

Short communication

Effects of magnetic field on the sol–gel transition
of methylcellulose in waterQ. Wang, L. Li ^{*}, G. Chen, Y. Yang*School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore*

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Abstract

The effect of a magnetic field (0.3 T) on the sol–gel transition of methylcellulose (MC) in water was studied by means of rheology. It has been found that (1) the magnetic field causes the sol–gel transition temperature of MC to shift to the lower temperature by about 3 °C, showing a salt-out like effect, (2) the magnetic field shows a weaker effect on the sol–gel transition when NaCl is present, and (3) the gel strength is not strongly affected by the magnetic field but a slight increase in the gel strength is observed. The possible mechanisms for these interesting phenomena are proposed and discussed.

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Keywords: Sol–gel transition; Methylcellulose; Magnetic field; Hydrogen bond; Salt**1. Introduction**

Water is the most curious substance because many physical properties of water are much different from other low-molecular-weight compounds. For example, unlike most low molecular weight compounds that are gases at room temperature, water is a liquid and has a high boiling temperature. The main reason for water to be unique is because of the strong tendency of water molecules to form hydrogen bonds with other water molecules. Each water molecule is simultaneously a hydrogen bond donor and a hydrogen bond acceptor. Water is also a good solvent for many biological substances due to its dipolar character.

Water is weakly diamagnetic. It is important to know if a magnetic field affects the structure and property of water and further affects the interaction of water with a solute in an aqueous solution, which will influence many physical properties of a solute such as hydration, solubility, interfacial tension, etc. The effects of magnetic fields on water have been studied in the literature (Ghauri & Ansari,

2006; Inaba, Saitou, Tozaki, & Hayashi, 2004; Iwasaka & Ueno, 1998; Yamamoto, Matsumoto, Yamaguchi, Shimazu, & Ishikawa, 1998; Zhou et al., 2000). However, a common conclusion on the magnetic effects on water has not been drawn. This would be due to the complexity of water structure and technical difficulty in observing water structure directly under a magnetic field.

Under an extremely strong magnetic field (14 T), it was proposed based on the near-infrared spectral results that the formation of hydrogen bonds is enhanced (Iwasaka & Ueno, 1998). The effect of a high magnetic field (6 T) on the melting point of H₂O and D₂O was studied (Inaba et al., 2004). However, the increases in melting temperature of H₂O and D₂O by the magnetic field (6 T) were only 0.0056 and 0.0218 °C, respectively, which were not significant (Inaba et al., 2004). These results were explained by the suppression of the thermal motion of water molecules by the magnetic field which caused the strengthening of hydrogen bonding (Inaba et al., 2004). A recent experimental study shows that a relatively weak magnetic field (0.75 T) increased the viscosity of water, which was interpreted by the stronger hydrogen bonds under the magnetic field (Ghauri & Ansari, 2006). However, the viscosity

^{*} Corresponding author. Tel.: +65 6790 6285; fax: +65 6791 1859.
E-mail address: mlili@ntu.edu.sg (L. Li).

increases were extremely small ($\Delta\eta < 0.002$) and further investigation is needed (Ghauri & Ansari, 2006). A simulation-based work proved that a relatively weak magnetic field (0.2 T) can weaken or even partly break hydrogen bonds and increase the number of monomer water molecules (Zhou et al., 2000). Based on these studies (Ghauri & Ansari, 2006; Inaba et al., 2004; Iwasaka & Ueno, 1998; Zhou et al., 2000), the effects of magnetic fields on hydrogen bonds of water have not reached to a stage of common conclusion.

The effects of magnetic fields on the sol–gel transition for polymeric hydrogels (here magnetic particles-filled hydrogels are excluded) have not been extensively studied. Yamamoto et al. investigated the effects of magnetic fields (0–5 T) on the gel–sol and gel–sol transition temperatures for agarose gels and methylcellulose gels, respectively (Yamamoto et al., 1998). They found that the magnetic effect reached the maximum (saturation) at 3 T and the magnetic field resulted in 1 °C increase in the gel–sol transition for agarose gels and 3.5 °C decrease in the sol–gel transition for methylcellulose gels (Yamamoto et al., 1998).

A methylcellulose (MC) aqueous solution is not a magnetic fluid. Heating a MC aqueous solution with a concentration about 1–3 wt% to above 60 °C (but below 80 °C) will turn the liquid solution into a solid gel. The sol–gel transition of MC in water occurs through the so-called hydrophobic association of MC chains. The breakage of the hydrogen bonds formed between water molecules and the polymer chains is a necessary precursor for the hydrophobic association of MC to take place (Li et al., 2002).

It is simple to anticipate that any factors affecting the formation or destruction of hydrogen bonds will influence the sol–gel transition of MC in water. For the thermoreversible MC hydrogels, temperature is the key factor controlling the sol–gel transition (Li et al., 2002). Xu et al., have recently systematically studied the effects of salts and salt mixtures on the sol–gel transition of MC in water (Xu, Li, Zheng, Lam, & Hu, 2004; Xu, Wang, Tam, & Li, 2004). When a salt-out salt such as NaCl is added into a MC aqueous solution, for example, the sol–gel transition temperature will shift to a lower temperature with increasing salt concentration. The reason for the phenomena is that the salt breaks the structure of water through the interactions between salt ions and water molecules (Hribar, Southall, Vlachy, & Dill, 2002). Some of original hydrogen bonding network formed by water molecules is destroyed by the salt and this effect is similar to increasing temperature.

If the dipolar moment and orientation of water molecules can be changed by a magnetic field, it is expected that the formation of hydrogen bonds between MC and water will be affected. Thus, the sol–gel transition of MC may be affected by a magnetic field. In this work, we apply a magnetic field (0.3 T) to the aqueous solutions of MC to study its effects on the sol–gel transition and the gel strength. The MC solutions containing NaCl are also examined.

2. Experimental

2.1. Materials and sample preparation

A cellulose derivative, methylcellulose with a trade name of SM4000, was obtained from Shinetsu Chemical Co. Ltd., Japan. The polymer has an average degree of substitution (DS) of 1.8 and an average molecular weight of 310,000 determined by light scattering. The material was used as received without further purification. Prior to use, it was vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature. NaCl was purchased from Sino Chemical Co. Ltd., Singapore, and used as received.

A pure MC aqueous solution (0.93 wt% or 1.53 wt%), was first prepared by dispersing the weighed MC powder into deionized water at 70 °C and kept in a refrigerator for stabilization. A homogeneous and transparent solution of MC was obtained. The weighed salt was then added into the MC solution to obtain the MC-salt solutions. All the sample solutions were prepared with deionized water from a Millipore water purifier. A low temperature (below 10 °C) was used to keep the MC solutions.

2.2. Magneto rheometer and rheological measurements

An advanced magneto rheometer (UDS 200, Paar Physica Co.) was used to obtain the dynamic functions under a magnetic field. Unlike a conventional plate rheometer, the magneto rheometer was equipped with an additional magneto cell that was used to generate a moderately strong magnetic field passing through the loading plates. The sample was placed between two plates (25 mm in diameter) with a fixed gap of 1.0 mm. The magnetic field could be controlled by the coil current (I). For this rheometer, the coil current, I , should be below 2.5 A in order to protect the coil against overheating. This magneto rheometer has been used for testing of many MR fluids (Li, Chen, & Yeo, 1999; Yang, Chen, Li, & Li, 2006). In this work, a current of 1.9 A was used. At $I = 1.9$ A, a magnetic field of about 0.3 Teslas (T) could be obtained. After each experiment, a demagnetizing procedure was required to cancel any residual magnetic field. It was observed that at a temperature near the sol–gel transition temperature of 61 °C, there was a slight heat effect caused by the magnetic-generating coil when the current of 1.9 A was applied for a long time (>30 min). But this effect was negligible within the short time of each measurement (≤ 10 min).

The storage modulus (G') and loss modulus (G'') were measured as a function of temperature at an angular frequency of 1 rad/s within a linear range of viscoelasticity. Each measurement was conducted after a stabilization period at a given magnetic field. The oscillatory strains of 5–30% were used to for the different-viscosity samples. The comparison experiments were conducted with or without a magnetic field implied.

3. Results and discussion

3.1. The sol–gel transition of MC aqueous solution under a magnetic field

To verify our hypothesis that the sol–gel system will be affected by a magnetic field in the pre-gel and the sol–gel transition regimes, the dynamic rheological measurements were carried out for several MC aqueous solutions under a given magnetic field ($I = 1.9$ A).

Fig. 1 shows G' and G'' for a 1.53 wt% MC aqueous solution in a heating process from 20 to 70 °C. Two parallel experiments were conducted to confirm the reproducibility of the sample under the magnetic field. The “a” curve was obtained without the magnetic field, while the “b” and “c” curves are two repetitive curves under the same magnetic field. The two repetitive experiments show the good reproducibility.

As shown in Fig. 1, G' in the vicinity of the sol–gel transition is not really affected by the magnetic field. Thus, we focus our discussion on G' of the gelling system. As already known, the sol–gel transition of the MC solution in the absence of the magnetic field occurs in a narrow temperature range around 61 °C. In Fig. 1, it is clearly observed that the G' curves (i.e. the “b” and “c” curves) with the magnetic field have a similar pattern with the curve “a” without the magnetic field but shift to the lower temperature region, which indicates a salt-out like effect. After the sol–gel transition temperature, all G' curves obtained with or without the magnetic field almost overlap, indicating the onset of a G' plateau for a gel network which is almost not affected by the magnetic field. The effect of the magnetic field on the gel strength will be discussed later.

This salt-out like effect can be explained through the role of hydrogen bonds of water or cage-like water structure surrounding the hydrophobic groups of MC, which would

have been affected by a magnetic field. It is easy to understand that if the magnetic field could weaken the interaction between water and MC in the system the hydrophobic moiety of the polymer chains could be exposed from the water cages more easily. As a result, an earlier (i.e. at a lower temperature) association of MC chains would become possible for gelation. The shift of the sol–gel transition is detectable (about 2–3 °C), but it is not as great as the salt effects by a salt-out salt (Xu, Li et al., 2004; Xu, Wang et al., 2004). For example, NaCl, a typical salt-out salt, can lower the transition temperature of MC at a rate of 2.4 °C per 100 mM of NaCl. The possible mechanism for this salt-out effect of NaCl is the competition between salt ions and polymer chains for water molecules (Xu, Li et al., 2004; Xu, Wang et al., 2004). Under a magnetic field, a different mechanism should exist since there are no salt ions that attract water molecules. Thus, the most possible mechanism for the salt-out like effect of the magnetic field would be that the interactions between MC chains and water molecules are weakened by the magnetic field.

The effects of magnetic fields on the sol–gel transition for polymeric hydrogels (here magnetic particles-filled hydrogels are excluded) have not been extensively studied. Two probable effects of magnetic field on a polymer aqueous solution consisting only of a water-soluble polymer and water may be considered. The magnetic field would affect hydrogen bonds of water. Some polymers may be orientated by a magnetic field due to their diamagnetic anisotropy. As a combined result, hydration (or dehydration) of a polymer would be influenced by magnetic field.

A few studies reported on the effect of magnetic field on water: (i) viscosity of water in a temperature range from 25 to 50 °C increases under a 0.75 T magnetic field (Ghauri & Ansari, 2006); (ii) melting point of water increases in the magnetic field (6 T) (Inaba et al., 2004); (iii) Under an extremely strong magnetic field (14 T), the formation of hydrogen bonds is enhanced (Iwasaka & Ueno, 1998). These results may indicate that hydrogen bonds among water molecules could be strengthened by a magnetic field. However, the study of the magnetic field effects on the sol–gel transitions of agarose and methylcellulose shows the opposite effects of magnetic fields (up to 5 T): the sol–gel transition temperature of agarose increased by 1 °C while that of methylcellulose decreased by 3.5 °C (Yamamoto et al., 1998). The result on methylcellulose is excellently consistent with what we have observed in Fig. 1 in this study. However, the mechanisms behind the experimental results were not proposed satisfactorily by the authors (Yamamoto et al., 1998).

The effects of magnetic field on orientation or alignment of biopolymers in aqueous solutions have been reported in the literature (Das & Chakrabarti, 2000; Yamagishi, Takeuchi, Higashi, & Date, 1990). For example, the significant orientation of fibrin fibers was observed under the magnetic field (1 T) (Yamagishi et al., 1990). On the other hand, a theoretical study on the orientation of semiflexible

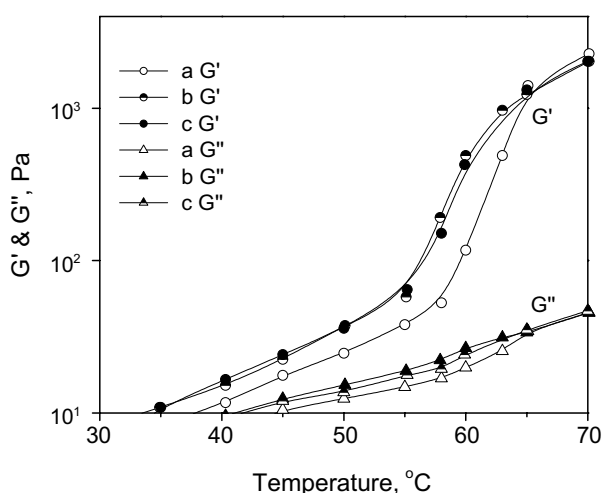


Fig. 1. Storage modulus G' and loss modulus G'' of MC (1.53 wt% SM4000) as a function of temperature in a heating process. A strain of 10% and angular frequency of 1 rad/s were applied. (a) Without a magnetic field; (b and c) under a magnetic field ($I = 1.9$ A).

biopolymers (such as filamentous actin and nucleic acids) in a magnetic field proves that a high-strength magnetic field of 12 T could stretch and orient the filamentous actin filaments in a dilute solution (Das & Chakrabarti, 2000). However, we have not found any studies on the effect of magnetic field on the molecular orientation of methylcellulose in aqueous solution from the literature. Since the methylcellulose polymer used is rigid and its molecular weight is very high (310,000 g/mol), the effect of magnetic field on the orientation of MC would be insignificant.

Based on our understanding and learning from the literature, we propose the following mechanism to explain the effect of magnetic field on the sol–gel transition of MC. The interactions between water molecules and MC are weakened by the magnetic field so that the dehydration of MC becomes easier, leading to a “salt-out” like shift of the sol–gel transition. This mechanism does not conflict with the literature results that hydrogen bonds among water molecules could be strengthened by magnetic field (Ghauri & Ansari, 2006; Inaba et al., 2004; Iwasaka & Ueno, 1998). When hydrogen bonds among water molecules are stronger in a magnetic field, hydration of a polymer will become more difficult but dehydration will be easier. Thus at the same time, the interactions between MC and water can be considered to become weaker in the magnetic field.

Our next hypothesis is that when a salt-out salt is present in a MC solution, the effect of the magnetic field will be weaker because the water molecules available for the formation of hydrogen bonds with MC chains are less than those in a salt-free MC solution. The similar rheological experiments were conducted for a 0.93 wt% MC solution containing NaCl (the salt concentration was varied from 0 to 0.8 M).

3.2. The sol–gel transition of MC in salt aqueous solutions under a magnetic field

We have conducted the rheological experiments for the MC solutions with 0.2, 0.4, and 0.8 M of NaCl, and the similar results were obtained. Fig. 2 illustrates the viscoelastic behavior of the MC aqueous solution (0.93 wt%) containing 0.8 M of NaCl. 0.8 M is the highest concentration of NaCl used in this work. As mentioned above, NaCl is well known as a typical salt-out salt, which is able to lower the sol–gel transition temperature of MC (Xu, Li et al., 2004; Xu, Wang et al., 2004). The capability of NaCl to lower the sol–gel transition temperature of a 0.93 wt% MC (SM4000) solution is shown in Table 1, which was obtained by the micro-DSC experiments previously (Xu, Li et al., 2004; Xu, Wang et al., 2004). Thus, the further shift of the G' curve to the left, as shown in Fig. 2 is no doubt caused by the magnetic field ($I = 1.9$ A). However, the magnetic effect in the presence of NaCl seems weaker than that in the absence of the salt as observed in Fig. 1. This may prove our hypothesis that the effect of the magnetic field is weaker when a salt is present. The similar

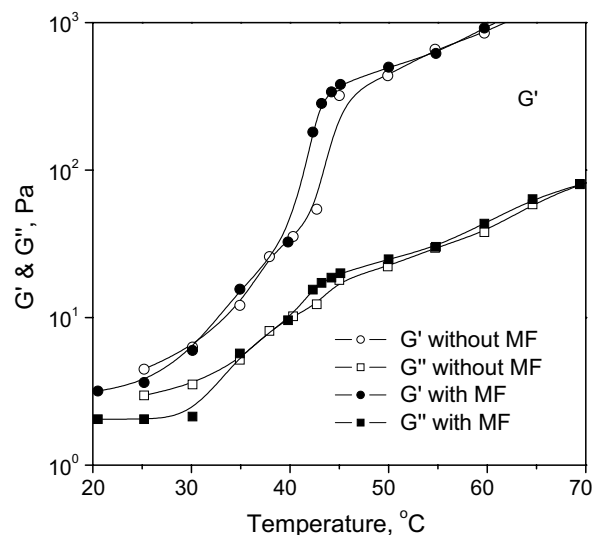


Fig. 2. Storage modulus G' and loss modulus G'' of MC/salt aqueous system (0.93 wt% SM4000 + 0.8 M NaCl) as a function of temperature in a heating process. An angular frequency of 1 rad/s was applied. MF denotes the magnetic field ($I = 1.9$ A).

Table 1

The sol–gel transition temperatures determined by micro-DSC for a 0.93 wt% MC aqueous solution with various salt concentrations of NaCl (Xu, Wang et al., 2004)

Salt conc. (M)	0	0.2	0.4	0.6	0.8
Peak temp. (°C)	61.1	55.3	50.1	46.8	43.1

trend could also be seen for the MC solutions with 0.2 and 0.4 M of NaCl.

Now, we believe that both a salt-out salt and a magnetic field can influence the sol–gel transition of MC aqueous solutions in the same direction (i.e. the salt-out direction) but in an independent way rather than in a cooperative way. Although the magnetic effect that we observed is not as great as the salt effect, our experimental results are the evidence that there is a magnetic effect on the sol–gel transition of MC.

As we discussed before, both the effects of a magnetic field and a salt-out salt are to decrease the hydration extent of MC in water, but with the different mechanisms that the salt competes with polymer chains for water molecules while a magnetic field weakens the hydrogen bonds between MC and water to result in an easier exposure of hydrophobic parts of the polymer. Therefore, these two effects can be considered to be independent. Furthermore, in a salt solution of MC, since the water structure may have been modified or partially destroyed by the salt ions, the further effect of a magnetic field on the water structure (or hydrogen bonds) will be weaker than that in a salt-free solution of MC.

Thus, the extent of the magnetic effect will be limited when a high concentration of NaCl is present, as the salt has provided already its salt-out effect in advance to the solution of MC and the superimposing of a magnetic field

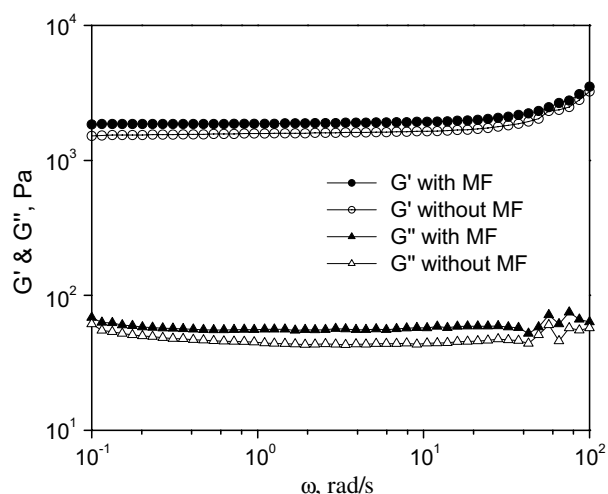


Fig. 3. Storage modulus G' and loss modulus G'' for a MC (1.53 wt% SM4000) hydrogel as a function of angular frequency at 70 °C. A strain of 3% was applied. MF denotes the magnetic field ($I = 1.9$ A).

will not further increase this effect too much. But the superimposed effect does exist in the vicinity of the sol–gel transition regime, as verified in this work.

3.3. Gel strength under a magnetic field

To examine if the magnetic field will affect the gel strength of a MC hydrogel, a comparison experiment was conducted on a well developed MC hydrogel, as shown in Fig. 3. G' and G'' were measured after a 30 min stabilizing period at 70 °C, which allowed the formation of a fully developed gel at the temperature (70 °C) without and with a magnetic field. As shown in Fig. 3, G' and G'' do not change remarkably with or without the magnetic field, but it is clear that both G' and G'' do increase slightly under the magnetic field.

It is reasonable that the strength of a MC hydrogel is not significantly affected by the magnetic field, because the gel network has already been well formed through the hydrophobic association. The water structure is no longer important for the gel as the breakage of the hydrogen bonds around the hydrophobes of MC has already occurred. However, the slightly increase in the gel strength under the magnetic field as observed in Fig. 3 may be explained by an increased resistance of the gel against the shear deformation, but this has not been experimentally

proved. In other way, if the hydrophobicity of water can be modified by a magnetic field to result in a “more hydrophilic” environment for MC chains, the hydrophobic association of MC may be strengthened to result in a stronger gel. This hypothesis needs to be experimentally verified by a future work.

4. Conclusions

It can be concluded from the above observation and discussion that the presence of a moderately strong magnetic field (0.3 T) does affect the sol–gel transition of a methylcellulose aqueous solution and a salt-out like effect is found. The above phenomenon has been explained to be due to the effect of a magnetic field on hydrogen bonds between polymer and water. The magnetic field may weaken hydrogen bonds or promotes the destruction of the cage-like water structure to result in an earlier hydrophobic association of MC. The similar results have been found in the MC aqueous solutions containing various contents of NaCl. However, the effects of the magnetic field and NaCl on the sol–gel transition of MC are independent with each other.

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