Multiple Thermal Gelation of Hydroxypropyl Methylcellulose and Kappa-Carrageenan Solutions and their Interaction with Salts

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Abstract: The multiple gelation behavior of aqueous solutions of kappa-carrageenan (KCG) and low molecular weight hydroxypropyl methylcellulose (HPMC) was studied with the presence of various salts. Multiple gelation behavior of aqueous solutions of HPMC/KCG/salt mixture were found. The shear viscosity of HPMC/KCG blend increased by one orders of magnitude, while the viscosity of HPMC/KCG/potassium chloride (KCl) mixture increased by three orders of magnitude as compared to HPMC solution at temperatures below apparent gelation. The dynamic elastic modulus of HPMC/KCG blend increased by two orders of magnitude, while the elastic modulus of HPMC/KCG/potassium chloride (KCl) mixture increased by three orders of magnitude as compared to HPMC solution at temperatures below apparent gelation temperature. The gel elastic modulus of the solution blend of HPMC/KCG/salt mixture decreased in the order of KCl > NaCl > $CaCl_2$. Thermal analysis revealed a linear relationship between the depression of melting temperature and the salt concentrations, which is independent of KCG. The free water content computed by enthalpy data showed that free water content decreased with increasing salt concentrations. The secondary peak which typically associated with bound water appeared in the mixture of HPMC and KCG in the presence of KCl. As the concentrations of KCl salt increased, the bound water peak also amplified and lifted to a higher temperature

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1. INTRODUCTION

Hydroxypropyl Methylcellulose (HPMC) (or Hypromellose) and carrageenans are both natural gums that are broadly used in pharmaceutical, food, cosmetic, biomedical, and industrial applications [1-6]. Aqueous HPMC solution is known to gel during heating which can be reversed during cooling. The low molecular weight HPMC solutions are frequently used with the presence of salt and other natural gums in food and pharmaceutical industries such as capsule manufacturing and delivery of ophthalmic drug solutions [1-5, 7, 8]. Carrageenans, an anionic linear hetero-polysaccharides extracted from red seaweed, is known to gel during cooling which can be reversed during heating [9]. Kappa-carrageenans (KCG) typically form structured double helices upon cooling and reverse to random coil conformation upon heating.

Gelation properties of KCG are highly influenced by the presence of cations. During gelation, KCG undergoes a disorder-order (coil → helix) transition which is followed by the aggregation of helical structures. The disorder-order transition occurs at a specific temperature called the transition temperature, which is highly dependent on the type of counter ions present and the total ionic concentrations [10, 11]. The influence of salts of monovalent cations follow the order $Rb^+ > Cs^+ \geq K^+ > NH_4^+ > (CH_3)_4N^+ > Na^+ > Li^+$ and those of divalent cations follow the order $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+} > Zn^{2+} > Co^{2+}$ [12-15]. At higher ionic strength, the negative charges of the sulfate group are shielded by cations which stabilizes the double helix structure and promote helix- helix aggregation. However, the gels formed with K^+ ions are the strongest and most stable and followed by those induced by Rb^+, Cs^+ and higher concentrations of Na^+ and Li^+ [16]. Divalent cations (Ca^{2+} and Cu^{2+}) also have the capability to promote gelation of KCG. However, gels formed from K^+ are stronger than those formed from Ca^{2+} [17]. The effect of KCl, NaCl, and $CaCl_2$ salts on the gel formation of aqueous KCG solutions followed the order of $K^+ > Ca^{2+} > Na^+$ according to Lai *et al.* Hermonsson *et al.* and Pekcan *et al.* [18-20]. However, Morris *et al*. found the sequence of effectiveness in increasing shear modulus followed the following order $Ca^{2+} > K^+ > Na^+$ [21]. The difference in these results may be due to the variation of experimental and analytical techniques, as well as solution and gel-aging conditions [18]. Zhang *et al*. showed that NaCl has the smallest effect on KCG gelation when compared with other salt solutions [22] while the gelation temperature of KCG/NaCl solutions is increased by increasing NaCl concentration [23].

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Moreover, anions also promote gelation via increasing aggregation of helix structures [22]. Zhang *et al*. also showed that the Cl^- has the lowest binding strength to KCG, hence the lowest effect on gelling in KCG [22].

Our previous research characterized gelation and gel dissolution of low molecular weight HPMC solutions as a function of salt type (NaCl, KCl, $CaCl_2$) and salt concentration. It was found that gelation temperature linearly decreased with increasing salt concentration [24, 25]. The phase behavior of aqueous blends of HPMC, KCG, and salt will naturally induce complex rheological behavior due to heat-gelling property of HPMC solution and cool-gelling property of KCG solution. This study systematically examines the complex phase behavior and phase transitions of the aqueous solutions of low molecular weight HPMC, KCG, and salt.

2. MATERIAL AND METHODS

2.1. Materials

The polymer, METHOCEL™ F5 LV Premium (hypromellose substitution type 2906) cellulose ether was provided by The Dow Chemical Company (Midland, MI), denoted as F5. The viscosity of F5 was 4.7 mPa.s which was measured at a 2 wt% aqueous solution at 20 ºC, and the methoxyl and hydroxypropoxyl contents were 28.8 wt% and 6.6 wt%, respectively. Kappa-carrageenan was obtained from CPKelco (Genugel carrageenan CP-130). Sodium chloride (NaCl), potassium chloride (KCl), and calcium chloride dihydrate ($CaCl_2.2H_2O$) were purchased from EM Science. All chemicals were used without further purification. All water was obtained from the laboratory Barnstead E-pure water filtration system, at >18 MOhm. Blend of 15 wt% F5 with KCG (0.1 wt% and 0.3 wt%) and with 0.008 to 0.5M salt (NaCl, KCl, $CaCl_2$) were dispersed in deionized water at 80 ºC, continuously stirred during the cooling process to room temperature, mixed for more than 3 hours at room temperature, and then stored at 4 ºC for more than 12 hours before running rheological testing.

2.2. Methods

2.2.1. Rheology

Dynamic oscillatory and stead shear flow experiments were carried out using AR2000 rheometer (TA instrument, New Castle, DE) with concentric conical fixture (stator inner radius 15mm, rotor outer radius 14mm, cylinder immersed height 42mm) in the linear viscoelastic region with a strain amplitude, γ, of 2%; a frequency, *f*, of 1Hz; and a heating or cooling rate of 1 °C/min. The free surface of solutions was covered with a thin layer of low-viscosity silicone oil (Sigma-Aldrich silicone oil – viscosity 5 cSt (25 °C), density 0.913 g/ml, boiling point > 140 °C) to prevent the dehydration of the samples at elevated temperatures. The nomenclature of gelation characteristics used in this paper was discussed in our previous papers [24, 25].

2.2.2. Thermal Analysis

Differential Scanning Calorimetry (DSC, Q-2000, TA Instruments) was used to determine the thermal characteristics of HPMC and KCG in several salt solutions. Approximately 10 milligrams of each sample were heated from -40 to 20 °C with a rate of 2 °C/min in a hermetically sealed pan.

The concentration of water (W_t) in the sample was computed using the total amount of water added to the HPMC/KCG solution. The types of water existed in a HPMC/KCG solution are free or bulk water (W_f), freezable/loosely bound water (W_{fb}), and non-freezable/tightly bound water which have been proposed for most hydrophilic polymers [26-28]. Hatakeyama *et al*. (1981 & 1998) demonstrated the different properties of bound (W_b) and free water [28, 29]. The detailed definition of W_t, W_b, and W_{fb} was given in [24, 25].

3. RESULTS AND DISCUSSION

3.1. Rheological Behavior of HPMC/KCG Blend with Various Concentrations of NaCl, KCl, and $CaCl_2$

Steady shear viscosity of aqueous solution of HPMC/KCG was measured as a function of shear rate as shown in Figure **1**. The aqueous solution of HPMC showed a Newtonian region at low shear rates where the viscosity was independent of shear rate. However, with the addition of 0.1% KCG, the range of Newtonian region was reduced and a shear thinning behavior was observed. With further addition of KCG (0.3%), a shear thinning behavior was dominant. Moreover, the viscosity of the solution of HPMC/0.3% KCG blend was increased more than one order of magnitude comparing to that of HPMC at frequencies less than 1 1/s. KCG appeared to interact with HPMC and formed a certain associated structure. Figure **2** shows steady shear viscosity of solutions of HPMC/KCG with various concentrations of NaCl, KCl, and $CaCl_2$. At the concentration level of 0.1% KCG in HPMC solution, viscosity did not increase significantly with the presence of salt (supplementary data Figure A).

However, at the concentration level of 0.3% KCG in HPMC solution, viscosity was increased two orders of magnitude in the presence of low concentration KCl (0.08M). An increase of viscosity at low shear rates was also observed with 0.08M of NaCl. However, when salt concentration was further increased to 0.38M and 0.39M for KCl and NaCl respectively, a viscosity profile that is similar to that of HPMC solution was observed. There appeared to be an optimal KCl and NaCl level that enhance the associated structure which formed in the solution of HPMC/0.3% KCG. There was no viscosity enhancement observed with the 0.08M and 0.37M addition of $CaCl_2$. This is in contrast with the effects of KCl and NaCl on the solution behavior of HPMC/0.3% KCG as well as previous research [10, 11]. The optimal concentration level of $CaCl_2$ could be less than 0.08M for the enhancement of the associated structure of the solution of HPMC/0.3% KCG before gelation temperature. Similar trend can be observed from dynamic rheological measurements presented next.

Figure **3** exhibits the typical heating curves of elastic modulus (G') acquired from oscillatory rheological experimnets of the solution of HPMC/0.3% KCG at different concentrations of NaCl, KCl, and $CaCl_2$. It is evident from Figure **3** as well as our previous publications, the gelation profile and gelation temperature of the solution of HPMC/0.3% KCG were very similar to that of HPMC solution[24, 25]. Similarly, the onset of gelation moved to a lower temperature as the concentrations of the salts (NaCl, KCl, $CaCl_2$) increased in the solution of HPMC/0.3% KCG. This is comparable to the effect of salt on the soluion of HPMC [24, 25]. When examine the elastic modulus (G') prior to the gelation temperature, the effect of salt on the dynamic modulus of the solution of HPMC/0.3% KCG showed similar trend as that of the steady shear viscosity of the solution of HPMC/0.3% KCG. The elastic modulus of the solution of HPMC/0.3% KCG increased 2 order of magnitude comparing to that HPMC solution around 10 °C. While with the addition of 0.08M of NaCl into the solution of HPMC/0.3% KCG, elastic modulus around 10 °C has increased 470 times to that of the HPMC solution (Figure **3a**). Similarly with the addition of 0.08M of KCl into the solution of HPMC/0.3% KCG, the elastic modulus around 10 °C increased by three orders of magnitude comparing with HPMC solution (Figure **3b**). However, further increasing NaCl and KCl concentration, the elastic modulus decreased to that of HPMC solution with 0.24M and 0.5M of NaCl and 0.5M KCl respectively. Adding $CaCl_2$ into the solution of HPMC/0.3% KCG led to the reduction of elastic modulus (~10 °C) comparing to that of the solution of HPMC/0.3% KCG; addition of 0.08 to 0.23M $CaCl_2$ led to the elastic modulus (~10 °C) comparable to that of the HPMC solution while addition of 0.37M and 0.5M of $CaCl_2$ led to a modulus one order of magnitude below that of the solution of HPMC/0.3% KCG. Table **1** and Figure **4** showed a summary of the elastic modulus at three different temperatures (10 °C, 20 °C, and 30 °C) for all three salts. It is evident that KCl is most effective at enhancing solution viscosity as well as solution elastic modulus (T<30 °C) at 0.08 M. The gel modulus of the solution of HPMC/0.3% KCG at temperatures above gelation temperature generally increased with increasing salt concentrations. Syneresis was the most probable cause of the reduction of gel modulus at temperatures between 60 to 80 °C as evident in Figure **3b** and **3c**. However, adding 0.08 to 0.5 M of NaCl, or KCl, or $CaCl_2$ into the solution of HPMC/0.1 % KCG always led to the reduction of elastic modulus as shown in supplementary data (Figure B).

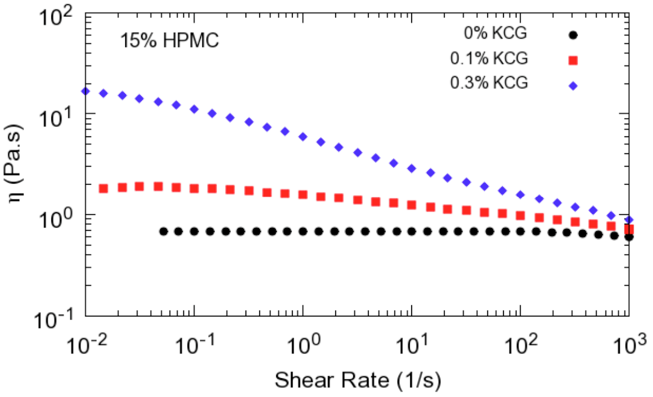

Figure 1: Shear rate dependence of shear viscosity for the aqueous solution of HPMC/KCG at 25 °C. Black – 15% HPMC, Red – 15% HPMC + 0.1% KCG, Blue – 15% HPMC + 0.3% KCG.

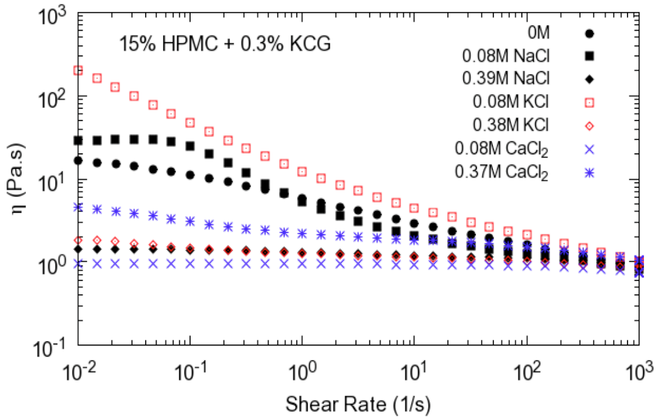

Figure 2: Shear rate dependence of shear viscosity for the aqueous solution of 15% HPMC and 0.3% KCG at various salt concentrations at 25 °C. Black – 15% HPMC + 0.3% KCG + NaCl, Red – 15% HPMC + 0.3% KCG + KCl, Blue – 15% HPMC + 0.3% KCG + CaCl2.

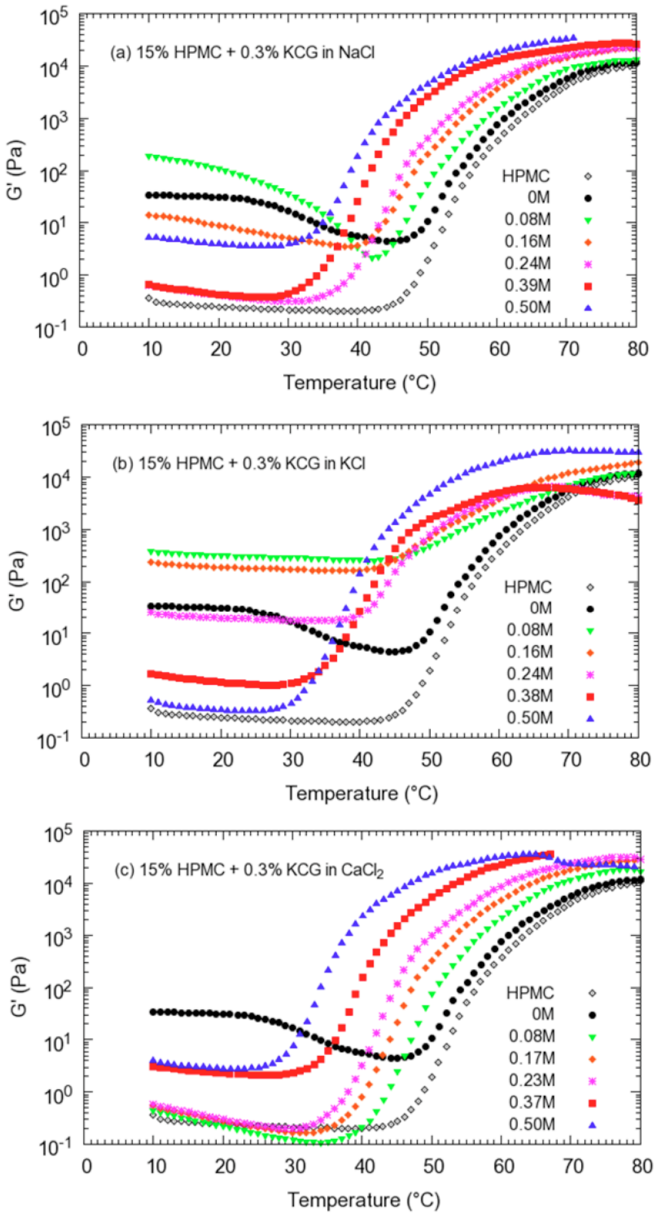

Figure 3: Temperature dependence of dynamic elastic modulus (G') of (a) 15% HPMC + 0.3% KCG in NaCl solution (b) 15% HPMC + 0.3% KCG in KCl solution (c) 15% HPMC + 0.3% KCG in $CaCl_2$ solution.

Table 1: The Elastic Modulus at Three Different Temperatures (10 °C, 20 °C, and 30 °C) for Various Salts Concentrations

Formulation	G' (T_{10}) Pa	G' (T_{20}) Pa	G' (T_{30}) Pa
HPMC	0.4	0.2	0.2
HPMC/0.3%KCG	34.3	31.3	16.8
NaCl			
0.08M	187.0	106.0	35.4
0.16M	13.9	9.0	5.1
0.24M	0.6	0.4	0.3
0.39M	0.7	0.4	0.4
0.50M	5.5	4.0	4.0
KCl			
0.08M	382.0	308.0	282.0
0.16M	237.0	189.0	171.0
0.24M	25.8	19.9	17.9
0.38M	1.7	1.2	1.1
0.50M	0.5	0.3	0.5
$CaCl_2$			
0.08M	0.4	0.2	0.1
0.17M	0.6	0.3	0.2
0.23M	0.6	0.3	0.2
0.37M	3.1	2.3	2.3
0.50M	4.0	2.9	7.8

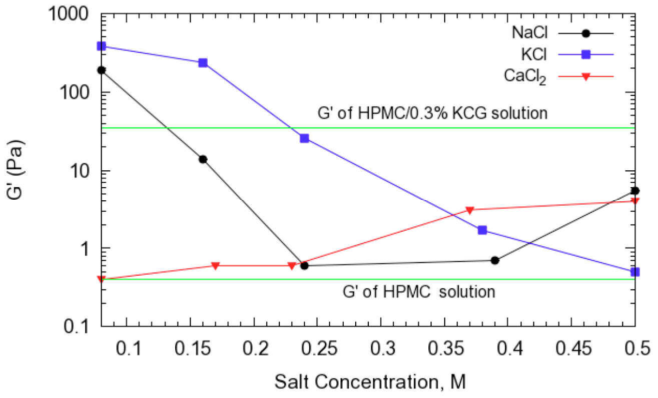

Figure 4: Summary of elastic modulus at 10 °C as a function of salt concentration in the solution of 15% HPMC/0.3% KCG.

Figure **5** shows the relative relationship of the dynamic elastic and loss spectrum of aqueous solution of HPMC/0.3% KCG/KCl. Addition of 0.3% KCG into HPMC solution led to solid like behavior (G' ≥ G") before apparent gelation transition. Such solid-like behavior maintained and both G' and G" further increased with addition of 0.08M of KCl into the solution of HPMC/0.3% KCG. However, further increasing concentration of KCl to 0.38 and 0.5M did not only reduce the magnitude of G' and G" but also led to a liquid-like behavior (G' < G") before apparent gelation transition which is similar to that of aqueous HPMC solution. Gelation transition temperature continuously decreased as KCl concentration increased which is similar to that of HPMC/salt solution [24, 25].

The onset of gelation that was measured by a series of matrices was defined in our previous publications [24, 25]. Onset gelation temperature 1,

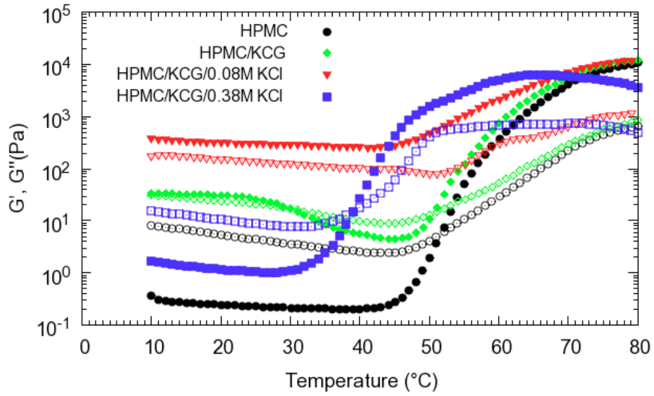

Figure 5: Temperature dependence of both elastic modulus (G' – filled symbol) and viscous modulus (G'' – open symbol) of aqueous solutions of HPMC/KCG/KCl. Black – 15% HPMC, Green – 15% HPMC/0.3%KCG, Red – 15% HPMC/0.3% KCG/0.08 KCl, Blue - 15% HPMC/0.3% KCG/0.38 KCl.

T_{heat} (G'_{min}), is defined as the temperature measured at minimum G' during heating. Onset gelation temperature 2, T_{heat} ($|\eta^*|_{min}$), is defined as the temperature measured at minimum $|\eta^*|$ during heating. Gelation temperature, T_{heat} (G' = G''), is defined as the temperature where *G*' = *G*'' during heating. Gel dissolution temperature, T_{cool} (G' = G'') is defined as the temperature where *G*' = *G*'' during cooling. These transition matrices decreased with increasing salt concentrations as shown in Figure **6**. The linear trend of gelation temperature, T_{heat} (G' = G''), and onset gelation temperature 2, T_{heat} ($|\eta^*|_{min}$), as a function of salt concentrations showed a coefficient of determination (R^2) values of 0.96 and 0.94 respectively. While the linear trend of onset gelation temperature 1, T_{heat} (G'_{min}), and gel dissolution temperature, T_{cool} (G' = G''), showed a R^2 value of 0.83 and 0.88 respectively. All transition matrices except gelation temperature 1 appeared to be independent of KCG and salt type, while gelation temperature 1, T_{heat} (G'_{min}), generally increased with the increasing concentration of KCG at the same concentration of the salt.

Figure **7** illustrates the elastic modulus, *G*', viscous modulus, *G*'' of the aqueous solution of HPMC/KCG/salt as a function of angular frequency at various temperatures during heating. At 25 and 35 °C, dynamic viscous modulus, G'', of 15% HPMC solution was greater than elastic modulus G' which indicates that the HPMC solution is in liquid state at 25 and 35 °C (as shown in Figure **7a**). However, the terminal behavior of G' of 15% HPMC solution showed a

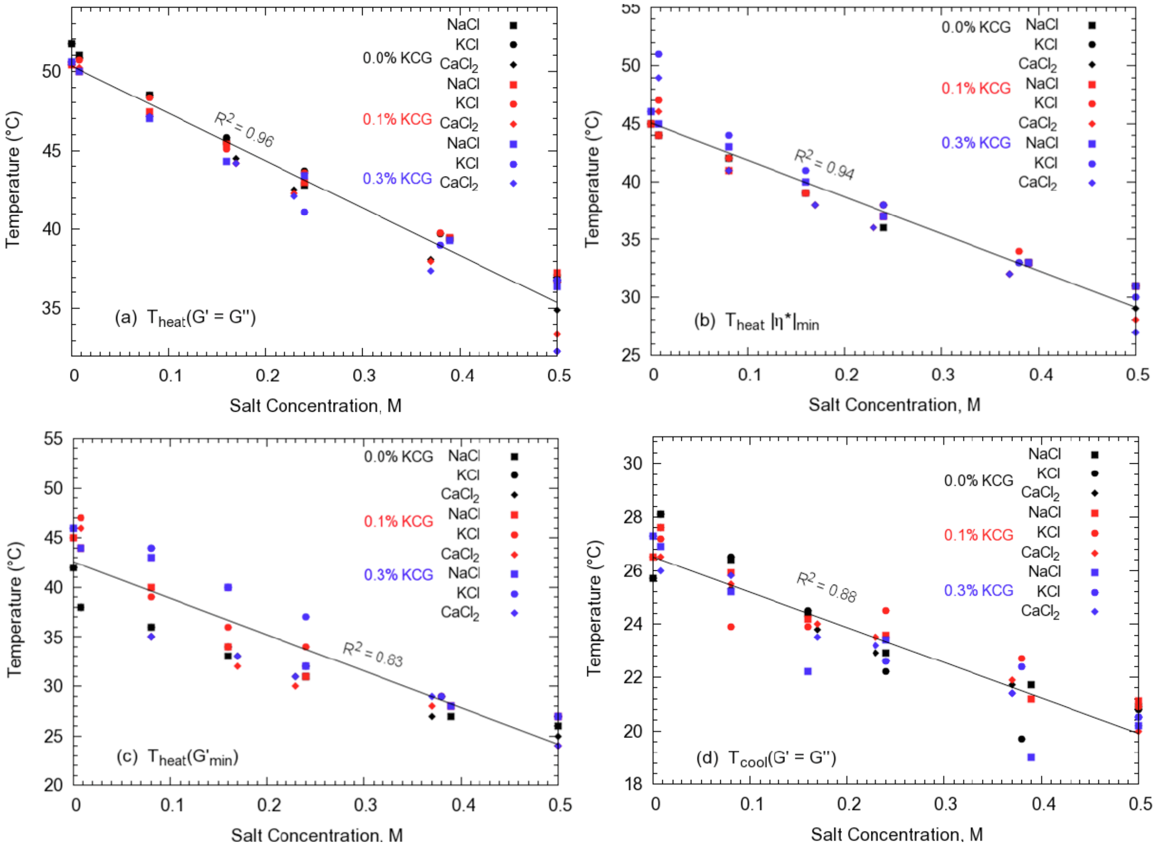

Figure 6: Gelation matrices as a function of salt concentrations (a) T_{heat} (G' = G'') (b) T_{heat} (|η*|min) (c) T_{heat} (G'_{min}) and (d) gel dissolution temperature, T_{cool} (G' = G''). Black – 15% HPMC in salt solution. Red – 15% HPMC + 0.1% KCG in salt solutions, Blue – 15% HPMC + 0.3% KCG in salt solutions.

frequency dependence of ~ $\omega^{1.4}$ instead of ~ ω^{2} which is a typical liquid behavior. This indicates there were polymer associations in HPMC solutions at 25 °C where polymers are not completely relaxed. As the temperature increased to 45 and 55 °C, terminal G' became greater than G'' which indicated a solid-like gel structure, a cross-over frequency appeared which indicated a relaxation time of the gel structure. This cross-over frequency shifted to a higher frequency (shorter relaxation time) at 55 °C. Furthermore, G' and G'' became less dependent on the angular frequency at temperatures above 55 °C. With the addition of 0.3% KCG into 15% HPMC solution, terminal G' became greater than G'' at 25 °C and the magnitude of terminal G' and G'' increased 4 and 2 order of magnitude comparing to that of HPMC solution at 25 °C respectively. The terminal frequency dependence of G' and G'' of the solution of HPMC/0.3%KCG was characterized by G'~G'' ~ $\omega^{0.1}$ (Figure **7b**). When the temperature increased to 35 °C and 45 °C, terminal G' remained greater than G'' and the terminal slope of G' and G'' became G'~G'' ~ $\omega^{0.40}$. When the temperature increased to 55 °C, the dynamic spectrum of G' and G'' of the solution of HPMC/0.3%KCG appeared to be similar to that of the HPMC solution with a slightly higher elastic modulus than that of HPMC solution. It was speculated that 0.3% KCG in HPMC solution helped to induce or nucleate a soft gel structure at temperatures 25 to 45 °C which was possibly templated on the partial helix structure of KCG. As temperature increased, the partial helix structure of KCG became unstable but association of HPMC polymer chains increased. A hard gel structure that was similar to that of HPMC solution formed after apparent gelation temperature identified in Figure **3**. With the addition of 0.08 M KCl, G' and G'' further increased and gelation is dominated by KCG in the temperature range between 25 °C to 45 °C (Figure **7c**). Terminal G' remained greater than G'' between 25 °C to 55 °C and the terminal slope of G' became G'~ $\omega^{0.1}$. However, further increasing the concentration of KCl to 0.5M in the solution of HPMC/0.3%KCG, G' and G'' decreased. Terminal G' only became greater than G'' at very low frequencies and the terminal slope of G' became G'~ $\omega^{0.5}$ at 25 °C. At temperatures 35 to 55 °C, the terminal slope of G' became G'~ $\omega^{0.2 \text{ to } 0.1}$ where the gelation of HPMC/KCl dominated (Figure **7d**) [24, 25].

3.2. Thermal Analysis of HPMC/KCG Solutions with Various Concentrations of NaCl, KCl, and CaCl$_2$

Differential Scanning Calorimetry thermograms were employed to investigate the interaction between polymers and water. Thermograms of HPMC solutions at different concentrations of KCG and KCl are shown in Figure **8**. The inception temperature of melting peak, as well as the size of endotherm peak, decreased as the concentration of the salt increased. The

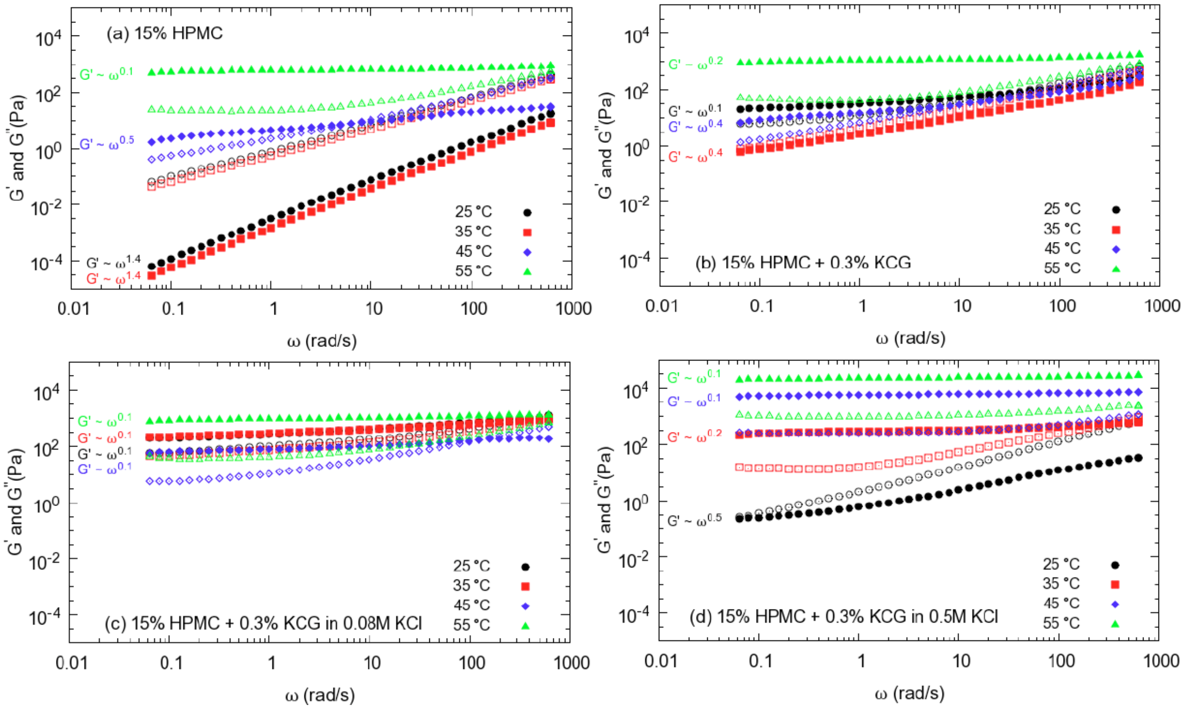

Figure 7: The frequency dependence of elastic modulus (G' – filled symbol) and loss modulus (G'' – open symbol) of aqueous solution of (a) 15% HPMC (b) 15% HPMC/0.3% KCG (c) 15% HPMC/0.3% KCG/ 0.08M KCl (d) 15% HPMC/0.3% KCG/0.5M KCl.

characteristic melting temperatures, T_{m1} and T_{m2}, can be determined as the peak temperature of the primary endothermic peak and secondary endothermic peak respectively. Secondary peaks were observed only when the concentration of KCl was more than 0.24M. Based on the research reported by Faroongsarng *et al*., Hatakeyama *et al*., Ping *et al*., and Nakamura *et al*., the appearance of secondary peaks are related to freezable/loosely bound water in the polymer solutions [26-29].

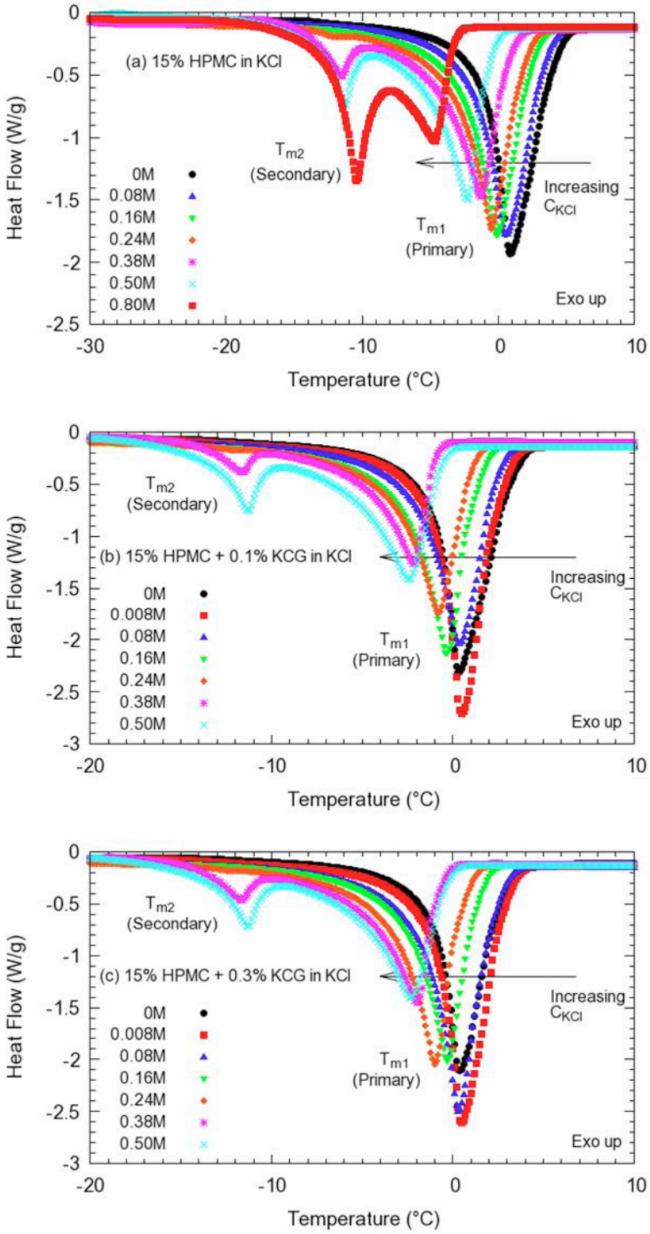

Figure 8: DSC thermograms of aqueous solution of (a) 15% HPMC (b) 15% HPMC/0.1% KCG (c) 15% HPMC/0.3% KCG with various concentrations of KCl.

There were no secondary peaks observed for NaCl and $CaCl_2$ as shown in supplementary data within the concentration range we studied (Figure C and Figure D). As discussed in our previous papers, the freezable bound water is loosely linked with polymer chains, while the non-freezable bound water is tightly bound to polymer chains [24, 25]. The mechanisms of the secondary melting peaks are not well understood. Therefore, further research is required to explain the absence of the secondary peaks of HPMC/KCG solutions containing NaCl and $CaCl_2$, which we may conjecture that it is due to lack of the freezable bound water.

The melting point (T_{m1}) as a function of total molar number of ions of NaCl, KCl, and $CaCl_2$ is given in

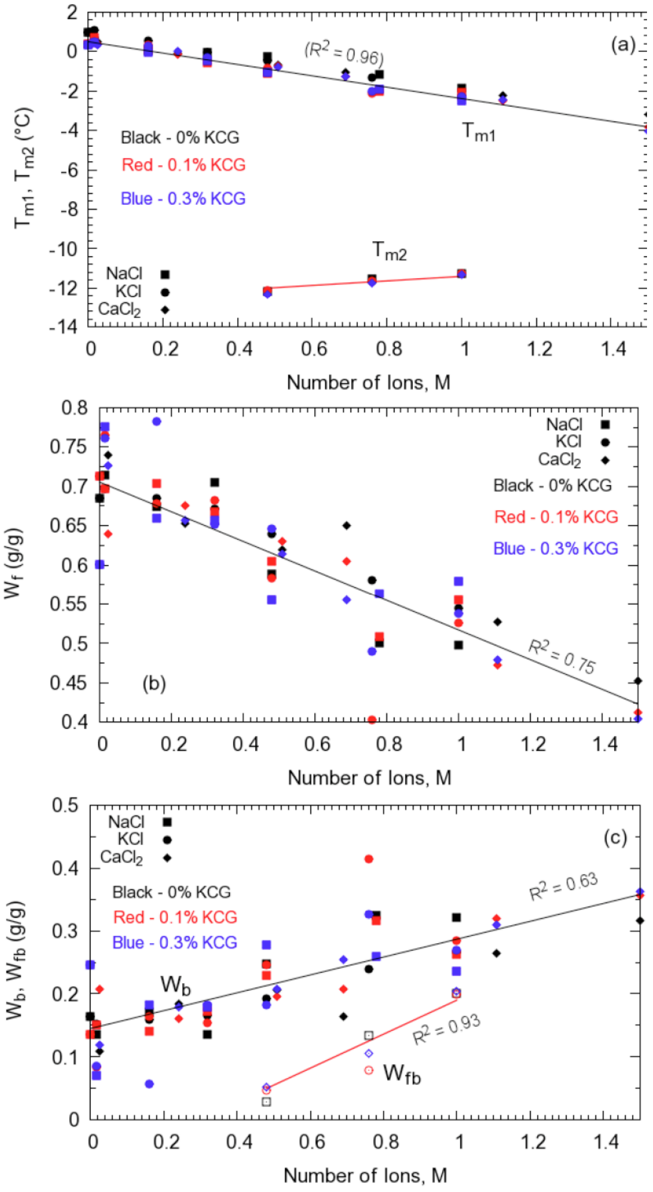

Figure 9: Characteristic thermodynamic parameters derived from DSC scans (a) depression of melting temperatures (T_{m1} and T_{m2}) as a function of ion concentration (b) free water (W_f) as a function of ion concentration (c) bound (W_b) and freezable bound (W_{fb}) water as a function of ion concentrations.

Figure **9a**. The melting temperature, T_{m1}, followed an approximate linear relationship with concentrations of salt ions. The secondary melting point (T_{m2}) slightly increased as the concentrations of KCl increased. Figure **9b** shows that the amount of free water of HPMC/KCG decreased with increasing salt concentration independent of KCG and salt types. Using equations from reference [24], the freezable and tightly-bound water content in the polymer chain were calculated and is shown in Figure **9c** which increased with increasing total amount of ions.

CONCLUSIONS

This research explored the complex phase behavior of aqueous solutions of HPMC/KCG/salt with focus on the concentrated solution of low molecular weight HPMC. The shear viscosity of HPMC/KCG blend increased by one orders of magnitude, while the viscosity of HPMC/KCG/ potassium chloride (KCl) mixture increased by three orders of magnitude as compared to HPMC solution at temperatures below apparent gelation. The dynamic elastic modulus of HPMC/KCG blend increased by two orders of magnitude, while the elastic modulus of HPMC/KCG/ potassium chloride (KCl) mixture increased by three orders of magnitude as compared to HPMC solution at temperatures below apparent gelation temperature. It was found that there was an optimal amount of salt that can enhance solution viscosity and solution elastic modulus most effectively at temperatures below apparent gelation temperature. Addition of 0.08M of KCl was most effective at enhancing solution viscosity as well as solution elastic modulus ($T < 30$ °C) in solution of HPMC/0.3M KCG. It was speculated that the gelation behavior at temperatures below apparent gelation temperature was dominated by the interaction of KCG and HPMC, and the impact of salt on such gel behavior follow the order: KCl > NaCl > $CaCl_2$.

The melting temperature of the polymer solution decreases linearly with increasing ion concentration of salts. The contribution of bound water in the polymer blend examined indicated that the amount of bound water increased with increasing salt concentration. Moreover, the DSC secondary peaks in the data that signify the freezable bound water were only found with the presence of KCl.

Additional experimentations are planned to investigate the role of water molecules in the multiple gelation behavior of aqueous solutions of HPMC/KCG/salt.

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SUPPLEMENTAL MATERIALS

The supplemental materials can be downloaded from the journal website along with the article.

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