Colloid Polym Sci (2008) 286:663–672
DOI 10.1007/s00396-007-1810-x

ORIGINAL CONTRIBUTION

# Effects of SDS on the sol–gel transition of konjac glucomannan in SDS aqueous solutions

**Wanchun Yin · Hongbin Zhang · Long Huang · Katsuyoshi Nishinari**

Received: 6 October 2007 / Revised: 21 November 2007 / Accepted: 21 November 2007 / Published online: 10 December 2007


**Abstract** The interaction between konjac glucomannan (KGM) and an anionic surfactant, sodium dodecyl sulfate (SDS) is studied by rheological, circular dichroism (CD), conductivity, electron spin resonance (ESR), and FT-IR measurements. Since KGM is a neutral polysaccharide and has no significant hydrophobic side groups, the critical micelle concentration value of SDS is not influenced with the addition of KGM, and no marked binding occurs between them. SDS makes no conformational changes of KGM with or without heat treatment. The weak alkaline character of SDS induces the deacetylation of KGM chains and makes it form gels with heat treatment. At the same pH value, the gelation time needed for KGM by using SDS as the coagulant is shorter than that by using $Na_2CO_3$. The addition of SDS promotes the gelation process of KGM, indicating that although the interaction is weak, SDS micelles seem to play an important role in the gelation of KGM.

**Keywords** Konjac glucomannan · Sodium dodecyl sulfate · Conformational transition · Critical micelle concentration · Micelles

**Abbreviations**

| | |
|---|---|
| KGM | konjac glucomannan |
| SDS | sodium dodecyl sulfate |
| CD | circular dichroism |
| ESR | electron spin resonance |
| cmc | critical micelle concentration |
| cac | critical aggregation concentration |
| PDMAEMA | poly(2-(dimethylamino)-ethyl methacrylate) |
| PEO | poly(ethylene oxide) |
| HMHEC | hydrophobically modified (hydroxyethyl) cellulose |
| HPMC | hydroxypropyl methyl cellulose |

## Introduction

Considerable efforts have been devoted toward studying the interactions between surfactants and polymers in solutions, which are not only for scientific interests, but also for industrial applications, such as in foods, pharmaceuticals, cosmetics, paints, coatings, detergents, tertiary oil recovery [1–3]. The interactions between surfactants and some polysaccharides [4–10] have also been reported; however, the interaction between surfactants and konjac glucomannan (KGM), which is a neutral polysaccharide and also has various applications in foods, pharmaceuticals, coating [11–13], has never been studied.

Derived from the tuber of *Amorphophallus Konjac C.* Koch [11], KGM is composed of $\beta$-(1→4) linked β-D-mannose and β-D-glucose in a molar ratio of 1.6:1 [14,

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15]. KGM backbone possesses some branches [11, 15] and a low degree of acetyl groups (approximately 1 acetyl group per 19 residues) [14, 16]. It is assumed that these acetyl groups predominated the solubility of KGM in water. The gelation mechanism of KGM has attracted much attention in the academic studies and industrial applications for a long time. It is well known that KGM generally forms a thermally irreversible gel in the presence of an alkaline coagulant such as $Na_2CO_3$ upon heating. Maekaji [16] concluded that KGM loses its acetyl groups upon alkaline treatment, and then deacetylated KGM aggregates with one another through linkages such as hydrogen bonds, by which the KGM chains form junction zones, thereby ultimately leading to gel formation. The added alkaline coagulant is believed to facilitate the deacetylation of the KGM chains. Now the idea, deacetylation inducing the gelation of KGM, seems to be widely accepted [17–19]. Alternatively, KGM can also form synergistic gels with other polysaccharides such as κ-carrageenan [20, 21], xanthan gum [22–24], gellan gum [25], acetan or deacetylated acetan [26] without involving the abovementioned deacetylation. The synergistic models of these binary mixtures have been presented on the basis of the intermolecular interaction, likely hydrogen bonding, supported by different characterization methods. In addition to these, Hirai et al. [27] suggested that KGM form a gel without alkaline coagulant, at the concentration above 8 wt%. By observing gelation kinetics in the presence of lyotropic series salts with alkaline coagulants, Case et al. [28] have suggested that hydrophobic interactions play an important role in the gelation process of KGM. The detailed gelation mechanism for KGM under different conditions has been still under clarification.

An anionic surfactant, sodium dodecyl sulfate (SDS), has been used in many cases to study the interactions existing in polymer-SDS systems. SDS has a negative charge and alkyl chain, which contributes to mainly electrostatic interaction and hydrophobic interaction existing in polymer-SDS systems. Then, SDS was employed in this work, to study the interaction between it and KGM. The gelation mechanism of KGM was also discussed.

## Experiment

### Materials and methods

Purified KGM sample was kindly supplied by Shimizu Chemical Co., Tokyo, Japan. The molecular weight of KGM was approximately $6.9\times10^5$ and its intrinsic viscosity using cadoxen as a solvent was 3.91 l/g [18].

SDS and $Na_2CO_3$ used in this study were of assay grade reagents (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), and were used without further purification.

### Preparation of KGM solutions

Powders of KGM were dispersed in double distilled/deionized water with stirring. The solutions were heated to 80°C and maintained at this temperature for 1 h and cooled to the room temperature.

For samples containing SDS, SDS was freshly dissolved in water at room temperature at a certain concentration, and then, the SDS solution was mixed with KGM aqueous solution at a weight ratio of 1:1, with gently stirring at room temperature. Ten minutes stirring was needed for diluting before the rheological measurements, and the measurement of pH value. For all samples containing $Na_2CO_3$, after the addition of $Na_2CO_3$ and 1 min stirring, the pH values were immediately measured. The pH values of all samples were measured by use of Metrohm 744 pH Meter (Bie & Berntsen Co., Herisau, Switzerland) at room temperature.

### Viscoelastic measurements

Tests were carried out in a stress-controlled rheometer, Rheostrees1 (ThermoHaake, Germany), using a 1.0 mm gap parallel-plate sensor (60 mm in the diameter of the plate). The sample was poured directly onto the lower parallel plate, which was heated to the testing temperature beforehand. The free-surface of all samples was immediately covered with low viscosity silicone oil to prevent the evaporation of water. Experiments were repeated to ensure that the addition of oil did not affect the data. Stress dependence of the storage and loss shear moduli, $G'$ and $G''$, was examined to determine a linear viscoelastic regime. Oscillatory measurements of $G'$ and $G''$ were performed at the frequency range from 0.01 to 10 Hz. Steady shear rate sweep measurements were carried out in the range from 0.01 to 100 $s^{-1}$. For samples with the addition of alkali, 20 μl of 2 M $Na_2CO_3$ was added to per 1 g KGM solution at the time $t$=0 and mixed.

### Gelation kinetic tests

When a solution prepared at a non-gelling temperature is kept at a certain gelation temperature, both moduli begin to increase with lapse of time. The evolution of storage shear modulus $G'$, loss shear modulus $G''$ and tanδ is recorded as a function of time under testing temperature. To avoid the destruction of the structure being formed, the testing stress should be as low as possible within the linear regime. In the present work, the applied stress was imposed at 0.2 Pa. In this paper, for simplicity, the gelation time, $t_0$ at 1 rad/s was determined as the intersection of $G'$ and $G''$, although the first order kinetics equation can be also used to obtain the kinetic parameters by fitting the rheological data [19], because it was difficult to detect the gelation time at

which $G'$ begins to deviate from the base line in the present experiment.

### Electrical conductivity

Conductivity was measured with a DDS-11A conductimeter (Shanghai Lei Ci Xin Ding Instrument Co., Shanghai, China) at room temperature.

### Circular dichroism

Circular dichroism (CD) spectra were recorded with a Jasco J-715 Spectropolarimeter (Jasco Co., Japan) in the range 190–500 nm with quartz cells with an optical path of 0.1 cm, under a nitrogen atmosphere. Instrument parameters were as follows: time constant 1 s, scan speed 100 nm/min, slit width 1 nm, step resolution 0.2 nm. Five scans were averaged for each solution and then corrected for background by the subtraction of a buffer blank.

### Fourier transform IR spectra measurement

Powders of native KGM were mixed with KBr and compressed into a thin film until no reduction in weight was observed. The gels formed by using SDS as the only coagulant, and the spin-labeled KGM as mentioned below were both frozen dried by using LGJ-10 freeze-drying machine (Beijing Four-cycle Scientific Technologic Machine Manufactory, China). Then the lyophilized samples were also mixed with KBr and compressed into a thin film. FT-IR spectra were obtained from these films, using a Paragon 100 Fourier Transform Infrared Spectrometer (Perkin Elmer Co., USA) in the range from 4,000 to 500 $cm^{-1}$.

### ESR measurement

KGM was spin-labeled with 4-amino Tempo (97%, Sigma Chemical Co., USA) through hydroxyl groups along the polymer chains as described previously [20–22, 29]. The spin-labeled KGM solutions were directly used to conduct the ESR measurement. The ESR spectra were recorded at 25°C on a Bruker EMX-8 spectrometer (Bruker Co., Germany) operating at X-band with 100 kHz magnetic field modulation at 1K and 9.985 mW microwave power to avoid power saturation. All spectra were determined by using a glass capillary with 0.5 mm diameter to contain the aqueous samples. Before measurements the spin-labeled KGM solutions were mixed with SDS solutions at the weight ratio of 1:1 with stirring for 4 h.

The rotational motion is usually described by rotational correlation time, $\tau_R$, which as an approximation, from the ESR spectra, can be calculated using Kevelson's expression [30] for isotropic rotation in the motional narrowing region by the following equation:

$$\tau_R = 6.6 \times 10^{-10} W_0 \left[ \sqrt{h_0/h_{-1}} + \sqrt{h_0/h_{+1}} - 2 \right] \quad (1)$$

where $W_0$ represents the peak-to-peak line width of the mid-field line (in gauss); and $h_{-1}$, $h_0$ and $h_{+1}$ are the peak-to-peak heights of the low-, mid-, and high-field lines, respectively. The constant $6.6 \times 10^{-10}$ has been calculated for di-tert-butyl nitroxide [31], but to a good approximation, it can be used for other nitroxide radicals as well [32, 33]. The average relative error for the rotational correlation time $\tau_R$ is lower than 10%.

## Results and discussion

It is known that SDS has a weak alkaline character, and that KGM forms a gel in the presence of alkaline coagulants with heat treatment. It is, therefore, necessary to see whether the pH value of KGM solutions is changed with the addition of SDS. Figure 1 shows the pH value of SDS and KGM/SDS mixed solutions, as a function of SDS concentration, with or without $Na_2CO_3$, which is a commonly used alkaline coagulant for KGM. It is clearly seen from this figure that, in the absence of $Na_2CO_3$, the pH values of pure SDS solutions and KGM in SDS solution all increased with increasing concentration of SDS, but quickly reached the final pH value around 9.0 because of the weak alkaline nature of SDS. In contrast with the alkalescence of SDS, $Na_2CO_3$ is a strong alkali. The addition of 40 mM $Na_2CO_3$ makes the pH values of SDS and KGM/SDS mixed solutions all sharply increase and keep constantly at 11.45. In the following, the interaction

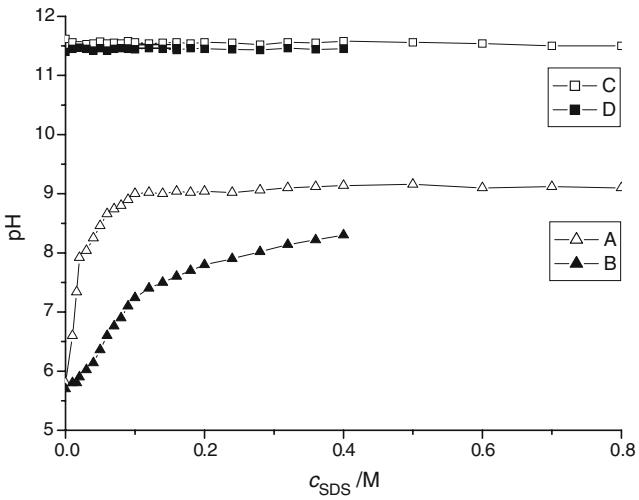


**Fig. 1** pH value of SDS and KGM/SDS solutions as a function of SDS concentration at 30°C *A*, aqueous solution of SDS alone; *B*, 0.8 wt% KGM in SDS solution; *C*, SDS aqueous solution with the addition of 40 mM $Na_2CO_3$; *D*, 0.8 wt% KGM in SDS solution with the addition of 40 mM $Na_2CO_3$

between SDS and KGM was studied in aqueous SDS solutions, with and without $Na_2CO_3$.

In the absence of $Na_2CO_3$

Since the addition of SDS increases the pH value of KGM solutions, the kinetic tests were done. Figure 2 shows the time dependence of $G'$ and $G''$ for 0.8 wt% KGM in 0.4M SDS solutions, at different temperatures. It is clear that, the addition of 0.4 M SDS solutions increases the pH value of 0.8 wt% KGM up to 8.30, and makes it form gels with heat treatment. The formed gels are elastic gels because the final tanδ is smaller than 0.1. This gelation process is dependent on the heating temperature. High heating temperature facilitates the gelation process, and low temperature delays it. In our previous studies (data not shown), the addition of 0.4 M SDS makes KGM solutions with different concentrations from 0.1 to 2.0 wt% form thermo-irreversible gels within 1 h, when heated at 80°C. The FT-IR spectra of KGM gels formed in SDS solutions (data not shown) confirmed the removal of acetyl groups, which showed a peak at 1,730 $cm^{-1}$ before mixing with SDS [18]. The alkaline property of SDS causes the deacetylation of KGM chains, just as other alkaline coagulant.

If both SDS and $Na_2CO_3$ make KGM form gels only through deacetylation, the gelation process of KGM will largely depend on the pH value and be independent on the type of the added alkali. From the result of Fig. 1, the pH values of SDS and KGM/SDS solutions depend on the concentrations of SDS. Figure 3 compares the kinetic tests for 0.8 wt% KGM by using SDS or $Na_2CO_3$ alone, at 80°C. It is clear that, the addition of 0.2 mM $Na_2CO_3$ adjusts the pH value of KGM solutions to be at 8.90. Although this pH value is also slightly higher than that of 0.8 wt% KGM solutions in the presence of 0.4M SDS, which is at 8.30; the gelation time, $t_0$ of KGM in the presence of 0.2 mM $Na_2CO_3$, is markedly longer than that of using 0.4 M SDS. It is also shown that, the gelation time $t_0$ of using 0.24 M SDS as the coagulant, (pH=8.0), is also shorter than that of using 0.2 mM $Na_2CO_3$ as the coagulant. These phenomena suggested that there are interactions between SDS and KGM, and they play important roles in the gelation process of KGM in SDS solutions.

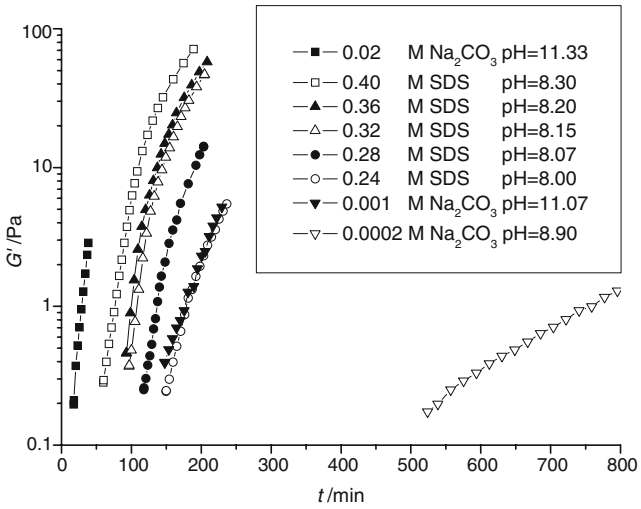


**Fig. 3** Time dependence of $G'$ for 0.8 wt% KGM aqueous solution with the addition of different concentrations of $Na_2CO_3$ or SDS($T$=80°C)

A general characteristic of surfactants is the formation of micelles in aqueous solution above a certain concentration, which is called the critical micelle concentration (cmc). When certain physical properties such as conductivity, surface tension, osmotic pressure and chemical shift are plotted

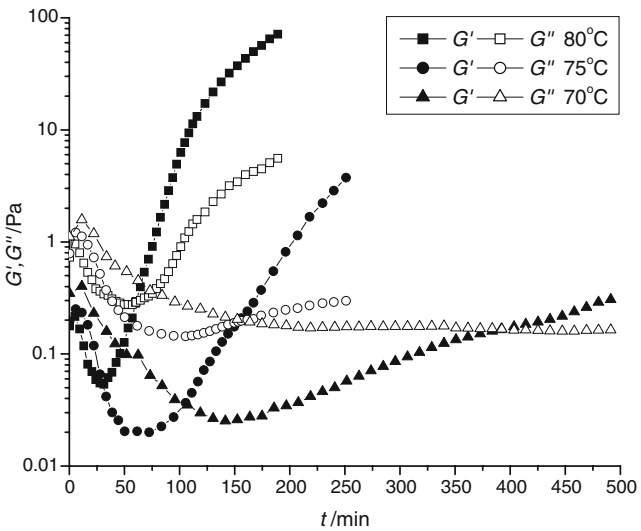


**Fig. 2** Time dependence of $G'$ and $G''$ for 0.8 wt% KGM in 0.4 M SDS solutions, pH=8.30, at different gelation temperatures

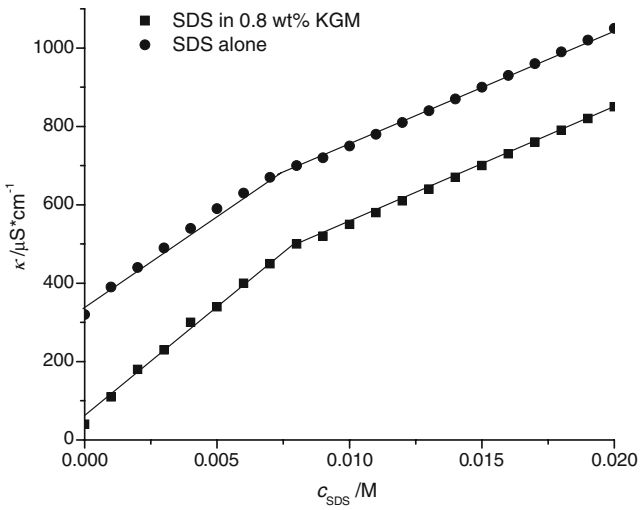


**Fig. 4** Electrical conductivities of SDS aqueous solution and 0.8 wt% KGM in SDS solution as the function of the final concentration of SDS ($T$=30°C)

against the surfactant concentration, each shows a break point at the cmc. Figure 4 showed the electrical conductivity measurements of SDS aqueous solution and 0.8 wt% KGM in SDS solution at room temperature. Each plot of the electrical conductivity ($\kappa$) against surfactant concentration furnishes two straight lines that intersect at the concentration corresponding to micelle formation, allowing identification of the cmc of the surfactant. Figure 4 shows that the conductivity increases with increasing concentration of SDS, and that the addition of KGM makes no effect on the cmc value of SDS, which is approximately 8 mM, identical to the reported value of pure SDS in water [34, 35]. This result resembles the cmc of SDS in the presence of xanthan gum [9]; but not the results of sodium hyaluronate [10], gelatin [36], chitosan [37] and PDMAEMA (poly (2-(dimethylamino)-ethyl methacrylate) [38], which lower the cmc value of SDS; either does not resemble the result of PEO [poly(ethylene oxide)] [39], which increases the cmc value of SDS. This suggests that though the interactions between SDS and KGM exist, it is very weak. The neutral KGM could not act as a nucleation site for surfactant aggregation, as some polyelectrolyte did [36–38].

Since dramatic changes always occurred in the rheological properties SDS-polymer mixed systems, viscoelastic measurements were done. The dynamic viscoelastic measurements for 0.4, 0.6, 0.8, and 1 wt% KGM in SDS solutions with different concentrations were conducted at 30 and 40°C. The stress was imposed within the linear viscoelastic regime. All the KGM solutions showed typical semi-dilute solution behavior, with or without the addition of SDS. Figures 5 and 6 showed the effects of the addition of SDS on the storage and loss shear modulus, $G'$ and $G''$, of KGM aqueous solutions with different concentrations at a frequency of 0.1 Hz, at 30 and 40°C, respectively. It shows that, the addition of SDS makes no significant changes in these four systems, which is not equal to the result of hydroxy(ethyl) cellulose [4], HMHEC [hydrophobically modified (hydroxyethyl)cellulose] [40], and hydrophobically modified poly(sodium acrylate) [41], where a sudden increase occurred in both $G'$ and $G''$. Figure 7 shows the zero-shear viscosity as a function of the SDS concentration, for 0.4, 0.6, 0.8 and 1 wt% KGM in SDS solutions, at 30 and 40°C. Corresponding to the dynamic viscoelastic measurements, the results of steady shear viscosity measurements also have no significant changes, which are also not equal to the changes of hydroxypropyl methyl cellulose (HPMC) [10], and hydrophobically modified poly(sodium acrylate) [42] with the addition of SDS. The different results of KGM comparing with these polymers are because of the lack of strong hydrophobic side groups on the backbone. The structure of SDS and the character of forming micelles with hydrophobic alkyl chains in the core of micelles, makes strong hydrophobic interactions between SDS and these hydrophobic polymers.

Wang et al. [6] studied the gelation process of MC in SDS solutions. Based on the results of gelation kinetic tests, which showed that both $G'$ and $G''$ values for MC/SDS mixed solutions are changed with the addition of SDS at different concentrations, they discussed the possibility of MC molecular entanglements in the presence of SDS. But from Figs. 2, 5, and 6 in the present paper, no such changes were observed on both moduli. It is reported by Ogawa et al. [43] that KGM molecule was bi-fold helix by X-ray diffraction method; however, Li et al. [44] argued that KGM molecule was an extending linear chain through TEM image. From our results, it seems the possibility of KGM molecular entanglements is neglected, but the further study should be done to clarify the details.

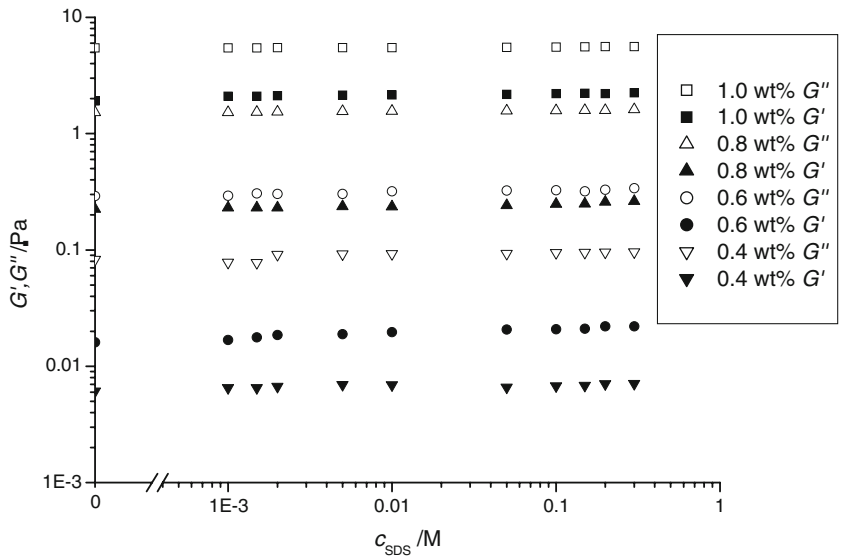


**Fig. 5** $G'$ and $G''$ ($\omega$=0.1 Hz) as a function of SDS concentration, $c_{SDS}$, for KGM at different concentrations and 30°C

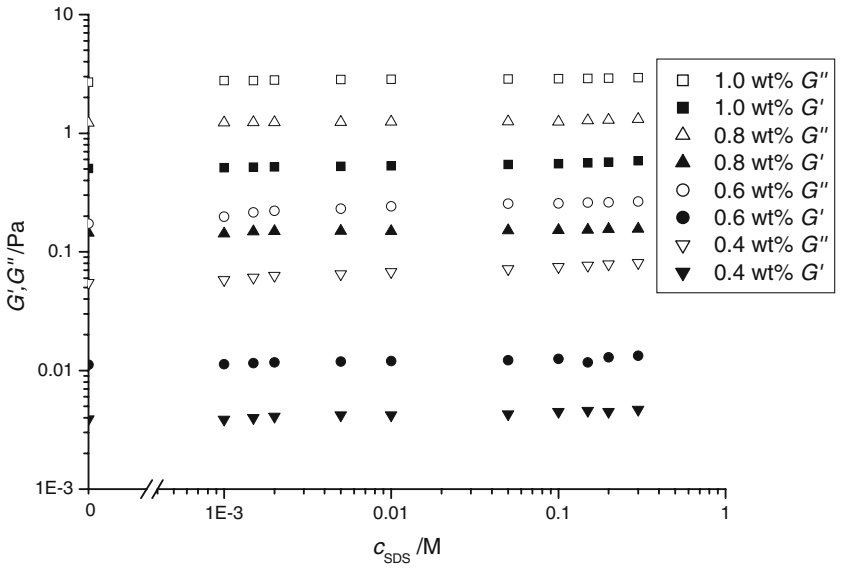


**Fig. 6** $G'$ and $G''$ ($\omega$=0.1 Hz) as a function of SDS concentration, $c_{SDS}$, for KGM at different concentrations and 40°C

For some proteins, i.e., zein protein [45], the addition of SDS could make proteins unfolding through electrostatic and hydrophobic interactions, the unfolding process is accompanied with the changes of viscosity. Molecular entanglement and unfolding are classified as molecular conformational changes, and SDS is also known to induce conformational changes of polymers [46, 47], taking into account the presence of the acetyl groups in the KGM backbones, optically active in the range 200–240 nm [24], CD measurements were conducted in this paper (data not shown). The results of CD measurements indicated that no conformational change of KGM occurred in the presence of SDS, with or without heat treatment. This result was in agreement with the results of gelation kinetic tests and viscoelastic measurements. Both moduli and zero-shear viscosity were not changed with the addition of SDS.

The spin-label and spin-probe techniques have been used to study a wide variety of polymers, both in bulk and in solution; and KGM was also studied by the ESR method [20–22, 29]. The shape and width of the electron spin resonance (ESR) spectrum of a spin label or probe is sensitive to the mode and rate of rotation of the radical. Thus, examination of the ESR spectrum of the labeled or probed polymer can yield information on the dynamics and relaxations of the polymer.

The spin probe results shown in Fig. 8 indicates the variation of rotational correlation time of $10^{-4}$ M 4-amino Tempo in SDS aqueous solution and KGM/SDS solution (the concentration of KGM is 0.8 wt%), as a function of SDS concentration. Figure 9 shows the ESR spectrum of 4-amino Tempo in SDS solution. The nitroxide free radical itself has a motionally narrowed three-lined pattern. Above

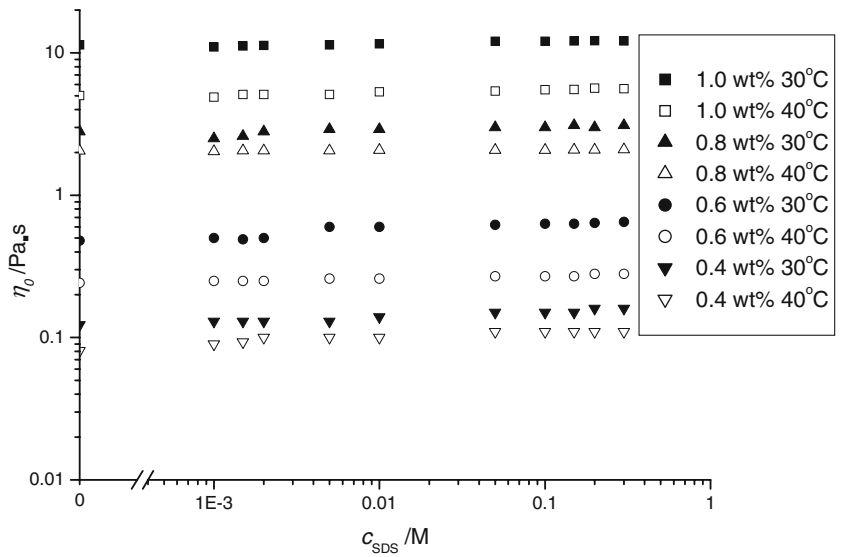


**Fig. 7** Zero-shear viscosity as a function of SDS concentration, $c_{SDS}$, for KGM at different concentrations and temperatures

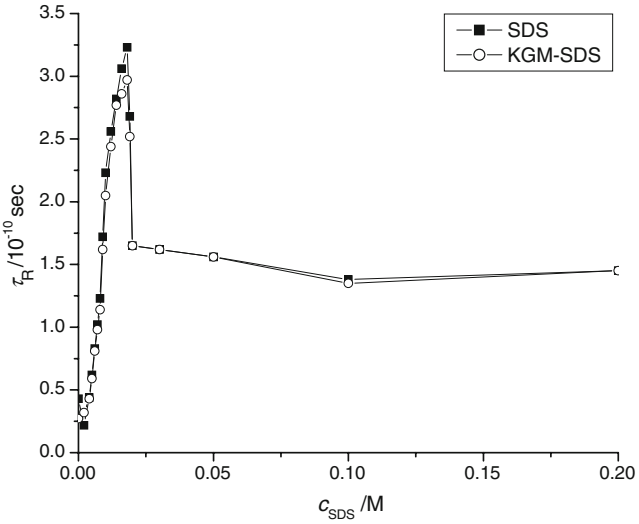


**Fig. 8** Variation of rotational correlation time, $\tau_R$, of 4-amino Tempo in SDS solution and KGM/SDS solution (the concentration of KGM is at 0.8 wt%; $T$=25°C)

the cmc value, 4-amino Tempo is solubilized in the micelles as evidenced by broadening of the high-field line, and by increasing of the rotational correlation time, $\tau_R$. Both the line width ratio and the height ratio are related to the concentration of SDS. From Fig. 8 it is found that, in KGM/SDS aqueous solution, the rotational correlation time values of 4-amino Tempo show no obvious difference or even a little smaller than that in the absence of KGM. This indicates that KGM interacts with SDS monomers only very weakly. When the concentration of SDS in the solution is equal, the spectrum of 4-amino Tempo in KGM/SDS aqueous solution is similar with that in SDS aqueous solution, so the spectra of 4-amino Tempo in KGM/SDS aqueous solution are not shown. In Fig. 8, the rotational correlation time increases with increasing concentration of SDS, it is indicative of slower molecular tumbling of the probes in the micelle than in water. This result is not identical to the results of Wang et al.'s [33], which showed the pronounced increase in rotational correlation time started at the concentration of cmc. This difference comes from the difference of experiments; their PEO samples were equilibrated for 2 days at 10°C and then stabilized for 3 h at 25°C before ESR spectroscopy. In our study, because of the weak alkaline character of SDS and to prevent further reaction, all samples were prepared through mixing high concentrated SDS solution with water or KGM aqueous solution at a weight ratio of 1:1 with mild stirring, then left 4 h at room temperature before ESR spectroscopy. The time for equilibration was not sufficient in the present study. The increase of rotational correlation time stops at saturation concentrations, where the regular free micelles start to form. Exceeding the saturation concentration, the rotational correlation time values decrease steeply with the increase of SDS concentrations. Ramachandran et al. [48] reported that most of the Tempo solubilized in the micelles is located at the micelle-water interface.

The spin-labeled KGM is confirmed identical to native KGM in chemical structure by FT-IR spectrum. Especially, the acetyl groups appearing at 1,730 $cm^{-1}$ are not removed after the spin-labeling reaction. Thus, the behavior of spin-labeled KGM could represent that of the native KGM. Compared with the 4-amino Tempo in aqueous solution, in spin label experiment, the nitroxide is covalently attached to KGM and the ESR spectrum becomes broader due to anisotropic effects arising from its restricted motion. Some contributions to mobility arising from rotation of the label molecule (4-amino Tempo) around the bonds linking it to the polysaccharide chains, however, may be expected.

Figure 10 shows the ESR spectra for 0.1 wt% spin-labeled KGM in 0.2 M SDS solution with or without heat treatment at 80°C. The ESR measurements were conducted at 25°C after the samples cooled. The addition of 0.2 M SDS made the line width broader and increased the rotational correlation time of 0.1 wt% KGM solution from $9.02\times10^{-11}$ s to $4.25\times10^{-10}$ s, the latter value is often

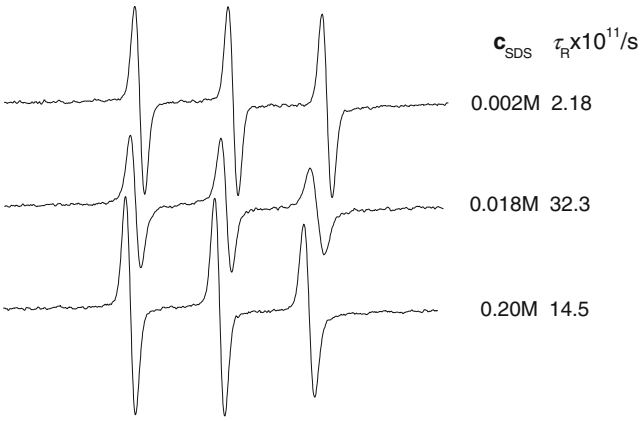


**Fig. 9** ESR spectra for $10^{-4}$ M 4-amino Tempo (spin probe) in SDS solution at different concentrations of SDS ($T$=25°C)

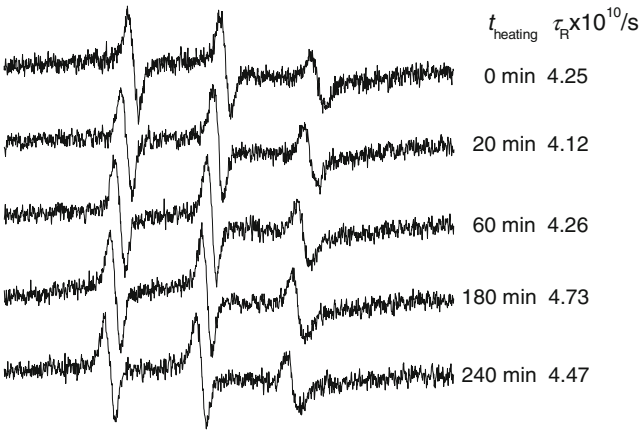


**Fig. 10** ESR spectra for 0.1 wt% KGM (spin-labeled) in 0.2 M SDS solution after heat treatment at 80°C for different times ($T$=25°C)

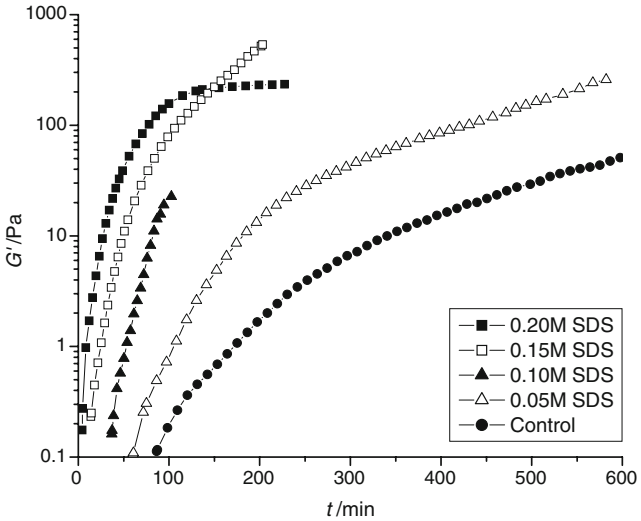


**Fig. 11** Time dependence of $G'$ for 0.8 wt% KGM in SDS solution at different concentration levels of SDS, in the presence of 40 mM $Na_2CO_3$ ($T$=70°C)

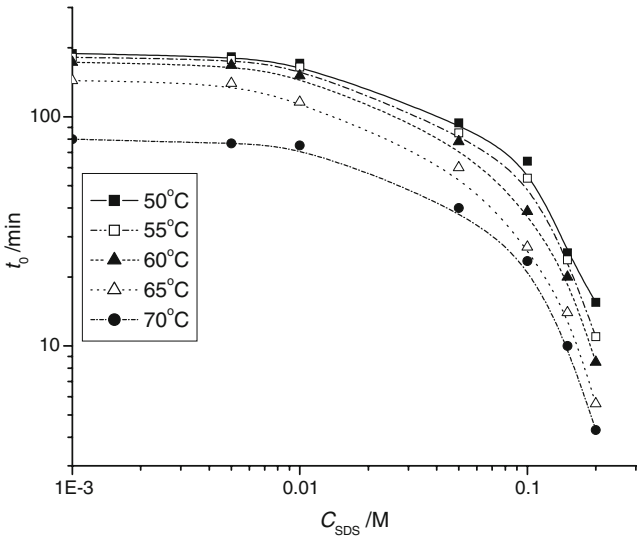


**Fig. 13** The gelation time ($t_0$) as a function of SDS concentration, for 0.8 wt% KGM in SDS solutions, in the presence of 40 mM $Na_2CO_3$, at different heating temperatures

referred to as "weakly immobilized" [32]. The increase of rotational correlation time is attributed to the restriction of KGM molecular motion by SDS micelles. But the heat treatment has no significant effects on the spectra. The result shows that, even after heating at 80°C for 4 h and the gels was already formed, the rotational correlation time is $4.47\times10^{-10}$ s, which is nearly equal to the value before heat treatment. In fact, along the heat treatment, the rotational correlation time keeps nearly constant. A similar result was also observed for 0.1 wt% spin-labeled KGM in 0.4 M SDS solution (data not shown), the rotational correlation time being not changed before and after the gel formation.

The results of spin-probe and spin-label experiments suggest that the interactions between KGM and SDS are very weak and near the interface region, just like PEO in SDS solutions [49]. The SDS micelles facilitate the deacylated KGM chains to form gel structure.

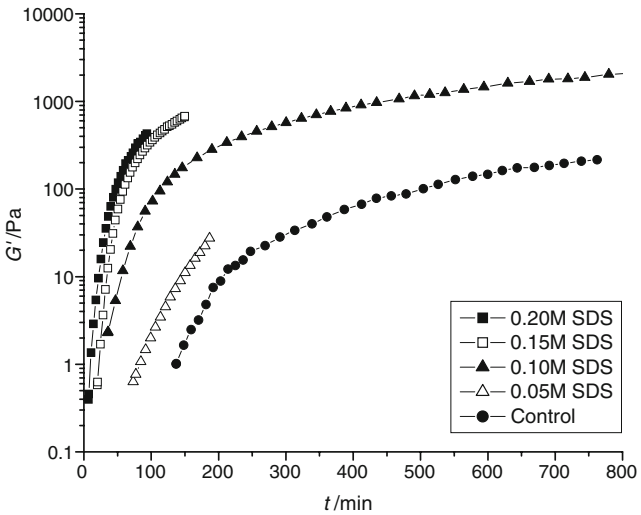


**Fig. 12** Time dependence of $G'$ for 1 wt% KGM in SDS solution at different concentration levels of SDS, in the presence of 40 mM $Na_2CO_3$ ($T$=60°C)

In the presence of $Na_2CO_3$

With the addition of $Na_2CO_3$, the interactions between KGM/SDS, KGM/$Na_2CO_3$ and SDS/$Na_2CO_3$ should all be considered. The effect of adding $Na_2CO_3$ into KGM solutions is not the focus in this paper.

As shown in Fig. 1, in the presence of 40 mM $Na_2CO_3$, the addition of SDS does not markedly influence the pH values of SDS solutions or KGM in SDS solutions. Figure 11 shows the gelation process of 0.8 wt% KGM in SDS solution at different concentrations of SDS, in the presence of 40 mM $Na_2CO_3$, at 70°C. The addition of SDS markedly promotes the gelation process of KGM, although the pH values were kept constant at 11.45 as shown in the curve D in Fig. 1. The addition of SDS also greatly assists the gelation process of 1 wt% KGM in the presence of 40 mM $Na_2CO_3$, which is shown in Fig. 12. Since the gelation process in 1 wt% KGM is faster than that in 0.8 wt% KGM, the heating temperature in Fig. 12 is set at 60°C.

Figure 13 shows the gelation time $t_0$ as a function of SDS concentration, for 0.8 wt% KGM in SDS solutions, in the

**Table 1** The gelation time, $t_0$ for 0.8 wt% KGM solutions, in the presence of $Na_2CO_3$ and SDS with different concentrations at 70°C

| $Na_2CO_3$ | 0.001 M SDS | 0.01 M SDS | 0.1 M SDS |
|---|---|---|---|
| 40 mM | 82 min | 74 min | 23.5 min |
| 30 mM | 88 min | 77 min | 30.5 min |
| 20 mM | 98 min | 85 min | 32 min |
| 10 mM | 103.5 min | 99 min | 33 min |

presence of 40 mM $Na_2CO_3$, at different heating temperatures. The results show that gelation time is largely depended on the heating temperature, which indicates deacetylation is still very important in these strong alkaline cases.

It is well known that the addition of salts greatly influences the character of SDS micelles. The increasing salt concentration screens the charge and reduces the surface potential, causing the decreases of cmc or cac (critical aggregation concentration), which means the minimum surfactant concentration at which polymer-surfactant complexes are formed. The growth and the shape of micelles are also influenced by the added salts concentration [50]. Salts dissolved into ions, then counterion effects [33] and coion effects [51] will influence the SDS micelles.

Table 1 shows that the SDS micelles influence greatly the gelation time of KGM solutions. The results in the presence of $Na_2CO_3$ are in agreement with the results in the absence of $Na_2CO_3$: both deacetylation and promoting by SDS micelles are very important in the gelation process of KGM in SDS solutions.

## Conclusion

The interaction between a nonionic polysaccharide, konjac glucomannan and an anionic surfactant, sodium dodecyl sulfate (SDS) has been studied. The interaction between KGM and SDS is weak, and occurs near the interface region. CD measurements show that SDS makes no conformational changes of KGM with or without heat treatment. The addition of SDS has not significantly changed the viscoelastic properties of KGM, and the cmc value of SDS is not influenced by the addition of KGM, which indicates that there are no significant hydrophobic side groups in KGM and no marked SDS binding to KGM. SDS makes KGM form gels with heat treatment not only because of its weak alkaline nature, but also by the formation of micelles. In the presence of $Na_2CO_3$, the addition of SDS also facilitates the gelation process of KGM. From these phenomena, it is assumed that KGM backbone has weak hydrophobic properties. SDS micelles play an important role in the gelation process of KGM, facilitating the deacetylated KGM chains to form the gel structure.

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