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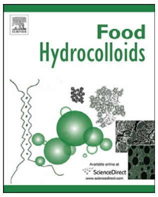

Monovalent and divalent salt effects on thermogelation of aqueous hypromellose solutions

Nalinda Almeida [a,1], Leela Rakesh [b,*], Jin Zhao [c,2]

[a] Science of Advanced Materials, Central Michigan University, Mt. Pleasant, MI 48859, USA
[b] Center for Applied Mathematics & Polymer Fluid Dynamics, Science of Advanced Materials, Department of Mathematics, Central Michigan University, Mt. Pleasant, MI 48859, USA
[c] Dow Pharma and Food Solutions, The Dow Chemical Company, Midland, MI 48674, USA

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ABSTRACT

The effect of salt on gelation behavior of concentrated low molecular weight Hydroxypropyl methylcellulose (HPMC, Hypromellose) solutions were investigated by using rheology measurements. Various gelation matrices were used to characterize gelation point as a function of salt concentrations. It was found that gelation temperature identified by frequency-independent loss tangents is similar to the gelation temperature at which minimum elastic modulus, *G*′, occurred during heating process. Thermal analysis showed that the melting temperature decreased linearly with increasing ion concentration of salts. The bound water analysis showed that the bound water increased as the salt concentration increased. Secondary peaks that represent the freezable bound water were also observed for solutions with NaCl and KCl.

1. Introduction

Hypromellose or Hydroxypropyl Methylcellulose (HPMC) and Methylcellulose (MC) are water soluble cellulose ethers obtained by substituting hydroxyl group of anhydroglucose with methoxyl and/or hydroxylpropyl groups. The resulting cellulose ethers can undergo thermo reversible sol–gel transitions. Cellulose ethers have many applications in food, pharmaceuticals, and cosmetic industries (Chen et al., 2006; Hoffman, 2002; Kumar & Banker, 1993; Lin, Wang, Wei, & Li, 2007; Perez, Sanchez, Pilosof, & Patino, 2008). Sol–gel transitions of HPMC and MC have been studied using different techniques including rheology (Bajwa, Sammon, Timmins, & Melia, 2009; Chen, 2007; Haque, Richardson, Morris, Gidley, & Caswell, 1993; Hussaina, Kearyb, & Craig, 2002; Kobayashi, Huang, & Lodge, 1999; Li et al., 2002; Silva et al., 2008), NMR (Haque et al., 1993), FTIR (Bajwa et al., 2009), dynamic light scattering (Kobayashi et al., 1999), small angle neutron scattering (Kobayashi et al., 1999), or DSC (Ford, 1999; Lam, Joshi, & Tan, 2007; Li et al., 2002). Based on these studies, various gelation mechanisms have been proposed (Bodvika et al., 2010; Carlssona, Karlströmb, & Lindman, 1990; Ibbett, Philp, & Price, 1992; Kobayashi et al., 1999). It is commonly accepted that gelation occurs due to the significant increase of the association density of HPMC chains above a critical temperature.

Gelation properties of HPMC and MC can be altered in the presence of salts and other additives (Liu, Joshi, & Lam, 2008; Xu, Li, Zheng, Lam, & Hu, 2004; Xu, Wang, Tam, & Li, 2004). It was found that the impact of salt on thermo gelation of aqueous HPMC solutions followed the Hofmeister series, which is similar to the impact of salt on precipitation of proteins (Liu et al., 2008; Mitchell et al., 1990; Xu, Li, et al., 2004; Xu, Wang, et al., 2004). Additionally, the effects of cations on gelation temperature is less significant than that of anions (Alexandridis & Holzwarth, 1997).

Previous researchers mainly focused onHPMC with high molecular weight (Mw ~ $8.6{*}10^4$ g/mol– $4.3{*}10^5$ g/mol) and very few research is done on high concentration of low molecular weight HPMC solutions (Liu et al., 2008; Silva et al., 2008; Xu, Song, Ping, Wang, & Liu, 2006). Therefore, this study examined the effects of salt on the viscoelastic properties of concentrated low molecular weight (Mw ~ 25,000 g/mol) HPMC solutions. Moreover, we also investigated the gelation/gel dissolution mechanism of HPMC as a function of salt type and salt concentration. The effect of salts on a different HPMC substitution type was examined in our previous publication (Almeida, Rakesh, & Zhao, 2014). This research also investigated the binding mechanism of water and HPMC chain using DSC which may influence the gelation behavior.

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[*] Corresponding author. Tel.: +1 989 774 6524.
E-mail addresses: edncalmeida@gmail.com (N. Almeida), lrakesh@aol.com (L. Rakesh), jzhao@dow.com (J. Zhao).
[1] Tel.: +1 989 400 2452.
[2] Tel.: +1 989 636 4828.

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2. Material and methods

2.1. Materials

The polymer evaluated was METHOCEL™ F5 LV Premium cellulose ether {hypromellose, HPMC USP (United States Pharmacopeia) substitution type 2906} that was supplied by The Dow Chemical Company in Midland, MI. The manufacturer's specification indicates that the viscosity of a 2 wt% HPMC solution at 20 °C is 4.7 mPa.s, and that the methoxyl and hydroxypropoxyl content are 28.8 wt% and 6.6 wt%, respectively. This polymer will be noted as F5 throughout this paper. Sodium chloride (NaCl), potassium chloride (KCl), and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) were purchased from EM Science. The molar concentration of the salts in the HMPC solutions is labeled as C_{NaCl}, C_{KCl}, and C_{CaCl_2}. Materials were used without further purification. Water used in the experiments was purified through Barnstead E-pure filter system and collected at 18 MOhm. F5 with 0–0.8 M salt (NaCl, KCl, $CaCl_2$) were dispersed at 80 °C in deionized water, continuously mixed at room temperature for more than 3 h, and then hydrated at 4 °C for a minimum of 12 h.

2.2. Methods

2.2.1. Rheology

Dynamic shear and steady flow measurements were conducted on AR2000 rheometer (TA instrument, New Castle, DE) with commercial computer software (Rheology Analysis Advantage Software Version 5.7.2, TA Instruments). A concentric cylinder fixture (stator inner radius 15 mm, rotor outer radius 14 mm, cylinder immersed height 42 mm) was used. To prevent dehydration of the solutions, a small amount of low-viscosity silicone oil (Fisher Chemical, S159-500, density 0.96 g/ml, boiling point > 140 °C) was placed on the top of the solution. For dynamic shear measurements, a small-amplitude oscillatory shear

$$\gamma = \gamma_0 \sin(\omega t) \tag{1}$$

was applied to the sample, and the resultant shear stress was measured as

$$\sigma(t) = \gamma_0 [G\prime(\omega) \sin(\omega t) + G\prime\prime(\omega) \cos(\omega t)] \tag{2}$$

with $G'(\omega)$ and $G''(\omega)$ being the storage and loss modulus, respectively. The complex viscosity, $|\eta^*|$, can also be obtained using the following equation:

$$\left|\eta^*\right| = \frac{\left(G\prime^2 + G\prime\prime^2\right)^{1/2}}{\omega} \tag{3}$$

A strain sweep was performed to find out the linear viscoelastic region (LVER) and to select a strain within the linear viscoelastic response of the material. A strain of 2% for all of the samples tested was within the LVER and therefore used throughout the dynamic measurements. Frequency scans were performed isothermally from 0.06 to 628 rad/s at temperatures from −5–80 °C with an increment of 5 °C temperature step. At each temperature, the solution is allowed to equilibrate for 30 min. Moreover, the frequency range was determined by the capability of the rheometer. The master curves were generated using the principle of time–temperature superposition (TTS) and shifted to a common reference temperature (T_{ref}) of −5 °C (Ferry, 1980; Macosko, 1994). The temperature sweeps were performed with 2% strain, 1 Hz frequency, and heating and cooling rates of 1 °C/min.

In order to thoroughly investigate gelation behavior, the matrices shown in Table 1 were used to characterize gelation and gel dissolution of polymer solutions at varying levels of salt concentrations.

Table 1
Key terminology and abbreviations used for gelation and gel dissolutions.

Nomanclature	Abbrevations	Definitions
Gelation temperature 1	T_{gel} (1)	The temperature where TTS failed (viscosity vs shear rate) or sharp increase of zero shear viscosity
Gelation temperature 2	T_{gel} (2)	The temperature that is independent of ω. (True Winter–Chambon transition occurs at $G' \approx G'' \sim \omega^n$ (Chambon & Winter, 1987; Winter & Chambon, 1986), while T_{gel} (2) determined in this paper did not show a true Winter–Chambon transition)
Gelation temperature 3	T_{heat} ($G' = G''$)	The crossover temperature, $G' = G''$ during heating
Onset gelation 1	T_{heat} (G'_{min})	The temperature measured at minimum G' during heating
Onset gelation 2	T_{heat} ($\|\eta^*\|_{min}$)	The temperature measured at minimum $\|\eta^*\|$ during heating
Gel dissolution temperature 1	T_{cool} ($G' = G''$)	The crossover temperature, $G' = G''$ during cooling

2.2.2. Thermal analysis

Differential Scanning Calorimetry (DSC) was carried out using DSC Q-2000 (TA Instruments) in hermetically sealed pans and the sample weighed approximately 10 mg. The samples were heated from −40 °C to 20 °C at 2 °C/min. Each sample was measured 3 times to ensure repeatability.

The water concentration (W_t) of each sample can be calculated based on the amount of water added during solution preparation. There are three types of water associated with hydrophilic polymers: (i) non-freezable bound water, (ii) freezable bound water, and (iii) free or bulk water (Faroongsarng & Sukonrat, 2008; Hatakeyama & Hatakeyama, 1998; Ping, Nguyen, Chen, Zhou, & Ding, 2001). It has been found that the properties of bound water (W_b) is significantly different from that of free water (Hatakeyama & Hatakeyama, 1998; Nakamura, Hatakeyama, & Hatakeyama, 1981). Freezable bound water is the water closely associate with polymer and can have melting and crystallizations peaks which can be detected when the water content is above its characteristic threshold limit. Free or bulk water has the melting and crystallization peaks that are close to 0 °C. The amount of free water (W_f) can be calculated from the melting peak close to 0 °C using the following equations:

$$W_f = Q/\Delta H(g/g) \tag{4}$$

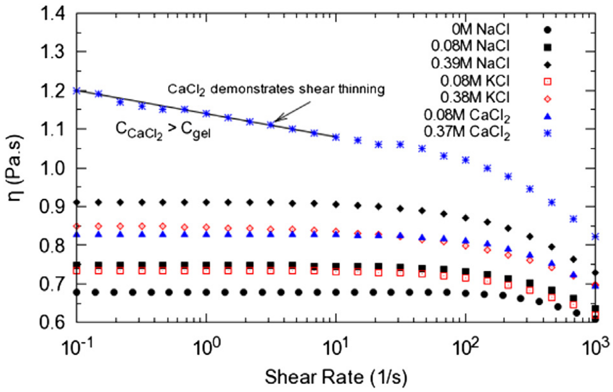

Fig. 1. Shear rate dependence of shear viscosity for various salt concentrations at 25 °C.