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Phase behavior of concentrated hydroxypropyl methylcellulose solution in the presence of mono and divalent salt

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ABSTRACT

Thermo reversible sol–gel transitions of hydroxypropylmethylcellulose (HPMC) are critical for many pharmaceutical, cosmetic, and food applications. This study examined the effects of salt (NaCl and $CaCl_2$) on the viscoelastic properties of concentrated low molecular weight HPMC solutions and found that the gelation temperature decreased linearly as a function of salt concentrations, independent of valency of cations and the mole concentration of anions. Thermal analysis showed that the depression of melting temperature can be fitted for both NaCl and $CaCl_2$ as a function of the total number of ions by a single linear curve, which was consistent with the melting point depression of pure water by NaCl and $CaCl_2$, but with a higher linear slope.

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1. Introduction

Hydroxypropylmethylcellulose (HPMC) (or hypromellose) is a non-ionic, linear polysaccharide that is obtained by modifying the hydroxyl position in cellulose. HPMC has been used in many applications such as thickeners, binders, and film-forming agents in the pharmaceutical, food, cosmetics, and ceramic processing industries (Clasen & Kulicke, 2001; Ford, 1999). Salts are commonly present in many of the formulations used.The rheological characteristics of the hypromellose solutions in the presence of salts is therefore crucial in designing the formulation and manufacturing process for these applications.

It is well known that HPMC can undergo thermo reversible sol–gel transition. Thermogelation of HPMC and other cellulose derivatives have previously been studied using rheology (Bajwa, Sammon, Timmins, & Melia, 2009; Haque & Morris, 1993; Hussaina, Kearyb, & Craig, 2002; Kobayashi, Huang, & Lodge, 1993; Li, Shan, Yue, Lam, Tam, & Hu, 2002; Silva et al., 2008), NMR (Haque, Richardson, Morris, Gidley, & Caswell, 1993), FTIR (Bajwa et al., 2009), dynamic light scattering (Kobayashi et al., 1993), small angle neutron scattering (Kobayashi et al., 1993), and DSC (Ford, 1999; Lam, Joshi, & Tan, 2007; Li et al., 2002). It has also been shown that the gelation mechanism of HPMC is a two stage process (Carlssona, Karlströmb, & Lindman, 1990; Ibbett, Kevin, & Price, 1992; Kobayashi et al., 1993), where the first stage occurs at low tempratures with association of HPMC or MC polymers and the second stage occurs at higher temperatures with a phase separated system. Recent studies using Cryo-TEM and other techniques have shown that HPMC gelation occurs due to aggregation and network structure formation (Bodvika et al., 2010).

The effect of salt on thermo gelation of HPMC has been previously studied using DSC and rheology measurements (Liu, Joshi, & Lam, 2008; Xu, Li, Zheng, Lam, & Hu, 2004; Xu, Wang, Tam, & Li, 2004). The gelation temperature of HPMC was increased or decreased by addition of salts where the degree of increase/decrease followed Hofmeister series (Liu, Joshi, & Lam, 2008; Mitchell, Ford, Armstrong, Elliott, Rostron, & Hogan, 1990; Xu, Li, et al., 2004; Xu, Wang, et al., 2004). More specifically, the thermo gelation temperature of HPMC in the presence of anions increased following the order of $SCN^- > ClO_4^- > I^-$ with SCN^- having the greatest increase, and decreased following the order of $NO_3^- \approx Br^- < Cl^- < F^- < H_2PO_4^- < S_2O_3^{2-} < SO_4^{2-}$ with SO_4^{2-} having the most depression on gelation temperature. The gelation temperature of other amphiphilic polymers in the presence of cations decreased in the following order: $Na^+ > K^+ > Li^+$, with the Na^+ having the greatest effect, however the effect of cations is less significant than that of anions (Alexandridis & Holzwarth, 1997). Additionally, it was found that the amount of depression of the

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Table 1
Zero shear viscosity of 15% E5 for various concentrations of salt.

Concentration of salts, NaCl (M)	η_0 (Pa s)			Concentration of salts, $CaCl_2$ (M)	η_0 (Pa s)		
	15 (°C)	25 (°C)	35 (°C)		15 (°C)	25 (°C)	35 (°C)
0.00	1.47	0.90	0.68	0.00	1.47	0.90	0.68
0.02	1.40	0.93	0.61	0.01	1.70	0.98	0.73
0.08	1.38	0.93	0.63	0.06	1.53	1.01	0.68
0.16	1.63	1.13	0.75	0.13	1.55	1.02	0.71
0.32	1.63	1.09	1.11	0.19	1.58	1.05	0.79
0.48	1.72	1.15	>10	0.36	1.54	1.05	>100
				0.50	1.82	1.32	>400

gelation temperature increased with increasing salt concentrations (Alexandridis & Holzwarth, 1997; Mitchell et al., 1990; Xu, Song, Ping, Wang, & Liu, 2006; Xu, Li, et al., 2004; Xu, Wang, et al., 2004).

The main objective of this study was to examine the effects of salt on the viscoelastic properties of concentrated low molecular weight HPMC solutions, as previous research mainly focused on high molecular weight HPMC and low concentration HPMC solutions (Liu, Joshi, & Lam, 2008; Liu, Joshi, Lam, & Tam, 2008; Silva et al., 2008; Xu et al., 2006). Both the rheological and thermal properties of a hypromellose solution with and without salts were investigated. NaCl and $CaCl_2$ were selected as model monovalent and divalent salts, respectively.

2. Experimental

2.1. Materials

The polymer used in this study was supplied by The Dow Chemical Company (Midland, Michigan, USA) under the trade name METHOCEL™ E5 LV Premium cellulose ether (a hypromellose labeled as United States Pharmacopeia (USP) substitution type 2910). The manufacturer's specifications indicated that the viscosity of a 2 wt% solution was 5 mPa s, at 20 °C and that the methoxyl and hydroxypropoxyl content are 28 wt% and 8.6 wt%, respectively. This polymer is noted as E5 throughout this paper. The polymer E5 was used without further purification. Water used in the experiments was purified through a Barnstead E-pure filter system and collected at 18 MOhm. Sodium chloride (NaCl) and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) were purchased from EM Science. E5 (15%) with 0–0.6 M salt (NaCl, $CaCl_2$) were dispersed at 80 °C with vigorous stirring in deionized water and were continously stirred at room temperature for more than 3 h. All solutions were hydrated at 4 °C for more than 12 h.

2.2. Rheology

Dynamic shear and steady flow measurements were conducted using an 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) was used. To prevent dehydration of the solutions, a small amount of low-viscosity silicone oil (Fisher Chemical, 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

$$\sigma(t) = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)] \tag{2}$$

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

$$|\eta^*| = \frac{\sqrt{G'^2 + G''^2}}{\omega} \tag{3}$$

A strain sweep was performed on all samples to locate the linear viscoelastic region (LVER). A strain amplitude γ of 2% was identified as well within the linear viscoelastic region and was used for both the dynamic temperature sweep as well as the dynamic frequency sweep. The temperature sweeps were performed at 2% strain and 1 Hz frequency with 1 °C/min of heating and cooling rates. The dynamic frequency sweep was performed at temperatures between −5 to 80 °C on each sample. The samples were annealed at each temperature for 30 min before the dynamic frequency sweep was performed. The master curves were generated using the principle of time-temperature-superposition (TTS) by shifting the appropriate dynamic frequency spectrum to a reference temperature (T_{ref}) of −5 °C.

2.3. Thermal analysis

Differential scanning calorimetry of the samples was done using DSC Q-2000 (TA Instruments) with hermetically sealed pans and sample weights of approximately 10 mg. The samples were heated from −40 °C to 20 °C at 2 °C/min. Each sample was measured three times to ensure reproducibility.

3. Results and discussion

3.1. Rheological behavior of HPMC solutions with various concentrations of NaCl and $CaCl_2$

The viscoelastic behavior of HPMC solutions was changed by the addition of various concentrations of salts. Fig. 1 shows the shear rate dependent viscosity at room temperature for 15% E5

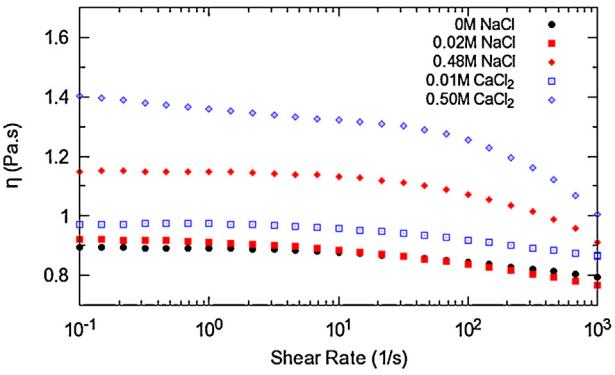

Fig. 1. Shear rate dependence of shear viscosity with salt concentrations at 25 °C.

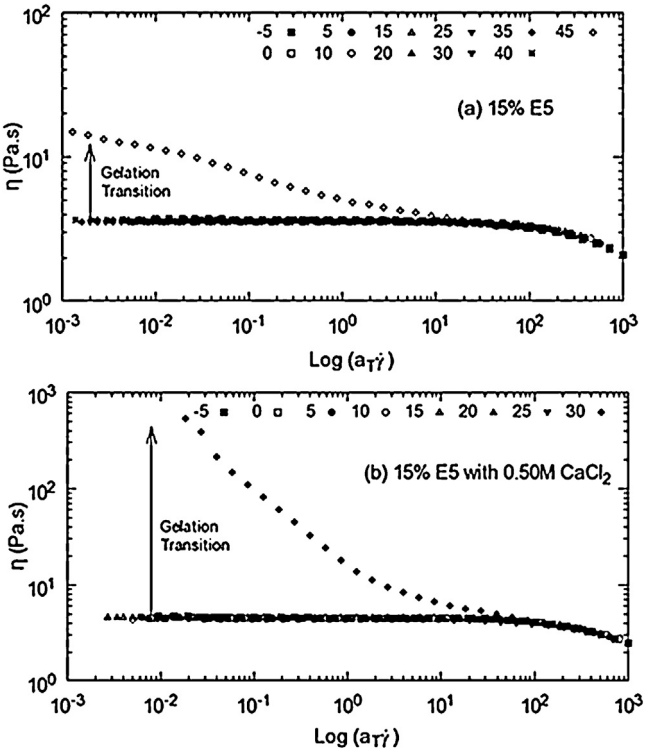

Fig. 2. Master curves of shear viscosity as a function of reduced shear rate (a) 15% E5 solution (b) 15% E5 solution with 0.50 M $CaCl_2$.

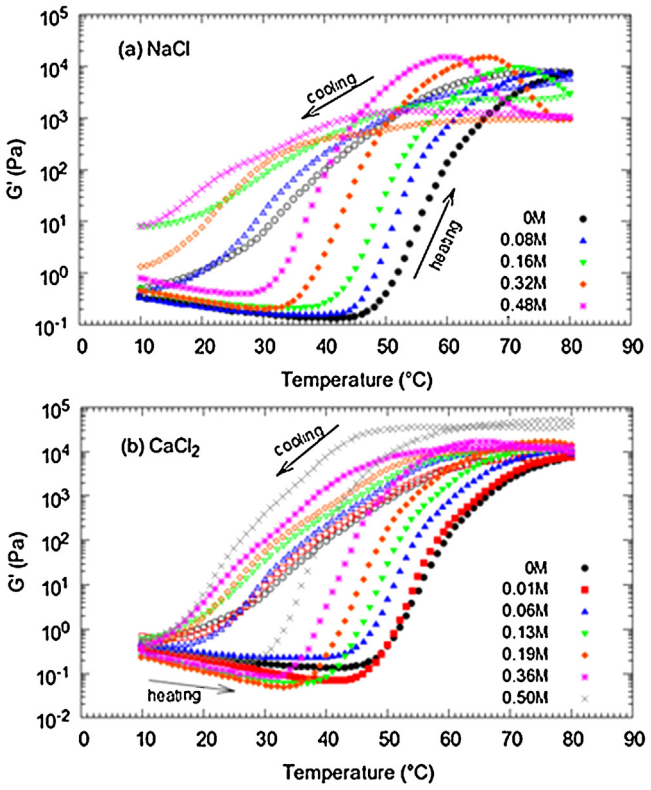

Fig. 3. Elastic modulus (G') as a function of temperature for 15% E5 solution with concentrations of (a) NaCl (b) $CaCl_2$. Filled and open symbol represent heating and cooling.

solution with and without salts. At the low shear rate, a Newtonian region was observed where the viscosity was independent shear rate, which indicated a zero shear terminal viscosity (η_0). Fig. 1 also shows the increases of zero shear viscosity as the salt concentration increases. Table 1 shows that the zero shear viscosity increased significantly when the temperature was above a critical temperature for a constant salt concentration (e.g. 35 °C for 0.48 M NaCl and 0.36 M $CaCl_2$) or when the salt concentration was above a critical concentration at a constant temperature (e.g. 0.48 M NaCl at 35 °C and 0.36 M $CaCl_2$ at 35 °C). Fig. 2 shows a typical master curve of 15% E5 solution and 15% E5 solution with 0.5 M $CaCl_2$. The gelation temperature was determined as the point of sharp increase of terminal viscosity, and as the point of failure of time temperature superposition. The gelation temperature identified from shear viscosity measurements was consistent with the gelation temperature determined from the dynamic measurements as shown in Fig. 4.

In order to characterize the gelation process and gel dissolution process, the key transition matrices are defined and described in Table 2.

Fig. 3 shows typical heating and cooling curves of rheological measurements of 15% E5 solutions with various concentrations of NaCl and $CaCl_2$. The onset of gelation temperatures shifted to lower temperatures with increasing NaCl and $CaCl_2$ concentrations. The various matrices of gelation temperature as well as gel strength (G'_{max}) obtained from this experiment are listed in Table 3 and also shown in Fig. 4.

The onset of gelation temperature 1 and 2 (T_{heat} (G'_{min}), T_{heat} ($|\eta^*|_{min}$)) and gelation temperature 1 (T_{heat} ($G' = G''$)) obtained from Fig. 3 were further analyzed in Fig. 4a and b. Linear curve fits were obtained for salt molar concentration dependances of T_{heat} ($|\eta^*|_{min}$), T_{heat} (G'_{min}), and T_{heat} ($G' = G''$) with relatively high coefficients of determination R^2 values, as shown in Fig. 4a. It appeared that both gelation temperature and onset of gelation decreased linearly as a function of salt concentrations independent of valency of cations as well as the molar concentration of anions. Fig. 4b shows the dependance of T_{heat} ($|\eta^*|_{min}$), T_{heat} (G'_{min}), and T_{heat} ($G' = G''$) as a function of total molar concentration of particles (ions) in the HPMC solutions. In this case, the transitions of $CaCl_2$ followed the same linear trend with NaCl at the concentration below 1 M, and had a significantly different trend from that of NaCl at higher molar concentrations of ions. Therefore, the interaction between water and strong electrolytes changed in the presence of HPMC. Usually the onset of gelation temperature can be influenced by the precipitation of HPMC chains. In this research, the precipitation behavior was not evident in Fig. 3, as there was no sharp drop of G' values before gelation transition. The drop of G' after gelation transition in Fig. 3a may be induced by syneresis of the gel which will be studied in more details in the future.

Fig. 4c and d shows maximum elastic moduli measured from temperature sweeps, as well as from master curves derived from frequency sweeps as a function of concentration of NaCl and $CaCl_2$. In general, the higher the salt concentration, the higher the elastic modulus of the gel. There may exist a critical salt concentration above which the gel modulus will increase significantly, as shown evidenced from Fig. 4c and d. Fig. 4d further shows that the functional dependance of G'_{max} is similar to HPMC solutions with $CaCl_2$ and NaCl lower than 1 M concentrations of ions. More research is needed to be done to further investigate the underlying mechanism of the impact of salt on gel modulus.

Usually, a dynamic spectrum of polymer solutions can be used to understand their structure and properties. To access a broad frequency range of materials, a principle, so-called time temperature superposition (TTS) is often used. It states that time and temperatures have equivalent effects on the rheological properties of linearly viscoelastic materials.

$$G'(\omega, T_r) = \frac{\rho(T_r)}{\rho(T)T} G'(a_T\omega, T) \quad (4)$$

Table 2
Key terminology and abbreviations used for gelation and gel dissolutions.

Matrix	Abbrevations	Definitions
Onset of gelation 1	T_{heat} (G'_{min})	The temperature measured at minimum G' during heating
Onset of gelation 2	T_{heat} ($\lvert\eta^*\rvert_{min}$)	The temperature measured at minimum η^* during heating
Gelation temperature 1	T_{heat} ($G' = G''$)	The crossover temperature, $G' = G''$ during heating
Maximum gel modulus during heating	G'_{max} (heat)	The maximum G' during heating
Gel dissolution temperature	T_{cool} ($G' = G''$)	The crossover temperature, $G' = G''$ during cooling
Onset gel dissolution temperature 1	T_{cool} ($\lvert\eta^*\rvert_{min}$)	The temperature measured at minimum η^* during cooling
Maximum gel modulus during cooling	G'_{max} (cool)	The maximum G' during cooling

Table 3
Summary of key matrices of gelation and gel dissolution behavior. The units for all transition temperatures are °C.

	T_{heat} (G'_{min})	T_{heat} ($G' = G''$)	T_{heat} ($\lvert\eta^*\rvert_{min}$)	G'_{max} (heat)[a]	T_{cool} ($G' = G''$)	T_{cool} ($\lvert\eta^*\rvert_{min}$)	G'_{max} (cool)[a]
NaCl (M)							
0	44	54.7	49	7.4	31.9	23	7.9
0.02	42	53.5	48	7.3	29.0	23	7.6
0.08	41	51.1	45	7.7	29.8	21	5.8
0.16	38	48.1	42	9.7	22.3	17	2.8
0.32	32	42.6	36	15.1	23.5	13	1.0
0.48	28	37.8	32	15.3	18.7	<12	1.3
$CaCl_2$ (M)							
0	44	54.7	49	7.4	31.9	23	7.9
0.01	43	54.2	48	7.6	31.3	23	2.6
0.06	42	50.8	46	11.7	30.2	21	11.9
0.13	41	48.4	45	13.0	27.3	19	11.0
0.19	37	45.6	42	16.9	26.4	17	13.4
0.36	34	42.2	39	13.4	26.1	<14	12.3
0.50	32	36.8	36	51.4	22.9	<14	37.4

[a] G'_{max} (heat) and G'_{max} (cool) values are in kPa.

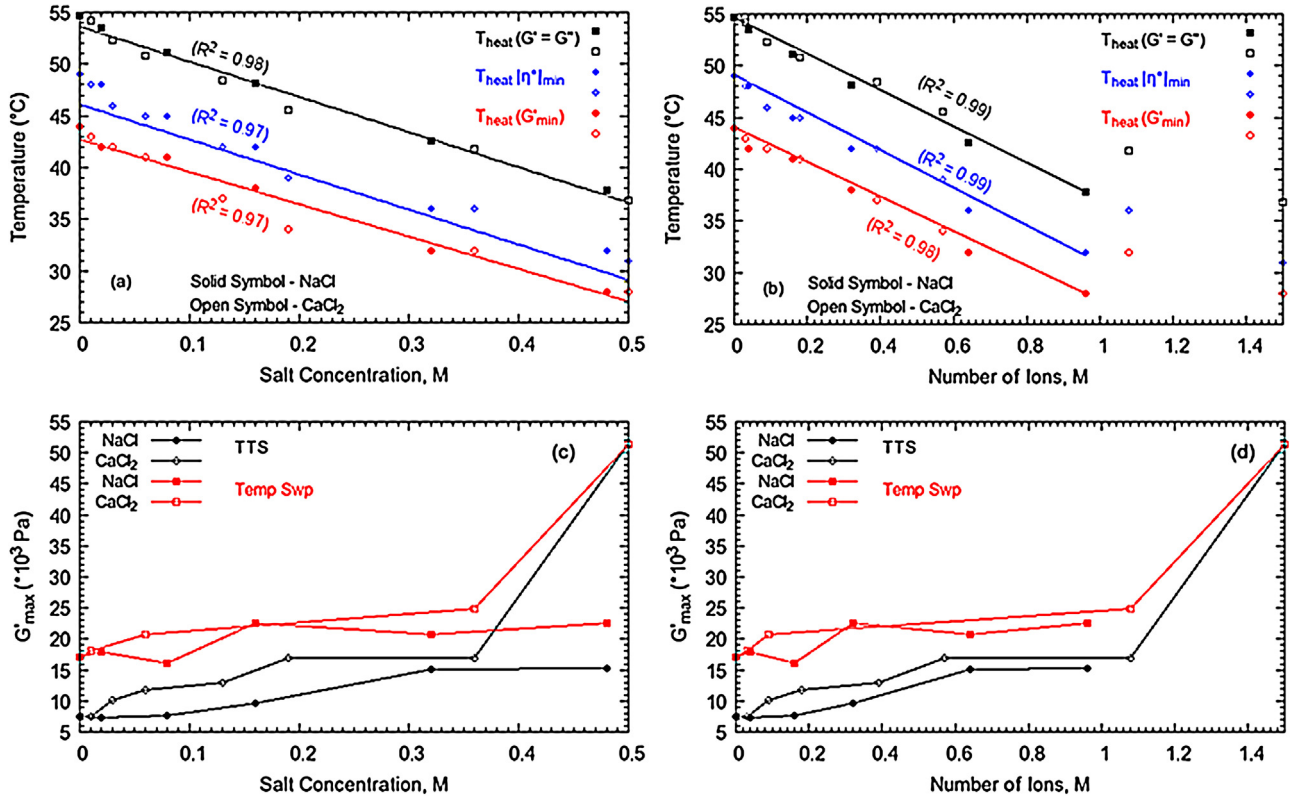

Fig. 4. (a and b) Onset of gelation 1 and 2 and gelation temperature 1 as a function of salt concentrations and number of ions; (c and d) the maximum elastic modulus as a function of salt concentrations and number of ions. (The data from temperature sweeps was noted as "Temp Swp"; the data obtained from TTS of frequency sweeps was noted as "TTS".)

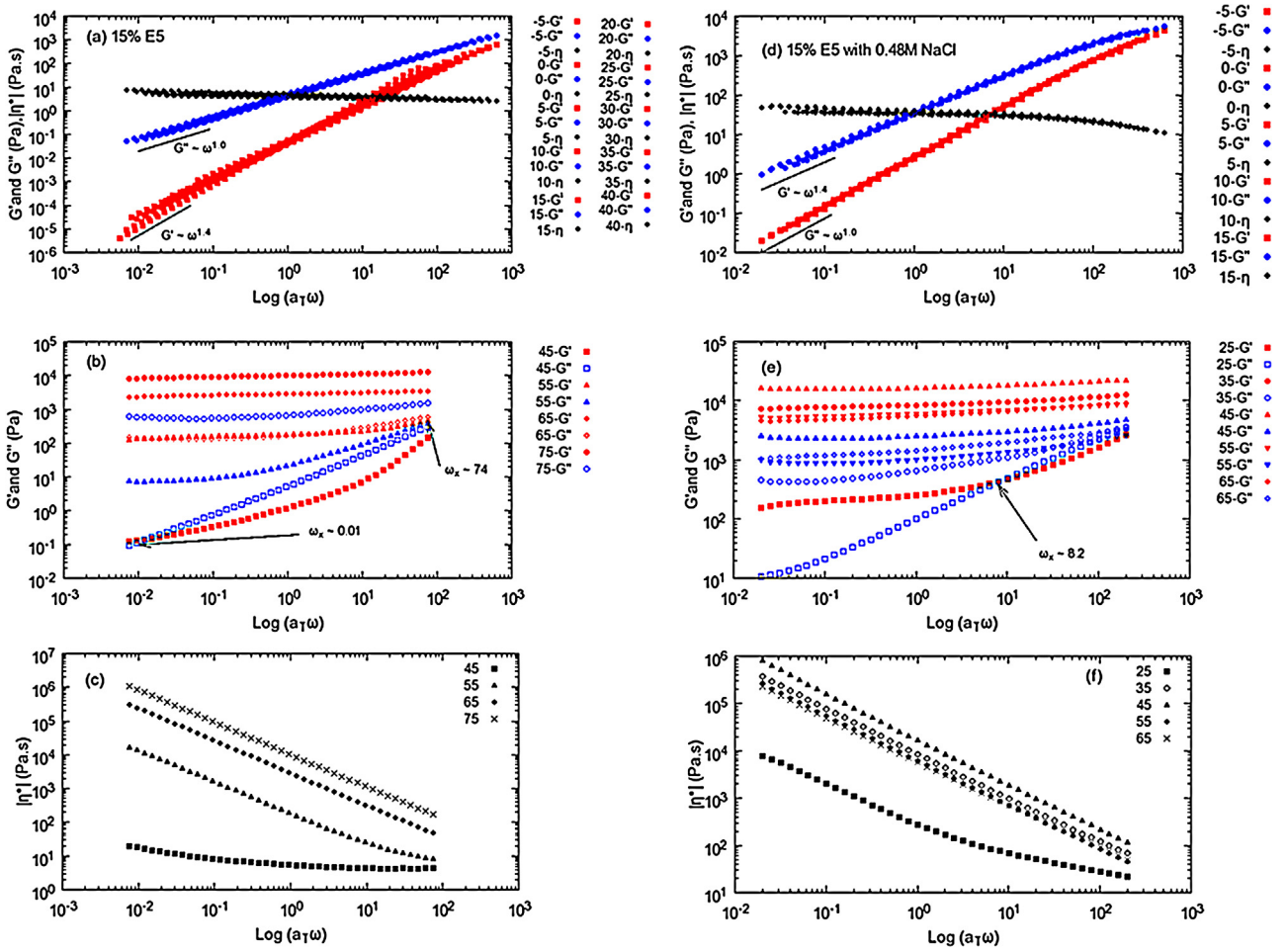

Fig. 5. Master curves of storage modulus, G', loss modulus, G'', and complex viscosity, $|\eta^*|$ as a function of reduced frequency for (a–c) 15% E5 solution; (d–f) 15% E5 solution with 0.48 M NaCl respectively.

$$G''(\omega, T_r) = \frac{\rho(T_r)}{\rho(T)T} G''(a_T\omega, T) \tag{5}$$

$$\left|\eta^*\right|(\omega, T_r) = a_T \frac{\rho(T_r)T_r}{\rho(T)T} \eta^*(a_T\omega, T) \tag{6}$$

where subscripts refer to conditions at a reference temperature, a_T is the ratio of relaxation times at two different temperatures, i.e., $\lambda_k(T)/\lambda_k(T_r)$; $\rho(T)$, is the density of polymer solutions at temperature T (Ferry, 1980; Macosko, 1994). However, this principle is only valid when all of the relaxation times, λ_k in the Maxwell equation have the same temperature dependence a_T (T).

Fig. 5 shows the storage modulus, G', loss modulus, G'', and complex viscosity, $|\eta^*|$ as function of reduced frequency, $a_T\omega$, for 15% E5 solutions and 15% E5 with 0.48 M NaCl solutions. It appeared that the master curve obtained by shifting frequency sweeps of −5 to 40 °C to a reference temperature of −5 °C followed a time temperature superposition as shown in Fig. 5a. Typical fluid-like behavior,

Table 4
Relaxation time and activation energy calculated from frequency sweep data and shift factor (a_T).

Concentration of salts	Activation energy, E_a (kJ/mol)	Relaxation time at crossover, τ_x (s)						
		25 (°C)	30 (°C)	35 (°C)	40 (°C)	45 (°C)	50 (°C)	55 (°C)
NaCl (M)								
0	13.5	–	–	–	–	67	0.3	0.01
0.02	13.5	–	–	–	74	25	0.12	<0.006
0.08	13.6	–	–	–	100	0.5	0.01	–
0.16	14.0	–	–	–	20	0.12	–	–
0.32	13.8	–	–	100	0.2	–	–	–
0.48	14.0	0.2	–	–	–	–	–	–
$CaCl_2$ (M)								
0	13.5	–	–	–	–	67	0.3	0.01
0.01	13.5	–	–	–	–	4	0.06	–
0.06	13.6	–	–	–	42	0.6	–	–
0.13	13.7	–	–	–	6	0.3	–	–
0.19	13.3	–	–	–	0.6	0.02	–	–
0.36	12.4	–	–	8	0.04	–	–	–
0.50	15.4	–	100	0.07	0.002	–	–	–

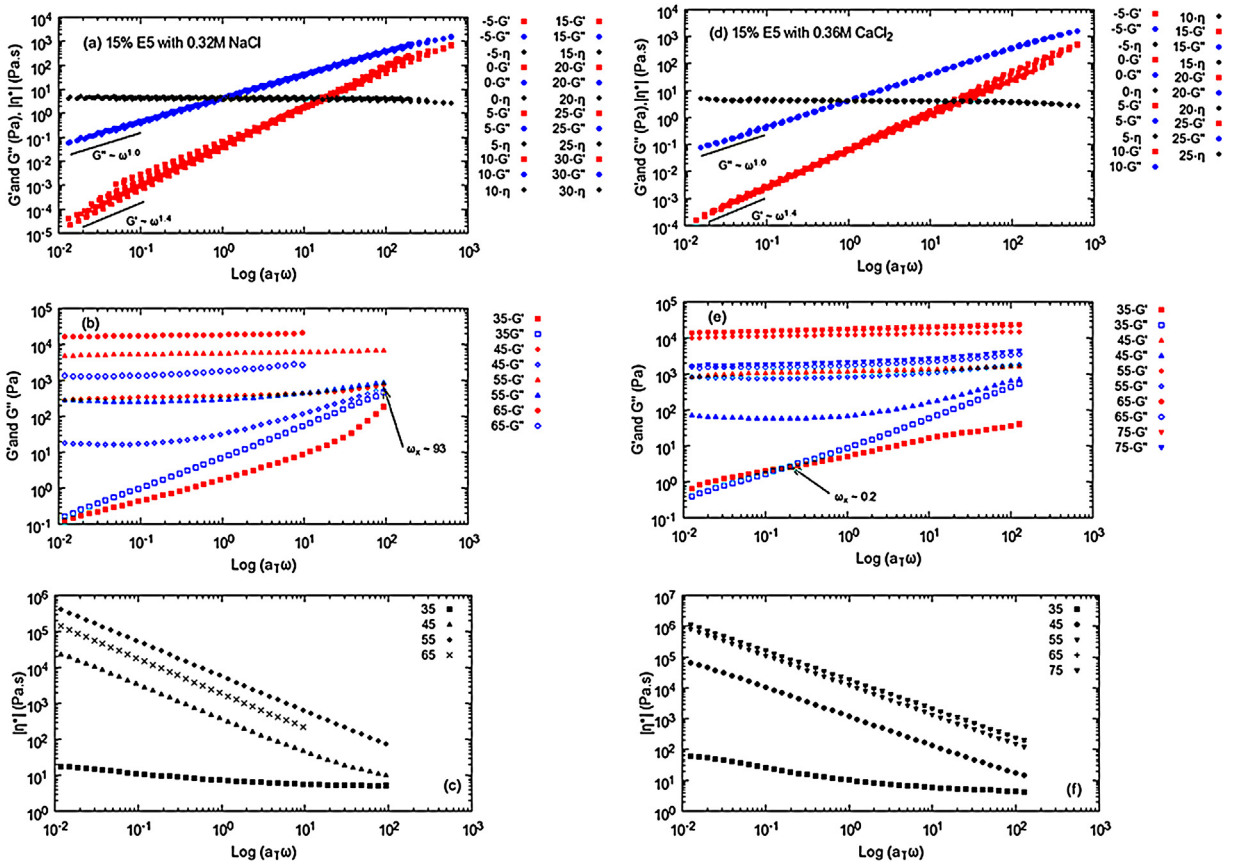

Fig. 6. Master curves of storage modulus, G', loss modulus, G'', and complex viscosity, $|\eta^*|$ as a function of reduced frequency for (a–c) 15% E5 solution with 0.32 M NaCl; (d–f) 15% E5 solution with 0.36 M $CaCl_2$ respectively.

i.e., $G'' \sim \omega^1$ and $G' \sim \omega^{1.4}$, was shown at low frequencies. However, when E5 solutions started to gel, i.e., above 40 °C, TTS failed when constructing the master curves from the scans obtained at 45 °C to 80 °C, as shown in Fig. 5b and c. Fig. 5b exhibits a crossover frequency, ω_x = 0.01 rad/s, at 45 °C. This crossover frequency shifted to higher frequencies as temperature increased and eventually moved out of the detectable range above 55 °C.

Similarly, Fig. 5d–f shows the storage modulus, G', loss modulus, G'', and complex viscosity, $|\eta^*|$ as a function of reduced frequency for 15% E5 solutions with 0.48 M NaCl. Again, TTS worked well at low temperatures for this solution, as shown in Fig. 5d. Typical fluid-like behavior, i.e., $G'' \sim \omega^1$ and $G' \sim \omega^{1.4}$, was shown at low frequencies. TTS failed when constructing the master curves above the gelation temperatures, as shown in Fig. 5e and f. The summary of relaxation time calculated from crossover frequencies is listed in Table 4. In general, the relaxation times shifted to lower value as temperature and salt concentration was increased.

Comparative master curves of 15% E5 solutions with 0.36 M $CaCl_2$ and 0.32 M NaCl are shown in Fig. 6. TTS worked well at low temperatures for both solutions as shown in Fig. 6a and d. Typical fluid-like behavior, i.e., $G'' \sim \omega^1$ and $G' \sim \omega^{1.4}$, was shown at low frequencies. Such slope defined by the $\log G'$ versus $\log \omega$ in the terminal region (lowest frequency range) is referred as terminal slope in polymer rheology. Fig. 6b and e shows that TTS failed when constructing the master curves above the gelation temperatures. Note that the transition of 0.36 M $CaCl_2$ solution occurred between 30 °C and 35 °C (as shown in Fig. 6a–c) versus that of 0.32 M NaCl solution which occurred between 35 °C and 40 °C (Fig. 6d–f). Additionally, the crossover frequencies of 0.36 M $CaCl_2$ solution shifted to a higher frequency compared to that of 0.32 M NaCl solution at the same temperature.

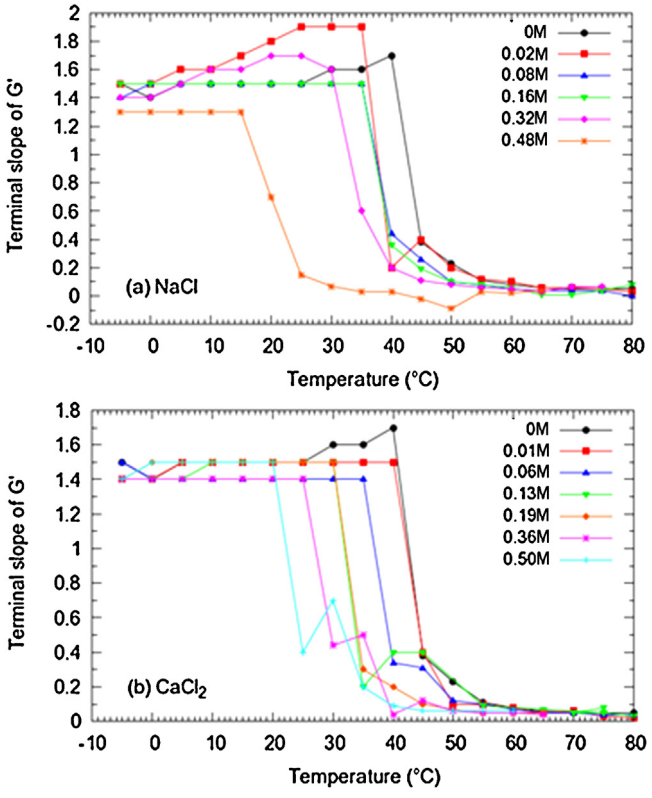

Fig. 7. The terminal slope of G' calculated from frequency sweep data of 15% E5 with concentrations of (a) NaCl and (b) $CaCl_2$.

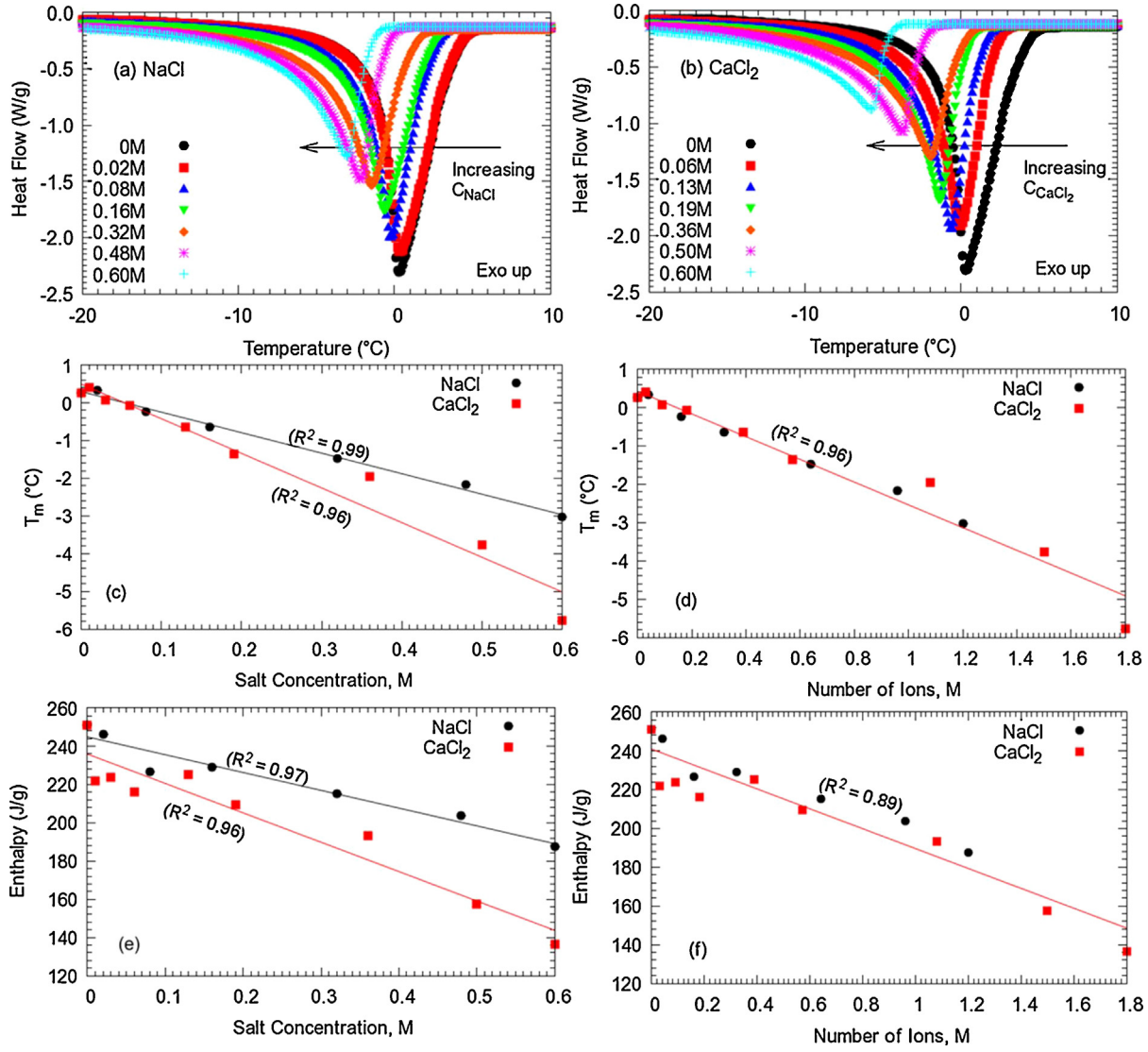

Fig. 8. DSC thermograms of 15% E5 solution with concentrations of (a) NaCl (b) $CaCl_2$; (c–d) melting temperature and (e–f) enthalpy as a function of salt and total ion concentration respectively.

The terminal slopes of the dynamic spectrum derived from frequency sweep data were plotted in Fig. 7 to demonstrate the change of slope during gelation transitions. These transitions were consistent with gelation transition obtained from dynamic temperature sweep data.

The shift factors a_T obtained from above TTS were also used to calculate the activation energy which is given by the Arrhenius equation:

$$\log(a_T) = \frac{E_a}{R}\left(1/T - 1/T_r\right) \quad (7)$$

where T_r is the reference temperature in degree K. Table 4 shows calculated activation energy from Eq. (7). The activation energy did not change significantly with salt concentrations, which suggest that the structure of the solution did not change as a function of salts below the gelation temperature.

3.2. Thermal analysis of HPMC solutions with various concentrations of NaCl and $CaCl_2$

Fig. 8a and b shows DSC thermograms of 15% E5 solution and 15% E5 solution with various concentrations of NaCl and $CaCl_2$ respectively. The melting temperature defined by the peak of endothermic thermogram decreased as the salt concentrations increased as shown in Fig. 8c and d. Fig. 8c shows that $CaCl_2$ depresses the melting temperature of the HPMC solution more than NaCl at the same molar concentration of salts. The melting temperature as a function of the total ion concentrations of NaCl and $CaCl_2$ is summarized in Fig. 8d. The depression of melting temperature can be fitted for both NaCl and $CaCl_2$ as a function of total number of ions by a single linear curve, which was consistent with the melting point depression of pure water by NaCl and $CaCl_2$, however, with a higher linear slope value (Ebbing & Gammon, 2009). This is in contrast with the effect of NaCl and $CaCl_2$ on the gelation temperature of 15% E5 solution as shown in Fig. 4 where the depression of gelation transitions were better fitted with the molar concentration of salt rather than the total molar concentration of ions. The enthalpy of melting for both NaCl and $CaCl_2$ also followed a similar linear relationship with salt concentrations (Fig. 8e and f).

4. Conclusions

In summary, this study examined the effects of salt on the viscoelastic properties of concentrated low molecular weight HPMC

solutions. It was found that the gelation temperature shifted to a lower temperature with increasing NaCl and $CaCl_2$ concentrations. Both gelation temperature and the onset of gelation decreased linearly as salt concentration increased independent of valency of cations and the mole concentration of anions. However, the transitions of $CaCl_2$ followed the same linear trend with NaCl at the concentration below 1 M and has significantly different trend from that of NaCl at higher molar concentrations. The elastic modulus of the gel also increased with increasing salt concentration. There may exist a critical salt concentration or the total ion concentration above which the gel modulus increased significantly.

It was shown that all of the solution rheology followed the principle of time-temperature superpostion below gelation temperature. The activation energy derived from TTS of the dynamic spectrum of low temperature solutions did not change significantly with salt concentrations, which may indicate that the solution structure did not have any effect with the addition of salt concentrations up to 0.5 M. Time temperature superpostion failed for all of the solutions above gelation temperature. It was also found that the characteristic crossover frequency shifted to higher frequencies as temperature and concentration increased. Thermal analysis showed that the depression of melting temperature can be fitted for both NaCl and $CaCl_2$ as a function of total number of ions by a single linear curve, which was consistent with the melting point depression of pure water by NaCl and $CaCl_2$ but with a higher magnitude of slope. The enthalpy of melting for both NaCl and $CaCl_2$ also followed a linear relationship with concentrations.

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