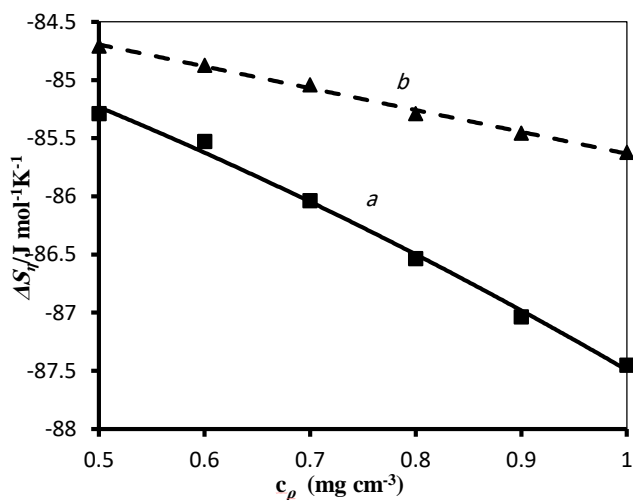


Fig. 5: CMC-Concentration dependence of ΔS_η , (a) is the HV-CMC and (b) is the LV-CMC

Conclusion

Photo-irradiation of carboxymethyl cellulose in the salt solution is expected to reduce their molecular weight, and improve the solvation quality of the system. Relative viscosity/temperature relationships can be conveniently employed to investigate these phenomena.

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